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Studies on Poly(vinyl Chloride). III. The Role of the Precipitated Polymer in the Kinetics of Polymerization of Vinyl Chloride

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Synopsis

In polymerization of vinyl chloride monomer, free radicals precipitate on or within aggregates of partially swollen dead polymer. Polymerization on the solid polymer is characterized by autoaccelerating rates due to a progressive reduction in termination rate. This reduction in termination rate is due to the fact that as the reaction progresses and more polymer accumulates there is a decrease in probability that chain transfer of polymer radicals to monomer will generate a mobile radical, which can readily terminate an occluded or stuck free radical. From the appearance of the particles of solid polymer in the system, it has been concluded that free radicals precipitate both on polymer particle surface and inside the open structure of polymer particles.

INTRODUCTION

Kinetic studies on the polymerization of vinyl chloride have been carried out by many investigators.[1–9] Studies by Bengough and Norrish,[2] Magat,[5] and Schindler and Breitenbach[7] indicate that the insoluble phase, poly(vinyl chloride), is responsible for a considerable acceleration of rate. Implicit in the hypotheses of these investigators is the assumption that free radicals stuck in or on the precipitated polymer have a greatly reduced opportunity for chain termination. Various mechanisms for correlating the rate data have been proposed. Such mechanisms have been less than completely definitive in both a qualitative and quantitative sense because the role ascribed to the precipitated polymer has been vague, and measurements indicating the size, shape, or number of polymer particles or the influence of these variables on rate have not been reported. A primary objective of the work reported here was to study both polymerization kinetics and particle properties to ascertain what control the latter exercise on rates of polymerization.

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EXPERIMENTAL

Preparation of Materials

The initiators benzoyl peroxide and α,α'-azoisobutyronitrile were purified by recrystallization from suitable solvents. Vinyl chloride, which polymerized at reproducible rates without inhibition, was prepared in the following manner. A high-purity commercial monomer was washed with aqueous sodium hydroxide to remove phenol and distilled at atmospheric pressure, the first and last 25% of the distillate being rejected. The middle cut was redistilled under vacuum on a manifold which had been carefully degassed by alternate evacuation to 10^{-3} mm. and flushing with vinyl chloride. Monomer was carefully degassed on the vacuum line, subsequently distilled under vacuum, condensed with Dry Ice in a bulb on the line, and stored out of contact with air until used. Dilatometers of 3–5 ml. capacity with calibrated Trubore capillaries were utilized, being loaded by distillation under vacuum.

Chlorobenzene was purified by distillation through a 4-ft. packed column. A fraction boiling with an 0.2°C. range around 131.2°C. was collected and used.

Methanol was distilled and a fraction boiling at 64.5–64.6°C. used.

Rate of Disappearance of Initiator and Efficiency of Initiation

Data in the literature on the decomposition of α,α'-azoisobutyronitrile are fairly consistent in indicating little if any solvent effect on the first order rates of decomposition. This greatly simplified the work with vinyl chloride which because of its volatility excludes measurements of nitrogen evolution. Using an average of values calculated by the rate constant expressions of Talat-Erben and Bywater,[10] Bawn and Mellish,[11] and Arnett[12] results in an estimated $k_d = 9.0 \times 10^{-5} \pm 0.9 \times 10^{-5}$ min.$^{-1}$.

Arnett and Peterson[13] have reported that radicals from α,α'-azoisobutyronitrile are 77% efficient at initiating polymerization of vinyl chloride (67% monomer in acetone) at 50°C. Experimental conditions, which they report, are quite close to ours, and we therefore assume that the same efficiency, $f = 0.77$, pertains.

Technique for Kinetic Runs

Initiator was introduced by direct weighing into dilatometers. In runs involving solvents, the solvent was next introduced through the dilatometer capillary by a long-needled hypodermic syringe. The dilatometer contents were then frozen by immersion in Dry Ice–acetone. Careful thawing under vacuum followed by repeated refreezing, evacuation, and rethawing permitted thorough degassing. Purified vinyl chloride was then distilled into the dilatometer and the dilatometer sealed off at the temperature of

Dry Ice–acetone. The dilatometer was slowly warmed to room temperature in a darkened hood and completely immersed in a thermostated bath at 47 ± 0.005°C. The dilatometer was at bath temperature within 2 min. With a cathetometer accurate to 0.01 cm., it was possible to measure easily volume changes equivalent to 0.01% conversion. The onset of polymerization in undiluted vinyl chloride was indicated by a sudden turbidity usually visible before any change of monomer level in the dilatometer capillary. Conversions were measured both volumetrically and gravimetrically, and results by both methods found to be in very good agreement up to 20% conversion. To assure an absence of photoinitiation, potassium dichromate was added to the thermostat water, and illumination from a diffused tungsten source was used. Under such conditions, purified monomer without initiator did not polymerize at 47°C. for several weeks.

In kinetic runs with chlorobenzene, the extent of conversion after a period of polymerization was determined by chilling the dilatometer and contents in a Dry Ice–alcohol bath. From the weights of monomer and polymer, isolated by precipitation in a large excess of methanol, conversions were determined and dilatometric observations converted to percentages of polymerization.

Particle Studies

Purified vinyl chloride and benzoyl peroxide were sealed in 7-mm. tubes and polymerized to varying degrees of conversion at 50°C. The tubes were opened and, after evaporation of monomer, the solid polymer shaken up in an aqueous detergent. Some of the solid polymer was dispersed; the dispersions were diluted to low polymer content, the diluted samples dried on collodion supported on 200-mesh stainless steel screens, shadowed with evaporated aluminum, and electron photomicrographs at 7050 diameters taken. A number of plates were made at each conversion to determine the size distribution. To sample a single run at various conversions, an alternative preparation of poly(vinyl chloride) involved polymerization at 50°C. in a heavy walled tube capped with a special crown closure with a small opening backed by a thick interliner of self-sealing rubber. At intervals, aliquots of the tube contents were removed with a calibrated syringe especially constructed to hold liquids under pressure. The aliquot was discharged into a solution of detergent. After evaporation of monomer, the portion of the polymer suspended as a dispersion was decanted and diluted; and electron photomicrographs taken. Conversions were determined by weighing the isolated polymer.

Electron photomicrographs of polymers polymerized in the presence of carbon black, methyl ethyl ketone, and methanol were also taken to determine the effects of inert solid surfaces, solvents, and precipitant on the form and size of poly(vinyl chloride) particles produced during polymerization.

TABLE I
Polymerization of Vinyl Chloride in the Presence of $CBrCl_3$ as Chain Transfer Agent

Tube	Wt. $CBrCl_3$, g.	Wt. $CH_2{=}CHCl$, g.	Wt. Bz_2O_2, g.	$\frac{[CH_2{=}CHCl]_0}{[CBrCl_3]_0}$	Polymer yield, %	Average DP
1	1.13	2.76	0.001	7.75	95	
2	2.05	1.84	"	2.84	100	
3	3.04	1.36	"	1.42	97	4.5
4	4.10	1.60	"	1.24	82	3
5	0.00	3.00	"		100	

Solubility of Low Molecular Weight Poly(vinyl Chloride) in Monomer

To prepare poly(vinyl chlorides) of low degree of polymerization (DP) for studies on the effect of polymer chain length on the solubility of poly(vinyl chloride) in monomer, vinyl chloride, bromotrichloromethane, and benzoyl peroxide in the quantities indicated in Table I were measured into glass tubes, evacuated at −78°C., and sealed off under vacuum. Tube contents were polymerized at 47°C. for 70 hr., cooled in Dry Ice, and opened. The contents of the tubes were then added to methanol.

Polymers from tubes 3 and 4 were to a large extent soluble in methanol. These polymers were recovered by evaporation of the solvent. To remove hexachloroethane from the methanol-soluble telomers produced in tubes 3 and 4, the samples were heated to 35°C. and held under a vacuum of <1.0 mm. for 16 hr., at which time they had attained constant weight. The other polymers were insoluble in methanol and were filtered, washed with methanol, and vacuum-dried to constant weight. The purified polymers differed in physical form as well as in solubility in vinyl chloride. Poly(vinyl chlorides) from tubes 1 and 5 were solid polymers; the telomer from tube 2 was a greasy solid; that from tube 3, a turbid liquid; and the product from tube 4, a clear liquid. Solubilities were measured in a threefold volume of vinyl chloride at room temperature and at 50°C. The telomer from tube 3 gave turbid solution at both room temperature and 50°C., due to insoluble high molecular weight components. The telomer from tube 4 was soluble at room temperature and at 47°C. in a threefold volume of vinyl chloride. From infrared analysis of polymer 4, it was estimated that the value of $n = 3$ characterized the telomer: $CCl_3(CH_2CHCl)_nBr$. This value is reasonable in view of the fact that telomers of structure, $CHBr_2(CH_2CHCl)_4Br$ and $CBr_3(CH_2CHCl)_4Br$ are liquid and semisolid greases, respectively.[14] The value of n for polymer from tube 3 was 4.5.

RESULTS

Kinetics of Polymerization of Vinyl Chloride at 47°C.

A typical conversion–time plot for vinyl chloride polymerization at 47°C. is presented in Figure 1. Data for low conversion are indicated on an expanded scale in Figure 1*a*. The reproducibility of experimental runs was quite good, and the 10% rate data agreed very well with results of Bengough and Norrish.[3] There has been disagreement[3,4,7–9] about the exact dependence of rate of polymerization of vinyl chloride on initiator concentration. Representative experimental data for both benzoyl peroxide (0.1–0.31 mole-%) and α,α'-azobisisobutyronitrile (0.06–0.27 mole-%) are included in Figure 2. Rates dC/dt at 5 and 10% conversions, where the conversion versus time plots were not of marked curvature, were measured tangentially[15] and are plotted logarithmically against the

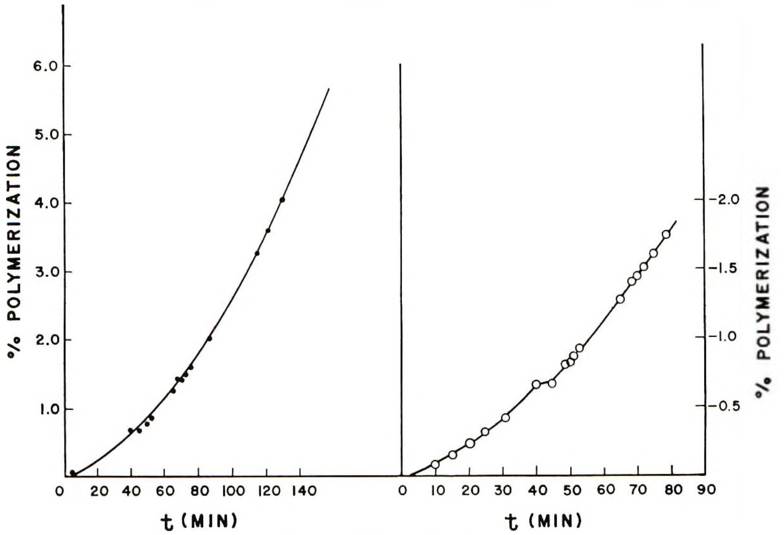


Fig. 1. Polymerization of undiluted vinyl chloride at 47°C., azobisisobutyronitrile initiator, 0.0175 mole/l.; (right, 1*a*) low-conversion data on an expanded scale.

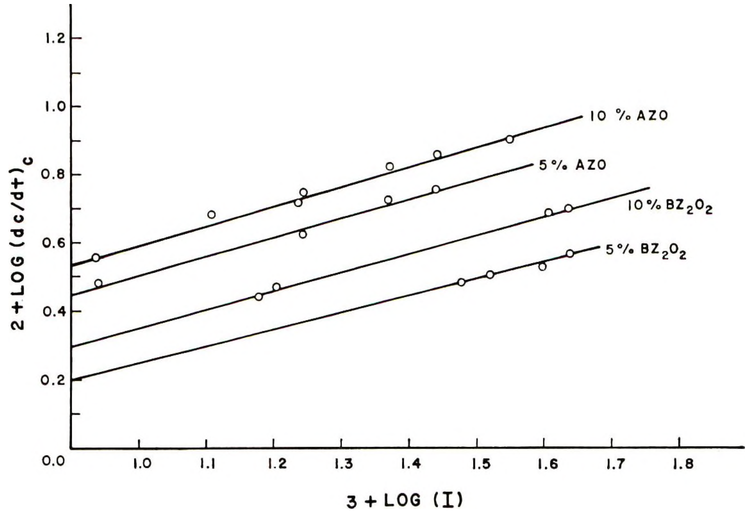


Fig. 2. Rate of polymerization at 47°C. of vinyl chloride at 5% and 10% conversions as functions of initiator concentrations. Initiators, α,α'-azobisisobutyronitrile and benzoyl peroxide.

logarithm of initial initiator concentration [I]. For benzoyl peroxide data, the initiator exponents are 0.50 and 0.55 at 5 and 10% conversions, respectively. For α,α'-azoisobutyronitrile initiator, exponents are 0.50 and 0.56 at the same conversions. These results do not differ markedly from the square-root dependence consistent with bimolecular termination. There is, however, a slight increase of the initiator exponent with conversion. For treatment of low conversion data, the square-root approximation is justified.

Detailed kinetic analysis of polymerization of vinyl chloride has been attempted in several ways. Bengough and Norrish have reported rates at low conversion proportional to the two-thirds power of the weight of polymer present. Mickley et al.[9] have recently presented evidence of deviations from the rate law of Bengough and Norrish at low conversions in precipitating media. Schindler and Breitenbach have reported that conversion of vinyl chloride can be represented as a quadratic function of time of polymerization. Magat has indicated that a nonsteady state analysis of kinetic data, essentially a long pre-effect, results in a reasonable quantitative fit of data on vinyl chloride polymerization.

Analysis of the experimental data of this research by each of the mechanisms proposed has been attempted, and a summary of the results is presented below.

The rate relationship of Bengough and Norrish is of the form:

$$-d[\mathrm{M}]/dt = K_0[\mathrm{I}]^{1/2}([\mathrm{M}] + K'W_p^{2/3}) \tag{1}$$

in which [M] and [I] are the concentrations of monomer and initiator, respectively; W_p, the weight of polymer at a particular conversion, C; K_0, and K', constants. This expression becomes on substitution of $C = ([\mathrm{M}_0] - [\mathrm{M}])/[\mathrm{M}_0]$ and $W_{\mathrm{M}0}$, the initial weight of monomer,

$$dC/dt = K_0[\mathrm{I}]^{1/2}\{(1 - C) + K''' (CW_{\mathrm{M}0})^{2/3}/[\mathrm{M}_0]\} \tag{2}$$

where $[\mathrm{M}_0]$ is the initial monomer concentration.

At low values of conversion for which $1 - C \approx 1$, the equation reduces to:

$$dC/dt = K_0[\mathrm{I}]^{1/2}\{1 + K''' (CW_{\mathrm{M}_0})^{2/3}/[\mathrm{M}_0]\} \tag{3}$$

predicting a linear relationship between dC/dt and $(CW_{\mathrm{M}_0})^{2/3}$. Figure 3 includes data for polymerization of vinyl chloride initiated by benzoyl peroxide at concentrations 0.0394M and 0.035M and by α,α'-azoisobutyronitrile at concentrations 0.0234M and 0.0086M. The arrow of each plot indicates 5% conversion. It is apparent that the data are only approximately consistent with the relationship proposed over a limited range of CW_{M_0}; and that there is a functional dependence of rate of polymerization on the amount of polymer in the system. An empirical kinetic expression similar to that of Bengough and Norrish:

$$dC/dt = K_0[\mathrm{I}]^{1/2}(1 + K_1C^{\alpha}) \tag{4}$$

has been fitted to experimental data from 0.5% to 10% conversion.

To determine values of α, eq. (4) has been used in the form:

$$dC/dt - K_0[\mathrm{I}]^{1/2} = K_0K_1[\mathrm{I}]^{1/2}C^{\alpha} \tag{5}$$

From extrapolations of rate data for benzoyl peroxide and α,α'-azoisobutyronitrile to zero conversion, and also from linear initial rates of poly-

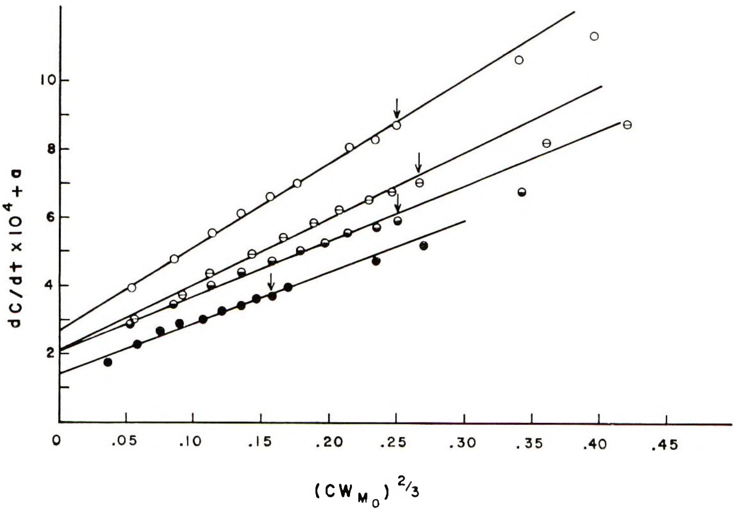


Fig. 3. Instantaneous rate of polymerization at 47°C. as a function of assumed surface area, $(CW_{M_0})^{2/3}$ g.$^{2/3}$: (○) $a = 0$, $[\mathrm{Azo}]^{1/2} = 0.153$ (mole/l.)$^{1/2}$; (⊖) $a = 0$, $[\mathrm{Bz_2O_2}]^{1/2} = 0.198$ (mole/l.)$^{1/2}$ (◒) $a = 0$, $[\mathrm{Bz_2O_2}]^{1/2} = 0.187$ (mole/l.)$^{1/2}$; (●) $a = -1$, $[\mathrm{Azo}]^{1/2} = 0.093$ (mole/l.)$^{1/2}$.

merization of vinyl chloride in chlorobenzene (Fig. 4), K_0 values have been obtained. These are $(K_0)_{\mathrm{Bz_2O_2}} = 1.09 \times 10^{-3}$ (l./mole)$^{1/2}$ min.$^{-1}$ for benzoyl peroxide at 47°C., and $(K_0)_{\mathrm{azo}} = 1.83 \times 10^{-3}$ (l./mole)$^{1/2}$ min.$^{-1}$. The extrapolated data are quite close to those in chlorobenzene.

Plotting log $(dC/dt - K_0[\mathrm{I}]^{1/2})$ versus log C results in straight lines (Fig. 5), and values of α tabulated in Table II have been obtained from the slopes of the straight lines of Figure 5.

The results tabulated in Table II demonstrate that no single value of

TABLE II

Polymerization of Vinyl Chloride at 47°C. Correlation of Instantaneous Rates as a Function of Conversion

Run	Catalyst	[I], mole/l.	$(dC/dt)_{C=0}$ × 10^4, min.$^{-1}$	α[a]	K_1
1	$\mathrm{Bz_2O_2}$	0.0350	2.06	0.57	10.3
2	"	0.0393	2.17	0.58	12.5
3	"	0.0299	1.88	0.55	9.6
4	"[b]	0.0688	2.86	0.67	12.7
5	Azo	0.0234	2.80	0.65	14.6
6	"	0.0086	1.71	0.46	12.0
7	"	0.0175	2.42	0.64	11.5
8	"	0.0275	3.03	0.60	11.7
				Avg.	11.9 ± 1.0

[a] α values are slopes of log $\{(dC/dt) - K_0[\mathrm{I}]^{1/2}\}$ vs. log C plots of Figure 5.

[b] Data of Bengough and Norrish.[3]

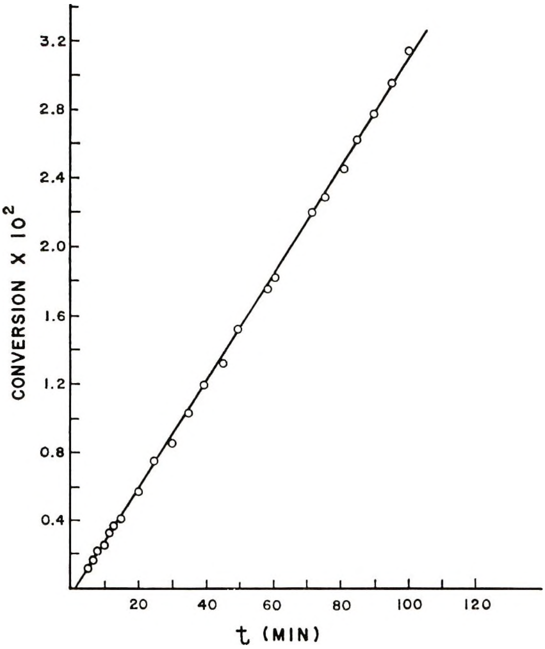


Fig. 4. Rate data for polymerization of vinyl chloride in chlorobenzene at 47°C. Weight fraction vinyl chloride = 0.54, $[\text{Azo}]^{1/2} = 0.156$ (mole/l.)$^{1/2}$.

α will accommodate all of the rate data for vinyl chloride. Data for a considerable number of runs indicate that only for faster rates of polymerization does α approximate 2/3. The trend in the data suggests that $\alpha = 2/3$ may be a limiting dependence on precipitated polymer at higher rates. The variation of α with rate of polymerization indicates a more complex dependence than the simple surface area relationship proposed by Bengough and Norrish. The failure of the simple mechanism of Bengough and Norrish has also been reported by Arlman and Wagner[4] and elaborated by Mickley et al.[9] Values of K_1 included in Table II are reasonably constant, and the value reported by Bengough and Norris agrees well with the data for the current research, suggesting that K_1 may be, as suggested by these authors, a dimensionless ratio of rate constants independent of type of initiator, amount, and physical form of solid polymer.

Analysis of kinetic data by Schindler and Breitenbach[7] was based on the hypothesis that the rate constant for termination of polymerization, k_T, is reduced by burial of free radials, k_T decreasing with conversion C in accordance with the law:

$$k_T = k_T^0/(1 + k^*C)^{1/2} \qquad (6)$$

In eq. (6), k_T^0 is the initial rate constant for termination and k^*, a dimensionless constant. According to this mechanism, the rate of polymerization becomes:

$$dC/dt = V_0(1 + k^*C)^{1/2} \qquad (7)$$

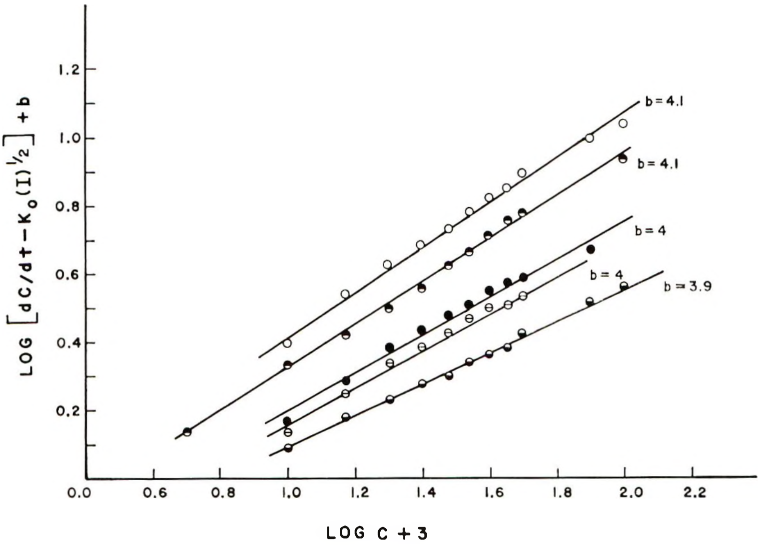


Fig. 5. Instantaneous rate of polymerization of vinyl chloride at 47°C. as a function of conversion C: (○) [Azo] = 0.0234 mole/l.; (◓) [Azo] = 0.0175 mole/l.; (●) $[\mathrm{Bz_2O_2}]$ = 0.0350 mole/l.; (⊖) $[\mathrm{Bz_2O_2}]$ = 0.0299 mole/l.; (◒) [Azo] = 0.0086 mole/l.

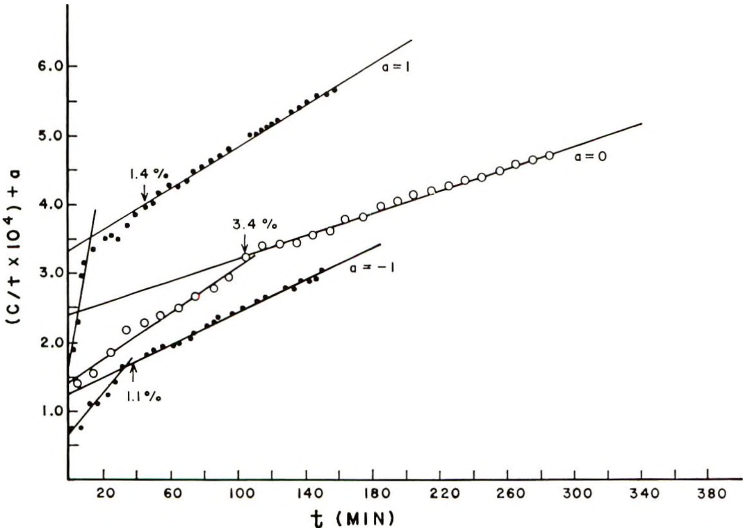


Fig. 6. Vinyl chloride data: C/t vs. t for $a = 1$, $[\mathrm{Bz_2O_2}] = 0.0350$ mole/l.; $a = 0$, [Azo] = 0.0086 mole/l.; $a = -1$, $[\mathrm{Bz_2O_2}] = 0.0299$ mole/l.

In eq. (7), $V_0 = (k_i[\mathrm{I}])^{1/2}k_p[\mathrm{M}]/(k_T^0)^{1/2}$. Integration of eq. (7) yields:

$$C/t = k^*V_0^2t/4 + V_0 \tag{8}$$

$$C = (k^*V_0^2t^2/4) + V_0t \tag{8a}$$

C/t versus t data for several runs are illustrated in Figure 6.

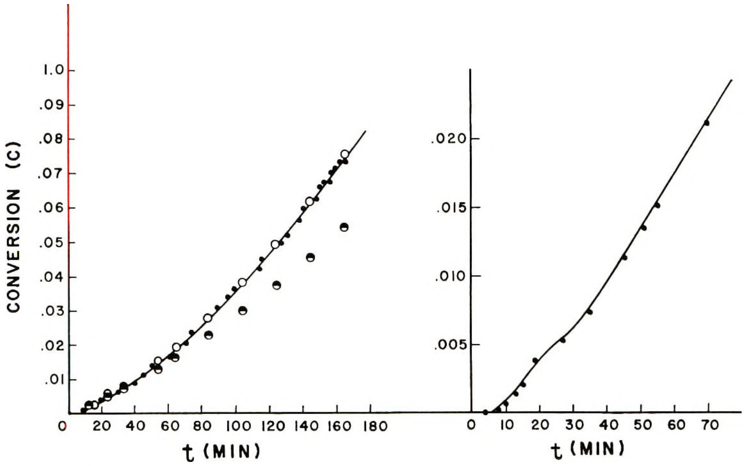


Fig. 7. Fitting of data for [Bz_2O_2] = 0.0350 mole/l. by $C = k^* (V_0t)^2/4 + V_0t$: (●) experimental data; (◓) $k^* = 50$; (○) $k^* = 110$. Plot at right indicates discontinuity of very low conversion data at $C \approx 0.005$.

The value of the dimensionless constant k^* reported by Schindler and Breitenbach was 50. Calculated conversions as a function of time for run 1, Table I, are presented in Figure 7 along with an enlarged reproduction of low conversion data. From the expanded scale, it appears that the early conversion data are not entirely continuous, a feature observed in many runs in this research and indicated by the data of Breitenbach and Schindler.[7] Included are the experimental data and calculated conversions based on $k^* = 50$ and $k^* = 110$. The value k^* which gives the best quadratic fit to the data is 110. The data of Schindler and Breitenbach yielding $k^* = 50$ were for ratios of [initiator]/[monomer] of the order 1×10^{-3}. The data for the run plotted are for [initiator]/[monomer] = 3×10^{-3} corresponding to faster rates of polymerization at 47°C. Table III includes a summary of representative results obtained by analysis of data by use of eq. (8).

A characteristic feature of the quadratic plots is the marked deviation from linearity at very low conversion for all runs. It is interesting to note

TABLE III
Polymerization of Vinyl Chloride at 47°C. with Benzoyl Peroxide and α,α'-Azoisobutyronitrile Initiators

[I], mole/l.	$V_0 \times 10^{4\,a}$	$V_0 \times 10^4$ exp.	k^*
0.0350	2.32	2.06	110
0.0299	2.25	1.88	90
0.0086	2.40	1.71	55
Schindler and Breitenbach			50

[a] Extrapolated value of V_0 from linear portion of quadratic plots of C/t vs. t.

that these deviations correspond to discontinuities observed in the conversion–time plots at conversions of the order 0.002–0.010.

There is a definite trend toward lower values of k^* as rates of polymerization decrease and our lowest rates of polymerization yield values of k^* close to those reported by Schindler and Breitenbach at similar levels of initiator. The "constant" k^*, unlike K_1, is not single-valued. It is rather to be considered an adjustable coefficient for fitting the experimental data by the quadratic function.

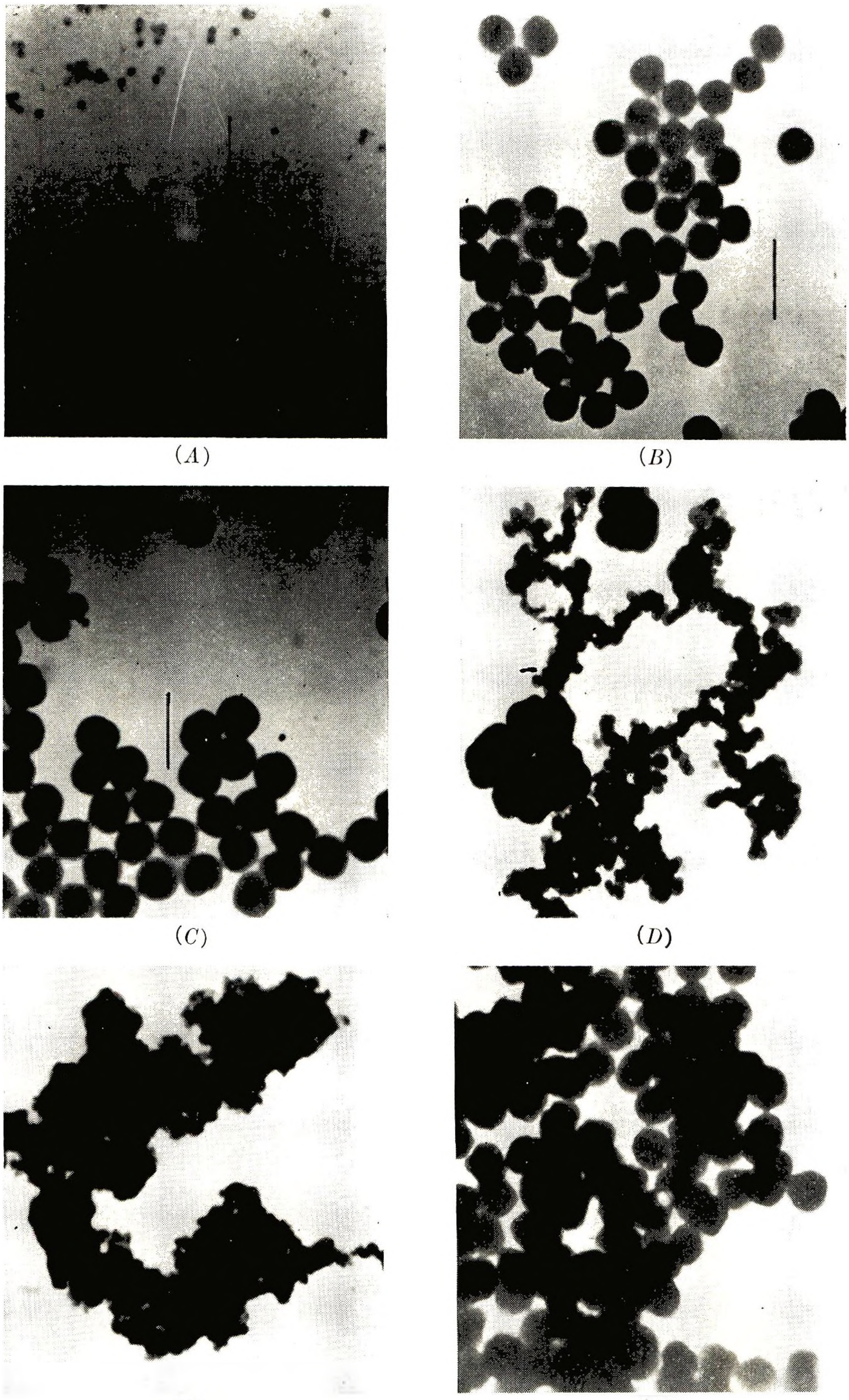
Nature of the Precipitated Polymer in Mass Polymerization of Vinyl Chloride

Electron photomicrographs (7050) of poly(vinyl chloride) particles isolated from mass polymerization batches at various conversions at 50°C. are included in Figure 8. Figure 9 illustrates the change in average particle diameter as a function of conversion. An unexpected feature was the uniformity in size (at a particular conversion) of polymer particles from different polymerizations. The size of particles appeared to be essentially a unique function of conversion, not of rate, in systems sampled between conversions of 0.01 and 0.30. The particles were found to be roughly spherical composites of smaller units and distributions of particle sizes were extremely narrow. Table IV includes a summary of particle size data for solid poly(vinyl chloride) isolated at conversions of 0.0017–0.30. Tabulated are particle sizes at the measured conversions, the weight of an individual particle, $W_p' = (4/3)\pi r^3 \rho$, in grams, and the number of particles per gram of monomer reacted, $N_p = C/(4/3)\pi r^3 \rho$. These data indicate a greater than fourfold decrease in number of polymer particles per gram of monomer at low conversions between 0.002 and 0.009. The structure of

TABLE IV
Particle Size and Weight as a Function of Conversion C in the Polymerization of Vinyl Chloride at 50°C.

C	Radius, r $\times 10^5$, cm.	$W'_p \times 10^{16}$, g.[a]	$N_p \times 10^{-11}$
0.0017	<0.50	<7.31	>23.2
0.009	1.45	178	5.10
0.045	2.55	971	4.65
0.096	2.95	1500	6.41
0.148	3.60	2740	5.40
0.300	4.8	6430	4.70

[a] In calculating the weight of a particle, it was assumed that the particles were densely packed and of the same density ρ = 1.40 g./cc. as solid poly(vinyl chloride). Swelling by monomer would result in a change in ρ but would not appreciably affect relative values of r. It has been shown[3] that the molecular weight (and presumably molecular weight distribution of poly(vinyl chloride) is not changed by conversion. Under these circumstances differences in swelling of the solid phase as a function of conversion should not be significant.


(A) (B)

(C) (D)

(E) (F)

Fig. 8. Electron photomicrographs (7050 diameters) of poly(vinyl chloride) particles of different conversions C from polymerizations carried out at 50°C. Fiducial mark on 8A–8C equals 1 μ; (A) $C = 0.0017$; (B) $C = 0.045$; (C) $C = 0.096$. (D) polymer formed in presence of carbon black: (E) polymer prepared in 60 vol.-% methanol; (F) added methyl ethyl ketone ($C \approx 0.10$).

particles at conversion 0.002 is uncertain. The particles observed may themselves be primary unaggregated units or particles which due to the interaction of the detergent and polymer are more or less flocculated. What is significant is a substantial change in particle size and number over a limited conversion range. Such a decrease is most probably the consequence of aggregation of the small insoluble particles to the larger units found at higher conversions. Aggregation at early conversion has been postulated by Mickley et al. It is in this range of conversion that precision dilatometry reveals a discontinuity in rate, initial rates falling off slightly before autoacceleration is manifested.

The character of poly(vinyl chloride) particles prepared by polymerization of monomer in the presence of a finely divided solid (carbon black) and in methanol (60 vol.-%) are included in Figures 8*D* and 8*E*. The polymer particles produced in either case had a different form from that obtained by mass polymerization. The irregular aggregates obtained with carbon black can be rationalized by postulation that poly(vinyl chloride) precipitated on the carbon black particles which served as nuclei for polymer deposition. Smaller particles of polymer are the consequence of secondary self-nucleation. Methanol in vinyl chloride should decrease the solubility of the lowest molecular weight polymer formed. Polymerization in the presence of methanol led to flocculent irregularly shaped aggregates. It is interesting to note that polymerization of vinyl chloride (40 vol.-%) in methanol resulted in faster rates than in bulk. The normalized rate $(dC/dt)/[\mathrm{I}]^{1/2}$ at 5% conversion in methanol was 34% faster than in the absence of methanol. Polymerization of vinyl chloride containing 3.8 mole-% of methyl ethyl ketone resulted in spherical particles of uniform size (Fig. 8*F*) similar in appearance, but smaller in size than those obtained by mass polymerization in the absence of solvent or precipitant.

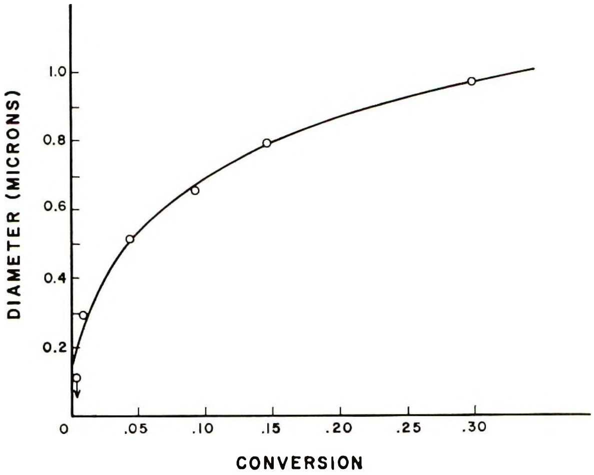


Fig. 9. Particle size of vinyl chloride polymer as a function of conversion.

Uniformity of particle size, continuous particle growth, and constancy of the number of particles per gram of monomer at conversions of 0.01–0.30 indicate growth of polymer on the particles existing in the system without appreciable secondary particle formation. At conversions of 0.30 or greater the incidence of nondispersible fused particle clusters increased and an occasional smaller spherical particle was observed indicative of a limited secondary nucleation.

From the observations made on particles from the different polymerization systems, it was concluded that the interaction of vinyl chloride polymer radicals with previously formed polymer is a process which can occur on the surface of other solids (e.g., carbon black). The process deposition is certainly in large measure, if not exclusively, a consequence of polymer insolubility in monomer.

Observations on the solubility of low molecular weight telomers of vinyl chloride are pertinent in defining the size at which polymer molecules precipitate from homogeneous system and as small colloidal units are readily accreted by larger polymer aggregates in the process of particle growth. The kinetics of polymerization indicate that polymer separates from monomer as free radicals, and this conclusion is substantiated by the solubility of polymer in monomer. A telomer of structure $CCl_3(CH_2CHCl)_{4.5}$—Br contains a small fraction which is insoluble in monomer at the temperature of polymerization.

Flory[16] has reported the following equation to describe the distribution of molecular sizes for polymerization in which chain transfer is the primary mode of molecular size regulation:

$$W_x = x(1 - p)^2 p^{x - 1} \tag{9}$$

in which W_x is the weight fraction of x-mers, and p, the probability of addition of another monomer unit, is defined by:

$$\bar{\bar{X}}_n = 1/(1 - p) \tag{10}$$

Calculation of cumulative weight fractions (ΣW_x) of polymers of average degree of polymerization ($\bar{\bar{X}}_n$) = 3.0 and 4.5 indicated that the soluble telomer contained a negligible fraction (<0.1%) of polymer molecules of DP > 25 and that less than 0.02% of the telomer of average DP = 4.5 was of DP > 32. From these data, we assume that somewhere in the molecular size range 25 < DP < 32, free radicals, like polymer molecules, lose their solubility in monomer and precipitate as small units which are accreted by larger aggregates of polymer. There they continue to add monomer units until chain transfer to monomer (or polymer) or termination with other free radicals occurs.

DISCUSSION

The inability to correlate experimental data for polymerization of vinyl chloride by simple kinetic rate expressions is very probably a direct consequence of interaction of the "dead" polymer with free radicals in the system. Kinetic analyses of polymerizations which yield polymers insoluble in monomer are rendered particularly difficult because of the probability of free-radical occlusion. Surface entrapment, as depicted by Bengough and Norrish, is a limiting mode of occlusion in which polymer radicals are temporarily isolated from one another, but not from monomer. Severe occlusion within tightly packed polymer particles not particularly swollen by monomer can shield free radicals from monomer as well, so that occlusion becomes in fact an act of termination. Depending on the mode and extent of radical entrapment and enclosure, many kinetic aberrations can appear. We believe that examination of the polymer produced in vinyl chloride permits a number of deductions about processes other than purely chemical mechanisms which are significant in determining the rates of polymerization. In evaluation of data, we have placed particular emphasis on the breakdown of simple mechanisms which have been offered for the polymerization of vinyl chloride. This has been done out of conviction that the essential role of heterogeneity in determining the rate of polymerization may be obscured by arbitrary fitting of rates by equations which apply at best to very restricted conditions of polymerization.

Particle Changes as a Function of Conversion

The nature of precipitated poly(vinyl chloride) changes with conversion. Onset of polymerization in vinyl chloride produces insoluble particles. Low-conversion particles ($r < 10^{-5}$ cm.) coalesce to aggregated units at conversions less than 0.01. The aggregates then grow in size by deposition of polymer, either as radicals or smaller polymer particles. At conversions of 0.01–0.30 there is little evidence for secondary particle formation. The limiting rate dependence on the 2/3 power of conversion proposed by Bengough and Norrish is applicable in a limited sense to this phase of polymer particle growth. Sticking of free radicals on the surface of particles where they add monomer units until released by chain transfer with monomer or terminate with another free radical increases the average lifetime of free radicals and rate of polymerization because of a lowered frequency factor for termination. The effect of surface capture on the rate of propagation should be small. The breakdown of the 2/3 power rate law is a consequence of simultaneous processes involving polymer particles. The aggregation of polymer particles, quite obvious at low conversion, proceeds throughout polymerization at a less rapid rate. There are several reasons for believing this. Attempts to disperse the polymer by detergents resulted in very limited dispersion. Most of the polymer was irreversibly flocculated. Very short treatment of nondispersible polymer with acetone resulted in limited dispersion. A strong evidence for aggregation was the observance of a meniscus during polymerization after an initial period of a uniformly turbid polymer–monomer mixture. To illustrate the significance of a meniscus, consider typical dimensions of one of the capillary dilatometers with volume equal to 3.00 ml. The capillary bore was 1.5 mm., so that a contraction of 1% in volume was equivalent to 1.70 cm. fall in capillary level. At 47°C., this volume change was equivalent to approximately 2.4% polymerization. For a considerable number of runs in such a dilatometer, contractions of the meniscus of 3.70–7.35 cm. were observed during periods of reaction of 145–150 min. Conversions as high as 0.06–0.11 were frequently measured before the meniscus was finally obscured by polymer. A definable, clear meniscus was considered evidence for polymer settling. Average rates of settling for these runs had to be no less than 1.8 cm./hr. to 3.0 cm./hr. to maintain a meniscus. Experimentally, the average diameter of a polymer particle dispersed from a 0.1 conversion polymer was 0.6 μ. Since the particles were approximately spherical, the rate of setting V_s should be, in accordance with Stokes' law:

$$V_s = 2/9g(\rho_{\text{solid}} - \rho_{\text{liquid}})r^2/\eta \tag{11}$$

The viscosity of vinyl chloride at 47°C., is 1.9 mpoise. Using this value of η, $\rho_{\text{solid}} = 1.40$, and $\rho_{\text{liquid}} = 0.86$, observed rates of settling correspond to particle diameters of 1.8–2.2 μ, each value considerably larger than the 0.6 μ diameter of polymer particles isolated from polymerization carried to 0.10 conversion. The large discrepancies between observed and calculated particle diameters are strong evidence for flocculation of particles, particularly since Kunkel[17] has reported that clusters of spherical particles yield smaller Stokes' law sedimentation diameters than correspond to the physical dimensions of the cluster. In addition, ignoring the swelling of polymer with monomer is equivalent to the assumption of too high a particle density for poly(vinyl chloride) suspended in monomer, a factor which would tend to make the calculated cluster diameters smaller than they actually were.

Kinetic Effects of Particle Changes

Kinetic consequences of the physical processes postulated are complex. Initial rapid coalescence of insoluble polymer particles removes a considerable amount of surface from the system. The discontinuity in rate indicated in Figures 1*a* and 7 suggests there may also be changes in kinetic coefficients of free radicals due to envelopment during rapid aggregation.

There is another unexplained experimental observation which is probably related to particle changes in the rapid coalescence of early polymerization. Breitenbach and Schindler[18] have reported that polymerization of vinyl chloride, containing low concentrations of extremely efficient chain transfer agents, not only yielded polymer of lowered degree of polymerization, but proceeded at initial rates faster than those of pure monomer. Additionally, in the presence of transfer agent, the usual autocatalysis was markedly suppressed. Using carbon tetrabromide as chain transfer agent there was an increase in initial rate with increasing CBr_4 concentration to a maximum at $[CBr_4]/[VCl] = 8 \times 10^{-4}$. At higher concentrations of chain transfer agent rates fell off. Using the chain transfer constant $C_{tr} \approx 50$ and $\bar{P}_0$ (the degree of polymerization in the absence of transfer agent)

= 740 reported by Breitenbach and Schindler, the calculated degree of polymerization at the level of maximum efficiency of chain transfer agent was 25, a value within the critical solubility limits already discussed. The coincidence of these data leads us to propose the following explanation for the anomalous observations of chain transfer activity.

Polymers of lower average degree of polymerization which are produced by chain transfer to carbon tetrabromide, contain increasingly larger fractions of partially soluble low molecular weight molecules as the concentration of transfer agent is increased. In addition, the precipitating particles of insoluble fractions may, by virtue of reduced molecular weight, be more stable and coalesce more slowly than particles of polymer of high degree of polymerization. Reduction of the rate of coalescence results in a substantially greater surface area for capture of mobile polymer free radicals. This hypothesis is also consistent with a maximum in the rate of polymerization as the concentration of transfer agent is increased; since the increase in fraction of soluble polymer as the average degree at polymerization goes down will eventually reduce the amount of the heterogeneous phase of insoluble polymer to an extent sufficient to result in eventual reduction of solid polymer surface, despite a lower rate of particle coalescence.

Suppression of autocatalysis in early conversion in the presence of very active chain transfer agents suggests that reaction of stuck radicals with the transfer agent produces smaller soluble radicals, which diffuse rapidly and terminate with one another. In this manner, a quasi-steady state is set up in early conversion. The absence of auto acceleration, in the presence of efficient chain transfer agents, indicates unequivocally that there is no rapid increase in free-radical concentration.

By contrast, polymerization, in the absence of added chain transfer agent, involves molecules of high degree of polymerization, low solubility, and rapid particle coalescence at low conversion. At very low conversions, rapid particle coalescence reduces particle surface area and may effectively terminate free radicals within the particles by confining them to a limited volume in close proximity so that they react with one another at an enhanced rate.

The incidence of particle coalescence also affords an explanation for the deviations from the rate law proposed by Bengough and Norrish. Assuming that free radicals are trapped on the surface of particles, coalescence reduces the surface/gram of polymer as polymerization progresses. Consequently, the value of α is less than the 0.67 predicted on spherical particles of independent identities.

In runs carried out in chlorobenzene, initial rates were constant even in the presence of a highly swollen polymer phase, which was apparent before any autocatalysis of rate.

Bamford and Jenkins[19] have demonstrated that in the polymerization of acrylonitrile, the higher the initial rate of polymerization to produce insoluble polymer radicals, the greater the opportunity for trapping of radicals. A comparison of (rates of polymerization)/$[I]^{1/2}$ for vinyl chlo-

TABLE V
Rates of Polymerization of Vinyl Chloride at 0.005 Conversion at 47°C.

Concn. azoisobutyronitrile initiator [I], (mole/l.)	$dC/dt \times 10^4$, min.$^{-1}$	$(dC/dt)/[\mathrm{I}]^{1/2} \times 10^3$
0.0234	3.8	2.5
0.0172	3.2	2.4
0.0175	3.5	2.6
0.0275	4.2	2.5
0.0086	2.7	3.0

ride at 0.005 conversion where the initial rapid aggregation occurs is given in Table V.

It is interesting to note that the value of $(dC/dt)/[\mathrm{I}]^{1/2}$ is 20% greater for the lowest rate than for the others. This observation, in addition to the dramatic effect of chain transfer agents, is consistent with some reduction of overall rate, because of the initial occlusion, by virtue of an enhancement of rate of termination of radicals confined to the small volume of the coalesced particles.

The alternative explanation of Breitenbach and Schindler, that mass polymerization of vinyl chloride in the absence of added chain transfer agent is slower than that with CBr_4 because of degradative chain transfer to monomer, is untenable for two reasons.

(*a*) The chain transfer processes with monomer and added chain transfer agent are competitive and not mutually exclusive.[20] Neither can suppress the other. As a consequence there can be no extension of kinetic chain length due to the action of added chain transfer agent.

(*b*) It is exceedingly questionable that a good case can be made for degradative chain transfer in the polymerization of pure vinyl chloride. Any variation of initiator exponent from 0.5 to 1.0, which has been interpreted as a characteristic of degradative chain transfer[21,22] in homogeneous systems cannot be so easily ascribed to degradative chain transfer in heterogeneous systems. Marked deviations of dependence of rate from $[\mathrm{initiator}]^{0.5}$ have been observed in the heterogeneous polymerization of acrylonitrile[23,24] in which polymerization there is no evidence for monomer chain transfer at all. Attempts[18] to relate to degradative chain transfer to monomer, the small deviations of vinyl chloride kinetics from a square root dependence on initiator may well have been misinterpretations of what is in reality a manifestation of phase heterogeneity. Mickley et al. have presented evidence for degradative chain transfer to tetrahydrofuran, but question its importance in transfer to monomer.

From available data, it is possible to estimate the extent of nondegradative chain transfer. The total number of chains initiated in time t is given by:

$$k_i It = 2fk_d It = R \qquad (12)$$

and the total moles of polymer P formed in time t are:

$$Cv_0\rho/M\bar{P}_n = P \tag{13}$$

where I is the moles of initiator; t, the reaction time; f and k_d have their usual significance; M is monomer molecular weight; $\bar{P}_n$ is number-average degree of polymerization of polymer; C is the conversion; v_0 is the initial monomer volume; and ρ is monomer density.

The average number of polymer molecules per free radical is:

$$P/R = Cv_0\rho/(2fk_dIt)(M\bar{P}_n) \tag{14}$$

Using data for run 5, Table II, at $C = 0.05$, $t = 93$ min., $v_0 = 2.917$ ml., $\bar{P}_n \approx 760$, $[\mathrm{I}] = 2.3 \times 10^{-2}$ mole/l., and the values $k_d = 9 \times 10^{-5}$ min.$^{-1}$, $f = 0.77$, we have

$$P/R = 4 \text{ polymer molecules/free radical}$$

Similarly for Run 6, Table II, where $[\mathrm{I}] = 8.6 \times 10^{-3}$ mole/l.

$$P/R = 6.8 \text{ at } C = 0.05$$

$$P/R = 8.7 \text{ at } C = 0.10$$

These data indicate several facts about chain transfer to monomer in vinyl chloride polymerization.

There is a considerable nondegradative chain transfer to monomer, resulting in a number of polymer molecules for each free radical utilized. In addition, P/R yields at a particular conversion parallel the initial kinetic chain lengths ν. Thus the 5% conversion P/R yields,

$$(P/R)_1/(P/R)_2 = 6.8/4 = 1.7$$

and,

$$\nu_1/\nu_2 = (dC/dt)_2/(dC/dt)_1 = 2.80/1.71 = 1.64$$

The increase in average P/R yield with conversion is indicative of an increase in the average lifetime of free radical during which, by virtue of chain transfer, an increased number of polymer molecules is formed.

These observations are readily interpretable on the basis of the heterogeneity of the polymerization, without involving any mechanism involving degradative chain transfer to monomer, thus requiring that the same act of chain transfer be extremely efficient in a nondegradative sense, and at the same time a mode of termination of chains.

Kinetic measurements and particle studies indicate that the period following initial agglomeration is primarily one of particle growth. Autoacceleration is due to the fact that the average lifetime of chain carriers increases; at least, the average useful radical lifetime during which propagation is effective increases. Continuous particle growth, the absence of secondary nucleation, and the approximate relationship between rate of polymerization and polymer surface area, indicate a predominant sticking of growing radicals on previously formed polymer surface in contact with monomer, rather than extensive burial out of contact with monomer because of occlusion. Comparison of our results with those of Bamford[19,25] dispose us to minimize extensive radical loss by burial as a factor in rates. The dependence of rate on initiator concentration (0.50–0.56) indicates little, if any, kinetically effective loss of radicals by occlusion. This is in sharp distinction to polymerization of acrylonitrile where free radicals are strongly occluded and is probably a consequence of greater solubility of poly(vinyl chloride) of low molecular weight in monomer and more swelling of polymer of high degree of polymerization by monomer than is the case for acrylonitrile. In addition, chain transfer to monomer, which is not significant in acrylonitrile polymerization, provides a mode of escape for radicals stuck in or on the surface of dead poly(vinyl chloride). Breakdown of the relationship, in which the increase in rate of polymerization is equated to the surface area of polymer particles, is predicted on particle changes. Flocculation of spherical particles to aggregates, probably relatively loosely packed aggregates, reduces available particle surface as flocculation progresses and as interstices between particles of the floc become filled with polymer. Interstitial polymerization eventually converts loose aggregates into dense ones in which individual particle identities are obscured. The K_1 values of Table I are to be regarded as the ratio of $(P_{\text{capture}})/(P_{\text{escape}})$, in which P_{capture} is the probability of free radical capture by polymer and P_{escape}, the probability of free radical escape from polymer surface by chain transfer to monomer.

The rate expressions of Schindler and Breitenbach and of Arlman and Wagner, like the surface-controlled process, are at best limiting expressions. Unlike the equation relating rate to particle surface area, these analyses fit conversion data by the first two terms of a power series with time as the independent variable. Such treatments are based on a reduction of the rate of termination in the presence of solid polymer, and assumptions are made that a significant percentage of free radicals is actually isolated in the solid polymer unavailable for termination, and that the steady-state hypothesis is applicable.

The incidence of occluded free radicals of long lifetime in the precipitated poly(vinyl chloride) has been recently reported by Magat.[26] This investigator reports significantly long after effects in the polymerization of vinyl chloride initiated by high energy radiation. Bawn[27] has indicated that an appreciable after-effect in vinyl chloride polymerization initiated by weak x-rays is observed only at temperatures (−20°C.) well below the range where poly(vinyl chloride) kinetics have been usually studied. His viewpoint is that ready chain transfer to monomer prevents extensive burial except at very low temperatures where the chain transfer is greatly reduced. The occlusion of radicals is not so large as to isolate free radicals to an extent which is reflected by a marked deviation of the initiator exponent from 0.5 toward 1.0. Acrylonitrile polymerization has been shown to involve extensive occlusion of free radicals (probably 1–10% of free radicals become occluded[19]). The initiator exponent for acrylonitrile polymerization has been reported to be as high as 0.82–0.90, and molecular weights of polyacrylonitriles from these reactions with abnormal initiator exponents exhibit an unusual maximum at about 55°C. No abnormal molecular weight–temperature relationship has been observed in vinyl chloride polymerization in the range between 20–70°C., and deviations of the initiator exponent from 0.5 are much less for vinyl chloride than for acrylonitrile, so that conclusion of a greatly reduced magnitude of free-radical burial in vinyl chloride polymerization seems warranted.

Mechanism of Polymerization for Vinyl Chloride

Experimental results for a number of kinetic investigations of polymerizations in which polymer is insoluble in monomer[1–7,19,23–25] emphasize the dramatic effects of precipitation on the rates of polymerization. The extensive investigations of Bamford and co-workers[19,23,25] on acrylonitrile have demonstrated the occlusion of polymeric free radicals in the insoluble phase and clearly indicated that occlusion of chain carriers results only in part in radical termination or burial. The autoacceleration of polymerization frequently observed in such systems is a consequence of the difference in magnitude of reduction of rate constants for propagation and termination processes because of occlusion. Accessibility of free radicals to monomer can persist under conditions of free-radical enclosure which reduce rates of bimolecular free-radical termination drastically. To summarize, the termination of free radicals is more extensively reduced by entrapment than the propagation rate. It must be emphasized, moreover, that values of both propagation and termination rate constants can change when the free radical is enmeshed in a solid polymer.

Evaluation of the several mechanisms proposed for polymerization of vinyl chloride in the light of knowledge about the effects of heterogeneity on polymerization rates and rate constants leads to a conclusion that the mechanisms presented are deficient not only in their limited success at correlation of experimental results, but also in their implication that single valued, invariant rate constants can characterize a mechanism in a system where physical processes lead to progressive changes in rate constants. The observations of the present investigation, particularly those on the interactions between insolubilized polymer radicals and polymer already formed, indicate that neither the assumption of a "pseudo-steady state" or the use of single-valued rate constants is valid. Bamford[19] and Magat[5] have questioned the validity of the assumption of a pseudo-steady state, and Magat has demonstrated that a nonsteady-state kinetic treatment can correlate the data for vinyl chloride polymerization kinetics. His use of single-valued rate constants is questionable, however, and the mechanism which follows has been devised to fit the known experimental facts. An endeavor will be made to indicate how the several mechanisms already proposed relate to the more general kinetic scheme.

The rate data are consistent with the mechanism of eqs. (15)–(27).

$$I \xrightarrow{k_d} 2R \tag{15}$$

$$R + M \xrightarrow{k_i} M^* \tag{16}$$

with

$$V_i = k_i[R][M]$$
$$= 2fk_d[I]$$

$$M^* + M \xrightarrow{k_p} M^* \tag{17}$$

with

$$V_p = k_p[M^*][M]$$

$$2M^* \xrightarrow{k_T} P \tag{18}$$

with

$$V_T = k_T[M^*]^2$$

$$M^* + M \xrightarrow{k_{tr}} P + M^* \tag{19}$$

with

$$V_{tr} = k_{tr}[M^*][M]$$

$$M^* + P \xrightarrow{k'_{tr}} P^* \tag{20}$$

with

$$V_{tr}' = k_{tr}'[M^*]f[P]$$

$$P^* + M \xrightarrow{k'_p} P^* \tag{21}$$

with

$$V_p' = k_p'[P^*][M]$$

$$P^* + M \xrightarrow{k_{tr}} P + M^* \tag{22}$$

with

$$V_{tr} = k_{tr}[P^*][M]$$

$$P^* + M^* \xrightarrow{k'_T} P \tag{23}$$

with

$$V'_T = k'_T[P^*][M]$$

$$P^* + P^* \xrightarrow{k''_T} P \tag{24}$$

with

$$V''_T = k''_T[\mathrm{P}^*]^2$$

$$\mathrm{M}^* + \mathrm{xy} \xrightarrow{k_{xy}} \mathrm{P} + \mathrm{y}^* \tag{25}$$

with

$$V_{xy} = k_{xy}[\mathrm{M}^*][\mathrm{xy}]$$

$$\mathrm{P}^* + \mathrm{xy} \xrightarrow{k_{xy}} \mathrm{P} + \mathrm{y}^* \tag{26}$$

with

$$V'_{xy} = k_{xy}[\mathrm{P}^*][\mathrm{xy}]$$

$$\mathrm{y}^* + \mathrm{M} \xrightarrow{k_{ri}} \mathrm{M}^* \tag{27}$$

with

$$V_{ri} = k_{ri}[\mathrm{y}^*][\mathrm{M}]$$

In this mechanism are summarized the various reactions which experimental evidence indicates are significant. Distinction is made between "mobile" soluble free radicals M* and occluded or surface-entrapped free radicals P*. The other symbols are I, initiator; R, initiator free radicals; M, monomer; P, polymer; xy, added chain transfer agent; y*, radical from chain transfer agent. For each reaction V gives the differential rate.

Reactions (15)–(18) are the initiation, propagation, and termination reactions of mobile soluble radicals. The equations describe the reactions of low DP polymer free radicals or solution polymerization as in chlorobenzene. Chain transfer to monomer by mobile radicals, eq. (19), or by free radicals on polymer, eq. (22), is the primary molecular weight control and a route by which free radicals on polymer became mobile ones. Reaction (20) concerns the sticking of mobile free radicals on polymer and is not specifically defined kinetically except as being a function of the amount of polymer f[P]. This process includes surface entrapment of mobile free radicals, free radical occlusion by rapid coalescence of a number of small mobile radicals (particularly important in initial polymerization), and penetration of a free radical into the open structure of a large polymer aggregate. An exact definition of f[P] is not easily envisioned, and the relative importance of chain transfer, precipitation, and/or adsorption is undetermined. Equation (21) indicates the propagation of radicals on polymer. A kinetic rate constant k'_p is associated with this process. This rate constant may be equal to or less than k_p for mobile radicals and is probably not single valued depending upon the extent and type of free radical occlusion and the accessibility of the free radical to monomer. Termination processes involving radicals enmeshed in polymer are represented in eqs. (23)–(24). Ready interaction of a stuck free radical with a mobile one eq. (23), is a very probable process for free radicals stuck on polymer surface and may be a predominant termination in systems with large surface areas of preformed polymer. Mutual termination of stuck radicals, eq. (24), is usually considered a very improbable event, but the incidence of ready chain transfer to monomer may favor such a process in vinyl chloride. Chain transfer of a stuck free radical to monomer deep inside a polymer cluster results in a mobile free radical with a limited opportunity to escape the polymer cluster. Its growth to a larger free radical increases its probability of becoming trapped, and it is probable that stuck free radicals can migrate toward one another by several transfer steps to form mobile radicals, which never escape the polymer mesh in which they are formed. The relative importance of the several terminations is contingent not only on the extent of polymerization but also the microscopic morphology of the heterogeneous polymer phase. Both k'_T and k''_T are assumed to be much smaller than k_T due to the lowered mobility of the stuck free radicals.

Chain transfer to an added substance xy is included in eqs. (26) and (27) to indicate the control this agent can have on degree of polymerization of both mobile and stuck free radicals as has been already discussed.

To determine the rate of polymerization in the absence of added chain transfer agent:

$$-d[\mathrm{M}]/dt = V_p + V'_p = k_p[\mathrm{M}^*][\mathrm{M}] + k'_p[\mathrm{P}^*][\mathrm{M}] \tag{28}$$

the concentration of free radicals [M*] and [P*] is required:

$$\begin{aligned} d[\mathrm{M}^*]/dt = 2fk_d[\mathrm{I}] &+ k_{tr}[\mathrm{P}^*][\mathrm{M}] \\ &- k_T[\mathrm{M}^*]^2 - k'_{tr}[\mathrm{M}^*]f[\mathrm{P}] - k'_T[\mathrm{M}^*][\mathrm{P}^*] \end{aligned} \tag{29}$$

$$\begin{aligned} d[\mathrm{P}^*]/dt = k'_{tr}[\mathrm{M}^*]f[\mathrm{P}] - k_{tr}[\mathrm{P}^*][\mathrm{M}] - k'_T[\mathrm{M}^*][\mathrm{P}^*] \\ - k''_T[\mathrm{P}^*]^2 \end{aligned} \tag{30}$$

Substitution of the total free-radical concentration $[R_t]$:

$$[\mathrm{R}_t] = [\mathrm{M}^*] + [\mathrm{P}^*]$$

results in:

$$\begin{aligned} d[\mathrm{R}_t]/dt &= 2fk_d[\mathrm{I}] - k_T[\mathrm{M}^*]^2 - 2k_T'[\mathrm{M}^*][\mathrm{P}^*] - k''_T[\mathrm{P}^*]^2 \\ &= 2fk_d[\mathrm{I}] - (k_T - 2k'_T + k''_T)[\mathrm{M}^*]^2 \\ &\qquad - k''_T[\mathrm{R}_t]^2 - 2(k_T - k''_T)[\mathrm{R}_t][\mathrm{M}^*] \end{aligned} \tag{31}$$

The solution of eq. (31) is not explicit except for specific relationships which permit the elimination of [M*].

Magat,[5] in a kinetic treatment for which he assumes the pseudo-steady state does not apply, has used a single-valued k_T which is equivalent to the assumption $k'_T = k''_T = k_T$. Under these conditions eq. (31) becomes:

$$d[\mathrm{R}_t]/dt = 2fk_d[\mathrm{I}] - k_T[\mathrm{R}_t]^2 \tag{32}$$

This differential is readily solved and has been used to correlate rate data and to estimate k_T/k_p. Values of k_T/k_p of 5–10 are reported which indicate an abnormally slow termination particularly when compared to the solution values of Burnett and Wright.[8] Magat has reported that his kinetc equation does not fit low conversion data, even very accurately determined low conversion data. In light of the more general mechanism, the low conversion deviations are easily explained. At low conversions where free radical mobility is higher, a larger average k_T is required than later in the reaction. The same may be true for k_p. No single-valued kinetic coefficient can fit the experimental data. It is interesting that the mathematical form of the Magat approximation is identical to that for a chemical pre-effect. This author has not directly related the autoacceleration to a chemical pre-effect, although it is implicit in his kinetic derivation. It is important to recognize that the good approximation of the experimental data by this treatment is the consequence of the similarity of the rate expression for the normal chemical pre-effect with invariant rate constants to a rate equation concerned with the kinetic consequences of free-radical sticking. Unfortunately, the very nature of the sticking excludes an exact solution. The good fit of experimental data by the nonsteady-state kinetic treatment by using a single-valued termination constant can be rationalized as strong evidence for a major contribution of cross termination between stuck and mobile free radicals for a significant fraction of the total reaction time. The relative rate constants for propagation and termination by their magnitude exclude a predominant mobile radical termination. The approximation of rates to a half-order catalyst dependence suggests an absence of free-radical burial or at least a very small percentage of free radicals buried. Because of the increased probability of free-radical sticking with higher conversion, the ratio of stuck free radicals to mobile ones increases with conversion; however, the increase in stuck radicals is moderated by chain transfer to monomer, which maintains sufficient radical mobility to effect chain termination.

The kinetic treatments of Bengough and Norrish, Arlman and Wagner, and Schindler and Breitenbach asssume a pseudo-steady state. The limited fit of data by these treatments has already been discussed in detail.

To conclude, we consider the mass polymerization of vinyl chloride to be analogous to that of acrylonitrile, in that the kinetics of both polymerizations are controlled by free-radical sticking on the precipitated polymer phase. A significant difference in the case of vinyl chloride is the ready chain transfer to monomer, which results in greater free radical mobility. In the case of vinyl chloride, as with acrylonitrile, exact kinetic analysis to yield significant rate constants appears to be an elusive and purposeless objective because of the influence of a heterogeneous, continuously varying precipitate that contains a significant fraction of the chain carrying free radicals, and superimposes environmental restrictions on the intrinsic reactivity of the free radicals.

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Résumé

Dans la polymérisation du chlorure de vinyle des radicaux précipitent à la surface ou à l'intérieur des aggrégats de polymère désactivé, partiellement gonflé. La polymérisation sur le polymère solide est caractérisée par une autoaccélération due à une diminution progressive de la vitesse de terminaison. Cette réduction de la vitesse de terminaison est due au fait qu'avec la progression de la réaction et l'accumulation plus grande de polymère, il y a une diminution de la probabilité de transfert de chaîne des radicaux polymériques sur le monomère, pour engendrer un radical mobile qui peut aisément terminer un radical libre occlus ou gelé. De l'apparition des particules de polymère solide dans le système, on a conclu que des radicaux libres précipitent aussi bien à la surface des particules de polymères qu'à l'intérieur de la structure ouverte de ces particules de polymère.

Zusammenfassung

Bei der Polymerisation von Vinylchlorid werden freie Radikale an oder in Aggregaten von partiell gequollenem toten Polymeren gefällt. Die Polymerisation am festen Polymeren wird durch eine Selbstbeschleunigung der Polymerisation durch fortschreitende Herabsetzung der Abbruchsgeschwindigkeit charakterisiert. Diese Herabsetzung der Abbruchsgeschwindigkeit ist dadurch bedingt, dass mit fortschreitender Reaktion und

Anhäufung von Polymerem die Wahrscheinlichkeit einer Bildung eines beweglichen Radikals, welches leicht eine Abbruchsreaktion mit einem okkludierten oder feststeckenden freien Radikal eingehen kann, durch Kettenübertragung der Polymerradikale zum Monomeren abnimmt. Aus dem Aussehen der festen Polymerpartikel im System wurde geschlossen, dass freie Radikale sowohl an der Polymerpartikeloberfläche als auch im Inneren der offenen Polymerpartikelstruktur ausgefällt werden.

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Kinetics of Free-Radical Polymerization of *p*-Vinylbenzyl Methyl Ether: Crosslinking by Initiator Free Radicals

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Synopsis

Kinetics of polymerization of *p*-vinylbenzyl methyl ether at low conversion either in bulk or in benzene have been found to be quite similar to those of the unsubstituted monomer styrene. Rates of polymerization initiated by peroxides or α,α'-azobisisobutyronitrile over the temperature range 50–70°C. have been found to be proportional to [Monomer][Initiator]$^{1/2}$ with an activation energy difference $E_{\text{propagation}} - {}^1/_2 E_{\text{termination}} \approx 6$ kcal./mole. Azo initiation leads to essentially unbranched poly(vinylbenzyl methyl ether) even at very high conversions, whereas initiation of undiluted monomer by diacyl peroxides results in some crosslinking at high conversion. Use of biacetyl as a photoinitiator of polymerization over the temperature range 0–60°C. with either bulk monomer or monomer solutions in benzene has been found in each instance to yield crosslinked, insoluble polymers at low degrees of conversion. Benzene solutions of soluble polymer have been converted to high molecular weight branched polymers by free radicals generated by photolysis of biacetyl, and a substantial preference of methyl free radicals to abstract benzyl hydrogens of poly(*p*-vinylbenzyl methyl ether) rather than add to solvent benzene has been observed.

Studies on mechanisms of polymerization of monomers which contain free-radical reactive substituents have indicated that free-radical chain transfer may result in crosslinking[1,2] or in a different order of polymerization rate on initiator by virtue of degradative chain transfer.[3–5] Huang[6,7] found that benzyl ethers are particularly susceptible to free-radical attack, yet Marvel and Overberger[8] found no evidence of crosslink formation in the free-radical polymerization of optically active *p*-vinyl *sec*-butylbenzyl ether. The *p*-vinylbenzyl grouping has been the basis on which a variety of amine, alcohol,[9] and other functional polymers have been synthesized, and, in the course of a program on functional monomers, a kinetic investigation of polymerization and determination of conditions under which crosslinking of poly(*p*-vinylbenzyl methyl ether) ensues has been carried out.

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EXPERIMENTAL

Materials

p-Vinylbenzyl methyl ether was synthesized by the method of Abramo and Chapin.[9] *p*-(β-Chloroethyl)benzyl chloride was refluxed with excess methanolic potassium hydroxide for 3 hr. and after dilution with water extracted into hexane. The hexane solution was dried, solvent removed, and, after addition of a trace of hydroquinone, the monomer was distilled under vacuum, b.p. 52°C./1–2 mm. On second distillation, a middle cut (50%) of constant boiling point was taken and stored with a trace of hydroquinone under nitrogen at − 30°C. Vapor-phase chromatography established 98% of the *para* and 2% of the *ortho* isomer. Analysis for halogen by the method of Liggert[10] established that the monomer contained less than 0.01% chlorine. Monomer densities were determined and found to be at temperatures indicated in parentheses 0.9681 (26°C.), 0.9570 (39°C.), 0.9471 (50°C.), 0.9412 (59.7°C.), and 0.9369 g./ml. (65°C.).

α,α'-Azobisisobutyronitrile, benzoyl peroxide, and lauroyl peroxide were recrystallized from suitable solvents and vacuum-dried at 25°C. for several days. Benzene, benzyl methyl ether, and biacetyl (Eastman White Label) were distilled from calcium hydride under nitrogen.

Technique for Kinetic Runs

The extent of polymerization was determined by measuring volume change in dilatometers of the type indicated in Figure 1. A solution of initiator in benzene was introduced through the Trubore capillary into B by a long-needled hypodermic syringe. The solvent was distilled off under vacuum, and monomer, after contact with Drierite to remove inhibitor, was introduced into A. After degassing by several freeze-thaw cycles (m.p. ∼−70°C.), under high vacuum, *p*-vinylbenzyl methyl ether was vacuum-distilled into B and cooled in liquid nitrogen. After warming to ambient temperature and introduction of nitrogen to a pressure of 30 cm. of mercury, the contents of B were frozen, and the dilatometer sealed off at C. In runs in benzene, the solvent was distilled under vacuum into B just before the dilatometer was sealed off.

Dilatometer contents were warmed to ambient temperature before complete immersion in a thermostated bath controlled to ±0.01°C. Volume changes were followed with a cathetometer. After each run, polymer was precipitated into hexane containing a trace of hydroquinone. The polymer precipitated as a viscous liquid which was washed free of monomer with hexane, dissolved in chloroform, and reprecipitated into hexane. After drying under vacuum at 50°C., polymer was isolated as a hard, brittle glass. Polymer density was determined in a density gradient column and found to be 1.088 g./ml. at 30°C. Conversions C were calculated from volume change by using experimentally determined correlations of volume change with per cent reaction.

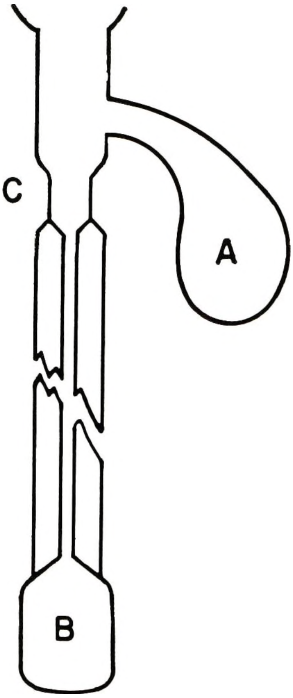


Fig. 1. Dilatometer for kinetic runs.

Dilatometric runs were carried out to no greater extent than $C = 0.40$ because of the appearance of gas bubbles in the viscous polymer. The nature of the gas is not certain, but it was established that the gas was not methane. For high conversions monomer consumption was determined by measurement of the differences in optical densities of solutions of polymer plus monomer in chloroform at 294 and 310 mμ. For solutions up to ~10% in monomer, a linear relationship between the difference in optical densities and monomer concentration was found to hold even in the presence of polymer.

Free-radical reaction of the benzyl hydrogens on polymer was studied by ultraviolet irradiation of solutions of poly(*p*-vinylbenzyl methyl ether) and initiators in benzene in a modified Ostwald viscometer. The solution of polymer and initiator in benzene was sealed off under nitrogen and the flow time for the solution determined. The solution in a thermostated bath (25°C.) was irradiated with a low wattage ultraviolet source and periodic readings of flow time measured.

RESULTS

Kinetics of Polymerization

Typical low conversion data for α,α'-azobisisobutyronitrile-initiated polymerization of undiluted *p*-vinylbenzyl methyl ether at 50°C. are

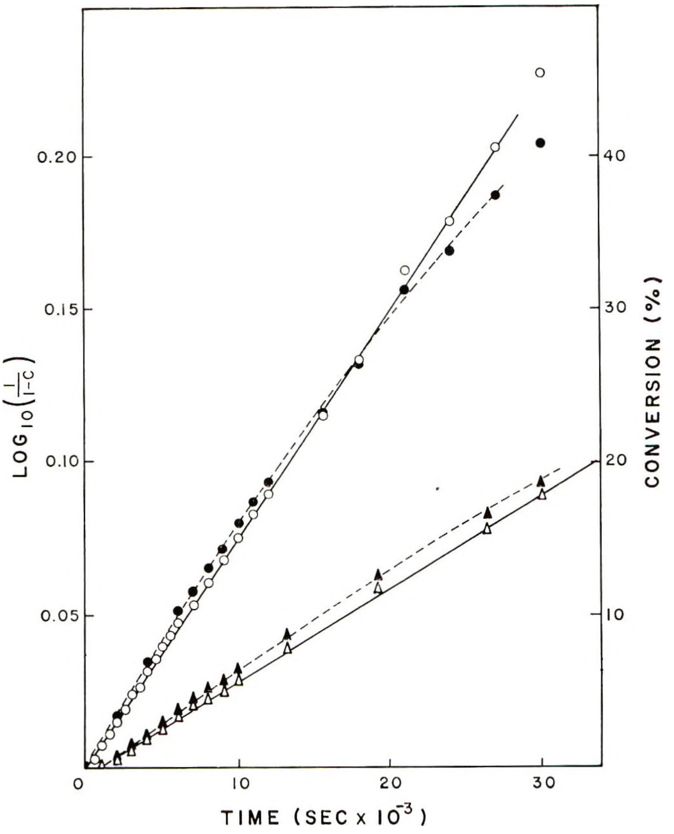


Fig. 2. Polymerization of *p*-vinylbenzyl methyl ether at 50°C. with α,α'-azobisisobutyronitrile initiator: (▲) conversion and (△) log $[1/(1 - C)]$ at [Azo] = 2.03×10^{-3} mole/l.; (●) conversion and (○) log $[1/(1 - C)]$ at [Azo] = 1.17×10^{-1} mole/l.

plotted in Figure 2. In Figure 3, data for benzoyl peroxide-initiated polymerization are presented. Plots of both conversion versus time and log $[1/(1 - C)]$ versus time, which corresponded to a process first-order in monomer, were reasonably linear at low conversion. At higher conversion log $[1/(1 - C)]$ plots were found to be quite linear for all runs up to conversions of about 50% where autoacceleration was observed, probably due to a Tromsdorff effect. To establish the order of polymerization rate in monomer, a series of runs was carried out in benzene at 50°C. over the monomer concentration range 0.965–6.40 mole/l. Figure 4 presents data for the depletion of monomer at constant initiator level in this concentration range, including undiluted monomer (6.40 mole/l.). From the initial slopes, initial rates R_p were determined. These data are plotted in Figure 5. The slope of the log rate versus log monomer plot of Figure 5 was found to be 1.09, approximately first-order in monomer as assumed from the linearity of log $[1/(1 - C)]$ plots for undiluted monomer. The ratio $R_p/[M]$ was found to increase by approximately 30% over the concentration range

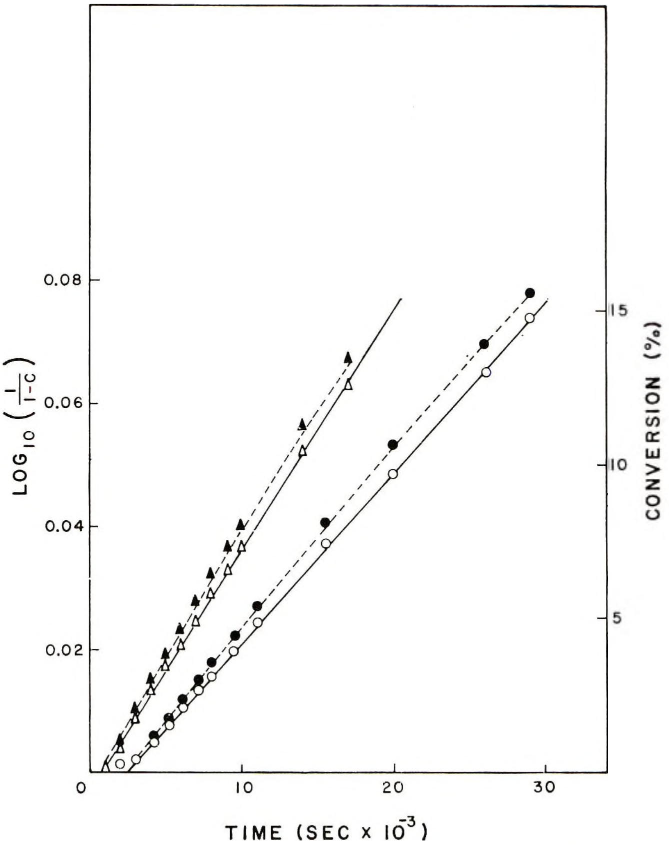


Fig. 3. Polymerization of *p*-vinylbenzyl methyl ether at 50°C. with benzoyl peroxide initiator: (▲) conversion and (△) log $[1/(1 - C)]$ at $[Bz_2O_2] = 7.85 \times 10^{-2}$ mole/l.; (●) conversion and (○) log $[1/(1(1 - C)]$ at $[Bz_2O_2] = 3.77 \times 10^{-2}$ mole/l.

studied, the ratio becoming larger at higher monomer concentration. This is characteristic of styrene polymerization in solution as well,[11] and Henrici-Olive and Olive have ascribed the monomer exponent greater than 1.0 to lowered efficiency of utilization of initiator free radicals in chain initiation in the presence of increasing concentrations of solvent.

To establish the order in initiator concentration, polymerization of undiluted monomer was carried out with α,α'-azobisisobutyronitrile varying from 0.598×10^{-2} to 11.72×10^{-2} mole/l. and benzoyl peroxide from 0.33×10^{-2} to 7.85×10^{-2} mole/l. From the linearity of the rate R_p versus $[\text{initiator}]^{1/2}$ plots of Figure 6, it was evident that the rate of polymerization of *p*-vinylbenzyl methyl ether for low conversion runs was quite normal and involved bimolecular free-radical termination. By using the reported value[12a] of the rate of decomposition for α,α'-azobisisobutyronitrile the ratio of kinetic parameters, $k_p(f/k_T)^{1/2} = 3.05 \times 10^{-2}$ $(\text{l./mole-sec.})^{1/2}$ was calculated. The factor f is the efficiency of initiation. The rate constant ratio for undiluted styrene at 50°C. is[12a] $k_p/k_T^{1/2} = 2.04 \times 10^{-2}$ (l./mole-sec.)$^{1/2}$, so it would appear that the *p*-methoxymethyl group exerts a slight accelerating effect on polymerization.

The variation of initial rate for undiluted monomer at different temperatures is summarized in Table I. From these data we have estimated

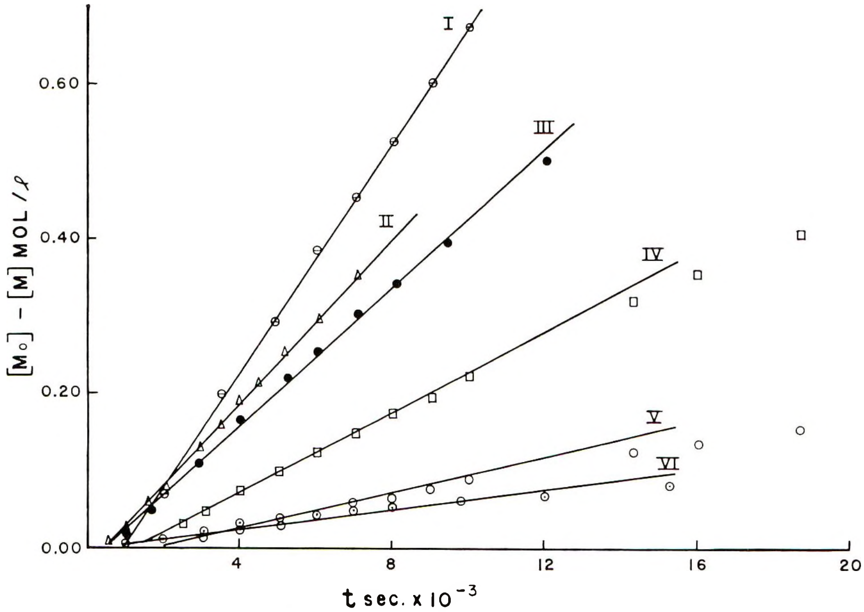


Fig. 4. Polymerization of *p*-vinylbenzyl methyl ether at 50°C. in benzene: Legend: (*I*) $[M_0]$ = 6.40 mole/l. (undiluted *p*-vinylbenzyl methyl ether); (II) $[M_0]$ = 4.81 mole/l.; (*III*) $[M_0]$ = 4.13 mole/l.; (*IV*) $[M_0]$ = 2.70 mole/l.; (*V*) $[M_0]$ = 1.36 mole/l.; (*VI*) $[M_0]$ = 0.96 mole/l. $[M_0] - [M]$ = mole/l. reacted; t = time in sec. [Azo] = 5.3×10^{-3} mole/l. for all runs.

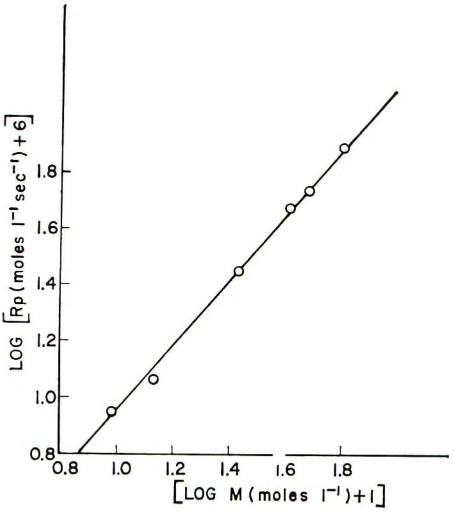


Fig. 5. Rate of polymerization of *p*-vinylbenzyl methyl ether at 50°C. as a function of monomer concentration in benzene.

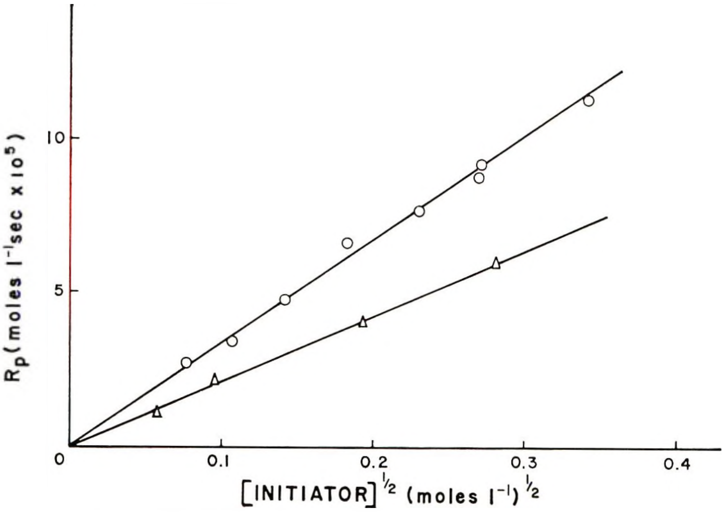


Fig. 6. Rate of polymerization at 50°C. as a function of initiator concentration: (○) α,α'-azobisisobutyronitrile; (△) benzoyl peroxide.

a value of the overall activation energy of polymerization $E_A = 21.2$ kcal./mole.

TABLE I
Rate of Polymerization of *p*-Vinylbenzyl Methyl Ether
([Azo] = 5.3×10^{-2} mole/l. for All Runs)

Temp., °C.	R_p, mole/l.-sec. $\times 10^5$	$k \times 10^5$ [a]
50.0	7.7	5.2
60.0	19.8	13.5
65.0	31.7	21.7
69.8	46.1	31.6

[a] $k = R_p/[M][I]^{1/2}$.

For a value of 30.5 kcal./mole for the activation energy of decomposition for the initiator,[12] $E_p - {}^1/_2E_T \approx 6$ kcal./mole. This value is within the 5.1–6.6 range reported for styrene.[12b]

Free-Radical Reactivity of the Benzyl Ether Substituent

Although the kinetics of polymerization indicated that in major details the polymerization mechanism was essentially the same as for styrene, there were observations which could only be interpreted as the consequences of free-radical reactions involving the benzyl ether function on polymer or monomer. As an example, azoisobutyronitrile-initiated polymerization of *p*-vinylbenzyl methyl ether either in bulk or in benzene solution to conversion as high as 90% resulted in soluble polymers of relatively constant intrinsic viscosity (at constant initial initiator concentration). The

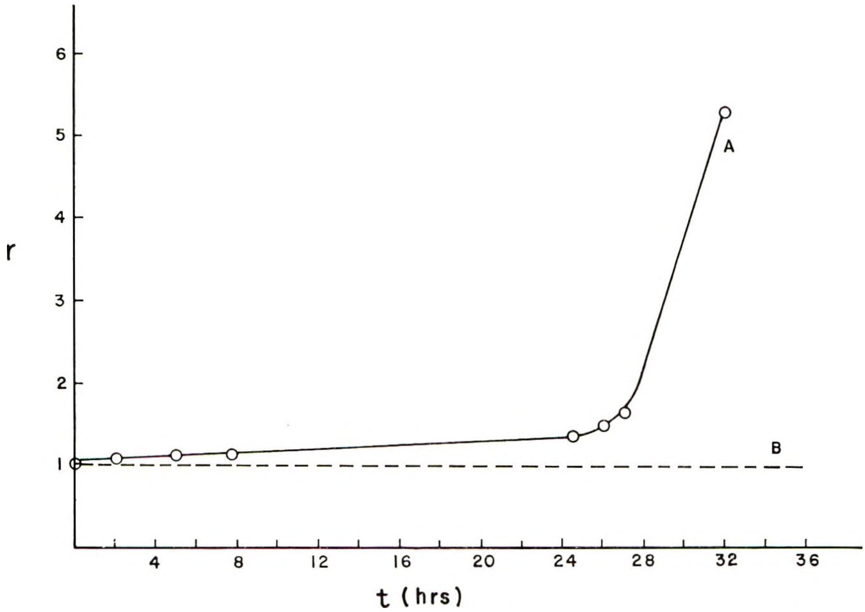


Fig. 7. Change in relative viscosity (r) of poly(p-vinylbenzyl methyl ether) in benzene on reaction with initiator free radicals: (A) photolysis of biacetyl at 25°C.; (B) thermal decomposition of lauroyl peroxide at 50°C.

effects of conversion and of initiator concentration on $[\eta]$ for runs with azobisisobutyronitrile initiator are summarized in Table II. The decrease in $[\eta]$ with increasing [Azo] for bulk polymerization obeys reasonably well (except for high conversion data) the $1/[\eta] \propto [I_0]^{1/2}$ predicted for a mechanism without chain transfer. Initiation of undiluted monomer with benzoyl peroxide or lauroyl peroxide, however, was found to produce limited amounts of insoluble gel at high conversions, particularly for high initiator concentrations. It was also found that photoinitiation with biacetyl as a source of free radicals over the entire temperature range of 0–60°C. for either undiluted monomer or solutions of p-vinylbenzyl methyl ether in benzene always yielded crosslinked insoluble polymer, even at low conversion. Additionally, it was demonstrated that a solution of soluble poly(p-vinylbenzyl methyl ether) in benzene containing biacetyl increased in molecular weight on irradiation. Poly(p-vinylbenzyl methyl ether) (prepared by azo initiation) of initial $[\eta] = 0.51$ was dissolved in purified benzene; [polymer] = 9.0 g./l. The solution was made 0.218M in biacetyl and sealed under nitrogen in an Ostwald viscometer. The solution at 25°C. was irradiated with a relatively weak 4-w. ultraviolet source, and flow times were measured periodically. A graph of the relative flow times $r = t/t_0$, where t_0 = 95 sec., is presented in Figure 7. The length of the period of slow viscosity increase is not considered to be significant because there may have been some terminators or transfer agents, such as chloroform introduced into solution with polymer. Of greater significance is the

TABLE II
Intrinsic Viscosity–Conversion at
[*p*-Vinylbenzyl Methyl Ether]$_0$ = 6.40 mole/l., 50°C.

[Azo], mole/l.	Conversion	[η]
0.186	0.225	0.54
0.186	0.302	0.51
0.186	0.344	0.52
0.186	0.494	0.54
0.186	0.639	0.69
0.0109	0.33	1.50
0.0218	0.29	1.19
0.036	0.36	1.14

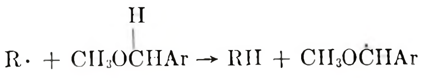
buildup of molecular weight due to a process that we interpret as precrosslink branching.

On thermal decomposition of lauroyl peroxide in the presence of preformed poly(*p*-vinylbenzyl methyl ether) in benzene, no change in the viscosity of solutions was observed. Repeat runs were carried out with the same polymer at the same concentration levels of initiator and polymer used in biacetyl runs. For reaction times at 50°C. as long as 200 hr., no appreciable changes in polymer viscosities were observed.

DISCUSSION

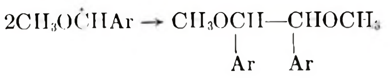
The observations that formation of crosslinked polymer depended on the type of initiator used and that the presence of aromatic solvent suppressed crosslink formation with peroxide initiators require explanation. The absence of crosslinks for α,α'-azobisisobutyronitrile initiator, even at high conversions of undiluted *p*-vinylbenzyl methyl ether, indicates that crosslinking is not caused by either: (*a*) hydrogen abstraction from polymeric units by cyanoisopropyl free radicals followed by polymeric free-radical coupling or (*b*) efficient chain transfer of poly(*p*-vinylbenzyl methyl ether) free radicals to polymer. The gradual increase in molecular weight at high conversions using the azo initiator may, however, be in part due to branching via poly(*p*-vinyl benzyl methyl ether) free-radical chain transfer to polymer as well as to a decrease in the rate of chain termination because of the Tromsdorff effect evident in rate measurements.

Assuming that crosslinks arise by virtue of reactions of the benzyl ether substituent reported by Huang[6] for benzyl methyl ether with alkyl free radicals:



$$\mathrm{R\cdot + CH_3O\overset{\overset{H}{|}}{C}HAr \rightarrow RH + CH_3O\dot{C}HAr} \qquad (1)$$

followed by



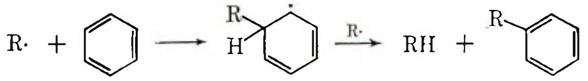
$$\mathrm{2CH_3O\dot{C}HAr \rightarrow CH_3O\underset{\underset{Ar}{|}}{C}H{-}\underset{\underset{Ar}{|}}{C}HOCH_3} \qquad (2)$$

the absence of crosslinks when azo initiator is used is in accord with the observations of Bickel and Waters[13] that cyanoisopropyl free radicals are very unreactive to benzyl methyl ether at 80–90°C. If the mechanism proposed in reactions (1) and (2) pertains, it is to be concluded from our results with azo initiator that poly(*p*-vinylbenzyl methyl ether) free radicals are also relatively inefficient at hydrogen abstraction from the benzyl ether function.

There is evidence to support the hypothesis that crosslinking arises because of the chain transfer reactivity of the benzyl ether substituent. Hiddema[14] has reported a chain-transfer coefficient, $C_{tr} = 6.0 \times 10^{-4}$ for polystyryl radicals reacting with benzyl methyl ether at 68°C. This value is an order of magnitude greater than for toluene or ethyl benzene, and approximately six times the estimated values for cumene[15–17] at the same temperature. Schulz et al.[18] have reported $C_{tr} \approx 5 \times 10^{-4}$ for polystyryl free-radical chain transfer to polystyrene, but these authors also present evidence that the measured value reflects highly reactive structural irregularities in polystyrene. For this reason the cumene structure may represent a better model for the tertiary hydrogen in polystyrene. Comparison of either the measured value of C_{tr} for polystyrene or of that for the model structure of cumene with C_{tr} for the benzyl ether group indicates a considerable reactivity of the benzyl methyl ether substituent to polystyryl free radicals and presumably to other more reactive alkyl or aryl free radicals.

In the absence of solvent benzene, alkyl or acyloxy free radicals from initiators, lauroyl peroxide, or benzoyl peroxide must react with polymer functional groups to a greater degree than the chain carrying poly(*p*-vinylbenzyl methyl ether) free radicals. This is the only explanation consistent with gelation at high conversions with peroxide initiators but not with azo initiation.

We are inclined to ascribe the failure to crosslink poly(*p*-vinylbenzyl methyl ether) by free radicals generated from lauroyl peroxide in the polymer solution in benzene to interception of a substantial fraction of the alkyl free radicals by the aromatic solvent:



(3)

Smid and Szwarc[19] have observed that the species (A) generated by addition of an ethyl radical to benzene is a hydrogen donor in the sense indicated in eq. (3). As such, free-radical intermediate (A) may react with *n*-undecyl free radicals from the initiator and also with α-methoxybenzyl radicals on polymer, thereby consuming most of the free radicals generated by lauroyl peroxide decomposition. Although there are no quantitative data available on the relative reactivities of *n*-undecyl free radicals toward addition to benzene and hydrogen abstraction from substituents on poly-(*p*-vinylbenzyl methyl ether), the observation presented in Figure 7, that the molecular weight of preformed poly(*p*-vinylbenzyl methyl ether) in benzene was essentially unchanged by free radicals generated by decomposition of lauroyl peroxide at 50°C., leaves little doubt that *n*-undecyl free radicals are being consumed essentially quantitatively by other reactions than processes involving hydrogen abstraction from the polymer. The mechanism indicated in eq. (3) may represent the role played by the solvent.

Extensive crosslinking observed in photoinitiated polymerization with biacetyl as photoinitiator is probably related to a faster relative rate of hydrogen abstraction from the polymer by free radicals from biacetyl than by those from lauroyl peroxide. Gel formation at low conversions over the wide temperature range observed requires that methyl (or acetyl) free radicals from the photoinitiator are much more reactive at chain transfer with poly(*p*-vinylbenzyl methyl ether) than *n*-undecyl free radicals. This is a not unreasonable assumption in light of the observations of Szwarc and Binks[20] that in competitive addition to benzene (k_{ad}) and abstraction of hydrogen from isooctane (k_{abs}) the ratios (k_{ad}/k_{abs}) are 0.29 for methyl free radicals, 2.9 for ethyl free radicals, and somewhat larger for *n*-propyl free radicals at 65°C. These data establish that the methyl free radical is possibly as much as an order of magnitude more reactive at hydrogen abstraction from isooctane than other *n*-alkyl radicals. A similar greater reactivity toward abstraction of more reactive benzyl hydrogens on polymer by primary methyl as compared to *n*-undecyl free radicals could account for the observations of this research.

Another factor favoring crosslinking by methyl free radicals in polymerization by biacetyl is the very slow rate of photoinitiation under our experimental conditions. Assuming a molecular weight between 10^4 and 10^5 for polymer of $[\eta] = 0.50$, an order of magnitude estimate of the rate of formation of crosslinks indicates a rate of formation of free radicals on polymer by reaction of free radicals from biacetyl of approximately 10^{-6}–10^{-5} mole free radicals/hr. This rate is several orders of magnitude slower than the rate of decomposition of α,α'-azoisobutyronitrile for lauroyl peroxide at 50°C. If as little as 1 or 2% of total free radicals generated photochemically abstract hydrogen to form polymer radicals (a conservative estimate) which then crosslink, the overall rate of photochemical free-radical generation is still much slower than for the thermal decomposition of the peroxide initiators, and polymer formed in a solvent free system will be of correspondingly higher degree of polymerization for photoinitiation. In view of the greater reactivity of methyl radicals toward polymeric structural units, crosslink formation by initiator free radicals at low conversions is additionally favored by the high molecular weight of initially formed polymer chains.

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Résumé

Des cinétiques de polymérisations du *p*-vinylbenzyléther à basse conversion soit pur dou dans le benzène se sont révelées être complétement similaires à celles du styrène non substitué comme monomère. Les vitesses de polymérisation initiée par les peroxydes ou l'α,α'-azobisisobutyronitrile à une gamme de température de 50 à 70°C étaient proportionnelles à (monomère)(initiateur)$^{1/2}$ avec une énergie d'activation: $E_{\text{propagation}} - {}^1/_2E_{\text{termination}} = 6$ Kcal/mole. L'initiation par l'azo conduit essentiellement à un poly(vinylbenzyl méthyl éther) non ramifié même à haute conversion; tandis que l'initiation de monomère non-dilué par les diacyl peroxydes fournit des liaisons transversales à haute conversion. L'utilisation du biacétyl comme photoinitiateur de polymérisation dans une gamme de température de 0 à 60°C avec soit du monomère pur ou en solution benzènique a fournit chaque fois des polymères pontés insolubles à bas degrés de conversion. Les solutions de benzène du polymère soluble ont été converties en polymères branchés à haut poids moléculaire par des radicaux libres méthyle pour prendre les hydrogénes benzyliques du poly(*p*-vinyl benzyl méthyl éther) plus vite que pour s'additionner au benzène utilisé comme solvant.

Zusammenfassung

Die Kinetik der Polymerisation von *p*-Vinylbenzylmethyläther bei niedrigem Umsatz in Substanz oder in Benzollösung war derjenigem des unsubstituierten Styrols ganz ähnlich. Die Geschwindigkeit der mit Peroxyden oder α,α'-Azobisisobutyronitril im Temperaturbereich von 50 bis 70°C genarteten Polymerisation ist zu [Monomeres] [Starter]$^{1/2}$ mit einem Aktivierungsenergieunterschied $E_{\text{Wachstum}} - {}^1/_2E_{\text{Abbruch}} \approx 6$ Kcal/Mol proportional. Azostart führt auch bei sehr hohem Umsat im wesentlichen zu unverzweigtem Polyvinylbenzylmethyläther; Start von unverdünntem Monomeren mit Diacylperoxyden ergibt dagegen bei hohem Umsatz eine gewisse Vernetzung. Die Verwendung von Biacetyl als Photostarter bei dr Polymerisation von Monomerem in Substanz oder in Benzollösung im Temperaturbereich von 0° bis 60°C liefert in jedem

Fall bei niedrigem Umsatz vernetzte unlösliche Polymere. Benzollösungen der löslichen Polymeren wurden durch photolytisch aus Biacetyl gebildete freie Radikale in hochmolekulare verzweigte Polymere umgewandelt; eine wesentliche Begünstigung der Benzylwasserstoff-abstraktion von Poly-*p*-vinylbenzylmethyläther durch freie Methylradikale gegenüber der Addition an das Lösungsmittel Benzol wurde beobachtet.

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Xylene-Stream Method for Obtaining Thin Polyethylene Specimens for Electron Microscopy

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Synopsis

A new technique is described for obtaining thin specimens from melt-crystallized polyethylene surface for studying the lamellar structure with the electron microscope. The specimen was first backed with carbon-gelatin backing and then the polyethylene side was exposed to a temperature-controlled xylene stream. After dissolving most of the specimen, a very thin layer of polyethylene which shows certain aspects of the original lamellar structure was obtained. Stereoscopic micrographs revealed the structure of polyethylene consisting of curved layers, concave, convex and other forms. These curved layers were identified by analysis of the Bragg fringes to be the crystalline lamellae. A special pattern resembling a spider in shape caused by a spherical crystal was investigated.

INTRODUCTION

The crystalline structure of the interior of the bulk polyethylene has been studied by the ultrasonic disintegration of the polyethylene after digestion with fuming nitric acid.[1] The crystal structure of the lamellar debris thus obtained was thoroughly studied;[2] however, the original spatial arrangement of the lamellae was not established. Organic solvents have been also utilized for the structural study of polyethylene. A melt-crystallized polyethylene was treated with the vapor of various solvents.[3] The difficulties existing in this technique have been also reported.[4] A multilayered polyethylene single crystal crystallized from a dilute solution has been partially dissolved with the solvents to obtain a detachment replica.[5] However, the procedure has not been successful for obtaining a specimen from the surface of bulk polyethylene.

A new technique is developed for obtaining a thin specimen from the surface of melt-crystallized polyethylene by evaporating the carbon on the surface, backing the treated carbon with gelatin, and then dissolving the most of the polyethylene with a xylene stream under controlled temperature.

EXPERIMENTAL

A commercial linear polyethylene in pellet form was melted in a glass capsule in vacuum and crystallized at 127°C. for a week. The crystal-

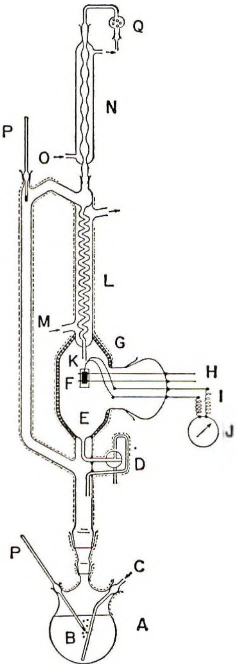


Fig. 1. Streaming solvent exposure apparatus: (A) distilling flask; (B) xylene; (C) air inlet; (D) three-way cock for flow rate determination; (E) sample chamber; (F) specimen; (G) heating tapes for sample chamber; (H) specimen support, tungsten wire 1 mm. dia.; (I) thermistor lead, tungsten wire 1 mm. dia.; (J) temperature indicator; (K) thermistor; (L) Graham condenser, temperature-controlled oil circulating through the outer jacket; (M) oil inlet; (N) Allihn condenser, water-cooled; (O) water inlet; (P) thermometer; (Q) drying tube. Dotted lines indicates insulation.

lized polyethylene block having a free surface was taken out of the capsule. A flat block measuring 10 mm. × 15 mm. in area of the free surface and 3 mm. in thickness was cut out from the crystallized block. The freely crystallized surface was backed with a carbon-gelatinbacking by the method previously reported.[6] After the gelatin was well air-dried, the uncoated polyethylene side was further cut to a uniform thickness of approximately 0.5 mm. The specimen thus prepared was then placed in the apparatus shown in Figure 1. The uncoated polyethylene side of the specimen was exposed to a stream of refluxing xylene. The temperature of the xylene was maintained within ±0.3°C. of an optional temperature between 108 and 110°C. by the oil circulating through the outer jacket of the condenser. A thermistor attached to the specimen detected the temperature of the streaming xylene flowing over the specimen. The sample chamber was also maintained at the same temperature as the xylene stream by heating tapes. The flow rate of the xylene was approximately 30 ml./min. After approximately 10 min. exposure, the temperature of the xylene stream was lowered to 70°C. to avoid any deposition of the dissolved polyethylene over the specimen when the specimen is taken out. When the specimen was

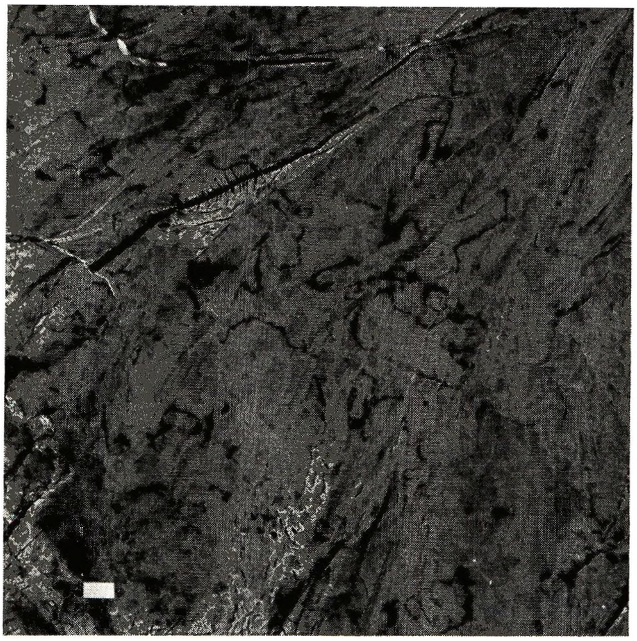


Fig. 2. Polyethylene surface remaining from the exposure to streaming xylene. Lamellar structure and Bragg fringes are noted. Bright field. The scale shows 1 μ.

taken out for visual inspection, the polyethylene in the central area where the action of the solvent had been strongest appeared to have been thoroughly removed. A very thin layer of polyethylene, however, still existed on the carbon–gelatin backing. The gelatin backing was then removed by the method described[6] except for the use of polystyrene backing instead of methyl methacrylate, and further treated with 5% sodium hydroxide solution to effect a thorough removal of any remaining gelatin. The resulting thin layer of polyethylene on the carbon film, representing the free surface of the crystallized polyethylene block, was subjected to the electron microscopic examinations.

RESULTS AND DISCUSSION

Observation of Thin Layer Specimen

A typical electron micrograph is shown in Figure 2, which shows presence of the thin layer of polyethylene remaining on the carbon film in various thickness. The direction of the streaks observed over the entire field of Figure 2 is not related to that of xylene flow. The thin layer of the polyethylene appears in layers of lamellae along with dark fringes. Most of these lamellae were found to show wavy forms with local convex or concave shapes. The crystal orientation of the lamellae was examined by electron diffraction; results are shown in Figure 3. The direction of streaks running diagonally from the upper right to the lower left corner of the brack-

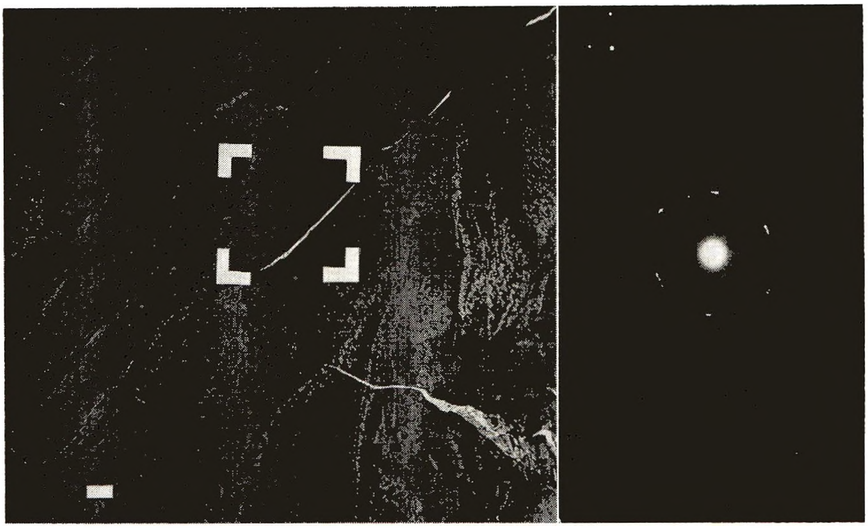
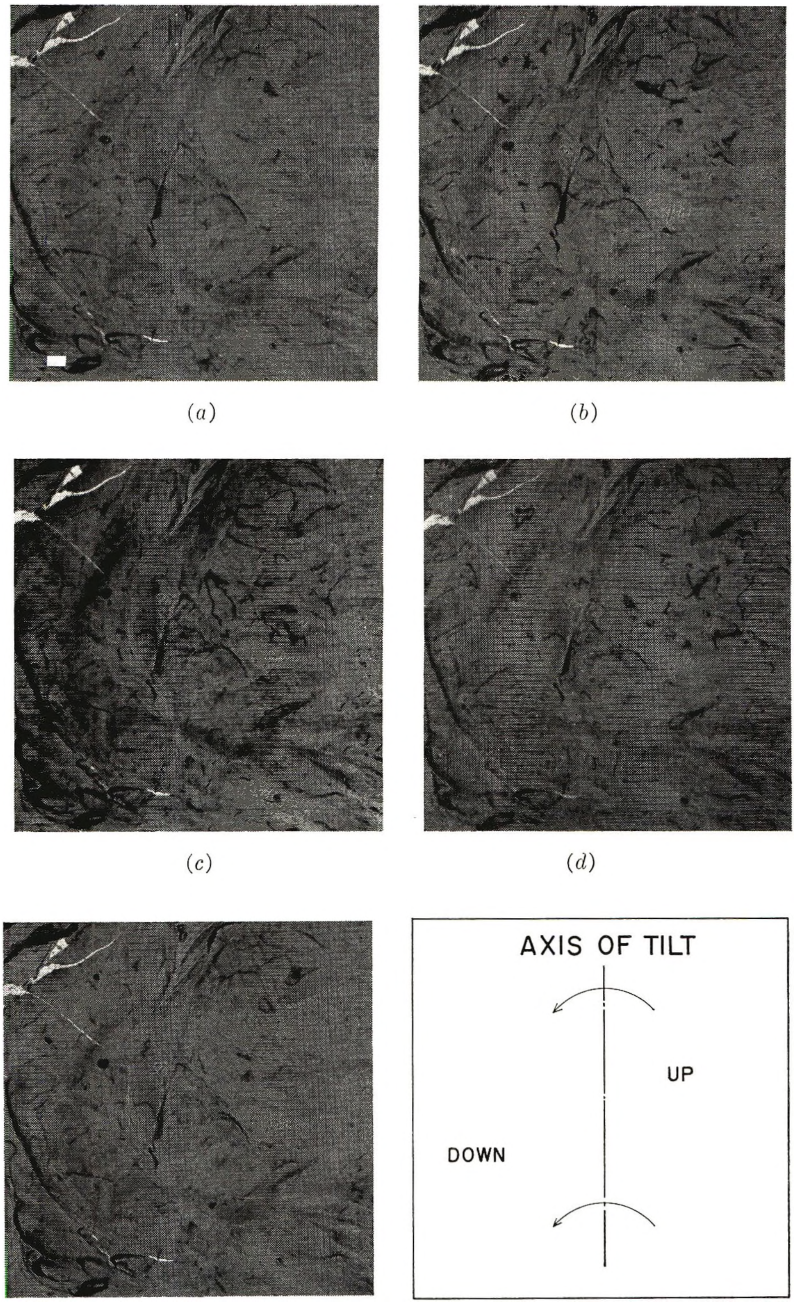


Fig. 3. Crystal orientation of polyethylene surface. Diffraction pattern corresponds to the bracketed area of the electron micrograph. Two white lines are due to cracks in the carbon.

eted area agrees with the *b* axis[7] as shown by the corresponding diffraction pattern. This proves that the original crystal orientation in the melt-crystallized polyethylene surface has not been altered during the course of the xylene stream exposure.

Bragg Fringe Due to Curved Lamella

The dark fringes were examined separately as shown in Figure 4 and proved to be the Bragg fringes caused by the crystalline structure of curved lamellae. The electron micrographs in Figure 4 were taken at various tilt angles of a specimen. As the observed plane was tilted, most of the dark fringes continuously changed both their positions and forms within a certain boundary and then entirely disappeared when they moved out of the boundary. Also, any of the two photographs in Figure 4 can be used as a set of stereoscopic photographs for the observation of waving lamellae. A certain type of curved lamella is considered to be the cause for the dark Bragg fringes or extinction contour lines in the bright field which change their positions and forms according to the degree of the tilt angle. The shift of the Bragg fringes resulting from the tilting is explained in Figure 5. As a convex lamella shown by its cross-section at position A is tilted to position B, a group of planes making the Bragg angle with the electron beams shift from position C to position D, resulting in the corresponding movement of the Bragg fringes. When the lamella is concave, the Bragg fringes will shift to the opposite direction. The distance of the displacement of each fringe line is related to the radius of curvature of the lamella and also to the angle between the tilt axis and the reflecting plane. The molecular chains packed within each lamella are locally so oriented that the



(a) (b)

(c) (d)

(e) (f)

Fig. 4. Shift of Bragg fringes resulting from the specimen tilt: (*a*) starting position; (*b*) tilted, 3.3°; (c) tilted, 6.6°; (*d*) tilted, 10°; (*e*) returned to starting position; (*f*) axis of tilt. Most of the Bragg fringes shift their positions and forms as the specimen is tilted. Any two combination among (*a*)–(*d*) can be also used as a set of stereoscopic photographs.

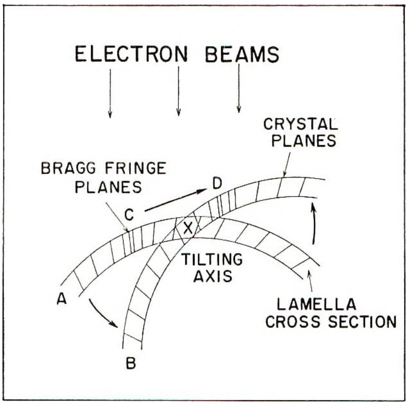
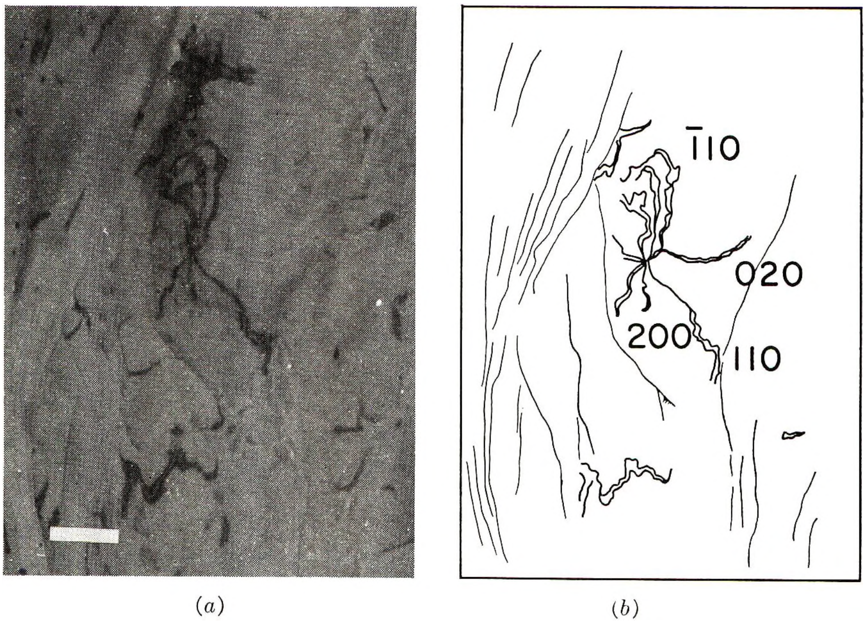


Fig. 5. Cross-sectional view of a curved lamella, explaining the shift of Bragg fringe by tilting. When the lamella in position A is rotated to the position B, the Bragg fringe caused by the planes position C move to the position D.

axes of the chains always maintain a certain definite angle with the curving surface of the lamella. This is analogous to the forced curving of a lamella having a staggered arrangement of molecular chain.

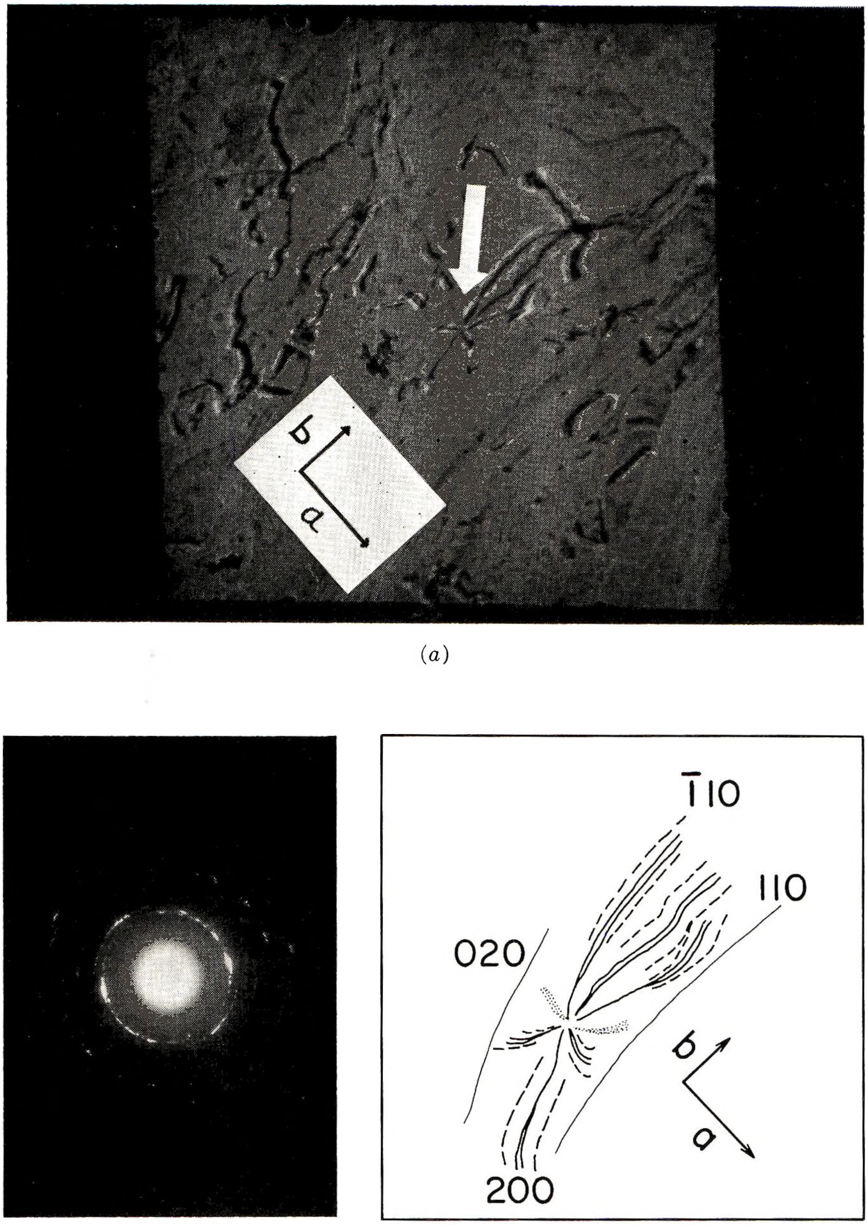
Spider-Shaped Fringes

A peculiar pattern of Bragg fringes resembling a spider in shape is observed on Figure 6*a*. The electron micrograph showed four pairs of



(*a*) (*b*)

Fig. 6. (*a*) Spider-like fringes indicating either a concave or a convex lamella, four double lines crossing at one point; (*b*) index for each line is given in the sketch.



(*a*)

(*b*) (*c*)

Fig. 7. Indexing the spider-like fringes: (*a*) limited area electron micrograph (*a* and *b* axes shown in the field indicate the predominant crystal axis of the entire field; the spider-like fringe is indicated by an arrow); (*b*) electron diffraction of (*a*); (*c*) sketch for the spider-like fringe indicated by the arrow in (*a*). Solid lines represent dark fringe lines and dotted lines the bright lines. Electron beam reflected by the parallel crystal planes cause the dark and bright lines. Bright lines shift from the dark lines along the direction perpendicular to the reflecting planes. The planes can be indexed when the *a* and *b* axes are known.

double fringes, all crossing at one point. Each pair of double fringes was indexed as shown by the Figure 6*b*. The intensity of the observed Bragg fringes in Figure 6*a* decreased the order 110, 200, 020, with 020 remarkably low in intensity. At the crossing point of these fringe lines the *c* axis of the crystal is parallel to the direction of the electron beam. These spider shapes were observed only occasionally in the study.

Indexing the Spider-Shaped Fringes

The indexing of the fringes of Figure 6 was performed by the following procedure, which depended on an indirect method beause of the delicacy of the Bragg fringes when exposed to the electron beams. A similar spider pattern on a different specimen is indicated by an arrow on a limited area electron micrograph shown in Figure 7*a*. The diffraction pattern obtained from the entire field of Figure 7*a* including the spider shape is given in Figure 7*b*. According to the diffraction pattern, the axes of the crystals of polyethylene predominate along the *a* and *b* axes, as indicated in Figure 7*a*. Here, the electron beams deflected by the crystalline planes resulted in bright images on both sides of the individual dark fringes. The displacement of the electron beams from the dark fringes to the bright images must have occurred mostly in the direction perpendicular to the (110) planes. For detailed discussion, the particular spider pattern is enlarged in the separate sketch shown in Figure 7*c*. The bright images for each of four dark lines shown by dotted lines in the sketch. It is assumed that the crystal axes *a* and *b* determined on the entire field of Figure 7*a* are also applicable to the spider shape under discussion. The direction of the shift from each dark line to the corresponding bright lines, perpendicular to the reflecting planes, agrees with the respective vector from the origin to the diffraction spot in Figure 7*b*. Therefore, the deflection of the electron beams from the dark fringes toward the bright images along the *a* axis must have been caused by a pair of planes indexed (200) and ($\bar{2}00$) and along the *b* axis by (020) and ($0\bar{2}0$) as shown in Figure 7*c*. The remaining two fringes are caused by two pairs of planes indexed as (110), ($\bar{1}\bar{1}0$), ($1\bar{1}0$), and ($\bar{1}10$). The double lines are caused by the curving of the lamella. Based on the above analysis on the spider-shaped pattern, indexing for Figure 6 is performed. Actually the 110 and $\bar{1}10$ in Figure 7*c* are reversed in Figure 6*b*, since as a result of the stereoscopic analysis it is found that the spider shape in Figure 7*c* is caused by a lamella in the form of a saddle and that in Figure 6*b* by a sphere.

Many other Bragg fringes not limited to the spider-shaped ones can be similarly indexed based on the direction of the lamella edge streaks (*b* axis) and also on the direction of the parallel shift in fringes.

Examination of the Xylene-Stream Method

A close visual observation of the polyethylene specimen after the exposure to the xylene stream revealed that the dissolution progressed either from its exposed surface or along a certain plane of cleavage existing within the thin

Fig. 8. Replica from free surface after xylene-stream exposure. Partial dissolution of the polyethylene surface lamellae is observed (× 21,000).

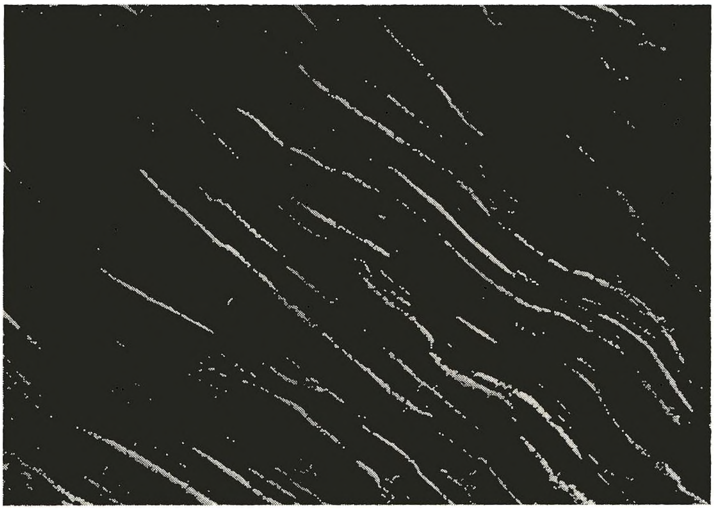


Fig. 9. A cross-sectional view of the piled-up lamellae obtained by the reported method, showing lamellar structure (× 24,000).

layer of polyethylene. To investigate the dissolution process of a lamella, a separate examination was carried out. A flat block cut from the melt-crystallized polyethylene was exposed to the xylene stream without the backing, the free surface being exposed to the flow of xylene for 30–60 sec. A surface replica of the exposed area showed a partial dissolution of the lamella as shown in Figure 8. The smooth areas represent the original surface of the undissolved lamellae, while the rough areas represent the newly exposed lamellae after the upper lamellae have been dissolved. A close study of Figure 8 supports the view that the dissolution of an exposed lamella starts from its edges and proceeds inward within its boundary. Thus, after the uppermost lamella has been dissolved, the second lamella surface is exposed relatively intact. Figure 9, showing a cross-sectional view of the piled up lamellae, was obtained by the carbon–gelatin backing method. Here, the dissolution of the lamellae seems to have followed a certain uniform process. It is believed, therefore, the reported method is capable of obtaining specimens fairly representative of the original lamellar structure.

No information is available now as to the extent of the alteration of lamellar thickness or the change in chain inclination caused as a result of the exposure of the specimen to the hot xylene. Further investigation is being made on this subject. The crystal orientation of the original polyethylene, however, is found to be unaltered as supported by the results of the examination shown in Figure 3. In addition, no precipitations of the dissolved polyethylene were noted under the exposure conditions described herein.

The method reported herein is not applicable to drawn polyethylene in studying the surface structure because of the relaxation of the material. The applicability of this method to quenched polyethylene has not been fully investigated yet. This technique is believed helpful for obtaining the thin specimens from melt-crystallized polymers.

The author expresses his thanks to Mr. H. Noake and Mr. M. Kizaki for useful discussions and encouragements in this work and is also grateful to Mr. S. Mitsuhashi for the offer of his facilities, and to Mr. M. Yoshioka for his assistance in this study.

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Résumé

Une nouvelle technique a été décrite pour obtenir un spécimen mince à partir d'une surface fondue d'un polyéthylène cristallisé pour étudier sa structure lamellaire en utilisant le microscope électronique. Tout d'abord ce spécimen a été doublé avec une doublure en carbone–gélatine et la paroi latérale de ce pollyéthylène a été exposée à un courant de xylène dont la température a été contrôlée. Après de dissolution de la plupart de spécimen, on a pu obtenir une très mince couche de polyéthylène présentant des divers aspects de la structure originelle lamellaire. Des micrographes stéréoscopiques révèlent que la structure de ce polyéthylène est constituée par des couches courbées en concave ou en convexe ou aux autres formes. Ces couches courbées ont été identifiées comme en étant une lamelle cristalline par des résultats obtenus avec des analyses de la bordure de Bragg. Un modèle spécial ressemblant à la forme d'arraignee causé par le cristal sphérique a été examiné.

Zusammenfassung

Ein neues Verfahren zur Gewinnung dünner, aus der Schmelze kristallisierter Polyäthylenoberflächenproben zur elektronenmikroskopischen Untersuchung der Lamellenstruktur wird beschrieben. Die Probe wurde zunächst auf der Oberfläche mit einem Kohle-Gelatinefilm beschichtet und die Polyäthylenseite dann dem Xylol-Strom ausgesetzt, dessen Temperatur reguliert wurde. Nach Auflösen des grössten Teils der Probe wurde eine sehr dünne Polyäthylenschichte erhalten, die gewisse Aspekte der ursprünglichen Lamellenstruktur erkennen liess. Die stereoskopischen Mikroaufnahmen zeigten die aus gebogenen Schichten in konkaven, konvexen und anderen Formen bestehende Struktur des Polyäthylens. Diese gebogenen Schichten wurden an Hand der Analyse der Braggschen Streifen als die kristallinen Lamellen identifiziert. Eine spezielle, durch einen kugelförmigen Kristall verursachte spinnenartige Figur wurde untersucht.

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Low Molecular Weight By-Products in the Ziegler Polymerization of Higher Terminal Olefins

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Synopsis

For the polymerization of *n*-octadecene-1 with catalysts derived from titanium tetrachloride and triethylaluminum, it has been shown that, in addition to polymerization of the olefin, the formation of isomerized olefin occurs. The latter is predominantly *trans*-*n*-octadecene-2 and its formation is favored by increase in Al:Ti mole ratio, in catalyst concentration, and in reaction temperature. It has also been shown that 1,1-disubstituted ethylene is present in the nonpolymeric reaction products. The influence of added *trans*-*n*-octadecene-2 or *trans*-*n*-octadecene-7 on the polymerization of *n*-octadecene-1 has been studied, and it is shown that the 2-isomer has the more pronounced effect on polymer yield and intrinsic viscosity. It has also been shown that no significant copolymerization of terminal with nonterminal octenes or octadecenes occurs under these conditions. Results indicate that, in polymerizations of this kind, the interaction of catalyst with isomerized monomer is probably an important factor in determining polymer yield and molecular weight. The isomerization reaction is also of interest as a general preparative method for *trans*-2-olefins.

INTRODUCTION

The occurrence of isomerization of monomer in the presence of the Ziegler catalyst has been demonstrated in the polymerization of butene-2, giving polymers of essentially polybutene-1 structure,[1] and in the polymerization of (*n*-1) methyl-1-alkenes (e.g., 4-methylpentene-1), yielding polymers having structures different from those expected from polymerization of a terminal olefin.[2] Conversion of terminal to nonterminal olefin (the latter being recovered from unpolymerized matter) was noted by Marvel and Rogers during the polymerization of *n*-octadecene-1 with Ziegler catalysts.[3] Medalia et al. detected small amounts of 1,2-disubstituted ethylene during the polymerization of butene-1 with titanium tetrachloride–triethylaluminum, but do not seem to have reported details of any further investigation.[4] The authors have already reported the presence of both *trans*-1,2-disubstituted ethylene and 1,1-disubstituted ethylene in unpolymerized matter from the polymerization of *n*-octadecene-1 with titanium tetrachloride–triethylaluminum,[5,6] and this paper discusses further work in this field.

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EXPERIMENTAL

Reagents

n-Octadecene-1 was prepared as described in a previous paper.[7]

The *trans*-*n*-octadecene-2, b.p. 124°C./0.05 mm., f.p. 14.6°C., n_D^{20} 1.4470, was obtained as a by-product from the polymerization of *n*-octadecene-1 with a catalyst derived from titanium tetrachloride and triethylaluminum (details in later section).

The internal olefin formed by heating *n*-octadecan-1-ol with phosphorus pentoxide (excess) at 300°C. for 24 hr. had physical constants (b.p. 222°C./72 mm., f.p. −3.6°C., n_D^{20} 1.4465, d_4^{20} 0.7877) closely resembling those previously reported for *trans*-*n*-octadecene-7,[8] and is referred to as such throughout this paper. It was fully appreciated that other homologs could be present, but it was not considered that these significantly affected our results, these being the effects of 2-isomer and isomer with the double bond much nearer the center of the chain.

Both nonterminal olefins were examined by infrared spectrosopy and gas chromatography. The position of the double bond in the 2-isomer was determined by ozonolysis, for which a stream of oxygen containing ozone (approx. 5%) was passed through a solution of the sample in chloroform at −22°C. for $1^1/_2$ hr. The white ozonide, after hydrolysis by heating with water for $1^1/_2$ hr. at 70°C., afforded acetaldehyde as the only product volatile at room temperature and atmospheric pressure. Examination of the nonvolatile matter (after removal of solvents) by gas chromatography revealed two main peaks, one in a position characteristic for a C_{18} hydrocarbon and probably due to *n*-octadecane from the original sample, the other presumably due to *n*-hexadecaldehyde.

Polymerization Procedure

This has been described in an earlier paper,[6] and has been modified only by the introduction of the nonterminal olefin in various amounts before the addition of catalyst components.

Examination of Nonpolymeric Reaction Products

Solvents were removed by fractional distillation and the residue examined by infrared spectroscopy and gas chromatography.

Internal olefin and terminal olefin in the unpolymerized matter were estimated from their respective infrared absorbances at 965 cm.$^{-1}$ (due to *trans*-1,2-disubstituted ethylene) and 910 cm.$^{-1}$ (due to terminal unsaturation).

Loss of unsaturation in unpolymerized matter was detected by iodine value, determined by Hanus' method.[9]

RESULTS AND DISCUSSION

Our earlier studies have shown that, for the polymerization of *n*-octadecene-1 with titanium tetrachloride–triethylaluminum catalyst systems,

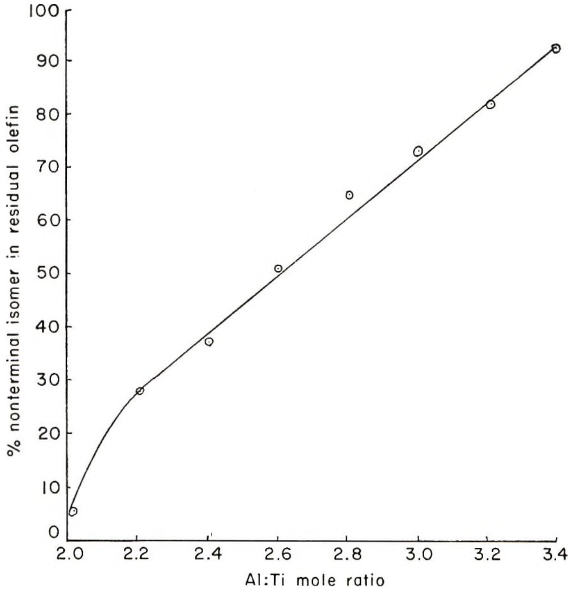


Fig. 1. Results obtained by infrared examination of acetone-soluble material from the polymerization of *n*-octadecene-1 with $TiCl_4$–$AlEt_3$ (30 hr., 25°C., $TiCl_4$:monomer mole ratio 0.035:1).

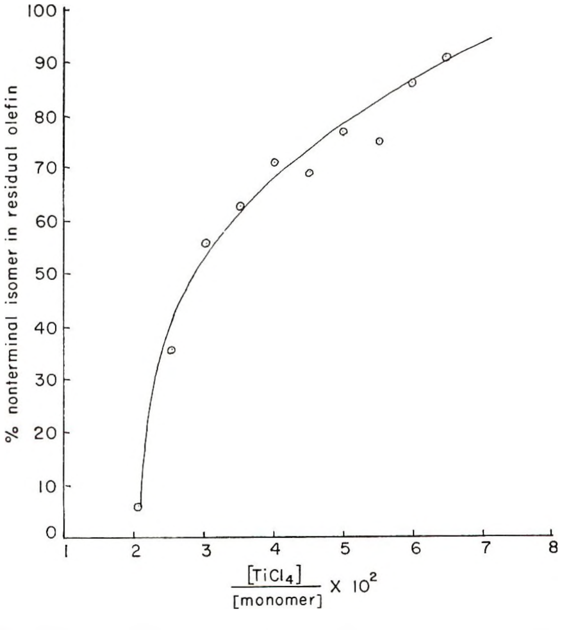


Fig. 2. Results obtained by infrared examination of acetone-soluble material from the polymerization of *n*-octadecene-1 with $TiCl_4$–$AlEt_3$ (30 hr., 25°C., Al:Ti mole ratio 2.8:1).

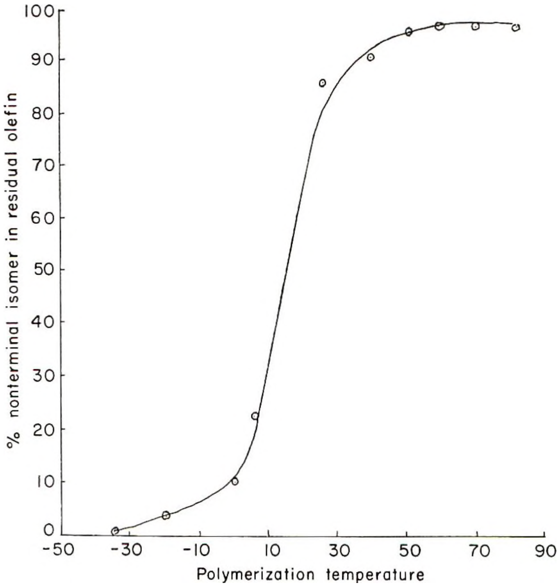


Fig. 3. Results obtained by infrared examination of acetone-soluble material from the polymerization of *n*-octadecene-1 with $TiCl_4$–$AlEt_3$ (72 hr., Al:Ti mole ratio 2.8:1, $TiCl_4$:monomer mole ratio 0.035:1).

both *trans*-1,2-disubstituted ethylene and 1,1-disubstituted ethylene are present in the nonpolymeric products.[5]

Further examination of the unpolymerized matter, using fractional distillation, infrared spectroscopy, and gas chromatography (Apiezon L on Celite 545 at 225°C.) has indicated the internal olefin and vinylidene compounds to be C_{18} and C_{20}, respectively. Some loss of unsaturation, as shown by iodine value determination, had occurred. This would seem to be in agreement with the findings of Marvel and Rogers, who have detected, using infrared spectroscopy, losses in unsaturation of olefin recovered from the polymerization of *n*-octadecene-1 with titanium tetrachloride–triisobutylaluminum.[3]

The olefinic C_{18} product was shown, by ozonolysis and infrared spectroscopy, to be mainly *trans*-*n*-octadecene-2, a result which supports the findings of Marvel and Rogers,[3] who have detected *trans*-*n*-octadecene-2 and *trans*-*n*-octadecene-3 in the polymerization of *n*-octadecene-1 with titanium tetrachloride–triisobutylaluminum.

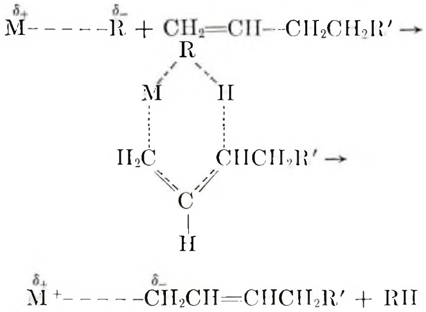
Using *n*-octadecene-1 and *trans*-*n*-octadecene-7 as reference materials, we have approximately determined, by infrared spectroscopy, the proportion of nonterminal to terminal isomer present in unpolymerized material, while varying polymerization conditions. Thus, we have found that the proportion of nonterminal to terminal olefin increases with Al:Ti mole ratio (Fig. 1), catalyst concentration (Fig. 2), and reaction temperature (Fig. 3). The two latter factors have been noted as potential promoters of isomerization in the polymerization of deuterated propylene.[10]

We have also shown that certain conditions (Al:Ti mole ratio 2.8:1, $TiCl_4$:monomer mole ratio 0.05:1, reaction temperature 60°C., reaction time 72 hr.) afford *trans-n*-octadecene-2 in 40% yield, giving less than 5% vinylidene compound. Some saturated C_{18} compound was present with the 2-olefin but was regarded as inert diluent for future experiments with the 2-olefin.

Suggested Mechanisms for Formation of Low Molecular Weight Liquid Products in Ziegler Polymerization

Our work has shown that only the solid phase of a titanium tetrachloride–triethylaluminum catalyst isomerizes *n*-octadecene-1 to its 2-isomer. No *cis–trans* isomerization or polymerization occurred when a mixture of *cis* and *trans-n*-octene-2 was added to the above catalyst at room temperature. However, Schimizu et al. have reported *cis–trans* isomerization during the polymerization at 60°C. of *n*-butene-2 with a titanium tetrachloride–triethylaluminum catalyst.[11]

Marvel and Rogers have suggested mechanisms for the isomerization of terminal olefin to the 2-isomer in the presence of the Ziegler catalyst.[3] They propose that isomerization occurs, via formation of a cyclic complex, at the M--R bond of the catalyst, where R is postulated to be H or alkyl.



$$\overset{\delta_+}{M}\text{-----}\overset{\delta_-}{R} + CH_2{=}CH{-}CH_2CH_2R' \rightarrow$$

$$\overset{\delta_+}{M}{}^{+}\text{-----}\overset{\delta_-}{C}H_2CH{=}CHCH_2R' + RH \qquad (1)$$

By a study of the effect of time on the polymerization of *n*-octadecene-1 with titanium tetrachloride–triethylaluminum, we have shown that mon-

TABLE I
Results from the Polymerization of *n*-Octadecene-1 with $TiCl_4$–$AlEt_3$[a]

Reaction time, hr.	Polymer yield, %	Internal isomer in residual *n*-olefin, %
1	23	12
4	34	20
6	39	20
8	47	28
12	55	45
24	57	60
30	56	70

[a] 30 hr., Al:Ti mole ratio 2.8:1, $TiCl_4$:*n*-octadecene-1 mole ratio 0.035:1.

omer is still isomerized after polymer yield has reached a constant value (Table I).

It could therefore be that, considering Marvel and Roger's mechanism, R is mainly H, and the hydride which remains after a termination reaction involving hydride ion transfer is more reactive to monomer isomerization than polymerization.

Effects of Added Nonterminal Olefin on the Polymerization of Higher Terminal Olefins with Titanium Tetrachloride–Triethylaluminum

Mixtures of *n*-octadecene-1 and *trans*-*n*-octadecene-7 were polymerized at 25°C. and the resulting polymers examined by infrared spectroscopy. Quantitative measurements of absorbance A at 1465 cm.$^{-1}$ (C—H deformation of —CH_2— group) and 1380 cm.$^{-1}$ (C—H deformation of C—CH_3 group) showed that, for all the proportions of nonterminal to terminal olefin investigated, the polymer had essentially the same ratio of methyl to methylene groups (Table II).

Another experiment, in which mixtures of *n*-octene-1 and *n*-octene-2 were polymerized, gave similar results (Table III).

TABLE II
Results from the Polymerization of Mixtures of *trans*-*n*-Octadecene-7 and *n*-Octadecene-1 with $TiCl_4$–$AlEt_3$

Mole ratio of nonterminal: terminal olefin	$\frac{A_{1380}}{A_{1465}}$
0	1.29
0.66	1.29
1.0	1.28
1.5	1.28
4.0	1.29
∞	No polymer formed

It was therefore concluded that no significant copolymerization occurs under the prevailing conditions. However, results in Table III do not rule out the possibility that *n*-octene-2 isomerizes to the terminal isomer and then polymerizes to yield polyoctene-1. However, conditions for the isomerization of 2-olefin to 1-olefin, which have been reported by other workers for *n*-butene-2 and *n*-pentene-2,[1,11] differ greatly from those used during the current work, and so it is unlikely that such a reaction occurs in this case.

Moreover, we have found that neither *trans*-*n*-octadecene-2 nor *n*-octene-2 (*cis*–*trans* mixture) are polymerized under the conditions used throughout these investigations.

We have shown that *trans*-*n*-octadecene-7 prepared by the dehydration of *n*-octadecan-1-ol with phosphorus pentoxide, and *trans*-*n*-octadecene-2 recovered from polymerizations already mentioned, have differing effects on the polymerization of *n*-octadecene-1 at 25°C.

The 7-isomer significantly decreases polymer yield only if present in greater concentration than the terminal olefin, whereas the 2-isomer has a much greater effect. Replacement of the nonterminal isomers by cyclohexane produced negligible effects on polymer yield. Increasing amounts of the 2-isomer caused a decrease in polymer intrinsic viscosity, whereas an increase was detected when this was replaced by the 7-isomer. Replacement of nonterminal olefin by cyclohexane gave a small increase in polymer intrinsic viscosity. Results are summarized in Table IV, from which no comparison should be drawn between individual figures quoted for *trans*-*n*-octadecene-2–*n*-octadecene-1 mixtures and those given for the other two systems. The polymers were prepared at different times, and the difference in intrinsic viscosities is most probably due to variation in experimental conditions. These results would seem to be in qualitative agreement with those of Coover, who has reported that the addition of *n*-octene-2 to a Ziegler polymerization reduces the molecular weight of the resulting polymer.[12]

TABLE III

Results from the Polymerization of Mixtures of *n*-Octene-2 and *n*-Octene-1 with $TiCl_4$–$AlEt_3$

Mole ratio of nonterminal: terminal olefin	$\frac{A_{1380}}{A_{1465}}$
0	1.31
0.11	1.31
0.25	1.33
0.43	1.28
0.67	1.33
1.0	1.33
1.5	No polymer formed

We have shown during these investigations that *trans*-*n*-octadecene-2 and *trans*-*n*-octadecene-7 do not polymerize under the conditions prevailing, and so it becomes of interest to examine the possible modes of interaction between nonterminal olefin and catalyst. Although Ziegler[13] has shown that terminal olefins are much more likely to react with aluminum alkyls (and presumably with Ziegler catalysts) than are nonterminal olefins, it is feasible that interaction by the latter becomes important with the high nonterminal olefin concentration encountered in these polymerizations. Results given in Table IV indicate that the changes in polymer yield and intrinsic viscosity caused by *trans*-*n*-octadecene-2 cannot be explained by dilution effects alone, and there remains the possibility that chemical interaction occurs. The most likely forms appear to be either that non-

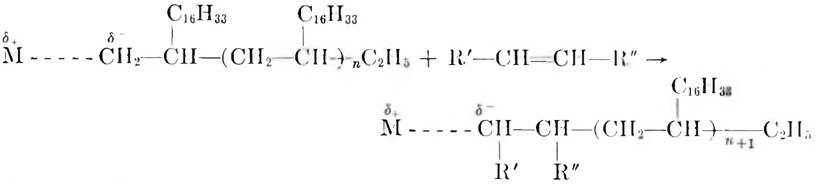
TABLE IV

Yields and Intrinsic Viscosities of Polymers Prepared by Polymerization of Mixtures of *n*-Octadecene-1 with *trans-n*-Octadecene-2, *trans-n*-Octadecene-7, or Cyclohexane with $TiCl_4$–$AlEt_3$[a]

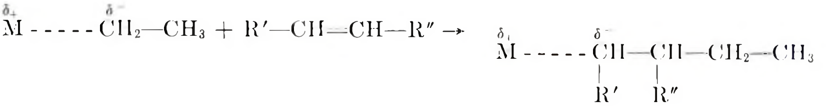
Non-terminal olefin or cyclohexane, mole/mole of terminal olefin	Polymer yield, %			Polymer intrinsic viscosity		
	trans-n- Octadecene-2	*trans-n-* Octadecene-7	Cyclohexane	*trans-n-* Octadecene-2	*trans-n-* Octadecene-7	Cyclohexane
0	55	56	56	1.04	0.6	0.6
0.09	56	—	—	0.98	—	—
0.11	—	53	—	—	0.6	—
0.20	45	—	—	1.03	—	—
0.25	—	52	—	—	0.63	—
0.33	44	—	54	0.98	—	0.65
0.43	—	52	—	—	0.70	—
0.50	37	—	—	0.82	—	—
0.66	—	51	—	—	0.78	—
0.72	27	—	—	0.76	—	—
0.75	—	—	56	—	—	0.65
1.0	No polymer	46	—	No polymer	0.86	—
1.29	"	—	51	"	—	0.64
1.50	"	35	—	"	0.96	—
1.98	"	—	56	"	—	0.69
3.0	"	—	56	"	—	0.80
4.5	"	—	48	"	—	0.92

[a] 30 hr., 25°C., Al:Ti mole ratio 2.8:1, $TiCl_4$:*n*-octadecene-1 mole ratio 0.035:1.

terminal olefin adds to a growing polymer chain [eq. (2)] or reacts with an active catalyst site [eq. (3)].

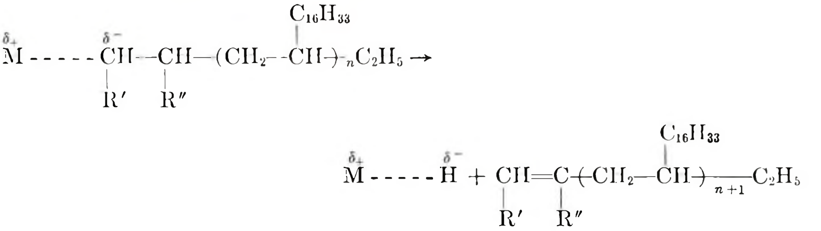


$$\overset{\delta_+}{\mathrm{M}}\text{-----}\overset{\delta^-}{\mathrm{CH_2}}-\overset{\mathrm{C_{16}H_{33}}}{\mathrm{CH}}-(\mathrm{CH_2}-\overset{\mathrm{C_{16}H_{33}}}{\mathrm{CH}})_n\mathrm{C_2H_5} + \mathrm{R'{-}CH{=}CH{-}R''} \rightarrow \overset{\delta_+}{\mathrm{M}}\text{-----}\underset{\mathrm{R'}}{\overset{\delta^-}{\mathrm{CH}}}-\underset{\mathrm{R''}}{\mathrm{CH}}-(\mathrm{CH_2}-\overset{\mathrm{C_{16}H_{33}}}{\mathrm{CH}})_{n+1}\mathrm{C_2H_5} \qquad (2)$$



$$\overset{\delta_+}{\mathrm{M}}\text{-----}\overset{\delta^-}{\mathrm{CH_2}}-\mathrm{CH_3} + \mathrm{R'{-}CH{=}CH{-}R''} \rightarrow \overset{\delta_+}{\mathrm{M}}\text{-----}\underset{\mathrm{R'}}{\overset{\delta^-}{\mathrm{CH}}}-\underset{\mathrm{R''}}{\mathrm{CH}}-\mathrm{CH_2}-\mathrm{CH_3} \qquad (3)$$

At this point there remains, attached to the catalyst surface, a hydrocarbon chain which cannot add on more terminal olefin, since otherwise copolymerization would have occurred. Lack of activity in respect of polymerization would be expected with this compound, in view of the well-known failure of α-branched aluminum alkyls to act as Ziegler catalysts, generally assumed to be due to steric hindrance. However, it seems unlikely that this would hinder the normal chain termination reactions, which involve hydride ion transfer. In the present instance, a trisubstituted ethylene would be obtained instead of the usual vinylidene compound.



$$\overset{\delta_+}{\mathrm{M}}\text{-----}\underset{\mathrm{R'}}{\overset{\delta^-}{\mathrm{CH}}}-\underset{\mathrm{R''}}{\mathrm{CH}}-(\mathrm{CH_2}-\overset{\mathrm{C_{16}H_{33}}}{\mathrm{CH}})_n\mathrm{C_2H_5} \rightarrow \overset{\delta_+}{\mathrm{M}}\text{-----}\overset{\delta^-}{\mathrm{H}} + \underset{\mathrm{R'}}{\mathrm{CH}}{=}\underset{\mathrm{R''}}{\mathrm{C}}-(\mathrm{CH_2}-\overset{\mathrm{C_{16}H_{33}}}{\mathrm{CH}})_{n+1}\mathrm{C_2H_5} \qquad (4)$$

We have already reported that the infrared spectra of polymers prepared during this work reveal absorption bands in positions characteristic for trisubstituted ethylenes,[5] thus supporting the concept of interaction between nonterminal olefin and a growing polymer chain.

It would seem reasonable to assume that the *trans-n*-octadecene-2, with only a small substituent at the double bond, is able to approach the catalyst surface more easily than the bulkier 7-isomer. Also, the double bond in the 7-isomer is somewhat more symmetrical electronically than in the 2-isomer, a factor which could well effect its reactivity. The *trans-n*-octadecene-2 would therefore be expected to have a greater likelihood of reacting at the catalyst surface, and thus to have a greater effect on polymer yield and molecular weight, than *trans-n*-octadecene-7. The occurrence of termination reactions described above would clearly be expected to reduce polymer molecular weight.

If, however, nonterminal olefin adds to an active catalyst site without subsequent detachment, the catalyst surface becomes covered with hydrocarbon chains, and it could well be that terminal olefin finds it increasingly difficult to reach the remaining active catalyst sites. Such conditions, which could well account for the unreacted terminal olefin recovered from some polymerizations, would be expected to reduce polymer yield. The *trans-n*-octadecene-2, when added to the polymerization of *n*-octadecene-1 with titanium tetrachloride–triethylaluminum, was found to reduce both polymer yield and molecular weight.

At present there does not seem to be sufficient experimental evidence to enable a full explanation to be offered of the effects of nonterminal olefins on polymer yield and molecular weight. It seems unlikely that the results mentioned in the foregoing can be due, to any significant extent, to impurities, as both nonterminal olefins and cyclohexane were carefully dried, distilled, and examined by infrared spectroscopy, gas chromatography, and iodine number determination before use. Possibly the main difference between *trans-n*-octadecene-2 and *trans-n*-octadecene-7 (or cyclohexane) is that the former reacts with catalyst and the latter merely acts as a diluent. Also, the differing polarities of nonterminal olefins and cyclohexanes may have to be taken into account. In order of decreasing polarity, 2-olefin > 7-olefin > cyclohexane. The 7-olefin could be loosely attached, by electrostatic forces, to the catalyst surface, and be less easily displaced by approaching terminal olefin than a nonpolar solvent such as cyclohexane.

It is probable that the explanation of the facts reported in this paper is very complex, and all the foregoing considerations must be taken into account.

The authors would like to express their gratitude to Dr. W. Gerrard for his valuable guidance throughout this work.

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Résumé

On a montré dans le cas de la polymérisation du *n*-1 octadécène avec des catalyseurs à base de tétrachlorure de titane et de triéthyle aluminium que outre la polymérisation de l'oléfine, il y avait la formation d'oléfines isomérisées. L'oléfine isomérisée est principalement le trans *n*-2-octadécène et sa formation est favorisée par un rapport molaire croissant aluminium-titane et une augmentation de la concentration en catalyseur et de la température de réaction. On a également montré que l'éthylène 1,1-disubstitué est présent dans le produit de réaction non-polymérique. L'influence de *n*-2-trans-octadécène additionné ou de trans *n*-7-octadécène sur la polymérisation de *n*-1-octadécène a été étudiée et on a montré que l'isomère 2 a un effet plus prononcé sur le rendement polymérique et sur la viscosité intrinsèque. On a également montré qu'il n'y a pas de copolymérisation significative avec l'octène terminal et non-terminal ou l'octadécène dans de telles conditions. Le résultat indique que dans les polymérisations de ce genre, l'interaction du catalyseur avec le monomère isomérisé est probablement un facteur important en ce qui concerne le rendement en polymère et son poids moléculaire. L'isomérisation est également intéressante comme méthode générale préparative *trans*.

Zusammenfassung

Bei der Polymerisation von *n*-1-Oktadecen mit von Titantetrachlorid und Triäthylaluminium abgeleiteten Katalysatoren wurde gezeigt, dass neben der Polymerisation auch eine Isomerisation des Olefins eintritt. Letztere führt vornehmlich zu trans-*n*-2-Oktadecen; seine Bildung wird durch Erhöhung des Molverhältnisses Aluminium: Titan, der Katalysatorkonzentration und der Reaktionstemperatur begünstigt. Die Anwesenheit des 1,1-disubstituierten Äthylens in den nicht-polymeren Reaktionsprodukten wurde nachgewiesen. Der Einfluss eines Zusatzes von trans-*n*-2-Oktadecen oder trans-*n*-7-Oktadecen auf die Polymerisation von *n*-1-Oktadecen wurde untersucht; es wurde gezeigt, dass das 2-Isomere den stärkeren Einfluss auf Polymerausbeute und Viskositätszahl besitzt. Weiters wurde gezeigt, dass unter diesen Bedingungen keine wesentliche Copolymerisation mit Oktenen oder Oktadecenen mit nicht-endständigen Doppelbindungen stattfindet. Die Ergebnisse lassen erkennen, dass bei Polymerisationen von dieser Art die Wechselwirkung zwischen Katalysator und isomerisierten Monomeren wahrscheinlich ein wichtiger Faktor für Polymerausbeute und Molekulargewicht ist. Die Isomerisationreaktion ist auch als allgemeine präparative Methode zur Darstellung von *trans*-2-Olefinen von Interesse.

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Some New Polymeric Semiconductors

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Synopsis

This paper deals with some new methods for synthesis of the polymeric semiconductors by conjugated reactions and also with electrophysical properties of the polymers. Elimination of hydrogen halides from α,β-dihalo derivatives by bases (calcium oxide or tertiary amines) yields polymers with conjugated bonds. The reaction proceeds at 200–300°C. under atmospheric or elevated pressures, acetylenes being the intermediates. α,β-Dihalo compounds with calcium carbide above 150°C. produce polyacetylenic copolymers by elimination of two moles of hydrogen halide, also by generating acetylene from calcium carbide. The identical reaction (elimination of water) was observed between carbonyl compounds and calcium carbide. Elimination of water from mono- and bifunctional phenols in the presence of zinc chloride under pressure above 200°C. yields polyphenylenes and polyhydroxyphenylenes, dehydrobenzene (benzyne) and hydroxybenzyne being intermediates. The polyhydroxyphenylenes prepared have a degree of polymerization from 4–5 to several thousand and are of interest as intermediates for thermostable resins, inhibitors etc. Linear polycyanamide and polycyanic acid were first prepared by polycondensation of urea with ammonium bicarbonate in the presence of zinc chloride. Analogous polymers were obtained from the ring-opening polymerization of melamine and cyanuric acid. The polymers show good semiconductor and ion-exchange properties. Polycondensation of ketones with ammonium bicarbonate also gave conjugated polymers. Thus, organometallic polymers were prepared from acetyl- and diacetyl ferrocene. We have also studied electrophysical, magnetic, and catalytic properties of the conjugated polymers prepared by the new methods. The electrical conductivity of the best specimens ranged from 10^{-3} to 10^{-6} ohm^{-1} cm.$^{-1}$; the number of electrons unpaired was 10^{18}–10^{19} spins/g.

Recently the authors have worked out a number of new methods for the synthesis, by polyconjugated reactions, of polymers and low molecular weight oligomers having systems of conjugated double bonds with or without benzene or ferrocene nuclei.

This investigation afforded polymers possessing semiconductor properties (electrical conductivities ranging from 1×10^{-1} to 1×10^{-11} ohm^{-1} cm.$^{-1}$) and low molecular weight oligomers which may be of importance as new intermediates in organic synthesis as well as intermediates for polymeric semiconductors.

Previously, such polymers were prepared by polymerization and polycondensation methods.[1–8]

We have proposed new methods of synthesis of polymers from monomers containing neither multiple bonds nor functional groups required for polycondensation reactions. These methods are based on conjugated reactions which could be depicted by the scheme:

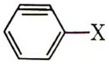
$$nA \rightarrow nB + ab$$
$$nB \rightarrow (B)n$$

Here A represents a starting compound which can be converted into a reactive monomer B with elimination of hydrogen halides or water (ab), and B represents a monomeric intermediate which polymerizes as rapidly as it is formed.

In most cases it is possible to obtain the B monomer beforehand by some method and polymerize it by a general method.

However, a number of monomers are often so unstable that their isolation is practically impossible. Some monomers are too toxic for general laboratory use. Moreover, the polymerization of monomers *in statu nascendi* may follow routes different from those of stable monomers as illustrated in the following derivatives (Ia, Ib)


Ia



Ib

have not been isolated in the free state, but their polymers and adducts are known.

Cyanoacetylene CH≡C—C≡N is not used in the preparation of polymeric semiconductors, but its polymers in the form of cyclized and dehydrogenated polyacrylonitrile are well known.

The theory of these reactions was considered by Emanuel and Knorre.[9]

A variety of new conjugated reactions for the syntheses of a number of polymers and oligomers, and also magnetic and electrophysical properties of the polymer obtained, will be considered below.

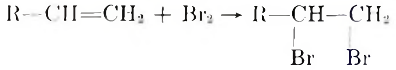
The electrical conductivity of the polymers was measured *in vacuo* by a method described previously.[10] A specimen was pelletized at elevated pressure. Prior to every measurement the pellets were kept for 5 hr. at 10^{-5} mm. Hg in order to remove readily desorbing substances (gases, water vapors, etc.) from the surface and out of the volume of the specimen.

The purity of the polymers was defined by ordinary elemental analysis, and the impurity content could not exceed 0.1%. As shown by some runs the presence of mineral salts (0.5–1.0%) in polymeric semiconductors with electrical conductivities from 10^{-2} to 10^{-9} ohm^{-1} cm.$^{-1}$ does not affect their conductivities, since these salts are insulators and they are not, moreover, included in the crystalline and submolecular structure of the polymer.

Dehydrohalogen Polymerization[11–18]

Polyacetylenic (polyene) hydrocarbons and their derivatives have been prepared in 60–80% yield by a one-step reaction involving the elimination of hydrohalic acids from dihalo derivatives of various compounds. Calcium oxide was employed as a dehydrohalogenating agent (acceptor). The reaction was carried out in a small (100 ml.) autoclave at temperatures from 200 to 350°C.

Compound having a double bond in the α-position were halogenated to the corresponding α,β-dichloro or dibromo derivatives [eq. (1)]:



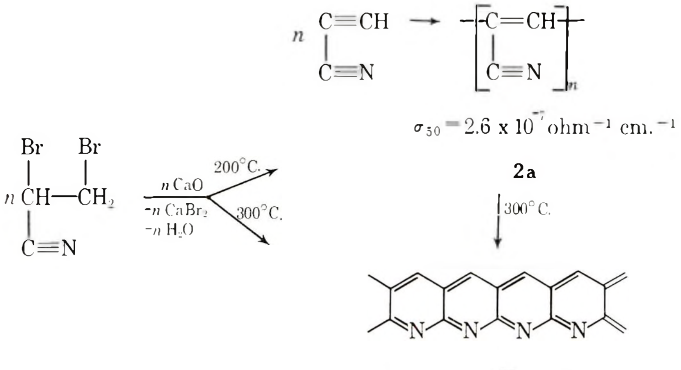
$$R{-}CH{=}CH_2 + Br_2 \rightarrow \underset{Br}{R{-}CH}{-}\underset{Br}{CH_2} \qquad (1)$$

(where R may be an alkyl, aryl, nitrile, alkoxy, or hydroxy group).

By this method a polyphenylacetylene having a molecular weight distribution similar to that obtained in the thermal polymerization of phenylacetylene was prepared.

Dibromoheptane and dibromononane gave rise to the polymers having a one-component signal in their ESR spectrum (1.1×10^{18} spins/g.); on the other hand, alkylacetylene polymers obtained by catalytic polymerization had no ESR signal, due to the migration of a double bond into the side chain.[11]

At 200°C. dibromopropionitrile was converted to a previously unreported polynitrileacetylene [eq. (2a)].



$\sigma_{50} = 2.6 \times 10^{-7}$ ohm^{-1} cm.$^{-1}$

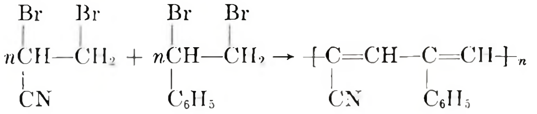
2a

$\sigma_{50} = 8.8 \times 10^{-5}$ ohm^{-1} cm.$^{-1}$

2b

At 300°C. cyclization involving the nitrile groups led to a structure similar to that of thermally treated polyacrylonitrile [eq. (2b)]. The electrical conductivity increased from $\sigma_{50} = 2.6 \times 10^{-7}$ ohm^{-1} cm.$^{-1}$ for the linear structure to $\sigma_{50} = 8.8 \times 10^{-55}$ ohm^{-1} cm.$^{-1}$ for the cyclic structure as chain conjugation increased.

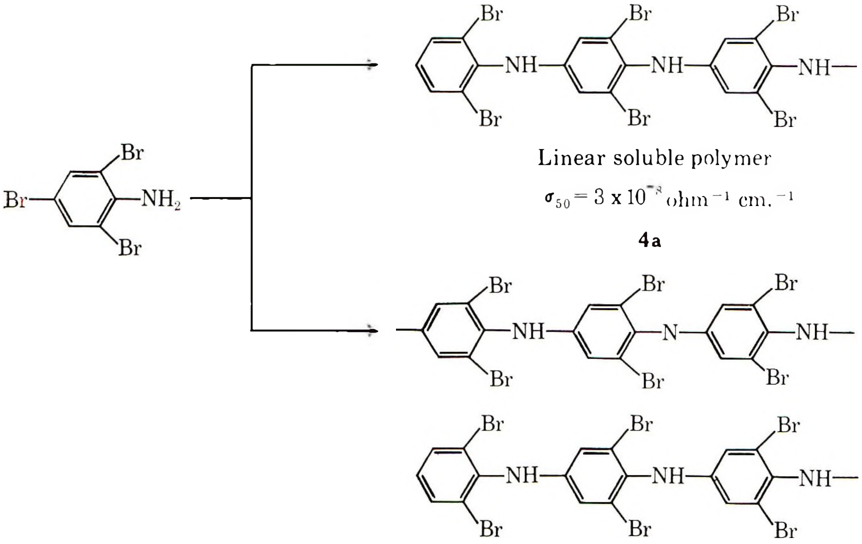
By mutual reaction of dibromopropionitrile and dibromoethylbenzene, corresponding copolymers have been synthesized [eq. (3)]



$$n\underset{CN}{\overset{Br}{CH}}{-}\overset{Br}{CH_2} + n\underset{C_6H_5}{\overset{Br}{CH}}{-}\overset{Br}{CH_2} \rightarrow {+}\underset{CN}{C}{=}CH{-}\underset{C_6H_5}{C}{=}CH{+}_n \qquad (3)$$

Some other examples of such reactions and some properties of the polymers obtained are listed in Table I.

An alternative form of intermolecular dehydrohalogen polycondensation is the formation of polymers from tribromoaniline and calcium oxide or aluminum chloride [eqs. (4)]



Linear soluble polymer

$\sigma_{50} = 3 \times 10^{-8}$ ohm^{-1} cm.$^{-1}$

4a

Crosslinear insoluble polymer

$\sigma_{50} = 2 \times 10^{-4}$ ohm^{-1} cm.$^{-1}$

4b

It is noteworthy that the reaction proceeds readily in the presence of aluminum chloride and involves the bromine atoms of the aromatic ring and the hydrogen atoms of the amino group, which has very low basicity in tribromoaniline. In the presence of aluminum chloride the reaction appears to involve only the polycondensation step without preliminary salt formation.

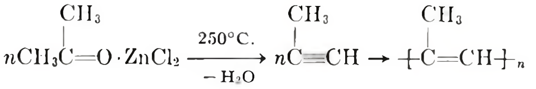
The electrical conductivity of the soluble polymers from tribromoaniline was about $\sigma_{50} = 1 \times 10^{-8}$ ohm^{-1} cm.$^{-1}$, and the molecular weights were about 5000, while electrical conductivity of insoluble polymers ranged from 1×10^{-3} to 1×10^{-4} ohm^{-1} cm.$^{-1}$. The soluble polytribromoaniline could be employed for preparing films.

Heteropolycondensation of Aldehydes or Ketones with Calcium Carbide[19-21]

According to another approach polyconjugated polymers have been prepared by the reaction of aldehydes or ketones with calcium carbide.

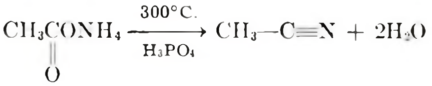
The stimulus for investigating this field was the discovery by Kargin and Kabanov[2] that polyacetylenes could be obtained by elimination of water from aldehydes or ketones by strong dehydrating agents.

In terms of aldol polycondensation the reaction is considered to proceed by a stepwise mechanism [eq. (5)]. But the direct elimination of water from the molecular complex of the carbonyl compound with zinc chloride and the subsequent polymerization of acetylenic compounds cannot be excluded.



$$n\,CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}{=}O\cdot ZnCl_2 \xrightarrow[-\,H_2O]{250°C.} n\overset{\overset{\displaystyle CH_3}{|}}{C}{\equiv}CH \rightarrow \left[\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH\right]_n \qquad (5)$$

A similar reaction, the elimination of water from ammonium salts, is known to proceed in the presence of dehydrating agents to give nitriles [eq. (6)]

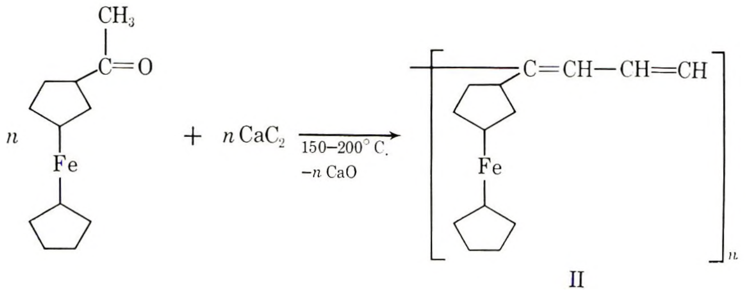


$$CH_3\underset{\underset{\displaystyle O}{\|}}{C}ONH_4 \xrightarrow[H_3PO_4]{300°C.} CH_3{-}C{\equiv}N + 2H_2O \qquad (6)$$

In the method worked out by the authors, zinc chloride was replaced by calcium carbide, which acted as both a condensing agent and a reactant, since it evolved acetylene, an intermediate in the copolymerization.

Acetylene was formed as a result of the reaction of calcium carbide with water eliminated from carbonyl compounds during heating. The reaction with calcium carbide has been studied for acetaldehyde, acetone, acetophenone, and the acetyl derivatives of ferrocene.

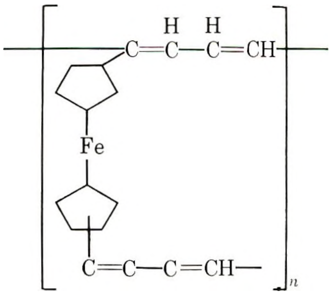
Consider the reaction for acetyl and diacetyl ferrocene [eq. (7)]



(7)

II

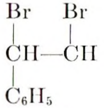
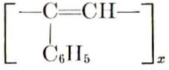
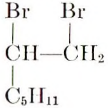
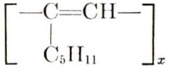
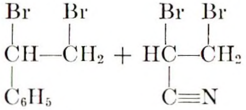
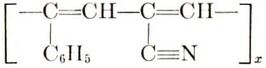
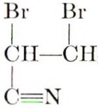
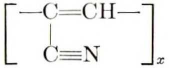
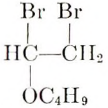
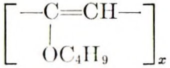
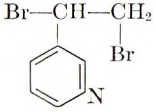
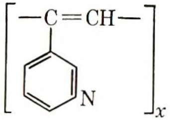
A polymer having the structure II was obtained from diacetyl ferrocene and two moles of the calcium carbide.

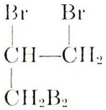
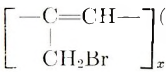
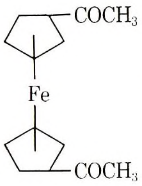
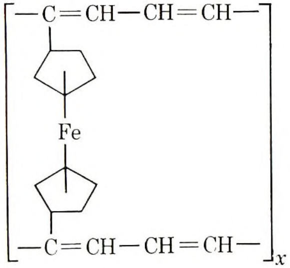
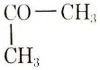
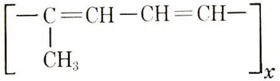
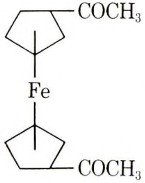
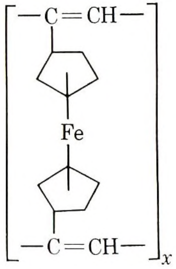


II

TABLE I

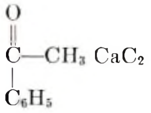
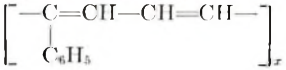
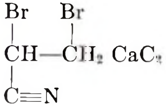
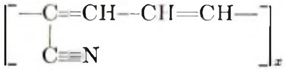
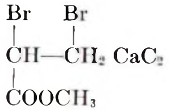
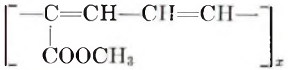
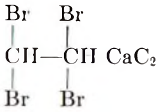
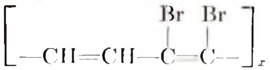
Characteristic Properties of New Polymers Consisting of a System of Polyconjugated Bonds

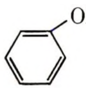
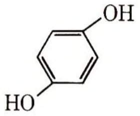
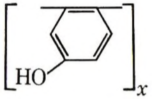
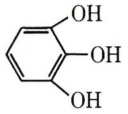
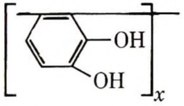
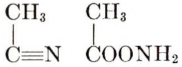
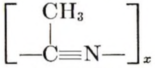
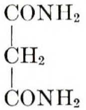
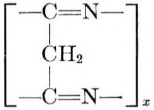
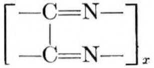
No.	Starting monomer	Polymer chain structures	σ_{50}, omh^{-1} cm.$^{-1}$	Activation energy E, e.v.	N, spins/g.	Magnetic susceptibility at H = 5500
		Dehydrohalogenation polymerization				
1	 $\underset{C_6H_5}{\overset{Br}{CH}}-\overset{Br}{CH}$	 $\left[-\underset{C_6H_5}{C}=CH-\right]_x$	1.8×10^{-11}	0.25	1.1×10^{18}	3.75×10^{-6}
2	 $\underset{C_5H_{11}}{\overset{Br}{CH}}-\overset{Br}{CH_2}$	 $\left[-\underset{C_5H_{11}}{C}=CH-\right]_x$	1.1×10^{-11}	0.2	10^{18}	—
3	 $\underset{C_6H_5}{\overset{Br}{CH}}-\overset{Br}{CH_2} + \underset{C\equiv N}{\overset{Br}{HC}}-\overset{Br}{CH_2}$	 $\left[-\underset{C_6H_5}{C}=CH-\underset{C\equiv N}{C}=CH-\right]_x$	1.3×10^{-11}	0.28	2.4×10^{19}	1.18×10^{-5}
4	 $\underset{C\equiv N}{\overset{Br}{CH}}-\overset{Br}{CH_2}$	 $\left[-\underset{C\equiv N}{C}=CH-\right]_x$	8.8×10^{-5}	0.01	6×10^{19}	1.97×10^{-5}
5	 $\underset{OC_4H_9}{\overset{Br}{HC}}-\overset{Br}{CH_2}$	 $\left[-\underset{OC_4H_9}{C}=CH-\right]_x$	1.5×10^{-11}	0.31	1×10^{18}	1.8×10^{-5}
6			7.15×10^{-12}	0.2	10^{19}	Small

7	 $\overset{Br}{\underset{CH_2B_2}{CH}}-\overset{Br}{CH_2}$		 $\left[-\underset{CH_2Br}{C}=CH-\right]_x$ (polymer from tribromopropane)	5.6×10^{-5}	0.3	10^{19}	1×10^{-5}
			Heteropolycondensation of ketones and calcium carbide				
8		CaC_2					
9	 $\underset{CH_3}{CO}-CH_3$	CaC_2	 $\left[-\underset{CH_3}{C}=CH-CH=CH-\right]_x$	0.9×10^{-12}	—	5.8×10^{17}	—
10		($ZnCl_2$)					
11				5.9×10^{-6}	—	—	—

(*continued*)

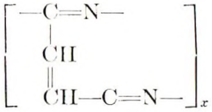
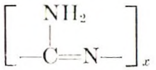
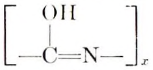
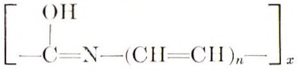
TABLE I (*continued*)

No.	Starting monomer	Polymer chain structures	σ_{50}, ohm^{-1} cm.$^{-1}$	Activation energy E, e.v.	N, spins/g.	Magnetic susceptibility at H = 5500
		Dehydrohalogen copolymerization with calcium carbide				
12	 $C_6H_5{-}C({=}O){-}CH_3$ CaC_2	 $[{-}C(C_6H_5){=}CH{-}CH{=}CH{-}]_x$				
		Oligomer	3×10^{-12}	0.12; 0.27	1.5×10^{17}	—
		Polymer	1.15×10^{-6}	0.1; 0.15	3×10^{18}	
13	 $BrCH(C{\equiv}N){-}CH_2Br$ CaC_2	 $[{-}C(C{\equiv}N){=}CH{-}CH{=}CH{-}]_x$				
		Oligomer	2×10^{-9}	0.71; 0.9	10^{19}	—
		Polymer	10^{-6}	0.05; 0.116	5×10^{20}	—
14	 $BrCH(COOCH_3){-}CH_2Br$ CaC_2	 $[{-}C(COOCH_3){=}CH{-}CH{=}CH{-}]_x$				
		Oligomer		0.12; 0.27	10^{16}	—
		Polymer	10^{-2}	—	10^{18}	—
15	 $CHBr_2{-}CHBr_2$ CaC_2	 $[{-}CH{=}CH{-}CBr{=}CBr{-}]_x$	10^{-1}	—	10^{16}	—

		Polydehydration of phenols				
16			3.2×10^{-8}	—	10^{19}	—
17			1.1×10^{-8}	0.16; 0.7	10^{18}	—
18			10^{-9}		10^{18}	
		Polydehydration of ammonium salts of carboxylic acids[a]				
19	 $CH_3{-}C{\equiv}N \quad CH_3{-}COONH_2$	 $[{-}C(CH_3){\equiv}N{-}]_x$	4×10^{-6}	0.09	7.5×10^{18}	−5
20	$HCOONH_2$	$[{-}HC{=}N{-}]_x$				
	$HCOONH_4$	via amide	2×10^{-6}	0.256	4.9×10^{18}	−126
		via salt	6×10^{-6}	0.07	3.6×10^{18}	—
21	 $CONH_2{-}CH_2{-}CONH_2$	 $[{-}C{=}N{-}{-}CH_2{-}{-}C{=}N{-}]_x$	4.6×10^{-6}	0.1	1×10^{18}	—
22	 $CONH_2{-}CONH_2$	 $[{-}C{=}N{-}{-}C{=}N{-}]_x$	1.6×10^{-5}	0.03	1.7×10^{18}	−2.6

(continued)

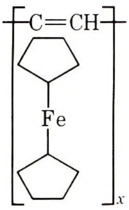
TABLE I *(continued)*

No.	Starting monomer	Polymer chain structures	σ_{50}, ohm^{-1} cm.$^{-1}$	Activation energy E, e.v.	N, spins/g.	Magnetic susceptibility at H = 5500
23	$CONH_2$—CH=CH—$CONH_2$	 $\left[\begin{array}{l} —C{=}N— \\ \quad \vert \\ \quad CH \\ \quad \Vert \\ \quad CH—C{=}N— \end{array}\right]_x$	1×10^{-4}	0.012	3.5×10^{19}	−5
	Polydehydration of both ammonium carbonates and urea					
24	NH_2—$CONH_2$	 $\left[\begin{array}{l} \quad NH_2 \\ \quad \vert \\ —C{=}N— \end{array}\right]_x$	1×10^{-11}	—	1×10^{18}	
25	$\begin{array}{l} NH_4O\diagdown \\ \qquad CO \\ HO\diagup \end{array}$	 $\left[\begin{array}{l} \quad OH \\ \quad \vert \\ —C{=}N— \end{array}\right]_x$	1×10^{-8}	—	1×10^{18}	—
26	$\begin{array}{l} NH_4\diagdown \\ \qquad C{=}O + CH_3CHO \\ HO\diagup \end{array}$	 $\left[\begin{array}{l} \quad OH \\ \quad \vert \\ —C{=}N—(CH{=}CH)_n— \end{array}\right]_x$	1×10^{-7}	—	1×10^{-8}	. .

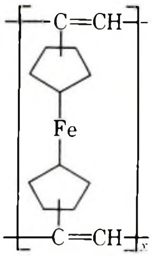
---

[a] These polynitriles were prepared from the ammonium salts of acetic, formic, oxalic, succinic, and maleic acids. The cyclic structure were for polymers 20a and b which were previously obtained from cyanic acid.

The elementary composition of this product coincides with calculated values (C, 74.91%; H, 6.3%; Fe, 19.2%). The heteropolycondensation reaction of acetyl and diacetyl ferrocene with calcium carbide gave polymers in 70–85% yields. The polymers obtained from acetyl or diacetyl ferrocene and zinc chloride as a result of water elimination (polycondensation) at 180–200°C. had the polyferrocenyl acetylene structures (IIIa, IIIb).



IIIa



IIIb

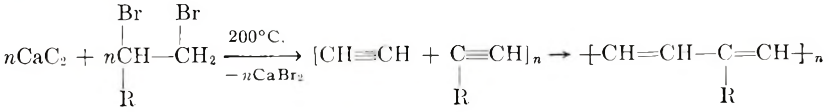
Characteristics of the polymers prepared are shown in Table I.

Heteropolycondensation of the other carbonyl compounds, such as aldehyde, acetone, and acetophenone with calcium carbide formed liquid tars and solid polymers. The elementary composition and a narrow signal in the ESR spectrum point to the presence of unpaired electrons (7×10^{16} spins/g.) characteristic of polyconjugated polymers.

Dehydrohalogenation Copolymerization[22]

The reaction of α,β-dihalo derivatives with calcium carbide at 200–230°C. leads to the formation of polymers both at atmospheric and at elevated pressures. Such methods of producing polymers are well known in macromolecular chemistry. An example is the reaction of sodium polysulfide with dihalo derivatives leading to Thiokols (polysulfide rubbers).

The reaction of calcium carbide with α,β-dihalo derivatives with or without an inert solvent began at temperatures above 150°C. with vigorous stirring. When carried out at normal pressure the reaction gave soluble oligomers with molecular weights ranging from 500 to 1000 which could be easily separated from inorganic material by extraction. Under pressure and at 200–300°C. the same reaction gave a considerable quantity of insoluble polymers. On the basis of the elementary composition, infrared and ESR spectra, as well as considerable electrical conductivity it may be concluded that both the oligomers and the polymers contained polyconjugated double bonds. Hence the reaction mechanism involves the intermediate formation of acetylene and its derivatives followed by their copolymerization [eq. (8)].



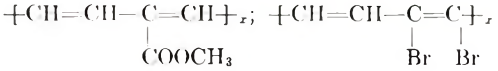
$$n\mathrm{CaC_2} + n\underset{\mathrm{R}}{\overset{\mathrm{Br}}{\mathrm{CH}}}\text{—}\overset{\mathrm{Br}}{\mathrm{CH_2}} \xrightarrow[-n\mathrm{CaBr_2}]{200^\circ\mathrm{C.}} [\mathrm{CH{\equiv}CH} + \underset{\mathrm{R}}{\mathrm{C}}{\equiv}\mathrm{CH}]_n \rightarrow \text{+}\mathrm{CH{=}CH{-}}\underset{\mathrm{R}}{\mathrm{C}}{=}\mathrm{CH}\text{+}_n \qquad (8)$$

Since the infrared spectra showed no triple bonds, while the polymers had high electrical conductivity, the reaction could involve only the copolymerization mechanism. The oligomers were soluble (and therefore easily recrystallizable), fusible compounds having comparatively low electrical conductivity ranging from 1×10^{-8} to 1×10^{-9} ohm^{-1} cm.$^{-1}$. When subjected to thermal polymerization at 200–300°C. the oligomers became infusible and insoluble, and the electrical conductivity rose to values of 1×10^{-3} to 1×10^{-6} ohm^{-1} cm.$^{-1}$. This was a convenient method for producing semiconductive polymers using oligomers as starting material. The oligomers could be considered to be biradicals.[2] For example, the oligomer obtained by reaction of dibromostyrene and calcium carbide presumably has the structure IV.

$$\cdot CH{=}CH{-}\underset{C_6H_5}{C}{=}CH{+}\underset{C_6H_5}{C}{=}CH{-}CH{=}CH{+}_x\underset{C_6H_5}{C}{=}CH{-}CH{=}CH\cdot$$

However, the question of terminal groups for the polyconjugated polymers still remains a moot point in the polymer chemistry. In cases such as the formation of some organosilicon, polyacetylenic, and other compounds, cyclic structures are not excluded.

It is of interest to note that the polymers obtained by dehydrohalogenation copolymerization of polar dihalo derivatives by calcium carbide had higher electrical conductivity, even though the comparatively mild conditions of synthesis (200–250°C.) precluded the formation of pyrolysis polymers. Notable is the copolymer (V) obtained from the methyl ester of dibromoacrylic acid, calcium carbide, and tetrabromoethane.



$$\text{+}CH{=}CH{-}\underset{COOCH_3}{C}{=}CH\text{+}_x;\ \text{+}CH{=}CH{-}\underset{Br}{C}{=}\underset{Br}{C}\text{+}_x$$

V

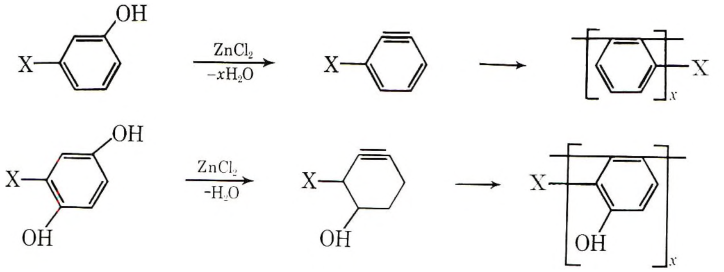
$$\sigma_{50} = 1 \times 10^{-2}\ \text{ohm}^{-1}\ \text{cm.}^{-1}$$

Table I lists starting monomers and structures and some properties of the polymers.

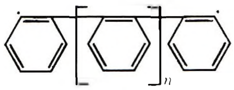
Polyhydration of Phenols[23]

The elimination of halogens from benzene derivatives is known to generate dehydrobenzene (benzyne), a species formed as an intermediate in a number of reactions. The phenols, like alcohols, lost water on heating with strong dehydrating agents, but since the dehydration products (benzyne and its derivatives) could not exist in a free state, the final products of the reaction were polymers.

This observation made for the first time in our previous communication[23] led to an essentially new method for preparing polyphenylenes and polyhydroxyphenylenes. Previously the water elimination reaction involving phenolic hydroxy groups had not been applied to the synthesis of polyphenylenes. The elimination of water from phenol and difunctional phenols starts at about 200°C. and gives both soluble, low molecular weight and insoluble, high molecular weight polyphenylenes. The reaction mechanism could be considered as involving the formation of benzyne or hydroxybenzyne intermediate and their subsequent polymerization [eqs. (9) and (10)].



According to this scheme the polymeric polyphenols are very likely to exist in the form of biradicals (VI).



VI

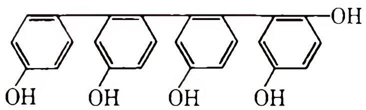
Highly conjugated systems and polycondensed aromatic hydrocarbons often exist in a biradical state which leads to further reactions.[25]

Thus, the soluble oligomeric fractions of polyphenylenes rapidly decrease in solubility during recrystallization, which is due to the presence of active centers causing the bridging of macromolecules.

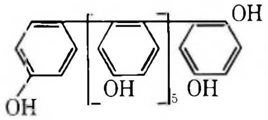
In previous publications[23,24] the influence of various factors on the synthesis of polyphenylenes from phenols has been investigated. In case of phenol the reaction usually started at temperatures above 300°C.; at 350°C. the yield of polyphenylenes reached 32% of theory.

The difunctional phenols at 200°C. formed mainly oligomers, i.e., 80% yields were obtained for low molecular weight polymers having a degree of polymerization of 3–8. An increase in the reaction temperature to 300–350°C. led to the formation of partially insoluble high molecular weight polyhydroxyphenylenes. All three bifunctional phenols studied, i.e., catechol, resorcinol, and hydroquinone, formed the corresponding polyhydroxyphenylenes.

Low molecular weight oligomers (molecular weight 350–650) of the structure VIIa or VIIb



VIIa



VIIb

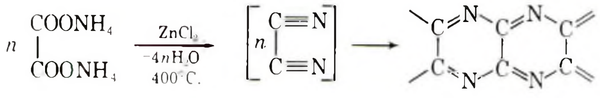
had melting points from 160 to 380°C. and were soluble in acetone, dioxane, and dimethylformamide. These oligomers can be of a considerable interest as prepolymers for producing formaldehyde, epoxy, and other resins and also as various intermediate products, antioxidant additives, etc. The electrical conductivity of the high molecular weight polyhydroxyphenylenes reached 1×10^{-7}–1×10^{-9} ohm^{-1} cm.$^{-1}$, which indicates the presence of conjugated aromatic nuclei. On the other hand, polyphenyl ethers, with benzene nuclei alternating with oxygen atoms, are good insulators with conductivities of 10^{-18} ohm^{-1} cm.$^{-1}$. Some properties of the polyhydroxyphenylenes prepared are shown in Table I.

Polydehydration of Ammonium Salts of Carboxylic Acids, Ammonium Carbonates, and Carbonyl Compounds[26–32]

The discovery of such reactions as thermal polymerization of nitrile groups in polyacrylonitrile, catalytic polymerization of nitriles involving a zinc chloride complex, and radiative polymerization of nitriles resulted in polynitriles, which are characterized by valuable semiconductor properties.

However, the nitriles are not always readily available and are highly poisonous.

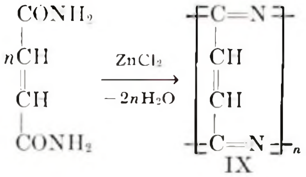
A method was suggested by means of which a variety of polynitriles could be obtained from ammonium salts of carboxylic acids. The method consisted in simultaneous elimination of water and polymerization of the reactive nitrile intermediates. Thus, for example, a paracyanogen polymer (VIII) was obtained from the diammonium salt of oxalic acid [eq. (11)].



VIII (11)

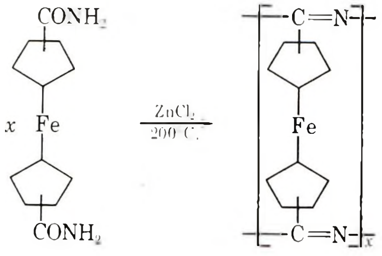
Polyhydrocyanic acid was prepared from ammonium formate in order to avoid the use of poisonous hydrocyanic acid. The reaction required heating of the ammonium salt at elevated pressure in the temperature range 350–400°C. with the use of an excess of zinc chloride and gave a polynitrile in 25–50% yield (depending on conditions). The yield was increased by removal of water formed during the reaction. Use of amides as starting materials also led to an increase of yield.

From the diamide of maleic acid the polynitrile IX was prepared.



IX (12)

Similarly, the diamide of ferrocene dicarboxylic acid gave a polyferrocenylene dinitrile (X).



X

(13)

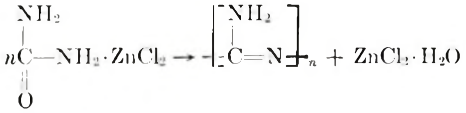
Whereas IX was prepared at 400°C. with 4 moles of zinc chloride per mole of the diamide, the elimination of water from the diamide of ferrocene dicarboxylic acid proceeded considerably more easily, even at 200°C. and with 2 moles of zinc chloride per mole of the diamide. The electrical conductivity of IX was about 1×10^{-4} ohm^{-1} cm.$^{-1}$ and that of X was 5×10^{-10} ohm^{-1} cm.$^{-1}$.

The polynitriles readily absorb silver and other noble metals from aqueous solutions of their salts.

The properties of the polynitriles prepared from ammonium salts are shown in Table I.

The polydehydration of urea and ammonium bicarbonate in the presence of zinc chloride has also been accomplished.[30-32]

Urea, on heating with an equimolar amount of zinc chloride at temperatures above 300°C. was observed to undergo water elimination which led to a linear polycyanamide [eq. (14)].

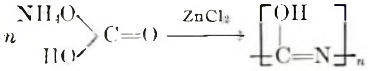


$$n\,\overset{NH_2}{\underset{O}{C}}\text{—}NH_2\cdot ZnCl_2 \rightarrow \left[-\overset{NH_2}{C}=N-\right]_n + ZnCl_2\cdot H_2O \qquad (14)$$

At 450°C. the yield of the polycyanamide reached 80%. Each monomeric unit of the polycyanamide molecule has an aromatic-like amino group which can be readily diazotized. In solution the polydiazo compound is stable at room temperature but decomposes at heating with nitrogen evolution.

The low molecular weight fractions of polycyanamide (oligomers) are colored brown (intrinsic viscosity $\eta = 0.035$), the fractions of higher molecular weight, colored black, are still soluble in acids ($\eta = 0.077$). Still higher molecular weight fractions are insoluble in any solvent. The oligomers seem to be used as a starting material for producing of thermally stable aldehydropolycyanamide resins.

Ammonium bicarbonate gave a linear polymer of cyanic acid (polycyanic acid) as a result of water elimination in the presence of zinc chloride [eq. (15)].

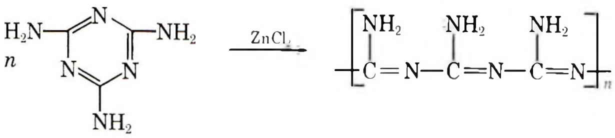


$$n\,\begin{matrix}NH_4O\\HO\end{matrix}\!\!>C=O \xrightarrow{ZnCl_2} \left[-\overset{OH}{C}=N-\right]_n \qquad (15)$$

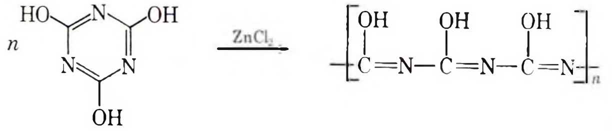
To date only the cyclic trimer of cyanic acid, i.e., cyanuric acid, was known.

Thus, linear polymers of polycyanamide and polycyanic acid were prepared from inorganic salts and urea. The structures of these compounds were confirmed by elementary analyses and by ESR spectra.

Linear polymers of cyanamide and cyanic acid were also prepared by polymerization of both melamine and cyanuric acid accompanied by cleavage of the triazine rings of these compounds on heating with zinc chloride in an autoclave at 450–500°C. [eqs. (16) and (17)].



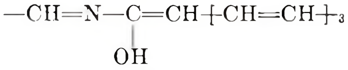
(16)



(17)

The properties of these polymers were similar to those of polymers prepared from urea and ammonium bicarbonate. The infrared spectra of the linear polycyanamide and poly(cyanic acid) were essentially different from those of the corresponding cyclic trimers (melamine and cyanuric acid).

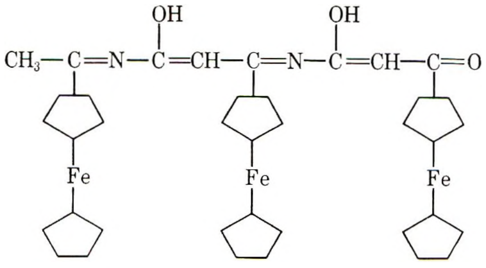
The joint conversion of ammonium bicarbonate and acetic aldehyde in the presence of zinc chloride led to a polymer having the structure XI.



$$-CH{=}N-\underset{\substack{|\\ OH}}{C}{=}CH\!+\!CH{=}CH\!+_3$$

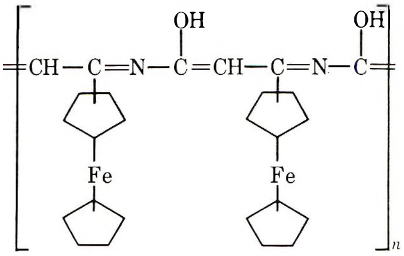
XI

The joint conversion of ammonium bicarbonate and acetyl or 1,1′-diacetyl ferrocene by means of zinc chloride (170–190°C., 5 hr.) gave a 60% yield of a polymer having a structure based on cyanic acid and ethynyl or 1,1′-diethynyl ferrocene [ferrocene-containing poly(vinylene hydroxynitriles)]. The resulting oligomers had the structure XII.



XII (Mol. wt. 720)

The macromolecular polymer chain structure was of the type XIII.



XIII

Oligomeric ferrocene-containing poly(vinylene hydroxynitriles) having a molecular weight of 725 (degree of polymerization 2–3) melted in the temperature range 250–350°C.; insoluble polymers were also obtained along with the oligomers. The structure and composition of these polymers were confirmed by elementary analysis and infrared spectra, as well as by hydroxy-group analysis. The presence of conjugated double bonds in the polymeric chains of the ferrocene-containing poly(vinylene hydroxynitriles) was confirmed by a narrow single-component signal in the ESR spectrum (unpaired electron concentration of 3.7×10^{18}/g.).

Structures and properties of the above polymers are shown in Table I.

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Résumé

On discute de certaines nouvelles méthodes de synthèse de polymères semiconducteurs par réaction conjuguée et également des propriétés électrophysiques de ces polymères. L'élimination d'acide hydrohalogéné au départ de dérivés dihalogénés α,β par des bases (oxyde de calcium ou amines tertiaires) permet l'obtention de polymères à doubles liaisons conjuguées. La réaction se passe à 200–300°C sous pression atmosphérique ou à pression élevée, des dérivés acétyléniques étant intermédiaires. Les dérivés dihalogénés α,β avec le carbure de calcium au-dessus de 150°C produisent des copolymères polyacétyléniques par élimination de deux molécules d'acide hydrohalogéné de la même façon que l'on forme de l'acétylène au départ de carbure de calcium. La réaction identique (élimination d'eau) a été observée entre les composés carbonylés et les carbures de calcium. L'élimination d'eau au départ de phénols mono- et bifonctionnels en présence de chlorure de zinc sous pression au-dessus de 250°C fournit des polyphénylènes et des polyhydroxyphénylènes, le déhydrobenzène (benzine) et l'hydroxybenzine étant des intermédiaires. Les polyhydroxyphénylènes préparés ont un degré de polymérisation de 4 à 5, jusque plusieurs milliers d'unités et sont intéressants comme intermediaires pour la formation de résines thermostables, des inhibiteurs, etc. Des polycyanamides linéaires et acides polycyaniques ont été pour la première fois préparés par polycondensation de l'urée avec le bicarbonate d'ammonium en présence de chlorure de zinc. Les polymères analogues résultaient de la polymérisation avec ouverture de cycles des mélamines et d'acides cyanuriques. Les polymères présentent des propriétés semiconductrices et échangeuses d'ions. La polycondensation de cétones avec le bicarbonate d'ammonium fournissait également des polymères conjugués. Donc des polymères organométalliques ont été préparés au départ de ferrocène acétyle et de diacétyle ferrocène. Nous avons également étudié les propriétés électrophysiques magnétiques et catalytiques des polymères conjugués préparés par les nouvelles méthodes. Les conductivités electriques des meilleurs échantillons variaient de 10^{-3} à 10^{-6} mho/cm, le nombre d'électrons non appariés étant de 10^{18} à 10^{19} sp/gr.

Zusammenfassung

In der vorliegenden Arbeit werden einige neue Methoden zur Synthese polymerer Halbleiter durch Konjugationsreaktionen sowie elektrophysikalische Eigenschaften der Polymeren beschrieben. Die Eliminierung von Halogenwasserstoffsäuren aus α,β-Dihalogenderivaten durch Basen (Calciumoxyd oder tertiäre Amine) führte zu Polymeren mit konjugierten Bindungen. Die Reaktion verläuft bei 200–300°C unter atmosphärischem oder erhöhtem Druck über Acetylene als Zwischenprodukte. α,β-Dihalogenderivate liefern mit Calciumcarbid oberhalb 150°C Polyacetylencopolymere durch Abspaltung von zwei Mol Halogenwasserstoffsäure und ebenso durch Entwicklung von Acetylen aus Calciumcarbid. Eine identische Reaktion (Eliminierung von Wasser) wurde zwischen Carbonylverbindungen und Calciumcarbid beobachtet. Die Eliminierung von Wasser aus mono- und bifunktionellen Phenolen in Gegenwart von Zinkchlorid unter Druck oberhalb 200°C liefert Polyphenylene und Polyhydroxyphenylene über Dehydrobenzol (Benzin) und Hydroxybenzin als Zwischenprodukte. Die dargestellten Polyhydroxyphenylene besitzen einen Polymerisationsgrad von 4–5 bis zu einigen tausend; sie besitzen als Zwischenprodukte für wärmebeständige Harze, Inhibitoren etc. Interesse. Lineares Polycyanamid und Polycyansäure wurden zuerst durch Polykondensation von Harnstoff mit Ammoniumbikarbonat in Gegenwart von Zinkchlorid dargestellt. Analoge Polymere entstanden bei der Ringöffnungspolymerisation von Melamin und Cyanursäure. Die Polymeren zeigen Halbleiter- und Ionenaustauschereigenschaften. Polykondensation von Ketonen mit Ammoniumbikarbonat führte ebenfalls zu konjugierten Polymeren. So wurden metallorganische Polymere aus Acetyl- und Diacetylferrocen dargestellt. Wir untersuchten auch die elektrophysikalischen, magnetischen und katalytischen Eigenschaften der nach den neuen Methoden dargestellten konjugierten Polymeren. Die elektrische Leitfähigkeit der besten Proben lag im Bereich von 10^{-3} bis 10^{-6} mho/cm; die Zahl der ungepaarten Elektronen betrug 10^{18}–10^{19} Spin/g.

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Copolymerization of 4-Cyclopentene-1,3-dione with *p*-Chlorostyrene and Vinylidene Chloride

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Synopsis

The copolymerization of 4-cyclopentene-1,3-dione (M_2) with *p*-chlorostyrene and vinylidene chloride is reported. The copolymers were prepared in sealed tubes under nitrogen with azobisisobutyronitrile initiator. Infrared absorption bands at 1580 cm.$^{-1}$ revealed the presence of a highly enolic β-diketone and indicated that copolymerization had occurred. The copolymer compositions were determined from the chlorine analyses and the reactivity ratios were evaluated. The copolymerization with *p*-chlorostyrene (M_1) was highly alternating and provided the reactivity ratios $r_1 = 0.32 \pm 0.06$, $r_2 = 0.02 \pm 0.01$. Copolymerization with vinylidene chloride (M_1) afforded the reactivity ratios $r_1 = 2.4 \pm 0.6$, $r_2 = 0.15 \pm 0.05$. The Q and e values for the dione ($Q = 0.13$, $e = 1.37$), as evaluated from the results of the vinylidene chloride case, agree closely with the previously reported results of copolymerization with methyl methacrylate and acrylonitrile and confirm the general low reactivity of 4-cyclopentene-1,3-dione in nonalternating systems.

INTRODUCTION

In previous papers of this series,[1,2] 4-cyclopentene-1,3-dione was shown to copolymerize readily with several common monomers. With methyl methacrylate and acrylonitrile the copolymers were always richer in comonomer than the feed over the entire feed composition range.[1] With styrene highly alternating copolymers were obtained.[2] This behavior of the dione is generally consistent with that of other cyclic monomers of similar structure.

An unusual feature of the copolymerization with styrene was that the copolymer composition curve approached 0.4 mole fraction styrene, rather than the simple alternation value of 0.5. Copolymerization involving a complex between styrene and the dione was suggested as a possible explanation for this behavior. To test the possibility that this effect was due merely to a distortion of the analytical data by the presence of fragments of the initiator (azobisisobutyronitrile), a distinct possibility since the molecular weight appeared to be low, the work was repeated and the data corrected for initiator from the nitrogen content. Although the corrections tended to raise the curve somewhat toward 0.5 mole fraction, the change was slight, and essentially the same copolymer composition curve was obtained as before.

To find out if this effect would be carried over to other cases of high alternation, the copolymerization of the dione with *p*-chlorostyrene was studied. A particular advantage of this system is that the copolymer compositions, as determined from the chlorine analyses, would be less affected by initiator fragments, trapped solvent, etc., than the styrene system, which involved carbon analyses.

Copolymerization studies of the dione with vinylidene chloride were also carried out to learn more of the general reactivity of the dione monomer itself, and to provide further information concerning the steric and electronic forces controlling the polymerization of cyclic monomers.

EXPERIMENTAL

Materials

The monomer, 4-cyclopentene-1,3-dione, was prepared from cyclopentenediol[3] and recrystallized three times from ether to give yellow crystals, m.p. 34°C. Vinylidene chloride and benzene were distilled under nitrogen and middle fractions were collected for use. The *p*-chlorostyrene was distilled under reduced pressure.

Polymerization Procedure

The desired molar ratios of 4-cyclopentene-1,3-dione and the comonomer were prepared and placed in thick-walled tubes along with about 10 ml. of benzene and 1 mole-% of azobisisobutyronitrile. The oxygen was removed by the usual degassing technique with a nitrogen flush, and the tubes were then sealed under about 1 mm. pressure of nitrogen. The polymerizations were carried out in a constant temperature bath with agitation.

The copolymers of *p*-chlorostyrene were prepared at 50°C. Precipitation of the copolymers occurred during the polymerization. After the polymerizations had proceeded to about 5–15% conversion, the tubes were opened and the contents were diluted with methanol (low dione feeds) or diethyl ether (high dione feeds). The solid granular polymers were collected, washed with benzene and ether, and dried under reduced pressure for several days.

The copolymers of vinylidene chloride were prepared at 65°C. The copolymers from the low dione feeds were soluble, and the solutions became viscous during the polymerizations. At high dione feeds the copolymers partially precipitated. After appropriate times the polymerizations were terminated, and the copolymers were caused to precipitate by the addition of methanol (low dione feeds) or diethyl ether (high and intermediate dione feeds). The polymers were collected, washed either with methanol or ether, and dried for several days under reduced pressure. Since the solubility characteristics of the copolymers vary considerably with the composition, further purification by reprecipitation was not performed in order to avoid possible separation and loss of some copolymer fractions.

Characterization and Analysis

All of the copolymers possessed strong infrared absorption at 1580 cm.$^{-1}$, characteristic of the highly enolic form of the β-diketone group.

The copolymers of *p*-chlorostyrene were insoluble or only very slightly soluble in the common solvents. The solubility of the vinylidene chloride copolymers was a function of the composition. At high dione content, the copolymers were insoluble in acetone and dioxane but were soluble in DMSO and DMF. At intermediate dione content, the copolymers were soluble in all four of these solvents. At low dione content the copolymers were insoluble but exhibited some swelling. All copolymers showed low solubility in methanol, carbon tetrachloride and chloroform.

The copolymers were analyzed for chlorine and the copolymer compositions were determined. The feed–copolymer composition data are re-

TABLE I
Data for Copolymerization of *p*-Chlorostyrene (M_1) with 4-Cyclopentene-1,3-dione (M_2)

Mole fraction M_1 in feed f_1	Time, min.	Conversion, %	Analysis for Cl, %[a]	Mole fraction M_1 in polymer F_1
0.05	120	9.50	12.48	0.40
0.10	120	16.28	14.23	0.46
0.20	120	14.68	16.34	0.55
0.30	120	11.35	15.72	0.53
0.40	120	17.68	15.72	0.53
0.50	90	14.40	16.12	0.54
0.70	90	11.20	18.36	0.64
0.80	90	5.05	19.72	0.70

[a] Crobaugh Laboratories, Inc., Charleston, West Virginia.

TABLE II
Data for Copolymerization of Vinylidene Chloride (M_1) with 4-Cyclopentene-1,3-dione (M_2)

Mole fraction M_1 in feed f_1	Time, min.	Conversion, %	Analysis for Cl, %[a]	Mole fraction M_1 in polymer F_1
0.05	90	3.91	16.65	0.23
0.10	90	4.20	24.93	0.34
0.20	150	12.83	37.12	0.50
0.30	150	15.54	42.87	0.58
0.40	150	7.05	59.34	0.80
0.50	150	6.44	62.97	0.86
0.60	150	17.42	61.70	0.84
0.70	150	13.15	68.27	0.93
0.80	15	1.86	66.21	0.90
0.90	15	2.42	68.90	0.94

[a] Galbraith Laboratories, Inc., Knoxville, Tennessee.

ported in Table I for copolymerization with *p*-chlorostyrene and in Table II for copolymerization with vinylidene chloride.

RESULTS

Copolymerization with *p*-Chlorostyrene

In Figure 1 the mole fraction *p*-chlorostyrene (M_1) in the copolymer F_1 is plotted against the mole fraction in the feed f_1. Solution of the copolymer equation by the Fineman-Ross[4] and Mayo-Lewis[5] methods are shown in Figures 2 and 3, respectively. From various r_1, r_2 combinations taken from

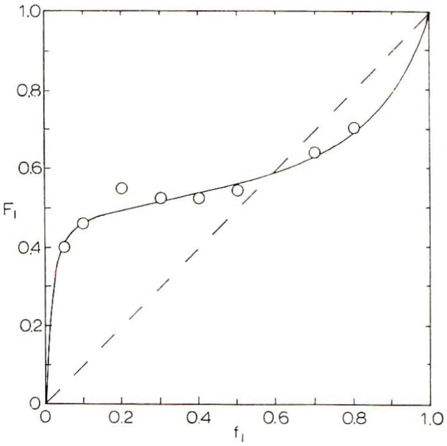

Fig. 1. Feed–copolymer composition plot for *p*-chlorostyrene (M_1), 4-cyclopentene-1,3-dione (M_2). The curve is for $r_1 = 0.32$, $r_2 = 0.02$.

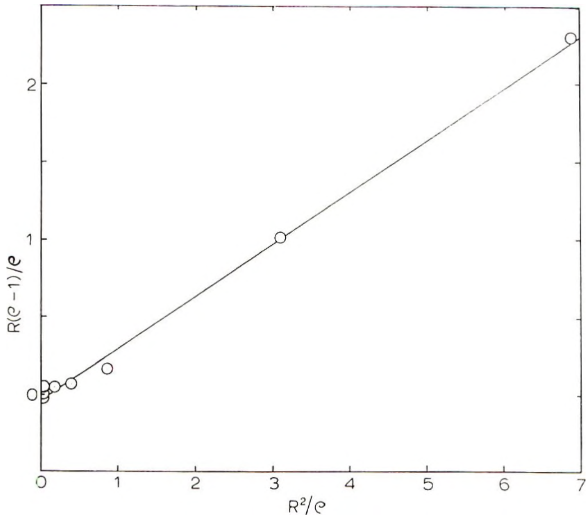

Fig. 2. Fineman-Ross plot for the copolymerization of *p*-chlorostyrene (M_1) with 4-cyclopentene-1,3-dione (M_2).

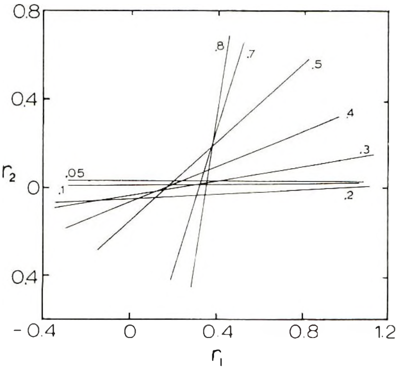

Fig. 3. Mayo-Lewis plot for the copolymerization of *p*-chlorostyrene (M_1) with 4-cyclopentene-1,3-dione (M_2).

within the area of intersection of Figure 3, copolymer composition curves were prepared with the aid of an IBM 7040 computer. The one which appeared to be the most accurate representation of the experimental data is shown in Figure 1. The reactivity ratios as determined by the three methods are tabulated in Table III.

TABLE III
Reactivity Ratios for the Copolymerization of
p-Chlorostyrene (M_1) with 4-Cyclopentene-1,3-dione (M_2)

Method	r_1	r_2
Fineman-Ross	0.34	0.03
Mayo-Lewis	0.30 ± 0.06	0.02 ± 0.01
Curve fitting	0.32	0.02 ± 0.01
Average	0.32 ± 0.06	0.02 ± 0.01

Copolymerization with Vinylidene Chloride

The feed–copolymer composition curve for the vinylidene chloride (M_1)–dione (M_2) system is shown in Figure 4. The data, plotted according to the Fineman-Ross method, were somewhat too scattered to provide reliable values for the reactivity ratios from a least-squares treatment over the entire range. However, a plot of the first four points ($f_1 = 0.05$–0.3), Figure 5, was reasonably linear, and values for the reactivity ratios were obtained (Table IV). Since the form of this portion of the copolymer curve

TABLE IV
Reactivity Ratios for the Copolymerization of
Vinylidene Chloride (M_1) and 4-Cyclopentene-1,3-dione (M_2)

Method	r_1	r_2
Fineman-Ross[a]	2.1	0.15
Mayo-Lewis	2.4 ± 0.6	0.15 ± 0.05

[a] Based upon data for $f_1 = 0.05$–0.3.

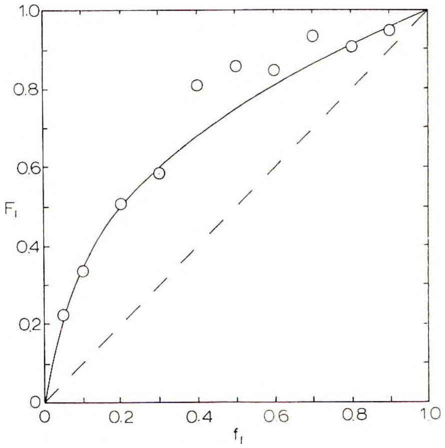

Fig. 4. Feed–copolymer composition plot for vinylidene chloride (M_1), 4-cyclopentene-1,3-dione (M_2). The curve is for $r_1 = 2.4$, $r_2 = 0.15$.

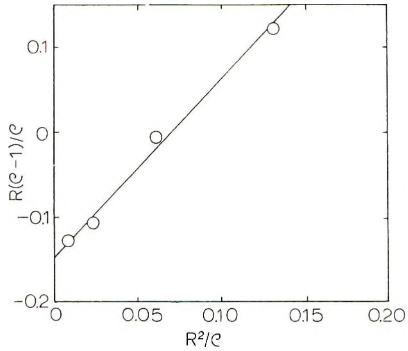

Fig. 5. Fineman-Ross plot for the copolymerization of vinylidene chloride (M_1) with 4-cyclopentene-1,3-dione (M_2).

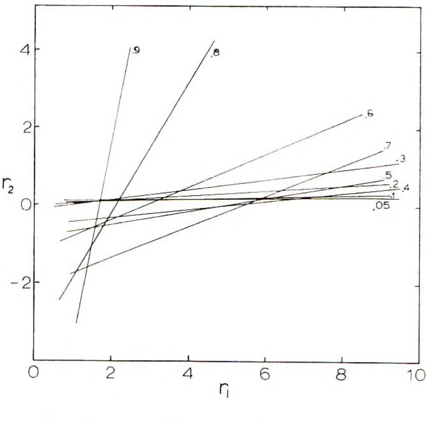

Fig. 6. Mayo-Lewis plot for the copolymerization of vinylidene chloride (M_1) with 4-cyclopentene-1,3-dione (M_2).

(Fig. 4) is determined largely by r_2 and affected little by small changes in r_1, a fairly accurate r_2 value may be obtained by this means. On the other hand, the r_1 value from the Fineman-Ross plot is not very accurate and is useful only as an estimate of the approximate magnitude.

Solution of the copolymer equation by the Mayo-Lewis method is shown in Figure 6. Here again a unique soution is difficult, since there appears to be two areas of maximum intersections, one for $r_1 = 2$ and another for $r_1 = 6$. In view of the approximate value for r_1, obtained from the Fineman-Ross treatment, the intersection at $r_1 = 2$ is the more reasonable value. From this area of intersection the r_1, r_2 values were evaluated (Table IV). Since the Mayo-Lewis values also seemed to provide the best copolymer composition curve to represent the experimental data, this curve was drawn in Figure 4.

From these reactivity ratios and the Q, e values for vinylidene chloride ($Q = 0.22$, $e = 0.36$),[6] the Q, e values for 4-cyclopentene-1,3-dione were calculated ($Q = 0.13$, $e = 1.37$). The good agreement between these values and those reported earlier from copolymerizations with methyl methacrylate and acrylonitrile[1] supports the reactivity ratio assignments.

DISCUSSION

The copolymerization of 4-cyclopentene-1,3-dione with *p*-chlorostyrene appears to be a typical alternating system, as evidenced by the composition curve of Figure 1. The copolymer equation was readily solved by the several methods and gave a unique pair of reactivity ratios, which described a composition curve closely following the experimental values over the entire range. These results thus fail to confirm the behavior of the styrene system, which approached 0.4 mole fraction styrene, and for which a unique pair of reactivity ratios could not be found.[2] If the polymerization involves a charge transfer complex, the *p*-chlorostyrene would be less able to donate an electron in such a situation than styrene and hence the different results obtained may represent a real difference in the polymerization mechanism. On the other hand, since different analytical techniques were used for the two systems, a determinate error could account for the apparent disparity in the results. Since the carbon analysis for the styrene–dione system would not be as accurate a measure of the copolymer composition as the chlorine analysis in the present case, error in the styrene copolymers is more probable. The question is still open, however. To provide a definite conclusion concerning the nature of these polymerizations, similar systems should be investigated to find other cases of unusual behavior. One such case appears to be the styrene–fumaronitrile system of Fordyce and Ham[7] which also approached a 0.4 mole fraction composition of the copolymers.

In copolymerization with vinylidene chloride, the dione exhibited the typical low reactivity associated with the cyclic monomers in general, which is consistent with the earlier results of copolymerization with methyl methacrylate and acrylonitrile. The Q, e values for the dione as reported here agree closely with those reported earlier[1] and thus confirm the original interpretation that, in comparison with maleic anhydride and *N*-butylmaleimide, the dione is of somewhat lower reactivity and has less polarity associated with the double bond system. In comparison with maleimide ($Q = 0.41$, $e = 1.33$),[8] the dione is a less reactive monomer as evidenced from its lower Q value but has about the same polarity as indicated by the closeness of the e values.

We express our appreciation to Mr. James B. Blair, undergraduate chemistry major, for assistance in the preparation of 4-cyclopentene-1,3-dione and to Mr. David A. Chapman, graduate research assistant, for computer programing.

This paper is taken from the Ph.D. dissertation of G. T. C. Li, West Virginia University, Morgantown, West Virginia, 1966.

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Résumé

La copolymérisation de la 4-cyclopentène-1,3-dione (M_2) avec le *p*-chlorostyrène et le chlorure de vinylidène a été rapportée. Les copolymères ont été préparés dans des tubes scellés sous atmosphère d'azote avec comme initiateur l'asobisisobutyronitrile. Les bandes d'absorption d'infrarouge à 1580 cm^{-1} révélaient la présence de dicétone-β fortement énolique et indiquaient que la copolymérisation avait eu lieu. Les compositions des copolymères étaient déterminées au départ d'analyses de chlore et les rapports de réactivité ont été évalués. La copolymérisation avec le *p*-chlorostyrène (M_1) était hautement alternante et fournissait les rapports de réactivité $r_1 = 0.32 \pm 0.06$; $r_2 = 0.02 \pm 0.01$. La copolymérisation avec le chlorure de vinylidène (M_1) fournissait les rapports de réactivité $r_1 = 2.4 \pm 0.6$, $r_2 = 0.15 \pm 0.05$. Les valeurs Q et e pour la dione ($Q = 0.13$, $e = 1.37$), telles qu'elles étaient évaluées au départ des résultats dans le cas du chlorure de vinylidène sont en bon accord avec les résultats rapportès antérieurement pour la copolymérisation avec le méthacrylate de méthyle et l'acrylonitrile et confirment la réactivité généralement basse de la 4-cyclopentadiène-1,3-dione dans des systèmes non-alternants.

Zusammenfassung

Die Copolymerisation von 4-Cyclopenten-1,3-dion (M_2) mit *p*-Chlorstyrol und Vinylidenchlorid wurde untersucht. Die Copolymeren wurden in zugeschmolzenen Gefässen unter Stickstoff mit Azobisisobutyronitril als Starter dargestellt. Infrarotabsorptionsbanden bei 1580 cm^{-1} liessen das Vorhandensein eines start enolischen β-Diketons erkennen und zeigten, dass Copolymerisation eingetreten war. Die Copolymerzusammensetzung wurde durch Chloranalysen bestimmt und die Reaktivitätsverhältnisse ermittelt. Die Copolymerisation mit *p*-Chlorstyrol (M_1) besass ausgeprägt alternierenden Charakter und lieferte die Reaktivitätsverhältnisse $r_1 = 0{,}32 \pm 0{,}06$, $r_2 = 0{,}02 \pm 0{,}01$. Die

Copolymerisation mit Vinylidenchlorid (M_1) ergab die Reaktivitätsverhältnisse $r_1 = 2{,}4 \pm 0{,}6$, $r_2 = 0{,}15 \pm 0{,}05$. Die aus den Vinylidenchloriddaten berechneten Q- und e-Werte für das Dion ($Q = 0{,}13$, $e = 1{,}37$) stimmen eng mit den früher bei der Copolymerisation mit Methylmethacrylat und Acrylnitril erhaltenen Werten überein und bestätigen die allgemein niedrige Reaktivität von 4-Cyclopenten-1,3-dion in nichtalternierenden Systemen.

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Stereoregularity of Poly(vinyl Ether)

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Synopsis

α-Methylvinyl isobutyl and methyl ethers were polymerized cationically and the structure of the polymers was studied by NMR. Poly(α-methylvinyl methyl ether) polymerized with iodine or ferric chloride as catalyst was found to be almost atactic, whereas poly(α-methylvinyl isobutyl ether) polymerized in toluene with BF_3OEt_2 or $AlEt_2Cl$ as catalyst was found to be isotactic. In both cases, the addition of polar solvent resulted in the increase of syndiotactic structure as is the case with polymerization of alkyl vinyl ether. *tert*-Butyl vinyl ether was polymerized, and the polymer was converted into poly(vinyl acetate), the structure of which was studied by NMR. A nearly linear relationship between the optical density ratio D_{722}/D_{736} in poly(*tert*-butyl vinyl ether) and the isotacticity of the converted poly(vinyl acetate) was observed.

INTRODUCTION

High-resolution nuclear magnetic resonance (NMR) has proved to be an effective means for determination of the microstructure of polymers. A number of structural studies of poly(vinyl alkyl ethers) by NMR have also been reported.[1,2]

Goodman and Fan[3] reported the NMR spectra of poly(α-methylvinyl methyl ether) for which only singlets were observed for α-methyl and methylene resonance, and they interpreted these results in terms of the syndiotactic structure of the polymers.

Relations between polymerization conditions of alkyl vinyl ether and the structure of the polymers have been reported.[4,5]

It may be reasonable to think that α-methylvinyl ether behaves in a manner similar to alkyl vinyl ether in polymerization. α-Methylvinyl isobutyl and methyl ethers were then polymerized, and the structure of the polymers was studied by NMR. As a comparison, *tert*-butyl vinyl ether was polymerized and the polymer was converted into poly(vinyl acetate), the structure of which was also studied by NMR.

EXPERIMENTAL

α-Methylvinyl ethers were prepared from isopropenyl acetate and alcohols by the method described by Crocker and co-workers.[6] *tert*-Butyl vinyl ether was synthesized by transetherification[7] from 2-*n*-butoxyethyl vinyl ether which was prepared from acetylene and 2-*n*-butoxyethyl alcohol. Monomer was washed with water, dried with potassium hydroxide, and distilled over metallic sodium just before use.

Polymerization was carried out as follows. Solvent and catalyst were introduced into an ampule equipped with a magnetic stirrer under a nitrogen atmosphere, and monomer was added after the desired temperature was attained. Polymer was purified by dissolution in benzene and precipitation into methanol.

Poly(*tert*-butyl vinyl ether) was converted into poly(vinyl alcohol) by hydrogen bromide[8] and then acetylated by acetic anhydride and pyridine.[9] Conversion was found to be complete from infrared spectra and elemental analysis.

NMR spectra were obtained with a Japan Electron Optics Laboratory 60 Mc./sec. spectrometer. Infrared spectra were obtained for films on salt plates. The viscosity was measured in benzene at 30°C. by use of an Ubbelohde viscometer.

RESULTS AND DISCUSSION

Polymerization of α-Methylvinyl Isobutyl Ether (MVIBE) and α-Methylvinyl Methyl Ether (MVME) and the Structure of the Polymers

Results of polymerization are shown in Tables I and II. Both PMVIBE and PMVME were white solids. In both cases, the addition of polar solvent caused the decrease in the polymer yield and in the viscosity. It is known that the addition of polar solvents causes an increase in the degree of polymerization in cationic polymerization of styrene,[10] while the reverse phenomenon is observed in case of alkyl vinyl ether.[11]

Infrared spectra are shown in Figures 1 and 2. In case of PMVME, there seem to be some differences between the infrared spectra of the polymers polymerized in a polar solvent and those polymerized in a non-

TABLE I
Results of Polymerization of α-Methylvinyl Isobutyl Ether at −78°C.

Sample	Catalyst	Solvent	Polymerization time, hr.	Yield, %	η_{sp}/c[a]
iB-BF-1	BF_3OEt_2	Toluene	46	5.9	0.17
iB-Al-1	$AlEt_2Cl$	Toluene	46	62.5	0.19
iB-Sn-1	$SnCl_4$	Toluene	16	—	—
iB-Fe-1	$FeCl_3$	Toluene	16	88.0	0.15
iB-FeC-1	$FeCl_3$	Toluene–CH_2Cl_2(40:5)	16	57.0	0.11
iB-FeC-2	$FeCl_3$	Toluene–CH_2Cl_2(20:25)	16	—	—
iB-I_2-1	I_2	Toluene	16	78.4	—
iB-I_2C-1	I_2	Toluene–CH_2Cl_2(40:5)	46	35.5	—

[a] Viscometry: 0.5 g./100 ml. in benzene at 30°C.

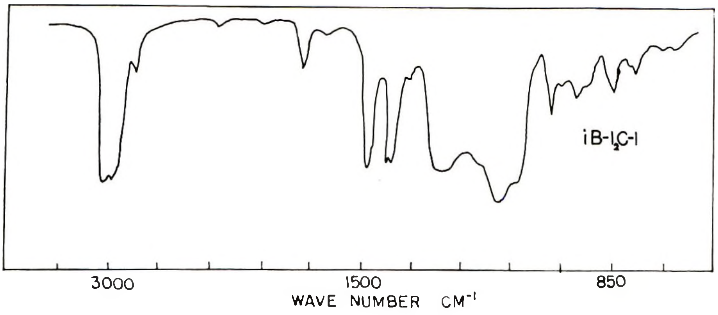

Fig. 1. Infrared spectrum of poly(α-methylvinyl isobutyl ether).

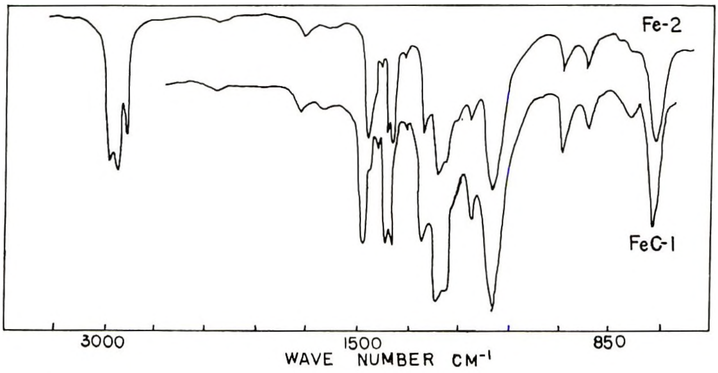

Fig. 2. Infrared spectra of poly(α-methylvinyl methyl ether).

polar solvent. The absorption at 810 cm.$^{-1}$ is stronger for the polymers obtained in polar solvent.

NMR spectra of PMVIBE and PMVME, determined in chloroform on 10% solutions at 50–55°C. are shown in Figures 3 and 4. For PMVIBE,

TABLE II
Results of Polymerization of α-Methylvinyl Methyl Ether at -78°C.

Sample	Catalyst	Solvent	Polymerization time, hr.	Yield, %	η_{sp}/c^a
Fe-1	$FeCl_3$	Toluene	4.5	5.9	0.16
Fe-2	$FeCl_3$	Toluene	6.5	61.9	—
Fe-3	$FeCl_3$	Toluene	16	77.6	—
FeC-1	$FeCl_3$	Toluene–CH_2Cl_2(40:5)	46	10.5	0.10
I_2-1	I_2	Toluene	4.5	31.4	0.14
I_2-2	I_2	Toluene	6.5	32.3	—
I_2C-1	I_2	Toluene–CH_2Cl_2(40:5)	46	21.0	0.12
I_2C-2	I_2	Toluene–CH_2Cl_2 (20:25)	46	—	—

[a] Viscometry: 0.5 g./100 ml. in benzene at 30°C.

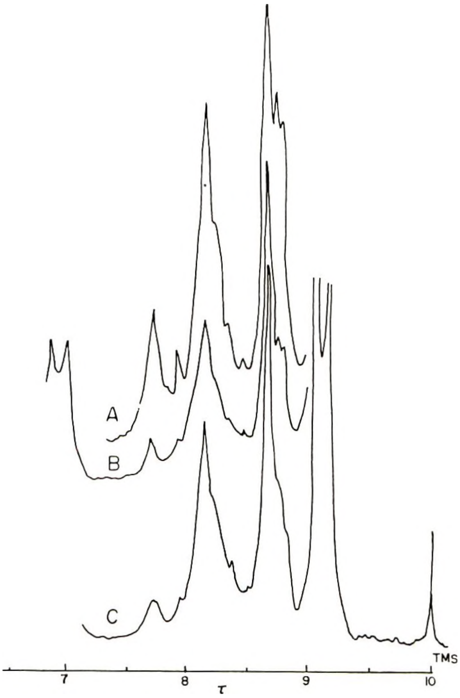

Fig. 3. NMR spectra of poly(α-methylvinyl isobutyl ether): (*A*) *i*-B-Fe C-1, polymerized with $FeCl_3$ in toluene–CH_2Cl_2(40:5); (*B*) *i*-B-BF-1, polymerized with BF_3OEt_2 in toluene; (*C*) *i*-B-Al-1, polymerized with $AlEt_2Cl$ in toluene.

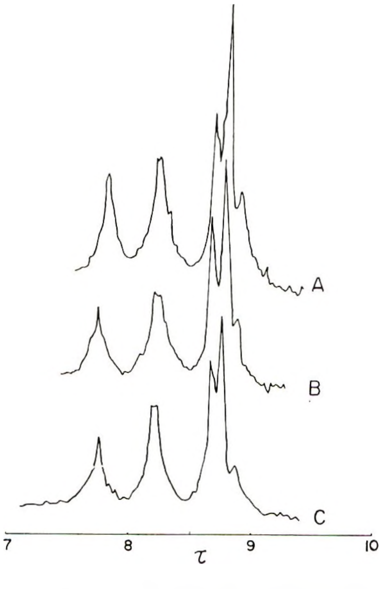

Fig. 4. NMR spectra of poly(α-methylvinyl methyl ether) (*A*) Fe-2, polymerized with $FeCl_3$ in toluene; (*B*) I_2-1, polymerized with I_2 in toluene; (*C*) I_2C-1, polymerized with I_2 in toluene–CH_2Cl_2 (40:5).

four multiplets are observed at 9.1, 8.75, 8.48–7.74, and 6.95 τ. A triplet at 8.82, 8.75, and 8.68 τ is due to α-methyl protons with different chemical configurations. Considering the polymerization conditions, i.e., the addition of polar solvent usually results in the decrease of isotacticity, these three absorptions may be assigned to isotactic, heterotactic, and syndiotactic configurations with increasing field. A multiplet at 8.48–7.74 τ is due to methylene protons in the main chain and methine protons in the side groups.

For PMVME, a triplet is observed at 8.86, 8.74, and 8.65 τ for all the polymers, which may be the absorptions due to syndiotactic, heterotactic, and isotactic α-methyl protons, respectively, as is the case with PMVIBE. For methylene protons, signals are observed at 7.74 and 8.16–8.22 τ. The areas under the peaks at 7.74 and 8.16–8.22 τ were determined and compared with the area of α-methyl peaks as shown in Table III. The areas per proton are 10–30% larger for methylene protons than for methyl protons. The same phenomenon is sometimes observed with poly(methyl methacrylates). This may be due to easy saturation of methyl protons in side chains, resulting in smaller area per proton.

TABLE III
Comparison of the Areas under the Peaks due to Methylene and Methyl Protons of Poly(α-methylvinyl Methyl Ether)

	Area, %[a]			Ratio of area	Stereoregularity in diad[b]			
		CH_2		CH_3 / CH_2	From CH_3		From CH_2	
Sample	CH_3	7.17 τ	8.16–8.22 τ	3 / 2	I, %	S, %	I, %	S, %
Fe-2	54	31	15	1.3	67	33	67	33
I_2-1	57	28	15	1.1	58	42	65	35
I_2C-1	54	28	18	1.3	54	46	61	39

[a] Total area is normalized to 100%.

[b] *I* and *S* indicate isotactic and syndiotactic configurations, respectively.

Then, diads determined from the methylene peaks under the assumption that the absorption at 7.74 τ is due to syndiotactic configurations and that at 8.16–8.22 τ due to isotactic ones, are compared with those calculated from the α-methyl proton triads. Although the agreement is not very satisfactory, partly because of unsharp and changeable spectra due to instability of the polymers, we may tentatively assign the singlet at 7.74 τ to syndiotactic equivalent methylene protons and the absorptions at 8.16–8.22 τ (they look like a quartet with a very small chemical shift) to isotactic ones.

The peak at 7.74 τ observed for PMVIBE may tentatively be assigned to syndiotactic methylenes, as is the case with PMVME, since it decreases with the increase of isotactic triads, as can be seen in Figure 3.

Although the reasons of the differences between our results and those reported by Goodman and Fan are not clearly known, one of them may be the unstableness of PMVME (PMVIBE is a stable polymer). It is quite necessary to determine NMR spectra shortly after dissolution. It is probable that the polymers of which they measured NMR spectra might be degraded.

The tacticity of the polymers, based on the assignment mentioned above, is listed in Tables IV and V. PMVME seems to be rather atactic polymer, whereas PMVIBE's which were polymerized in toluene with BF_3OEt_2 or $AlEt_2Cl$ as catalyst have isotactic structure. The addition of polar solvent caused the increase of syndiotactic configurations, as is the case with alkyl vinyl ether.

For PMVIBE, σ in terms of Furukawa's one-parameter model for isotactic polymerization based on enantiomorphic catalyst site[12] is calculated from the observed values of I. Then S and H are calculated from σ. This model seems to give a better fit to the experimental data as is shown in Figure 5, and it shows the possibility of control of monomer placement by catalyst asymmetry during isotactic polymerization of MVIBE. In case of PMVME, Bovey's one-parameter model[13] seems to be more applicable.

TABLE IV

Tacticity of Poly(α-methylvinyl Isobutyl Ether)

	Triad[a]				Calculated from σ	
Sample	I, %	H, %	S, %	σ[b]	H, %	S, %
iB-Fe-1	64	23	13	0.86	24	12
iB-FeC-1	44	29	27	0.75	38	19
iB-FeC-2	25	51	24	0.50	50	25
iB-I_2-1	58	28	14	0.83	28	14
iB-Sn-1	58	27	15	0.83	28	14
iB-BF-1	70	15	15	0.89	20	10
iB-Al-1	81	13	6	0.93	14	7

[a] I, H, and S indicate isotactic, heterotactic, and syndiotactic configurations, respectively.

[b] σ in terms of Furukawa's model, calculated from the observed value of I.

TABLE V

Tacticity of Poly(α-methylvinyl Methyl Ether)

	Triad[a]		
Sample	I, %	H, %	S, %
Fe-1	36	52	12
Fe-2	42	50	8
Fe-3	45	41	14
I_2-1	36	44	20
I_2-2	34	50	16
FeC-1	17	57	26
I_2C-1	24	60	16

[a] I, H, and S indicate isotactic, heterotactic, and syndiotactic configurations, respectively.

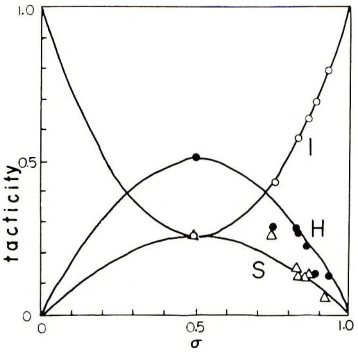

Fig. 5. Isotactic, heterotactic, and syndiotactic percentages as a function of σ: (○ *I* peaks; (●) *H* peaks; (△) *S* peaks.

Polymerization of *tert*-Butyl Vinyl Ether (*t*-BVE) and Structure of the Polymers

The results of polymerization are shown in Table VI. The effect of solvent on the viscosity is the same as that for α-methylvinyl ether.

TABLE VI
Results of Polymerization of *tert*-Butyl Vinyl Ether[a]

Sample	Catalyst	Solvent	Yield, %	η_{sp}/c[b]
TB-1	BF_3OEt_2	Toluene	96.8	1.04
TB-2	BF_3OEt_2	Toluene–CH_2Cl_2(50:4)	95.6	—
TB-3	BF_3OEt_2	Toluene–CH_2Cl_2(32:14)	83.8	—
TB-4	BF_3OEt_2	Toluene–CH_2Cl_2(20:25)	71.0	0.31
TB-7	BF_3OEt_2	Toluene–CH_2Cl_2(5:40)	79.0	0.17
TB-8	BF_3OEt_2	CH_2Cl_2–nitrobenzene (90:4)	67.2	—
TB-9	$SnCl_4$	Toluene	90.4	1.00
TB-13	$SnCl_4$	CH_2Cl_2	96.3	—

[a] Polymerization time: 2.5–4.5 hr.; polymerization temperature: −78°C.
[b] Viscometry: 0.5 g./100 ml. in benzene at 30°C.

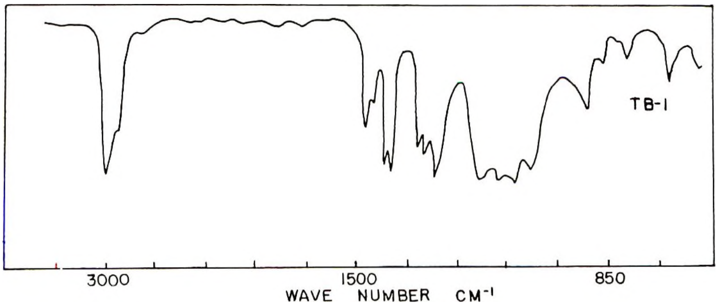

Fig. 6. Infrared spectrum of poly(*tert*-butyl vinyl ether).

TABLE VII
Tacticity of Poly(*tert*-butyl Vinyl Ether)

Sample	Triad[a]		
	I, %	*H*, %	*S*, %
TB-1	69	26	5
TB-2	63	32	5
TB-3	59	28	13
TB-4	32	51	17
TB-7	21	51	28
TB-9	30	47	23
TB-13	11	56	33

[a] *I*, *H*, and *S* indicate isotactic, heterotactic, and syndiotactic configurations, respectively.

The infrared spectrum is shown in Figure 6. Higashimura and coworkers proposed the optical density ratio D_{722}/D_{736} as the indication of the tacticity of the polymers.[5] The relative intensity ratio of the absorp-

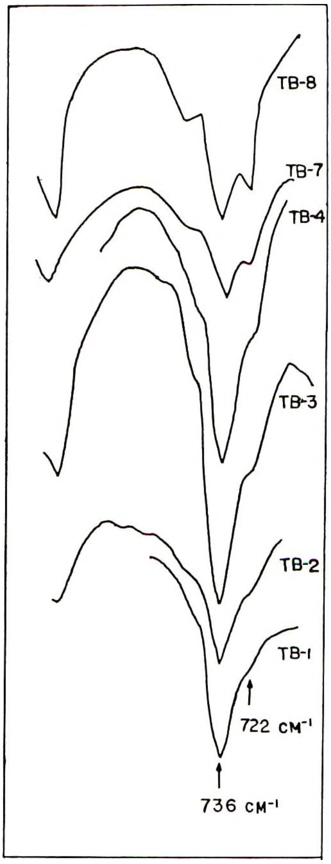

Fig. 7. Change of infrared spectra of poly(*tert*-butyl vinyl ether) with polymerization conditions.

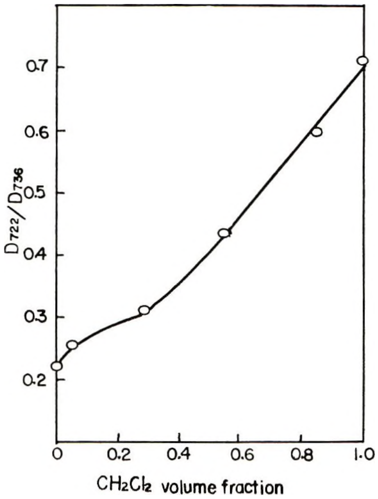

Fig. 8. Relationship between D_{722}/D_{736} and volume fraction of methylene chloride in polymerization system.

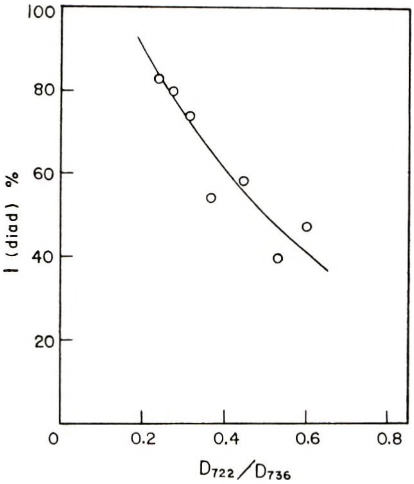

Fig. 9. Relationship between D_{722}/D_{736} and isotactic percentages (diads) of poly(*tert*-butyl vinyl ether).

tion at 722 and 736 cm.$^{-1}$ varied widely as the polarity of the solvent differed (Figs. 7 and 8).

PtBVE was converted into poly(vinyl acetate), NMR spectra of which were obtained in methylene chloride. Three peaks at 7.98, 8.00, and 8.02 τ for methoxy protons are assigned to isotactic, heterotactic, and syndiotactic configurations, respectively, according to Fujii et al.[14] and Murahashi et al.[15] The relative areas of triads are shown in Table VII. The polymers obtained in toluene are isotactic, whereas those polymerized in polar solvent have syndiotactic configurations, as already reported by Higashimura.[16]

There is a nearly linear relationship between D_{722}/D_{736} and I (isotactic fraction in terms of diads), as shown in Figure 9, indicating that D_{722}/D_{736} can be used as a measure of the tacticity of PtBVE.

The authors are indebted to Daicel Co. Ltd. for supplying the isopropenyl acetate.

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Résumé

Les éthers α-méthylvinyliques, isobutyliques et éthyliques ont été polymérisés cationiquement et les structures des polymères ont été étudiées par NMR. L'éther poly-α-méthylvinyléne méthylique polymérisait avec l'iode ou le chlorure ferrique comme catalyseur, et était essentiellement atactique alors que l'éther poly-α-méthylvinyl isobutylique polymérisait dans le toluène en présence de BF_3OEt_2 ou de $AlEt_2Cl$ comme catalyseur et était trouvé être isotactique. Dans les deux cas, l'addition de solvants polaires entraînait une augmentation de structure syndiotactique comme c'est la cas avec la polymérisation des éthers alkyle vinyliques. L'éther *tert*-butyl vinylique a été polymérise et le polymère a été transformé en acétate de polyvinyle dont la structure a été étudiée par NMR. Une relation environ linéaire entre le rapport des densités optiques D_{722}/D_{736} dans l'éther poly-*tert*-butyl vinylique et l'isotacticité de l'acétate de polyvinyle dans lequel celui-ci est converti a été observé.

Zusammenfassung

α-Methylvinylisobutyl- und -methyläther wurden kationisch polymerisiert und die Struktur der Polymeren mittels NMR untersucht. Mit Jod oder Eisen-III-chlorid als Katalysator polymerisierter Poly-α-methylvinyl-methyläther erwies sich praktisch als ataktisch, während in Toluol mit BF_3OEt_2 oder $AlEt_2Cl$ als Katalysator polymerisierter Poly-α-methylvinyl-isobutyläther isotaktisch war. In beiden Fällen führte der Zusatz eines polaren Lösungsmittels, ebenso wie bei der Polymerisation von Alkylvinyläthern,

zu einer Zunahme der syndiotaktischen Struktur. *tert*-Butylvinyläther wurde polymerisiert und das Polymere in Polyvinylacetat umgewandelt, dessen Struktur mittels NMR untersucht wurde. Es wurde eine nahezu lineare Beziehung zwischen dem Verhaltnis der optischen Dichte D_{722}/D_{736} im Poly-*tert*-butylvinyläther und der Isotaktizität des daruas erhaltenen Polyvinylacetates gefunden.

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Linear Polymers of Vinyl Aryl Monomers Containing Another Unsaturated Group

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Synopsis

The synthesis and the anionic polymerization of representative substituted styrenes, $CH_2{=}CH{-}C_6H_4R'$, where R′ is an ethylenic or acetylenic group attached directly or indirectly to the benzene ring, to linear polymers is described. In contrast, crosslinked polymers were obtained when radical and cationic initiators were used. The unpolymerized, unsaturated bonds in R′ in the resulting linear polymers were shown to be present by infrared spectroscopic methods and by the following post-reactions of these bonds: (*1*) the thermal- and radical-initiated crosslinking of the linear polymers through the unsaturated bonds in R′; (*2*) the post-bromination of these unsaturated bonds; (*3*) the post-copolymerization of these unsaturated bonds with vinyl monomers; and (*4*) the reaction of decaborane with the acetylenic bonds. The anionic copolymerizations of methyl methacrylate, acrylonitrile, and styrene with these monomers were performed and confirmed their behavior as substituted styrenes. Block copolymerizations with styrene and methyl methacrylate were also performed and the expected results obtained. Post-bromination of the linear polymers afforded self-extinguishing polymers. The linear polymers and copolymers may be classified as "self-reactive" polymers which yield thermosetting polystyrenes.

INTRODUCTION

Recently, the anionic polymerization of acrylic and methacrylic esters containing the allyl[1] and acetylenic groups[2,3] to linear polymers was reported. It was shown[1–3] that many multivinyl monomers are polymerized by radical and cationic initiators to insoluble, crosslinked polymers. Anionic initiators were shown[1] to polymerize some multivinyl monomers such as ethylene dimethacrylate and divinylbenzene to infusible, insoluble polymers because both unsaturated moieties react with the initiator.

In order to produce linear, soluble, fusible polymers by the anionic polymerization of multivinyl monomers having either two vinyl groups, or one vinyl group and one acetylenic group, it was necessary to select monomers with two groups such that only one was responsive to the polymerization initiator, while the other was unresponsive to the initiating and propagating conditions. In general, most vinyl groups are reactive with the types of radicals and cations used as polymerization initiators. However, marked differences are found in the reaction of anionic-type initiators on

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different vinyl moieties.[1-6] Accordingly, it should be possible to prepare linear polymers by the anionic polymerization of multivinyl aromatic monomers if the monomer contains one vinyl group, for example, $CH_2{=}CH{-}$ or $CH_2{=}\overset{|}{C}{-}CH_3$ attached directly to the electron-withdrawing aromatic group, and a second vinyl- or acetylenic-type group which is nonresponsive to anionic initiation. The linearity of the polymer may then be demonstrated by reacting the unpolymerized vinyl group or acetylenic group under other and different conditions after the linear polymer has been produced. For comparison with the related acrylic esters,[1-3] a number of substituted styrenes, $CH_2{=}CR{-}C_6H_4R'$ were chosen as representative compounds for this study; here R is H or CH_3 and R′ represents an unsaturated group attached directly or indirectly to the benzene ring.

The objective of this study is to prepare linear polymers of the $CH_2{=}C(R){-}C_6H_4{-}R'$ monomers of Table I by means of appropriate initiators,

TABLE I

$CH_2{=}\underset{\substack{|\\ R}}{C}{-}C_6H_4{-}R'$ Monomers

Monomers	R	R′
I	$-H$	*p*-$CH{=}CH_2$
II	$-CH_3$	*p*-$\underset{\substack{|\\ CH_3}}{C}{=}CH_2$
III	$-H$	*p*-$CH_2CH{=}CH_2$
IV	$-H$	*p*-$CH_2C{\equiv}CCH_3$
V	$-H$	*p*-$COOCH{=}CH_2$
VI	$-H$	*p*-$COOCH_2CH{=}CH_2$
VII	$-H$	*p*-$COOCH_2C{\equiv}CCH_3$
VIII	$-H$	*p*-$CH_2OCH_2CH{=}CH_2$
IX	$-H$	*p*-$CH_2OCH_2C{\equiv}CCH_3$
X	$-H$	*p*-$OCH{=}CH_2$
XI	$-H$	*p*-$OCH_2CH{=}CH_2$

and this paper describes the syntheses and polymerizations of these monomers under the influence of various radical, cationic, and anionic initiators. The chemical and spectroscopic methods used in determining the structure of the resulting polymers are given. Also described are the random and block anionic copolymerizations of some of the monomers with various other vinyl monomers.

EXPERIMENTAL

Materials

Reagents. Allyl alcohol, donated by Shell Chemical Company, was purified by distillation immediately before use, and the fraction boiling at 95.9–96.0°C. was used. 2-Butyn-1-ol was synthesized as previously recorded;[2] chloride b.p. 83°C.; bromide b.p. 106°C.

Solvents. Tetrahydrofuran, reagent grade, was purified according to the method given by Sorenson and Campbell[7] and refluxed over calcium hydride under deoxygenated, dried nitrogen, redistilled under helium into flamed receivers, and saturated with helium.

Toluene, A.R. grade, was purified according to the method of Vogel[8] and stored after vacuum distillation off calcium hydride into flamed receivers and saturated with helium.

Initiators. Sodium naphthalene was prepared according to the method of Scott[9] so that each milliliter of the tetrahydrofuran solution contained 23.4×10^{-5} mole of sodium naphthalene. Sodium benzalaniline was synthesized by the procedure given by Ringsdorf[10] as a 10.12% solution in tetrahydrofuran. *n*-Butyllithium, as a 15.08% solution in hexane, was obtained from Foote Mineral Company; only relatively fresh bottles were used. The initiator concentrations were determined after hydrolysis by titration for sodium hydroxide with dilute sulfuric acid. Benzoyl peroxide and analytical grade aluminum chloride were used as received.

Monomers

Styrene, divinylbenzene (50%), acrylonitrile, α-methylstyrene, methyl methacrylate, allylbenzene, allyl phenyl ether, and vinyl phenyl ether from commercial sources were purified by distillation, collected, refluxed over calcium hydride under deoxygenated dried nitrogen, redistilled, collected in flamed receivers and saturated with helium,[1,2] then stored over calcium hydride.

p-Diisopropenylbenzene (II) was obtained from Aldrich Chemical Company, recrystallized from ethanol and dried in a vacuum desiccator, m.p. 63.3°C. Before use, it was dissolved in tetrahydrofuran, 50 wt.-%, the solution saturated with helium, and allowed to stand over calcium hydride for at least 8 hr.

p-Divinylbenzene (I) was prepared by the method of Wiley,[11] m.p. 29.6–30.0°C., $n_D^{20} = 1.5842$. Before use, it was dissolved in tetrahydrofuran and the 50% solution saturated with helium and allowed to stand over calcium hydride for at least 8 hr.

Styrene-*p*-carboxylic acid (*p*-vinylbenzoic acid) was synthesized by the procedure recorded by Bissel and Spenger,[12] m.p. 127–128°C.

p-Allylstyrene (III) was prepared from *p*-vinylphenylmagnesium bromide and allyl bromide (b.p. 68–71°C.) following the method of Greber and Egle.[13] Some difficulty was encountered initially in preparing the Grignard reagent from *p*-bromostyrene; this was eliminated by the use at reflux temperature of tetrahydrofuran freshly distilled from lithium aluminum hydride as the solvent for the reaction. The yield of product was 58.2%; b.p. 59–60°C./2–3 mm.

ANAL. Calc'd. for $C_{11}H_{12}$: C, 91.67%; H, 8.33%. Found: C, 92.03%; H, 8.29%.

p-(2-Butyn-1-yl)styrene (IV) was prepared following the procedure[13] for allylstyrene above by using 1-bromo-2-butyne instead of allyl bromide. The yield was 39.8%; b.p. 63–66°C./3–4 mm. The bromide derivative of the monomer was prepared by treating approximately 1.0 g. of the monomer with a 25% solution of bromine in carbon tetrachloride at 0°C. for 4 days, evaporating the solution at 50 mm., and drying the product over sodium hydroxide in a vacuum desiccator.

ANAL. Calc'd. for $C_{12}H_{12}$: C, 92.3%; H, 7.70%. Found: C, 91.9%; H, 7.59%. Calc'd. for $C_{12}H_{12}Br_4$: Br, 67.07%. Found: Br, 66.54%.

Allyl(*p*-vinyl benzoate) (V) was prepared in a 50-ml. flask equipped with a reflux condenser and a Dean-Stark trap; in the flask were placed 118.4 g. (0.8 mole) styrene-*p*-carboxylic acid, 116.0 g. allyl alcohol (2 mole), 0.5 g. *p*-toluenesulfonic acid, 0.5 g. hydroquinone, and 350 ml. toluene. This mixture was refluxed until 14.2 ml. of water was collected in the trap, the toluene solution then neutralized with 10% aqueous sodium carbonate, dried over anhydrous magnesium sulfate, and distilled at 50 mm. pressure to remove the toluene. Tertiary butyl catechol (0.1 g.) was added to the crude ester and the product distilled. The yield was 138.0 g. (90%); b.p. 104–106°C./10 mm. The bromide derivative was prepared by reaction with bromine by the procedure given above.

ANAL. Calc'd. for $C_{12}H_{12}O_2$: C, 76.60%; H, 6.36%. Found: C, 76.30%; H, 6.34%. Calc'd. for $C_{12}H_{12}Br_4O_2$: Br, 62.96%. Found: Br, 61.87%.

Vinyl(*p*-vinyl benzoate) (VI) was prepared in a 250-ml. flask equipped with a reflux condenser and a nitrogen inlet from 37.0 g. of styrene-*p*-carboxylic acid (0.25 mole), 50.0 g. vinyl isobutyl ether (0.50 mole), 0.20 g. mercuric benzoate, and 0.05 g. hydroquinone; the mixture was heated to reflux under a slow nitrogen stream for 3 hr. and then distilled at 50 mm. pressure to remove by-products and excess vinyl isobutyl ether. Then 100 ml. of benzene was added to the crude ester, the solution washed with 10% aqueous sodium carbonate and with distilled water until neutral, dried over anhydrous sodium sulfate, and distilled. The yield was 22.7 g. (82%); b.p. 81–84°C./9–10 mm. The bromide derivative was prepared by the method given above.

ANAL. Calc'd. for $C_{11}H_{10}O_2$: C, 75.85%; H, 5.74%. Found: C, 75.45%; H, 5.70%. Calc'd. for $C_{11}H_{10}Br_4O_2$: Br, 64.74%. Found: Br, 62.88%.

2-Butyn-1-yl(*p*-vinyl benzoate) (VII) was prepared following the above procedure for the allyl ester by using 2-butyn-1-ol instead of allyl alcohol. The yield of product was 86.3%; b.p. 99–102°C./10–11 mm. The bromide derivative was prepared by the method given above.

ANAL. Calc'd. for $C_{13}H_{12}O_2$: C, 78.00%; H, 6.00%; O, 16.00%. Found: C, 77.60%; H, 5.80%; O, 16.52%. Calc'd. for $C_{13}H_{12}Br_4O_2$: Br, 61.54%. Found: Br, 62.21%.

(*p*-Vinylbenzyl) allyl ether (VIII) was prepared from *p*-(β-chloroethyl)-benzyl chloride, allyl alcohol, and sodium hydroxide following the method[14] of Chapin for saturated ethers. The yield was 68.6%; b.p. 83.5–86.0°C./0.5 mm.; 69°C./0.1 mm., $n_D^{20} = 1.5413$. The bromide derivative was prepared by the method given above.

ANAL. Calc'd. for $C_{12}H_{14}O$: C, 82.76%; H, 8.04%; O, 9.20%. Found: C, 82.80%; H, 8.07%; O, 9.18%. Calc'd. for $C_{12}H_{14}Br_4O$: Br, 64.83%. Found: Br, 64.18%.

(*p*-Vinylbenzyl) 2-butyn-1-yl ether (IX) was prepared by the same method[14] used for the allyl ether above by using 2-butyn-1-ol instead of allyl alcohol. The yield was 63.6%; b.p. 84–88°C./0.15–0.30 mm. The bromide derivative was prepared by the method given above.

ANAL. Calc'd. for $C_{13}H_{14}O$: C, 83.87%; H, 7.53%. Found: C, 83.82%; H, 7.50%. Calc'd. for $C_{13}H_{14}Br_4O$: Br, 63.42%. Found: Br, 62.66%.

Vinyl(*p*-vinyl phenyl) ether (X) was prepared from *p*-vinylphenol and vinyl isobutyl ether by the procedure given above for the vinyl(*p*-vinyl benzoate), mercuric benzoate being used as the catalyst. The yield was 77.4%; b.p. 90–91°C./12 mm.; b.p. 75–76°C./6 mm.

ANAL. Calc'd. for $C_{10}H_{10}O$: C, 82.18%; H, 6.85%. Found: C, 82.23%; H, 6.78%. Calc'd. for $C_{10}H_{10}Br_4O$: Br, 68.64%. Found: Br, 69.02%.

Allyl(*p*-vinyl phenyl) ether (XI) was prepared in a 250-ml. flask equipped with a reflux condenser and nitrogen gas inlet from 42.0 g. of sodium *p*-vinyl phenate (0.25 mole), 80 ml. tetrahydrofuran, 36.1 g. (0.3 mole) allyl bromide, and 0.1 g. tertiary butyl catechol; the mixture was refluxed under a slow nitrogen stream for 5 hr.; 100 ml. of toluene was added, the mixture cooled, and sodium bromide removed by filtration. The tetrahydrofuran was removed by distillation at 50 mm., the remaining toluene solution washed with distilled water until neutral and free of bromide; dried over anhydrous magnesium sulfate and distilled. The yield of product was 32.1 g. (76%); b.p. 82–85°C./6–7 mm. The bromide derivative was prepared by the method described above.

ANAL. Calc'd. for $C_{11}H_{12}O$: C, 82.50%; H, 7.50%. Found: C, 81.60%; H, 7.41%. Calc'd. for $C_{11}H_{12}Br_4O$: Br, 67.93%. Found: Br, 66.85%.

Vinylbenzyl allyl ether was prepared from vinylbenzyl chloride. A number of syntheses were performed with the use of commercial vinylbenzyl chloride[15] and sodium allylate in excess allyl alcohol or in tetrahydrofuran under a wide variety of experimental conditions to yield an ether which polymerized readily with radical and cationic initiators to infusible, insoluble polymers, but which, with various anionic initiators either refused to polymerize or did so to low yields and to low molecular weight, oily products. The same results were obtained when the vinylbenzyl allyl ether was highly fractionated through a 1-in. glass-helices-packed column at reflux ratios of 10:1 to 20:1 and the various fractions evaluated. Analysis by vapor-phase chromatography indicated 10–25% of an "impurity" in every preparation attempted even when highly fractionated samples of vinylbenzyl chloride, b.p. 82.7–83.0°C./5 mm., and 76.2–76.5°C./3.2 mm., $n_D^{20} = 1.5687$ were used.

An initial bluish-green color formed on the addition of sodium naphthalene to the monomer indicating the formation of an anion but this was followed by a rapid fading of the color.

In an attempt to destroy the impurity, another sample of vinylbenzyl allyl ether was distilled from sodium and the distilled product analyzed by vapor-phase chromatography. The distillate was shown to have the same ratio of impurities as the original untreated monomer. The results indicated that it was advisable to purify the vinylbenzyl chloride by other means, if possible. An attempt in this direction was made by partially polymerizing a sample of vinylbenzyl chloride with ultraviolet light initiation. After illumination for 127 hr., the viscosity of the vinylbenzyl chloride had increased slightly and the mixture gave a slight precipitate when a sample was added to methanol. Then, the vinylbenzyl chloride was carefully redistilled and the fraction distilling at 82.7–83.0°C./5 mm. was collected. Vinylbenzyl allyl ether was then prepared from it by reaction with sodium allylate. The isolated and purified product still possessed about 25% of the same type of impurities found in the earlier preparations as determined by vapor-phase chromatography.

Next, an attempt was made to purify vinylbenzyl allyl ether made above by partially polymerizing the impure monomer with *n*-butyllithium and heat, followed by distillation of the partially polymerized sample. After 12 hr. at 65°C. after injection with *n*-butyllithium the monomer had become slightly viscous, then acetic acid and *tert*-butyl catechol were added, and the monomer was distilled under nitrogen through an 18-in. glass-helices-packed column. The product was analyzed by vapor-phase chromatography and found to have the same ratio of impurities as the original untreated vinylbenzyl allyl ether.

A sample of the best fraction obtained gave the following analysis.

ANAL. Calc'd. for $C_{12}H_{14}O$: C, 82.76%; H, 8.04%; O, 9.20%. Found: C, 82.34%; H, 8.17, O, 9.20%; Cl, 1.29%.

Continued daily injection at room temperature of sodium naphthalene solution in the tetrahydrofuran solution of monomer over a period of a week to restore the anion color after fading finally caused noticeable polymerizations, as indicated by the viscosity increase.

All preparations yielded monomers containing chlorine, indicating that the impurity was contained in the vinylbenzyl chloride, which had been prepared by the chlorination of ethyl benzyl chloride followed by catalytic thermal dehydrochlorination according to the method of McMaster and Stowe.[16] They report the product as a mixture of *para* and 30–40% *ortho* isomers. The allyl ether synthesized from *p*-vinylbenzyl chloride prepared from the alcohol made according to the method of Chapin[14] polymerized readily with anionic initiators.

Before use, monomers III–XI were allowed to stand at least 8 hr. over calcium hydride, from which each was distilled under reduced pressure into a flamed receiver and then saturated with helium.

Polymerizations

Radical and Cationic. These polymerizations were carried out in rubber-capped serum glass vials with the use of 4 g. of the monomer and 0.02 g. benzoyl peroxide as the radical initiator and aluminum chloride as the cationic initiator. A typical polymerization was as follows. In a dry-box with a nitrogen atmosphere, into a thoroughly dried 5-ml. serum vial was placed the monomer and the initiator. The vial was then flushed with high-purity lamp-grade nitrogen and sealed. The samples containing radical initiators were placed in a 60°C. oven, while those containing aluminum chloride were kept at room temperature. At the end of 24 hr. the contents of the vials were examined and their solubility evaluated in acetone, toluene, dimethylformamide, and dimethyl sulfoxide.

Anionic. The apparatus and techniques used were substantially the same as those described[17] by Glusker et al. Before use the monomers were dried[17] over calcium hydride for at least 8 hr. and deoxygenated by bubbling helium through them for at least 2 hr. The reaction vessel consisted of a 100-ml. three-necked flask equipped by means of Y-tubes with a mechanical stirrer, gas inlet and outlet, thermometer, and a rubber serum bottle cap. After thorough flaming of the apparatus in a stream of helium, the solvent was added by means of syringe and needle through the serum cap. This was followed by the addition in the same manner of the monomer. The solution was then cooled to the desired temperature and the reaction initiated by injecting the solution of the initiator as rapidly as possible. The mole ratio of initiator to monomer was 1:500. The reaction was terminated by injecting 2 ml. of methanol. After termination, the polymer was isolated by pouring the reaction mixture into a tenfold excess of vigorously stirred methanol. The isolated polymer was washed again with methanol and dried to constant weight in a vacuum oven at 25°C. The infrared spectra of the monomers and polymers were recorded and the intrinsic viscosities of representative samples of the linear polymers determined. In addition to monomers I–XI, allyl phenyl ether and vinyl phenyl ether were also subjected to polymerization with *n*-butyllithium and sodium naphthalene at −78°C. and −40°C. as 25% and 50% solutions in tetrahydrofuran. In all cases, polymerization did not occur.

Copolymerization. The general procedure described above for anionic polymerization was used to prepare the copolymers. The comonomers were first mixed, then the copolymerizations were carried out in 25% tetrahydrofuran at −40°C.; the mole ratio of sodium naphthalene to mixed monomers was 1:100. The polymerizations were allowed to continue to obtain a perceptible degree of viscosity before they were terminated. The time varied from a few minutes to 1 hr., depending on the composition of the monomer mixture. The polymers were isolated by precipitation in nonsolvent, redissolved, and reprecipitated twice in a suitable solvent–nonsolvent system, the polymer solutions being carefully filtered before reprecipitation. The isolated copolymers were dried to constant weight in a vacuum oven at 25°C. In the copolymerizations with acrylonitrile, dimethylformamide was used as the solvent and methanol as the precipitant. In the remainder of the copolymerizations, acetone or benzene was used as the solvent and methanol as the precipitant.

Block Copolymerization. The same general procedure described above was used to prepare the block copolymers. They were prepared in a 25% tetrahydrofuran solution at −40°C. by first polymerizing one monomer with sodium naphthalene as the initiator, as above, then adding the second monomer,[18] allowing it to block-copolymerize before isolating the block copolymer. Most of the preparations consisted in adding the $CH_2=CHC_6H_4R'$ monomers to a styrene block previously prepared at −40°C. in a 25% tetrahydrofuran solution with the use of sodium naphthalene–styrene mole ratio of 1:100; conversion 93%; $[\eta] = 0.209$.

In one case, methyl methacrylate (10 mole-%) was added to 90 mole-% per cent of a block of III (Table III, $[\eta] = 0.594$).

Portions of the isolated copolymers were brominated and the composition calculated from the elemental analysis for bromine.[1]

Post-Reactions

Bromination of Linear Polymers. Into a 125-ml. glass-stoppered flask was placed 0.5 g. of polymer dissolved in 5 ml. of carbon tetrachloride. To this was added 2.00 g. of bromine in 3.00 g. of carbon tetrachloride. The mixture was stirred well, stoppered, and placed in a refrigerator at 0–5°C. for 7 days, then taken to dryness at room temperature at 15 mm. pressure, redissolved, reprecipitated twice, with 1:3 acetone–benzene as a solvent and methanol as precipitant, and dried in a vacuum oven at 30°C.

Thermal Crosslinking of Linear Polymers. Approximately 1.00 g. of each inhibitor-free linear polymer was dissolved in 5 ml. of benzene. Films were cast on glass plates and the solvent allowed to evaporate at room temperature. After being placed in an oven at 125°C. for 6 hr., the films were examined and found to be insoluble in acetone, benzene, carbon tetrachloride, and dimethylformamide.

Approximately 0.15 g. of the inhibitor-free linear polymers were heated at 250°C. for 15 min. on a Fisher-Johns melting point apparatus. The resulting masses were found to be insoluble in acetone and dimethylformamide.

Free-Radical Curing of Linear Polymers. Approximately 0.25 g. of each of the polymers was dissolved in 5 ml. of dry benzene and 0.002 g. of benzoyl peroxide was added to each solution. After being thoroughly mixed, the solution was poured onto glass plates, and solvent allowed to evaporate, and the plate placed in a 70°C. oven for 24 hr. The resulting film, at that time, was found to be insoluble in acetone, benzene, and dimethylformamide. To each of 2.5 g. samples of polymers of III, VII, and XI was added 0.2 wt.-% of benzoyl peroxide, then mixed thoroughly in a mortar and pestle and molded at 130°C. at 200 psi for 10 min. into a clear, hard, insoluble, infusible 1-in. disk.

Solutions of some of the linear polymers (Table II) were prepared in a number of monomers in which had been dissolved 0.10 wt.-% of benzoyl peroxide and the solution cast at 40°C. for 12 hr., 60°C. for 24 hr., and 100°C. for 48 hr. In all cases, colorless, insoluble, infusible polymers were obtained.

TABLE II
Post-Copolymerization of Some Linear Polymers with Other Monomers

Monomer		Polymer		
Parts	Monomer	Parts	Polymer	Resulting graft polymer
80	Styrene	20	III	Hard, insoluble, infusible
90	Methyl methacrylate	10	VI	Tough, insoluble, infusible
95	Ethyl acrylate	5	IX	Rubbery, insoluble, infusible
65	Divinylbenzene (50%)[a]	35	III	Very hard, insoluble, infusible

[a] Commercial grade.

Reaction with Decaborane. Samples of polymers IV, $[\eta] = 0.494$, and IX, $[\eta] = 0.322$, were reacted with 50% molar excess of decaborane in refluxing toluene and acetonitrile, according to the procedure previously recorded.[2,3]

ANAL. IV, calc'd. for $C_{12}H_{24}B_{10}$: C, 52.15%; H, 8.69%. Found: C, 54.56%; H, 8.53%.
IX, calc'd. for $C_{13}H_{26}B_{10}O$: C, 48.83%; H 8.07%. Found: C, 49.81%; H, 8.05%.

Both decaboronated polymers showed no appreciable softening up to 300°C. when heated on a Fisher-Johns melting point apparatus.

Viscosity Determinations

The intrinsic viscosities of representative samples of soluble polymers were determined in toluene solutions in a Canon 25-102 dilution viscometer. The bath temperature was maintained at 20 ± 0.02°C., and flow times were determined for at least three solution concentrations.

RESULTS AND DISCUSSIONS

The radical- and cationic-initiated polymerizations of III–XI would be expected to yield crosslinked, insoluble polymers since, in these structures, the styrene-vinyl group, (SV), in $CH_2{=}CHC_6H_4{-}$, and the second unsaturated structure in R′, are both susceptible to these types of initiators.

In order to demonstrate this point, III–XI were subjected to radical and cationic polymerizations with benzoyl peroxide and aluminum chloride, respectively, as the initiators; in each case, an insoluble, crosslinked gel was formed, indicating that both potential reaction sites had participated in the reaction. These results were compared with the polymerizations of the monovinyl monomers, methyl methacrylate and styrene, which are known to give soluble, fusible polymers, as well as with the polymerization of the multivinyl monomers, divinylbenzene (I) and diisopropenylbenzene (II), which are known to give crosslinked, infusible polymers.

On the other hand, it was believed that the anionic polymerizations of III–XI would lead to linear, soluble polymers with pendant unsaturated groups. These linear polymers would be the result of the selective polymerization solely through the vinyl group, A, of the respective monomers. In order to demonstrate this point III–XI were subjected to anionic polymerization reactions with *n*-butyllithium, sodium naphthalene, and sodium benzalaniline as initiators. The latter two are examples of radical-anion initiators.[10,19,20] The polymers formed in each case were soluble in a number of organic solvents and softened to viscous liquids or masses at higher temperatures. A summary of the results of the radical, cationic, and anionic polymerizations are shown in Table III.

TABLE III
Comparison of Radical, Cationic, and Anionic Initiation on Polymerization of Multivinyl Styrene

	Polymer with initiator[a]		
Monomer	Radical[b]	Cationic[c]	Anionic[d]
I	Crosslinked	Crosslinked	Crosslinked
II	"	"	"
III	"	"	Linear
IV	"	"	"
V	"	"	"
VI	"	"	"
VII	"	"	"
VIII	"	"	"
IX	"	"	"
X	"	"	"
XI	"	"	"

[a] 0.5% by weight on monomer.
[b] Benzoyl peroxide at 60°C.
[c] Aluminum chloride at 20°C.
[d] Sodium naphthalene at 0°C.

That the allyl group is not readily polymerized by anionic initiators was well demonstrated by the reluctance of allyl acetate, diallyl phthalate,[1] allyl phenyl ether, and allylbenzene to polymerization under comparable anionic conditions,[1] and by the synthesis of linear polymers from allyl acrylate and allyl methacrylate.[1] In a similar fashion, disubstituted acetylenic groups were shown[2,3] to be unresponsive to anionic initiation.

The formation under anionic initiation of linear, soluble polymers from III–XI in contrast to insoluble, crosslinked polymers from *p*-divinylbenzene (I) and diisopropenylbenzene (II) points to an essential difference between the two classes of monomers. All of them have two potentially polymerizable unsaturated groups; however, III–XI have only one vinyl group activated by the electron-withdrawing benzene ring, whereas di-

TABLE IV

Anionic Polymerization of $CH_2{=}CHC_6H_4{-}R'$ Monomers

Monomer	Monomer concn., %	Solvent[a]	Initiator[b]	Time, min.	Temperature, °C.	Conversion, %	[η], dl./g.
III	20	THF	SN	20	−78	98.6	0.780
III	20	THF	SN	60	−40	91.6	0.594
III	20	THF	SN	60	−20	86.4	0.476
III	20	THF	SN	60	0	72.9	0.357
III	20	THF	SN	60	20	67.2	0.136
III	20	THF	*n*-BuLi	60	−78	97.3	0.414
III	20	THF	SBA	20	−78	98.3	0.638
IV	30	THF	SN	20	−40	84.8	0.494
V	30	THF	SN	20	−40	80.2	0.316
VI	30	THF	SN	20	−40	81.7	0.337
VII	25	THF	SN	20	−40	81.8	0.276
VIII	25	THF	SN	20	−40	89.2	0.391
IX	25	THF	SN	20	−40	89.7	0.322
X	25	THF	SN	20	−40	79.6	0.307
XI	25	THF	SN	20	−40	84.4	0.363

[a] THF = tetrahydrofuran.

[b] SN = sodium naphthalene; SBA = sodium benzalaniline. BuLi used as a 15.08% solution in hexane; SN as a solution in THF containing 23.4×10^{-5} mole SN/ml.; SBA as a 10.12% solution in THF.

vinylbenzene and diisopropenylbenzene have two such activated vinyl groups and yield crosslinked polymers with anionic initiation.

The effects of temperature, initiator, solvents and monomer concentration of the polymerizations of III–XI are shown in Table IV; the results indicate that the polymerization is occurring substantially only through the styrene vinyl (SV) group, $CH_2{=}\overset{|}{C}{-}$, attached directly to the benzene ring.

A comparison of the infrared spectra of the monomers III–XI with those of the corresponding polymers indicate that only the SV group has polymerized substantially.

In the case of the styrenes, III, V, VI, VIII, X, and XI, which contain the SV group and a second $CH_2{=}CH{-}$ group, the spectra disclosed the disappearance of the styrene $CH_2{=}CH$ bands[12] at 7.15, 10.1, and 10.2 μ, while the olefinic bands(s)[13] at 6.95, 7.07, and 11.1 μ decreased correspondingly to the loss of the SV functions; this difference confirms the retention of the second $CH_2{=}CH$ function. In those styrenes (IV, VII, and IX) which contain the SV group together with a $-C{\equiv}C-$ group, the spectra showed the disappearance of the styrene bands while the acetylenic bands,[21] ($C{\equiv}CCH_3$), at 4.50 μ remained unchanged.[2]

Both the physical character of the polymers formed and the infrared spectra obtained are strong evidence that polymerization has occurred through the SV bond without affecting the second unsaturated bond in R′. The intrinsic viscosities of the polymers prepared at −78°C. were, as expected in anionic polymerizations, higher than those prepared at higher temperatures.

Since both sodium naphthalene and sodium benzalaniline exist as radical anions,[10,19,20,22,23] it was believed that the polymerizations initiated by them would exhibit some radical character and differ noticeably from those initiated by butyllithium. Differences, especially in the solubilities of the resulting polymers, might have been expected, since some radical polymerization of the R′ group and subsequent consequent crosslinking of the polymer could possibly have occurred. If such was the case, the degree of radical polymerization was so small as not to influence the polymer solubility appreciably. Due to the inherent differences between a radical-anion and a strictly anionic initiator, other differences in the polymerizations certainly are expected to have occurred. This aspect was not investigated at this time and is being considered for future studies along with kinetic measurements to determine the effect of initiator and monomer concentration on molecular weight, rate of polymerization, and microstructure. This investigation was intended primarily to establish the validity of the concept that monomers having one vinyl group activated by the electron-withdrawing benzene ring and another unactivated, unsaturated group can be predominantly polymerized through the vinyl group by means of appropriate anionic initiators.

Some relative values of their molecular weights may be estimated from the intrinsic viscosities given in Table IV from other viscosity–molecular weight relationships such as $[\eta] = 1 \times 10^{-4}M^{0.72}$ for polystyrene[24] in toluene. On this not too satisfactory basis, the lowest molecular weight of the polymers prepared is estimated to be of the order of 15,000–20,000, and the highest of the order of 135,000–150,000.

The linear polymers of the monomers containing acetylenic groups are relatively stable in air and give no evidence of increasing in viscosity or crosslinking when exposed to air for one week and are similar in this respect to the related linear polyacrylic esters.[2] The polymers containing pendant $CH_2{=}CH—$ groups show a marked tendency to crosslink on standing in air, and in this respect are similar to the linear polyacrylic allyl esters.[2] This tendency to crosslink is retarded by the addition of inhibitors. The polymers of III, V, and VI appear, qualitatively, to crosslink more readily than those of VII, X, and XI.

Post-Reactions of Linear Polymers

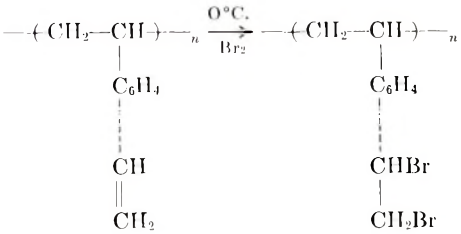
Several of the linear polymers prepared from III–XI were subjected to various post-reactions of the pendant unsaturated group. One of the purposes of these post-reactions was to lend support to the proposed linear structures by characterizing the products formed by these reactions. Among the reactions employed were the bromination of the pendant unsaturated group, as well as the thermal and radical crosslinking of the polymers through these groups.

The data on the dibromination of the linear polymers is summarized in Table V.

TABLE V
Dibromo Derivatives of $CH_2{=}CHC_6H_4R'$ Polymers

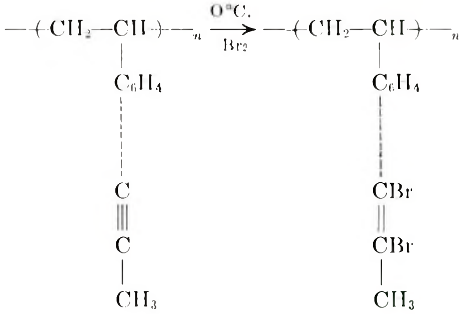
Polymer of monomer	Bromine, %	
	Calculated	Found
III	52.60	52.20
IV	50.60	51.39
V	47.84	47.24
VI	46.22	46.00
VII	44.38	44.46
VIII	47.88	47.01
IX	46.21	46.83
X	52.25	51.62
XI	50.00	48.76

The linear polymers obtained by the sodium naphthalene polymerization of III, V, VI, VIII, X, and XI at −40°C. were subjected to bromination with bromine as the brominating agent.[1] The amount of bromine found in the brominated polymer is in good agreement with the expected values.



$$-(CH_2-\underset{C_6H_4-CH=CH_2}{CH})-_n \xrightarrow[Br_2]{0^\circ C.} -(CH_2-\underset{C_6H_4-CHBr-CH_2Br}{CH})-_n$$

A comparison of the infrared spectra of the initial polymers and those of the brominated polymers disclosed by the disappearance of the carbon–carbon double bond at 6.95, 7.07, 10.35, and 11.10 μ. The subsequent appearance of a peak, in the region of 16.67–20.00 μ, attributable[21] to —C—Br was not investigated since this region is beyond the range of the available spectrophotometer. When preliminary tests were made with the use of chlorine instead of bromine as the halogenating agent, a small peak was observed at 14.84 μ attributable[21] to the C—Cl bond. The infrared spectra of the brominated linear polymers of IV, VII, and IX disclosed the disappearance of the acetylenic peak at 4.50 μ and the subsequent appearance of a peak at 6.03 μ attributable to a carbon–carbon bond.[2,21]

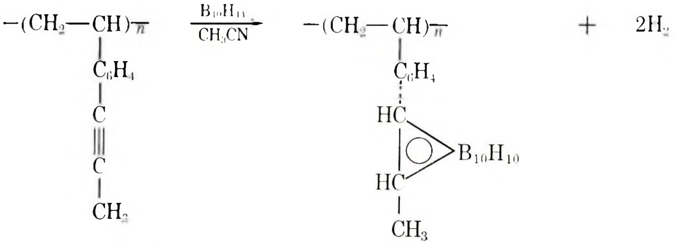


$$-(CH_2-\underset{C_6H_4-C\equiv C-CH_3}{CH})-_n \xrightarrow[Br_2]{0^\circ C.} -(CH_2-\underset{C_6H_4-CBr=CBr-CH_3}{CH})-_n$$

All of the brominated polymers were self-extinguishing when ignited in a flame and then withdrawn from the flame.

Further confirmation of the linear structure of these polymers and of the reactivity of the pendant unsaturated groups was obtained by both the thermal- and radical-induced crosslinking of the polymers through the unsaturated groups. The major portion of the radical-induced post-reactions consisted of casting films of the polymers from solutions containing benzoyl peroxide and heating the solvent-free films at 70°C. to produce insoluble, crosslinked films. The thermal-induced post-reactions were conducted in a similar manner, except that benzoyl peroxide was not included in the polymer solutions and heating was carried out at 125°C. Crosslinked films were also obtained in these thermal reactions.

The molding of the linear polymers of III, VII, and XI under heat and pressure to insoluble, infusible, shaped articles as the result of radical-induced crosslinking of the pendant unsaturated groups classifies these polymers as self-reactive, thermosetting polystyrenes. The linear polymers of IV and IX were both subjected to reactions with decaborane, acetonitrile being used as the catalyst. Elemental analyses indicated that the decaboronation reaction achieved in the case of polymer IV was 94% and of polymer IX was 97.2%.



The infrared spectra of the decaboronated product indicated a loss of the acetylenic peak at 4.50 μ and the presence of a BH peak at 3.92 μ.[2,3]

The reactivity of the acetylenic groups in the above post-reaction is additional evidence that the acetylenic function was substantially unaffected in the original polymerization.

The physical character of the polymers, the spectroscopic evidence, and these post-reactions prove conclusively that, in these new substituted styrenes, polymerization occurred anionicly only through the styrene vinyl group, SV, without affecting the second unsaturated group, R′. The random copolymerizations of the polymer of III with styrene and divinylbenzene, respectively, of VI with methyl methacrylate (MMA), of IX with ethyl acrylate (EA) yielded insoluble, infusible castings in all cases. These results show that these linear polymers act as crosslinking agents for monomers at relatively low concentrations; this is indicative of the presence of a multiplicity of active unsaturated pendant groups in the polymers.

Copolymerizations

The effect of the pendant unsaturated groups on III–XI are not known. Some change would be expected from the value of styrene and other substituted styrenes. In order to gain some insight into the reactivity of these monomers, some of them were subjected to anionic copolymerization with methyl methacrylate, styrene, and acrylonitrile at −40°C.

Experimental data is shown in Tables VI–VIII. The compositions of the copolymers were determined from their elemental analyses.

The $CH_2{=}CHC_6H_4R'$–methyl methacrylate (MMA) copolymerizations yielded the expected results. The copolymers consisted almost exclusively of MMA and can be compared[10,25] to the sodium naphthalene copolymerization of styrene with MMA. In the $-CH_2{=}CHC_6H_4R'$–acrylonitrile (AN) copolymerization, acrylonitrile is preferentially incorporated into the copolymer and the data is compatible with the sodium naphthalene-initiated styrene–acrylonitrile copolymerization.[26,27] In the $CH_2{=}CHC_6H_4R'$–styrene copolymerizations, styrene is preferentially incorporated into the copolymer and these results are in accord with the findings of Overberger[28] in other styrene-substituted styrene systems.

The procedure reported by Baer[18] and Zilkha[20] was used in the preparation of the block polymer. After the polymerization of styrene or III at −40°C., the second monomer was added and after 4 hr. the polymeriza-

TABLE VI
Copolymerization of Methyl Methacrylate (M_1) with $CH_2{=}CHC_6H_4R'$ (M_2)

M_1, mole-%	M_2, mole-%	M_2	Copolymer analysis		M_1 in copolymer, mole-%
			C, %	H, %	
77.3	22.7	III	60.20	8.02	~100.0
51.6	48.4	III	60.00	8.04	~100.0
24.8	75.2	III	60.10	8.01	~100.0
50.2	49.8	IV	59.76	7.76	99.6
49.4	50.6	V	59.25	7.62	98.9
53.4	46.6	VI	59.52	7.64	99.2
47.8	52.2	VII	59.64	7.66	99.4
56.9	43.1	IX	60.06	8.01	~100.0
46.7	53.3	XI	59.82	7.68	99.7

TABLE VII
Copolymerization of Acrylonitrile (M_1) with $CH_2{=}CHC_6H_4R'$ (M_2)

M_1, mole-%	M_2, mole-%	M_2	Conversion, %	Nitrogen in copolymer, %[a]	M_1 in copolymer, mole-%
76.4	23.6	III	7.6	26.39	~100.0
53.2	46.8	III	5.9	26.40	~100.0
27.1	72.9	III	4.2	26.25	99.4
51.5	48.5	IV	8.8	26.37	99.8
50.1	49.9	VI	9.7	26.33	99.5
49.2	50.8	VII	6.4	26.35	99.7
54.3	45.7	VIII	7.3	26.30	99.6
55.5	44.5	X	10.1	26.40	~100.0

[a] Corrected value.

TABLE VIII
Copolymerization of 50 mole-% of Styrene (M_1) with $CH_2{=}CHC_6H_4R'$ (M_2)

Monomer M_2	Conversion, %	Copolymer analysis		Br in brominated copolymer, %	Styrene (M_1) in copolymer, mole-%
		C, %	H, %		
III	5.1	91.91	7.89	25.60	72.8
V	4.8	85.21	7.12	23.57	74.6
VI	3.9	86.42	6.96	23.41	76.6
VII	4.4	86.52	6.81	24.82	75.1
VIII	5.5	88.69	7.80	23.48	76.7
IX	4.9	88.81	7.64	24.27	73.8
X	5.7	89.20	7.38	23.28	78.0

TABLE IX

Block Copolymerization of Polystyrene (M_1) with $CH_2{=}CHC_6H_4R'$ (M_2) at −40°C.

Poly-mer	Styrene in block, mole-%	M_2	M_2, mole-%	Conver-sion, %	Br in co-polymer, %	Block copolymer		[η], dl./g.
						Styrene, mole-%[a]	M_2, mole-%[b]	
A	95	III	5	99.6	8.48	94.1	5.9	0.224
B	90	III	10	100.0	13.75	89.2	10.8	0.228
C	85	III	15	97.0	17.91	85.0	15.0	0.224
D	75	III	25	96.8	26.84	73.2	26.8	0.263
E	90	IV	10	94.3	11.25	91.3	8.7	0.227
F	90	VI	10	99.8	13.65	88.8	11.2	0.230
G	90	VII	10	98.5	16.41	89.7	10.3	0.232
H	90	VIII	10	98.2	10.72	91.4	8.6	0.228
I	85	IX	15	97.3	16.08	86.6	13.4	0.241
J	85	XI	15	98.1	18.85	83.5	16.5	0.246

[a] By difference.

[b] Calculated from dibromo derivatives.

tion was terminated. The increase in $[\eta]$ from the original 0.209, post-reactions of bromination and thermal and radical crosslinking of the block styrene–$CH_2{=}CHC_6H_4R'$ copolymerization indicated that the $CH_2{=}CHC_6H_4R'$ monomers had reacted with the polystyrene anions. Since the polystyrene anions prepared by sodium naphthalene are "living" polymers,[28] undoubtedly the $CH_2{=}CHC_6H_4R'$ monomers constitute the termini of the polymer chains. The results are shown in Table IX.

Polymers A–J (Table IX) were converted to crosslinked polymers when mixed with 0.5 wt.-% benzoyl peroxide and heated at 110°C. for 3 min. Extraction in refluxing benzene of polymers C and G showed that 98.8 and 96.7%, respectively, of the polymer composition was insoluble after crosslinking. This probably indicates the presence of minor amounts of homopolystyrene. Block copolymerization of these monomers with polystyrene anions appears to afford a facile method of preparing "thermosetting" styrenes.

The III–methyl methacrylate block polymer (90:10 mole-%) was treated with refluxing acetonitrile to extract the methyl methacrylate homopolymer, dried, and weighed. Conversion of MMA was 62%; mole ratio of polymer of III–MMA in block copolymer was 93.55:6.44; $[\eta] = 0.664$. The infrared spectrum of the dried residual polymer showed the ester absorption band at 5.8 μ, indicative of the presence of the MMA in the copolymer. This product was converted to the infusible, insoluble state when heated at 150°C. for 15 min. or at 100°C. for 2 min. when mixed with 1.0 wt.-% benzoyl peroxide.

This paper is abstracted in part from a portion of the M.S. dissertation of T. R. Hoffend, University of Notre Dame, 1964.

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Résumé

La synthèse et la polymérisation anionique de styrènes substitués, $CH_2{=}CH{-}C_6H_4R'$ où R′ est un groupe éthylénique ou acétylénique attaché directement ou indirectement au noyau benzénique en vue d'obtenir des polymères linéaires, ont été décrites. On a obtenu des polymères pontés lorsque l'on utilisait des initiateurs radicalaires et cationiques. Les liaisons non polymérisées insaturées dans R′ dans le polymère linéaire résultant ont été démontrées par la méthode spectroscopique infrarouge et par les post-réactions suivantes de ces liaisons: (*a*) le pontage thermique initié par les radicaux des polymères linéaires au moyen de leurs liens insaturés à R′, (*b*) la postbromation de ces liens insaturés, (*c*) la postcopolymérisation de ces liens insaturés avec les monomères vinyliques; (*d*) la réaction du décarbrane avec les liens acétyléniques. Les copolymérisatins anioniques du méthacrylate de méthyle, de l'acrylonitrile et du styrène avec ces monomères ont été effectuées et elles confirment leur comportement comme styrène substitué. Les copolymérisations séquencées avec le méthacrylate de méthyle ont été également effectuées et les résultats attendus ont été obtenus. La postbromation de polymères linéaires fournissaient des polymères auto-extincteurs. Las polymères linéaires et copolymères peuvent être classifiés comme polymères réactionnels parce qu'ils fournissent des polystyrènes par durcissement thermique.

Zusammenfassung

Die Synthese und die anionische Polymerisation von repräsentativen substituierten Styrolen $CH_2{=}CH{-}C_6H_4{-}R'$, wo R′ eine direkt oder indirekt an den Benzolring gebundene Äthylen- oder Acetylengruppe ist, zu linearen Polymeren wird beschrieben. Bei Verwendung radikalischer oder kationischer Starter wurden dagegen vernetzte Polymere erhalten. Die nicht-polymerisatisierten ungesättigten Bindungen von R′ in den gebildeten linearen Polymeren wurden durch infrarotspektroskopische Methoden sowie durch folgende Reaktionen dieser Bindungen nachgewiesen: (*a*) thermisch und radikalisch gestartete Vernetzung der linearen Polymeren über die ungesättigten Bindungen in R′; (*b*) Copolymerisation dieser ungesättigten Bindungen mit Vinylmonomeren; und (c) Reaktion von Dekaboran mit den Acetylenbindungen. Die anionische Copolymerisation dieser Monomeren mit Methylmethacrylat, Acrylnitril und Styrol wurde durchgeführt und bestätigte ihr Verhalten als substituierte Styrole. Bei der Blockcopolymerisation mit Styrol und Methylmethacrylat wurde das erwartete Verhalten gefunden. Eine Nachbromierung der linearen Polymeren liefert flammensichere Polymere. Die linearen Polymeren und Copolymeren können als "selbst-reaktive" Polymere klassifiziert werden, die wärmehärtende Polystyrole liefern.

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Studies in Cyclocopolymerization. III. Copolymerization of Divinyl Ether with Certain Nitrogen-Containing Alkenes*

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Synopsis

The copolymerization of divinyl ether with fumaronitrile (A), tetracyanoethylene (B), and 4-vinylpyridine (C) has been studied, azobisisobutyronitrile being used as initiator. The compositions of the copolymers were calculated from their nitrogen and unsaturation content. Over a wide range of initial monomer composition, the mole fraction of A in the copolymers lies in the range 0.55–0.63, and the copolymers contained only 2–3% unsaturation, indicating a high degree of cyclization. The composition of the copolymers of B indicated that cyclization occurred to only a small extent, as the copolymers contained rather high unsaturation content. The values of $r_1 = 0.23$ and $r_2 = 0.12$ were obtained. The mole fraction of C in the copolymers lies between 0.85 and 0.998. If the assumption is made that $r_1 \simeq r_c \simeq 0$ and there is predominant cyclization, $r_2 = 32.0$ in this case. The difference in the composition of the copolymers is attributed to the difference between the electron density of the double bonds in A, B, and C.

INTRODUCTION

The copolymerization of 1,4-dienes with certain monoolefins has been shown to proceed by a bimolecular alternating inter-intramolecular mechanism.[1–4] In a recent paper from this laboratory,[5] a general copolymer composition equation for this copolymerization has been presented. The derived equation which relates copolymer composition to monomer feed composition in terms of five reactivity ratio parameters is given as eq. (1):

$$n = \frac{(1 + r_1x)\left[\dfrac{1}{[\mathrm{M}_2]} + \left(\dfrac{1}{a}\right)\left(1 + \dfrac{x}{r_3}\right)\right]}{\left(\dfrac{1}{a}\right)\left[\left(\dfrac{x}{r_3}\right) + \left(\dfrac{r_2}{x}\right) + 2\right] + \left(\dfrac{1}{[\mathrm{M}_2]}\right)\left[1 + \left(1 + \dfrac{r_2}{x}\right)(1 + r_cx)^{-1}\right]} \tag{1}$$

Here, $x = [\mathrm{M}_1]/[\mathrm{M}_2]$ is the mole fractional ratio of monomers in the feed, $n = [\mathrm{m}_1]/[\mathrm{m}_2]$ is the mole fractional ratio of monomers in the copolymer at

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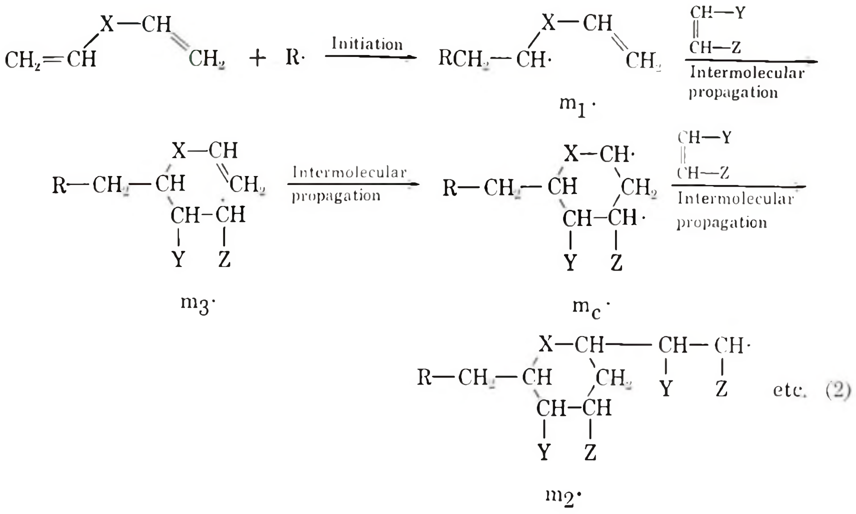
low conversions, $r_1 = k_{11}/k_{12}$; $r_2 = k_{22}/k_{21}$; $r_3 = k_{32}/k_{31}$; $r_c = k_{c1}/k_{c2}$; and $a = k_c/k_{32}$. The reactivity ratio parameters are defined in terms of the previously proposed kinetic scheme.[5] In certain special cases, eq. (1) can be approximated to simpler forms as previously described in detail and designated as (a), (b), and (c).

The general copolymer composition equation was further supported by the results of the most recent paper in this series,[6] in which copolymerization of 3,3-dimethyl-1,4-pentadiene and divinyl sulfone with acrylonitrile was reported and the reactivity ratio parameters for these systems were determined.

Copolymerization of 1,6-dienes with monoolefins has been studied by many authors, and general copolymer composition equations have been developed.[7–11] The dienes were found to be incorporated into the copolymer chain according to the alternating intra-intermolecular propagation mechanism.[11] In these copolymers, the diene radical undergoes direct cyclization to form a unimolecular repeating unit. In the present system of copolymerization of 1,4-dienes with monoolefins, the monoolefin is inserted into the propagating chain before cyclization, and the propagation proceeds by a bimolecular alternating inter-intramolecular mechanism. It can be illustrated as shown in eqs. (2).



This mechanism has been widely recognized; several systems have been investigated in which the 1,4-diene was 1,4-pentadiene, divinyl sulfone, divinyl ether, divinyldimethylsilane, or divinylaniline and the monoolefin maleic anhydride, acrylonitrile, fumaronitrile, methyl methacrylate, *N*-phenylmaleimide, vinyl acetate, or dialkyl fumarates and maleates.

With reference to the copolymerization kinetic scheme,[5] the fate of the intermediate radical, $m_3\cdot$, is governed by the relative rate of cyclization (k_c) and addition to the monomers 1 (k_{31}) and 2 (k_{32}). The present study was undertaken to provide further support of copolymerization by the alternating inter-intramolecular mechanism, and to study the effect of electronic character of the monoolefin on the relative rate of cyclization. The 1,4-diene used was divinyl ether; the monoolefins used were nitrogen-containing compounds. Copolymerization of the following systems was studied: (A) divinyl ether with fumaronitrile, (B) divinyl ether with tetracyanoethylene, and (C) divinyl ether with 4-vinylpyridine.

EXPERIMENTAL

Materials

Divinyl ether was obtained from Merck, Sharp and Dohme and was freshly distilled (under nitrogen) before copolymerization (b.p. 29°C.). Fumaronitrile was obtained from Monsanto Chemical Company and was carefully recrystallized from benzene and dried under vacuum (m.p. 96°C.). Tetracyanoethylene was obtained from Aldrich Chemical Company and was recrystallized from chlorobenzene. This yielded a white-grey precipitate having m.p. 200°C. after drying overnight in a vacuum oven at 50°C. 4-Vinylpyridine was obtained from K and K Laboratories and was freshly distilled (b.p. 60°C./13 mm.) through a 12-in. Vigreux column. Dimethylformamide (Fisher reagent) was purified in the following way: 10% methanol was added and the solution was distilled under normal pressure to remove the methanol. Dimethylformamide was distilled under reduced pressure (b.p. 76°C./39 mm.). Before using 1% P_2O_5 was added, and the mixture was stirred for 0.5 hr., then distilled under reduced pressure in a nitrogen atmosphere. Benzene (Fisher reagent) was dried over sodium and distilled before using.

Polymerization

For each system, the monoolefin was weighed and the divinyl ether measured, volumetrically directly into separate 25-ml. volumetric flasks and each diluted to volume with the solvent. The total monomer concentration was 3 mole/l. The concentration of azobisisobutyronitrile (AIBN) used as initiator was 1% by weight of the total monomer concentration. The solutions of monoolefin and AIBN were transferred to 12-mm. glass tubes, and the tubes were flushed with nitrogen and cooled in a Dry Ice–acetone bath, after which the solution of divinyl ether was added. When the mixture was nearly solid, the tubes were sealed. The copolymerizations of fumaronitrile and 4-vinylpyridine with divinyl ether were carried out at 60 ± 0.05°C. The copolymerizations of tetracyanoethylene with divinyl ether were carried out at 50 ± 0.05°C. Reaction time was such as to allow about 10% conversion. Total volume for each polymerization was approximately 10 ml.

The polymers were precipitated in a nonsolvent, filtered through fritted glass filter funnels, and dried in a vacuum oven at 50°C. for 48 hr. prior to analysis. The fumaronitrile copolymers which were prepared in dimethylformamide were precipitated in methanol, washed with methanol and then ethyl ether. The tetracyanoethylene copolymers, prepared in dimethylformamide, were precipitated in diethyl ether. The 4-vinylpyridine copolymers separated from solution during their polymerization in benzene and were then filtered and washed with ethyl ether. Their color varied gradually from red to yellow when the concentration of 4-vinylpyridine was decreased.

Analysis

The compositions of the copolymers were calculated from their nitrogen and unsaturation content.

Nitrogen. The analyses of nitrogen were done by the Kjeldahl method. The method was tested on polyacrylonitrile for the fumaronitrile and tetracyanoethylene copolymers, and on polyvinylpyridine for the copolymer of 4-vinylpyridine. A sample of each series was sent for verification to Galbraith Microanalytical Laboratories, Knoxville, Tennessee.

Residual Unsaturation. The determination of unsaturation was carried out in the following way for the fumaronitrile/divinyl ether copolymers: About 30 mg. of polymer was dissolved in acetone and an excess of bromine solution (20%) was added. The olefin was allowed to react with Br_2 for 30 min. The polymer was then reprecipitated in methanol, filtered, and dried. On the resulting polymer, analysis for bromine was carried out by the Volhardt and Schöniger method. The percentage of unsaturation was calculated from the bromine content.

For the tetracyanoethylene–divinyl ether copolymers, determination of unsaturation was carried out by the same method and also by infrared spectroscopy with a Perkin-Elmer Model 21 spectrophotometer, vinyl ethyl ether being used as reference compound.

RESULTS AND DISCUSSION

The compositions of the copolymers have been determined over a wide range of monomer feed compositions.

Divinyl Ether–Fumaronitrile

Table I shows data for the copolymerization of divinyl ether and fumaronitrile. Over a wide range of initial monomer composition, the molar fraction of fumaronitrile in the copolymer lies in the range 0.55–0.63. These values must be compared to 0.67, which is the predicted value for 2:1 molar alternating copolymers. Table I shows also the small amount of residual unsaturation (from 2.0 to 3.5%), thus indicating the high percentage of cyclization. The results are plotted in Figure 1.

The structure of the copolymer was verified by infrared spectra which showed the following absorptions: nitrile, 2260 cm.$^{-1}$; unsaturated ether, 1220 cm.$^{-1}$ (small absorption);[12] and cyclic ether, 1115 cm.$^{-1}$ (very strong).[12] The structure of the copolymer is well described by a cyclic repeating unit containing both monomers, alternating with fumaronitrile units, as indicated in the theory.

TABLE I

Divinyl Ether (M_1)–Fumaronitrile (M_2) Copolymers

M_2 (monomer mole fraction)	Reaction time, hr.	Conversion, %	N in the copolymer, %[a]	Unsaturation, % by weight	m_u/m_1[b]	m_2 (polymer mole fraction)	m_2'/m_2[c]	η_{red}, dl./g.[d]
0.92	5	7.56	23.4	2.0	0.057	0.626	0.437	
0.8	4	11.39	22.9	2.4	0.066	0.613	0.41	0.154
0.6	2	11.69	22.9	2.45	0.068	0.613	0.41	
0.5	1.5	8.56	22.7[e]	2.8	0.076	0.607	0.405	0.174
0.25	1.5	7.42	22.6	3.0	0.081	0.604	0.399	
0.15	2	6.71	21.8	3.1	0.08	0.59	0.332	0.138
0.05	2	3.93	20.7	3.5	0.082	0.55	0.242	0.114

[a] Nitrogen percentage was corrected on the basis of 95% found for polyacrylonitrile.

[b] Ratio of unsaturated ether to total ether.

[c] Ratio of noncyclized fumaronitrile to total fumaronitrile in the copolymer.

[d] Measured at 25°C. in dimethylformamide, c = 0.5 g./dl.

[e] Value given by Galbraith Laboratories: 22.71%.

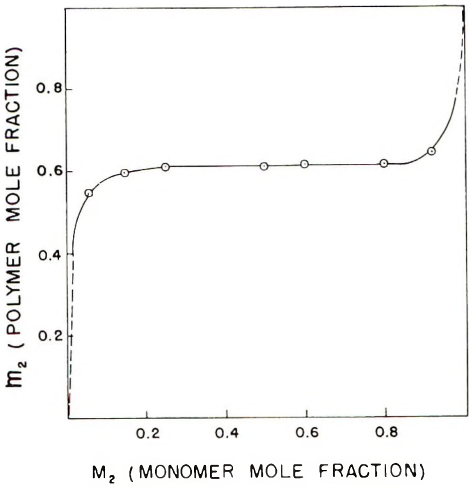


Fig. 1. Divinyl ether (M_1)–fumaronitrile (M_2) copolymers.

The composition of the copolymer was studied as a function of the total monomer feed concentration. The relative composition in monomers was kept constant: $[M_1] = [M_2] = 0.5$. These results are shown in Table II.

In the range $[M_1] + [M_2] = 1.1$–4.5 mole/l., the composition of the copolymer remains constant. The reactivity ratios r_1, r_2, and r_c could be obtained from eq. (3)[5]

$$m_1/m_2 = (1 + M_1r_1/M_2) \times (1 + M_1r_c/M_2)/[r_cM_1/M_2 + r_2M_2/M_1 + 2] \quad (3)$$

by using a digital computer method similar to that applied by Tidwell and Mortimer.[13] However, since this system approximates an alternating system, in which the molar ratio of olefin to diene approximates 2:0, the results most nearly fit special case (b)[5] in which both eqs. (1) and (3) reduce to eq. (4).

$$n = {}^1/_2 \quad (4)$$

Also, in this case, it seems that one must assume a kinetic effect of the penultimate unit. Such effects have been investigated for a few sys-

TABLE II

Variation of Total Monomer Concentration for Divinyl Ether–Fumaronitrile Copolymerization

$[M_1] + [M_2]$, mole/l.	N, % by weight	m_2 (molar fraction in polymer)
1.106	22.8	0.61
3.0	22.7	0.607
4.5	22.47	0.604

tems[14,15] and in particular for the copolymerization of fumaronitrile with styrene. The authors established that the rates of the copropagation steps are influenced by electrostatic repulsion between the nitrile groups in the monomer and the nonterminal nitrile groups in the attacking polymer radical. They developed a new composition equation, reduced to eq. (5) in the particular case of the fumaronitrile ($r_2 = 0$):[16]

$$r_1 = [(n - 1)/x^2 r_1'] + [(n - 2)/x] \tag{5}$$

where $r_1 = k_{111}/k_{112}$ and $r_1' = k_{211}/k_{212}$.

Application of eq. (5) to the fumaronitrile–divinyl ether copolymerization led to negative values of r_1 and r_1', showing the inadequacy of this kinetic model. The systems to which eq. (5) was applied did not show any cyclization, which is not the case for the fumaronitrile–divinyl ether system. More exact values would be obtained if a new kinetic equation were derived for the divinyl ether–fumaronitrile copolymerization. Such an equation should take into account both cyclization and influence of the penultimate unit in order to give a complete description of the copolymerization.

TABLE III

Divinyl Ether (M_1)–Tetracyanoethylene (M_2) Copolymers

M_2 (monomer mole fraction)	Reaction time, min.	Conversion, %	N, % by weight	m_2 (polymer mole fraction)	η_{red}, dl./g.[a]
0.25	50	5.71	23.69	0.392	0.0514
0.40	60	9.30	25.91	0.442	—
0.50	60	11.51	27.32[b]	0.477	0.067
0.60	25	6.37	28.51	0.506	—
0.80	30	4.45	31.11	0.574	—
0.90	30	5.75	33.16	0.64	0.0553

[a] Solvent: DMF; 25°C.; $c = 0.5$ g./dl.

[b] Value given by Galbraith Laboratories: 27.34%.

Divinyl Ether–Tetracyanoethylene

Table III shows data for the copolymerization of divinyl ether and tetracyanoethylene. The copolymer composition was quite different from that expected on the basis of an alternating bimolecular mechanism ($m_2 = 0.67$). Furthermore, the infrared spectrum showed a strong absorption in the 1630 cm.$^{-1}$ unsaturation region, suggesting that a cyclization occurred to only a small extent. These results are plotted in Figure 2.

The reactivity ratios r_1 and r_2 were determined by the Alfrey-Price equation, eq. (6).

$$r_2 = \frac{M_1}{M_2}\left[\frac{m_2}{m_1}\left(1 + \frac{M_1}{M_2} r_1\right) - 1\right] \tag{6}$$

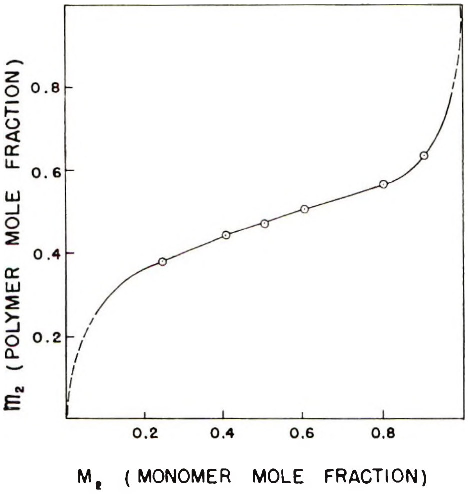


Fig. 2. Divinyl ether (M_1)–tetracyanoethylene (M_2) copolymers.

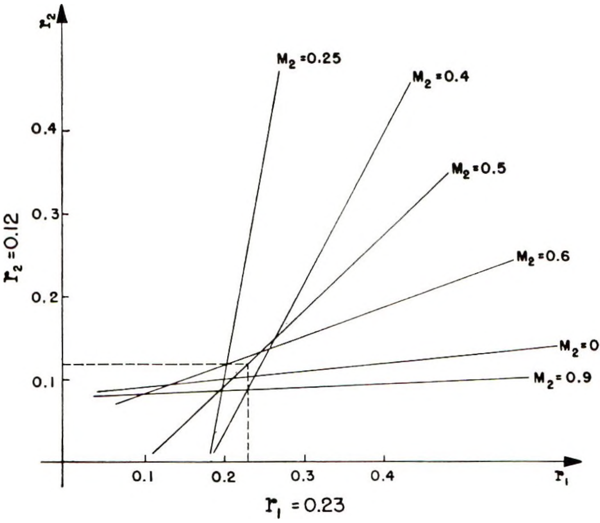


Fig. 3. Evaluation of r_1 and r_2 for divinyl ether–tetracyanoethylene copolymerization

The plot of r_2 against r_1 is shown in Figure 3. The values obtained were $r_1 = 0.23$, $r_2 = 0.12$. The linear method of Fineman and Ross[17] gave the values $r_1 = 0.2$; $r_2 = 0.11$ (Fig. 4).

Divinyl Ether–Vinylpyridine

Table IV shows data for the copolymerization of divinylether and 4-vinylpyridine. The mole fraction of 4-vinylpyridine in the copolymer lies between 0.85 and 0.998 indicating a high value of r_2. These results are plotted in Figure 5.

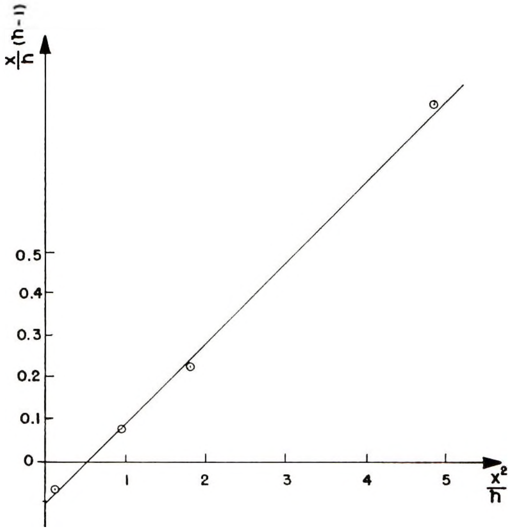


Fig. 4. Evaluation of r_1 and r_2 by Fineman and Ross method for divinyl ether–tetracyanoethylene copolymerization. $(x/n)(n - 1) = (x^2/x)(r_1 - r_2)$; $r_1 = 0.2$; $r_2 = 0.1$.

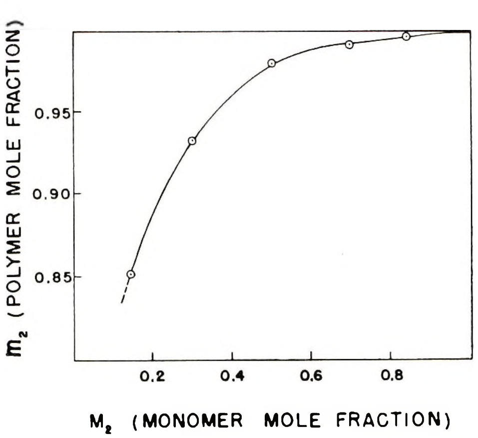


Fig. 5. Divinyl ether (M_1)–4-vinylpyridine (M_2) copolymers.

An attempt to use the digital computer method[5] for obtaining values for the reactivity ratios, r_1, r_2, and r_c, from eq. (3) gave negative values for r_1 or r_2, depending upon the initial estimates. However, when $1/n$ ($= [m_2]/[m_1]$) was plotted against $1/x$ ($= [M_2]/[M_1]$), using the results from Table IV (the last point was neglected since a very small error in determining $[m_2]$ results in an enormous difference in $1/n$) a straight line was obtained with an intercept of 2.0 as predicted from eq. (7).

$$n = 1/[(r_2/x) + 2] \qquad (7)$$

Equation (7) is the form to which eq. (1) reduces in the special case when the diene has a negligible tendency to add to its own radical, that is,

TABLE IV
Divinyl Ether (M_1)-4-Vinylpyridine (M_2) Copolymers

M_2 (monomer molar fraction)	Reaction time, hr.	Conversion, %	N, % by weight[a]	m_2 (polymer molar fraction)
0.15	5	6.1	11.9	0.848
0.30	4	5.6	12.45	0.931
0.50	1.3	3.68	13.1[b]	0.975[c]
0.70	2	9.65	13.2	0.987
0.85	1	7.53	13.3	0.998

[a] Percentage of nitrogen was corrected on the basis of the calculated nitrogen percentage in 4-vinylpyridine homopolymer, and of the nitrogen percentage found: 12.65%.

[b] Value given by Galbraith Laboratories: 12.40%.

[c] η_{red} = 0.30 dl./g. at 25°C. in DMF for the concentration $c = 0.5$ g./dl.

$r_1 \simeq r_c \simeq 0$, and there is also predominant cyclization. The slope of the line gave a value of 32.0 for r_2. It is reasonable to assume that under these conditions, divinyl ether has little tendency to add to its own radical, and since crosslinking was not observed, that there was also predominant cyclization.

The monomer reactivity ratios, r_1 and r_2 were also estimated by assuming $r_c \simeq r_1$, and substituting r_1 for r_c in eq. (3). Plots of r_1 versus r_2 were then made. Each experiment with a given feed ratio gives a curved line; the intersection of several of these lines allows an approximate evaluation of r_1 and r_2. By use of this method, r_1 was found to be 0.032 and r_2 was found to be 32.1.

From the results obtained it is interesting to compare the behavior of *p*-chlorostyrene,[18] 4-vinylpyridine, acrylonitrile,[5] fumaronitrile, and tetracyeanoethylene in their copolymerization with divinyl ether, as shown in Table V.

The ease with which divinyl ether adds to the monoolefins increases from 4-vinylpyridine to tetracyanoethylene. *p*-Chlorostyrene leads only to the homopolymer.[19]

The same order of reactivity is obtained when comparing the copolymerization rates as shown in Table VI. Tetracyanoethylene reacts most

TABLE V
Relative Composition of the Copolymers ([M] = [M_2] = 0.5)

Monoolefin	m_1[a]	e[b]
p-Chlorostyrene[c]	0.0000	−0.3
4-Vinylpyridine	0.025	−0.19
Acrylonitrile	0.251	+1.11
Fumaronitrile	0.393	>1.2
Tetracyanoethylene	0.523	>1.2

[a] m_1 is the molar fraction of divinyl ether in the copolymer.

[b] Value of e with respect to styrene.[20]

[c] Data of Allen and Butler.[19]

TABLE VI
Relative Copolymerization Rates

Monoolefin[a]	Temp., °C.	Reaction time, min.	Conversion, %
4-Vinylpyridine	60	80	3.68
Fumaronitrile	60	90	8.56
Tetracyanoethylene	50	60	11.56

[a] Initial feed monomer molar fraction: $[M_1] = [M_2] = 0.5$.

rapidly with divinyl ether and is incorporated into the copolymer to a greater extent than any other monoolefin studied, and also produces the most nearly alternating copolymer. The electron acceptor effect of the four $-C\equiv N$ groups of the tetracyanoethylene decreases the electronic density of the double bond and thus increases the affinity of the divinyl ether for the tetracyanoethylene.

It is interesting to compare these conclusions with the values of *e*, a measure of polarity. The effect of the cyanide groups becomes obvious when the copolymerization rates are compared with the copolymer compositions. This effect is strengthened when the number of cyanide substituents increases, thus decreasing the electronic density of the double bond to which they are attached and making it more active in its reaction with the diene.

The steric effect does not seem to be very important. Otherwise, the order in the copolymerization rates would be the reverse of that observed. Therefore, the electronic effect is predominant in these systems. The relative rate and composition of the copolymers may be explained on the basis of polarity: the greater the difference in polarity between the two comonomers, the greater the copolymerization rate and the greater the degree of incorporation of monoolefin in the copolymer.

The same explanation may serve to describe the relative importance of the cyclization. It has been observed that the comonomer plays a role in the yield of cyclization of the nonconjugated 1,6-dienes. The larger the

TABLE VII
Effect of Polarity Difference of Comonomers on Cyclization of 1,6-Diene

Comonomer	e	Δe	k_c/k_{12}[a]
Acrylic anhydride[b]	1.2		
		0.2	7.1
Methyl methacrylate	1.0		
Styrene	−0.8		
		2.0	0.25
Acrylic anhydride	1.2		

[a] Ratio of the cyclization rate constant of the 1,6-diene to the rate constant of the addition of the 1,6-diene (2) to the monoolefin (1).

[b] Data of Smets et al.[10]

TABLE VIII
Effect of Polarity Difference of Comonomers on Cyclization in 1,4-Diene

Monoolefin[a]	Cyclization, %
Acrylonitrile[b]	100
Fumaronitrile	96.3
Tetracyanoethylene	18.4

[a] Initial monomer concentration: $[M_1] = [M_2] = 0.5$.

[b] Data of Barton et al.[5]

difference in polarity between the diene and the monoolefin, the lower the cyclization yield, as shown in Table VII.

In the same way, the percentage of cyclization in the copolymerization of a 1,4-diene with a monoolefin may be related to the polarity difference of the two monomers. It is observed that the percentage of cyclization decreases when the polarity difference between the two monomers increases, as shown in Table VIII.

However, it should be pointed out that for the 1,6-diene, k_c is compared with k_{12}; and for the 1,4-diene, k_c is compared with k_{31}.[5] It can be considered that the addition reaction of the radical $m_3\cdot$ and a diene molecule is more favored as the difference in their polarity is increased. This is what is observed upon going from acrylonitrile to tetracyanoethylene. However the steric effect cannot be neglected and probably has an important role in the intermediary step of cyclization. Both factors must be taken into account. Their relative importance is difficult to determine.

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Résumé

La copolymérisation de l'éther divinylique avec le fumaronitrile (A), le tétracyanoéthylène (B) et la 4-vinylpyridine (C) a été étudiée utilisant l'asobisisobutyronitrile comme initiateur. La composition des copolymères a été calculée au départ de leur teneur en azote et en insaturation. Sur une grande gamme de compositions en monomères initiaux la fraction molaire de A dans les copolymères se situe entre 0.55 et 0.63, les copolymères contenaient uniquement 2–3% d'insaturation, ce qui indique un degré élevé de cyclisation. La composition des copolymères de (B) indiquaient une cyclisation peu prononcée ainsi que le montrait la teneur élevée en insaturation des copolymères obtenus. Les valeurs de $r_1 = 0.23$ et $r_2 = 0.12$ ont été obtenues. La fraction molaire de (C) dans les copolymères se situe entre 0.85 et 0.998. En admettant que r_1 est environ égal à r_c est environ égal à 0, et en admettant également qu'il y a essentiellement cyclisation, $r_2 = 32.0$ dans ce cas ci. La différence de composition des copolymères est attribuée à la différence entre les densités électroniques des doubles soudures dans (A), (B) et (C).

Zusammenfassung

Die Copolymerisation von Divinyläther mit Fumaronitril (A), Tetracyanäthylen (B) und 4-Vinylpyridin wurde mit Azobisisobutyronitril als Initiator untersucht. Die Zusammensetzung der Copolymeren wurde aus ihrem Stickstoff- und Doppelbindungsgehalt berechnet. Über einen weiten Bereich der Ausgangszusammensetzung der Monomerenmischung liegt der Molenbruch von (A) in den Copolymeren im Bereich von 0,55 – 0,63 und die Copolymeren enthalten nur 2–3% Doppelbindungen, was für einen hohen Cyclisierungsgrad spricht. Die Zusammensetzung der Copolymeren von (B) zeigte, dass Cyclisierung nur in geringem Ausmass auftritt, da die Copolymeren ziemlich stark ungesättigt waren. Es wurden die Werte $r_1 = 0{,}23$ und $r_2 = 0{,}12$ erhalten. Der Molenbruch an (C) in den Copolymeren liegt zwischen 0,85 und 0,998. Für den Fall, dass $r_1 \simeq r_c \simeq 0$ und dass vorwiegend Cyclisierung eintritt beträgt $r_2 = 32{,}0$. Die Zusammensetzungsunterschiede der Copolymeren werden auf Unterschiede in der Elektronendichte der Doppelbindungen in (A), (B) und (C) zurückgeführt.

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Synthesis of 1,4,5,6,7,7-Hexachloro- and Hexabromobicyclo-[2,2,1]-5-heptene-2-carboxylic Acid Vinyl Esters and Copolymerization with Acrylonitrile

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Synopsis

1,4,5,6,7,7-Hexachloro- and hexabromobicyclo-[2,2,1]-5-heptene-2-carboxylic acid vinyl esters have been prepared by esterification of the Diels-Alder addition products of hexachloro- and hexabromocyclopentadiene with acrylic acid. These monomers have been copolymerized with acrylonitrile to yield flame-retardant polymers. Copolymers having a chlorine content up to 18.35% or a bromine content up to 6.35% burn, but copolymers containing 25.0% or more of chlorine or 9.83% or more of bromine do not support combustion.

SYNTHESIS OF MONOMERS AND INTERMEDIATES

Hexachlorocyclopentadiene has been shown to undergo the Diels-Alder reaction with many dienophiles at temperatures between 20°C. and 200°C.[1-3] The addition product of acrylic acid and hexachloro-1,3-cyclopentadiene has been described in a patent.[4] Hexabromocyclopentadiene has been prepared from cyclopentadiene and potassium hypobromite,[5] but its acrylic acid adduct has not apparently been previously described.

The procedure of Straus et al.[5] has been modified to prepare hexabromocyclopentadiene. The diene synthesis of hexachlorocyclopentadiene with acrylic acid was carried out at 120°C. without solvent. The bromo compound reaction was carried out at 150°C. The addition products were soluble in ether and could be crystallized by addition of hexane to give yellow to brown crystals. The results are presented in Table I.

The vinyl esters of the Diels-Alder products were prepared at room temperature by use of a large excess of practical grade vinyl acetate.[6] The hexabromo compound was not very soluble in vinyl acetate; consequently it was necessary to use vigorous shaking during the reaction. It was demonstrated that the optimal reaction time was about 5–6 days.[6] After this time, the excess acid was removed by washing the solutions with water, sodium acetate and finally with sodium carbonate solutions. Then

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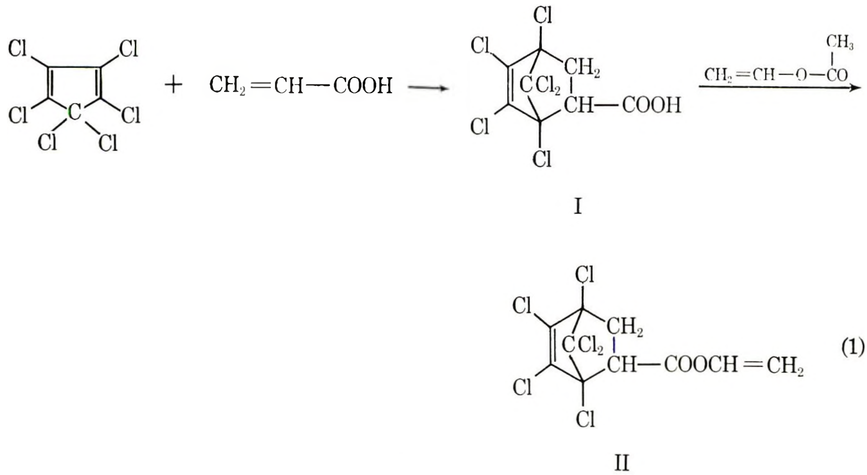
TABLE I

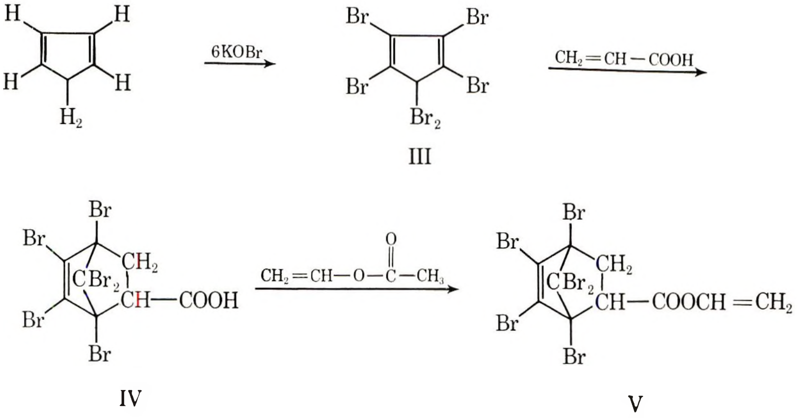
Monomers and Intermediates

Compound	Yield, %	M.p., °C.	n_D^{20}	Carbon, %		Hydrogen, %		Chlorine or bromine, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
I	54.2	178–179	—	27.86	28.03	1.17	1.37	61.69	61.50
II	68.6	163/5.0 mm.[a]	1.5428	32.31	32.48	1.63	1.76	57.36	57.22
III	52.8	85–86	—	11.12	11.30	0.00	<0.20	88.88	88.85
IV	76.0	272–273	—	15.71	16.14	0.66	0.58	78.60	78.80
V	61.6	79	—	18.84	18.96	0.95	1.43	75.20	75.47

[a] B.p.



(1)



(2)

the excess vinyl acetate was evaporated and the residues were purified by column chromatography. For the vinyl ester (II), alumina was used as absorbent and carbon tetrachloride as solvent. Pure vinyl ester (II) was then obtained by distillation under reduced pressure. The hexabromo vinyl ester monomer (V) was purified also by column chromatography using silica gel as absorbent and ether–hexane (1:19) as solvent. After repeated crystallization from hexane, there was obtained a white crystalline monomer (m.p. 79°C.). The results of the vinyl interchange reactions are summarized in Table I. The structure of these monomers was also investigated by NMR spectroscopy. The vinyl ester protons absorbed at 2.56 τ, 4.72 τ, and 5.13 τ for the hexachloro derivative and at 2.78 τ, 4.89 τ, and 5.29 τ for the hexabromo derivative. They had the expected splitting pattern of a vinyl ester. The tertiary ring proton is split into two doublets and absorbs at 6.24 τ for the hexachloro derivative and 6.23 τ for the hexabromo derivative. The methylene ring proton absorbs at 7.23 τ and 7.35 τ for the hexachloro and at 7.25 τ and 7.35 τ for the hexabromo derivative. Both of the ring protons are split into doublets, but, as expected, they do not have the same coupling constant. The spectra were taken in carbon tetrachloride solutions.

COPOLYMERS OF COMPOUNDS II AND V WITH ACRYLONITRILE

Copolymerizations were carried out in emulsion at 60°C. with the use of potassium persulfate as catalyst, sodium dodecylbenzenesulfonate as emulsifier, and decylmercaptan as modifier. The bromo compound V had a lower rate of copolymerization, but the copolymers exhibited better flame retardancy. Monomer II copolymerized better with acrylonitrile, but it was necessary to have more of that compound in the copolymers to obtain flame retardancy (up to 25% chlorine, see Table II). The flammability of the copolymers was investigated on pressed films. Copolymers with comonomer V did not burn when the bromine constant was 9.83% or higher. The viscosities of the copolymers were not influenced very much until a high percentage of comonomers of compound II and V was present in the charge. The results of copolymerization are summarized in Tables II and III.

EXPERIMENTAL

Reaction of Acrylic Acid with Hexachlorocyclopentadiene

A mixture of 400 g. (1.5 mole) hexachlorocyclopentadiene, 108 g. (1.5 mole) of acrylic acid, 1.0 g. of 4-*tert*-butylpyrrocatechol and 2.0 ml. of acetic acid was added to a 1-liter, round-bottomed flask and heated at about 120°C. for 24 hr. The solution became partially solid after 20–30 min., indicating that the reaction had started. Afterwards, the product was dissolved in 500 ml. of ether–hexane (1:1) mixture and filtered through charcoal. The solution was concentrated and the adduct crystallized after cooling to 0°C. to give 159 g. of product. Concentration of the filtrate gave additional material. After recrystallization of the combined portions from ether–hexane, 279 g. of pure adduct (54.2% of the theoretical) was obtained, m.p. 178–179°C. The results are given in Table I.

Esterification of 1,4,5,6,7,7-Hexachlorobicyclo-[2,2,1]-5-heptene-2-carboxylic Acid (I) with Vinyl Acetate

Copper resinate (0.320 g.) and mercuric acetate (3.840 g.) were dissolved in 900 ml. of practical grade vinyl acetate. The solution was cooled to 3–4°C. and 2.0 ml. of concentrated H_2SO_4 was added dropwise. The solution (brown color) was warmed to room temperature and 184 g. (0.534 moles) of compound I added. The solution was then left standing in a tube protected by dark paper from light for 144 hr. After this time, the solution was washed by 10% NaCl solution and water to remove H_2SO_4. To complete the neutralization 0.1% of Na_2CO_3 solution containing NaCl

TABLE II

Copolymers of Acrylonitrile and 1,4,5,6,7,7-Hexachlorobicyclo-[2,2,1]-5-heptane-2-carboxylic Acid Vinyl Ester (II)[a]

No.	Recipe of acrylonitrile and II, g./g	Charge ratio, acrylonitrile/II	Emulsifier, g.[b]	Modifier, mg.[c]	Potassium persulfate, g.	Time, hr.	Conversion, %	η_{inh}[d]	Cl in monomer mixture, %	Analyses of copolymer found C, %	H, %	N, %	Cl, %
1	20.0/5.0	80/20	0.5	14	0.25	24	92.0	3.93	11.5	60.57	4.88	—	9.41
2	15.5/6.0	72/28	1.0	28	0.50	24	94.5	1.84	16.0	57.68	4.63	18.43	13.96
3	20.0/8.7	70/30	1.0	28	0.50	24	68.6	1.85	17.4	59.61	4.80	—	14.03
4	20.0/11.6	63.9/36.6	1.0	28	0.50	24	95.2	1.72	21.0	56.35	4.27	17.55	18.35
5	10.0/9.4	51.5/48.5	0.5	14	0.25	24	94.7	1.86	27.8	52.95	4.04	14.48	25.00[e]
6	1.3/8.7	13.0/87.0	0.25	7	0.125	24	79.2	0.21	50.0	39.28	2.51	5.09	46.00[e]
7	0.0/5[f]	0.0/100[f]	0.25	7	0.125	24	78.0	0.08	57.4	33.07	1.83	—	56.70[e]

[a] All of the polymerizations were conducted at 60 ± 0.2°C. by tumbling the tubes end over end.

[b] Sodium dodecylbenzenesulfonate.

[c] Decylmercaptan.

[d] Determined in dimethylformamide on 0.5% solution at 30°C. All polymers were completely soluble.

[e] Do not support combustion.

[f] Homopolymerization.

TABLE III

Copolymerization of 1,4,5,6,7,7-Hexabromo-bicyclo-[2,2,1]-5-heptene-2-carboxylic Acid Vinyl Ester (V) with Acrylonitrile in Emulsion at 60°C.[a]

No.	Recipe of acrylo-nitrile and V, g./g.	Charge ratio, acrylo-nitrile/V	Emulsi-fier g.[b]	Modi-fier, mg.[c]	Potassium persulfate, g.	Time, hr.	Con-version, %	η_{inh}[d]	Br in monomer mixture, %	Analyses of copolymer found			
										C, %	H, %	N, %	Cl, %
1	10.0/0.87	92/8	0.5	14	0.25	24	90.6	2.21	6.0	63.29	5.55	23.64	6.17
2	10.0/1.36	88/12	0.5	14	0.25	24	95.2	2.43	9.0	62.97	5.43	23.39	6.17
3	10.0/1.90	84/16	0.5	14	0.25	24	79.4	3.07	12.0	64.19	5.50	23.17	6.35
4	10.0/2.50	80/20	0.5	14	0.25	24	87.6	2.66	15.0	61.10	5.09	22.99	9.83[e]
5	10.0/3.15	76/24	0.5	14	0.25	24	94.6	2.93	18.0	59.00	4.98	21.48	13.10[e]
6	10.0/3.87	72/28	0.5	14	0.25	24	89.1	2.27	21.0	56.04	4.92	19.23	17.35[e]
7	10.0/4.90	67/33	0.5	14	0.25	24	87.6	2.43	24.0	57.58	5.15	20.32	15.44[e]
8	10.0/5.60	64/36	0.5	14	0.25	24	84.4	2.22	27.0	54.44	4.14	18.77	20.56[e]
9	10.0/6.64	60/40	0.5	14	0.25	24	74.7	2.16	30.0	55.62	4.59	18.69	19.05[e]
10	5.0/5.67	46.8/53.2	0.25	7	0.125	24	80.0	1.64	40.0	47.26	3.79	14.88	29.53[e]
11	2.5/4.86	36/64	0.125	7	0.063	24	69.6	0.86	50.0	40.00	3.28	11.27	43.17[e]
12	0.0/3.80[f]	0.0/100[f]	0.125	7	0.063	24	Trace	—	75.6	—	—	—	—

[a] All of the polymerizations were conducted at 60 ± 0.2°C. by tumbling the tubes end over end.

[b] Sodium dodecylbenzenesulfonate.

[c] Determined in dimethylformamide on 0.5% solution at 30°C. All polymers were completely soluble.

[d] Decylmercaptan.

[e] Do not support combustion.

[f] Homopolymerization.

for good separation was used. The solution was dried over $CaSO_4$ and after 24 hr., the vinyl acetate was removed in vacuum to yield 200 g. of product. A 100-g. portion of this residue was used for chromatographic purification over 300 g. of alumina with CCl_4 as solvent. CCl_4 (150 ml.) was used for washing the column and then 360 ml. solution collected. After evaporation of CCl_4 in vacuum, 89.0 g. of yellow liquid was obtained. It was fractionally distilled, and the fraction boiling at 163°C./5.0 mm. was collected to yield 67.2 g. pure monomer.

Hexabromocyclopentadiene

In a 4-liter, three-necked, round-bottomed flask equipped with stirrer and thermometer, was placed 2 liters of distilled water. It was cooled to 0°C. and then with stirring 660 g. of potassium hydroxide was added first and then 90.8 ml. of bromine dropwise. The cooling was interrupted, and 16.5 g. of freshly distilled cyclopentadiene in 150 ml. of petroleum ether was added under vigorous stirring. The stirring was continued at room temperature for 18 hr. Then the dark brown crystalline material was filtered and recrystallized from petroleum ether. There was then obtained 38 g. of pure yellow crystalline compound, m.p. 85–87°C. The petroleum ether layer was separated, filtered through charcoal for decolorization, and concentrated to about 100 ml. On cooling to 0°C., there was obtained a brown crystalline product that was dissolved in petroleum ether, decolorized by charcoal and crystallized to yield 33 g. of yellow product, m.p. 85–86°C. The total yield was 71 g. (52.8%) (see Table I).

Reaction of Acrylic Acid with Hexabromocyclopentadiene

In a 1-liter, round-bottomed flask was placed 200 g. (0.37 mole) of hexabromocyclopentadiene, 26.7 g. (0.37 mole) of acrylic acid, 0.33 g. of 4-*tert*-butylpryocatechol, and 1.0 ml. of acetic acid. The mixture was stirred vigorously and heated to 150°C. for 16 hr. A black, solid product was obtained. It was dissolved in 300 ml. of ether, decolorized by charcoal, filtered, and recystallized from 300 ml. of hexane. This product was again recrystallized from ether–hexane (1:1) to yield 154 g. (76.0%) of 1,4,5,6,7,7-hexabromobicyclo-[2,2,1]-5-heptene-2-carboxylic acid (IV), m.p. 268–279°C. under decomposition. The results are summarized in Table I.

Esterification of 1,4,5,6,7,7-hexabromobicyclo-[2,2,1]-5-heptene-2-carboxylic Acid (IV) with Vinyl Acetate

In a 1-liter bottle were placed 0.160 g. of copper resinate, 1.920 g. of mercuric acetate, and 600 ml. of practical grade vinyl acetate. The solution was cooled to 3–4°C. and 1.0 ml. of concentrated H_2SO_4 was added dropwise. Then the solution was warmed to room temperature and 140 g. (0.23 mole) of compound II added. The hexabromo compound (IV) was slowly dissolved at room temperature (after 3 days) and then it was shaken for 24 hr. to complete the reaction. After this time, the solution was washed with 300 ml. of water followed by 200 ml. of 20% sodium chloride solution. The separation was difficult, therefore more sodium chloride was dissolved in the water layer to cause the organic layer to separate better. The vinyl acetate layer was separated, dried over $MgSO_4$, and the vinyl acetate removed under reduced pressure. This yielded 145.6 g. of an oily product.

For purification a 52 g. sample of this oil was dissolved in 120 ml. of ether–hexane (1:19) and purified by a chromatographic method with the use of 175 g. of silica gel and ether–hexane (1:19) solvent. After washing the column with 180 ml. of the solvent which was discarded, next 190 ml. of the solution was collected, the solvent removed, and the residue recrystallized from hexane to yield 32.0 g. of light yellow product, m.p. 79°C. By a similar purification of the remaining oil a total of 89.7 g. (61.6%) of pure product was obtained. The results are presented in Table I.

Copolymerization of Compounds II and V with Acrylonitrile

Emulsifier (sodium dodecylbenzenesulfonate, 1 g.) was placed in a 250-ml. pressure tube and the tube was filled with nitrogen. Then 70.0 ml. of oxygen-free water, 78 mg. of C_{10} mercaptan, 25 ml. of acrylonitrile, 0.5 g. of $K_2S_2O_8$, and the required amount of comonomer II and V were added. The emulsion was shaken for 15 min., then put in the polymerization bath at 60°C. After polymerization, the emulsion was poured into a large amount of methanol, filtered, and left standing in 1.5 liter of water for 24 hr., filtered again, and dried at 60°C. The results are summarized in Tables II and III.

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Résumé

Les esters vinyliques des acides 1,4,5,6,7,7-hexachloro- et hexabromo-bicyclo-[2,2,1]-5-heptène-2-carboxyliques ont été préparés par estérification des produits d'addition de la réaction de Diels-Alder au cyclopentadiène-hexachloré et hexabromé avec l'acide acrylique. Les monomères ont été copolymérisés avec l'acrylonitrile en vue de former des polymères retardant la combustion. Les copolymères ayant une teneur en chlore jusque 18.35% ou une teneur en brome jusque 6.35% brûlent; mais les copolymères contenant 25% ou plus de chlore et 9.83% ou plus, de brome ne supportent plus la combustion.

Zusammenfassung

1,4,5,6,7,7-Hexachlor- und -Hexabrombicyclo-[2,2,1]-5-hepten-2-carbonsäurevinylester wurden durch Veresterung des Diels-Alder-Additionsproduktes von Hexachlor- und Hexabromcyclopentadien und Acrylsäure dargestellt. Diese Monomeren wurden mit Acrylnitril zur Erzeugung nicht-entflammender Polymerer copolymerisiert. Copolymere mit einem Chlorgehalt bis zu 18,35% oder einem Bromgehalt bis zu 6,35% brennen, solche mit 25,0% Chlor oder mehr oder 9,83% Brom oder mehr unterhalten jedoch die Verbrennung nicht.

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Reactivity Ratios of Styrene and Methyl Methacrylate at 90°C.

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Synopsis

From the conversion–composition data of Gruber and Elias, the reactivity ratios of styrene (M_1) and methyl methacrylate (M_2) were calculated to be $r_1 = 0.55 \pm 0.02$ and $r_2 = 0.58 \pm 0.06$ at 90°C. The least-squares method was then used on these and literature values at other temperatures to obtain the Arrhenius expressions: $\ln r_1 = 0.04736 - (235.45/T)$, and $\ln r_2 = 0.1183 - (285.36/T)$. Using literature values for the homopolymerization steps, $A_{11} = 2.2 \times 10^7$ l./mole-sec., $E_{11} = 7.8$ kcal./mole, and $A_{22} = 0.51 \times 10^7$ l./mole-sec.$^{-1}$, $E_{22} = 6.3$ kcal./mole, activation energies and frequency factors were then calculated for the cross-polymerization steps: $A_{12} = 2.1 \times 10^7$ l./mole-sec., $E_{12} = 7.3$ kcal./mole, and $A_{21} = 0.45 \times 10^7$ l./mole-sec., $E_{21} = 5.7$ kcal./mole.

Introduction

The differential equation, namely,

$$\ln (M/M_0) = \int_{f_1^0}^{f_1} [1/(F_1 - f_1)]\, df_1 \qquad (1)$$

due to Skeist[1] has been solved by Lowry and Meyer[2] to yield:

$$M/M_0 = (f_1/f_1^0)^\alpha\, (f_2/f_2^0)^\beta\, [(f_1^0 - \delta)/(f_1 - \delta)]^\gamma \qquad (2)$$

where $\alpha = r_2/(1 - r_2)$; $\beta = r_1/(1 - r_1)$; $\gamma = (1 - r_1r_2)/(1 - r_1)(1 - r_2)$; and, $\delta = (1 - r_2)/(2 - r_1 - r_2)$. The other symbols have their usual meaning: $M = M_1 + M_2$; $M_0 = M_1^0 + M_2^0$; $f_1 = M_1/M = 1 - f_2$; and, $r_1 = k_{11}/k_{12}$, $r_2 = k_{22}/k_{21}$. For given values of the reactivity ratios, eq. (2) or more conveniently its logarithmic form may then be used to calculate mole conversion, $1 - (M/M_0)$, as a function of f_1, the change in monomer mixture composition. Alternatively, experimental values for f_1, f_1^0, M, M_0, may be inserted into eq. (2), and the equation then solved for the values of r_1 and r_2 consistent with the experimental data. This has recently been done for the case of styrene and methyl methacrylate at 60°C.[3] The purpose of this paper is to carry out a similar calculation at 90°C. where such information was not previously available. By means of the Arrhenius equation, these results are then compared with the values predicted at 90°C. by a least-squares treatment of the reactivity ratios as reported in the literature at various temperatures.

Experimental

For each polymer sample of Table I, r_2 was assigned values in the range of 0.4–0.8. To each assigned value of r_2, a Burroughs B5500 digital computer was used to calculate the corresponding value of r_1, consistent with the experimental data.[3] In this manner, a plot of r_2 versus r_1 then yields a straight line (Fig. 1) for each experimental sample of Table I. The intersection of the calculated straight lines then yields: $r_1 = 0.55 \pm 0.02$ and $r_2 = 0.58 \pm 0.06$, whereby the CL-2 curve is largely ignored. CL-2 has been given a little weight by selecting the intersection of CL-8, CL-6, and CL-4 as the solution, thereby balancing CL-2a somewhat against CL-2. In Figure 2, r_1, r_2 curves have been calculated for each of the analyses of Table I.

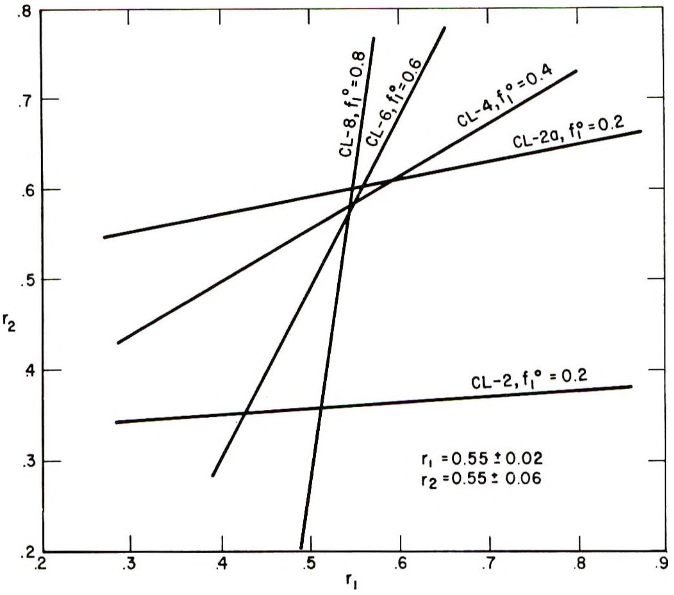

Fig. 1. Reactivity ratios from averaged copolymer analyses.

TABLE I
Conversion–Composition Data for the Solution Copolymerization of Styrene and Methyl Methacrylate at 90°C. in Dioxane[4]

Polymer sample	Monomers, g. Styrene	MMA	Conversion, wt.-%	f_1^0	f_1	Conversion, mole-%
CL-2	20.8	80.0	71.8	0.19996	0.05924	71.641
CL-2a	20.8	80.0	27.8	0.19996	0.18355	27.753
CL-4	41.6	60.0	62.6	0.39994	0.37579	62.564
CL-6	62.4	40.0	60.5	0.59994	0.63338	60.552
CL-8	83.2	20.0	61.5	0.79996	0.85974	61.590

In Figure 3, the monomer mixture composition f_1 has been calculated as a function of mole conversion according to eq. (2), $r_1 = 0.55$, $r_2 = 0.58$, and for the starting compositions, $f_1^0 = 0.2$, 0.4, 0.6, and 0.8. The experimental values from Table I are shown as dotted circles. Again it is

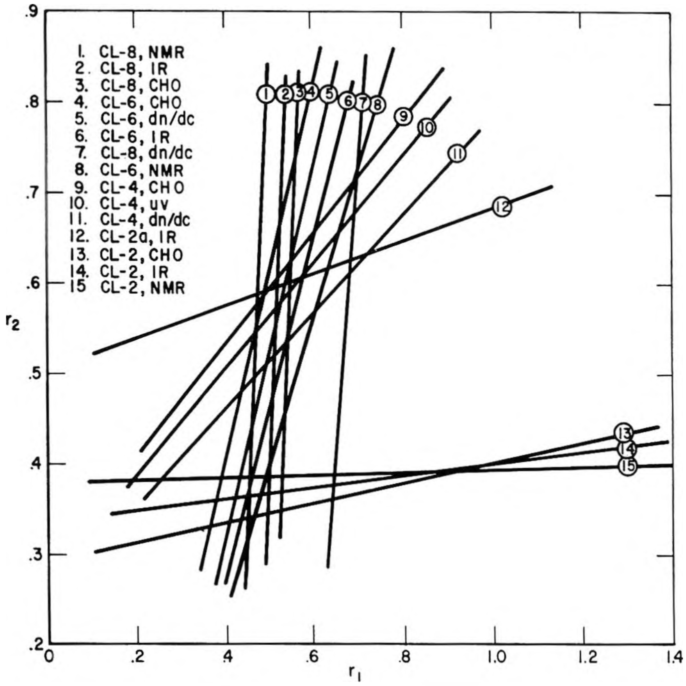

Fig. 2. Reactivity ratios from individual analyses.

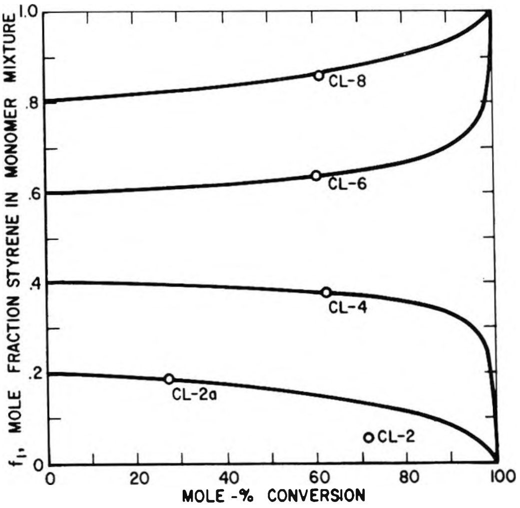

Fig. 3. Monomer mixture composition as a function of mole conversion for $r_1 = 0.55$, $r_2 = 0.58$.

TABLE II
Styrene-Methyl Methacrylate Copolymer Composition According to Various Analytical Techniques[4]

Polymer sample	Methyl methacrylate in copolymer, wt.-% From C,H,O	From IR	From UV	From NMR	From *dn/dc*	Average
CL-2	74.4	74.0	—	73.5	72.8	73.675
CL-2a	—	75.0	—	—	—	75.0
CL-4	58.1	(53.0)	57.7	—	57.0	57.600
CL-6	42.2	41.0	—	40.2	41.5	41.225
CL-8	23.0	23.5	—	24.1	21.5	23.025

evident that sample CL-2 is in poor agreement with the other experimental points, thus tending to justify our having ignored it in the calculation of the reactivity ratios.

The copolymerization of styrene and methyl methacrylate has been the subject of a fair number of experimental investigations. The results of these investigations are summarized in Table III. By substituting the Arrhenius expressions into the definitions of the reactivity ratios, one obtains:

$$\ln r_1 = \ln \left(\frac{A_{11}}{A_{12}}\right) - \left(\frac{E_{11} - E_{12}}{R}\right) \frac{1}{T} \tag{3}$$

and,

$$\ln r_2 = \ln \left(\frac{A_{22}}{A_{21}}\right) - \left(\frac{E_{22} - E_{21}}{R}\right) \frac{1}{T} \tag{4}$$

where the A's and E's correspond, respectively, to the frequency factors and activation energies for the various propagation rate constants as indicated by the subscripts.

TABLE III
Reactivity Ratios of Styrene (M_1) and Methyl Methacrylate (M_2)[a]

Reference	r_1	r_2	Temperature, °C.
Arlman et al.[6]	0.485	0.422	30
Wall et al.[7]	0.50	0.44	35
Lewis et al.[8]	0.50	0.50	60
Lewis et al.[9]	0.52	0.46	60
Wiley and Davis[10]	0.53	0.49	60
Wiley and Sale[11]	0.48	0.46	60
Meyer[3]	0.54	0.50	60
Meyer (present paper)	0.55	0.58	90
Doak et al.[12]	0.54	0.49	99
Lewis et al.[9]	0.59	0.536	131
Wiley and Sale[11]	0.60	0.55	132

[a] Taken in part from the compilation of Young.[16]

The methods of least squares (Figs. 4 and 5) applied to the data given in Table III yields:

$$\ln r_1 = 0.04736 - (235.45/T) \tag{5}$$

and

$$\ln r_2 = 0.1183 - (285.36/T) \tag{6}$$

i.e.,

$$A_{11}/A_{12} = 1.05$$

$$(E_{11} - E_{12})/R = 235.45$$

$$A_{22}/A_{21} = 1.13$$

$$(E_{22} - E_{21})/R = 285.36$$

In terms of the transition state theory,

$$r_1 = \exp\left\{(\Delta S_{11}\ddagger - \Delta S_{12}\ddagger)/R\right\} \exp\left\{-(\Delta H_{11}\ddagger - \Delta H_{12}\ddagger)/RT\right\} \tag{7}$$

and

$$r_2 = \exp\left\{(\Delta S_{22}\ddagger - \Delta S_{21}\ddagger)/R\right\} \exp\left\{-(\Delta H_{22}\ddagger - \Delta H_{21}\ddagger)/RT\right\} \tag{8}$$

the differences in heat of activation energies, $\Delta H_{11}\ddagger - \Delta H_{12}\ddagger = 468$ cal./mole, $\Delta H_{22}\ddagger - \Delta H_{21}\ddagger = 567$ cal./mole, and differences in entropies of

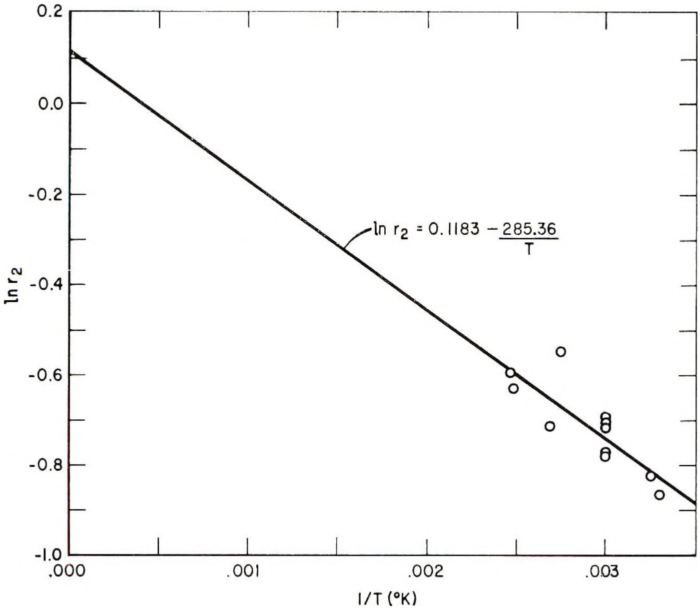

Fig. 4. Least-squares fit of literature values of r_1.

activation, $\Delta S_{11}\ddagger - \Delta S_{12}\ddagger = 0.09$ e.u., $\Delta S_{22}\ddagger - \Delta S_{21}\ddagger = 0.23$ e.u., may be readily calculated.

These values are in rather remarkably good agreement with the values obtained by Lewis et al.:[9,15] $\Delta H_{11}\ddagger - \Delta H_{12}\ddagger = 480$, $\Delta H_{22}\ddagger - \Delta \mathrm{H}_{21}\ddagger = 580$, $\Delta S_{11}\ddagger - \Delta S_{12}\ddagger = 0.12$, and $\Delta S_{22}\ddagger - \Delta S_{21}\ddagger = 0.19$, as determined from experiments at only two temperatures, 60 and 131°C.

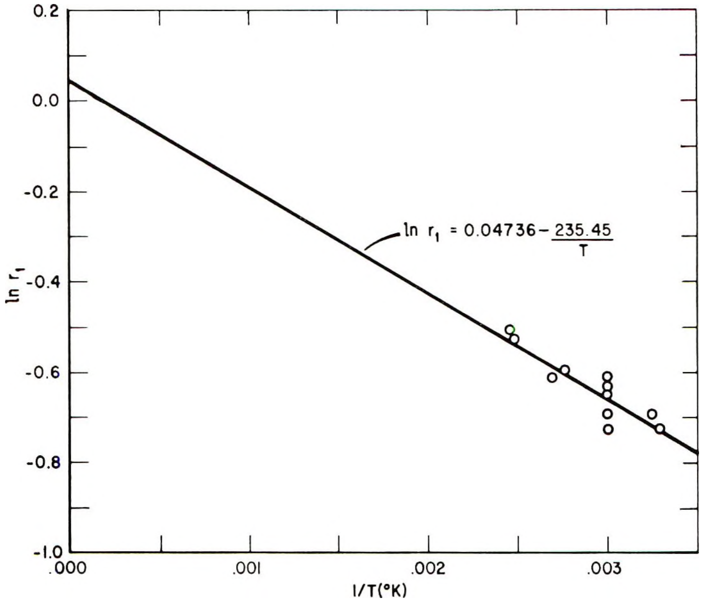

Fig. 5. Least-squares fit of literature values of r_2.

Since the propagation activation energies and frequency factors for the homopolymerization steps are known: $E_{11} = 7.8$ kcal./mole, $A_{11} = 2.2 \times 10^7$ l./mole-sec., and $E_{22} = 6.3$ kcal./mole, $A_{22} = 0.51 \times 10^7$ l./mole-sec.,[13] it can then be readily calculated that $E_{12} = 7.332$ kcal./mole, $A_{12} = 2.095 \times 10^7$ l./mole-sec., and $E_{21} = 5.733$ kcal./mole, $A_{21} = 0.4533 \times 10^7$ l./mole-sec.

Results and Discussion

Good agreement is observed between the experimental value (Table III), $r_1 = .55$, and the value obtained at 90°C. from the least-squares calculation, $r_1 = 0.548$. On the other hand, rather poor agreement is observed in the case of the other reactivity ratio: $r_2 = 0.58$ (experimental), whereas, $r_2 = 0.513$ (least squares). The source of the difficulty appears to arise because the experiments which are designed primarily to yield information concerning r_2, i.e., k_{22}/k_{21}, normally involve higher ratios of methyl methacrylate to styrene, which leads to greater experimental difficulties.

At 90°C., the specific rate constants for the four propagation steps are then calculated to be: $k_{11} = 530$, $k_{12} = 805$, $k_{22} = 805$, and $k_{21} = 1550$ (l./mole-sec.). From eqs. (5) and (6) it is evident that the differences in specific rate constants in this system are primarily due to the lower activation energies for the cross-polymerization steps rather than to differences in the frequency factors.

The author wishes to thank Professor D. H.-G. Elias, who kindly clarified certain aspects of their experimental work. Thanks are also due Dr. G. E. Molau for the use of his least-squares computer program.

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Résumé

Au départ de résultats de conversion–composition de Gruber et Elias, les rapports de réactivité du styrène (M_1) et du méthacrylate de méthyle (M_2) ont été calcules être égal à $r_1 = 0.55 \pm 0.02$ et $r_2 = 0.58 \pm 0.06$ á 90°C. La méthode des moindres carrés a été utilisée pour ces valeurs et celles de la littérature pour d'autres températures en vue d'obtenir les expressions d'Arrhénius: $\log r_1 + 0.04736 - (235.45/T)$, et $\log r_2 = 0.1188 - (285.36/T)$. Utilisant les valeurs de la littérature pour les étapes de la homopolymérisation $A_{11} = 2.2 \times 10^7$ l mole^{-1} sec^{-1}, $E_{11} = 7.8$ Kcal/mole et $A_{22} = 0.51 \times 10^7$ l mole^{-1} sec^{-1}, $E_{22} = 6.3$ Kcal/mole; des énergies d'activation et facteurs de fréquence ont ensuite été calculés pour des étapes de polymérisation croisée: $A_{12} = 2.1 \times 10^7$ l mole^{-1} sec^{-1}, $E_{12} = 7.3$ Kcal/mole et $A_{21} = 0.45 \times 10^7$ l mole^{-1} sec^{-1}, $E_{21} = 5.7$ kcal/mole.

Zusammenfassung

Aus den Umsatz–Zusammensetzungsdaten von Gruber und Elias wurden die Reaktivitätsverhältnisse von Styrol (M_1) und Methylmethacrylat (M_2) zu $r_1 = 0{,}55 \pm 0{,}02$ und $r_2 = 0{,}58 \pm 0{,}06$ bei 90°C berechnet. Mit der Methode der kleinsten Quadrate

wurden aus diesen Werten und aus Literaturangeben die Arrhenius-Gleichungen: ln $r_1 = 0{,}04736 - (235{,}45/T)$ und ln $r_2 = 0{,}1183 - (285{,}36/T)$ erhalten. Unter Benützung der Literaturwerte für die Homopolymerisation $A_{11} = 2{,}2 \times 10^7$ l Mol^{-1} sec^{-1}, $E_{11} =$ 7,8 kcal/Mol und $A_{22} = 0{,}51 \times 10^7$ l Mol^{-1} sec^{-1}, $E_{22} = 6{,}3$ kcal/Mol wurden Aktivierungsenergien und Frequenzfaktoren für die gekreuzten Wachstumsschritte berechnet: $A_{1,2} = 2{,}1 \times 10^7$ l Mol^{-1} sec^{-1}, $E_{12} = 7{,}3$ kcal/Mol und $A_{21} = 0{,}45 \times 10^7$ l Mol^{-1} sec^{-1}, $E_{21} = 5{,}7$ kcal/Mol.

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Kinetics and Mechanism of Acrylonitrile Polymerization by *p*-Toluenesulfinic Acid. II. Polymerization Mechanism

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Synopsis

The retardation of acrylonitrile (AN) polymerization by *p*-toluenesulfinic acid (TSA) in the presence of relatively strong acids has been further investigated. Conductance measurements supported the hypothesis that an ionic complex, presumably $RSO_2H_2^+$, is obtained by a reaction of the sulfinic acid with a proton. It is postulated that this complex is a chain transfer agent for the observed retardation. On the basis of this assumption, a kinetic scheme was developed involving additional termination steps by the complex. The scheme accounts for the maximum in initial rate observed on increasing the concentration of added sulfonic acid at a constant TSA concentration. It also provides an explanation for the elimination of the autoacceleration in the bulk polymerization of AN when strong acids are added. The orders derived from the kinetic equations are in good agreement with the orders evaluated from the kinetic experiments.

INTRODUCTION

The understanding of the mechanism of vinyl monomer polymerization by sulfinic acids is not at all clear, though it is known to be of the free-radical type.[1] The kinetic results found in the literature appear to be rather contradictory. The order of polymerization with respect to sulfinic acid concentration has been reported as 1.0–1.5 in methyl methacrylate[1] (MMA) and 0.5 in styrene.[2] Protons are known, in the case of MMA,[1] to enhance the rate of polymerization, whereas for the acrylic esters they act as inhibitors.[3] The influence of protons has also been studied in the emulsion polymerization of styrene and butadiene with aliphatic sulfinic acids.[4] In this particular case it was found, that increasing the concentration of protons resulted first in an acceleration and then in an inhibition of the polymerization. A maximal rate was found at pH 1.9.

Experimental results and a qualitative interpretation for the case of acrylonitrile (AN) polymerization by *p*-toluenesulfinic acid (TSA) are presented in Part I of this series.[5] It was found that the order of polymerization, with respect to the initiator was about 1.2 and that *p*-toluenesulfonic acid (TSOA) exhibited a cocatalytic effect. These results are similar to those obtained by Overberger[1] for MMA. We have also shown that the cocatalytic effect may be attributed to protons. Further increase in the concentration of the acid results in a retardation of the polymerization, a result very similar to that of Bredereck.[3] Orders of polymerization with respect to sulfinic acid initiator in 20% AN in dimethylformamide (DMF) solution, as well as in bulk, have been calculated and found to depend on the concentration of the strong acid added.

In solution, in the range 0.09–0.27*M* TSA, the orders found were as follows: 1.2 at 0.002*M*, 1.1 at 0.02*M*, and approximately 1.5 at 0.04*M* TSOA. A maximal activity occurred at about 0.02*M* sulfonic acid for three series of experiments, each at a constant concentration of TSA. The orders in bulk at 0.001*M* TSOA in the range of 0.005–0.013*M* TSA and at 0.09*M* TSOA in the range of 0.05–0.15*M* TSA, were 1.2 and 1.5, respectively.

It was observed that TSOA did not influence the rate of polymerization of AN by azobisisobutyronitrile (AIBN) in DMF solution. It thus appears that the polymerization is retarded through formation of a product between the TSA and TSOA.

In the bulk polymerization the addition of TSOA also diminishes and even eliminates the usually observed autoacceleration.

EXPERIMENTAL RESULTS

The experimental kinetic data have already been given in Part I. Some additional results directly concerning the theoretical treatment are reported below.

The postulated formation of ionic species, by an interaction of TSA with TSOA, has been substantiated from a study of the electrical conductance measurements of these acids in DMF solutions.

Conductivities were measured at 60°C. with an Industrial Instrument conductance bridge (Model RC-1) employing a Shedlovsky type cell. The conductivity of the TSA solution was found to increase with time, probably due to the formation of sulfonic acid through the disproportionation reaction. The specific conductance value for TSA is thus expected to be slightly too high. The specific conductance of 0.19*M* TSA in DMF was found to be 1×10^{-4} ohm^{-1} cm.$^{-1}$. The specific conductance of DMF solutions of TSOA alone and in the presence of 0.19*M* TSA were measured over a range of TSOA concentrations. The results are given in Figure 1. The specific conductance of the mixture TSA-TSOA is about four times greater than the sum of the separate specific conductances of TSA and TSOA solutions each of a concentration identical to that in the mixture. This result indicates the formation of a complex, presumably $RSO_2H_2^+$, which was already postulated by Bredereck[6] to be an intermediate in the disproportionation reaction of sulfinic acids. The concentration dependence of the equivalent conductance of TSOA alone in DMF shows that TSOA is a weak acid in this solvent.

DISCUSSION

The suggested kinetic scheme is based on initiation involving a bimolecular reaction between a trimer of TSA and a proton. Details of this mechanism will be given in Part III. In the equation for the initiation rate, it is therefore assumed that the order with respect to the proton is one. Because of side reactions, discussed in Part III,[7] the rate of initiation is given by the following equation:

$$R_i = k_i[\mathrm{T}]^n[\mathrm{H}^+] \tag{1}$$

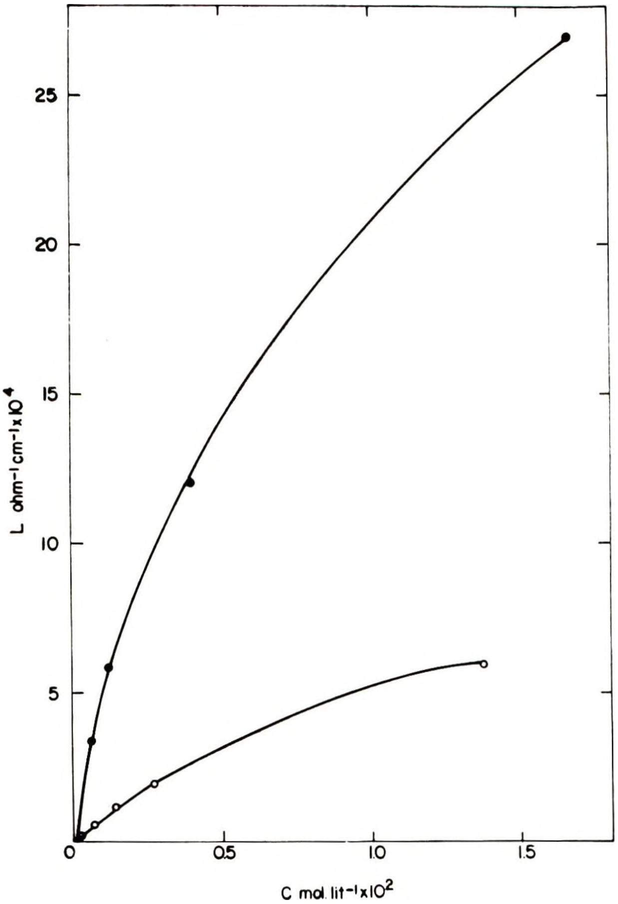

Fig. 1. Specific conductance of TSOA: (○) in DMF; (●) in presence of $0.19M$ TSA.

where k_i is the overall rate constant for initiation, [T] is the concentration of free TSA, and n is the order with respect to the initiator. Due to the formation of complex, the initial concentration of free sulfinic acid, [T], is

$$[\mathrm{T}] = [\mathrm{T}_0] - [\mathrm{Q}] \tag{2}$$

where $[T_0]$ is the total concentration of TSA and $[Q]$ is the concentration of the complex $RSO_2H_2^+$.

The stability constant K, for the formation of Q, is given by:

$$K = [Q]/[T][H^+] \tag{3}$$

Some other relations in the system are simply derived:

$$[T] = [T_0]/(1 + K[H^+]) \tag{4}$$

$$[Q] = K[H^+][T_0]/(1 + K[H^+]) \tag{5}$$

The rate of initiation will thus be

$$R_i = k_i\{[T_0]/(1 + K[H^+])\}^n[H^+] \tag{6}$$

In the work done in DMF solutions, the conditions are such that the concentration of TSOA added is always smaller than that of the sulfinic acid present (see Fig. 6 of Part I). Consequently, the values of $K[H^+]$, which is $[Q]/[T]$, are smaller than unity. The rate of initiation, formulated in eq. (6), has to increase with increasing concentration of protons in the solution. It was mentioned above that TSOA has no influence on the rate of free-radical polymerization of AN in DMF solution when AIBN is used as an initiator. It is suggested that the decrease in rate, illustrated in Figure 6 of Part I, is due to a retardation resulting from a reaction between the growing polymer chain and the complex of TSA and a proton. We suppose that the chain transfer to the complex leads to an ion-radical of a sulfur compound, and it is assumed that due to the adjacent aromatic ring this radical is sluggish in initiating polymerization by reaction with the monomer. It is further asserted that the positive charge on the ion-radical will prevent termination by mutual reaction. These radicals can, however, interact with a growing free radical and thereby contribute to the termination reaction. Stable ion-radicals of sulfur compounds formed from aromatic sulfones in concentrated sulfuric acid have recently been reported.[8]

In accordance with these kinetic assumptions, there are at least three types of termination mechanism for the growing chains in the system: the usual biradical termination with a rate constant of k_{t_2} and two terminations involved with the complex Q with rate constants of k_{t_1} and k'_{t_1},

$$X\cdot + Q \xrightarrow{k_{t_1}} P + Q\cdot \tag{7}$$

$$X\cdot + Q\cdot \xrightarrow{k'_{t_1}} \text{Product} \tag{8}$$

where $X\cdot$ is the growing chain radicals, P is polymer, and $Q\cdot$ is the radical obtained by the chain transfer.

The steady-state condition for the $Q\cdot$ radicals is:

$$k_{t_1}[X\cdot][Q] = k'_{t_1}[X\cdot][Q\cdot] \tag{9}$$

$$[Q\cdot] = (k_{t_1}/k'_{t_1})[Q] \tag{10}$$

Introducing the steady-state concentration of $Q\cdot$ in the overall rate equation for the termination of growing free radicals, one obtains:

$$R_t = 2k_{t_1}[X\cdot][Q] + k_{t_2}[X\cdot]^2 \tag{11}$$

Employing eq. (6) for the rate initiation and introducing the values of [T] and [Q] one obtains the following expression for the steady-state condition of the growing chain radicals.

$$k_i\left(\frac{[T_0]}{1 + K[H^+]}\right)^n [H^+] = k_{t_2}[X\cdot]^2 + 2k_{t_1}[X\cdot]\frac{K[H^+][T_0]}{1 + K[H^+]} \tag{12}$$

The DMF solvent introduces some complications in the kinetic scheme. It is known[9] that the order with respect to the initiator in the polymerization of AN in DMF solution is slightly higher than the values expected according to theory. Instead of the expected value of 0.50, the experimentally found values were 0.55–0.60. The rate of polymerization in DMF was also found to be lower than in other solvents. These results are explained[10] in terms of a retardation of the growing chain due to reaction with DMF molecule. It is reasonable to suppose that the presence of DMF will also increase the order with respect to the sulfinic acid initiator. For the sake of simplicity both the retardation due to the DMF, as well as any chain transfer to either monomer, polymer, or free sulfinic acid has been ignored.

The concentration of protons in the AN–DMF solution is not known, but if we assume that $[H^+]$ increases with increasing concentration of TSOA, we are then able to check the validity of eq. (12) with the experimental results.

By differentiating eq. (12) with respect to the proton concentration, $[H^+]$ and using $d[X\cdot]/d[H^+] = 0$, the maximum concentration of growing chains $[X\cdot]_{max}$, may be derived:

$$k_i\left(\frac{[T_0]}{1 + K[H^+]}\right)^n - \frac{nk_i[T_0]^n[H^+]K}{(1 + K[H^+])^{n+1}} = 2k_{t_1}\frac{(1 + K[H^+])[T_0]K - [T_0]K^2[H^+]}{(1 + K[H^+])^2}(X\cdot)_{max} \tag{13}$$

This equation may be arranged to give

$$(X\cdot)_{max} = \frac{\{1 - (n - 1)K[H^+]\}[T_0]^{n-1}k_i}{2k_{t_1}K(1 + K[H^+])^{n-1}} \tag{14}$$

The equivalent concentration of protons at the maximum rate, [h], can be obtained by inserting the value of $(X\cdot)_{max}$ into eq. (12):

$$k_ik_{t_2}\frac{\{1 - (n - 1)K[h]\}^2[T_0]^{n-2}}{K^2 2k_{t_1}^2(1 + K[h])^{n-2}} + \{1 - (n - 1)K[h]\}[h] - [h] = 0 \tag{15}$$

Calculation of the Value n

In deriving the value of n it is assumed that at low concentrations of protons, i.e., $0.002M$ TSOA, the biradical mechanism of termination dominates. The steady-state condition of eq. (12) can be written as:

$$k_i\left(\frac{[\mathrm{T}_0]}{1 + K[\mathrm{H}^+]}\right)^n [\mathrm{H}^+] = k_{t_2}[\mathrm{X}\cdot]^2 \tag{16}$$

The initial rate of polymerization will be: $R_p = k_p[\mathrm{X}\cdot][\mathrm{M}]$, where k_p is the propagation constant and $[\mathrm{M}]$ is the concentration of the monomer in solution. Inserting $[\mathrm{X}\cdot]$ from eq. (16) into the rate equation we obtain:

$$R_p = k_p(k_i[\mathrm{H}^+]/k_{t_2})^{1/2}\{[\mathrm{T}_0]/(1 + K[\mathrm{H}^+])\}^{n/2}[\mathrm{M}] \tag{17}$$

Further, we assume that in our calculation of n, i.e., at a TSOA concentration of $0.002M$, the change in proton concentration over the TSA range (0.09–$0.27M$) is negligible, since the TSOA is a much stronger acid as seen in the conductance results. The order of the polymerization with respect to the initiator, $n/2$, was calculated in Part I of this work from the slope of the log R_p versus log $[\mathrm{T}_0]$ curves. The value found was 1.2 ± 0.1 and thus the molecularity of primary radical formation according to eq. (6) is 2.4. Considering the above-mentioned retardation by DMF, the actual order of the reaction by which primary radicals are formed from TSA may be expected to be less than 2.4. The lowering of the order due to DMF was estimated as 10–20% of the calculated value. Inserting the value 2 for n in eq. (15) shows that [h] is independent of $[\mathrm{T}_0]$. It was indeed found that the concentration of TSOA at the position of maximum rate, obtained by varying the TSOA at a constant TSA, was independent of the latter concentration (see Fig. 6 of Part I).

The maximum rates must be proportional to $[\mathrm{T}_0]^{n-1}$, the only variable in eq. (14). It was found that the maximum rates were proportional to $[\mathrm{T}_0]$ to the power of 1.1 ± 0.1 which is in good agreement with the expected value.

When the monoradical termination is dominant, eq. (12) will have the form:

$$k_i\{[\mathrm{T}_0]/(1 + K[\mathrm{H}^+])\}^n[\mathrm{H}^+] = 2k_{t_1}[\mathrm{X}\cdot]K[\mathrm{H}^+][\mathrm{T}_0]/(1 + K[\mathrm{H}^+]) \tag{18}$$

Thus, at a constant concentration of TSOA, the rate of polymerization will be proportional to $[\mathrm{T}_0]^{n-1}$. Termination by chain transfer exclusively may be the case in certain bulk polymerizations, but we do not suppose that in solution polymerization the biradical termination can be neglected.

Mechanism of Heterogeneous Polymerization of AN with the Sulfinic–Sulfonic Catalytic System

It has been reported that the order of polymerization of AN in bulk with respect to TSA initiator is 1.2.[5] The order was calculated by the usual procedure from log–log plots of the initial rate versus catalyst concentration. The measurements were made at 60°C. in the presence of an initial concentration of 0.001M TSOA. The reaction was carried out at a relatively high temperature in order to diminish occlusion of growing radicals.[11] At 60°C. the results with pure sulfinic acid are not reproducible because of the cocatalytic effect of the sulfonic acid formed by the disproportionation reaction of TSA. The addition of 0.001M TSOA was found to yield reproducible kinetic results. (Conductivity measurements of pure sulfinic acid in DMF solution showed that the formation of sulfonic acid at room temperature is very slow and may be neglected. Accordingly, polymerization with pure sulfinic acid at 20–30°C. may yield reproducible results.)

The order obtained with respect to the TSA initiation in bulk is about the same as the order obtained in solution. This result is very peculiar, for it is well known that the usual order in bulk is higher than in solution. In experiments with pure sulfinic acid the autoacceleration observed is similar to that found with the usual free-radical catalysts. However, the autoacceleration is diminished by the addition of 0.001M sulfonic acid, vanishes entirely at higher concentrations of TSOA, and at 0.09M TSOA the rate decreases with the degree of conversion. This decrease of the rate with time is greater than that to be expected from the depletion of monomer (see Fig. 11, Part I).

We have tried to compare the molecular weights obtained in the bulk polymerization of AN both by sulfinic acid and by AIBN at the same temperature and initial rate. It was observed that the sulfinic acid polymer product could be easily dissolved in DMF while the product with AIBN was a swollen gel. It is possible that the transfer of free radicals from the growing chains to the retarder prevents transfer to the polymer chain, leading to branching. The similarity of the order found in bulk to that in solution, at low concentrations of TSOA, can be also explained by the chain transfer mechanism as this decreases the average molecular weight and makes the usual biradical termination much more available. The influence of the retardation is analogous to the case of the bulk polymerization of AN by AIBN, reported by Bamford,[11] when butyl mercaptan is added; the autoacceleration decreases and at relatively high concentrations the rate becomes constant. A chain transfer agent, in relatively high concentrations, may act as a retarder as in the above two cases, the molecular weights decrease, and small new radicals are formed. The small radicals can diffuse more easily into the aggregates of polymer and thereby terminate chain radicals growth.

Increasing the sulfonic acid concentration in the bulk, leads to the chains terminating through the retardation mechanism. Such a condition may give rise to a stationary state of the growing radicals, similar to the case of solution polymerization. Failure to detect EPR signals in the bulk product prepared with TSA–TSOA at 60°C. would indicate that the radicals formed by the chain transfer [eq. (7)] are disappearing, presumably according to the scheme shown in eq. (8). After one day at room temperature bulk product of TSA–TSOA showed the usual signals of buried polyacrylonitrile radicals.[12] For the initial rate the condition of steady state is expressed by eq. (18). In bulk, the constants k_i, K, and k_{t_1} may have different values, but the initial rate has to be proportional to the sulfinic acid concentration to the power of $n - 1$. The results obtained at $0.09M$ sulfonic acid in bulk show an order of 1.5 ± 0.1 which leads to a value of 2.5 for n, a value higher than in solution. It will be further shown,[7] that the initiation mechanism depends on the medium and n may vary from 2 to 3.

It is clear from Figure 11 of Part I that the polymerization rate decreases much more rapidly than the volume of monomer left, and eq. (18) may thus be considered correct only during the initial stages of the polymerization. The addition of acids in bulk polymerization may have an additional effect on the mode of aggregation, and thereby on the rate constants in the heterogeneous system. Indeed, inorganic acids were found to reduce the rate of bulk polymerization of AN by AIBN, in contradistinction to the case of solution where no effect on rate was found, (cf. Fig. 8, Part I). Such an effect was not taken into consideration in the kinetic scheme leading to eq. (18) and was ignored in the calculation of the order.

The rate of bulk polymerization with AIBN is decreased much more by the addition of sulfinic acid + sulfonic acid than by the addition of either acid alone. This special decrease can be attributed to the retardation by a complex formed by TSA and a proton.

On increasing the concentration of sulfonic acid the rate increases rather quickly and then decreases moderately. The molecular weights were found to decrease with increasing concentration of TSOA also in the range in which the rate decreases upon increasing the concentration of sulfonic acid.

Addition of phosphoric acid increases the rate though no decrease was found even at relatively high concentrations of the acid. The molecular weights were found to decrease but not to such an extent as in the case of sulfonic acid. It would seem that there is a correlation between the influence of the added acids on the molecular weight and on the autoacceleration. It was found possible to eliminate the autoacceleration by the addition of TSOA, whereas the addition of phosphoric acid, even up to high concentration ($0.55M$ H_3PO_4 to $0.19M$ TSA), only diminishes it.

It was also noted that the addition of relatively strong acids like perchloric and trifluoroacetic acids even at relatively low concentrations causes first a rapid polymerization and then, after a short while, leads to complete inhibition. We suppose that the change in retardation, observed upon addition of the various acids, is due to their varying acidity affecting the concentration of the complex, $RSO_2H_2^+$, produced in the system.

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Résumé

On a étudié le phénomène de retardement qui se présente au cours de la polymérisation de l'acrylonitrile au moyen d'acide *p*-toluène sulfinique (TSA) en présence d'acide relativement fort. Des mesures de conductance confirment l'hypothèse qu'un complexe ionique vraisemblablement $RSO_2H_2^+$, a été obtenu par réaction de l'acide sulfinique avec un proton. On admet que ce complexe est un agent de transfert pour le phénomène de retardement considéré. Sur la base de cette hypothèse, un schéma cinétique a été développé qui inclut des étapes supplémentaires de terminaison par ce complexe. Ce schéma rend compte du maximum observé dans la vitesse initiale en accroissant la concentration de l'acide sulfonique additionné pour une concentration constante donnée TSA. Il fournit également une explication pour l'élimination de l'autoaccélération dans la polymérisation en bloc de l'acrylonitrile lorsque l'on ajoute des acides forts. Les ordres qui résultent de ces équations cinétiques sont en bon accord avec les ordres évalués au départ d'expériences cinétiques.

Zusammenfassung

Die Verzögerung der Acrylnitril (AN)-Polymerisation durch *p*-Toluolsulfinsäure (TSA) in Gegenwart verhältnismässig starker Säuren wurde untersucht. Leitfähigkeitsmessungen lieferten eine Stütz für due Hypothese, dass durch eine Reaktion der Sulfinsäure mit einem Proton ein Ionenkomplex, wahrscheinlich $RSO_2H_2^+$, erhalten wird. Es wird angenommen, dass dieser Komplex bei der beobachteten Verzögerung als Kettenüberträger wirkt. Auf Grundlage dieser Annahme wurde eine kinetisches Schema mit zusätzlichen Abbruchsschritten durch den Komplex entwickelt. Das Schema kann das bei der Anfangsgeschwindigkeit mit zunehmender Konzentration der zugesetzten Sulfonsäure bei konstanter TSA-Konzentration beobachtete Maximum erklären, es liefert auch eine Erklärung für die Beseitung der Selbstbeschleunigung bei der Polymerisation von AN in Substanz bei Zusatz starker Säuren. Die aus den kinetishen Gleichungen abgeleitete Ordnung stimmt gut mit der aus den kinetischen Versuchen berechneten Ordnung überein.

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Kinetics and Mechanism of Acrylonitrile Polymerization by *p*-Toluenesulfinic Acid. III. Initiation Through Disproportionation

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Synopsis

A mechanism for radical formation from aromatic sulfinic acids through the disproportionation reaction is suggested. It is postulated that two parallel steps, one a bimolecular reaction and the other involving a trimer of sulfinic acid, yield sulfenyl sulfonate. This labile compound decomposes into free radicals or reacts with another molecule of sulfinic acid producing thiol sulfonate and sulfonic acid. This mechanism explains the variety and unusually high orders encountered in polymerization initiated by sulfinic acid initiators. The proposed kinetic scheme is in agreement with the proton dependence found for both the initiation as well as the disproportionation reactions.

Introduction

In the previous parts of this work,[1,2] the kinetics of acrylonitrile (AN) polymerization by *p*-toluenesulfinic acid (TSA) was reported and the mechanism of polymerization discussed. It was shown that at least part of the termination in the system is through chain transfer to a complex of sulfinic acid and a proton, which leads to retardation. The mechanism of initiation by aromatic sulfinic acids has not yet been evaluated, but it is known to be of a free-radical type.[3] In this paper a mechanism for the formation of free radicals from TSA is proposed.

It seems that the initiation step is connected with the disproportionation reaction of the sulfinic acid. The disproportionation reaction has been previously studied and is known to proceed according to the reaction:

$$3RSO_2H \rightarrow RSO_2SR + RSO_3H + H_2O \qquad (1)$$

The rate of reaction was measured in aqueous and acetic acid solutions.[4–6] It was found to be second-order with respect to the sulfinic acid and to be increased by acids. The polymerization of methyl methacrylate[3] (MMA) and AN[1,2] by sulfinic acids was also found to be enhanced by protons.

Bredereck[7] has suggested a mechanism for the disproportionation reaction of sulfinic acids involving catalysis by protons via formation of the

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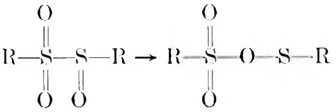
complex $RSO_2H_2^+$. By the abstraction of water from a molecule of sulfinic acid and a molecule of the complex, an intermediate compound, sulfinyl sulfone, RSO_2SOR (I), is formed. The sulfinyl sulfone oxidizes another molecule of sulfinic acid and the final products obtained are thiol sulfonate, RSO_2SR, and sulfonic acid.

Kice[8] has synthesized the sulfinyl sulfone (I) and studied kinetically its decomposition in dry dioxane. He found that the decomposition of I is monomolecular and that the rate of decomposition is not influenced by sulfinic acid added to the solution. This result stands in contradiction to the mechanism suggested by Bredereck. According to Kice, I goes through a relatively slow monomolecular rearrangement to the anhydride form, sulfenyl sulfonate (II).



$$\underset{\text{I}}{R-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-\underset{\underset{O}{\|}}{S}-R} \rightarrow \underset{\text{II}}{R-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-S-R} \qquad (2)$$

The sulfenyl sulfonate loses an oxygen in a relatively fast reaction with a molecule of sulfonic acid, forming the usual products [eq. (3)].

$$R-SO_2-O-S-R + RSO_2H \rightarrow R-SO_2-S-R + RSO_3H \qquad (3)$$

This mechanism is based on the results for the reaction carried out in acetic acid solutions in which the rate of reaction was found to be second-order with respect to the sulfinic acid. The sulfinyl sulfone as a starting material was shown to be capable of producing radicals, and it was assumed that the transition from I to II is through a homolytic scission of I.

It seems difficult to explain the mechanism of polymerization initiation according to this reaction scheme. We are presented with the following facts: (*a*) Kice[8] reported that the production of free radicals in dry dioxane solution is first-order with respect to the sulfinic acid; (*b*) in the polymerization of styrene[9] the order is 0.5, with respect to the sulfinic acid, indicating a monomolecular radical formation; (*c*) various aromatic sulfinic acids employed as initiators in the polymerization of MMA yield different orders, i.e., with *p*-trifluoromethylbenzenesulfinic acid and *p*-methoxybenzenesulfinic acid, orders of 1.0 and 1.5, respectively, were reported.[3] As the termination in this case is a bimolecular reaction, a bimolecularity or a trimolecularity has to be assigned to the respective initiation steps. Variation of the polymerization order with the type of substitution in the benzene ring of the sulfinic acid indicates that a reaction with another sulfinic acid molecule plays a direct role in the mechanism of radical formation.

The molecularity of radical formation in the polymerization of AN in DMF by sulfinic acids has also been found[1,2] to be above two. Such exceptional high orders indicate that the initiation step involves an associated form of the sulfinic acids. Indeed, sulfinic acids were shown by spectroscopical methods[10] to be highly associated, and a trimer form was concluded from cryoscopic studies.[11]

Experimental Results

The main experimental results are given in the earlier papers of this series.[1,2] In the polymerization of 20% AN in DMF solution it was found that the order with respect to TSA was 1.2 ± 0.1. A similar order for TSA was obtained in MMA.[3] It was shown[1,2] that in the presence of relatively strong acids a monoradical termination takes place through a chain-transfer mechanism. However, at low concentrations of the added acid the usual biradical termination is assumed to be dominant. With this assumption, the molecularity of radical formation is about 2.4.

Since styrene appears to behave differently, its bulk polymerization by TSA, in vacuum, was studied dilatometrically according to a procedure described previously for AN.[1] Contrary to the findings with AN, no influence of *p*-toluenesulfonic acid (TSOA) on the polymerization rate of styrene was observed. Plots of the degree of conversion versus time had the same shape as those obtained previously by Iring and Tudos.[9] The polymerization rate is relatively fast at the beginning, then it decreases, and then becomes constant.

Conductivity measurements[2] have shown that TSOA does not dissociate completely in DMF solutions, so that the concentration of protons could only be roughly estimated. Therefore, no attempt was made to evaluate the order of the polymerization with respect to the proton concentration.

p-Tolyl-*p*-toluenethiol sulfonate, which is a final product of the disproportionation reaction, was synthesized by heating TSA in aqueous hydrochloric solution for $^1/_2$ hr. with KI as a catalyst.[4] The brown oil obtained was recrystallized from ethanol solution to give white crystals, m.p. 75°C. The possible effect of thiol sulfonate on the thermal polymerization of AN was examined by itself and in combination with either TSA or TSOA. It was found that thiol sulfonate does not affect the polymerization.

Discussion

It is rather surprising that the order for aromatic sulfinic acids in the polymerization of various monomers varies so widely, from 0.5 to 1.5. The value of 1.5 implies that the molecularity of the radical formation reaction is three and it can be concluded that three molecules of TSA are involved in the initiation step. As a trimolecular reaction is not very likely, we have assumed that a trimer of TSA is the starting compound from which the primary radicals are produced. In order that this model be consistent, one has to assume that whenever the values of the order fall below 1.5, TSA will also contribute to a side reaction competing with the free-radical formation step. This last assumption is particularly necessary for the case of styrene, where the order is 0.5, as no plausible mechanism can be suggested for formation of free radicals in a mononomolecular decomposition of TSA.

It was shown that thiol sulfonate, the end-product of the disproportionation reaction, does not initiate polymerization by itself nor does it participate in the initiation by TSA. It must, therefore, be assumed that an intermediate compound in the disproportionation reaction is responsible for the radial formation.

Bredereck suggested that sulfinyl sulfone (I) is a possible intermediate in the disproportionation reaction of aromatic sulfinic acids. Kice[8] showed that this compound is capable of producing free radicals. However, it should be emphasized that sulfinyl sulfone has not been separated from TSA solutions undergoing a disproportionation reaction.

The molecularity of radical formation in MMA and AN was found to be larger than 2. In styrene, which is a relatively nonpolar monomer, the molecularity is one. Moreover, the rate of polymerization of styrene was found to be independent of TSOA in contrast to that of MMA and AN.

It would seem that there are two parallel mechanisms of initiation, one being dominant in polar and the other in nonpolar solutions.

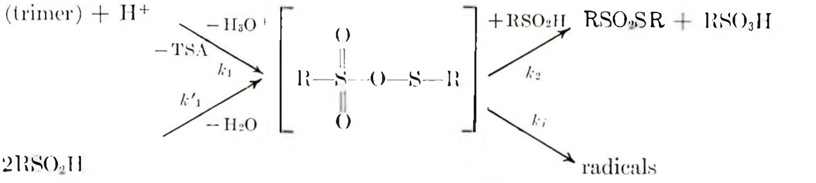
Trimers of aromatic sulfinic acids are known to exist both in polar and in nonpolar solvents. Although the cryoscopic experiments were carried out at a lower temperature than the polymerization reactions, it can be assumed that associated forms still exist in the polymerization mixtures. Let us designate by K the equilibrium constant of trimer with the monomeric sulfinic acid.

$$[T_3] = K[T]^3 \tag{4}$$

$[T_3]$ and $[T]$ being the concentration of the trimer and the monomer, respectively.

It is assumed that II may be formed by a bimolecular reaction of the trimer with a proton, extracting TSA and a water molecule. It is further postulated that II can be formed by a bimolecular reaction of monomeric TSA. The last reaction is slow as compared with the reaction of a trimer and a proton, but it may be dominant in nonpolar solvents where proton concentration is negligible.

We suppose that sulfenyl sulfonate is an intermediate compound in the disproportionation reaction formed according to reactions (5a) and (5b) in polar and nonpolar solutions, respectively. The intermediate compound may decompose into radicals or oxidize a TSA molecule yielding the usual products of the disproportionation reaction.



(5a)

(5b)

The sulfenyl sulfonate, a highly unstable substance, reaches a steady-state concentration after a short interval of time. The steady-state concentration of II can be derived from eqs. (6) and (7) for scheme (5a);

$$d[\mathrm{II}]/dt = k_1K[T]^3[H^+] - k_2[\mathrm{II}][T] - k_i[\mathrm{II}] = 0 \tag{6}$$

the concentration of the trimer is inserted according to eq. (4).

$$[\mathrm{II}] = k_1K[\mathrm{T}]^3[\mathrm{H}^+]/(k_2[\mathrm{T}] + k_i) \tag{7}$$

The rate of radical formation, R_i according to this scheme will be:

$$R_i = k_i\, k_1K[\mathrm{T}]^3[\mathrm{H}^+]/(k_2[\mathrm{T}] + k_i) \tag{8}$$

For scheme (5b)

$$d[\mathrm{II}]/dt = k_1'[\mathrm{T}]^2 - k_2[\mathrm{II}][\mathrm{T}] - k_i[\mathrm{II}] = 0 \tag{9}$$

$$(\mathrm{II}) = k_1'[\mathrm{T}]^2/(k_2[\mathrm{T}] + k_i) \tag{10}$$

The rate of initiation according to this scheme will be:

$$R_i = k_i\, k_1'[\mathrm{T}]^2/(k_2[\mathrm{T}] + k_i) \tag{11}$$

The rate of polymerization R_p for the case of biradical termination polymerization will be:

$$R_p = k_p(k_i[\mathrm{II}]/k_t)^{1/2}[\mathrm{M}] \tag{12}$$

where k_p is the propagation constant, k_t is the termination constant, and [M] is the monomer concentration.

It seems likely that the constants of the various steps of radicals formation and disproportionation reactions of sulfinic acid depend on the nature of the solvent employed. It is possible that the rather unusual observation of Overberger et al.[3] that the rate of polymerization of MMA with TSA in benzene solution is higher than that obtained in the bulk is due to the influence of the added benzene on those constants, resulting in an increase in the rate of radical formation.

The molecularity of initiation with respect to the sulfinic acid will depend on the ratio of $k_2[\mathrm{T}]$ to k_i in eqs. (8) and (11).

From eq. (8) when $k_2[\mathrm{T}] > k_i$, $R_i = k_ik_1K[\mathrm{T}]^2[\mathrm{H}^+]/k_2$, and the molecularity of radical formation n is 2. When most of II has dissociated into radicals, $k_2[\mathrm{T}] < k_i$, $R_i = k_1K[\mathrm{T}]^3[\mathrm{H}^+]$, and $n = 3$. For an intermediate case, the order will be between 2 and 3.

The monomolecularity of radical formation in styrene and anhydrous dioxane may be explained according to eq. (11), when $k_2[\mathrm{T}] > k_i$ and $R_i = k_ik_1'[\mathrm{T}]/k_2$.

The mechanism of disproportionation through the trimer provides an explanation for the second-order kinetics obtained in aqueous acidic solutions. The mechanism suggested by Kice for the disproportionation in acetic acid solution does not take into consideration the dependence on proton concentration although his experimental results do show such a dependence. The case of acetic acid solution is a special case because the order of the reaction was not found to depend on the nature of the substitution in the benzene ring.[6] It may be further assumed that in the case of aromatic sulfinic acids in acetic acid solution, the concentration of the complex, $\mathrm{RSO_2H_2^+}$, is relatively high, and I may be formed by a condensation of the complex, $RSO_2H_2^+$, with a molecule of sulfinic acid. This will result in a second-order reaction for the sulfinic acid and a dependence of the rate on the proton concentration.

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Résumé

Un mécanisme de formation de radicaux d'acides sulfiniques aromatiques par réaction de disproportionnement est présenté. On admet que deux étapes parallèles, l'une étant une réaction bimoléculaire et l'autre comportant un trimère de l'acide sulfinique fournissent toutes deux des sulféniles sulfonates. Ce dérivé labile se décompose en radicaux libres ou réagit avec une autre molécule d'acide sulfinique produisant un sulfonate de thiol et un acide sulfonique. Ce mécanisme explique la variété et les ordres inhabituellement élevés rencontrés au cours de la polymérisation initée par l'acide sulfinique. Le schéma cinétique proposé est en accord avec la fonctionalité de l'acidité trouvée aussi bien pour les réactions d'initiation que pour celles de disproportionnement.

Zusammenfassung

Ein Mechanismus der Radikalbildung aus aromatischen Sulfinsäuren durch Disproportionierung wird angegeben. Es wird angenommen, dass zwei parallele Schritte, einer als bimolekulare Reaktion und der andere über ein Trimeres der Sulfinsäure, Sulfenylsulfonat liefern. Diese labile Verbindung zerfällt in freie Radikale oder reagiert mit einem weiteren Sulfinsäuremolekül unter Bildung von Thiolsulfonat und Sulfonsäure. Dieser Mechanismus erklärt die Variabilität und ungewöhnlich hohe Ordnung, wie sie beim Sulfinsäurestart der Polymerisation anzutreffen sind. Das vorgeschlagene kinetische Schema steht mit der bei Start und Disproportionierung gefundenen Protonenabhängigkeit in Übereinstimmung.

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Grafting of Polyacrylonitrile to Granular Corn Starch

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Synopsis

Acrylonitrile grafts readily to granular corn starch in aqueous slurry when initiated by hydrogen peroxide plus activator. Prime evidence for grafting lies in the ease of separating PAN from starch in high yield when the initiator is azobisisobutyronitrile rather than peroxide. Grafting efficiencies are determined by extraction with appropriate solvents: dimethylformamide for homo-PAN, and boiling water for ungrafted starch. Grafting efficiencies of PAN range from 78 to 95%, $\bar{M}_n$ values for grafted PAN are 4,000 to 90,000, and frequency of attachment of side chains range from 300 to 1100 glucose units per chain. Increasing the monomer level, at fixed initiator concentration, tends to result in longer rather than more frequent side chains. AN behaves much as has been previously found for MMA, but the somewhat more efficient grafting at more frequent intervals and the more nearly uniform distribution of polymer in the starch granule suggest that AN penetrates the starch granule more readily than MMA.

INTRODUCTION

The grafting of poly(methyl methacrylate) (PMMA) to granular corn starch[1,2] or its unsaturated esters[3] by way of free-radical initiation has been described in previous papers from this laboratory. Means of separating ungrafted homopolymer of methyl methacrylate from the graft have been studied in detail.[4] This paper reports results of similar techniques used to prepare and characterize grafts of PAN (polyacrylonitrile) to granular corn starch.

Grafting of PAN to starch has already been carried out, but under conditions widely different from those here reported. Walrath et al.[5] prepared grafts to wheat starch by mutual or preirradiation from a ^{60}Co source. Kimura and co-workers grafted by initiation with ceric salt in solutions of potato amylose[6] or by use of reprecipitated starch peroxidized with ozone.[7] Fanta et al.[8] studied the effects of reaction conditions on composition of product obtained by initiation with ceric nitrate in dilute solutions of wheat starch.

EXPERIMENTAL

Materials

Unmodified and hypochlorite-oxidized starches were A. E. Staley production materials. The unmodified starch was defatted prior to use as previously described.[2] Commercial acrylonitrile (American Cyanamid), free of nonvolatiles and readily polymerizable, was used as received. All other reactants were reagent grade or equivalent.

Polymerization

The procedure was the same as previously described for methyl methacrylate.[1] On addition of the peroxide to the mixture containing all other reactants, the temperature rose from its initial 30°C. to a peak within the next 15 min. Total reaction time was 60–90 min. The product was filtered, washed with water, and dried in air at room temperature. Conversion of monomer to polymer was 95% or higher in each instance, except for those runs initiated with AIBN (azobisisobutyronitrile).

Characterization of Products

PAN Content by Acid Hydrolysis. The sample was refluxed for 6 hr. in 1*N* HCl. The PAN so recovered was washed thoroughly with water and dried to constant weight. This treatment causes no significant hydrolysis of the cyano groups. Samples so treated showed infrared spectra typical of that for a reference sample of PAN. Nitrogen content was not changed, as shown in the following: reference sample, 26.01% N; reference sample after acid treatment, 25.81% N; theory for PAN, 26.40% N. A similar technique for separating PAN from starch has been used previously[5–7] and has been shown not to reduce the nitrogen content of the PAN.[6]

Determination of Molecular Weight. Values of $\bar{M}_n$ were calculated from the equation of Onyon:[9]

$$[\eta] = 3.92 \times 10^{-4}\bar{M}_n^{0.75}$$

where $[\eta]$ is determined in DMF at 25°C.

Calculation of Grafting Efficiency. The following expression is used for both PAN and starch:

$$\text{Grafting efficiency (\%)} = \left(\frac{\text{total wt. polymer} - \text{wt. polymer extractable}}{\text{total wt. polymer}}\right) \times 100$$

RESULTS AND DISCUSSION

Qualitative Description of Products

The products are recovered in the form of fine white powders, similar in appearance to the original starch. Even the appearance of individual particles is changed hardly at all by the polymerization, as shown in Figures 1 and 2. Figure 1 is unmodified starch; Figure 2 is the product from run 12, containing about equal parts of starch and PAN. Even more striking, after acid hydrolysis to yield PAN analytically free of starch, the particles still look very similar to the original starch granules (Fig. 3).

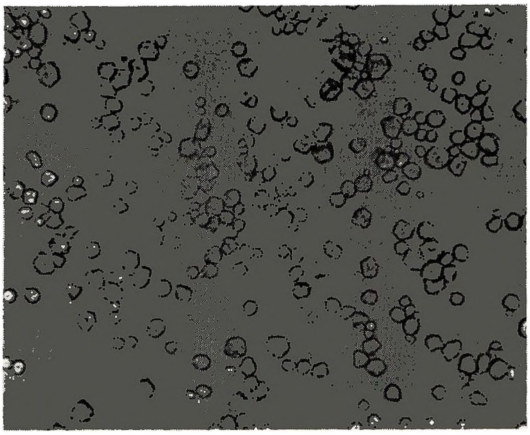

Fig. 1. Granular unmodified starch. 210×.

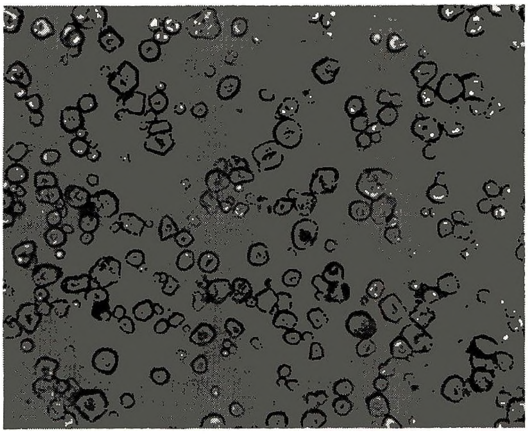

Fig. 2. Unmodified starch plus polyacrylonitrile, at 99.8 parts PAN per 100 starch (run 12). 210×.

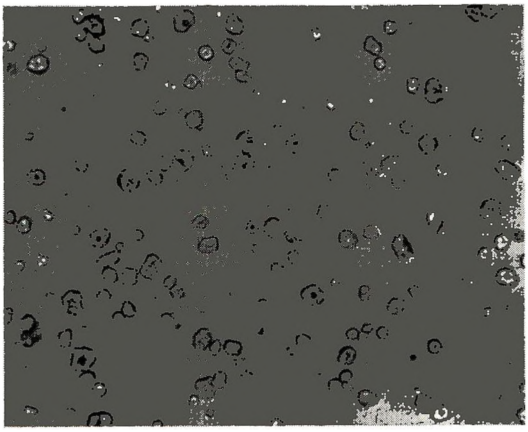

Fig. 3. PAN remaining after removal of starch by acid hydrolysis from product of Fig. 2. 210×.

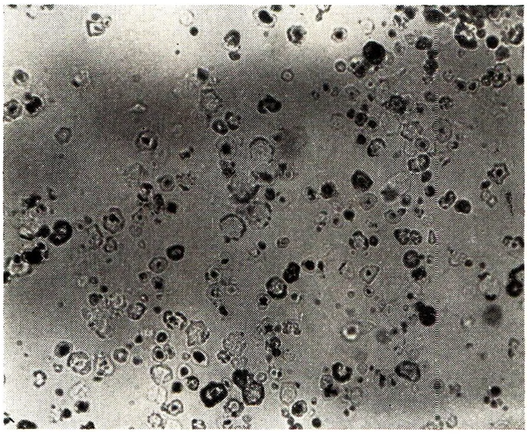

Fig. 4. Poly(methyl methacrylate) recovered by acid hydrolysis of its graft with starch (product from run 11, ref. 1).

The similarity is even more striking than is shown by PMMA recovered by the same process (Fig. 4).

The PAN grafts dissolve cleanly on heating at 100°C. for a few minutes in dimethyl sulfoxide. The solutions remain clear and gel-free on cooling to room temperature. After removal of starch by acid hydrolysis, the recovered PAN dissolves readily at room temperature in DMF. A small sediment, typically present, consists of dark particles amounting to less than 1% of the solid. Filtration removes these, giving a clear, gel-free solution. These observations indicate absence of substantial crosslinking in the grafted products, as was also observed with PMMA grafts.[1]

Extraction of Homopolymer

PAN. Ideally, the ungrafted portion of the PAN would be extracted by a liquid which is a powerful solvent for PAN but a complete nonsolvent for starch. Highly polar solvents suitable for PAN might also dissolve significant amounts of starch even at room temperature. Table I shows, however, that only minor amounts of starch should be extracted by DMF at 30°C.

TABLE I
Extractability of Starch by DMF

Starch	Starch dissolved, %[a]	
	30°C.	50°C.
Oxidized	0.47	1.03
Dextrin, 20% cold water-soluble	1.23	2.51

[a] 1.0 g. of starch at about 10% moisture content tumbled for 16 hr. in 100 ml. of DMF.

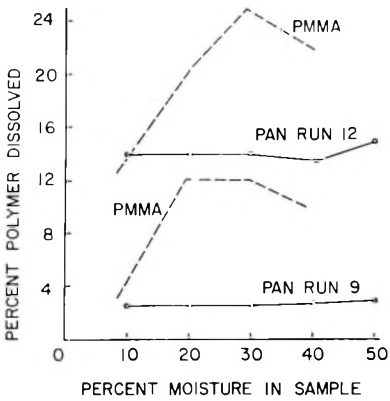

Fig. 5. Effect of moisture content of sample on extractability of (——) PAN with DMF at 30°C.; or (- - -) PMMA with 1,2-dichloroethane at 50°C.[4]

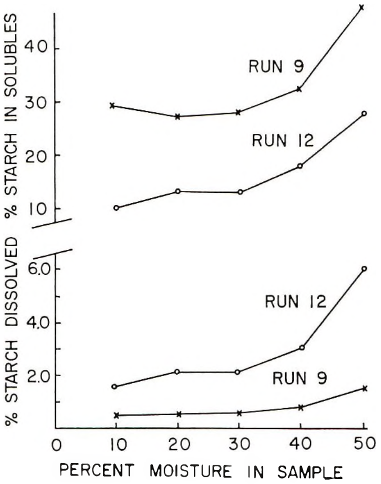

Fig. 6. Effect of moisture content of sample on extractability of starch from starch-PAN products with DMF at 30°C. (lower curves), and on composition of extracted solubles (upper curves).

Since moisture content of the sample influences the extractability of PMMA,[4] the effect was examined for two selected samples of PAN grafts. Products from runs 9 and 12 were extracted at varying moisture contents, with results as shown in Figure 5. For comparison, curves for two samples of PMMA grafts are included. The curves show that moisture has little if any effect on extractability of the homopolymer of acrylonitrile. This is probably due to the polarity of the solvent, which itself swells the granules enough to allow escape of ungrafted polymer.

Effect of moisture content on extractability of starch by DMF was also examined. Results are shown in Figure 6. The amount of starch extracted is relatively constant up to about 30% moisture content, but in-

TABLE II
Effect of Second Extraction with DMF

Run no.	Moisture content, %[a]	Extraction[b]	Extracted, wt.-%[c] PAN	Extracted, wt.-%[c] Starch	Starch in solubles, wt.-%[d]
9	20	1st	2.45	0.50	27
	20	2nd	0.36	0.21	52
	50	1st	2.91	1.51	48
	50	2nd	2.55	0.52	27
12	20	1st	14.2	2.1	13
	20	2nd	1.22	1.9	61
	50	1st	15.0	6.00	28
	50	2nd	0.25	0.51	67

[a] Adjusted by adding the required amount of water to the mixture of sample plus solvent.

[b] About 4.5 g. (dry basis) of sample tumbled 24 hr. at 30°C. in 100 ml. of DMF.

[c] Expressed as weight per cent of PAN and starch, respectively, contained in the original sample.

[d] Determined by 6 hr. reflux in 1N HCl of a portion of the solids recovered by removal of DMF from the extract.

creases at higher moisture levels. Extractions with DMF to remove homo-PAN were therefore carried out at 25% moisture content.

The curves in Figure 5 were derived from single extractions. To check the effect of a second extraction, samples from runs 9 and 12 at 20 and at 50% moisture content were re-extracted. Results are shown in Table II. With the exception of run 9 extracted at 50%, most of the extractable PAN, as well as starch, is removed in the first extraction. Moreover, the proportion of starch in the extract goes up significantly in the second extraction. Therefore, only a single extraction with DMF was used to obtain the data in Tables IV–VII.

Starch. It should be possible to separate ungrafted starch by extraction with water under suitable conditions. This approach has been studied with two selected grafts of PMMA, as shown in Table III.

A pertinent question is whether the extractability of starch would be influenced by prior removal of the extractable synthetic homopolymer. To check this question, samples were given two successive extractions with dichloroethane by the technique previously described.[4] After extraction, the solvent-free residues were then extracted with hot water, along with samples not given the prior solvent extraction. The figures in Table III indicate prior removal of homo-PMMA is not required. Also, extracting with two successive refluxings in distilled water for 3 hr. removes the same amount of starch as can be dissolved in 24 hr. in a Soxhlet extractor. In the two runs so designated, a little ammonia was added prior to reflux on the theory that if the mixture were slightly acidic, this could lead to removal of starch from graft by hydrolytic chain cleavage. The pH adjustment had little effect.

TABLE III
Water Extraction of PMMA/Starch Grafts

Product[a]	Prior PMMA extraction[b]	Starch extracted, %: Soxhlet[c]	Starch extracted, %: 2 Refluxes[d]
53.6% PMMA, 81% grafting efficiency, $\bar{M}_n$ = 190,000	Yes	64	65, 65
	No	—	68, 56[e]
51.5% PMMA, 76% grafting efficiency, $\bar{M}_n$ = 33,000	Yes	—	80
	No	—	84, 83[e]

[a] Prepared from oxidized starch.

[b] Two successive extractions by tumbling sample at 25% moisture content with 1,2-dichloroethane for 16 hr. at 50°C.

[c] 24 hr. extraction.

[d] Two successive refluxes of about 1.0 g. of sample in 100 ml. of distilled water for at least 4 hr.

[e] Ammonia added prior to reflux, to bring initial pH to about 8.0.

Based on the above observations, the procedure adopted for the PAN grafts was two successive 3-hr. refluxes in 100 ml. of distilled water of about 2.0 g. of graft. Some 70–90% of the starch removed was taken out in the first extraction. Calculations of the starch grafting efficiency are based on the total removed in the two extractions.

Starch containing a minor fraction of short-chain grafted PAN might carry PAN into aqueous solution. To determine PAN content, samples of the aqueous extract were refluxed with HCl. In no instance was insoluble product obtained from the second extract. In some runs, no solid was recovered from the first extract; in others, solid amounting to less than 1% of the total PAN was recovered. The single exception was run 17 (Table VI), in which some 59% of the PAN (identity established by infrared spectrum) in the original sample was recovered by acid hydrolysis of the aqueous extract. Note that most of the starch in this sample was extracted by hot water; in view of the low molecular weight (4,000) of the grafted PAN, it is not surprising that some graft copolymer was also water-soluble.

Evidence for Grafting

The evidence here presented rests on the difference between the results obtained with AIBN and peroxide. Table IV summarizes runs made with AIBN. Polymerizations were carried out as with peroxide except that temperature was maintained at 50°C. for 3 hr. (18 hr. for run 5). For unmodified starch (runs 1 and 2), the weight of extractable PAN was higher than theoretical. When allowance is made for probable solubilization of a little ungrafted starch, it appears that the PAN is about quantitatively removed. For runs 3–5 (oxidized starch), the removal of PAN is less than quantitative but is in every instance very much higher than shown in any run with peroxide (Tables V and VI). Removal of starch by extraction with water is quantitative for the samples derived from oxidized starch. With unmodified starch, the starch is much less readily extracted. This may reflect the difference between unmodified and oxidized starches themselves; the oxidized starch dissolves in water more quickly and at a

TABLE IV
Initiation with AIBN[a]

Run	Starch	AN, parts/100 parts starch in charge	AIBN level, mmole/AGU in starch	PAN, in product, parts/100 parts starch in product	PAN extracted in DMF, %[b]	Starch extracted in water, %[c]
1	Unmodified	50	10	4.3	113	48
2	Unmodified	50	25	23.1	107	44
3	Oxidized	50	10	9.6	91	101
4	Oxidized	50	25	14.3	82	99
5	Oxidized	100	25	129.	85	103

[a] Run with 100 parts dry basis of starch in 500 parts of water for 3.0 hr. at 50°C., except for run 5 which went 18 hr.

[b] About 3.0 g. of original sample at 25% moisture content tumbled with 200 ml. of DMF at 30°C. for 24 hr.

[c] About 1.0 g. of original sample extracted twice by refluxing 3 hr. in 100 ml. of distilled water.

TABLE V
Effect of Initiator Level[a]

Run no.	Starch	H_2O_2/Fe^{II}/ascorbic acid mmole[b]	PAN in product, parts/100 parts starch	Grafting efficiency[c]		$\bar{M}_n \times 10^{-3}$ of PAN[d]	AGU per chain[e]
				PAN	Starch		
6	Unmodified	10/–/2	40.6	88	91	49	850
7	"	10/1/–	43.9	94	95	61	910
8	"	100/1/10	52.4	81	70	35	500
9	Oxidized	10/–/2	54.6	96	79	33	390
10	"	10/1/–	54.3	92	32	89	1090
11	"	100/1/10	46.3	89	30	17	250

[a] All runs made with 50 parts of acrylonitrile/100 of starch.

[b] H_2O_2/ferrous ammonium sulfate/ascorbic acid per mole of contained anhydroglucose unit in the starch.

[c] Ratio of unextractable to total contained PAN or starch, respectively, ×100. For PAN, determined by a single extraction for 24 hr. at 30°C. in DMF at 25% moisture content of sample. For starch, determined by two successive 3-hr. extractions in refluxing water.

[d] Calculated from intrinsic viscosity at 25°C. in DMF, by using the equation[9] $[\eta] = 3.92 \times 10^{-4}\bar{M}_n^{0.75}$.

[e] Anhydroglucose units of total starch per grafted side chain of PAN.

TABLE VI
Effect of Monomer Level[a]

Run no.	Starch	Monomer, parts/100 parts starch charged	PAN in product, parts/100 parts starch	Grafting efficiency, %[b] PAN	Grafting efficiency, %[b] Starch	$\overline{M}_n \times 10^{-3}$ of PAN[c]	AGU per chain[d]
12	Unmodified	100	99.8	83	81	73	550
8	"	50	52.4	81	70	35	910
13	"	20	19.8	82	79	10	370
14	"	10	8.7	81	73	4	360
15	Oxidized	100	119.7	81	32	64	410
11	"	50	46.3	89	30	17	250
16	"	20	20.1	89	20	10	350
17	"	10	9.9	87	12	4	290

[a] All runs made at 100/1/10 mmole of H_2O_2/ferrous ammonium sulfate/ascorbic acid per mole of anhydroglucose unit.

[b] Ratio of unextractable to total contained PAN or starch, respectively, × 100. For PAN, determined by a single extraction at 30°C. in DMF at 25% moisture content sample, for starch, determined by two successive 3-hr. extractions in refluxing water.

[c] Calculated from intrinsic viscosity at 25°C. in DMF by using the equation[9] $[\eta] = 3.92 \times 10^{-4} \overline{M}_n^{0.75}$

[d] Anhydroglucose units of total starch per grafted side chain of PAN.

lower temperature than unmodified corn starch. In any event, starch and PAN are separable from each other in relatively high yield when initiation is with AIBN. This contrasts sharply with separability in products initiated with peroxide. PMMA/starch systems show similar behavior.[1,3]

Efficiency and Frequency of Grafting

Pertinent data from various runs are presented in Tables V and VI. Table V shows that as the amount of peroxide is increased, grafting efficiency of the PAN tends to decrease, molecular weight of the grafted chains decreases, and grafted chains are attached more frequently. Grafting efficiency of starch also decreases at higher peroxide level; this could be due to greater degradation of the starch at the higher level of peroxide.

A comparison of oxidized and unmodified starch at comparable initiator levels suggests that the oxidized starch is a little more susceptible to grafting. This is indicated by the higher PAN grafting efficiencies and the more frequent attachment of side chains with oxidized starch. Apparent differences in grafting efficiency of the starch may simply be due to the greater difficulty, noted above, of extracting unmodified starch with boiling water.

Table VI shows the effect of changing monomer level. As monomer level decreases, grafting efficiency of the starch drops sharply and molecular weight of the grafted PAN chains falls off. Efficiency and frequency of grafting PAN show little trend. As noted previously for PMMA,[2] the

TABLE VII
Graft Compositions, Oxidized Starch

Run no.	$H_2O_2/Fe^{II}/$ ascorbic acid, mmole	Monomer, parts/100 parts starch	AGU per chain		Parts/100 parts of product				$\overline{DP}_n$ of grafted PAN
					Homo-		Grafted		
			Total starch	Grafted starch	PAN	Starch	PAN	Starch	
15	100/1/10	100	410	130	10.4	30.9	44.1	14.6	1130
11	"	50	250	75	3.5	47.9	28.1	20.5	320
16	"	20	350	70	1.8	66.6	15.0	16.6	190
17	"	10	290	35	1.2	80.1	7.8	10.9	75
10	10/1/–	50	1090	350	2.8	44.1	32.4	20.7	1680
9	10/–/2	50	390	310	1.4	13.6	33.9	51.1	620

TABLE VIII
Comparison of Acrylonitrile with Methyl Methacrylate[a]

Starch	Monomer, parts/100 parts starch	$H_2O_2/Fe^{II}/$ ascorbic acid, mmole	Grafting efficiency, %		$\overline{DP}_n$ of grafted polymer		AGU per chain	
			AN	MMA	AN	MMA	AN	MMA
Unmodified	50	10/1/–	94	88	1150	2900	910	3700
Oxidized	"	"	92	90	1680	2800	1090	3500
Unmodified	50	100/1/10	81	72	660	1200	500	2000
Oxidized	"	"	89	75	320	240	250	350
Unmodified	100	100/1/10	83	69	1380	1800	550	1500
Oxidized	"	"	81	71	1200	450	410	330

[a] Data for MMA taken from reference 2.

predominant effect of increasing monomer level is longer chains rather than more chains.

Table VII shows calculated compositions of products derived from oxidized starch.

As an example of the significance of the figures, the product from run 15 can be described as follows. Each 100 parts of product contain 10.4 parts of PAN homopolymer, 30.9 parts of ungrafted starch, and 58.7 parts of grafted copolymer. The graft itself contains 44.1 parts of PAN and 14.6 parts of starch. In the graft, the PAN side chains have $\overline{DP}_n$ of 1130, and are attached at the rate of one chain for each 130 glucose units. The $\overline{DP}_n$ of the starch, hence the average number of PAN chains per starch chain, is not known.

From previous work with PAN–starch grafts, only Fanta et al.[9] report chain length and frequency of attachment of PAN. Typical values obtained from the main fractions of graft were one PAN chain, of average MW of 530,000, per 2600 anhydroglucose units. The lower values obtained in the present work may be due to the relatively high concentrations of reactants within starch granules, the locus where reaction appears to occur. Fanta et al. carried out the reactions in solutions of starch at 4% solids.

Comparison of Acrylonitrile with Methyl Methacrylate

Tables VIII and IX compare results obtained with the two monomers. Unmodified starch appears more susceptible to grafting by PAN than by MMA, as indicated by the higher grafting efficiencies and more frequent attachment of shorter chains with PAN. This probably reflects easier penetration of the starch granule by the highly polar AN than the much less polar MMA. This difference is also reflected in the appearance of the polymer particles remaining after removal of the starch. Some of the

TABLE IX
Comparison of Acrylonitrile with Methyl Methacrylate; at Various Monomer Levels[a,b]

Monomer, parts/100 parts starch	Grafting efficiency, %		$\overline{DP}_n$ of grafted polymer		AGU per chain	
	AN	MMA	AN	MMA	AN	MMA
100	81	71	1130	450	410	330
50	89	75	320	240	250	350
20	89	93	190	180	350	530
10	87	98	75	580	290	3500

[a] Oxidized starch; H_2O_2/ferrous ammonium sulfate/ascorbic acid at 100/1/10 mmole/mole of anhydroglucose unit.

[b] Data for MMA taken from Brockway.[2]

PMMA particles (Fig. 4) show heavy rings or crusts of polymer at the periphery. No such rings are evident in the PAN particles (Fig. 3).

With oxidized starch there is much less difference between the behaviors of the two monomers, at least at the 100 mmole level of peroxide. The chief difference is that as monomer level is lowered to 20 and 10 parts, frequency of chain attachment of PAN remains about constant and the chains become progressively shorter. PMMA, on the other hand, becomes much less frequently attached at monomer level of 10. This difference may also reflect a more ready penetration of the granule by AN than by MMA.

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Résumé

L'acrylonitrile se greffe facilement à des grains d'amidon de mais en suspension aqueuse lorsque la réaction est initiée par du peroxyde d'hydrogène en présence d'un activateur. Une première évidence pour le greffage est trouvée dans la facilité de séparer le PAN de l'amidon avec en rendement élevé lorsque l'initiateur est l'asobisisobutyronitrile plutôt que le peroxyde. Les efficacités de greffage sont déterminées par extraction avec des solvants appropriés: le diméthylformamide pour l'homopolyacrylonitrile et l'eau bouillante pour l'amidon non greffé. Les efficacités de greffage du polyacrylonitrile se situent entre 78 et 95%, les valeurs de $\overline{M}_n$ pour le PAN greffé sont de 4.000 à 90.000, et la fréquence d'attache de chaînes latérales se situe de 300 à 1100 unités glucosiques par chaîne. En augmentant la concentration en monomères à concentation en initiateur constante on obtient des chaînes latérales plutôt longues que fréquentes. L'acrylonitrile se comporte de facon semblable à celle qui a été trouvée précédemment pour le MMA, mais son greffage plus efficient à des intervalles plus fréquents et la distribution beaucoup plus uniforme des chaînes polymériques dans le granule d'amidon, suggèremt que l'acrylonitrile pénètre plus facilement au sein du granule d'amidon que le MMA.

Zusammenfassung

Acrylnitril wird bei Start mit Wasserstoffperoxyd plus Aktivator leicht auf gekörnte Maisstärke in wässriger Aufschlämmung aufgepfropft. Der Hauptbeweis für die Aufpfropfung liegt in der leichten Abtrennung des PAN von Stärke in hoher Ausbeute bei Start mit Azobisisobutyronitril an Stelle von Peroxyd. Pfropfausbeuten wurden durch Extraktion mit geeigneten Lösungsmitteln bestimmt: Dimethylformamid für Homo-PAN und seidendes Wasser für ungepfropfte Stärke. Pfropfausbeuten an PAN liegen im Bereich von 78 bis 95%, die $\overline{M}_n$ — Werte für das aufgepfropfte PAN betragen 4000 bis 90.000 und die Häufigkeit der Seitenketten liegt bei 300 bis 1100 Glukosereste pro Kette. Eine Erhöhung des Monomeranteils bei festgehaltener Starterkonzentration führt zu

einer Erhöhung der Länge und nicht der Häufigkeit der Seitenketten. AN verhält sich ähnlich dem früher untersuchten MMA, jedoch spricht die etwas wirksamere Aufpfropfung in häufigeren Intervallen und die einheitlichere Verteilung des Polymeren im Stärkekorn dafür, dass AN leichter in das Stärkekorn eindringt als MMA.

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Diffusion in Ethylene–Propylene Rubber

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Synopsis

A study of sorption in a copolymer of ethylene and propylene is presented. Long-time sorption and desorption measurements provided the actual diffusion coefficient in the limit of zero concentration gradient. An analysis of the diffusion–sorption data reinforced the Frisch hypothesis about diffusion in a polymer matrix. The better solvent deforms the microstructure, allowing a more marked dependence of the diffusivity upon concentration.

Introduction

Recently Frensdorff[1,2] presented a study of equilibrium sorption and diffusion in a copolymer of ethylene and propylene. The sorption data were obtained by the gravimetric procedure of Prager and Long.[3] The data were analyzed to obtain diffusion coefficients by two different methods, one employing the sorption data taken at short times and the other using the data taken at long times. The purpose of this paper is to reinforce the arguments of Frensdorff for the use of the latter method and to present additional data for sorption and diffusion in ethylene–propylene rubber.

Sorption into a finite slab has been used to measure diffusion coefficients in polymeric systems since Prager and Long.[3] By measuring weight pickup or loss in a polymer film exposed to a diluent vapor and using the mathematical description of the process, the diffusion coefficients can be obtained. The differential equation and the boundary conditions representing this sorption–desorption problem can be written†

$$\frac{\partial w}{\partial t} = \frac{\partial}{\partial x}\left(D\,\frac{\partial w}{\partial x}\right) \tag{1}$$

for $t < 0$ and $0 \leqslant x \leqslant l$: $w = w_0$; for $t \geqslant 0$ at $x = 0$ and $x = l$: $w = w_\infty$. Here w is the mass fraction of solvent, x is position in the slab, l is thickness of the slab, and D is the diffusion coefficient.

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† In this formulation, the diffusion coefficient is assumed to be constant, the mass-average velocity of the system is assumed to be zero. Consistent with this the system density is constant.

The fractional amount of diffusing material which is in the slab at any time is given by

$$M = \frac{1}{(w_0 - w_\infty)l} \int_0 w(x)dx \tag{2}$$

It can be readily shown from the solutions given by Crank[4] that

$$\lim_{t \to 0} (dM/dt^{1/2}) = -4(D/\pi l^2)^{1/2} \tag{3}$$

and

$$\lim_{t \to \infty} d\,(\ln M)/dt = -(\pi^2/l^2)D \tag{4}$$

Both of these equations present a method for experimental determination of the diffusion coefficient. The solutions, eqs. (3) and (4), are valid only for the case of a constant diffusivity. The use of these expressions in other cases must be justified.

If we consider a diffusing system in which the mass average velocity is zero, but the diffusion coefficient is not constant, the diffusion equation [eq. (1)] must be so modified that

$$D = D(w_0, \partial w/\partial x, x, t) \tag{5}$$

When the diffusion coefficient is only a function of concentration, eq. (1) has some interesting and useful properties. Ficken[5] has demonstrated uniqueness for any solution of this problem. Formal solutions of the problem for particular functions of concentration have been obtained by Stokes,[6] Fujita,[7] Boyer,[8] and Pattle.[9] These, however, are restricted to semi-infinite media. No analytical solutions have been presented for a bounded region. The only recourse, then, is a numerical solution. If we integrate eq. (1) numerically, we find that, at least for linear and exponential functions of concentration, the sorption curves conform to the behavior predicted by eqs. (3) and (4).

The results of the numerical integration of eq. (1) indicate that at short times when the concentration at the center of the slab had not changed from its value at $t = 0$, the amount of material in the slab, M, was a linear function of $t^{1/2}$. Fujita,[10] using the method of moments, also obtained this linear relation.

Crank, in his monograph,[4] reviews all the techniques to be used in conjunction with this fact. Extensive use of eq. (3) had been made in the study of diffusion in polymeric systems where the diffusion coefficient is strongly concentration dependent. The values of the diffusion coefficient obtained by using eq. (3) are not simple functions of the actual diffusivity. In fact, changing the boundary conditions in problem (1) from desorption to sorption conditions will give us a different value for the measured diffusivity.

In discussing the values provided by the analysis of the sorption–desorption experiments by using eq. (3), we shall designate these values as integral

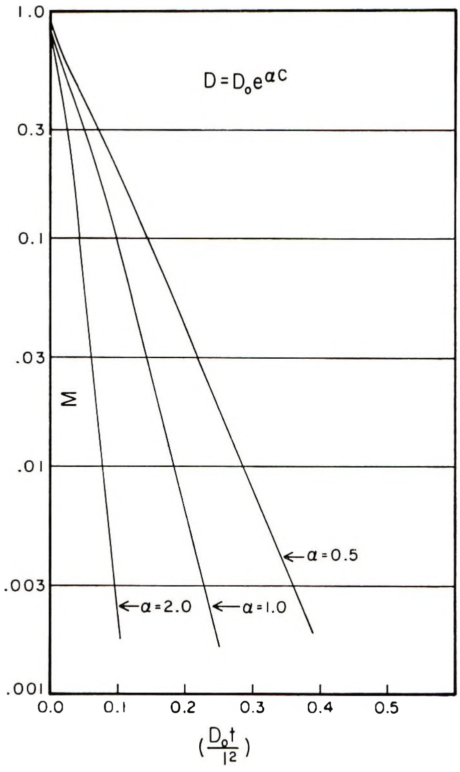

Fig. 1. Calculated curves for sorption into a finite slab for an exponential dependence of diffusivity upon concentration (long-time behavior).

diffusion coefficients. The value obtained for a sorption experiment is called an integral sorption diffusion coefficient $\bar{D}_s$; an integral desorption diffusion coefficient $\bar{D}_d$ is obtained from a desorption experiment. Equation (5) can be rewritten in the form:

$$\bar{D}_s \text{ or } \bar{D}_d = \lim_{t \to 0} \left[\frac{\pi l^2}{16} \left(\frac{dM}{dt^{1/2}} \right)^2 \right] \tag{6}$$

The only method we have available to measure the diffusion coefficient when it is a function of concentration is eq. (4). This property of the linear diffusion equation is equally a property of the nonlinear equation, since, at long times, the solution of the nonlinear equation approaches that of the linear equation. A physical argument can be made to justify this. At long times, the slab is nearly uniform in concentration, the gradients are small, the diffusion coefficient, it follows, is effectively constant over the thickness of the slab. The nonlinear equation becomes linear. Additional justification for the use eq. (4) for evaluation of the diffusivities in systems with variable diffusion coefficients is provided by Figure 1, which shows the sorption and desorption curves for two different functional dependencies of the diffusivity. The value of the slope of these curves is $-\pi^2/l^2$ times the

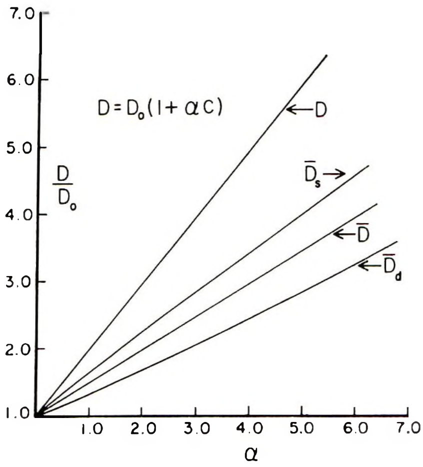

Fig. 2. Comparison of the various diffusivities for a linear dependence upon concentration.

value of the diffusion coefficient at the terminal concentration. The companion relation to eq. (6) is then

$$D(w_\infty) = \lim_{t\to\infty}\left[-\frac{l^2}{\pi^2}\frac{d}{dt}\ln M\right] \tag{7}$$

Zhurkov and Ryskin[11] and Frensdorff[1,2] have used the method, although they did not provide adequate justification for its use.

For concentration-dependent diffusivities, we can define an average diffusion coefficient over the range of concentration in an experiment by

$$\bar{D} = \frac{1}{w_c - w_\infty}\int_{w_\infty}^{w_0} D(w')dw' \tag{8}$$

The diffusion coefficients obtained by using eqs. (4), (6), and (7) can be ordered

$$D \geqslant \bar{D}_s \geqslant \bar{D} \geqslant \bar{D}_d \tag{9}$$

The calculated results for these coefficients are displayed in Figure 2, where we can see that all the curves in the figure have the same intercept. This suggests all the measured coefficients, D, $\bar{D}_d$, $\bar{D}_s$, should yield the same values when extrapolated to zero concentration.

Diffusion in Polymers

One characteristic of diffusion of penetrants in polymers is the marked concentration dependence of the diffusion coefficient. This is true primarily of good solvents. Poor solvents and fixed gases yield essentially constant diffusivities over a wide range of concentrations. Frisch[12] hypothesizes that the concentration dependence depends on the molecular size of the molecule and the distribution of micropores of molecular dimension in the polymer matrix. Fixed gases, such as O_2 and N_2, are of sufficiently small molecular dimension that they pass through the micropores without affecting the structure. Nonsolvents, since they do not interact with the polymer, do not change the structure and the diffusion coefficient remains independent of the concentration. Solvents do interact, deform the distribution of micropores, and consequently affect the diffusion coefficient. This can be seen by comparing the diffusion of water and ethyl acetate in poly(methyl acrylate).[13] The diffusivity of water, the nonsolvent, in the polymer is independent of concentration. The diffusivity of ethyl acetate, a good solvent, in the polymer changes 10-fold over the same concentration range.

The functional dependence of the diffusivity upon concentration is generally accepted to be exponential for reasonably low concentrations and linear at much lower concentrations. However, data obtained for diffusion in polymer solutions indicate that the functional dependence is not so well characterized over the whole concentration range and indeed does pass through a maximum[14] for some systems.

Experimental Verification

The sorption–desorption experiment described above restricts any material we study to a definite class which would provide an isotropic medium and constant surface conditions. To conform to these restrictions, the polymer must be above its glass transition temperature and it should be noncrystalline. Elastomers satisfy these requirements near room temperature. Only a few such materials have been subjected to extensive diffusion measurements. Frensdorff[1,2] added another to the set, ethylene–propylene rubber. In this investigation, we extend the study of the diffusional behavior in ethylene–propylene rubber to include two halocarbons, dichloromethane (methylene chloride) and trichloromethane (chloroform), and establish the concentration dependence conclusively.

Experimental

The gravimetric diffusion apparatus was similar in design to that of Prager and Long[3] and Frensdorff.[1,2] Sorption or desorption of vapor from the polymer samples, suspended from a quartz spiral, resulted in a deflection of the spring. A micrometer-slide cathetometer was used to measure this deflection as a function of time.

Hooke's law constants for the four springs used in this study ranged from 1.00269 ± 0.00618 to 1.00854 ± 0.00455 mm./mg. Since the cathetometer could be read directly to 1 μ, the precision of the balance was within 1 μg.

The entire apparatus, including the vapor manifold and balance case, was enclosed in an air bath. The temperature of the equipment was maintained at a constant value to within ±0.2°F.

The activity of the vapor was obtained from the pressure measurements. The pressure in the manifold and balance case were measured using a precision manometer and a micrometric manometer.

A 5-lb. polymer sample from a single polymerization batch was obtained from E. I. du Pont de Nemours, Inc.; it was reported to contain 41% propylene by weight.[15] The solvents used, dichloromethane (DCM) and trichloromethane (TCM), were analytical grade reagents, degassed before use.

The films were cast from a 5 wt.-% solution of the polymer in tetrachloroethylene. Two casting techniques were used. One method was to float a 5-in. diameter glass ring on clean mercury and to pour the polymer solution into the ring. The container was partially covered to minimize dust particles settling on the film while drying, which took approximately 36 hr. Samples had to be cut from the center of the film circle since adhesion to the glass strained the film, resulting in a non-uniform cross-section. As Frensdorff[1,2] reported, after exposure to a solvent such a film shrinks, perhaps due to relaxation of internal stresses established during casting. After solvent exposure and subsequent drying, the film was pressed between two polished steel plates separated by shims to insure uniform spacing. The first three films used were made in this fashion.

The films used in the later portion of the investigation cast on a flat, highly polished, steel plate, without restraining the fluid. The films were removed from the plate by soaking in acetone (a poor solvent). These samples were found to be more uniform than the previous ones (at least to the naked eye) and did not shrink upon exposure to solvent.

The film thickness was obtained by two different methods. The length and width of the films were obtained by averaging values measured at different points on the film. The thickness was calculated from the area and density of the sample. The thickness was also estimated by actual measurement with a vernier caliper. The two measurements were in reasonable agreement. The area measurements were believed to be more precise and were used in the calculations.

Procedural Detail

A run was begun in the following fashion. The manifold was evacuated to a pressure less than 20 μ Hg and the solvent in vapor source flask was allowed to boil for 15–30 sec. to degas the diffusate source. The vacuum source was then sealed and the manifold pressure was allowed to increase. Once the desired pressure level was reached, the vapor source was sealed. After the recording of the manifold pressure, the initial cathetometer setting, and the temperatures, the balance case was opened to the manifold, the timer started, and the cathetometer readings begun. Initially, the readings were at approximately 30-sec. intervals; as the sorption process approached equilibrium, the reading intervals were increased to 1 min. The experiment was stopped once no change (maximum 2 μ) was noted in the deflection of the spring. The temperature dependence of the equilibrium sorption and temperature fluctuations in the system caused, in some instances, an early abortion of a run and the equilibrium sorption value in these cases has to be estimated.

Preparation for a desorption run is as follows: The balance case is sealed, the manifold is opened to the vacuum source. The system is evacuated to less than 20 μ Hg. A liquid N_2 vapor trap preceded the vacuum pump. The balance case was then reopened, the timer started, and the run continued as in the sorption run described above.

Comments on the Data

A computer program was used to produce curves and punched card output of $(\text{time})^{1/2}$ versus residual diffusate and log of residual diffusate versus time. Visual examination of the curves indicated which portions of the curves were linear. The least-square error fit of straight lines to the data were made. The slope of these curves were used to calculate the appropriate diffusivities as specified by equations (3) and (4). Finally, a least-square error fit for the curves of the diffusivity–mass fraction data made to establish the value of D_0, the value of each diffusion coefficient at zero mass fraction.

The plot of log M versus time for one typical system run (MCE-9) in Figure 3 has the shape characteristic of the calculated sorption curve for an exponential dependence of the diffusivity upon weight fraction (Fig. 1).

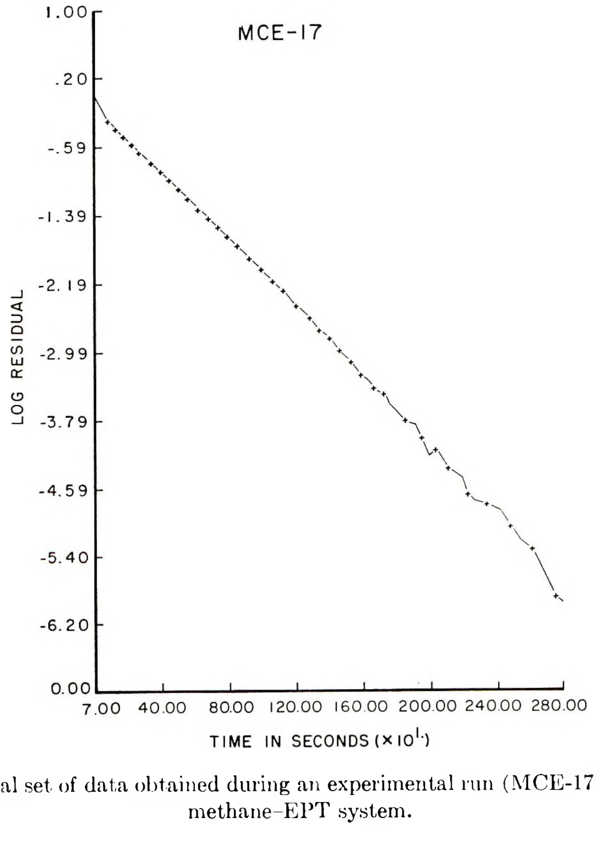

Fig. 3. Typical set of data obtained during an experimental run (MCE-17) for dichloromethane–EPT system.

There is an inflection point in the curve, which is not necessarily a property of eq. (1). The diffusion equation [eq. (1)] can be written with the same boundary condition. The function designating the change of diffusivity with concentration must be modified, however, in accordance with the redefinition of the problem.

The experimental data representing $(\text{time})^{1/2}$ versus M (the residual diffusate) do not always provide a linear relation at short times. Such behavior might be attributed to either of two experimental conditions.

When the stopcock was opened to allow vapor into or out of the weighing chamber, if particular care was not exercised to minimize the flow rate of the vapor, the spring balance oscillated, and the readings at short times had to be estimated. Another reasonable explanation is that the surface concentration did not reach its equilibrium value instantaneously and that this behavior is a reflection of this fact. Most runs during which no oscillation of the balance occurred were linear at extremely short times, indicating that the former explanation is the justifiable one.

Measurement of Diffusion Coefficients

It was feared initially that the data obtained at long times would not be as precise as the short time measurements. It can be readily seen from Tables I and II that the error in the slopes and therefore in the diffusivities were of the same order of magnitude for both methods. If any distinction exists between both techniques, the diffusion coefficient measured at long times had somewhat better precision. The average precision error in the trichloromethane (TCM) runs for D, the diffusivities, was 1.3%; that for $\bar{D}_d$ and $\bar{D}_s$, the integral coefficients, was 1.7%.

Accuracy is another problem. The scatter in the diffusion coefficient mass fraction curves was quite marked, especially in the DCM runs. This can be attributed to a number of factors.

Temperature control during the DCM runs was a problem. Room temperature on some days was higher than the desired operating temperature. Cooling of the air had to be accomplished by evaporating Dry Ice in the constant temperature box.

Although the buffer volume was large, (approximately 6 liters), the pressure changed in the course of a run approximately 0.5–1.0 mm. Hg. At moderate pressures, this change could affect the surface equilibrium concentration.

The scatter could not be definitely attributed to any systematic change of variable in the system and should be treated as random error.

A least-square error fit of the data in Figures 4 and 5 was made to straight lines and exponential curves. The results are presented in Table I and II along with the F-statistic, which provides a measure of the goodness of fit. The larger the value of the F-statistic, the more reliable the fit of the data. The curves plotted in Figures 4 and 5 are those obtained with the greater F-statistic.

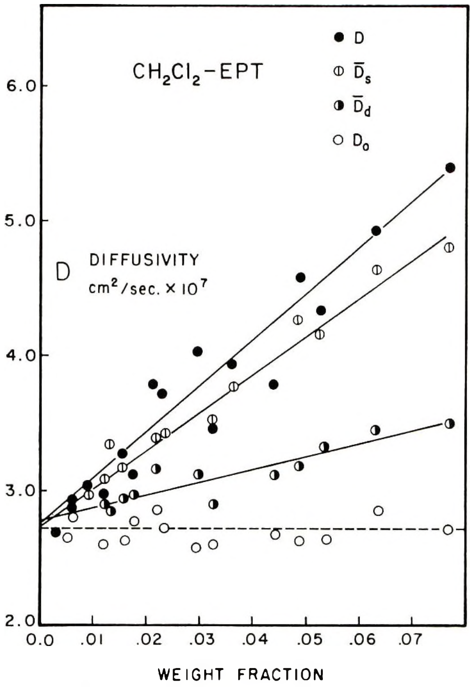

Fig. 4. Correlation of diffusivity–weight fraction data for the dichloromethane–EPT system at 30°C.

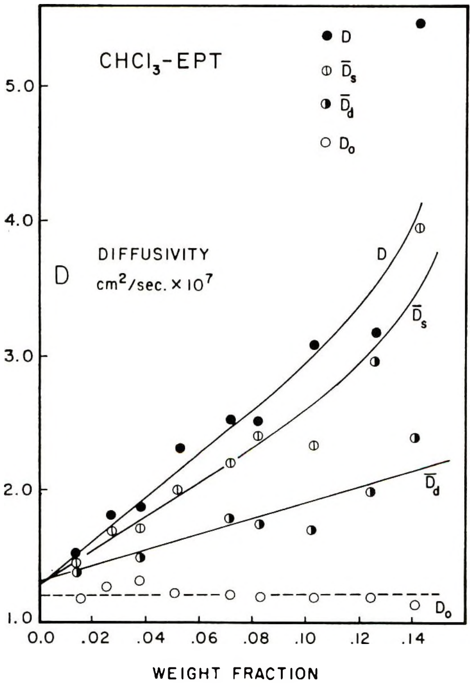

Fig. 5. Correlation of diffusivity–weight fraction data for the trichloromethane–EPT system at 30°C.

Concentration Dependence of the Diffusion Coefficients

It is more than apparent that the diffusivities are concentration-dependent. Prager and long[3] reported an exponential dependency* for diffusion of n-paraffins in polyisobutylene. A comparison of Figures 2, 4, and 5 tends to confirm the exponential dependence for the diffusion coefficient in these experiments. The value of the coefficients α are in the same range of values reported by Prager and Long[3] and for all the solvents used in the Frensdorff study[1,2] (see Tables I and II). The values of α (in the weight fraction–diffusivity function) are somewhat greater for the better solvent, chloroform. This is not unexpected. Frisch's theory of concentration-dependent diffusivities infers that the better solvent would deform the microstructure of the polymer matrix more readily and consequently have a more pronounced effect on the rate of diffusion.

TABLE I
Curve Fitting for Dichloromethane (DCM) Runs

Function	Diffusivity	Intercept of the curve at $C_2 = 0$, $D_0 \times 10^7$, cm.^{2}/sec.	α	F-Statistic
Exponential[a]	$D(C)$	2.898	8.191	6.772
Linear[b]	$D(C)$	2.808	6.119	7.483
Exponential	$\bar{D}_s$	2.788	7.863	11.353
Linear	$\bar{D}_s$	2.713	10.514	14.981
Exponential	$\bar{D}_d$	2.816	2.599	3.112
Linear	$\bar{D}_d$	2.805	2.904	3.503

[a] $D = D_0e^{\alpha c}$.
[b] $D = D_0(1 + \alpha c)$.

TABLE II
Curve Fitting for Trichloromethane (TCM) Runs

Function	Diffusivity	Intercept of the curve at $C_2 = 0$, $D_0 \times 10^7$, cm.^{2}/sec.	α	F-Statistic
Exponential	$D(C)$	1.237	9.293	22.150
Linear	$D(C)$	1.155	18.730	18.175
Exponential	$\bar{D}_s$	1.270	7.076	37.544
Linear	$\bar{D}_s$	1.092	15.834	13.575
Exponential	$\bar{D}_d$	1.362	3.258	4.457
Linear	$\bar{D}_d$	1.317	4.497	3.874

Solubility Data

The Flory-Huggins theory[16] of concentrated polymer solutions provides us with a relation between the activity a_1 of a solvent and its volume frac-

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* Actually, no real difference exists between an exponential and a linear function, since for small change in concentration $e^{\alpha w} \cong 1 + \alpha w$.

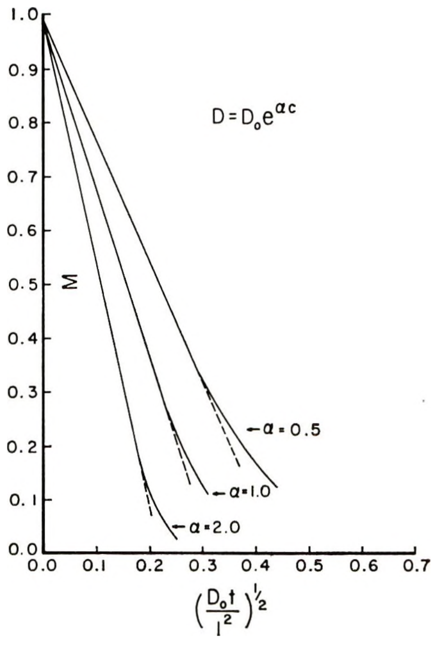

Fig. 6. Calculated curves for sorption into a finite slab for an exponential dependence of diffusivity upon concentration (short-time behavior).

tion V_1. If we restrict to low values of the volume fraction V_1 for systems where the interaction parameter χ_1 is a function of the volume fraction, the relation is

$$\ln (a_1/v_1) = (1 + \chi_1) - (1 + 2\chi_1 - \beta)v_1 \tag{10}$$

where a_1 is the activity of the solvent, $a_1 \cong p^0/\pi$ (p^0 being the vapor pressure and π the total pressure), v_1 is the volume fraction of solvent, $\beta = (\partial\chi_1/\partial v_1)_{v_1 = 0}$, and χ is the interation parameter between the solvent and the solute. Figure 7 indicates the relation between ln (a_1/v_1) and v_1 is linear. Table III presents the values of χ_1 and β observed in this study and in Frensdorff's work.[1, 2]

Conclusions

The solvents, trichloromethane and dichloromethane, are adjacent compounds in the homologous series of chloromethanes. The solubility data (Fig. 7) indicate that trichloromethane is a far better solvent. The diffusion data reinforce the Frisch hypothesis about the nature of diffusion in a polymer matrix. The larger molecule, trichloromethane, has a diffusion coefficient in the limit of zero solvent concentration 40% lower than dichloromethane, and the concentration dependence is more pronounced. The better solvent does indeed deform the microstructure,

TABLE III
Solubility Data

	χ_1			β			
System	10°C.[a]	30°C.[b]	40°C.[a]	10°C.[a]	20°C.[a]	30°C.[b]	40°C.[a]
EPT–CH_2Cl_2	1.30	0.883	1.12	−1.20	−1.14	1.234	1.86
EPT–$ChCl_3$	—	0.207	—	—	—	0.396	—

[a] Data reported by Frensdorff.[1,2]

[b] Data reported in this study.

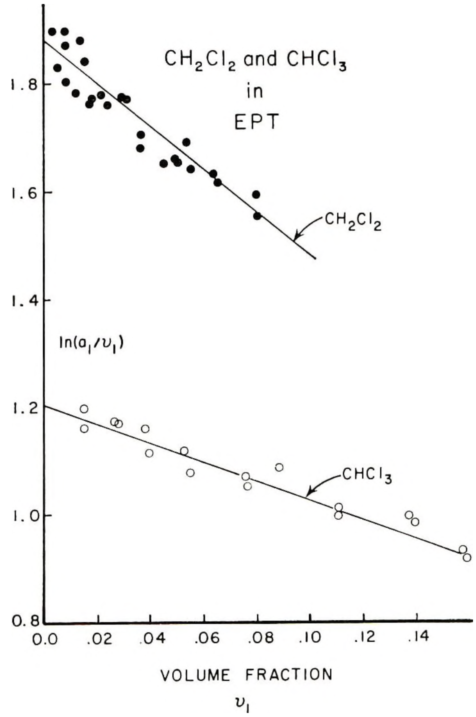

Fig. 7. Correlation of equilibrium sorption data for both trichloromethane and dichloromethane in EPT at 30°C.

allowing a more marked dependence of the diffusion coefficient upon concentration.

The technique of measuring diffusivities at long times suggested by the work of Frensdorff[1,2] has been demonstrated to be a valid approach yielding the actual diffusion coefficients.

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Résumé

Une étude de la sorption d'éthylène et de propylène dans un copolymère est présentée. Des mesures de sorption à longue durée et de désorption fournissent un coefficient de diffusion réel dans les limites de gradient de concentration nul. Une analyse des données de diffusion-sorption confirme l'hypothèse de Frisch concernant la diffusion dans une matrice de polymère. Meilleur est le solvant, plus la microstructure est déformée, ce qui permet une dépendance plus marquée de la diffusibilité en fonction de la concentration.

Zusammenfassung

Es wird über eine Untersuchung der Sorption in einem Äthylen-Propylencopolymeren berichtet. Langzeit-Sorptions-und Desorptionsmessungen lieferten den aktuellen Diffusionskoeffizienten für die Grenze des Konzentrationsgradienten gleich Null. Ein Analyse der Diffusions-Sorptionsdaten bekräftigte neuerlich die Hypothese von Frisch über die Diffusion in einer Polymermatrix. Das bessere Lösungsmittel deformiert die Mikrostruktur und führt damit zu einer stärker ausgeprägten Abhängigkeit der Diffusionsfähigkeit von der Konzentration.

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Preparation and Characterization of Some Cellulose Graft Copolymers. Part IV. Some Properties of Isolated Cellulose Acetate–Styrene Graft Copolymers*

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Synopsis

A series of purified graft copolymers of cellulose acetate and polystyrene, which were prepared and characterized during the course of an earlier investigation, have been used for some initial property studies. Grafts with high molecular weight backbones and low molecular weight side chains and vice versa, and with both side chains and backbones of high and low molecular weights, were prepared. The graft polymers were found to be insoluble in most solvents but soluble in dimethylformamide and pyridine and in mixtures of solvents for each component. Films cast from mixtures of the grafts and homopolymers showed that the grafts were compatible with the homopolymer of the component with a higher molecular weight. A graft copolymer with high molecular weight backbone and side chains was found to be compatible with both homopolymers separately and with a mixture of both across a wide range of compositions. A blend of the high and low molecular weight grafts was also found to be highly compatible with both homopolymers. The permeability, diffusion, and sorption of gases and water vapor in the grafts and in the corresponding homopolymers was also studied. In the case of water vapor, the sorption in cellulose acetate was much higher than in polystyrene whereas the diffusion was much lower. It was found that the graft polymers showed both diffusion and solution behavior closer to that of cellulose acetate, whereas the permeability constants were more intermediate between those of the two homopolymers. The gas permeability and diffusion constants were found to be intermediate between the values obtained with the two homopolymers.

INTRODUCTION

There have been many interesting and valuable studies of the properties of grafted fibers and films. In general, the accessible side chain homopolymer has been removed by extracting to constant weight with a suitable solvent. In very rare cases the accessible backbone homopolymer has also been extracted. It is known, however,[1,2] that these extraction treatments usually remove only part of both of the homopolymers. Furthermore, the usual techniques of heterogeneous grafting are known to lead to the formation of graft copolymers with few disproportionately long side chains having very wide molecular weight distributions.[3] During the

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* Presented in part at the American Chemical Society Meeting, Detroit, Michigan, April 7, 1965.

course of an extensive investigation into the radiation grafting of styrene to cellulose acetate it was found that a combination of extraction, solution, and precipitation procedures led to graft copolymers which were substantially free from both homopolymers.[1-4]

These methods could also be applied to graft copolymers which were prepared in solution. Here the molecular weight distribution of the side chains would be normal and the chain length could be controlled by changes in monomer concentration and the radiation dose rate. The molecular weight of the backbone, on the other hand, could be controlled by the choice of substrate polymer. A small correction needs to be made for the radiation degradation accompanying the grafting.[5] Four samples of graft copolymer with varying backbone and side chain molecular weights were prepared, purified, and characterized, as described in the experimental section. A number of properties of these materials, and also of the corresponding homopolymers, were determined and the results of this study will now be described.

EXPERIMENTAL

Two grades of cellulose acetate (CA) were used to provide the two different backbone lengths, one DS = 2.25 and a viscosity-average molecular weight of 120,000 was obtained from the Celanese Corporation, and the other DS = 1.84 and molecular weight 55,000 was obtained from the Eastman Kodak Corporation. The grafting experiments were carried out at 25°C. in 50:50 styrene–pyridine solution under vacuum after degassing. Two dose rates were used for the irradiation to provide the two different side chain lengths; these were 7,600 and 320,000 rad/hr. These produced grafts with side chains of viscosity-average molecular weights of 130,000 and 32,000, respectively. After grafting the solutions were poured into a large excess of benzene and the insoluble gel fraction allowed to separate overnight. This was freeze-dried and the residue extracted with a 70:30 acetone–water mixture. The highest molecular weight was checked for freedom from homopolymers by a density gradient ultracentrifugation technique.[4] A small amount of polystyrene was found still to be present. This was found to have been removed after a further extraction with benzene and all samples were extracted to constant weight with benzene.

TABLE I
Characteristics of Graft Copolymers

Sample	Combined polystyrene, %	$\bar{M}_v$ (CA)	$\bar{M}_v$ (PS)	Attached to acetate groups, %
P_3	45.0	54,000	119,000	49.3
P_4	44.1	111,000	119,000	49.0
P_5	28.0	54,000	32,000	44.4
P_6	18.2	111,000	32,000	47.4

The characteristics of the four graft copolymers are given in Table I. The molecular weights of the backbones were estimated from separate degradation experiments under simulated grafted conditions.[5] Those of the side chains were determined directly after removing the cellulose acetate by acid hydrolysis;[3,4] the percentage of grafted side chains attached to ester groups was determined by cold alkaline hydrolysis.[5]

The compatibility studies were conducted as described in the text. The gas and water vapor permeability and diffusivity measurements were made by using the high-vacuum technique described elsewhere.[6] Water vapor sorption measurements were made on a quartz helix microbalance under high vacuum conditions.

RESULTS AND DISCUSSION

Solubility and Viscosity

All the four graft polymers and the four corresponding homopolymers were soluble in dimethylformamide. A 1% solution of each in this solvent was titrated to precipitation point with water, methanol, and toluene. The results are shown in Table II. The grafting can be seen to have increased the tolerance towards nonsolvents for the least soluble component. The polystyrene component of the graft exerts by far the strongest influence. The tolerance of the grafts to water and methanol, for example, is much closer to that of the polystyrene, and their tolerance to toluene is enhanced tremendously over the cellulose acetate.

The intrinsic viscosity of the grafts and their homopolymers in mixed solvents and nonsolvents is a more subtle indicator of the solution behavior. Two grafts with the same length of polystyrene side chains but with different grades of cellulose acetate as backbones were examined in a number of solvent mixtures, and the results are summarized in Table III. As would be expected, adding nonsolvent for one component tended to reduce the viscosity of the graft towards that of the other component. It was interesting in the case of the acetone–toluene mixtures that although neither was a solvent for the graft copolymer, the mixtures were solvents across a wide range of compositions.

TABLE II
Solubility Limits of Grafts and Corresponding Homopolymers

	Nonsolvent to precipitate 10 ml. of 1% solution								
	H_2O			MeOH			Toluene		
	CA	PS	Graft	CA	PS	Graft	CA	PS	Graft
Graft P_3	6.36	0.28	0.30	29.5	3.6	4.0	21	∞	500
P_4	2.85	0.28	0.30	45.1	3.6	3.6	37	∞	450
P_5	6.36	0.40	0.50	29.5	5.1	7.4	21	∞	500
P_6	2.85	0.40	0.55	45.1	5.1	7.4	37	∞	500

TABLE III
Intrinsic Viscosities of Grafts and Corresponding Homopolymers in Mixed Solvents and Nonsolvents

Solvent 2	Solvent 2, %	PS	[η] CA	P_3 Graft
	Graft P_3, Solvent 1 = Dimethylformamide			
Toluene	0	0.36	0.96	0.76
"	20	0.37	0.95	0.78
"	40	0.38	0.93	0.78
"	60	0.39	0.90	0.78
"	80	0.39	Insol.	0.78
"	90	0.39	Insol.	0.52
"	100	0.39	Insol.	0.48
Water	2	0.25	0.96	0.68
"	20	Insol.	0.95	Insol.
	Graft P_4, Solvent 1 = Acetone			
Toluene	0	Insol.	2.80	Insol.
"	15	Insol.	2.76	1.66
"	30	Insol.	2.44	1.53
"	35	0.27	2.16	1.04
"	45	0.32	Insol.	1.01
"	60	0.37	Insol.	Insol.
"	100	0.39	Insol.	Insol.

Film Compatibility Studies

It is of considerable interest to investigate the tolerance of the isolated graft copolymers for both homopolymers in the solid state. In particular,

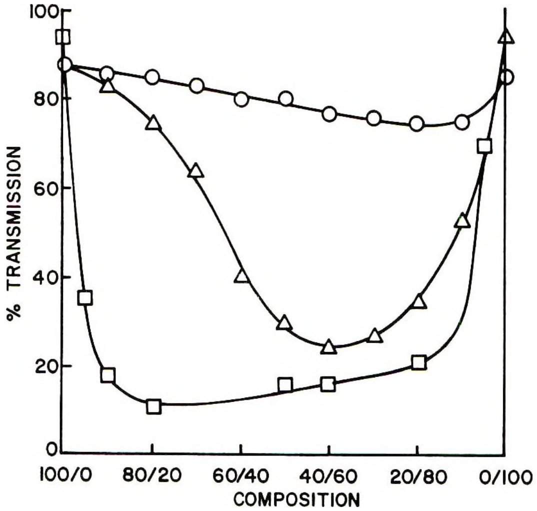

Fig. 1. Light transmission vs. composition of blends of cellulose acetate and polystyrene and the P_3 graft copolymer: (□) CA/PS; (△) P_3 graft/CA; (○) P_3 graft/PS.

a knowledge of the degree to which a graft copolymer can compatibilize mixtures of the two homopolymers is of value. Studies along these lines were carried out by using the three graft copolymers, P_3, P_4, and P_6. The films were prepared from mixed solutions in dimethylformamide and dried

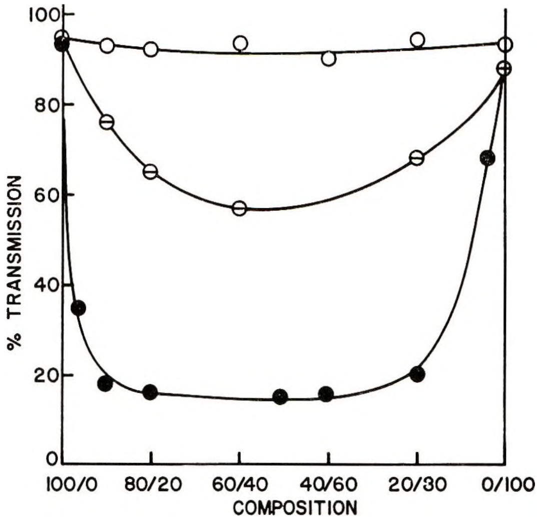

Fig. 2. Light transmission vs. composition of blends of cellulose acetate and polystyrene and the P_6 graft copolymer: (●) CA/PS; (⊖) P_6 graft/PS; (○) P_6 graft/CA.

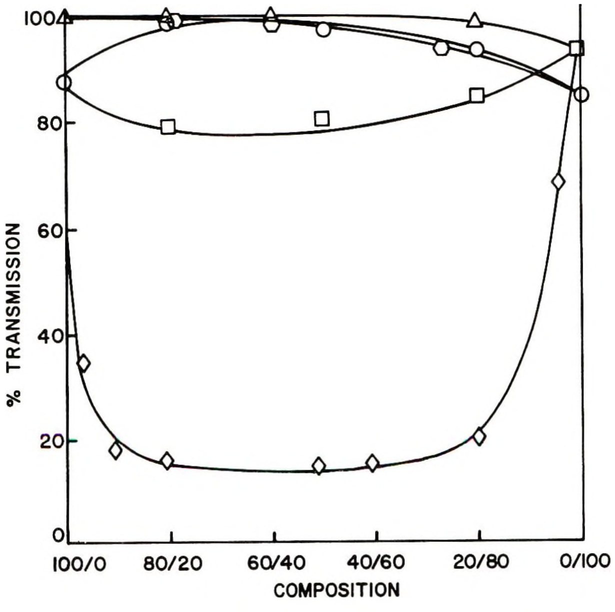

Fig. 3. Light transmission vs. composition of blends of cellulose acetate and polystyrene and the P_4 graft copolymer and a 50:50 blend of P_3 and P_6 graft copolymers: (◇) CA/PS; (□) blend of P_3 and P_6/CA; (○) blend of P_3 and P_6/PS; (△) P_4 graft/CA; (⬡) P_4 graft/PS.

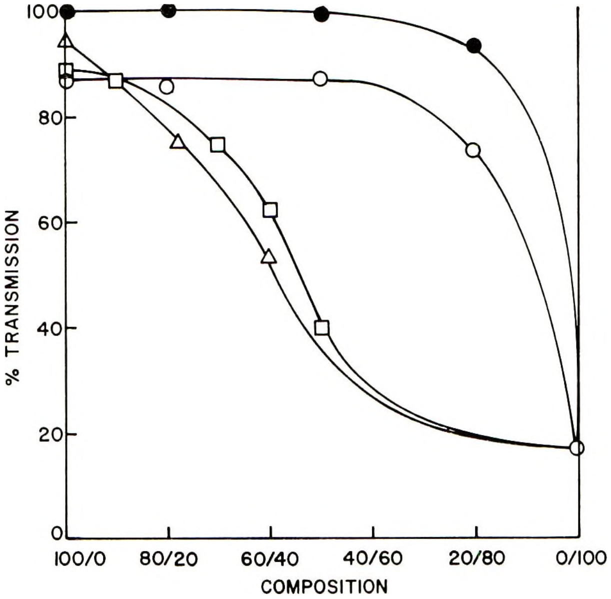

Fig. 4. Light transmission vs. composition of the graft copolymers and a 50:50 blend of cellulose acetate and polystyrene homopolymers: (△) P_6 graft/homopolymer blend; (□) P_3 graft/homopolymer blend; (○) P_3 + P_6 blend/homopolymer blend; (●) P_4 graft/homopolymer blend.

in desiccators at room temperature under slight vacuum. All the graft copolymers alone gave clear films, and it was originally thought that comparatively sharp transitions from clear to cloudy films would be observed. However, this was not so, and a rather gradual change from clear to opaque film was observed. The actual light transmissions of the films were therefore measured. The results were rechecked after considerable annealing of the films and found to be virtually unchanged. A figure of 75% light transmission was arbitrarily selected as indicating the limit of compatibility. The resulting data for the two component mixtures are presented in Figures 1–3.

Considering the two-component diagrams, the extreme incompatibility of physical mixtures of the two homopolymers is apparent. The first graft copolymer, however, is more tolerant towards cellulose acetate than the corresponding physical mixtures, especially at the lower percentages of added homopolymers. The tolerance of the first graft polymer (P_3) towards polystyrene is remarkable, and only minor cloudiness developed with the least compatible mixtures. The results obtained with the second graft (P_6) are shown in Figure 2 and are essentially the reverse of the previous results. The graft is now completely compatible with the cellulose acetate and essentially incompatible with polystyrene. Considering now the results obtained with the third graft polymer (P_4), which has equal and comparatively long backbone and side chains, it can be seen (Fig. 3) that the graft is compatible with each of the two parent homopolymers across the whole range of compositions. A fourth series of experiments were conducted in which a graft consisting of equal parts by weight of the first two grafts was used. The results are shown also in Figure 3. Again complete compatibility can be seen at all proportions. The im-

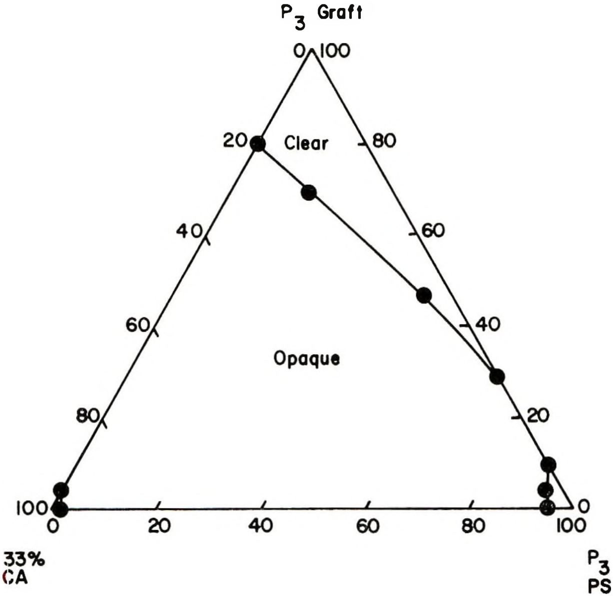

Fig. 5. Phase diagram of blends of cellulose acetate, polystyrene, and the P_3 graft copolymer. (A light transmission of 75% has been selected as the compatibility limit.)

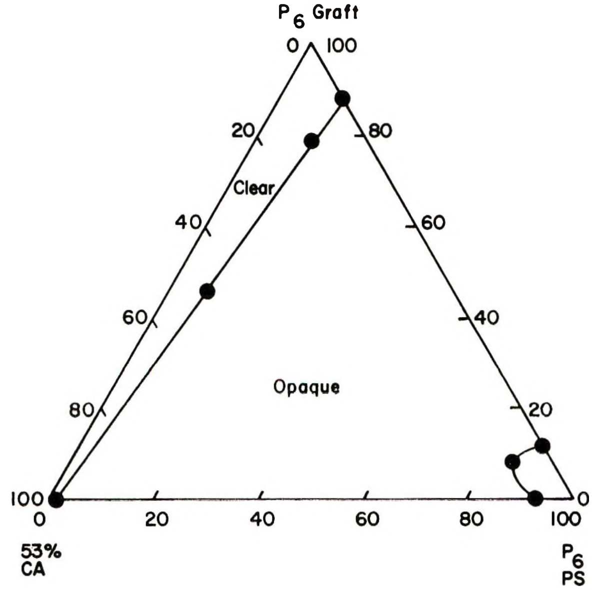

Fig. 6. Phase diagram of blends of cellulose acetate, polystyrene, and the P_6 graft copolymer. (A light transmission of 75% selected as compatibility limit.)

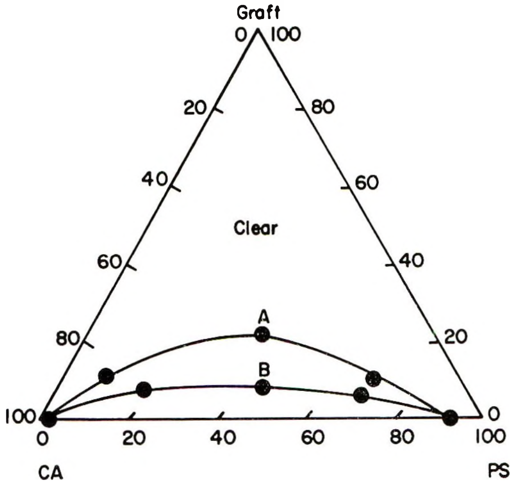

Fig. 7. Phase diagrams of blends of cellulose acetate, polystyrene, and (*A*) the $P_3 + P_6$ blended grafts and (*B*) P_4 graft copolymer.

portance of molecular weight on the compatibility is clearly shown since each graft is compatible with the component having the higher molecular weight. Presumably the compatibility arises from the local mixing of the same polymeric species and a certain minimum size is necessary for this to be favored. On the other hand, if the domains become too large as with the homopolymers alone, then the films will obviously become opaque. The molecular weight distribution seems less important in view of the good compatibility shown by the mixed graft copolymer.

The three-component mixtures, graft plus both homopolymers, have also been studied, and the results are presented in Figures 4–7. The results parallel closely the results of the two-component study. There was little additional compatibilization of the two homopolymers with the first two grafts except with high proportions of added graft. It can be seen from Figure 4, for example, that about 75% of graft copolymer (P_3 or P_6) is needed to compatibilize equal parts of cellulose acetate and polystyrene. With the more evenly balanced high molecular weight grafts, P_4 or 50:50 blends of P_3 and P_6, only a comparatively small proportion of graft is needed. The relative compatibilities of all the four systems studied are further illustrated in the phase diagrams presented in Figures 5–7. A somewhat similar compatibility study has recently been made by Bandcret and co-workers,[7] but with block copolymers of styrene and methyl methacrylate.

Permeability Properties

Polystyrene has a water sorption of less than 0.02%, whereas cellulose acetate sorbs about 17% at saturation. A study of the water vapor diffusion and sorption properties of the grafts should therefore be particularly rewarding. The sorption isotherms for cellulose acetate and the

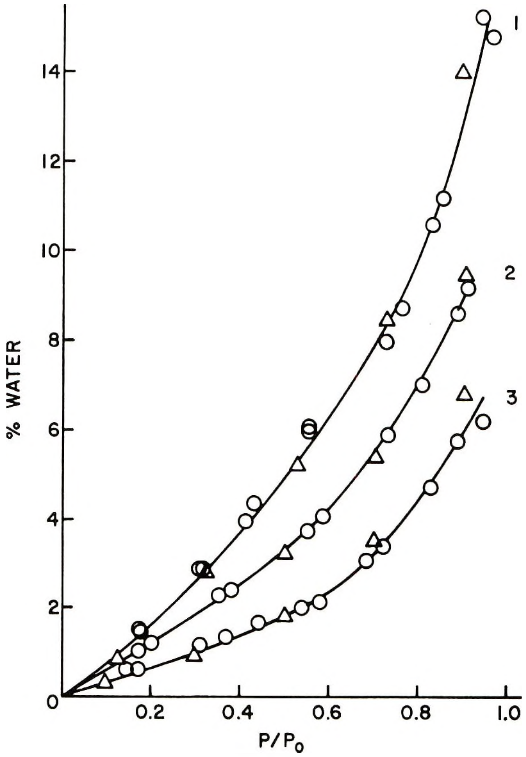

Fig. 8. Water vapor sorption isotherms at 25°C.: (○) equilibrium values; (△) from the P/D data; for (*1*) cellulose acetate, (*2*) P_6 graft copolymer, and (*3*) P_3 graft copolymer.

two grafts based on the same material are shown in Figure 8. The isotherms are based on the total weight of material and considerable reduction in the water sorption can be seen. When the water sorptions are based on the cellulose acetate content only the values are still reduced; for example, at 65% R.H. the water contents are 7.3, 5.9, and 5.0% for the 0, 18.1, and 44.1% polystyrene contents, respectively.

The diffusion constants have also been determined by the time lag technique and are shown in Figure 9. Since the concentrations vary so widely, the diffusivities are presented for convenience as a function of relative vapor pressure. The corresponding concentrations may be found from Figure 8. In the case of polystyrene the concentrations of water vapor were too small to measure directly; however, since the permeability and the diffusion constants were independent of the vapor pressure the solubility coefficient was calculated as 0.393 cm.^{3} STP/cm.^{3}/cm. Hg. This leads to a water vapor sorption of 0.013% at saturation. The diffusion constants of the graft copolymers are much closer to those of cellulose acetate than to the polystyrene values. The actual values at 50% R.H. are 1.8, 2.2, 3.4, and 28.0 × 10^{-8} cm.^{2}/sec. for the cellulose acetate, grafts, and polystyrene, respectively. The values for the grafts are very close to those calculated on the cellulose acetate content only. Since the dif-

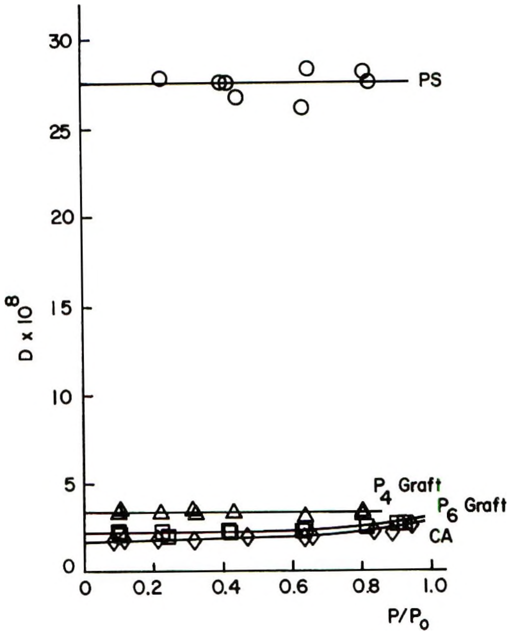

Fig. 9. Diffusion constants for water in polystyrene, cellulose acetate, and the P_4 and P_6 graft copolymers at 25°C. and various vapor pressures.

fusion constant for polystyrene is nearly sixteen times faster than for cellulose acetate, diffusion through the latter apparently becomes essentially rate determining. This could be interpreted to indicate that the graft polymer films contain domains of each polymer type. Diffusion in the polystyrene domains would be sufficiently fast to be negligible compared with the low diffusivity cellulose acetate domains which govern the overall rate of diffusion. Since the grafted films are quite transparent, the domains must be smaller than a few thousand Angstroms; they could still be large enough to be distinct domains compared with the size of a diffusing water molecule. This behavior again illustrates one of the major differences between random and graft copolymers. The properties of grafts often retain to a considerable degree those of one of the homopolymers, whereas random copolymers have properties lying on a curve between those of corresponding homopolymers.

The diffusion constants for the graft with the highest polystyrene content were independent of concentration up to 4.5% water content. The cellulose acetate and the lowest polystyrene graft had diffusivities which increased in parallel fashion at higher water contents with a maximum increase of about 40% of the original low water content values. The permeability constants for all four polymers were determined directly and are shown in Figure 10 as a function of the relative vapor pressure. Cellulose acetate and both grafts showed increasing permeabilities with vapor pressure, whereas polystyrene was found to have pressure-independent permeability constants. It can be seen that the grafting reduced the permeability sharply compared with cellulose acetate; for example, at 65% R.H. the permeability constants were 17, 11.5, and 9.6 × 10^{-7}

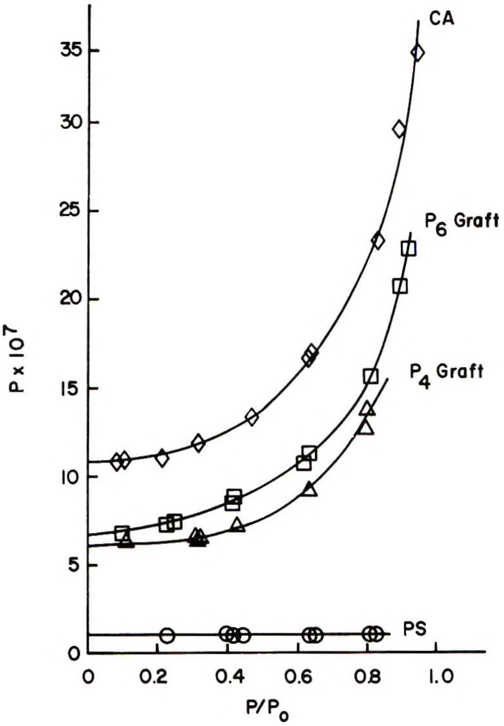

Fig. 10. Permeability constants for water in polystyrene, cellulose acetate, and the P_4 and P_6 graft copolymers at 25°C. and various vapor pressures.

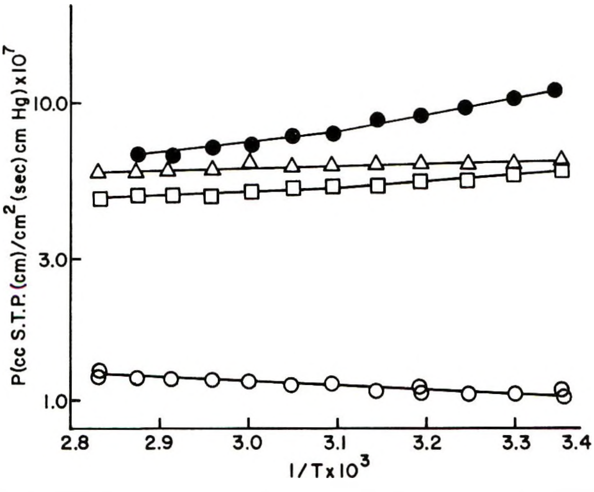

Fig. 11. Temperature dependence of the permeability constants at about 0.2 relative vapor pressure for polystyrene, cellulose acetate, and the P_4 and P_6 graft copolymers: (●) cellulose acetate; (△) P_6 graft copolymer; (□) P_4 graft copolymer; (○) polystyrene.

cm.^{3} STP/cm./cm.^{2}/sec./cm. Hg for the cellulose acetate and two grafts, respectively. The corresponding value for polystyrene was, however, only 1.1×10^{-7}. Since the diffusivities of the grafts were greater than those of cellulose acetate, it is clear that the whole reduction in the permeability is due to the decreased solubility of water in the graft copolymers.

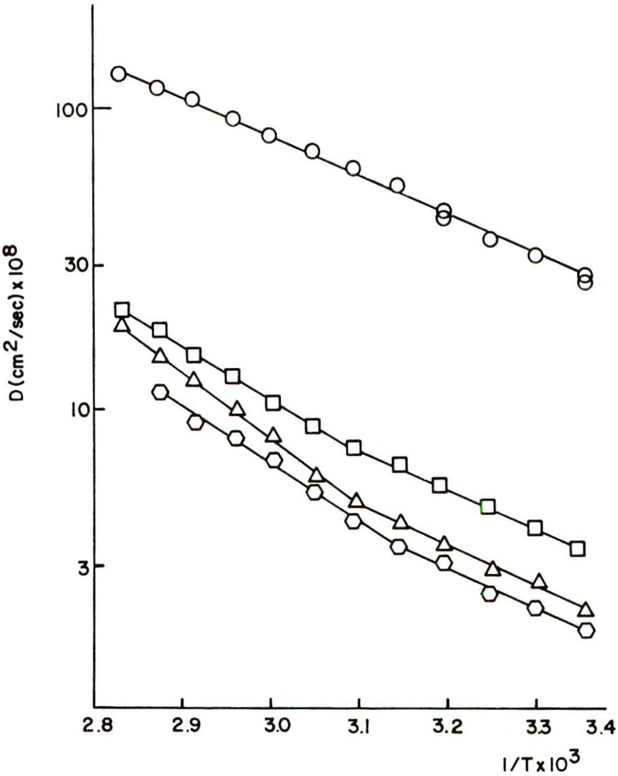

Fig. 12. Temperature dependence of the diffusion constants for polystyrene, cellulose acetate, and the P_4 and P_6 graft copolymers: (⬡) cellulose acetate; (△) P_6 graft copolymer; (□) P_4 graft copolymer; (○) polystyrene.

The quotient of the permeability and diffusion constants gives the solubility coefficient, and so an isotherm can be constructed from these values. These are included in the sorption isotherms presented in Figure 8 and agree completely with the actual measured equilibrium values. The isotherms are of the normal mixing BET type IV variety and the agreement is surprising in view of previous findings, e.g., with ethyl cellulose.[6] This is believed to be the first case of non-Henry law sorption, where the "dynamic" solubility agrees with the equilibrium values. It demonstrates the different nature of the water sorbed in cellulose acetate compared with ethyl cellulose and some other polymers. It could be that the type of clustering of the water molecules, which is believed to occur in ethyl cellulose, does not take place and the time-lag diffusivities

TABLE IV

The Permeability and Diffusivity of Water Vapor (less than 30% R.H.) in the Graft Copolymers and Homopolymers[a]

Polymer	Temp., °C.	P_{25}°C. × 10^7, cm.^{3} STP/cm.^{2}/cm. /sec./cm. Hg	P_0 × 10^7, cm.^{3} STP/cm.^{2}/cm. /sec./cm. Hg	E_p, kcal./mole	D_{25}°C., cm.^{2}/sec. × 10^8	D_0 × 10^3, cm.^{2}/sec.	E_d, kcal./mole
Polystyrene		1.1	2.41	0.5	28.0	6.49	6.0
P_4 graft	<50	5.9	1.6	−0.3	3.4	0.73	6.0
	>50	—	1.6	−0.3	—	24.3	8.2
P_6 graft	<50	6.4	3.9	−0.8	2.2	0.65	6.1
	>50	—	3.9	−0.8	—	72.4	10.2
Cellulose acetate	<50	11.0	0.11	−2.73	1.8	0.54	6.1
	>50	—	0.52	−1.8	—	46.9	9.0

[a] E_p, E_d, P_0, and D_0 are the activation energies and pre-exponential factors for permeation and diffusion, respectively.

TABLE V

Permeability and Diffusivity of Oxygen and Carbon Dioxide in the Graft Copolymers and Homopolymers

		Carbon Dioxide					Oxygen					
Polymer	$D_{25°}$C., cm.^{2}/sec. × 10^8	D_0, cm.^{2}/sec. × 10^8	E_d, kcal./mole	$P_{25°}$C., cm.^{3} STP/cm.^{2}/cm./sec./cm. Hg × 10^{11}	P_0 × 10^6, cm.^{3} STP/cm.^{2}/cm./sec./cm. Hg × 10^{11}	E_p, kcal./mole	$D_{25°}$C., cm.^{2}/sec × 10^8	D_0 × 10^3, cm.^{2}/sec. × 10^8	E_d, kcal./mole	$P_{25°}$C., cm.^{3} STP/cm.^{2}/cm./sec./cm. Hg × 10^{11}	P_0 × 10^6, cm.^{3} STP/cm.^{2}/cm./sec./cm. Hg × 10^{11}	E_p, kcal./mole
Poly-styrene	6.4	0.128	8.7	69.0	7.41	5.5	11.0	125	8.3	25.0	971	9.0
P_4 Graft	1.8	0.039	8.7	100.0	0.31	3.4	7.0	4.5	6.6	15.5	1.57	5.5
P_6 Graft	0.75	0.012	8.5	19.0	1.23	5.2	5.2	0.054	4.1	4.9	0.11	4.6
Cellulose Acetate	0.54	5.82 × 10^{-4}	6.9	11.0	3.47	6.2	2.9	2.64	6.8	6.1	0.27	5.0

include the time taken for cluster formation; however, the independence of the time-lag diffusivities on the concentration precludes this explanation. The more polar nature of cellulose acetate compared, for example, with ethyl cellulose apparently leads to less tendency to cluster and a greater proportion of free water molecules in the system.

The temperature dependence of the permeability and the diffusion constants were also determined, and the results are shown in Figures 11 and 12. There was evidence of a weak transition at about 50°C. in the case of cellulose acetate and the graft copolymers. Weak transitions at 55 and 60°C. have been found by dilatometry for similar grades of cellulose acetate by Russell and Van Kerpel[8] and by Mandelkern and Flory,[9] respectively. The activation energies E_p, E_d, and pre-exponential factors are given in Table IV. The values of the activation energies below the glass transition are similar for all four polymers. Above 50°C. the activation energy for cellulose acetate is about 3 kcal. higher, and this increase is also reflected in those of the graft copolymers in keeping with the role of this component in determining the water vapor diffusivities as discussed previously.

However, the much greater solubility of water in the cellulose acetate leads to greater flux in the cellulose acetate, i.e., the polystyrene acts essentially as inert filler domains. This leads to a permeability constant about in proportion to the cellulose acetate content, as shown in Figure 10.

The permeability and diffusion constants were determined also for carbon dioxide and oxygen across the temperature range of 25–90°C. Quite linear Arrhenius plots were obtained with no inflections. The activation energies and pre-exponential factors are given in Table V together with the actual values of the diffusion and permeability constants at 25°C. In general, the values for the grafts lie between those of the two homopolymers. The differences in the diffusivities between the homopolymers themselves were not as large as in the case of water vapor, particularly in the case of oxygen. The diffusivities, therefore, were not so close to those calculated on the cellulose acetate content only as was shown with water vapor although in the case of carbon dioxide similar results were found. The permeability and diffusion constants of the graft copolymers were found to be much more dependent on the conditions of film formation than was the case with the homopolymers. The values given in Table V were determined on films cast from dimethylformamide solution and dried under vacuum at 40°C. A study of the changes in the diffusion and sorption properties of graft copolymer films prepared under different conditions is under investigation in these laboratories and will be reported in a later publication.

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Résumé

Une série de copolymères greffés purifiés d'acétate de cellulose et de polystyrène qui ont été préparés et caractéristés au curs d'une étude antérieure a été utilisée pour certaines études de propriétés initiales Des produits greffés avec des chaînes principales de poids moléculaire élevé et de courtes chaînes latérales et réciproquement et à la fois avec des chaînes latérales et principales de aut et bas poids moléculaires ont été préparés. Les polymères greffés sont insolubles dans la plupart des solvants mais solubles dans la diméthylformamide et la pyridine et dans des mélanges des solvants pour chacun des composants. Les films coulés au départ des mélanges de ces polymères greffés et des homopolymères montraient que les polymères greffés étaient compatibles avec l'homopolymère du composant de poids moléculaire le plus élevé. Le copolymère greffé avec une chaîne principale de poids moléculaire élevé et a chaîne latérale également de poids moléculaire élevé est compatible avec les deux homopolymères pris séparément et avec un mélange des deux sur un vaste domaine de composition. Un mélange de greffés de hauts et de bas poids moléculaires était également entièrement compatible avec les deux homopolymères. On a également étudié la perméabilité, la diffusion et la sorption des gaz et de la vapeur d'eau dans ces polymères greffés, de même que dans ces polymères correspondants. Dans le cas de la vapeur d'eau la sorption au sein de l'acétate de cellulose était beaucoup plus élevée que dans le polysthrène, tandis que la diffusion était beaucoup plua basse. On a trouvé que les polymères greffés montraient à la fois un comportement à la diffusion et à la solution plus proche de celui de l'acétate de cellulose, alors que les constantes de perméabilité étaient plutôt intermédiaires entre celles des deux composants.

Zusammenfassung

Eine Reihe gereinigter Pfropfcopolymerer aus Celluloseacetat und Polystyrol, die im Verlaufe einer früheren Untersuchung dargestellt und charakterisiert worden waren, wurden für orientierende Untersuchungen ihrer Eigenschaften herangezogen. Es wurden Pfropfpolymere mit hochmolekularer Hauptkette und niedermolekularen Seitenketten und umgekehrt, sowie mit Seiten- und Hauptkette mit hohem oder niederem Molekulargewicht dargestellt. Die Pfropfpolymeren waren in den meisten Lösungsmitteln unlöslich, lösten sich aber in Dimethylformamid und Pyridin und in Gemischen von Lösungsmitteln für jede Komponente. Filme aus Mischungen der Pfropfpolymeren und Homopolymeren zeigten, dass die Pfropfpolymeren mit dem Homopolymeren der Komponente mit höherem Molekulargewicht verträglich waren. Ein Pfropfcopolymeres mit hochmolekularer Hauptkette und hochmolekularen Seitenketten war mit den beiden Homopolymeren getrennt, sowie mit einer Mischung beider über einen breiten Zusammensetzungsbereich verträglich. Eine Mischung der hoch- und niedermolekularen Pfropfpolymeren zeigte ebenfalls eine hohe Verträglichkeit mit beiden Homopolymeren. Weiters wurde die Permeabilität, Diffusion und Sorption von Gasen und Wasserdampf in den Pfropfpolymeren und den entsprechenden Homopolymeren untersucht. Im Falle von Wasserdampf war die Sorption in Celluloseacetat viel höher als in Polystyrol, während die Diffusion viel geringer war. Die Pfropfpolymeren waren in ihrem Diffusions- und Lösungsverhalten dem Celluloseacetat ähnlicher, während die Permeabilitätskonstanten mehr zwischen denjenigen der beiden Homopolymeren lagen. Die Gaspermeabilitäts- und -diffusionskonstanten lagen in der Mitte zwischen den für die beiden Homopolymeren erhaltenen Werten.

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Polymerization of Methyl Methacrylate with Butyllithium–Diethylzinc Complex

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Synopsis

The low-temperature polymerization of methyl methacrylate initiated with butyllithium–diethylzinc has been studied in toluene and in toluene–tetrahydrofuran and toluene–dioxane mixtures in various proportions. The polymerization process is typically anionic; it is characterized by a very rapid initiation reaction, and the absence of termination and chain transfer reactions, the molecular weight increasing proportionally with the degree of conversion. With toluene as a solvent, the polymer chains are associated, as is shown by viscometric measurements; moreover the polymers produced are highly polydisperse ($M_v/M_n = 5.4$). The kinetics are very complicated and vary with the range of the catalyst and monomer concentrations. In pure toluene in the presence of the organometallic complex, butyllithium–diethylzinc, the monomer addition is more stereospecific than when butyllithium alone is used as catalyst. By adding tetrahydrofuran to the reaction mixture, the polymer chain association disappears; concomitantly the stereochemical structure of the polymer changes from an isotactic to a mainly syndiotactic configuration. In toluene–tetrahydrofuran mixtures containing from 1 to 10 vol.-% tetrahydrofuran, the kinetics of polymerization can easily be interpreted by assuming the presence of two propagating reactive species which are in equilibrium with each other: the ion pair and the THF-solvated ion pair. The energy of activation of propagation for the free ion pair is equal to 7.5 kcal./mole; for the solvated ion pair a value of 5.5 kcal./mole was found, including the solvation enthalpy of the organometal with tetrahydrofuran. The existence of any relation between the reactivity of the propagating species and the tactic incorporation of the monomeric units has been discussed. The polymerization in mixtures of toluene–dioxane is intermediate between that in pure toluene and that in toluene–THF mixtures; the reaction mechanism however cannot be interpreted with the usual kinetic scheme. The experimental data concerning the rate dependence on catalyst and monomer concentrations are briefly summarized.

INTRODUCTION

The kinetics of the polymerization of methyl methacrylate with organolithium compounds at low temperatures in polar and in nonpolar solvents has been described in detail by Glusker[1–3] and Bywater[4,5] and their coworkers. It has been shown that the initiation reaction is very fast and that any chain transfer or termination process must be excluded. Glusker[3] presented a kinetic scheme which explains the dependence of the rate of polymerization upon monomer concentration, initiator concentration, and solvent composition. In order to explain the broad molecular weight distributions of the polymer obtained in toluene solution he proposed a mechanism involving two interconvertible states of greatly differing kinetic activity, for which the exchange of activity is very slow compared with the addition of monomer.[6]

From the point of view of the internal structure of the polymer, as it can be determined by nuclear magnetic resonance spectroscopy following the method of Bovey and Tiers,[7] isotactic, syndiotactic, and iso-syndio-block polymers can be prepared by working in solvents of varying polarity;[8,9] the isotactic propagation is observed in media such as toluene in which the polymer chains are highly associated. In order to explain this stereoregulatory effect, Furukawa[10] proposed a multicenter coordination mechanism involving a transition state for the propagating species, in which the polar function of the monomer and that of the last monomeric unit of the growing polymer are coordinated to more than one active center of the complex or associated catalyst and are consequently restricted in their free rotation. It is on the basis of Furukawa's hypothesis that the polymerization of methyl methacrylate initiated with a soluble diethylzinc–butyllithium complex has been examined in the present work. Previous NMR experiments indeed had shown the existence of 1:1 stoichiometric alkyllithium–diethylzinc complexes.[11] The polymerization will be considered successively from the point of view of the internal structure of the polymer and of their reaction kinetics.

RESULTS AND DISCUSSION

Tacticity of the Polymers

The strong complexing properties of diethylzinc for a growing chain should influence its stereoregularity, according to Furukawa's mechanism.[10] The tacticities of poly(methyl methacrylate) formed in toluene and in toluene–tetrahydrofuran mixtures at −60°C. with butyllithium or with butyllithium–diethylzincate as catalyst are given in Table I.

As expected, the isotacticity of the polymers for both series decreases as the polarity of the medium increases. However the complex shows a stronger stereoregulating power than butyllithium at low tetrahydrofuran content in the range of 0–3% tetrahydrofuran. The influence of the temperature on the tacticity of poly(methyl methacrylate) prepared with the complex is shown in Table II.

In a polar medium, the syndiotacticity decreases with an increase of temperature in favor of a heterotactic structure, while in a nonpolar medium, isotacticity remains practically unchanged. The influence of the degree of conversion, of the concentration of catalyst, and of monomer in toluene and in toluene–2% THF are reported in Tables III and IV, respectively. Although these factors are of minor importance, it can be seen that the isotacticity increases slightly with increasing concentration of catalyst, decreasing initial concentration of monomer, and increasing conversion.

TABLE I
Tacticity of Poly(methyl Methacrylate) Formed in Toluene–Tetrahydrofuran Mixtures[a]

Solvent				Tacticity		
THF, vol.-%	Toluene, vol.-%	Catalyst	Yield, %	*I*, %	*H*, %	*S*, %
0	100	BuLi	84	76	13	11
		BuLi–ZnEt$_2$	86	95		
1	99	BuLi	87	38	27	35
		BuLi–ZnEt$_2$	73	71	21	8
2	98	BuLi	83	25	42	33
		BuLi–ZnEt$_2$	88	67	22	11
3	97	BuLi	87	15	39	46
		BuLi–ZnEt$_2$	96	61	23	16
5	95	BuLi	84	18	36	46
		BuLi–ZnEt$_2$	100	18	39	43
10	90	BuLi	81	18	32	50
		BuLi–ZnEt$_2$	90	18	32	50
20	80	BuLi	88	18	32	50
		BuLi–ZnEt$_2$	92	7	27	66
100	0	BuLi	39	18	32	50
		BuLi–ZnEt$_2$	95	7	27	66

[a] $[\text{MMA}]_0 = 0.46$ mole/l.; $[\text{Cat}]_0 = 2.30 \times 10^{-2}$ mole/l.; -60 ± 1°C.

TABLE II
Tacticity of Poly(methyl Methacrylate) Formed at Different Temperatures[a]

			Tacticity		
Solvent	Temp., °C.	Yield, %	*I*, %	*H*, %	*S*, %
Toluene	−70	94	82	9	9
	−30	94	79	15	6
	0	~85	~75	~18	7
THF	−70	100	8	21	71
	−30	100			~60
	0	75	12	36	52
Dimethoxyethane	−70	82			~72
	−30	94	~13	~30	~57
	0	65	10	39	51

[a] $[\text{MMA}]_0 = 0.46$ mole/l.; $[\text{BuLi–ZnEt}_2]_0 = 0.93 \times 10^{-2}$ mole/l.

The influence of the initial monomer concentration can be interpreted as a polar effect similar to that of tetrahydrofuran, although less pronounced. When the conversion increases, the current monomer concentration, and as a consequence the polarity of the medium, decreases so that the isotacticity increases. It is also possible, in agreement with the interpretation of Glusker[3] that the isotactic growth of the chain occurs only when the first monomeric units are already incorporated in an atactic conformation of 8 to 10 units; this effect also would increase on the average the percentage of isotactic linkages with conversion.

TABLE III
Influence of the Degree of Conversion and the Concentrations of Catalyst and Monomer on the Isotacticity of Poly(methyl Methacrylate) Formed in Toluene Solution at −60°C.

$[MMA]_0$, mole/l.	$[BuLi–ZnEt_2]$ 10^2, mole/l.	Yield, %	Tacticity		
			I, %	*H*, %	*S*, %
0.93	0.46	93	74	18	8
0.46	0.23	93	79		
	0.46	6	68	27	5
		27	78	13	9
		42	81	14	5
		50	81	16	3
		66	78		
		76	79	19	2
		92	88	10	2
	0.93	48	74	19	7
		62	83		
		91	89		
		93	90		
	2.30	86	95		
0.23	0.23	94	92		
	0.46	85	89		

TABLE IV
Influence of the Concentration of Catalyst and Monomer on the Tacticity of Poly(methyl Methacrylate) Formed with $BuLi–ZnEt_2$ in Toluene–2 vol.-% THF Solution at −60°C.

$[MMA]_0$ × mole/l.	$[Cat]_0$ × 10^2, mole/l.	Yield, %	Tacticity		
			I, %	*H*, %	*S*, %
0.46	0.93	88	70	18	12
0.46	0.46	90	62	20	18
0.46	0.23	85	60	20	20
0.23	0.46	94	64	21	15
0.12	0.46	42	67	20	13

Polymerization Kinetics

The kinetics of polymerization of methyl methacrylate in the presence of butyllithium–diethylzinc complex have been examined in three different media: in pure toluene, in toluene–tetrahydrofuran, and in toluene–dioxane mixtures. The three systems will be considered separately.

Polymerization in Toluene–Tetrahydrofuran Mixtures. On addition of butyllithium–diethylzinc at −60°C. to a toluene–THF solution of methyl methacrylate, "living" polymers are formed which are capable of further growth upon addition of fresh monomer. The initial rates of polymerization are directly proportional to the monomer concentration (Table V); by plotting the logarithm of M_0/M, i.e., the ratio of the initial monomer concentration to the current monomer concentration versus

TABLE V
Polymerization of Methyl Methacrylate Initiated with BuLi–ZnEt$_2$ in Toluene–Tetrahydrofuran Mixtures[a]

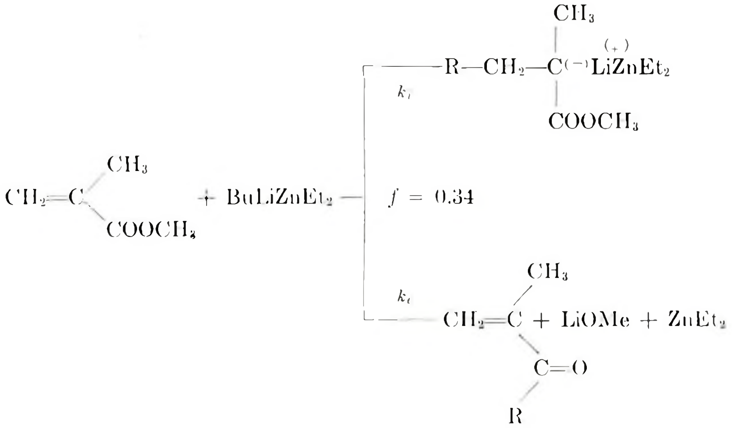
[THF]		$[MMA]_0$, mole/l.	$10^3 R_p$, mole/l.-sec.
Vol.-%	Mole/l.		
1	0.12	0.23	0.44
		0.46	0.86
		0.93	1.80
2	0.24	0.12	0.24
		0.23	0.66
		0.46	1.32
		0.70	2.00
		0.93	2.62

[a] $[Cat]_0 = 0.46 \times 10^{-2}$ mole/l.; -60°C.

time, linear plots passing through the origin are obtained; they remain linear up to high degree of conversion (the maximum conversions are indicated in Fig. 1). These results indicate that the initiation reaction is much faster than the propagation and that the concentration of active chain ends must remain constant throughout the reaction. It is therefore interesting to compare the experimental number-average molecular weight with the theoretical value as calculated from eq. (1):

$$\bar{M}_{n\,\text{theo}} = 100\alpha[M]_0/[Cat]_0 \qquad (1)$$

where 100 is the molecular weight of methyl methacrylate, α is the degree of conversion, and $[M]_0$ and $[Cat]_0$ are the initial monomer and catalyst concentrations, respectively. Indeed during the initiation step a considerable fraction of the catalyst is lost by side reaction with the ester



$$CH_2{=}C(CH_3)(COOCH_3) + BuLiZnEt_2 \begin{cases} \xrightarrow{k_i} R{-}CH_2{-}C(CH_3)(COOCH_3)^{(-)}\,{}^{(+)}LiZnEt_2 \\ f = 0.34 \\ \xrightarrow{k_t} CH_2{=}C(CH_3){-}C({=}O){-}R + LiOMe + ZnEt_2 \end{cases} \qquad (2)$$

$$\underset{k_1\,\downarrow\,MMA}{P^{(-)}Li^{(+)}ZnEt_2} + THF \overset{K}{\rightleftharpoons} \underset{k_2\,\downarrow\,MMA}{P^{(-)}Li^{(+)}ZnEt_2\cdot THF} \qquad (3)$$

$$R_p = \{k_1 + k_2K(THF)\}f[Cat][M] \qquad (4)$$

TABLE VI

Molecular Weight Data for Poly(methyl Methacrylate) Formed with Butyllithium–Diethylzinc in Toluene–Tetrahydrofuran Mixtures

Temperature, °C.	THF		[MMA], mole/l.	$[Cat]_0$ × 10^2, mole/l.	Yield, %	$[\eta]$ (25°C., C_6H_6)	$\bar{M}_v$	$\bar{M}_n$	f	$\bar{M}_v/\bar{M}_n$
	Vol.-%	Mole/l.								
−60	1	0.12	0.46	0.46	86.5	0.24	58,700	23,000	0.38	2.5
−60	1	0.12	0.46	0.70	100	0.22	51,400	17,300	0.38	3.0
−60	2	0.24	0.46	0.93	43.0	—	—	7,000	0.31	3.0
−60	2	0.24	0.46	0.70	100	0.17	36,200	17,300	0.38	2.1
−60	2	0.24	0.46	0.46	90	0.21	49,300	27,000	0.33	1.8
−60	2	0.24	0.46	0.23	84.7	0.44	130,400	42,300	0.40	3.0
−60	2	0.24	0.23	0.46	94	0.14	29,000	13,700	0.34	2.1
−60	2	0.24	0.12	0.46	42.6	—	—	3,500	0.30	—
−60	5	0.61	0.46	0.46	54.6	—	—	18,600	0.30	—
−75	2	0.24	1.86	0.70	7.5	—	—	5,900	0.33	—
−75	10	1.23	0.46	0.46	80.7	0.20	46,000	26,600	0.30	1.7
−50	1	0.12	0.46	0.46	22.2	—	—	6,200	0.36	—
−40	1	0.12	0.46	0.23	31.4	—	—	19,000	0.33	—

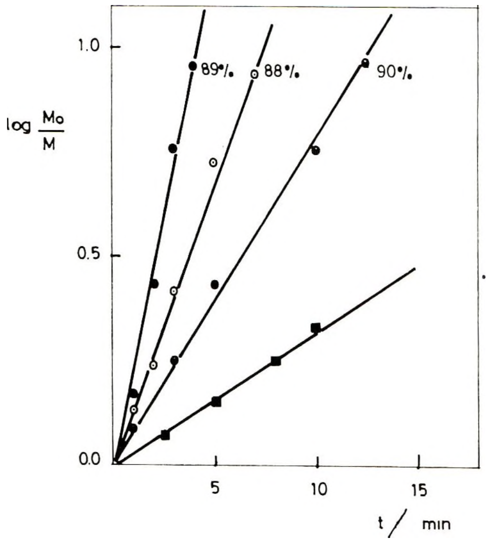


Fig. 1. Polymerization of methyl methacrylate with BuLi–ZnEt$_2$ in toluene–2% tetrahydrofuran at −60°C. and [MMA] = 0.46 mole/l. and various [Cat]$_0$: (■) 0.23 × 10^{-2} mole/l.; (⊗) 0.46 × 10^{-2} mole/l.; (⊙) 0.93 × 10^{-2} mole/l.; (●) 1.44 × 10^{-2} mole/l.

function of the monomer [eq. (2)], with the consequence that the experimental number-average molecular weight is appreciably greater than expected. The initiation efficiency f is therefore given by

$$f = [P]/[Cat]_0 \tag{5}$$

where [P] is the concentration of polymer molecules. The results of these determinations are summarized in Table VI. Within experimental error, the efficiency remains practically constant ($f = 0.34$) and independent of the monomer and catalyst concentration and of the tetrahydrofuran content.

This result is indeed logical if one considers the efficiency as arising from the competition of two bimolecular reactions of the catalyst with the double bond (k_i) or with the ester function (k_e) of the monomer [eq. (2)] inasmuch as the order of both reactions is the same, f must be equal to $k_i/(k_i + k_e)$. In connection with this, attention should be called to the fact that the absence of a termination reaction during the polymerization process indicates that the living chain end of the polymer, in contrast with the catalyst, does not react with the ester function of the monomer. The explanation for it must be sought in the large steric hindrance of the polymeric anion that prevents it to react with the bulky ester group. There is another interpretation for the low initiation efficiency. According to Glusker[3] the value of 0.34 which was also found in the fluorenyllithium-initiated polymerization of methyl methacrylate in toluene–tetrahydrofuran could be due to a pseudocyclization reaction leading to the formation of trimers, etc., as represented further in the reaction scheme for the polymerizations in pure toluene. The presence of these oligomers has been demonstrated in the polymerizations in nonpolar medium; their existence in a good solvating medium can also be assumed, although not demonstrated.

The pseudomonomolecular rate constants as determined from the slopes of the log $[M_0]/[M]$ plots (Fig. 1) versus time are summarized in Table VII; they depend upon the first power of the initial initiator concentration (Fig. 2).

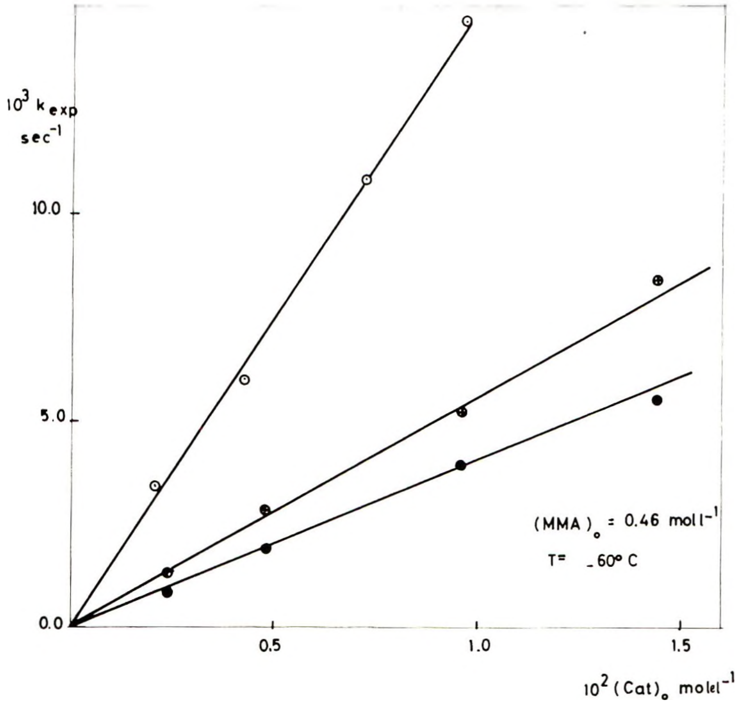


Fig. 2. Dependence of the apparent first-order rate constants on the catalyst concentration in polymerization of methyl methacrylate; with BuLi–ZnEt$_2$ in toluene–tetrahydrofuran mixtures at −60°C.: (⊙) 10 vol.-% THF; (⊕) 2 vol.-% THF; (●) 1 vol.-% THF.

The reduced rate constants, $k_{exp}/[\mathrm{Cat}]_0$ are themselves a linear function of the concentration of tetrahydrofuran (Fig. 3). The rate of polymerization may therefore be represented by eq. (6):

$$R_p = k_{\mathrm{exp}}[\mathrm{M}] = \{k_1 + k'[\mathrm{THF}]\}f[\mathrm{Cat}]_0[\mathrm{M}] \quad (6)$$

The occurrence of two rate constants k_1 and k' reflects the existence of two different reactive centers, one of which is solvated with tetrahydrofuran; both are probably in equilibrium with each other. The first-power dependence on catalyst concentration indicates the following:

TABLE VII
Rates of Polymerization of Methyl Methacrylate Initiated with Butyllithium–Diethylzinc in Toluene–Tetrahydrofuran Mixtures at $[MMA]_0 = 0.46$ mole/l.

Temperature, °C.	[THF] Vol.-%	[THF] Mole/l.	$[Cat.]_0 \times 10^2$, mole/l.	$k_{exp} \times 10^3$, sec.$^{-1}$
−60	1	0.12	1.44	5.5
			0.93	3.9
			0.46	1.9
			0.23	0.8
	2	0.24	1.44	8.2
			0.93	5.1
			0.46	2.9
			0.23	1.3
	5	0.61	0.46	4.4
	10	1.23	0.93	14.7
			0.70	10.8
			0.42	6.0
			0.21	3.4
−75	1	0.12	0.46	0.7
	2	0.24	0.46	0.8
	5	0.61	0.46	1.4
	7	0.86	0.46	2.1
	10	1.23	0.46	2.7
−50	1	0.12	0.41	3.5
	1	0.12	0.46	4.8
	3	0.36	0.41	5.8
	4	0.48	0.23	3.5
	5	0.61	0.41	7.4

(*1*) The polymer chains are very poorly or not associated at all. This conclusion is confirmed by viscosity measurements (Table VIII). When a living system consists mainly of unassociated chains the viscosity must remain the same when the living chain ends are killed (methanol addition). In pure toluene as a solvent, the difference in flow time is quite large; in the presence of tetrahydrofuran, on the contrary, the difference is practically negligible.

(*2*) The equilibrium does not deal with any ionization phenomenon but with the interconversion into one another of two different ion pairs. (Free ions are not likely to occur in such media.[12])

(*3*) The efficiency does not change with respect to the concentration of catalyst and of tetrahydrofuran. This has already been discussed on the basis of Table VI.

A kinetic scheme consistent with the experimental data is given in eqs. (2) and (3). After an instantaneous initiation, characterized by an efficiency of 0.3–0.4, monomer is consumed by two reactive species which are in equilibrium with each other.

$$K = \frac{[P^{(-)}Li^{(+)}ZnEt_2 \cdot THF]}{[P^{(-)}Li^{(+)}ZnEt_2][THF]} \tag{7}$$

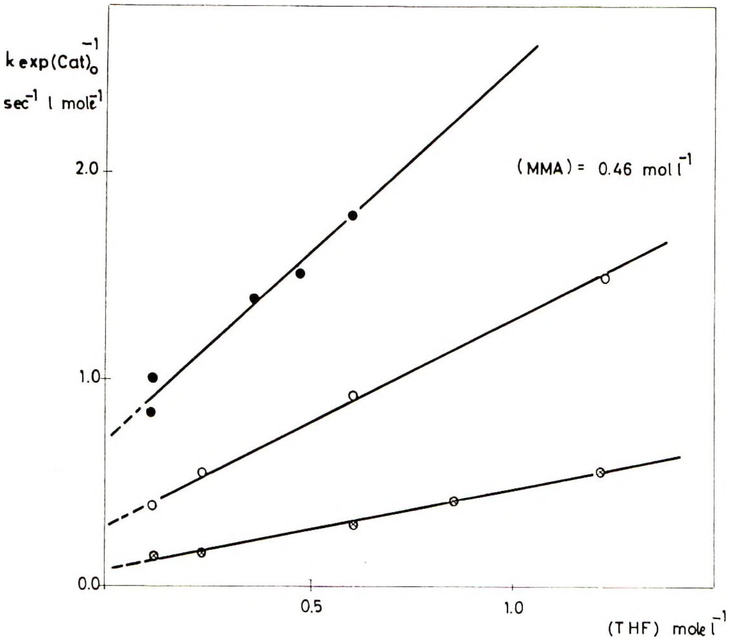


Fig. 3. Dependence of the rate constants on the tetrahydrofuran concentration in polymerization of methyl methacrylate with BuLi–ZnEt$_2$ in toluene–tetrahydrofuran mixtures: (⊗) −75°C.; (○) −60°C.; (●) −50°C.

The rate of polymerization is equal to the sum of the monomer additions at the two centers.

$$R_p = \{k_1 + k_2K[\mathrm{THF}]\}[\mathrm{P}^{(-)}\mathrm{Li}^{(+)}\mathrm{ZnEt}_2][\mathrm{M}] \tag{8}$$

The concentration of living chains can be expressed in function to the initial concentration of catalyst.

$$f[\mathrm{Cat}]_0 = [\mathrm{P}^{(-)}\mathrm{Li}^{(+)}\mathrm{ZnEt}_2] + [\mathrm{P}^{(-)}\mathrm{Li}^{(+)}\mathrm{ZnEt}_2\cdot\mathrm{THF}] \tag{9}$$

$$f[\mathrm{Cat}]_0 = [\mathrm{P}^{(-)}\mathrm{Li}^{(+)}\mathrm{ZnEt}_2]\{1 + K[\mathrm{THF}]\} \tag{10}$$

$$[\mathrm{P}^{(-)}\mathrm{Li}^{(+)}\mathrm{ZnEt}_2] = f[\mathrm{Cat}]_0/(1 + K[\mathrm{THF}]) \tag{11}$$

TABLE VIII

Viscosity Measurements at −60°C. "Living" Poly(methyl Methacrylates)[a]

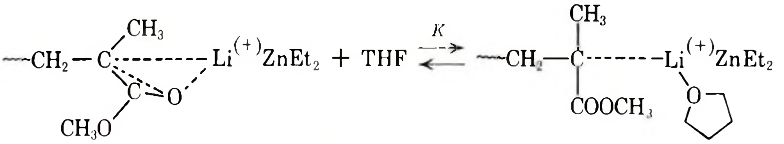
Reaction medium	Flow time, min.:sec. Living	Flow time, min.:sec. Terminated
Toluene	36:33	20:41
Toluene–1% THF	10:55	10:4
Toluene–2% THF	11:5	10:5
Toluene–3% THF	8:45	8:36
Toluene–4% THF	9:45	9:37
Toluene–5% THF	9:00	8:56
Toluene–5% Dioxane	13:10	11:10

[a] $[\mathrm{MMA}]_0 = 0.46$ mole/l.; $[\mathrm{Cat}]_0 = 0.70 \times 10^{-2}$ mole/l.

The rate of polymerization is therefore given by eq. (12):

$$R_p = \{k_1 + k_2K[\mathrm{THF}]\}f[\mathrm{Cat}]_0/(1 + K[\mathrm{THF}])[\mathrm{M}] \tag{12}$$

This rate equation, eq. (12), agrees with the experimentally determined one [eq. (6)] if the product $K[\mathrm{THF}]$ is small compared to unity, i.e., if the concentration of active chains is practically equal to $f[\mathrm{Cat}]_0$. A low value for the equilibrium constant is acceptable if one considers that tetrahydrofuran must compete with the last ester function of the growing polymer chain for complexing with the lithium cation [eq. (13)]. Indeed not only is the probability of reaction much greater for an intramolecular, than for an intermolecular complexation with tetrahydrofuran, but the carbonyl group of the ester function carries a partly negative charge on account of the charge delocalization of the carbanion endgroup.



(13)

The kinetic scheme as described here differs markedly from that given by Glusker[3] for the fluorenyllithium-initiated polymerization of methyl methacrylate in toluene–tetrahydrofuran mixtures. In Glusker's experiments the dependence upon initiator concentration was one-half order, while the dependence upon tetrahydrofuran concentration is one-half order at low concentration and second order at high concentrations. The reason for this marked difference between the two systems must evidently be found in the nature of the catalyst. Table IX summarizes the data necessary to determine the energy and the entropy of activation of both reactions. The low value of the activation energy ($E_{a,1}$ = 7.5 kcal./mole) and the great negative value of the activation entropy ($\Delta S_1\ddagger$ = -25 e.u.) of the nonsolvated propagation reaction are typical for an anionic polymerization. The activation energy $E'_{a,2}$ of the tetrahydrofuran-complexed propagating species (5.5 kcal./mole) consists of a true activation energy ($E_{a,2}$) and of a complexation enthalpy (ΔH_c):

$$E'_{a,2} = E_{a,2} + \Delta H_c \tag{14}$$

TABLE IX

Activation Parameters of the Polymerization of Methyl Methacrylate in Toluene–Tetrahydrofuran Mixtures[a]

Temperature		k_1f, l./mole-sec.	k_1, l./mole-sec.	k_2Kf, l.^{2}/mole^2-sec.	k_2K, l.^{2} mole^2-sec.
°C.	°K.				
−75	198	0.08	0.27	0.38	1.3
−60	213	0.3	1.0	0.98	3.3
−50	223	0.7	2.3	1.8	6.0

[a] $E_{a,1}$ = 7.5 kcal./mole; $E'_{a,2} = E_{a,2} + \Delta H_c$ = 5.5 kcal. mole^{-1}; $\Delta S_1\ddagger$ (−60°C.) = −25 e.u. — (unit of concentration: mole l.$^{-1}$).

It must be pointed out that there is no direct correlation between the kinetic results and the way of incorporation of the monomers. The ratio of the apparent rate constants k_1/k_2K[THF] is not equal to the ratio of the isotactic to the syndiotactic diads (calculated from Table I). It is therefore not permissible to associate with the species propagating with the rate constant k_1 an almost isotactic propagation and to the species propagating according to k_2K[THF] a syndiotactic propagation. For each propagating species, two steps should be considered. While the kinetic rate-determining step consists in the formation of a complex between a living chain end and the next monomer, the isotactic, syndiotactic, or heterotactic incorporation of monomer should be to a great extent thermodynamically controlled. It is possible for example, that some physical property of the medium (e.g., its polarity) favors a syndiotactic conformation over an isotactic one, so that the monomer should be incorporated in such a way that the most stable helix is retained.

Polymerization in Toluene. When the polymerization of methyl methacrylate is initiated with butyllithium–diethylzinc in toluene solution at low temperature, the molecular weight of the polymer increases linearly with the degree of conversion (Fig. 4). After completion, the reaction can start again at −60°C. upon addition of fresh monomer, and the molecular weight of the living polymer increases further. These statements

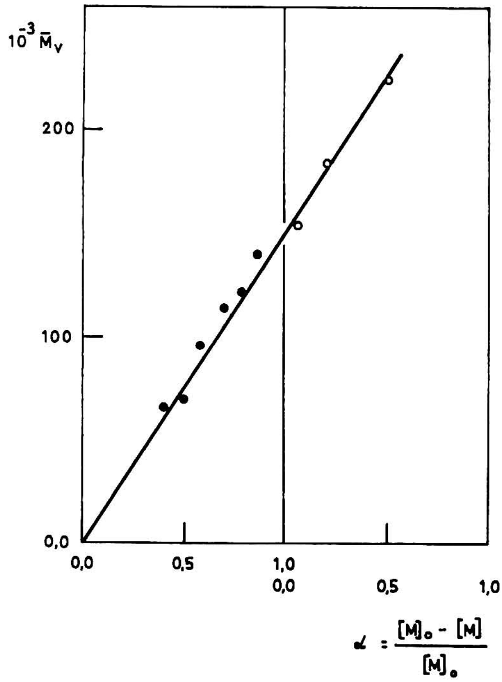
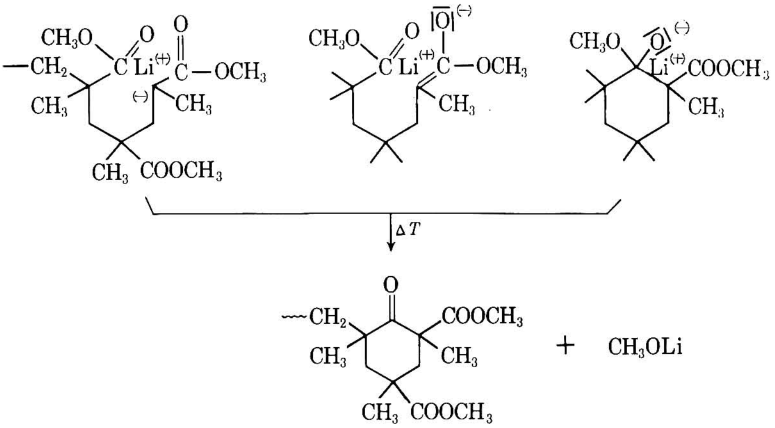


Fig. 4. Molecular weight of PMMA as a function of the degree of conversion: (●) polymerization initiated with BuLi–ZnEt$_2$; (○) further polymerization of the living system after addition of fresh monomer.

signify that: (*1*) transfer or termination reactions are excluded; (*2*) the initiation reaction is instantaneous; and (*3*) the concentration of active chains, or the initiation efficiency, remains constant throughout the whole polymerization process. On the other hand, when the polymerization is carried out at 0°C., a self-termination reaction must occur, probably due to an intramolecular cyclization reaction as shown in eq. (15), the existence of which has been proved by Goode et al.[13] for the polymerization



(15)

of methyl methacrylate in the presence of Grignard reagent at 0°C. The last step of the cyclization reaction, i.e., the loss of lithium methoxide, is irreversible; indeed a living polymer, first brought to 0°C. and then cooled further to −60°C. is no longer able to start a new polymerization reaction.

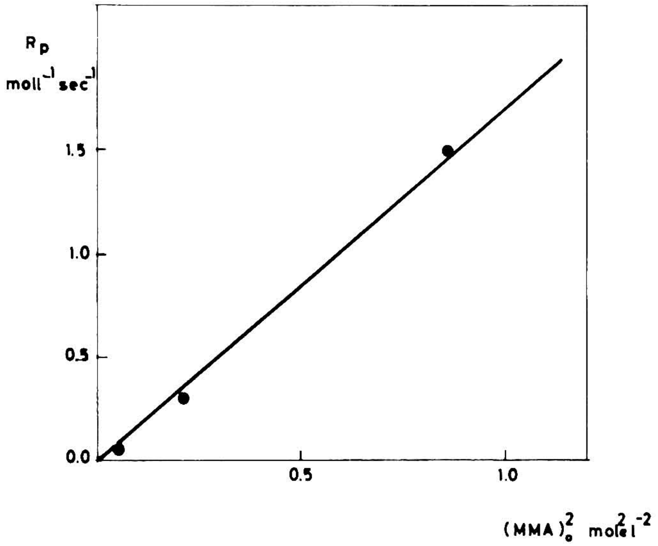


Fig. 5. Influence of the monomer concentration on rate of polymerization of methyl methacrylate with BuLi–ZnEt$_2$ in toluene at −60°C., $[\mathrm{Cat}]_0 = 0.23 \times 10^{-2}$–$0.93 \times 10^{-2}$ mole/l.

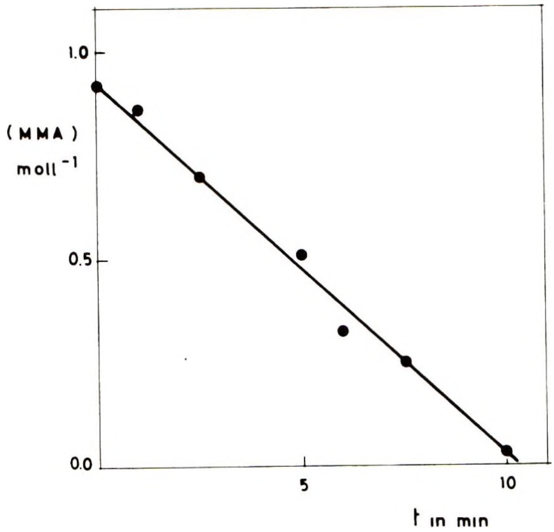


Fig. 6. Polymerization of methyl methacrylate with BuLi–ZnEt$_2$ in toluene at −60°C. $[\mathrm{Cat}]_0 = 0.93 \times 10^{-2}$ mole/l.

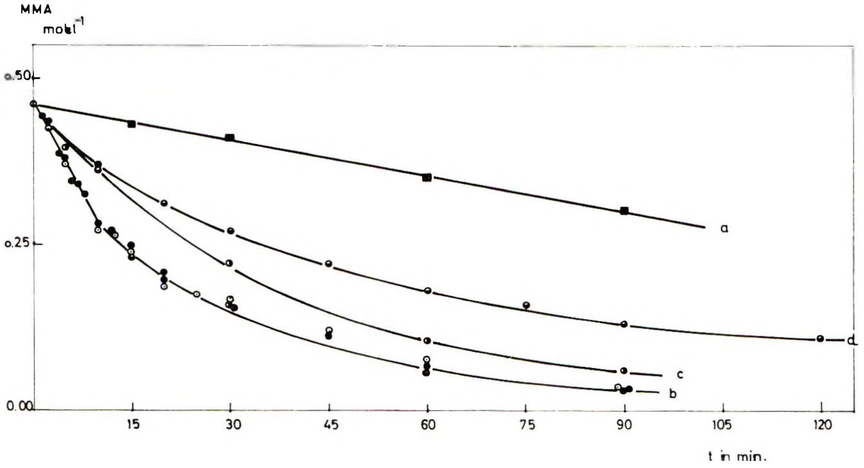


Fig. 7. Influence of catalyst concentration on polymerization of methyl methacrylate with BuLi–ZnEt$_2$ in toluene at −60°C.: (■) $[\mathrm{Cat}] = 0.093 \times 10^{-2}$ mole/l.; (●) $[\mathrm{Cat}] = 0.23 \times 10^{-2}$ mole/l., $\bar{M}_v/\bar{M}_n = 5.1$; (⊗) $[\mathrm{Cat}] = 0.46 \times 10^{-2}$ mole/l., $\bar{M}_v/\bar{M}_n, = 4.1$; (⊙) $[\mathrm{Cat}] = 0.93 \times 10^{-2}$ mole/l., $\bar{M}_v/\bar{M}_n = 4.3$; (◑) $[\mathrm{Cat}] = 1.38 \times 10^{-2}$ mole/l.; (◒) $[\mathrm{Cat}] = 1.84 \times 10^{-2}$ mole/l., $\bar{M}_v/\bar{M}_n = 5.7$.

As was already pointed out in the previous section, the living polymer chains are associated in pure toluene solution, as shown by viscosity measurements (Table VIII).

From the kinetic point of view, the rate dependence on monomer and catalyst concentrations appears to be much more complicated so that no general kinetic scheme can be presented. While the initial rate of poly-

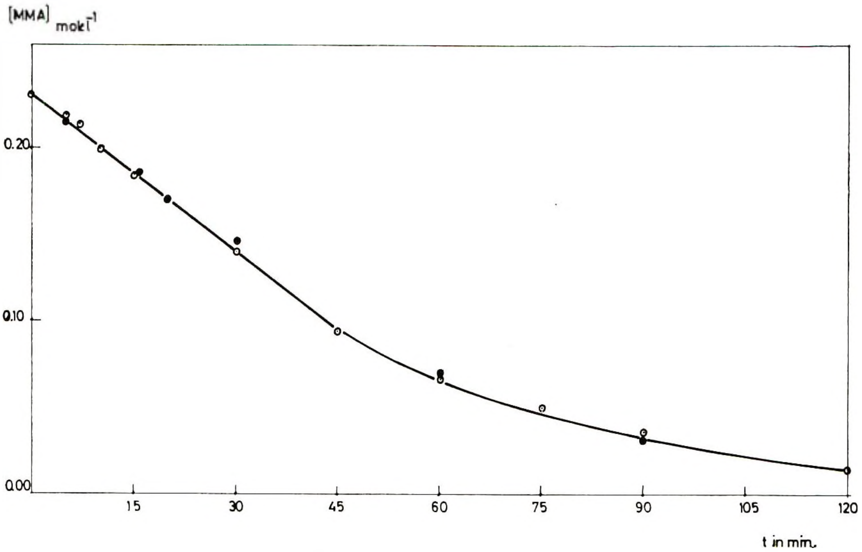


Fig. 8. Polymerization of methyl methacrylate with BuLi–ZnEt$_2$ in toluene at −60°C and [Cat] = 0.23×10^{-2} mole/l.: (⊙) first reaction; (●) further reaction after addition of fresh monomer.

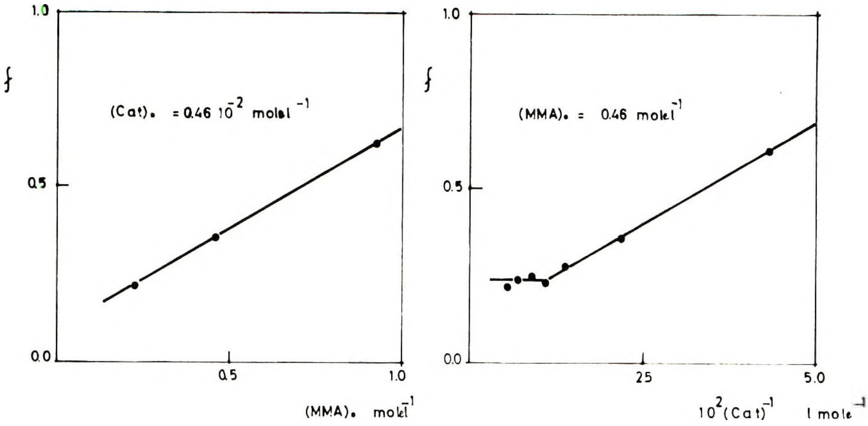


Fig. 9. Dependence of the initiation efficiency on the initial monomer and catalyst concentrations; reaction in toluene at −60°C.

merization depends upon the second power of the monomer concentration (Fig. 5), on the other hand, the observed order with respect to the current monomer concentration varies from zero to two, depending the range of the catalyst concentration.

Figure 6 shows a zero-order reaction up to very high degree of conversion. Contrarily, in Figure 7, curve *c* corresponds to a strictly first-order reaction with a constant half-life time of 27 min. while curve *d* shows an almost second-order reaction for which the reciprocal of the monomer concentration is a linear function of the time. Not only does the concentration of catalyst affect strongly the order of reaction with respect to the current monomer concentration, but there exists a domain of catalyst concentration (curve *b*) where the rate of reaction is independent of the amount of catalyst; above a given concentration, the rate even decreases (curves *c* and *d*). Furthermore, in agreement with previous observations by Bywater et al.,[4] a sudden change in monomer consumption was observed in the second part of some reactions and was concomitant with a color change from yellow to a Tyndall blue, this last being due to the formation of high polymeric agglomerates. The yellow color itself that is most pronounced at high initial monomer concentration, corresponds to the solvation of the living chain ends by free monomer. The reproducibility of the measurements is quite satisfactory; e.g., when a second quantity of pure monomer, equal to the first one, is added to a living system, the rate of monomer consumption is practically the same as for the previous one, as shown in Figure 8. With respect to the initiation efficiency in pure toluene, Figure 9 shows that the efficiency increases with monomer concentration to constant catalyst concentration; inversely, at constant monomer concentration, it remains only constant at low catalyst concentration, then increases linearly. These results must be related to the data of Tsuruta et al.[15] for the *n*-butyllithium-initiated polymerization of methyl methacrylate in hexane solution. They found that several products are formed during the initiation step and that the product distribution is a function of the concentrations of both monomer and catalyst.

The overall energy of activation has been determined from the initial rates of polymerization at different temperatures (Table X). The low value of 7.0 kcal./mole is in striking contrast with the 37 kcal./mole for the isoprene polymerization in hexane solution as described by Morton and coworkers.[14] In the present case, the enthalpy of association is unknown and must be relatively high; therefore it cannot be included in the low value of 7 kcal./mole as it was in Morton's system.

TABLE X
Determination of the Energy of Activation for the Polymerization in Toluene[a]

Temperature		$R_p \times 10^5$, mole/l.-sec.
°C.	°K.	
−40	233	1.29
−50	223	0.76
−60	213	0.34
−70	203	0.14

[a] $[\mathrm{MMA}]_0 = 0.46$ mole/l.; $[\mathrm{Cat}]_0 = 0.46 \times 10^{-2}$ mole/l.

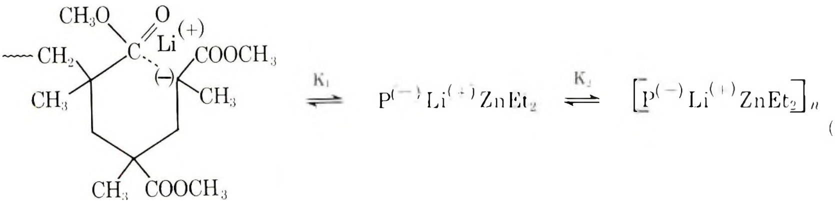
The high negative value of the entropy of activation (−40 e.u. at −60° C.) corresponds to a highly ordered structure of the intermediary complex for stereoregular monomer addition. A last very important point that should be stressed is the unusually high ratio $\bar{M}_v/\bar{M}_n$ of the viscosity-

TABLE XI
Molecular Weights Data of Poly(methyl Methacrylate) Initiated with $BuLi-ZnEt_2$ in Toluene at −60°C.

$[MMA]_0$, mole/l.	$[Cat]_0 \times 10^2$, mole/l.	Yield, %	$\bar{M}_v$	$\bar{M}_n$	f	$\bar{M}_v/\bar{M}_n$
0.93	0.46	93	117,000	29,500	0.63	4.0
0.46	1.84	52.3	34,000	5,900	0.22	5.7
0.46	1.38	20.8	—	—	0.24	—
0.46	1.15	42.1	---	6,700	0.25	—
0.46	0.93	91	84,000	19,700	0.23	4.3
0.46	0.70	100	123,000	24,000	0.28	5.1
0.46	0.46	92	106,000	26,000	0.36	4.1
0.46	0.23	93	156,000	30,700	0.61	5.1
0.23	0.46	85	112,000	19,000	0.22	5.9

average molecular weight to the number-average molecular weight (Table XI):

In order to interpret such an anomalous polydispersity, as well as the previous kinetics results, it can be assumed that open polymer chains exist in equilibrium with pseudocyclized chains (K_1) and with associated chains (K_2) according to eq. (16). The pseudocyclic endgroups are the less re-



(16)

active, and as suggested by Glusker and co-workers,[6] they can go over into more active species by a bimolecular mechanism; this exchange reaction is, however, much slower than the monomer addition. Moreover, it may be that in pure toluene, in addition to chain association and agglomeration (Tyndall effect) and solvation by free monomer, the lithium methoxide and dialkylzinc produced as side-products in the course of the initiation process, act as solvating and complexing agents with respect to the living polymer chains and directly affect the kinetics of polymerization.

Polymerization in Toluene–Dioxane Mixtures. Toluene and dioxane have nearly the same dielectric constant 2.38 and 2.20, respectively. It therefore seemed interesting to compare the polymerization process in toluene–dioxane mixtures with that in pure toluene and in toluene–tetrahydrofuran mixtures. The experimental results, however, suggest a reaction mechanism at least as complicated as in pure toluene; therefore the kinetic results will only be briefly summarized. The initial rates of polymerization vary with the monomer concentration, and the curves pass through a maximum at about $1M$ solution (Fig. 10). The influence of the concentration of catalyst is shown in Figure 11. The rate is proportional to the catalyst concentration only over a narrow range of concentration that itself is dependent on the dioxane content; above this region the rate

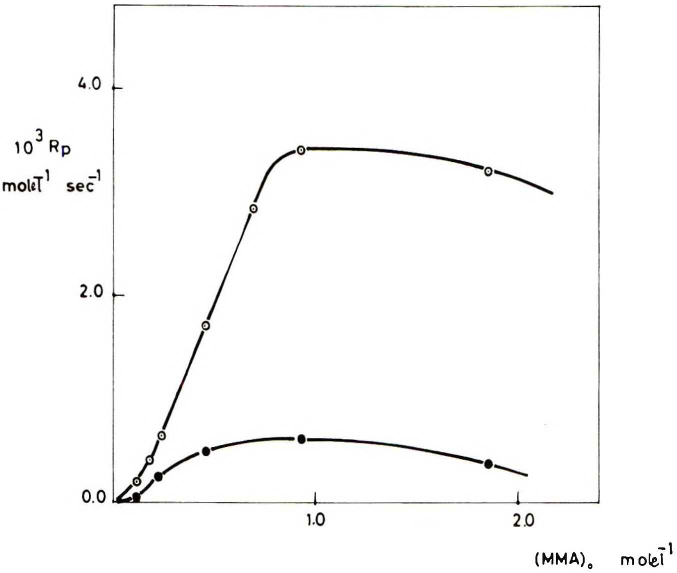


Fig. 10. Dependence of the rate on monomer concentration for polymerization of methyl methacrylate with BuLi–ZnEt$_2$ in toluene–dioxane at −60°C.: (⊙) [dioxane] = 0.59 mole/l., [Cat] = 0.70 × 10^{-2} mole/l.; (●) [dioxane] = 0.12 mole/l., [Cat] = 0.23 × 10^{-2} mole/l.

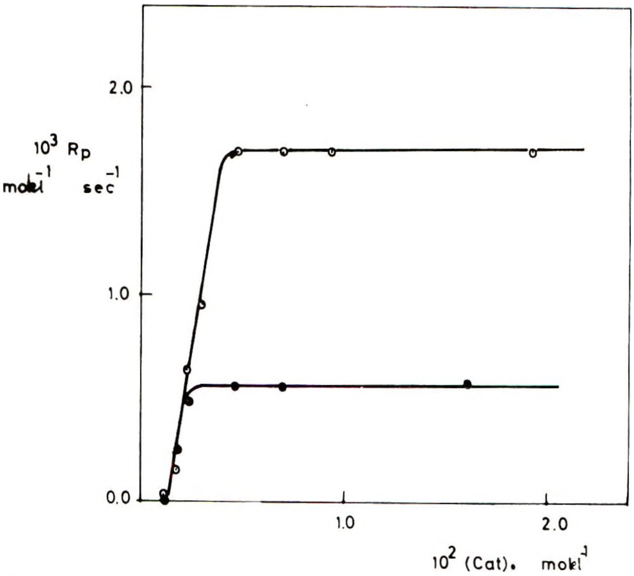


Fig. 11. Dependence of rate on the catalyst concentration in polymerization of methyl methacrylate with BuLi–ZnEt$_2$ in toluene–dioxane at −60°C. and [MMA] = 0.46 mole/l.: (●) 1 vol.-% dioxane; (⊙) 5 vol.-% dioxane.

becomes independent of the catalyst concentration. As expected, the addition of dioxane to the polymerization system increases the rate of polymerization, to a smaller extent, however, than the addition of tetrahydrofuran, probably on account of the solvation of the growing chain ends.

EXPERIMENTAL

Materials

Diethylzinc.[16] On refluxing a mixture of ethyl bromide and ethyl iodide over a zinc–copper couple under an argon atmosphere, ethylzinc halide is formed; this, upon heating under reduced pressure, forms diethyl zinc and zinc halide. The diethylzinc was purified by fractional distillation under reduced pressure and then distilled on a vacuum line into tubes which are stored at −25°C. in the absence of light.

***n*-Butyllithium.**[17] *n*-Butyllithium was prepared from *n*-butyl chloride and an excess of lithium in hexane or toluene solution under argon atmosphere. The reaction mixture was filtered and kept at −25°C. in small vessels provided with a rubber cap.

Butyllithium–Diethylzinc. Diethylzinc was distilled into a butyllithium solution of known molarity in order to obtain a molar ratio of 1/1. The lithium concentration of the solution was determined by potentiometric titration, the zinc concentration by complexiometric titration with EDTA in the presence of Eriochrome Black T as an indicator.

Monomer. Methyl methacrylate (U.C.B.) was shaken repeatedly with dilute alkali and distilled water, distilled under reduced pressure, and stored over sodium sulfate. Before use it was dried for 2 days under stirring over calcium hydride and distilled on a vacuum line into ampules which were filled with argon. The purity was checked by gas chromatography.

Solvents. Toluene (analytical grade, Carlo Erba) was dried over lithium aluminum hydride and filtered before use. Tetrahydrofuran (E. Merck), dimethoxyethane (Fluka), and dioxane (Carlo Erba) were dried over sodium–potassium alloy and distilled into ampules filled with argon.

Polymerization Procedure

The polymerizations were carried out in tubes filled with argon and covered with a rubber cap. Before use the inert gas was passed through a butyllithium solution in order to eliminate traces of oxygen and moisture. When the ampules were completely dry and filled with argon, solvent and monomer were introduced with a syringe (Hamilton type) through the rubber cap and the solution flushed with dry argon for $^1/_2$ hr. After thermostating at low temperature, the initiator was introduced with a syringe. The polymerization was stopped by injecting 1 ml. of methanol. The polymer was precipitated by pouring the solution into vigorously stirred petroleum ether (b.p. 50–80°C.); the polymer was dissolved in dioxane and reprecipitated into water containing some hydrochloric acid. The purified polymer was collected and dried *in vacuo* at 40°C. Each point in the monomer consumption–time curves results from a separate experiment; good reproducibility of the data was controlled in this way.

To examine the association, a viscometer was attached to the ampules and the flow times of the completely polymerized system were measured before and after addition of a few drops of methanol.

Characterization of the Polymers

Intrinsic viscosities were determined in chloroform and in benzene solution at 25 ± 0.01°C.; viscosity-average molecular weights were calculated by using the equations[5,18]

$$[\eta]_{\mathrm{CHCl_3}}^{25^\circ\mathrm{C.}} = 6.48 \times 10^{-5} \, \bar{M}_v^{0.78}$$

and

$$[\eta]_{\mathrm{C_6H_6}}^{25^\circ\mathrm{C.}} = 5.7 \times 10^{-5} \, \bar{M}_v^{0.76}$$

Number-average molecular weights above 15,000 were determined in benzene solution at 25°C. with a Fuoss-Mead osmometer. The molecular weights below 15,000 were determined in benzene solution at 37°C. with a Mechrolab vapor-pressure osmometer.

The tacticities of the polymers are determined by means of a Varian A 60 NMR apparatus. Spectra of 10% solutions of the polymer in chloroform were taken.

Polymerizability of Methyl Methacrylate by Means of Diethylzinc and Alkoxides

Methyl methacrylate dissolved in toluene or tetrahydrofuran and thermostatted at 0°C. for 3–7 days in the presence of 5 mole-% diethylzinc undergoes no polymerization.

During the polymerization of methyl methacrylate by butyllithium diethylzinc, methoxide is formed during the initiation step. It is therefore worthwhile to know if alkoxides, which are always present in the reaction system, are able to initiate the polymerization of methyl methacrylate. The experiments, carried out in toluene or tetrahydrofuran solution with monomer and 1–5 mole-% alkoxide at room temperature for 3 hr. were all completely negative.

CONCLUSIONS

Butyllithium–diethylzinc complex exerts a strong stereoregulating effect on the polymerization of methyl methacrylate; this effect is stronger than that of butyllithium alone.

In toluene solution the association of polymeric growing chains and their association with some foreign substances as lithium oxide and diethylzinc formed during the initiation influence strongly the reaction mechanism; different associated active species are assumed to be in equilibrium with each other and to intervene in the overall rate expression. Consequently the kinetics of polymerization are complicated, and depend on the range of concentration of initiator and monomer where they are examined. The very high $\overline{M}_v/\overline{M}_n$ ratio was also interpreted on the same basis. An almost completely isotactic poly(methyl methacrylate) is obtained at high degree of conversion with a relatively high $[\mathrm{Cat}]_0/[\mathrm{M}]$ ratio.

In the presence of tetrahydrofuran (1–10%) chain association is prevented on account of the great solvating power of THF. The kinetics are easily explained on the basis of an equilibrium between ion pairs and THF-solvated ion pairs, both species giving chain propagation. There is, however, no correlation between the relative importance of both propagation reactions and the structural composition, as resulting from NMR measurements. The isotactic content of the polymers decreases strongly with an increasing THF content in the solution.

In toluene–dioxane mixtures the situation is intermediate with respect to the two previous ones. Larger quantities of dioxane are necessary for the dissociation of the chain aggregates.

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Résumé

La polymérisation du méthacrylate de méthyle initiée par un complexe butyllithium-diéthylzinc a été effectuée à basse température (−60°C) dans le toluène, dans des mélanges toluène–tétrahydrofurane et toluène–dioxanne en différentes proportions. La polymérisation est typiquement anionique: réaction d'initiation très rapide, absence de réactions de terminaison et de transfert de chaîne, proportionalité directe entre le poids moléculaire du polymère et le taux de conversion. Dans le toluène comme solvant les chaînes polymériques sont associées, ainsi qu'il ressort des mesures viscosimétriques; en outre les polymères sont fortement polydispersés ($M_v/M_n = 5.4$). La cinétique s'avère très complexe et varie avec le domaine de concentrations de catalyseur et de monomère utilisées. Dans le toluène pur l'addition du monomère est plus fortement stéréospécifique en présence de l'organométallique double, butyllithiumdiéthylzinc, qu'en présence de butyllithium seul. Par addition de tétrahydrofuranne au milieu réactionnel, l'association des chaînes polymériques disparaît; concomittament la structure stéréochimique du polymère passe d'une configuration isotactique à une configuration principalement syndiotactique. Dans les mélanges toluène–tétrahydrofuranne, contenant de 1 à 10 % vol. de tétrahydrofuranne la cinétique de polymérisation peut être interprêtée aisément en admettant l'existance de deux espèces propagatrices, en équilibre l'une avec l'autre: la paire d'ions et la paire d'ions solvatée; l'énergie d'activation de propagation pour la paire d'ions s'élève à 7.5 kcal/mole; pour la paire d'ions solvatée, on trouve une valeur de 5.5 kcal/mole, y compris l'enthalpie de solvatation de l'organométal par le tétrahydrofuranne. On discute de la possibilité d'existence d'une corrélation entre la réactivité des sites propagateurs et la tacticité d'addition des unités monomériques. La polymérisation dans des mélanges toluène–dioxanne est intermédiaire entre celle dans le toluène et dans les mélanges toluène–tétrahydrofuranne. Le mécanisme réactionnel ne peut toutefois pas être interprêté au moyen d'un schéma cinétique habituel; on présente uniquement les résultats expérimentaux relatifs à l'influence des concentrations en catalyseur et monomère sur la vitesse de polymérisation.

Zusammenfassung

Die Tieftemperaturpolymerisation von Methylmethacrylat bei Start mit Butyllithium–Diäthylzink wurde in Toluol sowie in Toluol–Tetrahydrofuran- und Toluol–Dioxan-Mischungen von verschiedener Zusammensetzung untersucht. Es handelt sich um einen typisch anionischen Polymerisationsprozess, der durch eine sehr rasche Startreaktion und das Fehlen von Abbruchs- und Übertragungsreaktionen charakterisiert wird das Molekulargewicht nimmt proportional zum Umsatz zu. In Toluol als Lösungsmittel sind, wie Viskositätsmessungen zeigen, die Polymerketten assoziiert; ausserdem sind die gebildeten Polymeren stark polydispers ($M_v/M_n = 5{,}4$). Die Kinetik ist sehr kompliziert und hängt vom Bereich der Katalysator- und Monomerkonzentration ab. In reinem Toluol ist die Monomeraddition in Gegenwart des metallorganischen Komplexes Butyllithium–Diäthylzink stärker stereospezifisch als bei Verwendung von Butyllithium allein als Katalysator. Bei Zusatz von Tetrahydrofuran zur Reaktionsmischung verschwindet die Polymerkettenassoziation gleichzeitig erfolgt eine Änderung der stereochemischen Struktur des Polymeren von einer isotaktischen zu einer hauptsächlich syndiotaktischen Konfiguration. In Toluol–Tetrahydrofuranmischungen mit 1 bis 10 Vol% Tetrahydrofuran kann die Polymerisationskinetik leicht durch Annahme des Vorhandenseins zweier wachsender reaktiver Spezies, die miteinander im Gleichgewicht sind, gedeutet werden: das Ionenpaar und das THF-solvatisierte Ionenpaar. Die Aktivierungsenergie des Wachstums für das freie Ionenpaar beträgt 7,5 kcal/Mol, für das solvatisierte Ionenpaar wurde, einschliesslich der Solvatisierungsenthalpie der metallorganischen Verbindung mit Tetrahydrofuran, ein Wert von 5,5 kcal/Mol gefunden. Das Bestehen einer Beziehung zwischen der Reaktivität der wachsenden Spezies und dem taktischen Einbau des Monomerbausteins wurde diskutiert. Die Polymerisation in Toluol–Dioxangemischen liegt zwischen derjenigen in reinem Toluol und derjenigen in Toluol–THF-Mischungen; ihr Reaktionsmechanismus kann aber nicht mit einem konventionellen kinetischen Schema dargestellt werden. Die Versuchsdaten über die Abhängigkeit der Geschwindigkeit von Katalysator- und Monomerkonzentration werden kurz zusammengefasst.

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Thermodynamics of Polymerization. Part IV. Free Energy Changes of Binary Copolymerization Systems

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Synopsis

Using a statistical thermodynamic method we discuss the general shape of a free energy change versus composition curve for a binary copolymerization system. This simple theoretical approach gives reasonable agreement with the experimental results.

In Part II[1] of this series attention has been drawn to the free energy change of copolymerization. It is the purpose of this paper to examine the free energy change of copolymerization from a more general point of view. Generally speaking, this point of view does not yield quantitative results but important semiquantitative deductions often result. The only arbitrary assumption which is made in this treatment is that the elementary steps of the reaction are completely reversible.[1-3]

If the heats of polymerization per mole of AA, BB, AB, and BA pairs are denoted by H_{AA}, H_{BB}, H_{AB}, and H_{BA}, respectively, the heat of copolymerization per mole is given by[4]

$$\Delta H = -\{H_{AA}X_A + H_{BB}X_B + P_{AB}X_A[(H_{AB} + H_{BA}) - (H_{AA} + H_{BB})]\} \quad (1)$$

where X_A and X_B are the mole fractions of monomer units A and B, respectively, and P_{AB} is the probability that a B monomer unit will occupy a site adjoining an A monomer unit in the copolymer.

If we introduce the following definitions[1,4]

$$\Omega = H_{AB} + H_{BA} - (H_{AA} + H_{BB}) \quad (2)$$

$$\psi = P_{AB}/X_B \quad (3)$$

then eq. (1) becomes

$$\Delta H = -\{H_{AA}X_A + H_{BB}X_B + X_AX_B\psi\Omega\} \quad (4)$$

The entropy change of copolymerization per mole ΔS is given by[3]

$$\Delta S = -(S_{AA}X_A + S_{BB}X_B + X_AX_B\psi\chi) - R[(1 - \psi X_B)\ln(1 - \psi X_B) + \psi X_B \ln \psi X_B] \quad (5)$$

where S_{AA} is the entropy change per mole of reaction AA and similarly for S_{BB}. χ is the parameter given by

$$\chi = S_{AB} + S_{BA} - (S_{AA} + S_{BB}) \tag{6}$$

where S_{AB} and S_{BA} are the corresponding entropy changes, per mole, for the reactions AB and BA, respectively.

Next, let us consider the general shape of a free energy change versus composition curve for a binary copolymerization system in the vicinity of either end of the binary. The free energy change of copolymerization at some particular composition will be given by the equation

$$\begin{aligned}\Delta F &= \Delta H - T\Delta S \\ &= -(H_{AA}X_A + H_{BB}X_B + \Omega X_A X_B \psi) + T(S_{AA}X_A + S_{BB}X_B \\ &\qquad + X_A X_B \chi\psi) + RT[(1 - \psi X_B) \ln (1 - \psi X_B) \\ &\qquad + \psi X_B \ln \psi X_B]\end{aligned} \tag{7}$$

To simplify the following treatments, it is assumed that ψ is independent of X_B. This assumption can be regarded only as a first approximation, since there is no doubt that ψ depends on X_B with the exception of random copolymers, alternating copolymers, and block copolymers. However, in the vicinity of the end of binary, ψ is independent of X_B and $\psi \cong 1$.[4] Differentiating ΔF with respect to X_B at constant temperature, we find

$$\begin{aligned}\frac{\partial \Delta F}{\partial X_B} &= (H_{AA} - H_{BB}) - T(S_{AA} - S_{BB}) - \\ &\qquad \psi(1 - 2X_B)(\Omega - \chi T) + RT\psi \ln [\psi X_B/(1 - \psi X_B)]\end{aligned} \tag{8}$$

In the vicinity of the end of binary, we may say that $(1 - \psi X_B) \cong 1$. Thus

$$\begin{aligned}\frac{\partial \Delta F}{\partial X_B} &\cong (H_{AA} - H_{BB}) - T(S_{AA} - S_{BB}) - \psi(1 - 2X_B) \\ &\qquad (\Omega - \chi T) + RT\psi \ln \psi X_B\end{aligned} \tag{9}$$

If ψ is not zero, so that $\ln \psi X_B \to -\infty$ as $X_B \to 0$, $(\partial \Delta F/\partial X_B)$ will always be negative at sufficiently small values of X_B, regardless of the sign of any term. Thus the introduction of the first comonomer units into a homopolymer will always result in a decrease in free energy of the system; hence, a pure homopolymer in the presence of a comonomer is always thermodynamically unstable. This conclusion has important ramifications in connection with the important process of copolymerizing impurities such as oxygen from its environment.[5]

If Ω is positive and χ is negative or zero, ΔF as a function of X_B will be concave downward at all compositions below the ceiling temperature as shown in Figure 1. Let us consider a general case for which Ω is a large positive value. It is assumed that $\chi \cong 0$ from experimental data of Orr[6] as well as from his theoretical discussion.[6] It therefore allows that χ has comparatively little effect on ΔF although Ω affects ΔF markedly. At a temperature T_1 well below the ceiling temperatures of either component, the free energy change versus composition curves would appear sche-

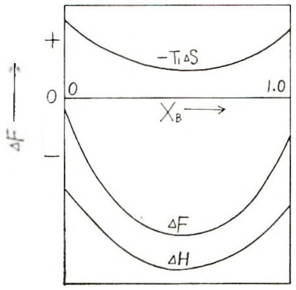

Fig. 1. Free energy change vs. composition for a copolymer when Ω is positive and $T = T_1$.

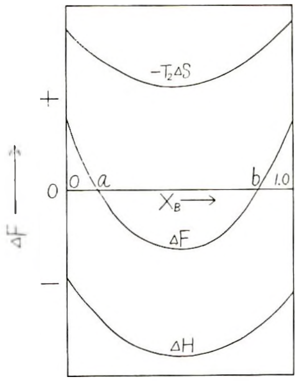

Fig. 2. Free energy change vs. composition for a copolymer when Ω is positive and $T' = T_2$.

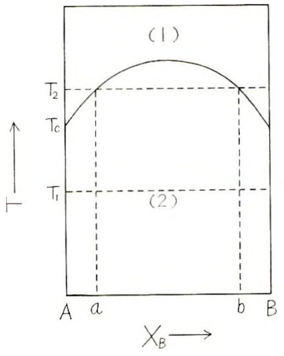

Fig. 3. Modified phase diagram corresponding to free energy curves of Figs. 1 and 2. (At T_2, free energy diagram is given by Fig. 2.): (*1*) monomer; (*2*) copolymer. T_c = ceiling temperature.

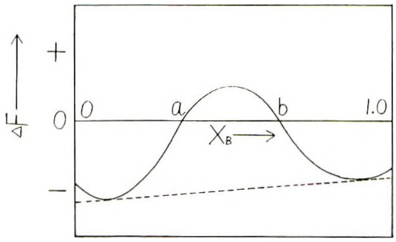

Fig. 4. Free energy change vs. composition for a copolymer when Ω is a large negative value and $T = T_1$.

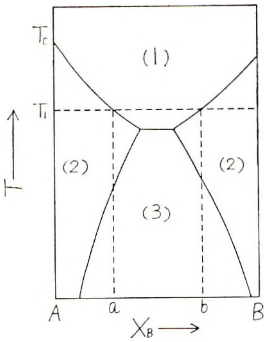

Fig. 5. Modified phase diagram corresponding to free energy curve of Fig. 4. (At T_1, free energy curve is shown by Fig. 4.): (*1*) monomer; (*2*) copolymer; (*3*) two copolymers of different compositions. T_c = ceiling temperature.

matically as shown in Figure 1. Above the ceiling temperature of both components at temperature T_2, the curves would appear as shown in Figure 2. This gives rise to a ceiling temperature maximum and a modified phase diagram as shown in Figure 3.

When Ω is a large positive quantity, the introduction of two types of monomer unit into a polymer chain raises the ceiling temperature for polymerization. Joshi[7] found experimentally that the monomer units alternate along the chain only when $\Omega > 0$. Therefore, the maximum ceiling temperature occurs at a polymer structure of the regular alternation. The alternating copolymerization of sulfur dioxide and isobutene might appear to be a typical example of the maximum ceiling temperature.[8]

A positive value of Ω reflects an attractive interaction between unlike neighbors. Since this attraction would be more pronounced in the copolymer, and because of the strong bonding resulting from this attraction, the ceiling temperature of the copolymer relative to both homopolymers would be increased.

It is easily shown that the maximum ceiling temperature occurs also when $\Omega \cong 0$. This result is consistent with the experimental data of Richardson and North.[9] They found the maximum in ceiling temperature for the copolymerization of acetaldehyde and propionaldehyde.

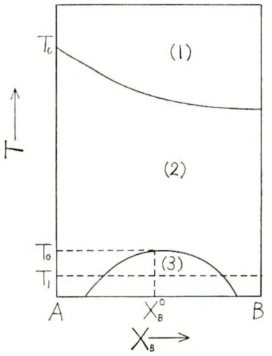

Fig. 6. Modified phase diagram for a copolymer when Ω is a small negative value. (At T_1, free energy curve is given by Fig. 7.): (*1*) monomer; (*2*) copolymer; (*3*) two copolymers of different compositions. T_c = ceiling temperature.

Let us now consider the case of a large negative value of Ω. At some temperature T_1 below the ceiling temperature of the homopolymers, the curves would appear as shown in Figure 4. The free energy curve for the copolymerization would exhibit minima, since $\Omega < 0$.

The most stable situation at various compositions is: (*a*) $0 < X_B < a$, polymer is stable; (*b*) $a < X_B < b$, monomer is stable; (*c*) $X_B > b$, polymer is stable.

This gives rise to a ceiling temperature minimum, and results from a repulsive interaction between unlike nearest neighbors and hence a weakening of the copolymer structure. In the case of a repulsive interaction, Ω will be negative and clustering will occur.[1] The modified phase diagram associated with this type of system is shown in Figure 5, with Figure 4 being associated with T_1.

There will be a repulsive interaction between unlike nearest neighbors in the copolymerization of vinyl monomer with cyclic monomer, and hence the cross-propagation reaction occurs with difficulty.[10] In this copolymerization Ω must be negative, indicating the production of block copolymers.[1] Tsuda et al.[10] found the block copolymer for the copolymerization of styrene and β-propiolactone.

If a case is considered for which Ω is less negative than in the former case, the ceiling temperature minimum is not realized. This modified phase diagram is shown in Figure 6. As the temperature is lowered, however, the ΔH term will begin to dominate in the free energy expression. As discussed above, near the ends of the binary ΔF is always negative, so the complete curve will be as shown in Figure 7.

Consider now a copolymer of composition a. It will have a value of ΔF equal to ΔF_a and negative. Therefore this copolymer is stable relative to pure homopolymer A and B. The same is true for copolymer b. Consider copolymer x, however. It might have a negative value of ΔF but we have to question whether or not ΔF could be lower by dissociating the copolymer. If it dissociates into two copolymers of different compositions, the lowest

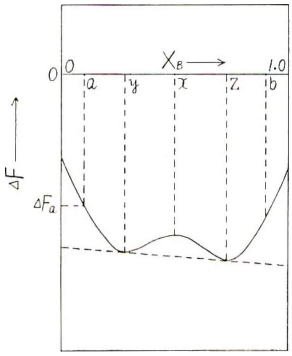

Fig. 7. Free energy change vs. composition for a copolymer when Ω is a small negative value.

stable value of ΔF which can be attained by the decomposition is ΔF at compositions y and z, respectively. These copolymers are in equilibrium with one another since component B would have the same chemical potential in both. This is because for $\Omega < 0$, $(H_{AB} + H_{BA}) < (H_{AA} + H_{BB})$ and AA and BB pairs are energetically favored over AB pairs. Hence, at low enough temperatures two copolymers having different compositions will be formed.

It is important to note that compositions y and z are not necessarily associated with the minima of the ΔF versus X_B curve. The free energy changes at composition y and z may be different from the minimum values, since the important criterion for equilibrium is that the chemical potential of a given component is the same in both copolymers, not that the free energy change of each copolymer be a minimum. Thus, copolymers to the left and the right of y and z, respectively, are stable, whereas copolymers of composition between y and z are unstable and will dissociate into two different types of copolymers.

In connection with Figure 7 it will be observed that two inflection points exist between y and z. Let us calculate the maximum critical temperature T_0 where decomposition will occur and the composition of the copolymer X_B^0, at this temperature. These points are shown in Figure 6. Above the temperature T_0, the curve of ΔF versus X_B is everywhere concave downward. Below this temperature, two minima will occur as already discussed and there will be two inflection points where $\partial^2 \Delta F/\partial X_B^2 = 0$.

As the temperature is raised toward T_0, the minima will move closer together in composition and as a result so will the inflection points. At T_0, both minima and the inflection points will coincide at the same temperature. Thus T_0 is the temperature where both $\partial^2 \Delta F/\partial X_B^2$ and $\partial^3 \Delta F/\partial X_B^3$ equal zero at the critical composition X_B^0.[11]

$$\partial^2 \Delta F/\partial X_B^2 = -2\psi(\chi T_0 - \Omega) + [\psi R T_0/X_B^0(1 - \psi X_B^0)] = 0 \quad (10)$$

$$\partial^3 \Delta F/\partial X_B^3 = -\, R T_0 \psi(1 - 2\psi X_B^0)/[X_B^0(1 - \psi X_B^0)]^2 = 0 \quad (11)$$

Hence, we find

$$T_0 = [2\Omega X_B{}^0(1 - \psi X_B{}^0)]/[2\chi X_B{}^0(1 - \psi X_B{}^0) - R]$$

$$= \Omega/(\chi - 2R\psi) \tag{12}$$

$$X_B{}^0 = 1/2\psi \tag{13}$$

When $\chi = 0$ or $\chi < 0$, Ω must be negative in order for T_0 to be positive. A negative value of Ω indicates a repulsive interaction between unlike components and block copolymer will occur.[1] Thus, from eq. (12), the larger this repulsive interaction, the higher the temperature will be where decomposition begins. As a generalization, we might say that virtually all systems with negative Ω and χ should give two copolymers of different compositions. Thermodynamically, of course, copolymers of composition in the region $y < X_B < z$ are unstable at this temperature, and two copolymers of different compositions y and z will be favored. This is not found experimentally. The reason for this lack of agreement with theory is related to the fact that unless Ω is a sufficiently large negative value, T_0 will be so low that the kinetics of the decomposition in the copolymer will be infinitesimally fast, and thus a copolymer will be generally found which is actually metastable.

Up to the present time, little quantitative work has been done which would provide a check on the foregoing theory. Nevertheless, there is qualitative evidence available to support the general validity of the concepts set forth.

Anderson et al.[12] observed formation of two copolymers of different compositions in the copolymerization of styrene and 5-methylhex-1-ene. This copolymerization product is a mixture of block copolymers, the chain backbones consisting mainly of one monomer type with short blocks of the other. They pointed out that the different catalytic sites may produce copolymer molecules of different composition. Although this might be the case, the thermodynamic explanation presented above can probably be applied to this case.

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Résumé

Utilisant une méthode thermodynamique statistique, nous avons discuté l'allure générale de la variation de l'énergie libre en fonction de la courbe de composition pour un système de copolymérisation binaire. Cette approche théorique simple donne un accord raisonnable aved les résultats expérimentaux.

Zusammenfassung

Die allgemeine Gestalt der Kurve: Änderung der freien Energie gegen Zusammensetzung für ein binäres Copolymerisationssystem wurde auf statistisch-thermodynamischer Grundlage diskutiert. Diese einfache theoretische Betrachtung liefert eine brauchbare Ubereinstimmung mit den Versuchsergebnissen.

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Method of Calibrating Gel Permeation Chromatography with Whole Polymers

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Synopsis

Column systems for gel permeation chromatography are usually calibrated by eluting a series of sharp polymer fractions of known molecular weights and by correlating their elution volumes with molecular size or weight. A different method for calibration is proposed in which only one polymer sample, with a broad, well-characterized molecular weight distribution, is used. The cumulative distribution and the integrated, normalized GPC chromatogram are successively superimposed, and molecular weights and corresponding elution volumes are correlated. It is found that calibration curves obtained in this manner show a definite curvature. A possible explanation and correction for this behavior is given, based on the concentration dependence of elution volumes.

Gel permeation chromatography (GPC) is at present the most convenient and rapid technique for the fractionation of polymers on an analytical and preparative scale. Details of the method and of the instrumentation have been presented in the literature.[1-4] Any particular column combination has to be calibrated experimentally. The usual way to do this is to run a series of sharp fractions and to correlate their elution volumes with their molecular weights, which have to be measured by some independent method. Customarily the point of maximum recorder response is assigned to the measured average molecular weight. However, this elution volume only corresponds to that molecular weight species within the fraction which is present in the largest amount. The determination of the proper point would require a more detailed knowledge of the separation process than is currently available. The decision on the exact point of the elution curve to use for correlation with molecular weight is even more difficult when a whole polymer with a wide distribution is used for calibration.

The complete molecular weight distributions of several whole polyisobutenes have been previously determined in this laboratory by column fractionation.[5] It seemed desirable to utilize this information for the calibration of GPC. This was done by integrating the chromatogram and comparing the normalized values with the corresponding data on the integral molecular weight distribution. Table I shows this calculation for

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TABLE I
Calibration of GPC by Comparison with Known Molecular Weight Distributions (Run 269)

Elution volume, cc.	Area under GPC curve	Σ Areas	I (area)	Corresponding molecular weight
165	2	2	0.001	—
160	9	11	0.007	1,200
155	21	32	0.020	2,800
150	40	72	0.046	5,500
145	68	140	0.089	8,900
140	121	261	0.167	14,400
135	211	472	0.302	22,700
130	295	767	0.490	37,500
125	310	1,077	0.688	62,500
120	250	1,327	0.848	99,000
115	153	1,480	0.946	144,500
110	64	1,544	0.987	182,500
105	19	1,563	0.999	—
100	2	1,565	1.000	—

the case of Vistanex LM-MS polyisobutene. The calibration curve shown in Figure 1 was obtained in this manner from the known distribution of the whole polyisobutene. It should be noted that the set of points exhibits a definite curvature. A possible explanation for this behavior was found when the dependence of elution volume on polymer concentration was documented.[6] It was shown over a wide range of molecular weights that the apparent molecular weight M_A decreases with increasing concentration c in the manner shown in eq. (1). (The concentration is given in weight per cent.)

$$1/M_A = (1/M) + kc \tag{1}$$

The slope constant k for the set of columns used in this investigation (one column each of 10^3, 10^4, 10^5, and 10^6 A. nominal pore size, 1,2,4-trichlorobenzene as the solvent, 150°C. operating temperature) was found to be 225×10^{-8}. From eq. (1), the following relation can be obtained

$$-dM_A/dc = kM^2/(1+kcM)^2 = kM_A^2 \tag{2}$$

or approximately

$$\Delta M_A = 225 \times 10^{-8}\, M_A^2\, \Delta c \tag{3}$$

An inspection of any GPC chromatogram makes it obvious that the various molecular weights, corresponding to their respective elution volumes, are present at different concentrations, corresponding to their respective recorder responses. According to eq. (3), the concentration correction would affect the low concentration, high molecular weight end of the chromatogram to the greatest extent. The corrections for the data in Table I are given in Table II. Figure 1 shows the uncorrected values from Table I

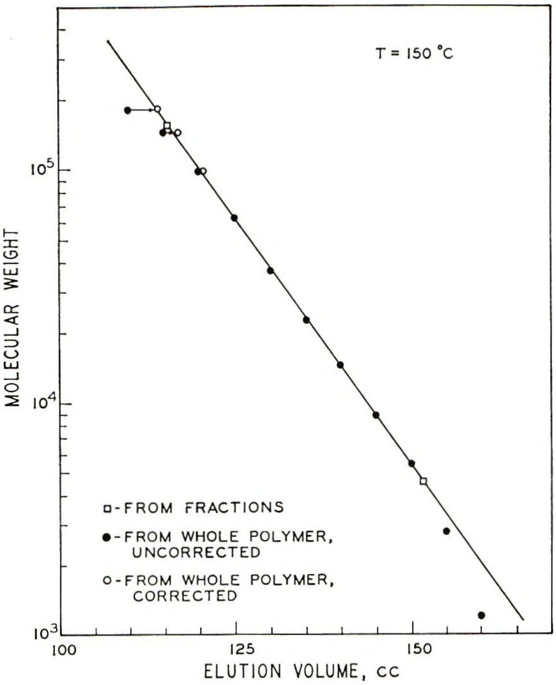

Fig. 1. GPC calibration with whole polyisobutene; application of concentration correction.

(solid circles) and the three points from Table II where the correction made a significant difference (open circles). All points now correspond to results obtained at identical concentration, with the maximum concentration on the chromatogram taken as unity. The upper part of the calibration curve after correction is in excellent agreement with the line passing through the points obtained from runs on sharp fractions (open squares).

TABLE II

Correction for Concentration Dependence According to Equation (3) (Run 269)

Elution volume, cc.	Relative concentration	$M_A^2 \times 10^{-8}$	$225 \times 10^{-8} M_A^2$	ΔM_A
160	0.03	0.01	2.25	2
155	0.07	0.08	18.0	17
150	0.13	0.30	67.5	60
145	0.22	0.79	178	140
140	0.39	2.07	466	285
135	0.68	5.15	1,160	370
130	0.95	14.1	3,170	160
125	1.00	39.1	8,800	—
120	0.81	98.0	22,100	4,200
115	0.49	209	47,000	24,000
110	0.21	333	74,300	59,000

The down curvature at the lower end is probably due to the poor fractionation efficiency of this particular column combination in the very low molecular weight range.

It is thus shown that a GPC run on one or two well-characterized, broad-distribution polymers represents a simple and rapid method of calibrating a GPC instrument.

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Résumé

Des systèmes de colonnes pour chromatographie par perméation sur gel sont habituellement calibrés par élution d'une série de fractions polymériques étroites de poids moléculaire connu et en reliant leur volume d'élution avec la grandeur moléculaire ou leur poids moléculaire. Une méthode différente pour le calibrage est proposée utilisant uniquement un échantillon polymérique avec une distribution de poids moléculaire large et bien caractérisée. La distribution cumulative et le chromatogramme intégré de chromatographie par perméation sur gel sont superposés successivement et les poids moléculaires et les volumes d'élution correspondants se relient entre-eux. On a trouvé qu'une courbe de calibrage obtenue de cette façon montre und coupure nette. Un explication possible et une correction pour ce comportement est donnée basée sur la dépendance des volumes d'élution en fonction de la concentration.

Zusammenfassung

Säulensysteme für die Gelpermeationschromatographie werden gewöhnlich durch Eluierung einer Reihe scharfer Polymerfraktionen von bekanntem Molekulargewicht und Aufstellung einer Beziehung zwischen ihrem Eluierungsvolumen und Molekulargewicht oder Molekülgrösse geeicht. Es wird eine andersartige Eichmethode mit Verwendung nur einer Polymerprobe mit einer breiten wohldefinierten Molekulargewichtsverteilung vorgeschlagen. Die kumulative Verteilung und das integrierte, normalisierte GPC-Chromatogramm werden schrittweise überlagert und Molekulargewichte und entsprechende Eluierungsvolumina zueinander in Beziehung gesetzt. Die so erhaltenen Eichkurven zeigen eine bestimmte Krümmung. Eine mögliche Erklärung und eine Korrektur für dieses Verhalten wird auf Grundlage der Konzentrationsabhängigkeit der Eluierungsvolumina angegeben.

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Poly(chloral-1,3-Dioxolane Diol)

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Synopsis

Chloral and cyclic formals were copolymerized in the presence of acidic catalysts and controlled amounts of water to diols of varying compositions and molecular weights. Cyclic oligomers were formed irreversibly as by-products from the monomers and were also obtained by depolymerization. Condensation of the diols with diisocyanates yielded linear polyurethanes of improved flame resistance.

INTRODUCTION

Chloral has been polymerized in the presence of acidic or basic catalysts. Since the polymers formed where insoluble and decomposed below their melting points,[1] no commercial use has been found. Internal plasticization with dichloroacetaldehyde,[2] ethylene oxide,[3] or formaldehyde[4] has been reported. Earlier attempts to prepare linear acetals from chloral and diols or coacetals from chloral, formaldehyde, and diols have failed.[5]

It is also known that cyclic formals can be homopolymerized or copolymerized with formaldehyde[6] but copolymers with other aldehydes have not been described.[3]

It has now been found that chloral and cyclic formals copolymerized rapidly in the presence of strong Brønsted or Lewis acids and controlled amounts of water. The rates of copolymerization at 0°C. were fast, approaching instantaneous conversion in some cases, and yielded close to alternating diols. This is in contrast with the slow, cationic homopolymerization of chloral.[1]

High molecular weight copolymers of chloral and cyclic formals could be prepared, where the nature and concentration of catalyst and of cocatalyst were found to determine the composition and the molecular weight of the copolymers.[7]

This paper describes the synthesis of relatively short-chain diols and of condensation polymers derived from them.

RESULTS AND DISCUSSION

The cationic copolymerization of chloral with cyclic acetals was found to be limited to nonsubstituted cyclic formals. Presumably steric rather than electronic effects are responsible for the inability of substituted cyclic acetals to undergo copolymerization, as has been suggested to explain the absence of homopolymerization of the latter.[8]

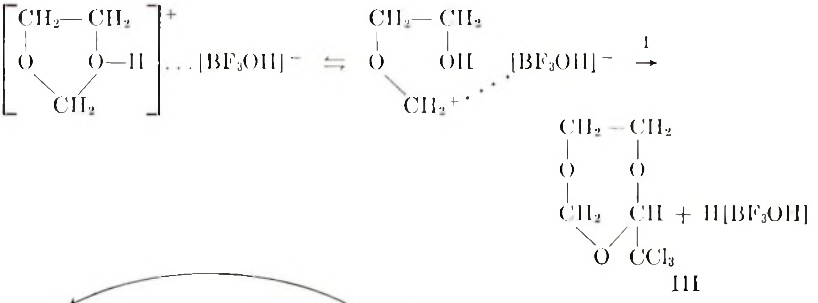
When chloral was copolymerized with nonsubstituted cyclic formals of varying ring sizes under comparable conditions, a lesser chloral content of the copolymers was obtained with 1,3-dioxepane (Table I).

TABLE I
Copolymerization of Equimolar Mixtures of Chloral and Formals[a]

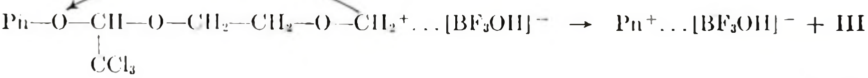
Formal	Yield, %	Petroleum ether soluble, %	Chloral in polymer, %
1,3-Dioxolane	84.5	7.6	44.1
1,3-Dioxepane	55.7	28.4	20.1
1,3,6-Trioxocane	78.9	17.4	41.7

[a] Temp. 5°C.; water content below 0.5%; time 24 hr.; catalyst: 0.1 mole-% $BF_3 \cdot Et_2O$.

The copolymerization was found to compete with an irreversible insertion of chloral into the formal ring during the polymerization and with an irreversible depolymerization. In both cases new, cyclic coacetals of the cyclic formal monomer with one or two chloral units were isolated. More general aspects of this insertion of chloral into cyclic acetals are discussed elsewhere.[9] The case of copolymerization of chloral (I) with dioxolane (II) was studied in detail, since close to alternating copolymers were obtained in the presence of 1.5% of water, starting with equimolar mixtures of I and II. The cyclization reaction may be formulated from the monomers [eq. (1)] as well as from the polymer [eq. (2)].



(1)



$$\text{Pn—O—}\underset{\text{CCl}_3}{\text{CH}}\text{—O—CH}_2\text{—CH}_2\text{—O—CH}_2^+ \ldots [\text{BF}_3\text{OH}]^- \rightarrow \text{Pn}^+ \ldots [\text{BF}_3\text{OH}]^- + \text{III}$$

(2)

The 2-trichloromethyl-1,3,5-trioxepane (III) was also obtained from anhydrous equimolar mixtures of I and II at room temperature with PF_5 almost instantaneously in over 80% yield, apparently with little if any initial polymer formation. A depolymerization of a diol at 80°C. with toluenesulfonic acid also yielded over 80% of III, supporting an alternating structure of the copolymer.

When pure, anhydrous III was subjected to a variety of polymerization conditions (e.g., −80°C., phosphorus pentafluoride as catalyst) it was found to be probably thermodynamically stable with respect to polymer.[10] These observations indicated that III formed irreversibly from the monomers as well as by unzipping from the polymer during polymerization. The copolymerization therefore resembles the polymerization of ethylene oxide, where 1,4-dioxane is formed irreversibly without establishment of a concentration equilibrium. In the case of ethylene oxide,[11] depolymerization of growing chains rather than dimerization appears to predominate.

The relative rates of cyclization and of copolymerization of equimolar amounts of I and II in the presence of 1.5% of water at 5°C. were found dependent on the type and concentration of cationic initiator and on time of polymerization (Table II). Since the apparent rates of conversion with concentrated sulfuric acid as a catalyst were exceedingly slow, it could not be compared with boron trifluoride etherate (intermediate) and antimony pentachloride (fastest rate) at the same concentration.

The molecular weights and chlorine contents of periodically withdrawn samples (Table II) were determined from analytical data by correcting for III according to the equation,

$$M_1 = 221 M_m W_1/(22{,}100 - M_m W_{III})$$

where M_1 is the molecular weight of linear copolymer, 221 is the molecular weight of III, M_m is the molecular weight of mixture (experimental), W_1 is the weight per cent of linear polymer, and W_{III} is the weight per cent of III.

The weight percentages of components were determined initially by careful extraction with hexane, which dissolved III selectively. Later, a quantitative infrared method was developed for determining percentage of III in the copolymers, based on comparison of intensities of absorptions of polymer at 8.05 μ and of III at 7.8 μ, both of which were found to be specific. Since the errors in both methods were in the order of ±3%, calculations of absolute rates and exact degrees of polymerization were not attempted.

Figure 1 shows that the rate of polymerization with boron trifluoride etherate or antimony pentachloride as catalysts initially exceeded the rate of cyclization, while the reverse was true with sulfuric acid as catalyst. In all three cases, a time-dependent minimum was observed in the content of III in the polymer (Fig. 2). This shows that the rate of cyclization from the monomers decreased earlier than the rate of polymerization, presumably since dimerization is a second-order reaction with respect to monomer while polymerization is of the first order. The later relative increase in the yield of III is attributed mainly to depolymerization which becomes noticeable with the slowdown in propagation resulting from monomer depletion. It is also evident from Table II that the composition of

TABLE II

Copolymerization of Chloral (I) with 1,3-Dioxalane (II) vs. Cyclization to 2-Trichloromethyl-1,3,5-trioxepane (III)[a]

Catalyst	Time	Yield, %	Polymer yield, %	Yield of III, %	III in total products, %	$\overline{M_n}$ total products (found)	$\overline{M_n}$ polymer (calc.)	Cl in total products (found), %	I in polymer (calc.), mole-%
0.2 mole-% H_2SO_4	10 days	53.1	20.7	32.4	61	341	2240	46.0	42.7
	28 "	62.0	27.3	34.7	56	372	2933	44.7	40.4
	52 "	72.4	27.5	44.9	62	338	2714	46.2	43.2
	142 "	73.4	27.2	46.2	63	—	—	—	—
0.02 mole-% $BF_3 \cdot$ether	17.5 hr.	50.7	32.1	18.7	37	412	852	43.8	41.2
	2 days	66.2	49.6	16.6	25	461	721	45.2	44.2
	6 "	79.4	58.7	20.7	26	396	552	44.8	43.6
	14 "	80.4	57.9	22.5	28	372	537	45.3	44.8
	118 "	83.6	57.7	25.9	31	—	—	—	—
0.02 mole-% $SbCl_5$	0.2 hr.	82.0	64.8	17.2	21	605	1140		
	5 "	83.3	58.3	25.0	30	497	1075		
	24 "	85.0	54.5	30.5	36	443	1016		
	48 "	88.7	55.2	32.5	37	468	1340		
0.004 mole-% $SbCl_5$	1 hr.	20.9	14.0	6.9	33	495	1264		
	3.7 "	45.2	35.3	9.9	22	540	906		
	6.3 "	75.9	56.9	19.0	25	605	1442		
	94 "	92.2	70.0	22.2	24	557	1070		

[a] Molar ratio I/II = 1; temp.: 5°C.; water content: 1.5%.

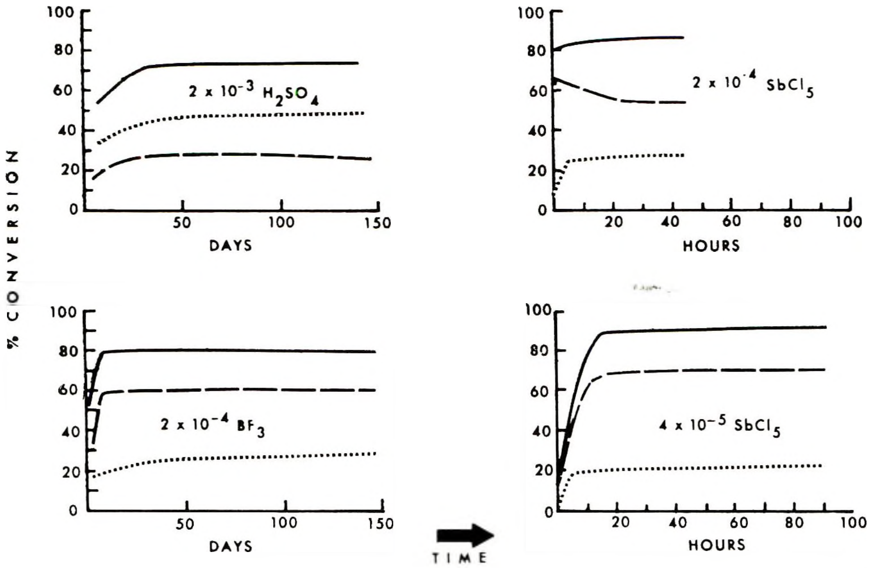


Fig. 1. Copolymerization of chloral-dioxolane (1.5% H_2O): (——) total yield; (- - -) linear; (· · ·) cyclic. Temperature, 5°C.; catalyst listed as mole/mole monomer.

the copolymer was independent of the type of catalyst, of overall conversion, and of molecular weights, which confirms an alternating copolymer composition.

The role of water in initiation and termination steps becomes apparent from examining Table III, which is based on the final samples of Table II. Table III shows that the moles of polymer chains produced per mole of catalyst was of the same order of magnitude as the molar ratio of water to catalyst except for the reaction catalyzed by sulfuric acid. The initiation, transfer, and termination by water in this copolymerization suggests the usual mechanism for cationic polymerizations of cyclic ethers or aldehydes.[12] However, this mechanism may have to be modified to include an explanation why copolymerizations of cyclic formals with chloral are possible but apparently not with other aldehydes.[3] The observed spontaneity of the copolymerization contrasts with the rather slow cationic homopoly-

TABLE III
Termination Process

Catalyst	Catalyst, mole-%	Molar ratio water/catalyst	Number of polymer chains/mole catalyst
H_2SO_4	0.2	45/1	5.6/1
BF_3·ether	0.02	450/1	260/1
$SbCl_5$	0.02	450/1	230/1
$SbCl_5$	0.004	2250/1	1820/1

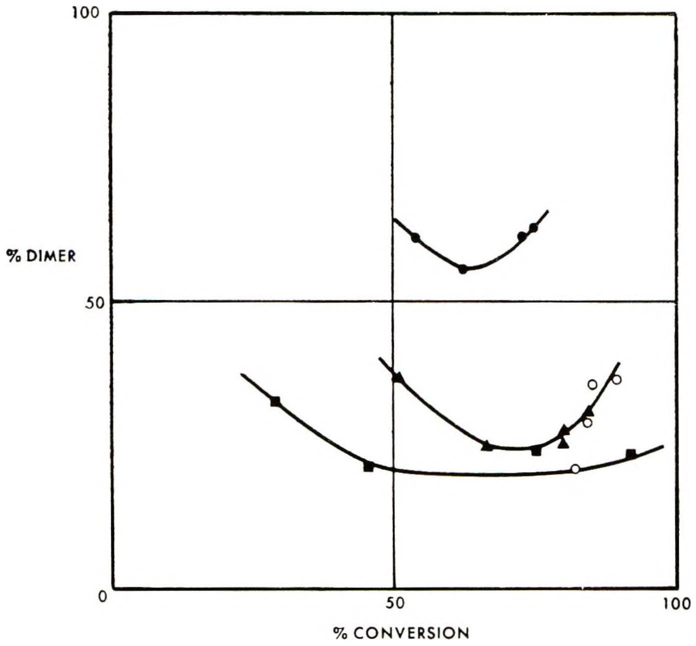


Fig. 2. Yield of dimer as a function of total conversion: (●) 2 × 10^{-3} H_2SO_4; (▲) 2 × 10^{-4} BF_3; (○) 2 × 10^{-4} $SbCl_5$; (■) 4 × 10^{-5} $SbCl_5$.

merization of chloral, especially with such catalysts as BF_3 or $SbCl_5$. The formation of chloral carbonium ions has been suggested as the rate-determining step in the propagation of the latter[1] as well as in the difficult syntheses or hydrolyses of acetals from chloral and alcohols.[5] Steric hindrance of the addition reaction of chloral to carbonium ions has been discounted as reason for its relative passivity towards electrophilic agents, as the same should apply to nucleophilic catalysts. This is not the case, since anionic polymerizations of chloral are quite rapid.[1] On first consideration, the absence of steric hindrance in an approaching formal carbonium ion would explain conveniently the ease of copolymerization. However, when the water content of equimolar mixtures of the comonomers was lowered to approach a truly anhydrous state, it was found that gradually less copolymerization occurred. Water-soluble crystalline poly-1,3-dioxolane with negligible chlorine content was isolated. This observation suggests that water or chloral hydrate is required for copropagation of chloral with formals. Other aldehydes except formaldehyde, which have not been reported to undergo copolymerization with cyclic formals, do not form stable hydrates. Therefore, it is likely that chloralhydrate rather than water participates in propagation. The nature of the propagating transition stage remains the subject of further research.

The probable absence of termination reactions not involving water was confirmed by meticulous extraction of two diols with petroleum ether. The functionalities of these copolymers, calculated from $\overline{M}_n$ and hydroxyl numbers were 1.85 and 2.10 hydroxyl groups per mole, respectively. No evidence for fluoro- or chloromethyl endgroups derived from catalyst decomposition was detectable by NMR, infrared, or mass spectroscopic techniques which, however, does not exclude their presence completely.

The hydroxyl endgroups may be of the alcohol or the hemiacetal type of either chloral or formaldehyde. It is likely that chloral hemiacetal endgroups predominated. This is indicated by the location and shape of the hydroxyl band (μ = 2.95) on the infrared spectrum of the diols which resembled that of chloral hydrate rather than of poly-1,3-dioxolane (μ = 2.80–2.90). Furthermore, a hydroxyl analysis with phthalic anhydride yielded only one-third of the value found with acetic anhydride. This may be attributed to reduced reactivity of chloral hemiacetal due to its more acidic hydroxyl group and to steric factors. The reduced activity of chloral hemiacetal endgroups towards esterification with phthalic anhydride was substantiated by hydroxyl determinations of chloral ethyl hemiacetal by both methods. With phthalic anhydride, no endpoint could be obtained in the titration, while a value of 285 (theoretical 290) mg. KOH/g. was found with acetic anhydride. Excess pyridine was used in both methods.

Additional proof for completeness of functionality of the diols was obtained by reacting them with diisocyanates to thermoplastic polyurethanes. In this case, the reactivity of the chloral hemiacetal seems not to be diminished since urethane formations have been observed.[13,14] The resulting polymers formed solutions of high viscosity, indicating high molecular weights. It was also attempted to chain extend a prepolymer, formed from one mole of diol with two moles of an 80/20 mixture of 2,4- and 2,6-toluene diisocyanate with 1,4-butanediol. However, partial decomposition during the curing stage of cast films prevented the preparation of faultless test specimens. Decomposition is thought to have occurred at formal–urethane linkages derived from formal hemiacetal-terminated diols. Such a structure has been reported to be thermally unstable.[15] It was established independently that decomposition was not due to thermal depolymerization by exposing diols to curing temperatures. The weight losses of the diols were found negligible, as expected from a polyacetal containing 1,4-dioxabutane units. Thermal stabilization of the polyurethanes was possible by chain-extending the prepolymers with 4,4′-methylenebis(2-chloroaniline) to yield clear, bubble-free films. The formal–urethane group is believed stabilized by the higher basicity and additional hydrogen bonding of the resulting urea linkages.

The cast films showed a tensile strength of 2300 psi and elongation of 215% and were self-extinguishing (ASTM D 568-61) when their chlorine content was above 25%.

EXPERIMENTAL

Analyses

The following instruments were used in spectral analyses: a grating infrared spectrometer from Perkin-Elmer, Model 521 for qualitative spectra; a Perkin-Elmer infrared spectrometer, Model 21 for quantitative analysis of the cyclic dimer; an NMR spectrometer from Varian, Model A-60. The molecular weights were determined in a vapor-pressure osmometer from Mechrolab, Inc., Model 302 (number-average molecular weight), Vapor-phase chromatography was carried out with a Beckman GC2A instrument. Hydroxyl numbers were determined in acetic anhydride.

Purification of Reagents

Highest purity chloral from Eastman was dried over 5 A. molecular sieves, distilled through a 12-in. Vigreux column and stabilized with 0.5% of hydroquinone. The 1,3-dioxolane was dried over calcium hydride, refluxed over sodium and distilled. During all operations and transfers a dry nitrogen atmosphere was maintained and glassware was flamed out.

Analysis of chloral showed 1.2% of chloroform, 0.8% of carbon tetrachloride, and 100 ppm H_2O (vapor-phase chromatography).

1,3-Dioxolane contained 0.4% of a low-boiling impurity, 0.2% of a high-boiling impurity (vapor-phase chromatography), and 15 ppm H_2O (Karl Fischer titration).

Reagent grade H_2SO_4, $SbCl_5$, and BF_3 etherate were used without further purification.

Technique of Polymerization Study

Flamed-out three-necked flasks (100–500 ml.), provided with stirrer, thermometer, nitrogen flush, and inlet for the reagents were used. The monomers were injected from syringes, the flask cooled to 5°C., and the catalyst injected. Samples (20–30 g.) were taken periodically, weighed, dissolved in 50 ml. diethyl ether and neutralized with triethanolamine. The ether solution was washed with 200 ml. water in a separatory funnel, the water layer was decanted and washed with 50 ml. ether. The ether layers were combined and evaporated in a rotary evaporator at 40°C. and 12 mm. Hg to constant weight. Linear polymer was thus recovered quantitatively. Losses in chloral–dioxolane dimer ranged from 2 to 5%. The mixture of linear copolymer and dimer was weighed and analyzed as such.

The amount of cyclic dimer was determined from the infrared spectrum of the mixture. The ratio of the absorption bands at 7.8 μ (dimer) and 8.05 μ (polymer) was used. Since Beer's law did not hold exactly, a calibration curve was made up for known mixtures, containing between 1 and 80% of the pure dimer in pure linear copolymer. The solvent was *o*-xylene in a 0.05 mm. sodium chloride cell.

Preparation of Pure Diol

Chloral (4 mole) and 1,3-dioxolane (4 mole) were mixed in a 1-liter three-necked flask and cooled to 5°C. Water (13.2 ml.) was added, and when the exothermic chloral hydrate formation was completed, BF_3 etherate (0.20 ml.) was added. An argon atmosphere was maintained over the reaction mixture while stirring. After 10 days, acetone (500 ml.) and triethanolamine (2 ml.) were added and the solution washed with water (three times, 1 liter). The aqueous layer was each time decanted and the polymer layer finally dried on a steam bath. The copolymer–dimer mixture (644 g., 74% conversion) was extracted in a liquid–liquid extractor with hexane. The mixture was stirred and kept at 50°C. during extraction for 14 days. The extracted copolymer was dried in a rotary evaporator (yield: 47% based on monomers); hydroxyl number: 141 mg. KOH/g.; number-average molecular weight: 836; calculated OH functionality: 2.10).

The infrared spectrum was quite similar to the spectrum of polychloral as described by Novak and Whalley.[1] In general, the chloral-dioxolane spectrum showed broader absorption areas than polychloral.

Additional absorption peaks at 6.9 and 8.5 μ and broad absorption regions between 9.3 and 10.2 μ were due to formal-type linkages. A band was visible at 2.9 μ, indicating hydroxyl endgroups.

The NMR spectrum showed the following absorptions: terminal OH: 4.58 ppm; $—O—C(CCl_3)H—O$: 5.05–5.32 ppm; $—OCH_2—O$: 4.75–5.05 ppm; and $O—CH_2—CH_2—O—$: 3.7–4.3 ppm.

The hexane extract was dried in a rotary evaporator (yield: 17%; m.p. 29°C.). A loss of 10% of material remained unaccounted for.

Preparation of 2-Trichloromethyl-1,3,5-trioxepane

Anhydrous chloral (29.4 g., 0.2 mole) and 1,3-dioxolane (14.8 g., 0.2 mole) were mixed at room temperature. Phosphorus pentafluoride gas (20 ml.) was injected from a syringe. After an exothermic reaction had subsided the sample was allowed to stand at room temperature for 72 hr. The resulting white cake was dissolved in 100 ml. dioxane, neutralized with $NaHCO_3$, washed twice in water, and decanted. The oily bottom layer was crystallized at 5°C.; yield: 36.5 g. (82.5%); m.p. 29.5–30°C.; b.p. 122–123°C./17 mm. Hg; n_D^{25} 1.4911.

ANAL. Calc'd. for $C_5H_7Cl_3O_3$: C, 27.1%; H, 3.17%; Cl, 48.1%; mol. wt. 221. Found: C, 27.38%; H, 3.18%; Cl, 47.85%; mol. wt. 266.

The infrared absorption spectrum revealed absence of C=O or OH groups. There was a sharp band at 7.8 μ and a broad band at 10.85 μ, both not present in linear copolymer. The nuclear magnetic resonance spectrum confirmed the structure.

2-Trichloromethyl-1,3,5-trioxepane by Depolymerization of Diol

Diol (28.2 g.), toluenesulfonic acid (1 g.), and anhydrous benzene (100 ml.) were refluxed for 2 hr. in a Dean-Stark apparatus, where 0.8 ml. of water were separated. Excess sodium bicarbonate was added to the warm solution for neutralization, filtered, and fractionated. The yield in 2-trichloromethyl-1,3,5-trioxepane was 23.2 g. (82.4%).

Preparation of Chloral–Dioxolane Urethane Film

Chloral dioxolane copolymer (30 g.) of molecular weight 836 and hydroxyl number 141 mg. KOH/g., tetrahydrofuran (30 ml.), and a 80/20 mixture of 2,4- and 2,6-tolylene diisocyanate (13.2 g.) were refluxed for 4 hr. under a nitrogen atmosphere. A solution of 4,4′-methylenebis(2-chloroaniline) (1.94 g.) in tetrahydrofuran (10 ml.) was added and the solution cast on glass plates, treated with a fluorocarbon release agent. After air drying for 3 days, a hard, tough sheet of film was obtained which was self-extinguishing (ASTM-D 568-61); elongation: 215%; tensile strength: 2300 psi.

The authors are indebted to Messrs. W. Harple, G. Vickers, and L. P. Carr for determining and interpreting spectral data and vapor-phase chromatography analyses and to Mr. G. Hurt for establishing a spectral method for the dimer determination.

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Résumé

Le chloral et des formals cycliques ont été polymérisés en présence de catalyseurs acides et de quantités contrôlées d'eau; on a obtenu ainsi des diols de composition variable et de poids moléculaire variable. Des oligomères cycliques ont été formés de façon irréversible comme produits secondaires au départ de monomères et ont également été obtenus par dépolymérisation. La condensation des diols avec les diisocyanates fournissait des polyuréthanes linéaires de résistance à la flamme améliorée.

Zusammenfassung

Chloral und cyclische Formale wurden in Gegenwart saurer Katalysatoren und kontrollierter Wassermengen zu Diolen verschiedener Zusammensetzung und verschiedenen

Molekulargewichtes copolymerisiert. Als Nebenprodukte wurden aus den Monomeren irreversibel cyclische Oligomere gebildet, diese wurden auch durch Depolymerisation erhalten. Kondensation der Diole mit Diisocyanaten lieferte lineare Polyurethane mit verbesserter Flammenbeständigkeit.

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High-Resolution NMR of Crosslinked Polymers: Effects of Crosslinked Density and Solvent Interaction*

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Synopsis

Measurements have been made of the dependence of nuclear magnetic resonance bandwidths of polymers on the degree of crosslinking. Poly(methyl methacrylates) and poly(hexadecyl acrylates) were studied. Three regions of behavior are apparent: (*1*) in lightly crosslinked materials, bandwidths are quite insensitive to the degree of crosslinking, and the networks behave almost as linear polymers in solution; (*2*) in moderately crosslinked material, bandwidths are significantly affected by the degree of crosslinking; and (*3*) in highly crosslinked materials, bandwidths are extremely sensitive to crosslink density, and the polymer peaks become so broad that they disappear almost completely. These results indicate that segmental motion of a polymer in solution is not a function solely of its molecular weight, and that a certain degree of crosslinking is required to restrict polymer motion at the segmental level. The solvent (benzene) peak is always a singlet in swollen poly(methyl methacrylate) systems with swelling ratios up to 6.4 (regions *1* and *2*, above) but as the swelling ratio further decreases to 3.5 (region *3*), the solvent peak splits into a doublet; this phenomenon may indicate the existence of two different arrangements of solvent molecules in the swollen network, for which interchange is not sufficiently rapid to produce a single line.

Introduction

The high-resolution nuclear magnetic spectra of polymers in solution in most cases exhibit broader absorption bands than those of small molecules; this is ascribed to the restricted segmental motion of the macromolecules.[1] In these systems, the line width dependence on variables such as molecular weight and concentration is not clear: Bovey[1] reports bandwidths of polystyrene are insensitive both to the degree of polymerization (20 to 10,000) and concentration (up to 50%); Ullman[2] describes a theoretical treatment indicating possible dependence on molecular weight of NMR spin-spin relaxation time, and in turn, the bandwidth of isolated polymer molecules; and Liu[3] observes a marked dependence of NMR bandwidth of poly(ethylene oxides) on molecular weight above a certain molecular weight and concentration, although this dependence vanishes completely in dilute solution.

* Presented at the 149th Meeting, American Chemical Society, Detroit, Michigan, April 1965.

This paper reports NMR line-broadening effects of swollen crosslinked polymers. Since translation and rotation are eliminated, NMR data of such swollen networks yield information on segmental motion of the chain and on solvent mobility, provided that the segments move reasonably rapidly so that high resolution spectra may be obtained; furthermore, since the molecular weight is infinite, any molecular weight effect would be accentuated in the present case. Polymers studied in this paper include syndiotactic poly(methyl methacrylate) (PMMA), conventional crosslinked poly(methyl methacrylate) (C-PMMA), conventional poly(hexadecyl acrylate) (PHA), and crosslinked poly(hexadecyl acrylate) (C-PHA).

Experimental

Soluble PMMA was obtained from the Rohm and Haas Company, Philadelphia. Crosslinked PMMA was synthesized at 80°C., in bulk, from redistilled, degassed monomer, α,α'-azobisisobutyronitrile being used as the radical initiator and ethylene glycol dimethacrylate as crosslinking agent; C-PHA polymers were prepared by ^{60}Co γ-radiation of the linear polymer at 30°C.[4] The crosslinked polymers were purified by extracting soluble polymer with benzene, and crosslink densities estimated from equilibrium swelling ratios.[5] Weight swelling ratios in benzene are 3.5, 6.4, 18, 23, 37, 75 for C-PMMA polymers and 8.5, 13.5, 14.9, 19.3, 23 for the C-PHA systems.

The solvents and polymers were stored in a nitrogen atmosphere, and degassed and sealed *in vacuo* prior to use. NMR spectra were obtained at 35°C. with a Varian A-60 spectrometer. Linewidths were measured in cycles per second. The widths given for the polymer proton are corrected for the linewidths of the solvent peak to compensate for any difference in spectrometer resolution or sample inhomogeneity.

Results and Discussion

Tables I and II summarize the data obtained from the NMR bandwidth measurements. Bandwidths of the polymers are quite insensitive to the degree of crosslinking when the swelling ratio is high; for C-PMMA of swelling ratios 37 and 75, the difference in bandwidths is less than 1 cps. It is evident from these data that lightly crosslinked networks behave as linear polymers in solution. As the crosslink density increases, mobility is reduced, and linewidth broadens markedly. If bandwidths are plotted versus swelling ratio (Fig. 1), a region is apparent in which the bandwidth is very sensitive to the degree of crosslinking: decreasing the swelling ratio of C-PMMA from 18 to 6.4 effects a bandwidth increase of about 15 cps, while a further decrease in swelling ratio to 3.5 results in a bandwidth increase of more than 100 cps. At this point, the high-resolution peaks of the polymer disappear almost completely. A broad NMR band at 120 cps is obtained for the highly crosslinked sample (C-PMMA, swelling ratio 3.5) only at the elevated temperature of 60°C.

TABLE I
NMR Data of Crosslinked Poly(methyl Methacrylate) at 35°C., in Benzene

Equilibrium swelling ratio	Measured swelling ratio	Bandwidth of ester methyl, cps	Bandwidth of backbone methyl, cps
3.5	3.5	>100	>100
6.4	6.4	21.5	30.5
18	18	9.5	15.5
23	23	6.4	12.4
23	18.5	6.6	13.4
23	12	7.4	14.6
23	8.35	8.1	15.1
23	5.4	9.9	15.9
23	3	10.9	16.9
37	37	4	11.5
75	75	3.7	10.7
∞	—	3.7	9

These results indicate that segmental motion of a polymer in solution, under ordinary conditions, is not a function solely of its molecular weight and that a certain degree of crosslinking is required to restrict polymer

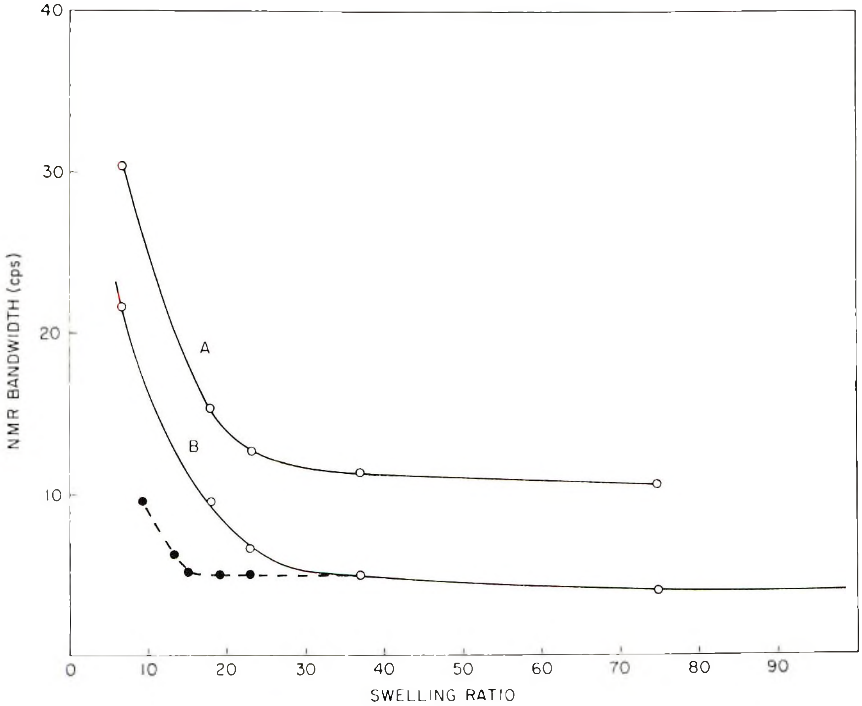

Fig. 1. Dependence of NMR linewidth on swelling ratio in benzene: (——) for crosslinked poly(methyl methacrylate) (the backbone α-methyl protons are represented by curve *A*, the ester methyl protons by curve *B*); (- - -) protons of the side chain group in poly(hexadecyl acrylate).

TABLE II
NMR Data of Crosslinked Poly(hexadecyl Acrylate) at 35°C., in Benzene

Equilibrium swelling ratio	Measured swelling ratio	Bandwidth of ester alkyl group, cps
8.5	8.5	9.5
13.5	13.5	6.4
14.9	14.9	5.0
19.3	19.3	5.0
23	23	5.0
∞	—	5.0

motion at the segmental level. While in this study, the crosslinking is via chemical bonds, crosslinks also may be formed temporarily through physical entanglements of linear polymer chains; the latter phenomena will be reported elsewhere.[3]

From Figure 1 it is seen that the NMR bandwidths of the ester methyl and the backbone α-methyl groups are about equally sensitive to the crosslink density. This may reflect the stiffening effect of a rigid PMMA chain on the ester methyl side group.

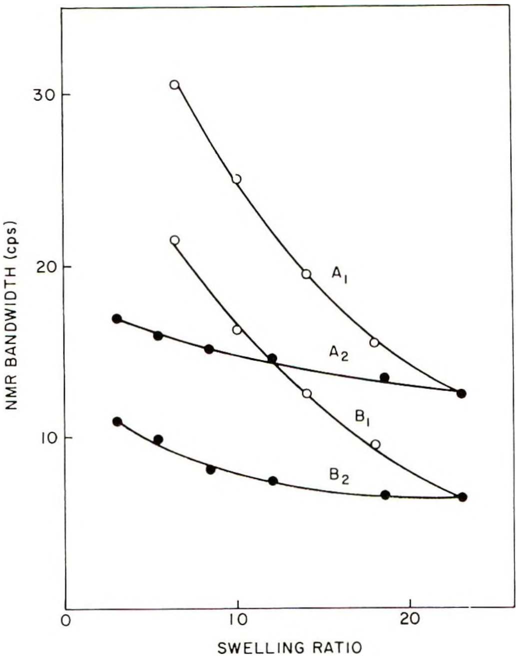

Fig. 2. Effect of swelling on NMR linewidths for crosslinked poly(methyl methacrylates) in benzene at indicated equilibrium swelling ratios (○); (●) NMR linewidths of a lightly crosslinked polymer (equilibrium swelling ratio of 23) swollen to the indicated points. The upper pair of lines (A_1 and A_2) represent the backbone α-methyl protons and the lower pair (B_1 and B_2) the ester methyl protons.

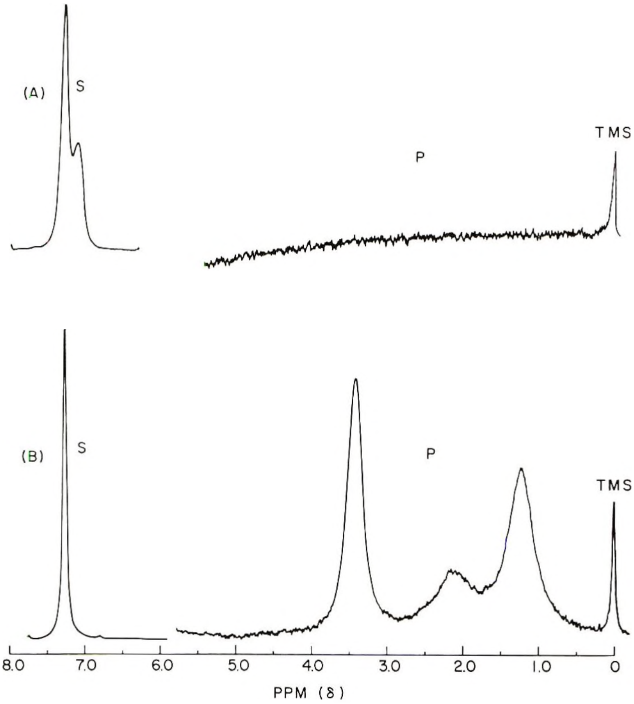

Fig. 3. Effect of crosslink density on the high resolution NMR spectra of poly(methyl methacrylates) and solvent benzene: (*A*) crosslinked polymer of maximum swelling ratio 3.5, swollen to its equilibrium value; (*B*) polymer of maximum swelling ratio 23, swollen to a swelling ratio of 3.5. Peaks S, P, and TMS are solvent, polymer, and reference absorption lines, respectively.

The backbone proton spectra of the C-PHA are complex, and only the bandwidth of the ester alkyl group was examined. Segmental motion in C-PHA, measured by ester alkyl bandwidths, is greater than that in C-PMMA at similar degrees of crosslinking, so higher crosslink densities are required to limit segmental mobility in C-PHA. Bandwidths of C-PMMA increase rapidly at swelling ratios less than 23; the bandwidth of the C-PHA increases rapidly only when the swelling ratio is less than 15.

Figure 2 compares partially swollen, lightly crosslinked C-PMMA (of equilibrium swelling ratio 23) with more densely crosslinked C-PMMA samples at their equilibrium swelling ratios. Bandwidths of the tightly crosslinked polymers (equilibrium swelling ratio less than 23) are broader than those of partially swollen loose networks (maximum swelling ratio, 23); at swelling ratios greater than 23, this behavior is not pronounced.

The solvent bandwidth, in comparison with the polymer, broadens very little: restriction of molecular motion of the solvent or sample inhomogeneity may cause bandwidth broadening. Although these effects cannot be separated at present, they are small and do not alter the qualitative picture of polymer bandwidths as a function of swelling ratio. We have treated the data conservatively by assuming that the latter phenomenon is responsible for broadening.

It is also significant that the solvent NMR peak is always a singlet in swollen polymer systems with swelling ratios up to 6.4, but as the swelling ratio further decreases to 3.5, the solvent peak splits into a doublet (Fig. 3). For comparison, the C-PMMA of maximum swelling ratio 23 was swollen to the same extent (3.5), and its spectrum shown in the same figure. These doublet solvent peaks may indicate the existence of two different arrangements of solvent molecules in the network, for which interchange is not sufficiently rapid to produce a single frequency. Some of the solvent molecules may interact strongly with the polymer, while others may be freely tumbling in the macrovoids likely to exist in highly crosslinked networks.[6] Since free solvent molecules are present, the migration mechanism of solvent through swollen crosslinked networks (such as cured paint films and semipermeable membranes) may be hydrodynamic flow, where the macroscopic flow rate is high and the semipermeability of the network is low.

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Résumé

Des mesures ont été effectuées concernant la dépendance de la largeur de bande de résonance nucléaire magnétique des polymères en fonction du degré ce pontage. On a étudié le polyméthacrylate de méthyle et le polyacrylate de hexadécyle. Trois régions de comportement sont nettes: (*1*) pour des matériaux faiblement pontés, la largeur de bande est pratiquement insensible aux degrés de pontage et les réseaux se comportent pratiquement comme des polymères linéaires en solution; (*2*) dans un matériau modérément ponté, la largeur de bande est affectée de façon significative par le degré de pontage; et (*3*) dans des matériaux hautement pontés, les largeurs de bande sont extrêmement sensibles à la densité de pontage et les pics des polymères deviennent si larges qu'ils disparaissent presque complètement. Les résultats indiquent que la mobilité segmentaire d'un polymère en solution n'est pas seulement une fonction de son poids moléculaire et qu'un certain degré de pontage est requis pour diminuer le mouvement polymérique au niveau segmentaire. Le pic du solvant (benzène) est toujours un singlet dans le système gonflé de polyméthacrylate de méthyle avec des rapports de gonflement jusque 6.4 (régions 1 et 2 ci-dessus). Mais lorsque le rapport de gonflement décroit plus fort jusque 3.5 (région 3), le pic du solvant se scinde en un doublet; ce phénomène peut indiquer l'existence de deux arrangements différents des molécules de solvant dans le réseau gonflé pour lequel l'interéchange n'est pas suffisamment rapide pour produire une ligne simple.

Zusammenfassung

Die Abhängigkeit der kernmagnetischen Resonanzbandenbreite von Polymeren vom Vernetzungsgrad wurde gemessen. Polymethylmethacrylate und Polyhexadecylacrylate wurden untersucht. Es treten drei Verhaltensbereiche auf: (1) bei schwach vernetzten Systemen ist die Bandenbreite gegen den Vernetzungsgrad ziemlich unempfindlich und das Netzwerk verhält sich fast wie ein lineares Polymeres in Lösung; (2) bei mässig vernetzten Systemen wird die Bandenbreite durch den Vernetzungsgrad deutlich beeinflusst und (3) bei hochvernetzten Systemen ist die Bandenbreite gegen die Vernetzungsdichte äusserst empfindlich und die Polymermaxima werden so breit, dass die sie fast völlig verschwinden. Diese Ergebnisse zeigen, dass die Segmentbewegung eines Polymeren in Lösung nicht bloss eine Funktion seines Molekulargewichtes ist und dass zur Einschränkung der Polymerbewegung auf der Segmentstufe ein gewisser Vernetzungsgrad erforderlich ist. Das Lösungsmittelmaximum (Benzol) ist in gequollenen Polymethylmethacrylatsystemen mit Quellungsgraden bis zu 6,4 (die oben angegebenen Bereiche 1 und 2) immer ein Singulett, bei weiterer Abnahme des Quellungsgrades auf 3,5 (Bereich 3) spaltet sich aber das Lösungsmittelmaximum in ein Dublett; diese Erscheinung spricht für ein Bestehen zweier verschiedener Anordnungen der Lösungsmittelmoleküle im gequollenen Netzwerk, zwischen welchen der Austausch nicht genügend rasch ist, um eine einzige Linie zu erzeugen.

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Radiation-Induced Bulk Polymerization of Maleimide

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Synopsis

Radiation-induced bulk polymerization of maleimide in both solid and liquid states was studied. Benzoquinone inhibited the liquid-state polymerization and retarded solid-state polymerization. The results of ESR study showed that solid monomer irradiated at 61°C. gave a spectrum, the concentration of which slowly decreased without changing the shape at 61°C. The radical detected at 61°C. was shown not to be the main propagating species. Overall rate polymerizations in the liquid and solid states were expressed, respectively, by first-order and zero-order rate equations with respect to the concentration of monomer. The overall rate constants in liquid and solid states were proportional to $I^{0.9}$ and $I^{1.0}$, respectively.

INTRODUCTION

The polymerizations of maleimide and its derivatives by free-radical initiators[1-5] and anionic catalysts[3,6,7] have been studied by several groups of workers. We have already reported[8] that maleimide polymerized in both liquid and solid states with γ-ray irradiation and that in both states post-polymerization was not observed.

In this paper, results of a further detailed study of radiation-induced bulk polymerization of maleimide are presented.

EXPERIMENTAL

Materials and Polymerization Procedure

Preparative and purification procedures of maleimide were same as reported in the previous paper.[8] Benzoquinone (G.R. grade) and AIBN (G.R. grade) were used without purification. Procedures of polymerization and separation of polymer from the reaction mixture were also same as previously reported.

Irradiation Conditions

Irradiations were performed at Sumitomo Atomic Energy Industries, Ltd., with a ^{60}Co source (5000 curies) in the dose rate range from 1.3×10^4 to 1.7×10^5 rad/hr. and to total doses of 6.3×10^3 to 4.1×10^6 rad. Irradiation temperature was over the range of −196 to 100°C.

ESR Spectrum Measurement

The ESR spectrum was measured with the use of a Japan Electron Optics ESR spectroscope (Model JES-3B). Estimation of the amount of radicals from the intensity of the ESR spectrum was made with the use of a benzene solution of DPPH (10^{-3} mole-%) as a standard.

RESULTS AND DISCUSSION

Nature of Propagating Species

Since maleimide is polymerized in solution with both radical initiator and anionic catalyst, the polymerization by γ-rays may proceed either by a free-radical or by an anionic mechanism. In order to determine the nature of the propagating species, the influence of benzoquinone on polymer yield was studied. The results are summarized in Table I.

TABLE I
Influence of Additives on Polymer Yield[a]

Benzoquinone, mg.	Irradiation temperature, °C.	Irradiation time, hr.	Polymer yield, wt.-%	Phase
6.8	100	1.0	0.0	Liquid
None	100	1.0	53.0	Liquid
9.5	86	24	6.3	Solid
None	86	24	25.6	Solid

[a] Conditions: dose rate, 1.7×10^5 rad/hr.

As shown in Table I, in the liquid state no polymerization occurred in the presence of the radical scavenger (benzoquinone). This result suggests that the polymerization of maleimide in liquid state proceeds by a free-radical mechanism.

Polymerization in the solid state was considerably retarded by the addition of benzoquinone. In addition, the study of the solid-state polymerization initiated by AIBN confirmed that a free radical was capable of propagation in the solid state.[10] These results suggested that the γ-ray-induced polymerization in the solid state proceeded at least partially by a free-radical mechanism.

Electron Spin Resonance of Irradiated Monomer

It was already reported[8] that the product obtained from solid monomer irradiated at 0°C. gave a ESR spectrum, whereas that from solid monomer irradiated at 85°C., under which condition polymerization occurred, did not give a detectable ESR spectrum.

Solid monomer irradiated at −196°C. for 20 hr. at a dose rate of 1.7×10^5 rad/hr. gave the spectrum as shown in Figure 1. The shape of the spectrum gradually changed with warming the sample (Fig. 1*A* → Fig. 1*D*).

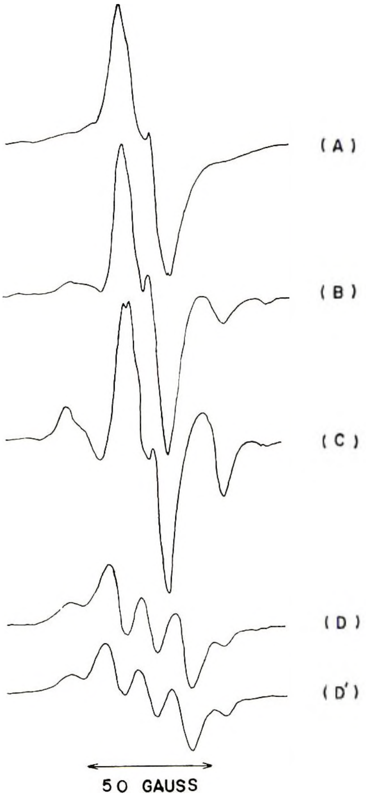

Fig. 1. Change in the ESR spectrum of irradiated monomer with warming: (*A*) at −196°C.; (*B*) at −78°C.; (*C*) at 0°C.; (*D*) at 60°C. after 24 hr. at 60°C. Wavelength of spectroscope, 3.16 cm.; frequency of the main magnetic field, 100 kc./sec.

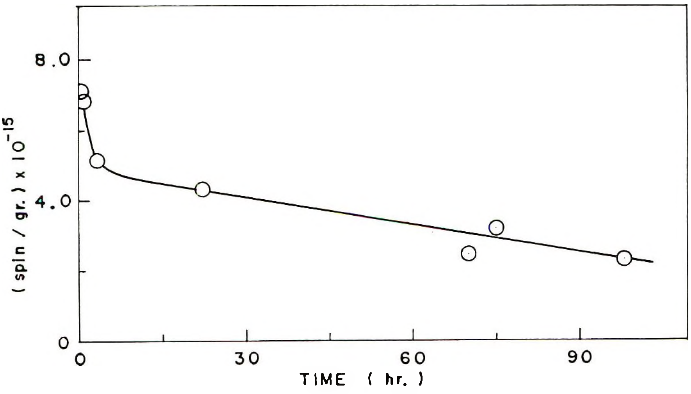

Fig. 2. Change of the concentration of radicals after stopping the irradiation. Conditions of irradiation: dose rate, 1.7 × 10^5 rad/hr.; irradiation temperature, 61°C.; irradiation time, 22 hr.; conditions after irradiation: temperature, 61°C.

The quantity of radicals produced by γ-ray irradiation scarcely changed below −80°C., whereas it gradually decreased above −80°C. The concentration of the radicals was observed to be 1.8×10^{17}/g. at −196°C. and decreased to 1.5×10^{16}/g. after the sample was kept at 60°C. for 24 hr. The shape of the spectrum (Fig. 1*D*) did not change above 60°C., and the spectrum gradually decayed with time; it almost disappeared after the sample was kept at 70°C. for 24 hr. The spectrum (Fig. 1*D*) decayed only slightly when the sample was allowed to stand several days at room temperature or when air was introduced into the sample. These results indicate that the radical detected at 60°C. was very stable. Solid monomer irradiated at 61°C. for 22 hr. at a dose rate of 1.7×10^5 rad/hr. gave a spectrum (Fig. 1*D′* which was very similar to the spectrum shown in Figure 1*D*). The concentration of the spectrum decreased slowly as the sample was allowed to stand at 61°C., as shown in Figure 2, while the shape did not change.

The experimental results of the post-polymerization at 61°C. with a dose rate of 1.7×10^5 rad/hr. are summarized in Table II. Post-polymerization at 61°C. for 22 hr. was slight. On the other hand, as shown in Figure 2, about half of the radicals remained after storing the sample at 61°C. for 30 hr.

TABLE II
Post-Polymerization at 61°C.

Irradiation[a] temperature, °C.	Conditions after irradiation		Polymer yield, wt.-%
	Temperature, °C.	Time, hr.	
61	—	—	6.2
61	61	22	6.9
−78	61	22	0.4

[a] Conditions: irradiation time, 22 hr.; dose rate, 1.7×10^5 rad/hr.

The results of the measurements of ESR spectrum and polymerization suggest that the stable radical detected at 61°C. is not the main propagating species.

Influence of Irradiation Time on Polymer Yield

Figures 3 and 4 show the influence of irradiation time on polymer yield of solid- and liquid-state polymerizations with various dose rates. The overall rate of solid-state polymerization at a dose rate of 1.7×10^5 rad/hr. at 86°C. is shown to be independent of irradiation time up to a conversion of 40 wt.-%, i.e., it follows the zero-order rate equation with respect to the concentration of monomer. Under different polymerization conditions, a linear relationship between polymer yield and irradiation time was also observed up to a conversion of about 10 wt.-%. On the other hand, the time–conversion curve of liquid-state polymerization was S-shaped. This

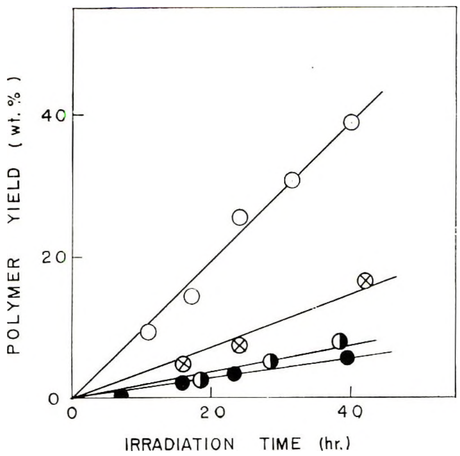

Fig. 3. Time–conversion curve of solid-state polymerization (○) 1.7 × 10⁵ rad/hr., 86°C.; (●) 1.7 × 10⁴ rad/hr., 61°C.; (⊗) 7.0 × 10⁵ rad/hr., 86°C.; (◑) 2.5 × 10⁴ rad/hr., 86°C.

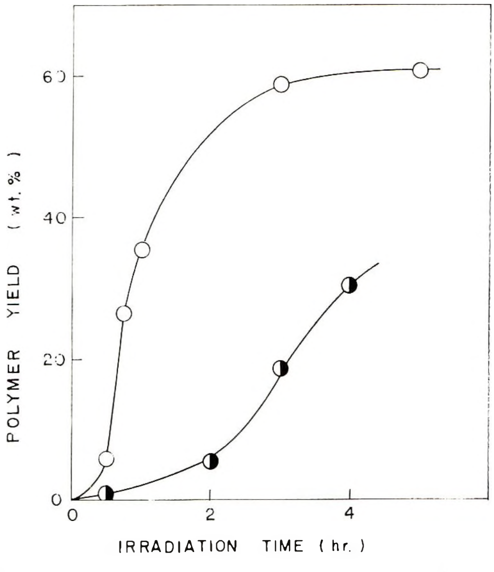

Fig. 4. Time–conversion curve of liquid-state polymerization at 100°C.: (○) 1.7 × 10⁵ rad/hr.; (◑) 1.3 × 10⁴ rad/hr.

type of the time–conversion curve has been observed either in polymerizations which have an induction period caused by impurity in the monomer, or in polymerization in which long-lived propagating species exist. Since this polymerization has been found not to show a post-effect,[8] it is suggested that the behavior of the conversion curve be attributed to a small amount of impurity in the monomer.

In order to exclude traces of air in the monomer crystal, further careful degassing was performed by melting the monomer under vacuum after the usual degassing process. The careful degassing increased the rate of liquid-state polymerization in the early stage, as shown in Figure 5. We concluded, therefore, that the S-shaped curve in Fig. 4 resulted from the retardation of free-radical type polymerization by traces of oxygen in the early stage of polymerization.

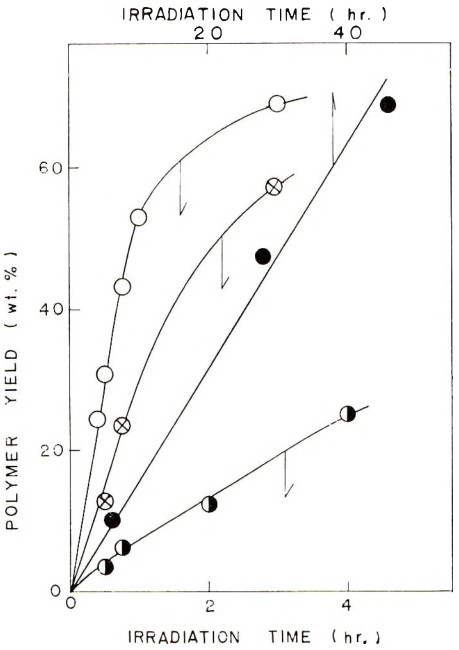

Fig. 5. Time–conversion relationship under carefully degassed conditions: (○) 1.7 × 10^5 rad/hr., 100°C.; (●) 1.7 × 10^5 rad/hr., 86°C.; (⊗) 4.6 × 10^4 rad/hr., 100°C.; (◑) 1.3 × 10^4 rad./hr., 100°C.

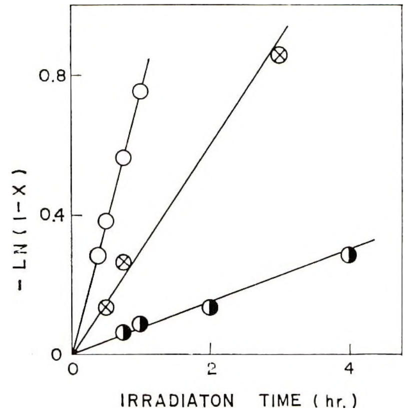

Fig. 6. Plot of $-\ln(1 - X)$ vs. irradiation time in liquid-state polymerization at 100°C. under carefully degassed conditions: (○) 1.7 × 10^5 rad/hr.; (⊗) 4.6 × 10^4 rad/hr.; (◑) 1.3 × 10^4 rad/hr.

The careful degassing process also increased the rate of solid-state polymerization, but the time–conversion relationship remained linear, as shown in Figure 5. This increase in the polymerization rate is suggested to be caused by the complete degassing, or by a change in crystallite size.

As seen in Figure 6, $-\ln(1 - X)$ (where X is conversion) was approximately proportional to irradiation time in the liquid-state polymerization up to a conversion of about 60% with carefully degassed monomer. This result shows that the overall rate of liquid-state polymerization could be approximately expressed by a first-order rate equation with respect to the concentration of monomer.

Kinetics of Liquid-State Polymerization

The overall rate is approximately equal to the propagation rate R_p, which is given by the equation:

$$R_p = k_p[\mathrm{P}^*][\mathrm{M}]$$

where k_p is the propagation rate constant and $[\mathrm{P}^*]$ is the concentration of propagating radical. R_p observed was expressed by a first-order rate equation with respect to $[\mathrm{M}]$, as was mentioned above. This result indicates that $[\mathrm{P}^*]$ was independent of reaction time, and that a steady-state treatment could be applied to the propagating radical. This observation is consistent with the result previously reported that the life of the propagating species is short.[8]

It is known that the overall rate of free-radical polymerization, in which steady-state treatment is applicable to the propagating radical, is always proportional to $I^{0.5}$ when mutual termination of propagating radicals prevails. The overall rate constant evaluated from Figure 6 was found to be proportional to $I^{0.9}$, as is shown in Figure 7. This result indicates that termination, whose rate was proportional to $[\mathrm{P}^*]$, prevailed.

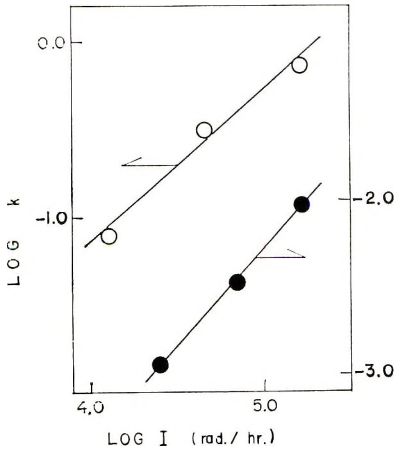

Fig. 7. Log-log plots of the overall rate constants vs. dose rate: (○) liquid state (100°C.); (●) solid state (86°C.).

Kinetics of Solid-State Polymerization

Since the life of the propagating species of this polymerization was found to be short,[8] a steady state with respect to the propagating species is considered to be realized. The overall rate, which is nearly equal to R_p, was found to be independent of reaction time in spite of the consumption of the monomer. This result indicates that the rate of propagation in the solid state can be expressed by the equation $R_p = k_p(\mathrm{P}^*)$, where (P^*) denotes the moles of propagating species. The overall rate constant evaluated from Figure 3 was found to be proportional to dose rate, as is shown in Figure 7. This result indicates that the termination rate was proportional to (P^*).

Post-Effect in Solid-State Polymerization

In most radiation-induced solid-state polymerizations which proceed by a radical mechanism it has been observed that post-polymerization occurred and that the rate of in-source polymerization was proportional to dose rate. These results have been adequately interpreted by the slow mutual termination.[11]

In this solid-state polymerization, however, no post-effect was observed, while the overall rate was proportional to dose rate. The former result indicates the occurrence of rapid termination, and the latter result indicates the insignificance of the mutual termination. The rapid first-order termination may be ascribed to either of the following two terminations: (*1*) degradative transfer or (*2*) termination with stable radicals which do not serve as initiators.

In connection with the above, it was reported that *N*-substituted maleimides such as *N*-phenylmaleimide (m.p. 90°C.)[9] and *N*-butyl maleimide (m.p. ca. 20°C.) exhibited the post effect.[10] Absence of a post-effect for maleimide, therefore, indicates that a degradative transfer might occur by producing a maleimidyl radical (*N*-maleimide radical). The result of the ESR study mentioned previously might imply the occurrence of termination with stable radicals produced by γ-irradiation. A further detailed study on the mechanism of termination will be reported in the near future.

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Résumé

La polymérisation en masse induite par radiation du maléimide à l'état liquide et solide a été étudiée. La benzoquinone inhibait la polymérisation à l'état liquide, et retardait la polymérisation à l'état solide. Le résultat d'une étude ESR montrait que le monomère solide irradie à 60°C. donnait un spectre de radicaux don la concentration décroissait lentement sans changer leur forme à 61°C. Le radical détecté à 61°C, n'était pas l'espèce propagatrice habituelle. Les vitesses de polymérisation globales aux états liquide et solide sont exprimées repectivement par des équations de premier ordre et d'ordre zéro en ce qui concerne la concentration en monomère. Les constantes de vitesse globale aux états solide et liquide sont proportionnelles à l'exposant $I^{0.9}$ et $I^{1.0}$ respectivement.

Zusammenfassung

Die strahlungs-induzierte Polymerisation von Maleinimid in Substanz im festen und flüssigen Zustand wurde untersucht. Benzochinon verhinderte die Polymerisation in flüssiger Phase und verzögerte sie in fester Phase. Die Ergebnisse einer ESR-Untersuchung zeigten, dass festes, bei 61°C bestrahltes Monomeres ein Spektrum lieferte, dessen Intensität ohne Gestaltsänderung bei 61° langsam abnahm. Das bei 61°C gefundene Radikal war nicht mit der wachsenden Hauptspezies identisch. Die Bruttogeschwindigkeit der Polymerisation in flüssiger und fester Phase konnte durch einen Geschwindigkeitsausdruck erster Ordnung in Bezug auf die Monomerkonzentration dargestellt werden. Die Bruttogeschwindigkeit war in flüssiger Phase proportional zu $I^{0.9}$ und in fester Phase zu $I^{1.0}$.

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Radiochemical Determination of Low Unsaturations in Polyisobutene. Stoichiometry of the Reaction Between Chlorine and Branched Double Bonds

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Synopsis

In a previous paper, the radiochemical determination of low unsaturation in polyisobutene was effected by reacting radiochlorine with the double bonds. The reaction is one of substitution rather than addition, and the derivation of true unsaturation values required an assumption to be made regarding the number of chlorine atoms (one or two) incorporated per double bond. In this paper the assumption is tested by examining the stoichiometry of the chlorination of suitable model compounds of known or measurable unsaturation under the experimental conditions used previously. It is found that reaction leads to a monochloro product rather than the dichloro product previously assumed. Conclusions regarding the chain termination process in isobutene polymerization are re-examined in the light of this result.

INTRODUCTION

It has been shown in a previous paper[1] that polyisobutene prepared in methylene chloride solution at −78°C. with stannic chloride as catalyst exhibits unsaturation only at the chain ends. The number of double bonds per chain was estimated by reaction with radiochlorine. In considerations of the mechanism of chlorination, polyisobutene may be regarded as a substituted olefin, $R_1CH_3C{=}CH_2$, or possibly $R_1CH{=}C(CH_3)_2$. The chlorination of olefins may proceed by free-radical or ionic mechanisms and may give addition or substitution products, depending on the structure of the olefin and the chlorination conditions employed. An ionic substitution reaction to give the monochloro product is predominant for branched olefins such as isobutene, which has been the subject of numerous investigations;[2-6] the main product of chlorination is methylallyl chloride (93%). The effect of various parameters on the mechanism has recently been investigated by Poutsma;[6-8] in general, the dark chlorination of olefins in the absence of solvent is predominantly ionic for olefins having at least two alkyl groups substituted at one end of the double bond. Dilution of the olefin in a nonpolar solvent was found to favor the ionic pathway.

It is to be expected, therefore, that the chlorination of polyisobutene in carbon tetrachloride solution[1] would follow the substitution mechanism.

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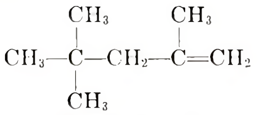
Owing to the relatively high chlorine concentrations used in this work as compared to the above mechanistic studies, however, further reaction of the monochloro product with excess chlorine must be considered.[2]

The chlorination of olefins can be followed by constructing curves of the amount of chlorine incorporated in the olefin for a fixed reaction time against chlorine concentration in the reaction mixture.[1,9] The curves show a distinct break, and the derivation of unsaturation values depends upon this break corresponding to the endpoint of a stoichiometric reaction. McNeill[9] found that for butyl rubber chlorination, the reaction consisted of the stepwise incorporation of two chlorine atoms per double bond, and this stoichiometry was assumed in the derivation of the polyisobutene unsaturations,[1] since the double bond structures in the two systems are comparable. The results obtained indicated approximately 0.5 double bond per chain, which suggests that not all chain-terminating reactions in the polymerization result in a terminal double bond. Although this can be accounted for in terms of anion capture processes,[1] it is clearly desirable to resolve the uncertainty by testing the validity of the above assumption. This has now been done by chlorinating model compounds for the unsaturated structures present in polyisobutene, the unsaturations of which were either known or could be determined by other methods.

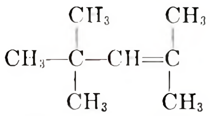
EXPERIMENTAL

The unsaturated compounds studied were diisobutene, two isomers: 2,4,4-trimethyl pent-1-ene (I) and 2,4,4-trimethyl pent-2-ene (II) (both from Koch-Light Laboratories Ltd.), triisobutene, 2,4,4,6,6-pentamethyl hept-1-ene (III) (kindly made available by Dr. J. D. Burnett, I.C.I. Ltd., Plastics Division),



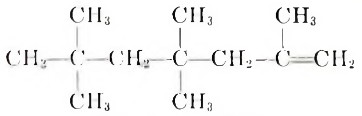
$$CH_3{-}C(CH_3)_2{-}CH_2{-}C(CH_3){=}CH_2$$

Diisobutene (I)



$$CH_3{-}C(CH_3)_2{-}CH{=}C(CH_3)_2$$

Diisobutene (II)



$$CH_3{-}C(CH_3)_2{-}CH_2{-}C(CH_3)_2{-}CH_2{-}C(CH_3){=}CH_2$$

Triisobutene (III)

and low molecular weight polyisobutene, oligomeric material, number-average molecular weight <1000, obtained[10] from the thermal degradation of a polyisobutene of molecular weight 100,000.

The olefinic materials were chlorinated as solutions of approximately 10 mg. of dimer or trimer, or 30 mg. of low molecular weight polymer, respectively, in 15 ml. of A.R. carbon tetrachloride, by use of the apparatus and techniques previously described.[1] After 3 hr. reaction in the dark at 25°C., radioactive impurities (Cl_2 and HCl) were removed by repeated extraction of the organic solution with aqueous sodium thiosulfate.[9] 10-ml. portions of the purified solutions were counted, and the chlorine content of the product was calculated by using the known specific activity of the chlorine supply.

The molar unsaturation of the low molecular weight polyisobutene was estimated by the iodine–mercuric acetate method of Gallo et al.[11]

RESULTS

The chlorination results for the low molecular weight polymer are given in Table I and Figure 1. The results of the iodine–mercuric acetate determination of molar unsaturation are given in Table II. The results for chlorination of the diisobutene isomers and triisobutene are collected in Table III and illustrated in Figure 2.

TABLE I
Chlorination of Low Molecular Weight Polyisobutene[a]

Cl in reaction mixture, wt.-%	Counts/min. for 10 ml. solution	Polymer in 10 ml. solution, mg.	Cl in polymer, mg.	Cl in polymer, wt.- %
23.05	753	21.0	1.273	5.71
19.20	711	21.0	1.200	5.42
14.72	691	21.0	1.170	5.29
7.69	588	21.0	0.995	4.55

[a] Specific activity of chlorine (CCl_4 soln.) = 591 counts/min./mg. Cl.

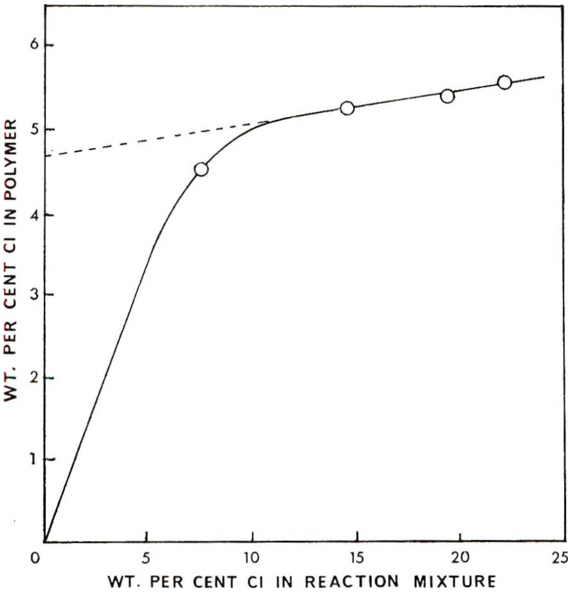


Fig. 1. Chlorination of low molecular weight polyisobutene.

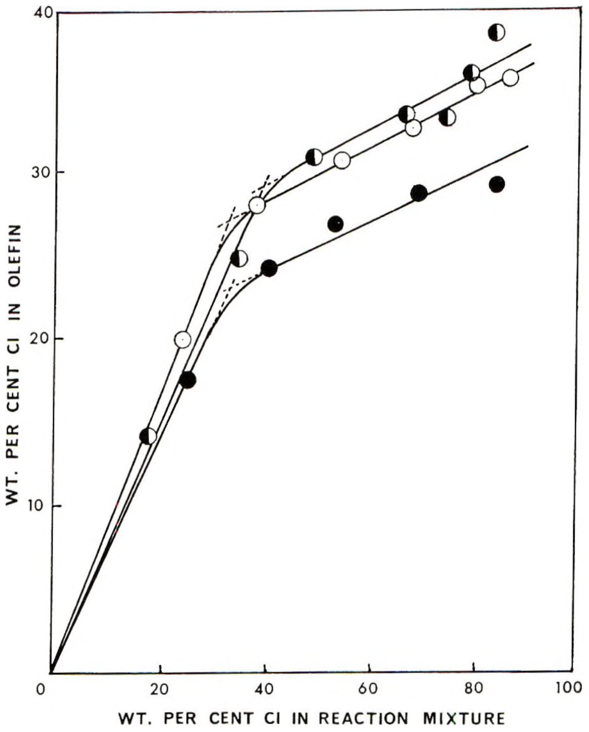


Fig. 2. Chlorination of (◐) diisobutene (I), (⊙) diisobutene (II), and (●) triisobutene.

TABLE II
Unsaturation of Low Molecular Weight Polyisobutene by the Iodine–Mercuric Acetate Method

Sample	Polymer in solution, mg.	Titer, ml.	Blank, ml.	Unsaturation, mole-%
1	94.5	19.34	22.74	6.72
2	90.5	21.34	24.50	6.50

DISCUSSION

Low Molecular Weight Polyisobutene

It is evident from Figure 1 that, as found previously for high molecular weight polyisobutene,[1] the gradient of the linear portion following the break in the chlorination curve is small. The weight per cent unsaturation,[1] U_W, was determined as for the high molecular weight samples by extrapolating this linear portion to the vertical axis. This gives U_W equal to 4.75.

The relationship between the weight per cent unsaturation and the mole per cent unsaturation, U_M, is

$$U_M = U_W M_1/35.5x$$

where M_1 is the molecular weight of the unsaturated chain unit (i.e., the monomer molecular weight) and x is the number of chlorine atoms incorporated in the olefin per double bond. By substituting the mean value of U_M from the iodine–mercuric acetate unsaturation determinations (Table II) and $U_W = 4.75$, it is found that $x = 1.14$. In view of the fact that the iodine–mercuric acetate method has been found to give about 80–100% of the true unsaturation for compounds with this type of branched double bond structure,[11] it can be concluded that the true value of x is close to unity.

TABLE III

Chlorination of Diisobutene and Triisobutene[a]

	Cl in reaction mixture, wt.-%	Counts/minute, 10 ml. solution	Cl in product, wt.-%
Diisobutene (I)	18.6	522	13.6
	34.7	1120	24.7
	50.7	1532	30.9
	67.5	1650	33.2
	74.4	1651	32.8
	79.2	1890	35.8
	84.0	2137	38.6
Diisobutene (II)	25.0	808	19.8
	37.9	1244	27.8
	54.8	1402	30.6
	68.2	1550	32.5
	80.0	1770	35.5
	85.6	1788	35.7
Triisobutene (III)	26.2	693	17.8
	39.7	1009	24.0
	53.2	1170	26.8
	69.0	1284	28.7
	82.7	1295	28.9

[a] Specific activity of chlorine (CCl_4 soln.) = 474 counts/min./mg. Cl.

Diisobutene Isomers and Triisobutene

It can easily be calculated that for the incorporation in the dimer of one and two atoms of chlorine by substitution, the Cl in the product would be 24 and 39 wt.-%, respectively. Similarly, the incorporation of one and two atoms of chlorine in the trimer would give Cl values of 17.5 and 30 wt.-%. The observed results are collected in Table III and illustrated in Figure 2. In contrast to the polymer chlorinations, the curves show a steeply inclined slope beyond the break. Owing to the steepness of the gradient, extrapolation to the axis was not justified; two linear portions are clearly defined, however, and the weight per cent unsaturation was calculated (as in the case of butyl rubber chlorination[9]) by extrapolating these to an intersection.

The weight per cent unsaturation values obtained from Figure 2 are 28 for diisobutene (I), 27 for diisobutene (II), and 22 for the trimer. These values are about 13 and 25% higher than the theoretical values for the incorporation of one Cl atom per double bond in dimer and trimer, respectively, and clearly fall very far short of the theoretical values for two Cl atoms per double bond.

For the reaction of chlorine by substitution to give the monochloro product, it would be expected that in the region of Figure 2 where there is an excess of olefin in the reaction mixture (i.e., before the break in the curve) 50% of the available chlorine would enter the olefin. In fact, the amount is greater. This is an indication either that the procedure for removal of radioactive impurities from the product was not completely efficient (the amount of such material to be removed is very much greater than in the case of the polymer experiments), or that some side reaction, such as addition, is occurring to a small extent.

As in the experiments on low molecular weight polyisobutene, therefore, the results for the dimer and trimer point unequivocally to the fact that the break in the chlorination curve corresponds to completion of reaction to give the monochloro product.

TABLE IV
Unsaturation of High Molecular Weight Polyisobutene[a]

Polymer	$\bar{M}_n$	U_W	U_M	No. of double bonds per chain
IB 1	45,700	0.085	0.134	1.09
IB 2	49,100	0.078	0.123	1.08
IB 3	40,500	0.089	0.140	1.01
IB 4	100,000	0.049	0.080	1.43
F 1	376,000	0.012	0.018	1.21
F 2	190,000	0.026	0.040	1.36
F 3	125,000	0.036	0.056	1.25
F 4	77,000	0.052	0.082	1.13
F 5	32,000	0.128	0.202	1.15

[a] See McGuchan and McNeill.[1]

High Molecular Weight Polyisobutene

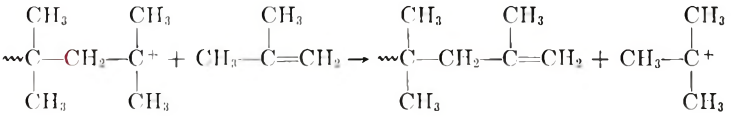
It is clear from the foregoing discussion that the assumption made in the derivation of molar unsaturations in high molecular weight polyisobutenes[1] was unsound, and that the unsaturated structures in polyisobutene and butyl rubber behave differently towards chlorine. The reason for this difference is not understood. When the results are recalculated on the basis of the incorporation of one chlorine atom per double bond, the data of Table IV are obtained.

The measured unsaturations are close to one double bond per chain. The biggest deviation from unity occurs with the higher molecular weight samples, for which the accuracy of the radiochemical method is at its lowest.

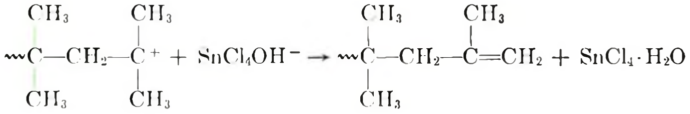
The fact that the samples show a mean value of 1.19 chlorine atoms per chain is probably an indication that side reactions such as addition of chlorine are occurring to a small extent. It may readily be shown by plotting U_M against the reciprocal of the molecular weight[1] that the conclusion that unsaturation is exclusively terminal remains unaltered.

Since the true unsaturation is close to one double bond per chain, it follows that the main chain-breaking reaction during the cationic polymerization of isobutene is proton transfer. Termination by capture of a hydroxyl group from the anionic catalyst residue does not occur under the polymerization conditions used. Transfer reactions leading to the formation of saturated endgroups derived from the solvent are also unimportant in this system.

Proton transfer could be accomplished by transfer to monomer (1) or by the termination reaction (2):



$$\sim\!\!\sim\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C^{+}}} + CH_3{-}\overset{CH_3}{C}{=}CH_2 \rightarrow \sim\!\!\sim\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2{-}\overset{CH_3}{C}{=}CH_2 + CH_3{-}\underset{CH_3}{\overset{CH_3}{C^{+}}} \qquad (1)$$



$$\sim\!\!\sim\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C^{+}}} + SnCl_4OH^{-} \rightarrow \sim\!\!\sim\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2{-}\overset{CH_3}{C}{=}CH_2 + SnCl_4\cdot H_2O \qquad (2)$$

The present study does not distinguish the two mechanisms of double-bond formation, but it does give quantitative support to the conclusions of Norrish and Russell[12,13] that every chain-breaking reaction results in the formation of a terminal double bond.

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Résumé

Dans une publication précédente, la détermination radiochimique de la faible insaturation au sein de polyisobutylène était réalisée par réaction du chlore radioactif avec les doubles soudures. La réaction est une réaction de substitution plutôt que d'addition et l'obtention de vraies valeurs d'insaturation nécéssitait l'hypothèse en ce qui concerne le nombre de atomes de chlore (un ou deux) incorporés par double liaison. Dans ce manuscrit, l'hypothèse est testée en examinant la stoèchiométrie de la chloration de composés modèles correspondants dont l'insaturation est connue ou mesurable dans les conditions expérimentales utilisées précédemment. On a trouvé que la réaction mène à un produit monochloré plutôt qu'aux produits dichlorés prévus précédemment. Les conclusions concernant le processus de terminaison de chaîne dans la polymérisation de l'isobutène sont dès lors réexaminées sur la bare de ce nouveau résultat.

Zusammenfassung

In einer früheren Arbeit wurde die radiochemische Bestimmung eines niedrigen Doppelbindungsgehaltes in Polyisobuten durch Reaktion von Radiochlor mit den Doppelbindungen bewerkstelligt. Diese Reaktion ist mehr eine Substitutionsreaktion als eine Additionsreaktion und die Gewinnung wahrer Doppelbindungsgehalte erfordert eine Annahme über die Anzahl (eins order zwei) der pro Doppelbindung eingebauten Chloratome. In der vorliegenden Arbeit wird diese Annahme durch Ultersuchung der Chlorierungsstöchiometrie geeigneter Modellverbindungen von bekanntem oder messbarem Doppelbindungsgehalt unter den früher angewendeten Versuchsbedingungen getest. Es zeigt sich, dass die Reaktion zu einem Monochlorprodukt und nicht zu dem früher angenommenen Dichlorprodukt führt. Die Schlussfolgerungen bezüglich des Kettenabbruchprozesses bei der Isobutenpolymerisation werden im Lichte dieses Ergebnisses überprüft.

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Stress–Strain Behavior of Swollen Polymeric Networks

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Synopsis

The network parameters of swollen, solution-crosslinked polymer filaments can be collected from deswelling measurements in solutions of nonpermeating polymer or, as shown in this paper, from the stress–strain relation when in equilibrium with the surrounding solvent. The degree of swelling, at which the partial molar free energy of elasticity equals zero, is found to vary with solvent power in agreement with earlier findings on other systems. Comparison with results of studies on rubber networks crosslinked in the absence of diluent show that previously observed discrepancies between theory and experiment can be attributed to the deficiency of the single term involving the one-third power of the volume fraction of polymer in the swollen network to describe the contribution of the partial elastic free energy.

INTRODUCTION

The swelling pattern of crosslinked polymer networks is customarily assumed to be governed by the sum of two additive free energy terms which represent the balancing forces behind the equilibrium state, viz., a mixing term representing the free energy of mixing the polymer with the solvent and an elastic term which accounts for the entropy decrease accompanying the stretching of the chains. Although it is, in fact, immaterial whether these terms are considered to be two separate free energies or only one—as their sum equals the free energy involved in the difference between the number of ways in which the chains can be placed on the lattice sites before and after swelling—this concept has proved on the whole to be very successful in relating the swelling behavior to such primary network parameters as crosslink density and Huggins' interaction parameter.

There remain, however, a number of discrepancies between the current treatments of the elastic free energy, one of which is concerned with the significance of the logarithmic term in eq. (1)

$$F_{\mathrm{el}} = kTG[1/2(\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3) - \ln \alpha_x\alpha_y\alpha_z] \quad (1)$$

where G is the number of chains present and α_x, α_y, and α_z the extension ratios in the x, y, and z direction, respectively. Flory and Wall[1,2] predict a factor 1/2 in front of this term (for tetrafunctional crosslinks), whereas James and Guth[3] reject it altogether. The term is of no consequence for

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deformations at constant volume and becomes negligible for high degrees of free swelling if the crosslinks have been introduced in the dry state, but is of critical importance if the crosslinking has taken place in solution. For this case, eq. (1) can be written[4]

$$F_{\mathrm{el}} = kTG\,[3/2(q_1/q_0)^{2/3} - 3/2 - \ln (q_1/q_0)] \qquad (2)$$

from which it is seen that the controversial term becomes of comparable magnitude to the first if the relaxed degree of swelling q_0 is large enough. In this equation q_1 represents the equilibrium degree of free swelling.

This principle has been used in attempts to discriminate experimentally[5,6] between the different treatments of the elastic free energy, but a critical evaluation is rendered difficult by the almost insurmountable problem of counting the number of effective crosslinks by an independent method, thereby accounting for loose chain ends, loops, and the like.

Furthermore, it has become evident that there exists no *a priori* relationship between q_0 and the amount of diluent present at the time of crosslinking. One would intuitively expect this to be the case, particularly for low degrees of crosslinking. Although this has been confirmed only for the latter case provided that the networks are swollen in the same solvents as those in which they were prepared,[5,6] it has become clear that the relaxed degree of swelling varies greatly with solvent power and molecular weight between crosslinks when studied in a range of other solvents. This behavior can be accommodated by assuming that the chains in the relaxed network follow a similar pattern of perturbation by preferential polymer–solvent interaction as is customarily assigned to free chains. Experiments on lightly crosslinked poly(methyl methacrylate) networks have quantitatively supported this.[7] However, the calculation of q_0 values was based on thermodynamic swelling equilibrium in solvents and solutions of nonpermeating polymer, and any interpretation in terms of long-range polymer–solvent interaction should therefore equally well apply to the free energy of mixing. In other words, there is no certainty about the correct value for the Huggins' interaction parameter to be used in those expressions which lead to the observed q_0 values. Although it is possible to present arguments which provide some justification for a single value for the interaction parameter for all networks if the solvents are poor, it was considered appropriate to test the solvent power dependence of q_0 without recourse to the interaction term. This was achieved by studying the stress–strain behavior of a solution-crosslinked nitrile rubber sample in equilibrium with a number of solvents and polymer solutions. The values for q_0 were determined from the entropy decrease as a result of extension only and further used to discuss some features of other related work on crosslinked rubber.

EXPERIMENTAL

Preparation of the Filament

An acrylonitrile–butadiene copolymer (33/67) was used for the preparation of the gel filament. The sample, tradenamed Chemigum N-7, was supplied by courtesy of The Goodyear Tyre and Rubber Co. (S.A.) Pty., Limited., Uitenhage, Cape Province. The sample, as received, showed finite swelling in benzene, indicating a slight extent of crosslinking. The low molecular weight species and additives were removed by Soxhlet extraction with benzene and the residue, approximately 75%, was homogenized in a Waring Blendor and adjusted to the desired concentration. Benzoyl peroxide, 2 g./100 g. of dry rubber, was added. The final solids content of the blend was 5.57 wt.-%.

The solution was extruded from a syringe into Pyrex tubes of 5.5 mm. bore, frozen in liquid air, sealed under vacuum, and subsequently cured at 45°C. for 5 days. The filaments were removed from the tubes by deswelling in methanol and, after extraction, kept in benzene containing 0.1% α-naphthylamine as antioxidant.

Degree of Swelling

The equilibrium degree of free swelling of the filament in four solvents—acetone, n-butyl acetate, benzene, and toluene—was determined by equilibrating small pieces in excess solvent for 48 hr. They were then blotted, weighed in a closed vessel, and dried to constant weight at 110°C. The samples in butyl acetate were washed with acetone prior to drying. In the calculation of q_1 the volumes of rubber and solvents were assumed to be additive.

In order to determine the equilibrium degree of swelling under various loads the two ends of the slightly deswollen filament were fitted into cylindrical aluminum adapters and impaled with steel pins. The filament was then mounted vertically in the swelling agent, contained in a cylindrical glass tube provided with a water jacket to allow for the circulation of thermostat water. The distance between two reference marks on the filament was read with a cathetometer when equilibrium was attained. Varying loads were applied to the swollen filament by suspending a calibrated chain of a chainomatic balance from the lower adapter at different lengths.

The changes in cross-sectional area were followed photographically. Each exposure included part of the upper adapter which served as a reference when the photograph was measured under a suitable measuring microscope. The portion of the filament between the reference marks was cut out and its rubber content determined after all readings had been taken.

A period of at least 24 hrs. was allowed to attain equilibrium under each load. Light was avoided as much as possible and antioxidant was added to the swelling agent to prevent oxidative degradation.

All experiments were carried out at a constant temperature of 25 ± 0.1°C.

RESULTS AND DISCUSSION

The experimental data are appropriately expressed in terms of the abovementioned parameters by using the statistical theory of rubber elasticity, which predicts for the configurational entropy as a result of swelling and stretching, according to Hermans[4]

$$S_{el} = kG \ln \alpha_x\alpha_y\alpha_z - 1/2kG(\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3) \qquad (3)$$

For a freely swollen filament, stretched in the x direction from length l_1 to l, one has then

$$\alpha_x\alpha_y\alpha_z = q/q_0$$

$$\alpha_x = l/l_0$$

$$\alpha_y = \alpha_z$$

and, since the crosslinks were introduced in an isotopic state,

$$l_1/l_0 = (q_1/q_0)^{1/3}$$

Inserting this in eq. (3) and writing $\lambda = l/l_1$ one obtains[8]

$$S_{el} = kG[\ln (q/q_0) - (q_1/q_0)^{2/3} (\lambda^2/2 + q/q_1\lambda) + 3/2] \qquad (4)$$

At equilibrium, where $\partial F_{\text{total}}/\partial q = 0$, the force required to stretch the filament from l_1 to l equals $f = -T\partial S_{el}/\partial l$, which gives

$$f = RTA_1N_dq_0^{-2/3}q_1^{-1/3} [\lambda - q/q_1\lambda^2] \qquad (5)$$

Here, N_d represents the number of moles of chains per unit volume of dry rubber, A the cross-sectional area of the filament, and q the degree of swelling. The subscripts d, zero, and 1, attached to the symbols, refer to the dry, relaxed, and swollen unstretched state, respectively.

Recalling further that $Al = qV_d = V$, the volume of the filament, eq. (5) can be rearranged to

$$f/l = BA_1/l_1 - Bl_1A/l^2$$

where $B = RTN_dq_0^{-2/3}q_1^{-1/3}$.

Thus, an experimental plot of f/l against A/l^2 should give a straight line for each solvent. Values for B, A_1, and l_1 follow from the slope and the intercept and from the equality $A_1l_1 = V_1$.

Figure 1 shows the results for toluene, acetone, and solutions of nonpermeating polymer in acetone. Similar plots were obtained from the measurements in the other solvents. It is observed that the experimental points for the solutions fall essentially on the same line as obtained for pure acetone itself. This is in keeping with expectation since $l_1q_1^{-1/3} = l_d$ and $A_1q_1^{-1/3}/l_1 = V_d/l_d^2$, and the slope and intercept are therefore independent of q_1. For this reason, any difference between the f/l versus A/l^2 plots for the various solvents is a mere reflection of the respective q_0 values, as N_d is obviously constant.

The numerical data are listed in Table I. The solvent dependence of q_0 is here shown by the variations of $N_d/q_0^{2/3}$. This is seen to increase with decreasing solvent power (i.e., smaller q_1 values), but does not vary with concentration of the acetone solutions, in agreement with results from pre-

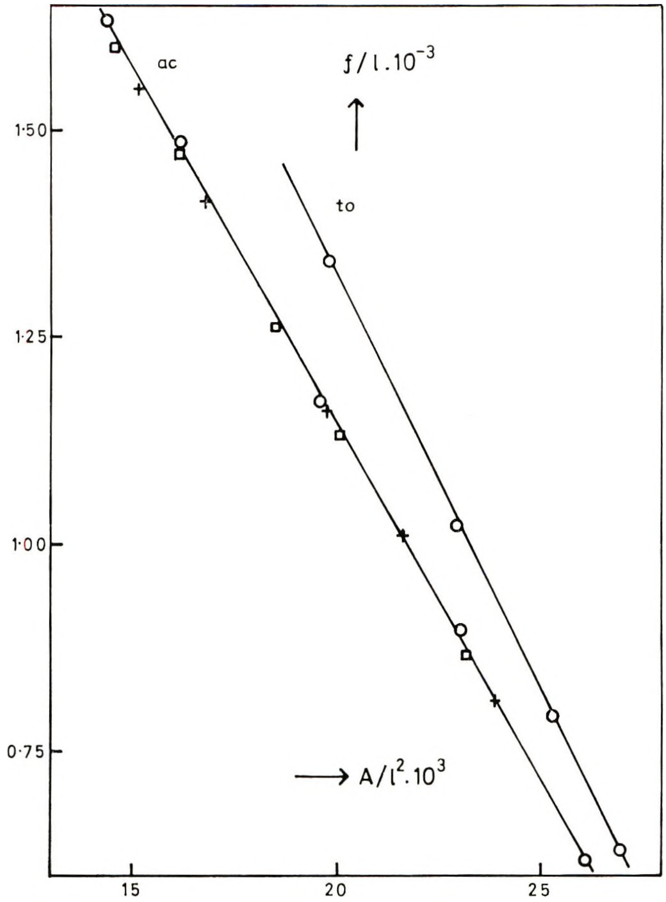

Fig. 1. Plots of f/l versus A/l^2 for the filament in toluene, acetone, (+) a 2% polymer solution, and (□) 4% polymer solution in acetone. The lines for *n*-butyl acetate and benzene fall between the ones for acetone and toluene.

vious studies.[7] Separate values for N_d and q_0 can in principle be obtained from additional modulus measurements on the dry rubber, when adequate allowance is made for the effect of diluent at the time of crosslinking. This

TABLE I
Parameters and Dimensions of the Swollen, Unstretched Filament Obtained from Plots in Figure 1

Swelling agent	q_1	$N_d/q_0^{2/3} \times 10^6$	l_1, cm.	A_1, cm.^{2}	V_1, cm.^{3}
Acetone	34.71	3.65	3.12	0.324	1.012
2% polymer solution in acetone	24.29	3.63	2.77	0.256	0.708
n-Butyl acetate	30.12	3.81	2.97	0.295	0.878
Benzene	27.84	3.89	2.90	0.280	0.811
Toluene	18.84	4.22	2.54	0.216	0.549

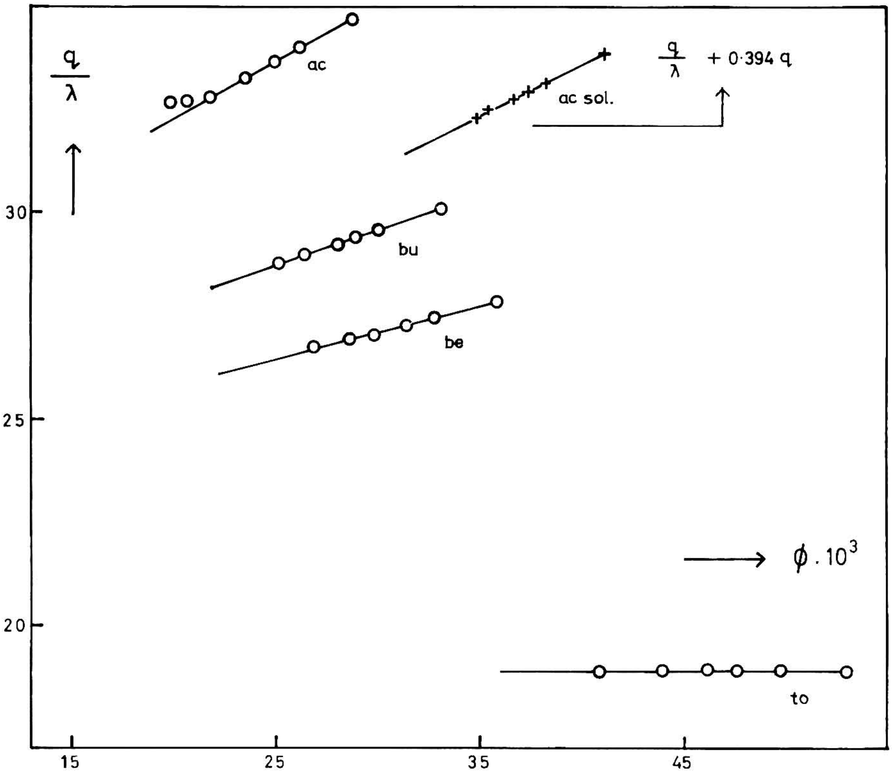

Fig. 2. q/λ versus ϕ plot according to eq. (7) for the filament in the four solvents and (+) in a 2% polymer solution in acetone ($\pi_{\text{osmo.}} = 12.3 \times 10^3$ dyne/cm.^{2}).

procedure is complicated, however, by the failure to attain steady equilibrium values and the very limited degree of reversibility. Local alignment of adjacent chains on evaporation of the solvent may well be responsible for this behavior. This possibility was further supported by the finding that the vacuum-dried filament, when re-immersed in benzene, swelled only to one-third of its original volume.

The network parameters were therefore obtained by considering the total swelling entropy of the network in equilibrium with the solvent or solution. To this end, a term for the entropy of mixing, as given by Flory and Huggins, is added to eq. (4). Differentiation with respect to the number of moles of solvent, multiplication by $(-T)$, and addition of the van Laar heat of dilution term then yields for the partial molar free energy of the solvent.

$$\partial F_{\text{tot}}/\partial n_s = RT\{\ln(1-\phi) + \phi + \chi\,\phi^2 + N_d \bar{V}[\phi_1{}^{1/3}/q_0{}^{2/3}(1/\lambda) - \phi]\} \qquad (6)$$

where n_s is the number of solvent moles, χ the Huggins' interaction parameter, $\bar{V}$ the molal volume of the solvent and $\phi = q^{-1}$. For the case of equilibrium with pure solvent one has $\partial F_{\text{tot}}/\partial n_s = 0$, so that eq. (6), on expansion of the logarithmic term with omission of powers of ϕ higher than the second, becomes, upon rearrangement

$$q/\lambda = (q_0^{2/3}/\phi_1^{1/3}) + [q_0^{2/3}(1/2 - \chi)\phi]/N_d\bar{V}\phi_1^{1/3} \tag{7}$$

According to this equation plots of q/λ against ϕ should be linear, which is confirmed by experiment as shown in Figure 2. Values for q_0 follow then from the intercepts, and χ and N_d can be obtained from the slopes by using the respective values of $N_d/q_0^{2/3}$ previously found from the f/l versus A/l^2 plots.

For the case of equilibrium with a polymer solution $\partial F_{\text{tot}}/\partial n_s$ will be equal to $-\pi\bar{V}$. The left-hand side of eq. (7) should then be replaced by $q/\lambda + (\pi q_0^{2/3}/RTN_d\phi_1^{1/3})q$, where π denotes the osmotic pressure of the external solution. An example is shown in Figure 2 for the filament in a 2% poly(methyl acrylate) solution in acetone.

The results are listed in Table II. From the values for $N_d = \rho/\bar{M}_c$, the average molecular weight between crosslinks is calculated to be 31,500. The apparent density of the rubber ρ is 0.941. This value for $\bar{M}_c$ still needs to be corrected for the finite molecular weight of the primary molecules[9] which is unknown in this case. An estimate of $M \cong 3 \times 10^5$ for this emulsion-polymerized sample seems, however, quite plausible. This gives for the effective molecular weight between crosslinks an approximate value of 26,000.

The values for q_0 in the different solvents are seen to vary with solvent power expressed by the second virial coefficient A_2. This result therefore provides additional experimental evidence to the previous conclusion that the chains in a network at a degree of swelling q_0, at which the partial molar elastic free energy equals zero, may be perturbed by preferential polymer–solvent interaction as encountered in free chains. The linear relationship between q_0 and A_2 permits the evaluation of the unperturbed chain dimensions of the nitrile rubber.[10] For the ratio $(\langle r_0^2\rangle/\bar{M}_c)^{1/2}$ of the unperturbed root-mean-square chain displacement to the square root of the molecular weight an approximate value of 0.80×10^{-8} was calculated, which compares well with 0.83×10^{-8} as found for natural rubber.[9]

The experimental values for χ fall within a small numerical range, indicating narrowly spaced physical affinities between the rubber and the

TABLE II

Parameters of the Filament Obtained from the Plots in Figure 2

Swelling agent	q_1	q_0	$N_d \times 10^5$	$A_2 \times 10^4$	χ	χ (osmo.)
Acetone	34.71	23.47	2.99	3.49	0.477	—
2% polymer solution in acetone	24.29	23.50	2.99	3.49	0.477	—
n-Butyl acetate	30.12	22.00	2.98	2.38	0.472	—
Benzene	27.84	21.33	3.02	1.84	0.485	0.482
Toluene	18.84	18.89	2.98	0.00	0.501	0.500

four solvents. In practice, this is not a disadvantage owing to the relatively high value of M_c. The χ values appear to be constant in this range of polymer concentration and are in agreement with results from osmometry. A number of better solvents have also been tried, but the experimental work becomes increasingly difficult when dealing with higher degrees of swelling. Moreover, very high degrees of swelling were found to affect the reversibility, as did elongations larger than about 1.4. This feature is noticeable in the Figures 2 and 3 for the filament in acetone and is probably due to rupture of the chains.

Previous experimental work on the deformation of swollen networks has been confined almost exclusively to networks crosslinked in the dry state. In these cases $q_0 \simeq 1$, and any of the above-mentioned features involving the solvent dependence of q_0 would therefore remain unnoticed. However, the data of Gee[11,12] seem to provide some indication of their presence. Here, the increase in volume of the filament on stretching followed the theoretical predictions quite closely for good solvents whereas the volume increase in poor solvents was found to be consistently larger. For good solvents, i.e., high degrees of swelling $\phi_1^{1/3} \gg \phi_1$ and, when $q_0 \simeq 1$, it follows from eq. (6) that $q/q_1 \simeq \lambda^{1/2}$. In the case of poor solvents the term ϕ_1 may not be neglected without introducing a more serious error, and a corresponding reasoning applies to solution-crosslinked networks where q_0 is much larger than unity. The relation between q and q_1 should therefore be written

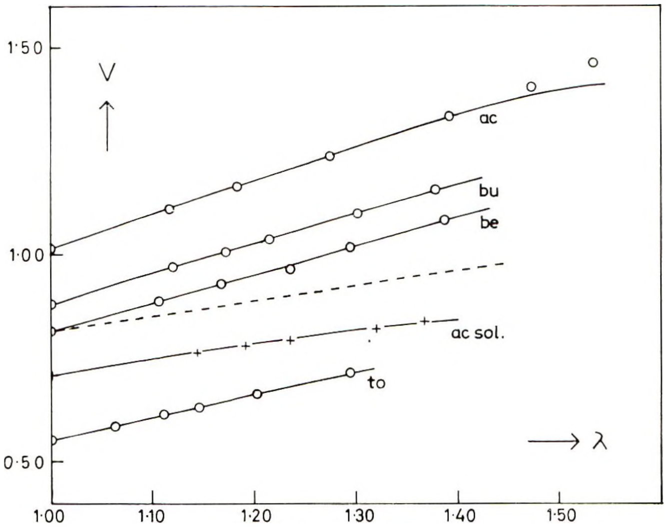

Fig. 3. Volume increase of the filament on elongation in the four solvents. Lines according to eq. (8), points experimental. Dotted line represents $V = \lambda^{1/2}V_1$ for benzene.

$$\frac{q}{q_1} = \left[\left(\frac{\phi_1{}^{1/3}}{q_0{}^{2/3}} - \phi_1\right)\Big/\left(\frac{\phi_1{}^{1/3}}{q_0{}^{2/3}}\frac{1}{\lambda} - \phi\right)\right]^{1/2} \tag{8}$$

and is shown graphically in Figure 3 for the filament stretched in the various solvents. The solid lines for acetone, *n*-butyl acetate, and benzene represent eq. (8). The dotted line drawn for benzene obeys the simple equation $q/q_1 = \lambda^{1/2}$, which stays well below the experimental points.

It should be remarked that crosslinking in the dry state does not necessarily imply that $q_0 = 1$ irrespective of the swelling agent. In good solvents one may expect q_0 to exceed unity to some extent, depending on solvent and chainlength between crosslinks, whereas, alternatively, q_0 may well be smaller than unity if the solvent is very poor. In this latter case it is obviously impossible to reach such a degree of swelling, but this does not, in principle, detract from its usefulness. However, in either case, values for $q_0^{2/3}$ will never be so much different from unity as to affect the issues critically.

Thanks are due to the Research Committee of the University of Cape Town for an equipment grant.

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Résumé

Les paramètres de réseaux de filaments polymériques gonflés et pontés en solution peuvent être obtenus par des mesures de dégonflement dans des solutions d'un polymère non-diffusant ou comme on le montre dans le manuscrit au départ de la relation tension–étirement lorsqu il se trouve en équilibre avec le solvant environnant. Le degré de gonflement, pour lequel l'énergie libre molaire partielle d'élasticité est égale à zéro, était trouvé varier avec le pouvoir solvant en accord avec des données antérieures sur d'autres systèmes. La comparison avec des résultats d'études sur des réseaux caoutchouteux pontés en absence de diluants montrait que les écarts observés précédemment entre la théorie et l'expérience peuvent être attribués à des déficiences du terme unique comportant une puissance un tiers de la fraction de volume du polymère dans le réseau gonflé en vue de décrire la contribution de l'énergie libre élastique partielle.

Zusammenfassung

Die Netzwerkparameter von gequollenen, in Lösung vernetzten Polymerfäden können aus Enfquellungsmessungen in Lösungen eines nicht-permeationsfähigen Polymeren oder—wie in der vorliegenden Arbeit gezeigt wird—aus dem Spannungs-Dehnungsverhalten bei Gleichgewicht mit dem umgebenden Lösungsmittel erhalten werden. In Übereinstimmung mit früheren Befunden an anderen Systemen ergibt sich eine Abhän-

gigkeit des Quellungsgrades, für welchen die partielle molare freie Elastizitätsenergie gleich Null ist, von der Güte des Lösungsmittels. Ein Vergleich mit Ergebnissen an Kautschuknetzwerken, die in Abwesenheit eines Verdünnungsmittels vernetzt worden waren, zeigt, dass die früher beobachteten Widersprüche zwischen Theorie und Experiment auf die mangelhafte Beschreibung des Beitrages der partiellen elastischen Energie durch einen einzelnen, die ein-drittel-Potenz des Volumsbruches des Polymeren im gequollenen Netzwerk enthaltenden Term zurückgeführt werden können.

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Some Considerations of the Kinetics of the Acid Hydrolysis of Poly- and Oligosaccharides. Part III. The Disaccharides 2-*O*-(α-D-Glucopyranosyluronic Acid)-D-Xylose, 2-*O*-(4-*O*-Methyl-α-D-Glucopyranosyluronic Acid)-D-Xylose, and 2-*O*-(4-*O*-Methyl-α-D-Glucopyranosyl)-D-Xylitol*

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Synopsis

Rate equations have been formulated for the formation and depletion of the hydrolysis product(s) of the title disaccharides. They are based on the assumptions that (*1*) the rate of acid hydrolysis of the disaccharides is according to first order, and (*2*) the rate of depletion of the hydrolysis product(s) is constant in the early periods while it approaches first order in the more advanced stages of the reactions. By using experimental rate data from the literature the rate constants of the hydrolysis of the disaccharides and of the depletion of the hydrolysis product(s) have been computed. The validity of the assumptions underlying the rate equations advanced has been confirmed by (*a*) the agreement between experimental and calculated values and (*b*) the similar values for the rate constant of the depletion of xylose formed in the hydrolysis of the two biouronic acids. Also discussed are some implications arising from the magnitude of the hydrolysis rate constant of methylaldobiouronic acid and of the depletion rate constant of xylose in relation to complete hydrolysis of polysaccharides.

The kinetics of acid-catalyzed hydrolysis of the disaccharides 2-*O*-(α-D-glucopyranosyluronic acid)-D-xylose(I) (aldobiouronic acid), 2-*O*-(4-*O*-methyl-α-D-glucopyranosyluronic acid)-D-xylose(II) (methylaldobiouronic acid), and 2-*O*-(4-*O*-methyl-α-D-glucopyranosyl)-D-xylitol (III) (xylitol bioside) are of interest from several points of view. From the pure carbohydrate chemistry angle the effect of substituents in the two sugar units on the rate of cleavage of the glycosidic bond is of interest. As the two biouronic acids (I and II) constitute a structural component in the xylan of woods, other land plants, hemicelluloses, and pulps, the rate of their hydrolysis is of interest in relation to the elucidation of the chemical structure of xylans. In the analysis of woods, plant, and pulp polysaccharides for constituent sugars, a complete hydrolysis of monosaccharides is one of the prerequisites; therefore the rate of hydrolysis of the two biouronic acids is of special interest. Finally, because of the fact that wood pulps,

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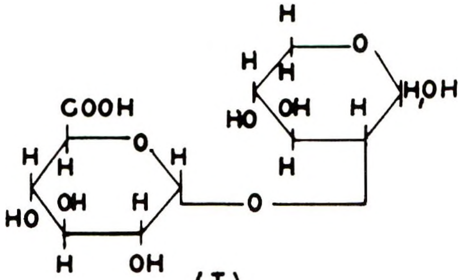
* For Part II, see Meller.[1]

particularly those produced by acid pulping processes, contain these structures in their xylan fraction,[2] influencing their properties, the rate of hydrolysis of these disaccharides is of considerable interest to the pulp and paper industry.



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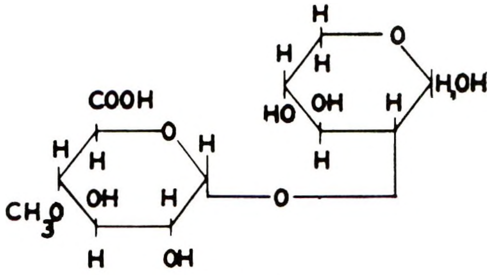

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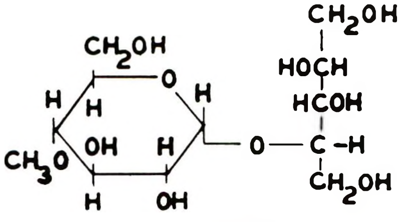

(III)

RATE OF HYDROLYSIS OF METHYLALDOBIOURONIC ACID AND XYLITOL BIOSIDE IN 1*N* SULFURIC ACID AT 95–100°C.

The rate of hydrolysis of methylaldobiouronic acid and xylitol bioside in 1*N* sulfuric acid at 95–100°C. (steam bath) has been measured by Whistler and Richards.[3] The progress of hydrolysis with the former disaccharide has been followed by measuring the xylose formed. The change in optical rotation has been followed in the hydrolysis of the xylitol bioside.

Hydrolysis of the xylitol-bioside yields xylitol in the *meso* form and 4-*O*-methyl-D-glucose, while that of the methylaldobiouronic acid results in the formation of xylose and 4-*O*-methyl-D-glucuronic acid. The criterion that the change in optical rotation of the acid solutions of the xylitol bioside measures the extent of hydrolysis is that neither the disaccharide nor its hydrolysis products should yield further reaction products which affect the optical rotation of the solutions. In acid solutions of the methylaldobiouronic acid the xylose content measures the extent of hydrolysis when neither the disaccharide nor the xylose formed enter into any further reactions.

Whistler and Richards computed the first-order rate constant from the results of their measurements and found that it decreased considerably with the progress of hydrolysis. Realizing that this was probably due to loss of the hydrolysis products, they assumed that the rate constant derived from the first measured value of the progress of hydrolysis approximated the true hydrolysis rate constant for the conditions used.

Formulation of the Kinetics of Hydrolysis of Disaccharides and Depletion of Reaction Products

The exact formulation of the kinetics of acid hydrolysis of both biouronic acids and of the xylitol bioside, based on the measured values of xylose present in the reaction mixture or on the optical rotation, requires the knowledge of the rate of formation and depletion of the hydrolysis products and also of the depletion of the disaccharides as such. The term depletion refers to disappearance of the hydrolysis products and also of the disaccharides by whatever reactions are involved (e.g., polymerization, transglycosidation, or formulation of furaldehydes, etc.).

While there is little doubt that the rate of hydrolysis of these disaccharides (i.e., the formation of the hydrolysis products) is according to first order and that the rate of their depletion is probably very small, the formulation of the kinetics of the depletion of the hydrolysis products involves a complex problem.

The depletion of xylose in sulfuric acid solutions over a wide range of temperatures has been extensively studied by Kobayashi[4–6] and by Root et al.[7] They regarded the rate of xylose disappearance as first order, because the plots of log (C_x/C_{x_0}) against time of acid treatment were essentially linear (where C_x is xylose concentration at any instance and C_{x_0} is initial xylose concentration). However, Root[8] points out that with increasing C_{x_0} the slope of the linearized plots increases slightly while the intercept with the ordinate decreases.

Accepting that the kinetics of both the hydrolysis of methylaldobiouronic acid and the depletion of xylose is according to first-order and that the depletion of the disaccharide as such is negligibly small, the well-known rate equation expressing the relationship between xylose concentration C_x and time of hydrolysis t is

$$C_x = [D_0 k_I/(k_I' - k_I)][e^{-k_I t} - e^{-k_I' t}] \qquad (1)$$

where k_I is the first-order hydrolysis rate constant of disaccharide, k_I' is the first-order depletion rate constant of xylose, and D_0 is the initial concentration of disaccharide.

This rate equation failed to satisfy the experimental results of Whistler and Richards.

It is well known that under the influence of aqueous acid solutions, reducing sugars form di-, tri-, and oligosaccharides, furfural, and nonreversible degradation (condensation) products. Since the progress of hydrolysis of the disaccharide (methylaldobiouronic acid) has been followed by measuring the xylose present in the hydrolyzate,[3] and since the concentration of the "reversion" and decay products of xylose has not been determined, the formulation of the kinetics of hydrolysis of the disaccharide and of the depletion of xylose advanced here is based on the following assumptions: (*a*) the rate of hydrolysis of the disaccharide is first order, and (b) the rate of xylose depletion is first order in the more advanced stages of the reactions while it is constant during the early period of the reactions.

The rate equation for the hydrolysis of the disaccharide and the depletion of xylose in the more advanced stages is identical with eq. (1), while for the earlier stages it is

$$C_x = D_0\,(1 - e^{-k_I t}) - Ct \tag{2}$$

In this rate equation, C is a rate coefficient of the depletion of xylose. Although formally C is a zero-order rate constant, the rate of xylose depletion should not be regarded to conform with zero-order kinetics. It arises from the assumption made for the depletion of xylose in the early periods of the reactions in acid solution.

Hydrolysis of Xylitol Bioside

Since the progress of the hydrolysis of this disaccharide has been followed by measuring the change in optical rotation of the hydrolyzate,[3] eq. (2) becomes

$$\alpha^0 = \alpha_\infty{}^0 - (\alpha_\infty{}^0 - \alpha_0{}^0)e^{-k_I t} - C't \tag{2a}$$

Here α^0 is the measured optical rotation at time t, $\alpha_0{}^0$ is the measured optical rotation of xylitol bioside, $\alpha_\infty{}^0$ is the calculated optical rotation of 4-*O*-methyl-α-D-glucose, and C' is the depletion rate coefficient of 4-*O*-methyl-α-D-glucose.

Table I lists the values for the progress of hydrolysis of this disaccharide found experimentally by Whistler and Richards and calculated by eq. (2a). The values for $\alpha_\infty{}^0$, k_I, and C' were obtained by using the experimental values and an equation described in previous papers.[9,10]

The agreement between experimental and calculated values is very satisfactory. Also the value of $\alpha_\infty{}^0$ calculated and that of the literature,[11] i.e., $[\alpha]_{\infty\mathrm{D}}^{20}$ (c = 0.7 in water) = +61, is in good agreement, which lends support to the validity of the assumptions made for deriving eq. (2). (The solution used by Whistler and Richards contained 0.04 g. xylitol bioside

TABLE I

Rate of Hydrolysis of 2-*O*-(4-*O*-Methyl-α-D-Glucopyranosyl)-D-Xylitol in 1*N* Sulfuric Acid at 95–100°C.

	α^0	
t, min.	Experimental[a]	Calculated[b]
0	0.33	0.33
15	0.26	0.26
30	0.22	0.21
60	0.16	0.16
90	0.138	0.14
120	0.13	0.13
180	0.12	0.12
300	0.11	0.10

[a] Data of Whistler and Richards.[3]

[b] $\alpha^0 = 0.14 - (0.14 - 0.33)e^{-3.2 \times 10^{-2}t} - 1.2 \times 10^{-4}\,t$ [eq. (2a)].

per 10 ml.; $\alpha_{\infty}^0 = (61 \times 0.04/10)\,(194/328) = 0.144$; molecular weight of the disaccharide = 328, that of 4-*O*-methyl-α-D-glucose = 194.)

The hydrolysis rate constant computed by Whistler and Richards [1.0×10^{-2} min.$^{-1}$ ($\log_{10}$ base) = 2.303×10^{-2} min.$^{-1}$ ($\log_e$ base)] is lower than that obtained by using eq. (2a) (3.2×10^{-2} min.$^{-1}$).

Hydrolysis of Methylaldobiouronic Acid

The experimental xylose values of the hydrolysis of methylaldobiouronic acid found by Whistler and Richards and calculated by means of eq. (2) are listed in Table II. The value for the constants k_I and C were obtained as before.[9,10]

TABLE II

Rate of Hydrolysis of 2-*O*-(4-*O*-Methyl-α-D-Glucopyranosyluronic Acid)-D-Xylose in 1*N* Sulfuric Acid at 95–100°C.

	% Hydrolysis *X*	
t, min.	Experimental[a]	Calculated[b]
60	7.4	7.4
120	13.7	13.5
180	18.3	18.5
240[c]	22.5	22.4
300	26.1	25.45

[a] Data of Whistler and Richards.[3]

[b] $X = 100\,(1 - e^{-20.08^{-4}t}) - 6.58 \times 10^{-2}\,t$ [eq. (2)].

[c] Interpolated value.

The agreement between experimental and calculated values is very satisfactory except for the value for the highest hydrolysis time. This is in line with the limitation set in the formulation of the kinetics of depletion of xylose.

The approximate rate constant computed by Whistler and Richards [5.7×10^{-4} min.$^{-1}$ ($\log_{10}$ base) = 13.1×10^{-4} min.$^{-1}$ ($\log_e$ base)] is lower than the value obtained by means of eq. (2) [20.08×10^{-4} min.$^{-1}$ ($\log_e$ base)]. It should be mentioned that the primary object of these authors was to compare the rate of hydrolysis of the two disaccharides.

RATE OF HYDROLYSIS OF METHYLALDOBIOURONIC ACID AND ALDOBIOURONIC ACID IN 0.5*N* SULFURIC ACID AT 100°C.

Roudier and Gillet[12,13] have followed the progress of hydrolysis of methylaldobiouronic acid and aldobiouronic acid in 0.5*N* sulfuric acid at approximately 100°C. (boiling water bath) by measuring the xylose content of the hydrolyzates. They found that the hydrolysis of the former disaccharide was accompanied by a slight demethylation. These authors appreciated the effect of xylose depletion and applied a correction which was based on the results of measurements of the loss in weight on subjecting xylose to the conditions under which the disaccharide hydrolysis measurements were made. They did not advance a rate equation expressing the relationship between the measured (i.e., uncorrected) xylose values and time of hydrolysis. The hydrolysis rate constant of the disaccharides was com-

TABLE III

Rate of Hydrolysis of 2-*O*-(4-*O*-Methyl-α-D-Glucopyranosyluronic Acid)-D-Xylose and 2-*O*-(α-D-Glucopyranosyluronic Acid)-D-Xylose in 0.5*N* Sulfuric Acid at 100°C.

	2-*O*-(4-*O*-Methyl-α-D-glucopyranosyluronic acid)-D-xylose				2-*O*-(α-D-Glucopyranosyluronic acid)-D-xylose		
	Xylose formed (X), %				Xylose formed (X), %		
	Experimental[a]		Calculated			Calculated	
Time t, hr.	First run	Second run	Eq. (2)[b]	Eq. (1)[c]	Experimental[a]	Eq. (2)[d]	Eq. (1)[e]
1	4.3						
2		8.39	8.0		7.4	6.4	
4	14.4		14.6		12.5	12.9	
6	19.6	24.5	20.9		15.2	17.9	
8	26.5		26.7		23.3	23.0	
10	30.5	30.7	32.0		28.1	27.7	
12	36.4		36.9	38.1	27.7		30.8
14		44.1	41.5	42.0	31.5		34.1
16					36.1		37.2
18					37.5		39.7
20		52.7		50.8	42.9		42.0
25		50.7		55.1	45.6		46.5
30	57.7	58.3		57.7	47.2		49.2

[a] Data of Roudier and Gillet.[13]

[b] $X = 100(1 - e^{-0.042t}) - 0.225t$.

[c] $X = 145.2(e^{-0.045t} - e^{-0.014t})$. Mean $k_I = 0.0435$ hr.$^{-1}$.

[d] $X = 100(1 - e^{-0.036t}) - 0.25t$.

[e] $X = 184(e^{-0.035t} - e^{-0.016t})$. Mean $k_I = 0.0355$ hr.$^{-1}$.

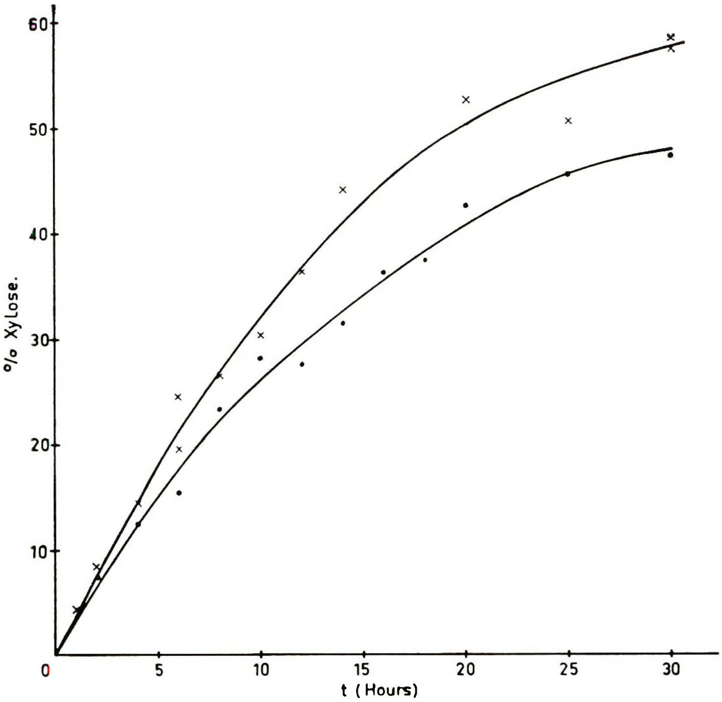

Fig. 1. Hydrolysis of biouronic acids in 0.5N sulfuric acid at 100°C.: (×) experimental and (——) calculated values for 2-O-(4-O-methyl-α-D-glucopyranosyluronic acid)-D-xylose; (●) experimental and (——) calculated values for 2-O-(α-D-glucopyranosyluronic acid)-D-xylose.

puted by means of a rate equation of first-order by using the "corrected" xylose values. The correction was computed by assuming that the disaccharides deplete at the same rate as xylose does.

The experimental values of Roudier and Gillet and the calculated values obtained by using eqs. (1) and (2) are listed in Table III. The constants k_I and C were computed as before[9,10] from the experimental values; k_I' was evaluated by using the value of k_I.

The values for the hydrolysis rate constants calculated by means of eqs. (1) and (2) are quite close. Also the values for the depletion rate constant for xylose formed in the hydrolysis of both disaccharides are similar. The experimental and calculated values agree reasonably well. The former show some scatter, and the closeness of agreement between experimental and calculated values can be seen in Figure 1.

All these results may be regarded as support to the essential validity of the assumptions made in the formulation of the kinetics of the hydrolysis of these disaccharides and of the depletion of xylose.

The values for the rate constant of hydrolysis of both disaccharides derived by Roudier and Gillet are close to those obtained in the present study. For methylaldobiouronic acid, 2.9×10^{-4} min.$^{-1}$ ($\log_{10}$ base), Roudier and Gillet; 3.15×10^{-4} min.$^{-1}$ ($\log_{10}$ base), present study. For aldobiouronic acid, 2.1×10^{-4} min.$^{-1}$ ($\log_{10}$ base), Roudier and Gillet; 2.5×10^{-4} min.$^{-1}$ ($\log_{10}$ base), present study.

Interpolation from the rate data of Kobayashi[4–6] gives a value of 1.1×10^{-2} hr.$^{-1}$ for the xylose depletion rate constant at 100°C. in 0.5*N* sulfuric acid, which is about 25% lower than the average value shown in the Table III. When it is considered that both values are essentially approximate values, the agreement cannot be regarded as unsatisfactory.

"COMPLETE HYDROLYSIS" OF XYLAN AND DEPLETION OF XYLOSE

It is customary in the analysis of polysaccharides of woods, other land plants, wood pulps, and isolated polysaccharide fractions (hemicelluloses) to treat the test sample first with 72% sulfuric acid at room temperature for a short period (1–2 hr.)[14–16] With insoluble samples, an extensive swelling and dispersion as well as some hydrolysis of the polysaccharides take place.[12–14] The reaction mixture is subsequently diluted to 3% with respect to sulfuric acid concentration and the hydrolysis "completed" either by refluxing for several hours (5–8 hr.) or by autoclaving at 15 psi (120°C.) for a shorter period (1–2 hr.). Similar hydrolysis conditions are also often used in studies on the chemical structure of polysaccharides.[16] During the "secondary" hydrolysis the reactions may take place—at least for a period—under heterogeneous conditions.[9,10]

Based on the magnitude of the rate constants for the hydrolysis of methylaldobiouronic acid derived in the present study, a 99% hydrolysis at 100°C. in 0.5*N* sulfuric acid would require 110 hr. while in 1*N* sulfuric acid it would require 38 hr. By interpolation to 3% sulfuric acid concentration the time required for 99% hydrolysis would be approximately 90 hr. at 100°C. The temperature coefficient of the rate of hydrolysis of methylaldobiouronic acid is not known, but assuming a value for the energy of activation of 30 kcal./mole., the time required for 99% hydrolysis at 120°C. in 3% sulfuric acid would amount to approximately 10 hr.

The rate of acid hydrolysis of the methylaldobiouronic acid unit as a structural component in wood xylans is not known. However, based on the values for methylaldobiouronic acid content of a large number of woody angiosperm xylans,[17] as an average, one methylaldobiouronic acid unit can be taken to be present for every ten xylose units. In gymnosperm xylans as well as in wood pulps, particularly in sulfate pulps, it is much lower.[2] Thus, in the extreme case of incomplete hydrolysis the ultimate xylan content would be affected by 10%. On the other hand, if the hydrolysis of these units is complete, the extent of xylose loss would amount to 3% on the basis of methylaldobiouronic acid, corresponding to 0.3% on xylan basis.

It is widely maintained that the arabinose side units of xylan in woods and other land plants are rapidly hydrolyzed even with very dilute acid solutions.[14–17] As the degree of other type of branching in hardwood xylans is very moderate,[18] during the secondary hydrolysis 90% of all xylans can be considered as essentially a polymer of 1 → 4-linked β-D-xylose units of different degrees of polymerization. Based on the values for the rate constant of hydrolysis for xylobiose in 1N sulfuric acid (at 60, 70, and 80°C.) and the energy of activation of 32.7 kcal./mole[19] and assuming that the dependence of the rate is in accord with Hammett's acidity function,[19,20] the time necessary for 99% hydrolysis in 3% sulfuric acid solution at 100°C. would be approximately 28 min., while at 120°C. it would amount to approximately 3 min. The rate of hydrolysis of poly(1 → 4)-β-D-xylose (i.e., xylan free from side branches) is not known, and therefore it is difficult to assess the extent of xylose loss occurring when this type of xylan is fully hydrolyzed. There is, however, probably little doubt that under homogeneous conditions poly(1 → 4)-β-D-xylopropanose hydrolyzes faster than poly(1 → 4)-β-D-glucopyranose (cellulose). The rate constant of hydrolysis of xylobiose is about seven times greater than that of cellobiose in 1N sulfuric acid.[19] It is about a hundred times greater than that of the depletion of xylose (see foregoing section).

It may be of relevance to mention here that mannobiose hydrolyzes about twice as fast as cellobiose, while glucosylmannose and cellobiose hydrolyze at about the same rate.[19] The rate of decay of glucose, mannose, and galactose in acid solution is much lower than that of xylose.[4,21,22]

In closing, it should be emphasized that the knowledge of the rate of hydrolysis of xylans and other polysaccharides in woods, hemicelluloses, and wood pulps as well as that of the depletion of their hydrolysis products would make it possible to place the determination of constituent saccharides through complete hydrolysis on a firm base. In the absence of this it may appear advisable to hydrolyze a test sample under two (or more) conditions and to determine, after separation, two (or more) constituent monosaccharides in each hydrolyzate.

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Résumé

Des équations de vitesse ont été établies pour la formation et l'épuisement des produits d'hydrolyse de disaccharides susmentionnés. Ces équations sont basées sur les hypothèses que: (*a*) la vitesse d'hydrolyse acide des disaccharides est du premier ordre, (*b*) la vitesse d'épuisement des produits d'hydrolyse est constante dans les premières périodes tandis qu'elle approche du premier ordre dans les étapes avancées de la réaction. Utilisant les résultats expérimentaux des vitesses provenant de la littérature, des constantes de vitesse d'hydrolyse de disaccharides et de disparition des produits d'hydrolyse ont été évaluées. La validité des hypothèses sur la base des équations de vitesse avancées sont confirmées par (*a*) l'accord entre les valeurs expérimentales et calculées et (*b*) par les valeurs semblables pour la constante de vitesse de disparition de xylose formé en cours d'hydrolyse des deux acides biouroniques. On a discuté également des conséquences résultat de la grandeur de la constante de vitesse d'hydrolyse de l'acide méthyl-aldobiouronique et de la constante de vitesse de disparition du xylose en rapport avec l'hydrolyse complète des polysaccharides.

Zusammenfassung

Geschwindigkeitsgleichungen für Bildung und Umsetzung der Hydrolysenprodukte der im Titel genannten Disaccharide wurden aufgestellt. Sie beruhen auf der Annahme, dass (a) die Geschwindigkeit der sauren Hydrolyse der Disaccharide erster Ordnung entspricht und (b) die Umsetzungsgeschwindigkeit der Hydrolysenprodukte in der Anfangsperiode konstant ist und sich im fortgeschritteneren Reaktionsstadium der ersten Ordnung nähert. Aus experimentellen Geschwindigkeitsdaten aus der Literatur wurden die Geschwindigkeitskonstanten der Disaccharidhydrolyse und der Umsetzung der Hydrolysenprodukte berechnet. Die Gültigkeit der den aufgestellten Geschwindigkeitsgleichungen zu Grunde liegenden Annahmen wurde bestätigt: (*a*) durch die Übereinstimmung zwischen experimentellen und errechneten Werten und (*b*) durch ähnliche Werte für die Geschwindigkeitskonstante der Umsetzung der bei der Hydrolyse der beiden Biuronsäuren gebildeten Xylose. Schliesslich werden einige Folgerungen diskutiert, die sich aus der Grösse der Hydrolysengeschwindigkeitskonstante der Methyl-aldobiuronsäure und der Umsetzungsgeschwindigkeitskonstante der Xylose für die vollständige Hydrolyse von Polysacchariden ergeben.

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Phenyl-Substituted Polyquinoxalines

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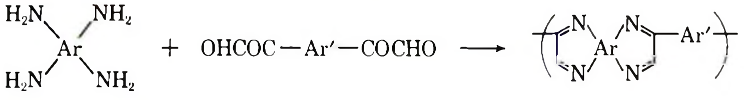
Synopsis

Four phenyl-substituted polyquinoxalines have been prepared by the reaction of combinations of two tetraamines, 3,3′-diaminobenzidine and 3,3,′4,4′-tetraaminodiphenyl ether, with two bisbenzils, 4,4′-dibenzil and 4,4′-oxydibenzil. The polymers were prepared by melt and solution polymerizations. Melt condensations were performed at 180, 220, and 280°C. and samples were periodically removed and characterized. The solution polymerizations consisted of two stages, initially forming an intermediate molecular weight polymer (η_{inh} 0.6–1.0) which was advanced at 400°C. to final polymer (η_{inh} 1.5 to 2.2). Clear yellow films, cast from *m*-cresol solution, exhibited good toughness and flexibility. The phenyl-substituted polyquinoxalines exhibited excellent oxidative and thermal stability. Polymer decomposition temperatures in air were generally about 550°C. Isothermal aging at 371°C. (700°F.) in air showed weight retentions as high as 93 and 50% after 100 and 200 hr., respectively. Weight-average molecular weight determination by light-scattering technique on a polymer with an η_{inh} of 2.16 suggested a value of 247,000. Certain physical properties of the phenyl-substituted polyquinoxalines are compared with those of the corresponding ordinary polyquinoxalines to illustrate the advantageous effect of introducing a phenyl group on the quinoxaline ring.

INTRODUCTION

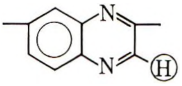
Several investigators[1–3] have recently reported the preparation of high molecular weight polyquinoxalines which exhibit excellent hydrolytic and thermal stability. These polymers were prepared from the reaction of an aromatic bis(*o*-diamine) with an aromatic bisglyoxal as indicated in eq. (1).



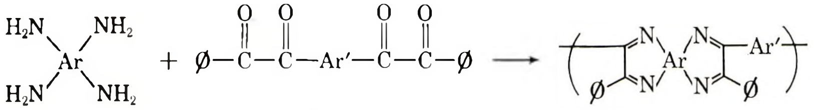
(1)

where Ar = Ar′ = aromatic.

The polyquinoxalines possess a favorable combination of unique properties which makes them excellent candidates for potential use as high temperature structural materials. The isothermal aging at 316°C. (600°F.) in air is outstanding but at 371°C. (700°F.), oxidative degradation occurs at a moderate rate. Infrared spectroscopic study of polyquinoxaline samples which had been subjected to an isothermal aging study at 371°C. (700°F.) in air suggested that oxidative breakdown occurred at the pyrazine hydrogen on the quinoxaline ring.

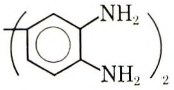


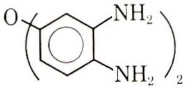
Therefore, in an attempt to improve the oxidative stability, a phenyl group was substituted for the pyrazine hydrogen by preparing phenyl-substituted polyquinoxalines as indicated in eq. (2).

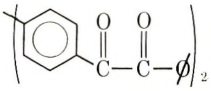

(2)

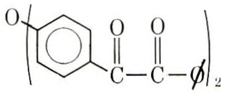
where Ar = Ar′ = aromatic.

Four polymers have been prepared by the reaction of combinations of two tetraamines, 3,3′-diaminobenzidine (I) and 3,3,′4,4′-tetraaminodiphenyl ether (II), with two bisbenzils, 4,4′-dibenzil (III) and 4,4′-oxidibenzil (IV).


I


II


III


IV

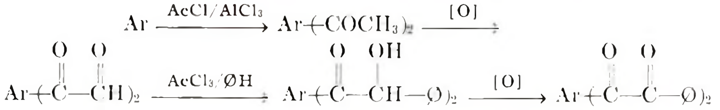
EXPERIMENTAL DISCUSSION

Monomers

3,3′,4,4′-Tetraaminodiphenyl ether was synthesized following the procedure of Foster and Marvel.[4]

3,3′-Diaminobenzidine was purchased from a commercial source and purified.

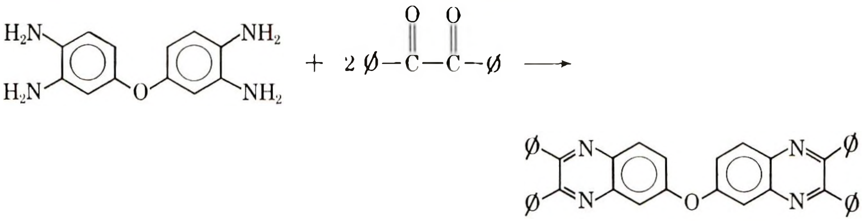
The aromatic dibenzils were obtained in good yields following a modification of a known procedure[5] by the phenylation of the bisglyoxals using benzene and aluminum chloride. The resulting bisbenzoins were subsequently oxidized to the corresponding bisbenzils as indicated in eqs. (3):



$$\mathrm{Ar} \xrightarrow{\mathrm{AcCl/AlCl_3}} \mathrm{Ar}(\mathrm{COCH_3})_2 \xrightarrow{[\mathrm{O}]} \mathrm{Ar}(\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{H})_2 \xrightarrow{\mathrm{AcCl_3/\phi H}} \mathrm{Ar}(\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}\mathrm{H}-\phi)_2 \xrightarrow{[\mathrm{O}]} \mathrm{Ar}(\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\phi)_2 \quad (3)$$

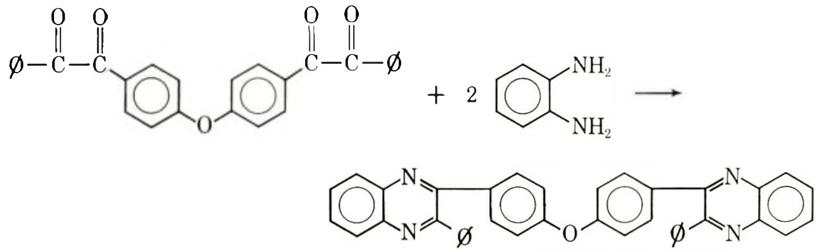
Model Compounds

Two model compounds were prepared in quantitative yield by melt condensation at 180–250°C. as shown in eqs. (4).



2, 2′, 3, 3′-Tetraphenyl-6, 6′-oxydiquinoxaline

V


(4)

p, p′-Di[2-(3-phenylquinoxalyl)]
diphenyl ether

The model compounds were characterized as shown in Table II and also by ultraviolet and infrared spectroscopy (Figs. 1, 2*a*, and 2*b*).

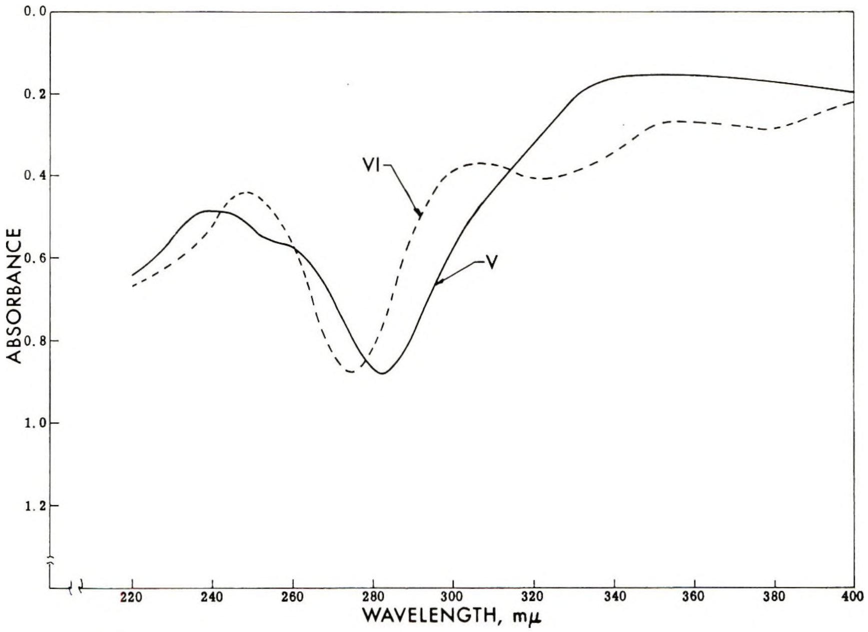


Fig. 1. Ultraviolet spectra of model compounds. Concentration = 1 mg./100 ml. H_2SO_4.

Polymers

The phenyl-substituted polyquinoxalines were prepared by melt and solution polymerization. Melt polycondensations were performed by introducing a polymerization tube containing an intimate, stoichiometric mixture of tetraamine and bisbenzil under an inert atmosphere into a preheated oil bath at 180–200°C. A melt readily formed with the evolution of volatiles. The temperature was increased to 380°C. during 3 hr. and maintained at 380–400°C. for 1 hr. The resulting polymer exhibited extremely good adhesion to glass as evidenced by pulling glass away from

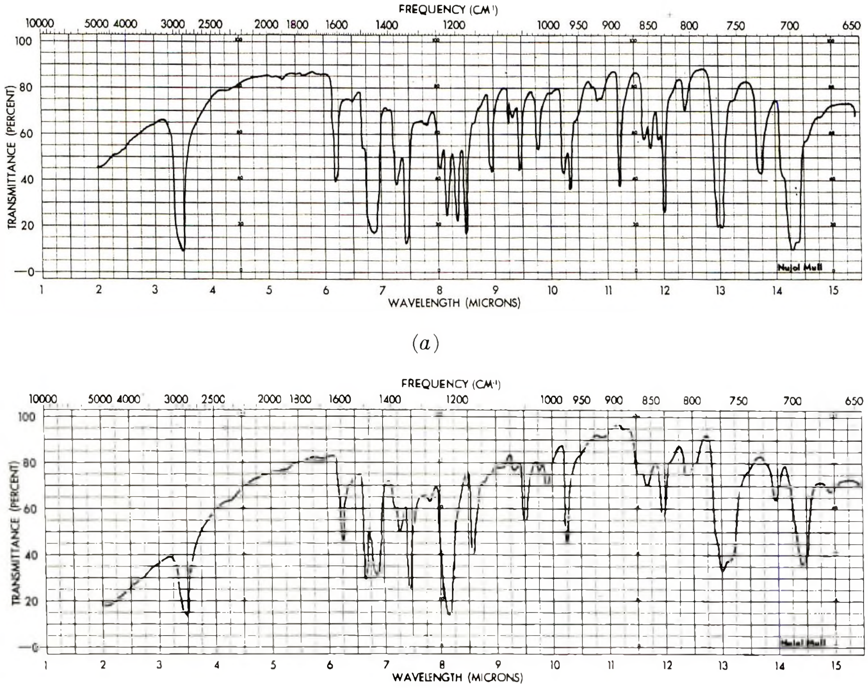
TABLE I
Characterization of Reactants

Reactant	M.p., °C.	Lit. m.p., °C.	Formula	Elemental analysis					
				Calculated			Found		
				C, %	H, %	N, %	C, %	H, %	N, %
I	177.5–178	179–180$_6$	$C_{12}H_{15}N_4$	67.26	6.59	26.15	67.18	6.47	26.11
II	150–151	149.5–151$_4$	$C_{12}H_{14}N_4O$	62.58	6.13	24.35	62.41	6.03	24.12
III	205–206	203–204$_7$	$C_{28}H_{18}O_4$	80.37	4.34	—	80.24	4.31	—
IV	107–108	106.4–107.4$_7$	$C_{28}H_{18}O_5$	77.41	4.18	—	77.33	4.11	—

TABLE II
Characterization of Model Compounds

Model compound	M.p., °C.	Elemental analysis[a]		
		C, %	H, %	N, %
V	264.5–265.5	80.31	5.06	11.04
VI	226–227	80.17	5.11	10.98

[a] Calculated for $C_{34}H_{26}N_4O$: C, 80.61%; H, 5.17%; N, 11.06%:



(*a*)

(*b*)

Fig. 2. Infrared spectra of model compounds: (*a*) 2,2′,3,3′-tetraphenyl-6,6′-oxydiquinoxaline (V); (*b*) *p*,*p*′-di[2-(3-phenylquinoxalyl)]diphenyl ether (VI).

the side of the polymerization tube upon cooling. The extremely tough polymer had to be pulverized in a Wiley Mill.

The course of the melt condensation was studied using 3,3′,4,4′-tetraaminodiphenyl ether and 4,4′-oxydibenzil at 180, 220, and 280°C. Samples were periodically removed and characterized by inherent viscosity, polymer melt temperature, and ultraviolet spectroscopy. See Table III.

Solution polymerization was performed in a variety of solvents such as *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAC), and *m*-cresol over a temperature range of −10–202°C. High molecular weight polymers, as suggested by inherent viscosities (0.5% H_2SO_4 solution at 25°C.) > 1.0 dl./g. could not be obtained directly in refluxing DMF or

TABLE III

Effect of Temperature and Time on the Melt Condensation of 3,3′,4,4′-tetraaminodiphenyl Ether and 4,4′-Oxydibenzil

Reaction time	Reaction temperature								
	180°C.			220°C.			280°C.		
	η_{inh}[a]	PMT[b]	λ_{max} (K_{sp})[c]	η_{inh}	PMT	λ_{max} (K_{sp})	η_{inh}	PMT	λ_{max} (K_{sp})
3 min.	0.09	154	286(33,000)	0.21	210	287(38,500)	0.42	280	287(43,000)
1 hr.	0.10	171	286(35,100)	0.23	220	287(39,600)	0.45	300	288(45,000)
72 hr.	0.12	181	287(37,700)	0.26	260	287(40,300)	0.46	310	288(46,200)

[a] η_{inh} = inherent viscosity (0.5% H_2SO_4 at 25°C.), dl./g.

[b] PMT = polymer melt temperature, °C.

[c] λ_{max} = wavelength (mμ) and K_{sp} = specific absorbance (1 mg./100 ml. H_2SO_4).

DMAC. This presumably was due to the limited solubility of the polymer which precipitated from solution as the condensation progressed. However, polymers with η_{inh} of 0.6–0.8 were obtained which could be further advanced to high molecular weight polymers by heating to 400°C. for 1 hr. in an inert atmosphere. The polymers remelted, foamed, and resolidified during this thermal treatment to yield polymers with inherent viscosities generally about 1.5.

In *m*-cresol, the polymerization was generally conducted by adding a slurry of the bisbenzil to a vigorously stirred slurry of the tetraamine at ambient temperature. After about half of the bisbenzil was added, a clear reddish solution formed, and a slight exotherm was observed. Upon complete addition of the bisbenzil, the viscous red solution was stirred at 120°C. for 3 hr. This solution contained 30% solids and was conveniently used in application work. The inherent viscosities of the polymers at this stage were about 1.0. Obviously, the molecular weight of the phenyl-subsitituted polymers can be conveniently controlled when the polymerization is conducted in *m*-cresol by altering the reaction time and/or temperature. Polymers with inherent viscosities of 1.0 are readily formed but fail to grow appreciably upon further heating. For example, stoichiometric quantities of 3,3′,4,4′-tetraaminodiphenyl ether and 4,4′-oxydibenzil were heated for 3 hr. at 120°C. in *m*-cresol to yield a polymer with an inherent viscosity of 1.0. Further heating at the reflux temperature for 72 hr. resulted in an inherent viscosity of 1.2. However, when this polymer was isolated by quenching the *m*-cresol solution with methanol, followed by heating at 400°C. for 1 hr. in an inert atmosphere, the inherent viscosity increased to 2.0. The stability of the *m*-cresol solution is excellent, as shown by characterizing the polymer solution and polymer isolated periodically over 30 days.

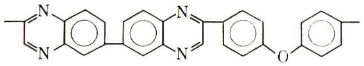
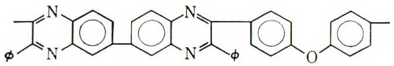
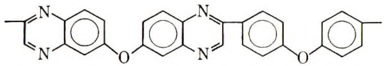
Clear yellow films, cast from *m*-cresol solutions containing 10% solids, exhibited high tensile strength and excellent flexibility after curing up to 300°C.

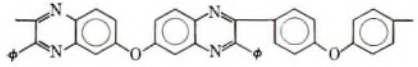
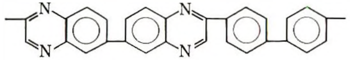
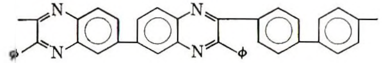
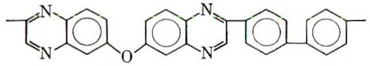
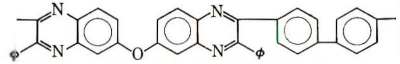
EVALUATION

Certain physical properties of the phenyl-substituted polyquinoxalines are compared with those of the corresponding polyquinoxalines in Table IV. All the polymers were prepared initially as prepolymers in *m*-cresol and subsequently isolated and advanced via melt polymerization at 400°C. for 1 hr. in an inert atmosphere. The ordinary polyquinoxaline prepolymers obtained from *m*-cresol failed to exhibit true polymer melt temperatures apparently due to the rapid reaction at the melt temperature to form the quinoxaline ring. Introduction of the phenyl group apparently sterically hinders the formation of the quinoxaline ring somewhat and consequently provides a prepolymer with a true polymer melt temperature.

A representative polymer from each quinoxaline system is used to illustrate the difference in the properties of the final polymers. Equation (5) indicates the preparation of the two polymers.

TABLE IV
Characterization of Polyquinoxalines

Polymer repeating unit	η_{inh}, dl./g.[a]	PDT, °C.[b]		T_g,[c] °C.	% Weight retention at 371°C. in air after[d]		Formula	Elemental analysis[e]		
		Air	Helium		100 hr.	200 hr.		C, %	H, %	N, %
	2.06	510	530	388	60	0	$C_{28}H_{16}N_4O$	79.08 (79.23)	3.74 (3.80)	12.91 (13.20)
	2.05	520	550	420	80	40	$C_{40}H_{24}N_4O$	82.11 (83.31)	4.29 (4.20)	9.60 (9.72)
	1.61	510	540	382	70	0	$C_{28}H_{16}N_4O_2$	76.53 (76.35)	3.79 (3.66)	12.59 (12.72)

	2.16	550	560	437	93	50	$C_{40}H_{24}N_4O_2$	80.90 (81.06)	4.09 (4.08)	9.39 (9.45)
	1.42	530	540	386	70	0	$C_{28}H_{16}N_4O$	—	—	—
	1.50	530	550	404	90	45	$C_{40}H_{24}N_4$	—	—	—
	1.75	520	540	390	64	0	$C_{28}N_{16}N_4O$	78.89 (79.23)	3.71 (3.90)	12.74 (13.20)
	1.71	530	550	410	78	35	$C_{40}H_{24}N_4O$	82.01 (83.31)	4.17 (4.20)	9.43 (9.72)

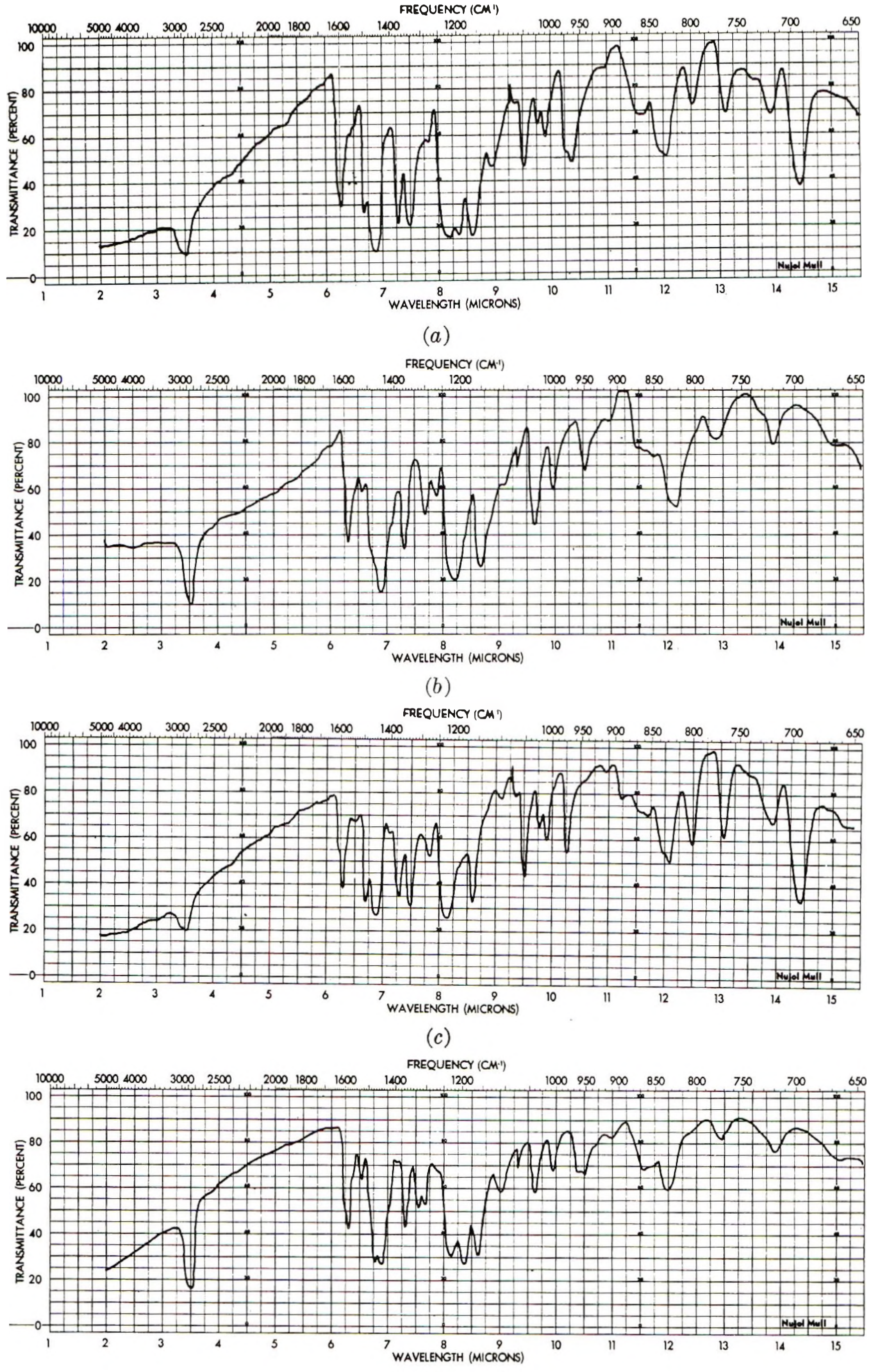
[a] η_{inh} = inherent viscosity (0.5% H_2SO_4 at 25°C.).

[b] PDT = polymer decomposition temperature, ±10°C., determined using a Stanton thermobalance.

[c] T_g = glass transition temperature, determined utilizing dielectric properties of polymer.

[d] Particle size of 140–240 mesh.

[e] Calculated values reported in parentheses.



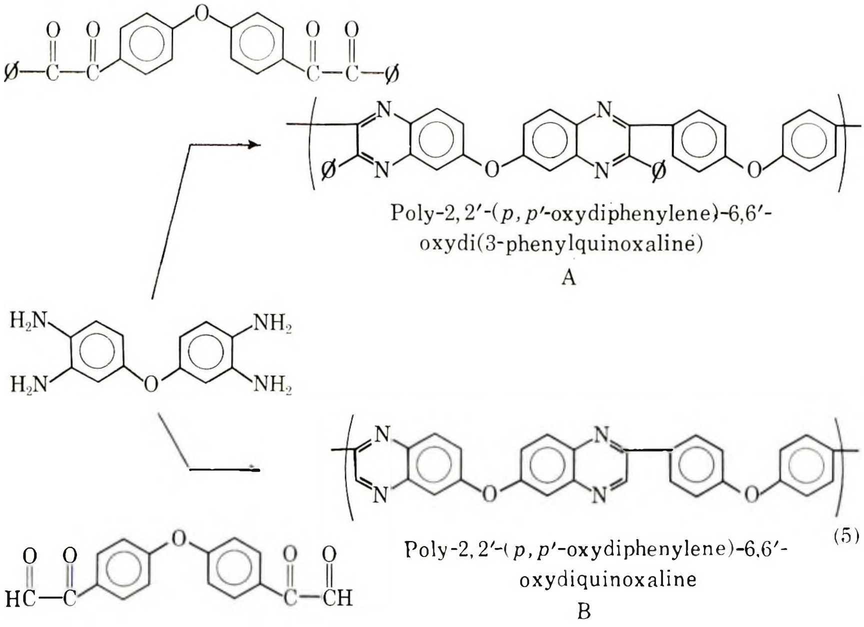
(a)

(b)

(c)

(d)

Fig. 3. Infrared spectra of polyquinoxalines: (*a*) poly-2,2′-(*p*,*p*′-oxydiphenylene)-6,6′-oxydi(3-phenylquinoxaline) (A); (*b*) poly-2,2′-(*p*,*p*′-oxydiphenylene)-6,6′-oxydiquinoxaline (B); (*c*) poly-2,2′-(*p*,*p*′-oxydiphenylene)-6,6′-di(3-phenylquinoxaline); (*d*) poly-2,2′-(*p*,*p*′-oxydiphenylene)-6,6′-biquinoxaline.


Poly-2,2′-(p,p′-oxydiphenylene)-6,6′-oxydi(3-phenylquinoxaline)
A

Poly-2,2′-(p,p′-oxydiphenylene)-6,6′-oxydiquinoxaline
B

(5)

The infrared spectra of representative polyquinoxalines are shown in Figures 3*a* through 3*d*.

The ultraviolet spectrum of a phenyl-substituted polyquinoxaline with an $\eta_{\text{inh}} = 1.84$ is compared with that of the corresponding ordinary polyquinoxaline ($\eta_{\text{inh}} = 1.61$) in Figure 4. Both curves are very similar with

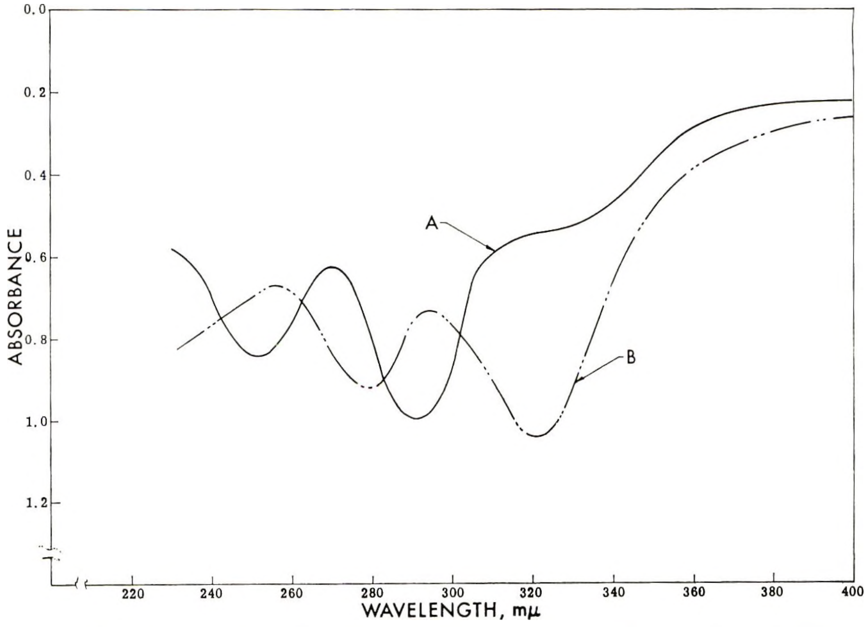


Fig. 4. Ultraviolet spectra of polyquinoxalines. Concentration = 1 mg./100 ml. H_2SO_4.

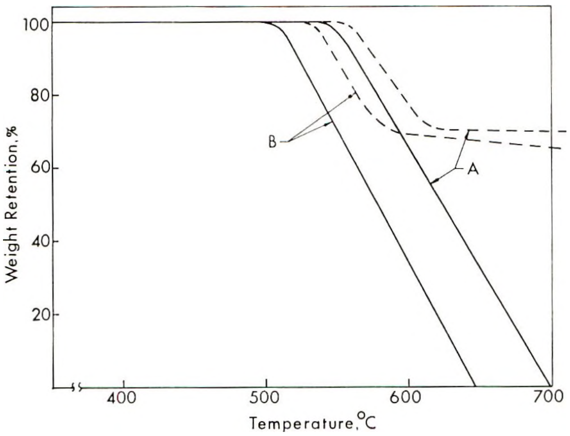


Fig. 5. Thermograms of polyquinoxalines: (——) air; (- - -) helium. ΔT = 6.67°C. min.$^{-1}$. Particle size = 140–240 mesh.

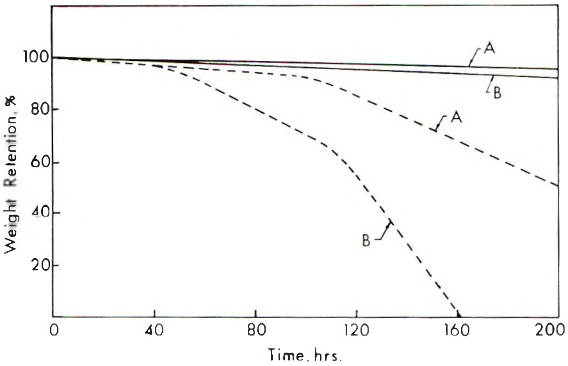


Fig. 6. Isothermal weight loss curves of polyquinoxalines in air: (——) 316°C. (600°F.); (- - -) 371°C. (700°F.). Particle size = 140–240 mesh.

about 40 mμ between the two λ_{max} in each curve. It is interesting to note the pronounced hypsochromic shift in the λ_{max} of the phenyl-substituted polyquinoxaline spectrum which is apparently attributed to the steric effect of the phenyl groups on the quinoxaline ring.

Oxidative and Thermal Stability

As shown in Table IV, the phenyl-substituted polyquinoxalines exhibited slightly higher polymer decomposition temperatures in air and helium (Fig. 5) and higher glass transition temperatures than the ordinary polyquinoxalines. Also, the polyphenylquinoxalines exhibit better oxidative stability as shown by the isothermal weight loss study at 316°C. (600°F.) and at 371°C. (700°F.) in air (Fig. 6). It should be noted that at 316°C. (600°F.) in air, both polymer systems exhibit excellent oxidative stability retaining about 92–95% of their weight after 200 hr. It is also interesting to note that the most stable phenyl-substituted polymer was prepared from the two diphenyl ether reactants. This polymer also exhibited the highest glass transition temperature which was surprising since the presence of the diphenyl ether moieties should impart more flexibility to the polymer.

Hydrolytic Stability

Hydrolytic stability of the phenyl-substituted polyquinoxalines was evaluated by refluxing samples of 140–240 mesh particle size in 40% aqueous potassium hydroxide for 6 hr. The polymer was recovered in quantitative yield and exhibited no change in its inherent viscosity, elemental analysis, and infrared spectrum.

Molecular Weight

Light scattering, in sulfuric acid, of a polyphenylquinoxaline having an inherent viscosity of 2.16, indicated a molecular weight of 247,000; a Brice-Phoenix light-scattering photometer was used.

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Résumé

Quatre polyquinoxalines phénylsubstituées ont été préparées par réaction de combinaisons de deux tétraamines, la 3,3′-diaminobenzidine et l'éther 3,3′-4,4′-tétraaminodiphénylique, avec deux bisbenzyles, le 4,4′-dibenzyle et 4,4′-oxydibenzyle. Les polymères ont été préparés par polymérisation à l'état fondu et en solution. La condensation à l'état fondu a été exécutée à 180, 220 et 280°C, et des échantillons ont été périodiquement enlevés et caractérisés. Les polymérisations en solution consistaient en deux étapes, initialement formation d'un polymère de poids moléculaire intermédiaire (une viscosité intrinsèque de 0.6 à 1.0) qui est alors poussée à 400°C au polymère final (η_{inh} = 1.5 à 2.2). Des films clairs jaunes coulés de leur solution dans le *m*-crésol, manifestailont une bonne dureté et flexibilité. Les polyquinoxalines substituées aromatiques manifestent une stabilité excellente à l'oxydation et à la chaleur. Les températures de décomposition des polymères à l'air se situent généralement vers 550°C. Le viellissement isotherme à 371°C (700°F) à l'air montrait des rétentions en poids aussi élevées que 93% et 50% après 100 et 200 heures respectivement. La détermination du poids moléculaire moyen en poids par la technique de diffusion lumineuse sur un polymère qui avait une viscosité inhérente de 2.16 suggère une valeur de 247.000. Certaines propriétés physiques des polyquinoxalines substituées aromatiques sont comparées à celles des polyquinoxalines ordinaires correspondantes en vue d'illustrer l'effet avantageux de l'introduction d'un groupe phényle dans le noyau quinoxalinique.

Zusammenfassung

Vier phenyl-substituierte Polychinoxaline wurden durch die Kombinationsreaktion zwischen zwei Tetraminen, 3,3'-Diaminobenzidin und 3,3',4,4'-Tetraminodiphenyläther mit zwei Bisbenzilen, 4,4'-Dibenzyl und 4,4'-Oxydibenzyl dargestellt. Die Polymeren wurden durch Schmelz- und Lösungspolymerisation gewonnen. Schmelzkondensationen wurden bei 180°, 220° und 280°C durchgeführt und periodisch Proben entnommen und charakterisiert. Die Lösungspolymerisation bestand aus zwei Stufen, wobei zuerst ein Polymeres mit mittlerem Molekulargewicht (η_{inh} 0,6 bis 1,0) erhalten wurde, das bei 400°C in das polymere Endprodukt (η_{inh} 1,5 bis 2,2) überging. Klare, gelbe, aus *m*-Kresollösung gegossene Filme zeigten gute Festigkeit und Biegsamkeit. Die phenylsubstitutierten Polychinoxaline besassen ausgezeichnete Oxydations- und Wärmebeständigkeit. Die Zersetzungstemperaturen der Polymeren lagen in Luft allgemein bei etwa 550°C. Die isotherme Alterung bei 371°C (700°F) in Luft zeigte Gewichtsretentionen in der Höhe von 93% und 50% nach 100 bzw. 200 Stunden. Die Bestimmung des Gewichtsmittels des Molekulargewichts durch Lichtstreuungsmessungen an einem Polymeren mit $\eta_{inh} = 2{,}16$ lieferte einen Wert von 247.000. Um den vorteilhaften Effekt der Einführung einer Phenylgruppe am Chinoxalinring zu zeigen, wurden gewisse physikalische Eigenschaften der phenyl-substituierten Polychinoxaline denjenigen der entsprechenden gewöhnlichen Polychinoxaline gegenübergestellt.

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Environmental Effects in Free-Radical Polymerizations. Part III. Vinyl Chloride and *n*-Butyraldehyde

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Synopsis

The properties of poly(vinyl chloride) samples prepared by a free-radical process in the presence of *n*-butyraldehyde have been studied from the point of view of polymer tacticity, branching, molecular weight, and relative crystallinity. The postulate of a polymer radical–aldehyde complex, invoked to explain the increased crystallinity, was tested. The polymers had a lower degree of polymerization and branching than normal, and these parameters rather than increased syndiotacticity were responsible for the high degree of crystallinity. Both molecular weight and branching affect the crystallinity, since polymer samples prepared in the presence of various transfer agents with similar molecular weights were less crystalline than those prepared in aldehyde, but yet more crystalline than high molecular weight bulk polymer. Polymers prepared in aldehyde had a lower degree of branching than those formed in other transfer agents. It was concluded that aldehyde was effective in increasing the crystallinity of poly(vinyl chloride) in these two ways, and so appeared to be unique among the transfer agents. There was no evidence for assuming any complexing between polymer radicals and aldehyde.

INTRODUCTION

The stereoregularity of a polymer chain is determined by the mode of addition of monomer to the growing chain end, so it is a useful guide to the mechanism of propagation. Since crystalline poly(vinyl chloride) (PVC) is produced by free-radical polymerization in aliphatic aldehydes,[1] it might be deduced that the growth process differed from that giving amorphous bulk polymer. Crystalline, presumably stereoregular, polymer can be obtained by free-radical methods at very low temperatures. Fordham et al.[2] have reported that PVC prepared at −70°C. is more crystalline than normal; the aldehyde-prepared polymer is even more crystalline. The configuration of the entering monomer molecule in polymerization is determined to some extent by the interactions between this molecule and the growing radical, and also by the interactions between the terminal growing unit and the penultimate and other groups in the chain. Steric and electrostatic interactions control the mode of addition and generally favor syndio-

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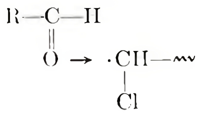
tactic addition in a free-radical polymerization. Bovey[3] has obtained evidence of preferred syndiotacticity in the low-temperature polymerization of methyl methacrylate and established that the activation energy of the isotactic addition was 0.8 kcal./mole. greater than the syndiotactic. Fordham[4] has calculated a theoretical value of 0.5 kcal./mole. With monomers having more polar and bulky side groups this difference in activation energy is much higher, and syndiotactic block formation is favored even at high temperatures. This seems to be the case with fluorinated and chlorinated vinyl acetates, which are normally obtained with free-radical initiators in a highly crystalline syndiotactic form.[5] Fordham et al.[2] consider that the crystalline samples of PVC prepared at −70°C. have a syndiotactic block structure, and suggest that the ratio of the optical densities infrared absorption bands at 635 and 692 cm.$^{-1}$ can be used to measure syndiotacticity. This ratio varies considerably with the temperature of polymerization. Burleigh[1] considers that highly crystalline PVC, produced with a monomer:aldehyde ratio of unity is also predominantly syndiotactic; D_{635}/D_{692} is 4.3, compared to 2.7 for the sample polymerized at −70°C. and 1.5 for normal bulk polymer. The aldehyde polymer shows 13 lines in its x-ray powder diffraction pattern while normal PVC shows only 4 diffuse lines. This is obviously due to the large increase in stereoregularity. The x-ray diffraction results are also consistent with a syndiotactic structure in the basic unit cell; recently Rylov et al.[6] have compared the electron diffraction pattern of PVC prepared in aldehyde with the unit cell assigned by Natta and Corridini,[7] i.e., orthorhombic, a = 10.6 A., b = 5.4 A., and c = 5.1 A., and syndiotactic configuration. Rosen et al.[8] have also reported the ability of various aldehydes to induce increased crystallinity. They found that all aromatic aldehydes except *p*-dimethylaminobenzaldehyde are completely ineffective, whereas aliphatic aldehydes are effective in increasing order from acetaldehyde to the butyraldehydes. For an α substituent the effectiveness is in the order, methyl > H > Cl > OH. The formation of a π complex between the aldehyde and growing radical is suggested as likely to favor syndiotactic orientation. The suggested structure of this complex is I.



$$\begin{array}{ccc} R{-}C{-}H & & \\ \Vert & & \\ O & \rightarrow & \cdot CH{-}\sim \\ & & | \\ & & Cl \end{array}$$

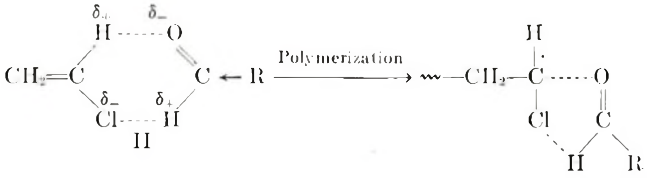
I

The effect of varying the substituent will be to raise or lower the electron density around the carbonyl group and so increase or decrease the stability of the complex. These inductive effects are in the order of observed activity.

Rosen[9] has more recently reported that lowering the temperature of the polymerization does not appreciably alter the crystallinity of the aldehyde polymer. Indeed, the infrared spectrum of the aldehyde polymer is closer to that of the polymer prepared at low temperature (−80°C.) than to that of the syndiotactic polymer prepared by urea canal complex polymerization in the solid state.

Minsker et al.[10] have also polymerized vinyl chloride in the presence of widely different organic reagents, but only aldehydes were found to be effective in producing crystalline polymer. Polymers from styrene, methyl methacrylate, methyl acrylate, and vinyl acetate formed in aldehyde solution were completely amorphous. It is concluded that the effect is specific to vinyl chloride and aldehydes, and it is suggested there is a strong dipole interaction between monomer and aldehyde molecule. Similar conclusions have been reached by Sumi et al.[11] who polymerized vinyl chloride in various π-complexing solvents. None, except diallyl phosphite, produced any crystallinity in the polymer, so that it is concluded that π-complexing was not responsible for the crystallinity found with aldehydes.

Razuvaev et al.,[12] by analogy with the effect of polar and bulky side-groups on the stereoregularity of polymers, proposed a different type of complex to explain the increased crystallinity. This involves the formation of a cyclic complex (II) between vinyl chloride and the aldehyde:



(1)

The complex so formed has the effect of increasing the size of the substituent on both monomer and growing radical. The nature of the substituent, R, on the aldehyde has been shown to affect the degree of crystallinity of the resulting polymer. It is possible to relate the ability to produce crystalline polymer to the Hammett constant. Addition of compounds which could complex with the aldehyde, i.e.; those containing hydroxyl groups, greatly reduce the efficiency of the aldehyde.

Bovey and Tiers[13] have shown that the NMR spectrum of deuterated PVC prepared in the presence of *n*-butyraldehyde is indistinguishable from that of normal polymer prepared in cyclohexanone solution. Both samples have the same low degree of tacticity, despite their differences in crystallinity. They suggest that the increased crystallinity can only be due to reduction in the degree of branching, and postulate a similar radical–aldehyde complex, as did Burleigh to explain the anomalous reduction in the degree of branching. They also found very small differences in the tacticity of the polymer prepared at low temperature; the changes they did find were considered to be too small to explain the observed change in crystallinity. They estimated an activation energy difference between isotactic and syndiotactic placements of 0.2 kcal./mole, compared with Burleigh's estimate of 0.6 kcal./mole. Increasing crystallinity was due to reduction in the degree of branching with lowering temperature.

Rosen and Burleigh[14] also postulated a similar type of radical–aldehyde complex to explain the increased crystallinity of acrylonitrile polymers prepared in an aldehyde environment. They deduced from infrared analysis that the more crystalline polymers were more syndiotactic. More recently, however, it has been shown that the increased crystallinity in polyacrylonitrile is due to the extremely low molecular weights of the samples.[15] Polymers formed in other media, of similar molecular weights show the same relative increase in crystallinity, but acrylonitrile polymers do not show the same large increase in crystallinity as vinyl chloride polymers. An analogous polymer, polymethacrylonitrile (PMAN), which is normally amorphous, shows no tendency to become crystalline when prepared in the presence of an aldehyde, and NMR spectroscopic analysis shows no evidence of any change in tacticity. The spectrum is identical to that of the normal heterotactic polymer.[16]

Although formation of radical–aldehyde complexes has been suggested to account for increased syndiotacticity, the evidence for their existence is still conflicting. Only polymers which are normally partially crystalline, polyacrylonitrile (PAN) and PVC, show increased crystallinity in the presence of aldehyde: change from amorphous to crystalline polymer by the same method has not been achieved. The polymers do not show any increase in tacticity.

We have studied the properties of the PVC samples and characterized them, as far as possible, with respect to degree of polymerization, degree of branching, stereoregularity, and crystallinity, in order to determine the effect of each of these parameters on the final properties of the polymers.

EXPERIMENTAL

Materials

Vinyl chloride, (Matheson Co. Ltd.), after drying in a silica gel tower, was collected in a Dry Ice trap and fractionally distilled under vacuum three times. The middle 80% cut was retained in each distillation, and the final product was stored in the dark as a gas.

n-Butyraldehyde was purified as previously described.[15]

Techniques

Vinyl chloride was polymerized at 50°C. in a stainless steel dilatometer which could be evacuated to 10^{-4} torr. A pressure trap was mounted at the end of a stainless steel extension tube to prevent it from being excessively cooled on distilling monomer and aldehyde into the vessel. The degree of conversion obtained on polymerization was measured from the weight of polymer produced. To isolate the polymer, the reaction vessel was cooled to −30°C. before opening, and the monomer was vented off as the system slowly warmed up. The polymers were purified by washing with a large excess of methanol, filtered, and vacuum dried. Further purification was achieved by repeated precipitation from solution with methanol.

Molecular weights were measured by viscosity in cyclohexanone solution at 25°C. by using the relationship,[17]

$$[\eta]_{\text{lim}} = 2.4 \times 10^{-4}\, \bar{M}_n^{0.77}$$

which is applicable in the region 10^4–10^6 for the bulk samples.

Number-average molecular weights $\bar{M}_n$ for the low molecular weight samples were determined by ebulliometry in dioxane solution under an atmosphere of nitrogen.[18]

To achieve most accurate results a standard (tristearin) was used. The relevant relationship is

$$\bar{M}_n = M_s\, (\Delta d/\Delta C)_{s,c=0}/(\Delta d/\Delta C)_{sc=0}$$

where $\Delta d/\Delta c$ is the change of galvanometer deflection in relation to change in concentration, and Δd is proportional to the boiling point increase, M_s is the molecular weight of tristearin. Table I shows $(\Delta d/\Delta c)$ for various samples.

The polyhydrocarbon reduction products were also studied by ebulliometry (Table II) with toluene as solvent with a calibration value of 28.4.

Number-average molecular weights from ebulliometry were accurate to 10%, and compared favorably with those determined by endgroup analysis, based on elemental analysis (Table II).

The x-ray powder diffraction patterns were measured on a Phillips diffractometer, model PW 1051, on polymer samples either as films or as very fine powders. Thin films of hydrocarbon polymers were obtained by vacuum melting and pressing between sheets of cellophane. The samples

TABLE I

Molecular Weights by Ebulliometry

Polymer no.	$(\Delta d/\Delta c)_{c\to 0}$	Number-average molecular weight $\bar{M}_n$
C1	5.05	4,100
C2	2.90	7,100
C3	5.40	3,800
C4	6.60	3,100
C5	7.30	2,800
A1	9.60	2,140
N1	7.10	2,900
N2	11.0	1,870
N3	13.6	1,510

TABLE II

Endgroup Analysis

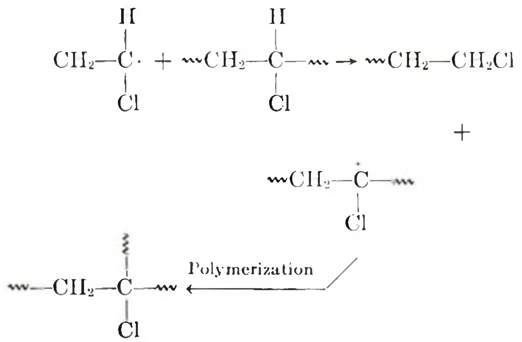
	Chemical analysis		Degree of polymerization	
Polymer no.	C, %	H, %	Analysis	Ebulliometer
N3	39.8	5.18	22 ± 2	23
C3	37.3	4.90	65 ± 6	58

were then recrystallized at a slow standard rate of cooling. Within a sample, crystallinity measurements were found to be reproducible by this method.

Infrared spectroscopic measurements were carried out on a Hilger spectrophotometer, H-800, and a Perkin-Elmer Infracord, on samples in the form of Nujol mulls, films cast from solution, molten films, and KCl disks by conventional methods. Molten films were made for studying the hydrocarbon polymers produced by the reduction of PVC, for measurement in the region 1300–1400 cm.$^{-1}$. For quantitative study of the hydrocarbon bands the samples had to be in an amorphous state as crystallinity alters the intensities of these bands. A heated cell, similar in design to that described by Richards and Thomson,[19] was used. The polymer sample was inserted between two rock salt plates kept at a constant temperature by means of controlled heaters. Film thickness was determined by metal washers of known thickness. The working temperature of the plates was generally 140°C.

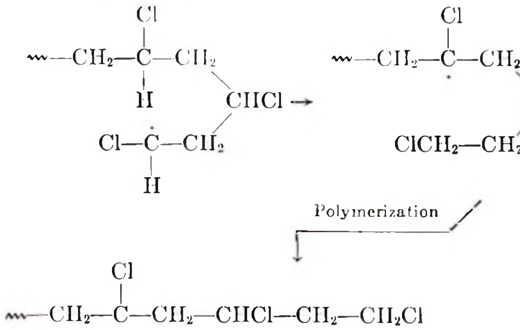
The Degree of Branching

The degree of branching is determined from the number of endgroups but this determination requires a definition of a branch. There are three possible ways in which branches can be produced: (*1*) by polymerization through a terminal double bond of a chain; (*2*) by intermolecular transfer to polymer, which produces long branches [eq. (*2*)];



(2)

(*3*) by intramolecular transfer to polymer ("back-biting"), which produces short chains [eq. (*3*)].



(3)

Polymerization through terminal double bonds is unlikely to contribute significantly in vinyl chloride polymerization.

From a knowledge of the number of chain ends and the molecular weight, the degree of branching can be found. Since determination of terminal $-CH_2Cl$ groups in PVC is not precise,[20] polymer is reduced with lithium aluminum hydride without degradation to a branched hydrocarbon.[21] The terminal methyl groups can be estimated by infrared spectroscopy as in the case of polyethylene. A modified reduction technique[22,23] with dry, peroxide-free tetrahydrofuran (THF) or decalin as solvent was used. Reduction was about 99% complete.

TABLE III
Molecular Weight Changes During Reduction

	Degree of polymerization	
Polymer no.	PVC sample	Reduced product
C2	111	119
C5	43	48
A1	33	30

PVC (1 g.) in THF, under an atmosphere of pure dry nitrogen, was reduced with lithium aluminum hydride (2.5 g.) under reflux for 3 days. The THF was then distilled off and decalin added. The mixture was further refluxed for 7 days. On cooling, anhydrous ethyl acetate was added dropwise to destroy the excess lithium aluminum hydride. Sufficient 50% aqueous nitric acid was added to remove the inorganic residues, and the organic layer separated and repeatedly washed with water. The polymer residue was isolated, purified by repeated dissolution in boiling carbon tetrachloride, and precipitated from methanol.

The above method gave a reproducible produce whose chain branching was identical to that of the original polymer. No significant chain degradation occurred during reduction (Table III).

RESULTS

Polymerization of Vinyl Chloride

Imoto et al.,[24] in an extensive study of the radical polymerization of vinyl chloride in acetaldehyde solution, found no anomalous rate dependences; the rate was proportional to monomer concentration and to square root of initiator concentration.

In order to compare the properties of polymers formed in *n*-butyraldehyde with those formed in other solvents a series of polymers was prepared. The relevant details of the polymerization are set out in Table IV. From these results it is obvious that *n*-butyraldehyde is an efficient chain-transfer agent.

TABLE IV
Vinyl Chloride Polymer Samples

Transfer agent S	Polymer no.	Polymerization temp., °C.	Molecular weight $\bar{M}_n \times 10^{-3}$	$\frac{[I]^a}{[M]} \times 10^{-3}$	$\frac{[S]^b}{[M]}$
None	O1	50	66.5[c]	1.36	
Carbon tetrachloride	C1	35	4.10	6.30	4.3
	C2	50	7.10	1.36	3.0
	C3	50	3.80	6.30	4.3
	C4	65	3.10	1.36	4.3
	C5	80	2.80	1.36	4.3
n-Butyl alcohol	A1	50	2.14	1.36	10.1
n-Butyraldehyde	N1	50	2.90	1.36	0.61
	N2	50	1.87 2.14[c]	1.36	0.90
	N3	50	1.51	1.36	1.08

[a] [I] = initiator concentration, [M] = monomer concentration.
[b] [S] = transfer agent concentration.
[c] Viscosity determined.

Degree of Branching

The reduced hydrocarbon polymers in the amorphous state, i.e. at 140°C. show infrared absorption bands at 1378 cm.$^{-1}$ due to methyl and at 1350 and 1367 cm.$^{-1}$ due to the methylene vibrations.[25] The ratio of the optical densities of the bands at 1378 and 1350 cm.$^{-1}$ was used as a quantitative estimate of the degree of branching.

Various hydrocarbons of known CH_3/CH_2 ratio were used for calibration, and so a Beer's law relationship was established. Cyclohexane was taken as an arbitrary zero. From the calibration results in Table V, the methyl contents of the hydrocarbon polymers were determined, and from the known number-average molecular weight, and assuming two terminal methyl groups per main chain, the degree of branching was determined. The results in Table VI clearly indicate that there is less branching in the lower molecular weight polymers than in the bulk polymer (01). Also despite the similarity in molecular weights polymer formed in aldehyde has less branches than those formed in other media.

TABLE V
Calibration Results

Standard hydrocarbon		$\frac{CH_3}{CH_2}$ ratio	D_{1378}/D_{1350}
n-Decane	$C_{10}H_{22}$	0.25	4.64
n-Dodecane	$C_{12}H_{26}$	0.20	3.86
n-Hexacosane	$C_{26}H_{54}$	0.083	2.01
n-Octacosane	$C_{28}H_{58}$	0.077	1.84
n-Dotriacontaine	$C_{32}H_{66}$	0.067	1.77
n-Hexatriacontane	$C_{36}H_{74}$	0.059	1.54
Cyclohexane	C_6H_6	0.000	0.46

TABLE VI
Degree of Branching

No.	$\frac{D_{1378}}{D_{1350}}$	Total concn. of methyl groups per 10^3 C atoms	Branches per 10^3 C atoms
O1	0.78	16	15
C1	0.84	20	4.0 ± 2.0
C2	0.73	14	4.9
C3	0.90	23	5.6
C4	1.02	29	7.5
C5	1.08	32	8.5
A1	1.12	34	4.1
N1	0.86	21	0[a]
N2	1.14	35	1
N3	1.23	40	0[b]

[a] Value was negative (−1.0).
[b] Value was negative (−2.5).

Crystallinity of Polymer Samples

The x-ray diffraction patterns were used as a measure of the degree of crystallinity. Unoriented crystalline polymer normally gives a pattern consisting of a series of fairly sharp lines superimposed upon a diffuse band due to scattering from the amorphous regions. The integrated intensities of each of these contributions can be used to measure the degree of crystallinity. PVC prepared by radical means is poorly crystalline,[26] but not completely amorphous. The position and angular limits of the amorphous scattering cannot be determined exactly, as the polymer cannot be obtained amorphous. Crystallinities were therefore compared by the relative area under all the crystalline bands, correcting for the background scatter.

TABLE VII
d Spacings of Crystalline PVC from X-Ray and Electron Diffraction (E.D.) measurements

Reflection no.	*d*, A.		Relative intensity	
	X-ray	E.D.	X-ray	E.D.
1	5.25	5.27	0.42	Medium
2	5.10	5.09	0.45	"
3	4.71	4.62	0.77	Strong
4	3.71	3.65	1.00	Medium
5	2.90	2.85	0.09	Very weak
6	2.56	2.60	0.04	" "
7	—	2.52	—	" "
8	2.35	2.31	0.11	Weak
9	2.29	2.26	0.17	"
10	2.09	2.06	0.15	"
11	—	1.82	—	Very weak
12	—	1.74	—	"
13	—	1.69	—	"

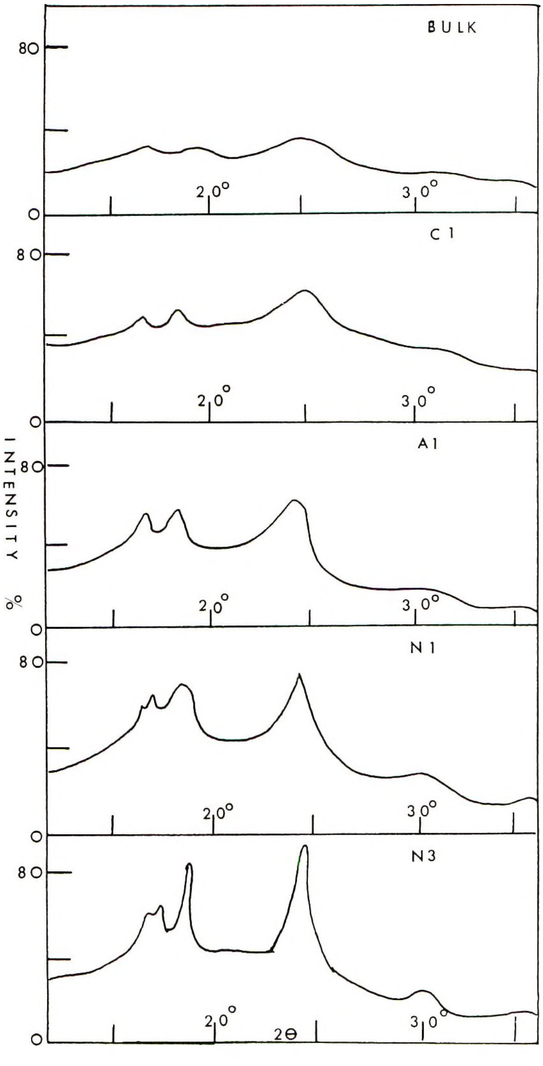


Fig. 1. X-ray diffraction patterns of PVC: (*a*) bulk; (*b*) C1; (*c*) A1; (*d*) N1; (*e*) N3.

The x-ray diffraction pattern for the various samples are shown in Figure 1. The samples prepared in aldehyde are distinctly more crystalline than any other samples. The most crystalline sample, N3, prepared in aldehyde, also shows 9 lines compared with the 4 diffuse bands shown by bulk PVC (Fig. 1*a* and 1*e*). The interplanar distances and the relative intensities of the lines for N3 are shown in Table VII and compared with those obtained by Rylov et al.[6] by electron diffraction.

In general there is a sharpening and increase of intensity of the four basic reflections as the molecular weight decreases; but with *n*-butyl alcohol samples extra, rather diffuse bands appear at 2.5 and 2.9 A. The intensities of the reflections as measured by the areas under the peaks are given

TABLE VIII
Comparison of Polymer Crystallinities

No.	Relative crystallinity	Branches per 10^3 C atoms	$(\bar{M}_n)^{-1} \times 10^4$
C2	0.25	4.9	1.41
C1	0.42	4.0	2.44
C4	0.30	7.5	3.23
C5	0.40	8.5	3.57
A1	0.55	4.1	4.67
N1	0.74	0	3.45
N2	0.96	1	5.35
N3	1.00	0	6.62

along with molecular weights and branching index in Table VIII. In Table VIII sample N3 is arbitrarily taken as completely crystalline. There is no simple correlation between the relative crystallinity and reciprocal molecular weight alone, as in PAN, but however if the degree of branching is approximately constant, as in samples N1, N2, and N3, there is a linear increase in crystallinity with reciprocal molecular weight. It is evident that both molecular weight and the degree of branching are important factors in determining the crystallinity of PVC.

Crystallinity of the Hydrocarbon Reduction Product

The reduction products were also highly crystalline and showed diffraction patterns (Fig. 2) rather similar to that of polyethylene,[27] i.e., two main bands at 4.15 and 3.76 A. The product obtained by reduction of bulk PVC, 01, showed a marked amorphous band, whereas the reduced samples of the aldehyde prepared polymers showed only a very weak band. The relative crystallinity was measured from the ratio of the area of the two

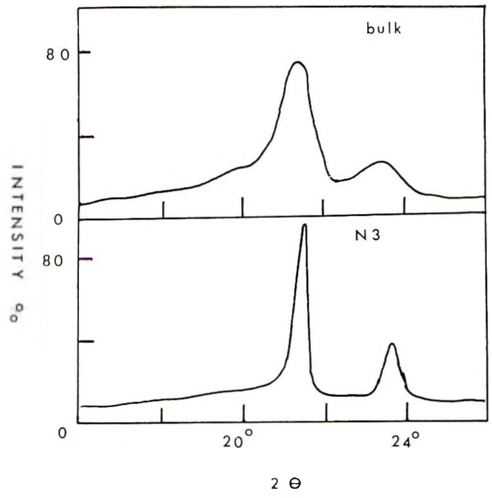


Fig. 2. X-ray diffraction patterns of Reduced PVC: (*a*) bulk; (*b*) N3.

bands, relative to the most crystalline sample N3. In exactly the same way as with the PVC samples, decreasing the branching increased the crystallinity (Table IX).

TABLE IX
Crystallinity of Hydrocarbon Samples

No.	Relative crystallinity	Branching per 10^3 C atoms
O1	0.47	15.
C3	0.85	5.6
N3	1.00	0

DISCUSSION

The postulation of radical–aldehyde complex formation arose from the apparent correlation between crystallinity and syndiotacticity in PVC. This correlation depends on the ratio of infrared absorption at 635 and 692 cm.$^{-1}$, assigned to syndiotactic and isotactic forms, respectively. However, the situation is much more complicated, since both bands show fine structure[28–30] and changes in crystallinity as well as tacticity alter the value of the ratio.

NMR measurements have revealed that the media in which polymerizations are carried out have no effect on the tacticity of PVC, and that polymer prepared at low temperature or in aldehyde media is not stereoregular although crystalline.[13] Tincher[31] has obtained a more direct measure of tacticity and has shown that the stereoregularity of PVC formed in aldehyde is very little different from that obtained in bulk. There is a small, possibly insignificant reduction in the proportion of heterotactic triads (from NMR measurements), but this would not be expected to affect the crystallinity.

The results described in this work support the view of Bovey and Tiers[13] that decreased branching is responsible for the increased crystallinity of PVC. Where the polymer is unbranched, as with polyacrylonitrile, the crystallinity of the polymer is dependent on molecular weight only so that polymers of the same molecular weight prepared in different media exhibit the same degree of crystallinity.[15] The effectiveness of aldehyde in giving highly crystalline PVC arises from their ability to reduce branching and molecular weight simultaneously. When only one of these properties is altered, the change in crystallinity is not so great, so that polymers of the same molecular weight and different degrees of branching show differing tendencies to crystallize.

The ability of aldehydes to reduce chain branching can be explained by strong association between the polymer molecule and aldehyde to such an extent as to sheath the macroradical. Such sheathing would make it unlikely that "back-biting" intramolecular transfer to polymer could take place and so short chain branching would be eliminated. Normal molecular interaction of this kind would not be likely to affect the rate very greatly, whereas complex formation involving the growing radical might well do so.

Note: Our attention has been drawn to an important reference, O. C. Bockman, *J. Polymer Sci. A*, **3,** 3399 (1965), which describes similar work and conclusions. Low molecular weight PVC (D.P. less than 50) prepared in the presence of transfer agents, butyraldehyde, chloroform, tetrahydronaphthalene, and THF were similarly crystalline, but exhibited the same tacticity, as measured by NMR spectroscopy. The degree of branching of the transfer polymers were not measured, however, and no distinction was found in their degrees of crystallinity. Each transfer agent was equally effective in producing crystalline samples. The reduction in molecular weight alone increased the crystallinity of the PVC samples.

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Résumé

Les propriétés d'échantillons de chlorure de polyvinyle préparés par un processus radicalaire en présence de N-butyraldéhyde ont été étudiées du point de vu de la tacticité des polymères, de la ramification, de leur poids moléculaire et de la cristallinité relative. On a examiné le bien-fondé du postulat d'un complexe aldéhyde radical polymérique postulé généralement pour expliquèr la cristallinité croissante. Les polymères ont un degré de polymérisation plus bas et une ramification plus basse que normalement et ses paramètres plutôt qu'une syndiotacticité croissante, sont responsables du haut degré de cristallinité. Le poids moléculaire et le degré de branchement affectent la cristallinité puisque des échantillons de polymères préparés en présence de différents agents de transfert avec des poids moléculaires similaires, sont moins cristallins que ceux préparés en présence d'aldéhyde, mais ils sont déjà plus cristallins toutefois que les polymères en bloc de poids moléculaire élevé. Les polymères préparés en présence d'aldéhyde ont un degré de ramification plus faible que ceux formés en présence des agents de transfert. On en conclu que l'aldéhyde est particulièrement efficace en augmentant la cristallinité du chlorure de polyvinyle de ces deux façons et ainsi apparaît être unique parmi les agents de transfert. Il n'y a pas d'évidence pour supposer quelques complexations entre les radicaux polymériques et l'aldéhyde.

Zusammenfassung

Durch einen radikalischen Prozess in Gegenwart von n-Butyraldehyd erhaltene Polyvinylchloridproben wurden in Bezug auf Polymertaktizität, Verzweigung, Molekulargewicht und relative Kristallinität untersucht. Die zur Erklärung der erhöhten Kristallinität gemachte Annahme eines Polymerradikal-Aldehydkomplexes wurde überprüft. Die Polymeren besassen einen niedrigeren Polymerisationsgrad und geringere Verzweigung als die normalen; diese Parameter und nicht eine erhöhte Syndiotaktizität, waren für den hohen Kristallinitätsgrad verantwortlich. Sowohl Molekulargewicht als auch Verzweigung beeinflussen die Kristallinität, da die in Gegenwart verschiedener Kettenüberträger dargestellten Polymerproben mit ähnlichem Molekulargewicht weniger kristallin als die in Aldehyd dargestellten, aber doch stärker kristallin als hochmolekulare, in Substanz erhaltene Proben waren. Die in Aldehyd dargestellten Polymeren besassen einen niedrigeren Verzweigungsgrad als die in anderen Überträgern gebildeten. Man kam zu dem Schluss, dass Aldehyd auf diesen beiden Wegen eine Erhöhung der Kristallinität von Polyvinylchlorid bewirkt und daher eine einzigartige Stellung unter den Kettenüberträgern einnimmt. Es wurden keine Hinweise auf eine Komplexbildung zwischen Polymerradikalen und Aldehyd erhalten.

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NOTES

Preparation of Mono and Poly-2-oxazolidones from 1,2-Epoxides and Isocyanates

In an earlier investigation Speranza and Peppel[1] reported that vinylcyclohexene diepoxide and a commercial epoxy resin, Epon 828, gave polymeric products upon reaction with 2,4-toluenediisocyanate. The polymers were not characterized and no detailed study was reported. Later, Sandler, Berg, and Kitazawa[2] reported that the polymers isolated by Speranza and Peppel were poly-2-oxazolidones based on a comparison of their infrared spectra to that of model compounds that were synthesized.[2] It was also shown at that time that dimethylformamide (DMF) is not always necessary and that temperatures below 140–160°C. in DMF favor trimerization of the isocyanate rather than addition to the 1,2-epoxide. The trimer, triphenylisocyanurate, m.p. 280°C upon being heated in DMF at 140–160°C. with phenylglycidyl ether gave the known 2-oxazolidone.

We now report some additional examples of the reaction of mono- and diepoxides with mono- and diisocyanates as shown in Table I. The results of experiment indicate that oxazolidone formation can occur even in the absence of a catalyst when heated in DMF for 6 hr. at 160°C. Presumably some amine present in DMF or DMF alone acts as the catalyst. Omission of DMF and catalyst in example 8 gave no reaction. The addition of catalyst in the absence of solvent in example 7 gave a quantitative yield of poly-2-oxazolidone from bisphenol A diglycidyl ether (DGBA) and 2,4-toluenediisocyanate.

Although Gulbins and Hamann[3] earlier indicated that Lewis acids such as zinc chloride or ferric chloride are effective catalysts, they gave no experimental evidence in support. Table I indicates that a Lewis acid catalyst such as zinc bromide acts as an effective catalyst. Pyridine seems to be less effective than tetramethylammonium iodide in catalytic power. However, more data is needed to describe the relative effectiveness of Lewis acids and bases in their ability to catalyze 2-oxazolidone formation.

The molecular weight of two of the polymers (experiments 9 and 11) were determined to be in the range of 2800 as determined in DMF using vapor-phase osmometry. Whether the molecular weights can be increased by suitable variation of the catalyst, solvent, or reaction conditions is yet to be determined.

The use of 1,6-hexanediisocyanate in experiment 10 gave a gelled polymer of unknown structure. Since epoxides and bases catalyze the trimerization of isocyanates to isocyanurates the polymer may contain isocyanurate groups which may be responsible for its being crosslinked.[4] A similar observation using 1,6-hexanediisocyanate under slightly different conditions has been reported.[5,6] Using 2-vinylcyclohexane monoepoxide also causes phenylisocyanate to trimerize rather than to condense when heated in DMF with TMAI catalyst at 150°C. for 6 hr.

Using a diisocyanate prepolymer Adiprene L-315 in experiment 16 with bisphenol A diglycidyl ether gave a polymer which shows the characteristics of poly-2-oxazolidones. Several diisocyanate prepolymers were prepared as earlier described[7] and were reacted similarly to give poly-2-oxazolidones with no free isocyanate groups.

This reaction therefore offers an additional method of curing diisocyanates or diisocyanate prepolymers in place of the more common one using diamines.

TABLE I. Preparation of Monomeric and Polymeric Substituted 2-Oxazolidones from 1,2-Epoxides and Isocyanates

Experiment No.	Epoxide, moles	Isocyanates, moles	Catalyst, g.	Solvent	Reaction conditions		2-Oxazolidone	M.p., °C.	Yield, %	Characteristic infrared spectral bands and comments,[c] μ
					hr.	°C.				
1	3-Phenoxy-1,2-propylene (0.10)	Phenyl (0.10)	TMAI[a] (0.2)	DMF	6	160	3-Phenyl-5-phenoxymethyl	137–8	28	5.60 (w) 5.65 (w) 5.68 (mw) 5.70 (m) 5.72 (m) 5.72 (ms) 5.75 (s) 5.78 (ms) 5.80 (m) 5.81 (ms) 7.08 (s)
2	3-Phenoxy-1,2-propylene (0.10)	Phenyl (0.10)	Pyridine (0.2)	DMF	6	160	3-Phenyl-5-phenoxymethyl	136–7	14	Same as above
3	3-Phenoxy-1,2-propylene (0.10)	Phenyl (0.10)	$ZnBr_2$ (0.2)	DMF	6	160	3-Phenyl-5-phenoxymethyl	136–7	33	Same as above
4	3-Phenoxy-1,2-propylene (0.10)	Phenyl (0.10)	None	DMF	6	160	3-Phenyl-5-phenoxymethyl	136–7	15	Same as above
5	3-Phenoxy-1,2-propylene (0.20)	2,4-Toluenedi- (0.10)	TMAI (0.20)	DMF	6	160	2,4-di[3-(5-phenoxymethyl-2-oxazolidonyl)] toluene	60–63	78	5.50 (w) 5.55 (mw) 5.57 (m) 5.60 (s) 5.62–5.72 (vs) 5.75 (s) 5.85 (s) 5.90 (m) 7.10 (vs)

6	DGBA[b] (0.050)	Phenyl (0.10)	TMAI (0.20)	DMF	6	160	2,2-bis(3-phenyl-5-phenoxymethyl 2-oxaolidone)-propane	40	93	5.55 (w) 5.70 (s) 5.77 (s) 7.10 (s)	5.65 (s) 5.75 (s) 5.85 (s)
7	DGBA (0.025)	2,4-Toluene-di- (0.50)	TMAI (0.20)	None	2	120	Polymer[d] (brittle)	Softens 70–80 m.p. >300	100	5.60 (w) 5.68 (mw) 5.72 (ms) 5.80 (vs) 7.10 (vs)	5.65 (w) 5.70 (m) 5.75 (s) 5.85 (vs)
8	DGBA (0.025)	2,4-Toluene-di- (0.050)	None	None	2	120				No reaction	
9	DGBA (0.050)	2,4-Toluene-di- (0.050)	TMAI (0.20)	DMF	20	160	Polymer Mol. wt.[f] 2880	Softens 175–185	91	5.52 (w) 5.60 (ms) 5.65 (vs) 7.10 (vs) (No absorption at 4.25–4.60 μ)	5.75 (m) 5.63 (ms) 5.84 (ms)
10	DGBA (0.050)	1,6-Hexamethylene-di- (0.050)	TMAI (0.20)	DMF	6	160	Polymer gelled	—	79	5.68 (m) 6.80 (m) 8.05 (m) (No absorption at 4.25–4.60 μ)	5.90 (vs) 12.0 (m)
11	DGBA (0.050)	4,4′-di-phenyl-methane-di- (0.050)	TMAI (0.20)	DMF	6	160	Polymer Mol. wt.[f] 2870	Softens 170 m.p. 190–5	100	5.55 (mw) 5.80 (m)	5.70 (s) 7.10 (s)
12	Epon 828 (0.050)	2,4-Toluene-di- (0.050)	TMAI (0.4)	None	2	120	Polymer (soft)	—	100	—	

(continued)

TABLE I (*continued*)

Experiment No.	Epoxide, moles	Isocyanates, moles	Catalyst, g.	Solvent	Reaction conditions hr.	Reaction conditions °C.	2-Oxazolidone	M.p., °C.	Yield, %	Characteristics infrared spectral bands and comments,[c] μ
13	"	"	"	"	6	160	Polymer (hard)	Softens 90–100	100	4.38 (m) 5.75 (s) 5.82 (vs) 7.10
14	DGBA (0.050)	2,4-Toluenedi- (0.050)	TMAI (0.4)	"	2	120	Polymer (hard)	—	100	—
15	"	"	"	"	6	160	Polymer (hard)	Softens 170–180 m.p. <300	100	5.68 (vs) 5.83 (vs) 7.15 (vs)
16	DGBA (0.050)	2,4-Toluenedi- (0.050)	None	"	6	160	Liquid (viscous)		100	4.43 (vs) 5.75 (w) 5.77 (m)
17	DGBA (3.4 g.)	Adiprene L-315 (17.8 g.)	TMAI (0.06)	"	2	120	Polymer	Softens 65–70 m.p. <300	100	5.60 (w) 5.63 (w) 5.68 (m) 5.75 (s) 5.80 (s) 5.85 (s)

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[a] Tetramethylammonium iodide (Eastman Chemical Co.).

[b] Diglycidyl ether of Bisphenol A. (Dow Chemical Co.)

[c] 2-Oxazolidone (Allied Chem. Co.) has a broad maximum between 5.75–5.80 μ.

[d] When Epon 828 was used in its place similar results were obtained. This polymer and that from DGBA had residual isocyanate groups because of the stoichiometry of this reaction. This experiment was first performed by Speranza and Peppel.[2]

[e] Polyurethane prepolymer terminated with free isocyanate groups. NCO = 9.5%. (E. I. du Pont de Nemours & Co., Inc.).

[f] The molecular weights were determined at Galbraith Labs in Knoxville, Tenn. using vapor-phase osmometry in DMF.

TABLE II
Elemental Analysis

Experiment No.	N, % Calculated	N, % Found
5	5.90	5.04
6	4.85	4.41
9	5.45	5.52
10	5.51	7.40
11	4.75	5.07

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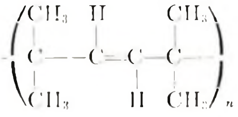
α,ω-Glycols from Copolymers of Isobutylene and 2,5-Dimethyl-2,4-hexadiene

Synopsis

Isobutylene has been copolymerized with 2,5-dimethyl-2,4-hexadiene using a boron trifluoride catalyst in petroleum ether solution. Ozonization of the products followed by reduction with lithium aluminum hydride has furnished polyisobutylene glycols in good yield.

INTRODUCTION

Polymerization of 2,5-dimethyl-2,4-hexadiene with cationic catalysts proceeds rapidly at low temperatures to give a crystalline product which probably has structure I.[1]



$$\left(-\mathrm{C(CH_3)_2-CH{=}CH-C(CH_3)_2}-\right)_n$$

I

Because 2,5-dimethyl-2,4-hexadiene apparently polymerizes only by 1,4-addition, its copolymers with isobutylene should have unsaturation exclusively in the main chain and should give rise to difunctional glycols when their ozonides are reduced with lithium aluminum hydride. A similar cleavage reaction performed on butyl rubber containing 2 mole-% isoprene has been reported previously.[2]

Copolymers having inherent viscosities close to 0.4 were prepared by treating mixtures of isobutylene and 2,5-dimethyl-2,4-hexadiene with 1.0–2.2% boron trifluoride in petroleum ether solution at −78°C. The presence of unsaturation in the copolymers shown in Table I is not evident from the NMR or infrared spectra. Vinyl protons, which are present in very low concentration, are not visible in the NMR. A band in the infrared region at 985 cm.$^{-1}$ characteristic of *trans*-disubstituted olefins occurs in poly(2,5-dimethyl-2,4-hexadiene) but not in the copolymers. However, the copolymers decolorize bromine in carbon tetrachloride solution and are cleaved by ozone to products which correspond closely in molecular weight to the values predicted from equal monomer reactivities. This is especially true in the case of the 40:1 copolymers, which theoretically should give glycols having molecular weights close to 2230.

TABLE I

Isobutylene-2,5-dimethyl-2,4-hexadiene Copolymers and Derived Glycols

Starting molar ratio[a]	BF$_3$, %	Viscosity at 30°C.[b]	M.W. of derived glycol	Monomer ratio[d] in polymer
160:1	1.0	0.44[c]	5870	105:1
40:1	1.0	0.40	2190	39:1
40:1	2.2	0.42	1970	35:1

[a] Isobutylene:2,5-dimethyl-2,4-hexadiene.

[b] Inherent viscosity measured as 0.5% solution in toluene.

[c] An average of two polymerizations.

[d] Calculated from the actual molecular weights determined from hydroxyl equivalents in cleaved products.

Polyisobutylene glycols were obtained by ozonization of the polymers in cyclohexane solution followed by reduction of the ozonides with lithium aluminum hydride. The molecular weights of the glycols were determined by acetic anhydride–pyridine hydroxyl endgroup analysis[3] and were used to calculate the actual monomer ratios in the starting copolymers assuming 100% conversion of double bonds to ozonides.

EXPERIMENTAL

Materials

Isobutylene was the pure grade supplied by Phillips Petroleum Co.

2,5-Dimethyl-2,4-hexadiene was obtained from the Aldrich Chemical Co.

Cyclohexane was Matheson, Coleman and Bell practical grade, purified by extracting with concentrated sulfuric acid and distilling from calcium hydride.

Ozone was generated from a Welsbach Laboratory Ozonator, Model T-23, using oxygen at a flow rate of about 600 ml./min.

Petroleum ether was Mallinckrodt reagent grade, b.p. 30–60°C.

Isobutylene-2,5-dimethyl-2,4-hexadiene Copolymer (40:1 mole ratio). A solution of 20 g. of isobutylene and 1.0 g. of 2,5-dimethyl-2,4-hexadiene in 150 ml. of petroleum ether was cooled to −78°C. in a 250-ml. pressure tube under a slow stream of nitrogen. Three 30-ml. portions of boron trifluoride gas 25°C. and 720 mm. Hg were added at 3-min. intervals from a hypodermic syringe. After 30-min. and 60-min. periods, additional 30-ml. portions of boron trifluoride were injected. At the end of the total reaction time of 1.5 hr. the mixture was poured into 30 ml. of methanol containing 1 g. of sodium bicarbonate. After standing for 15 min. the solution was decanted and the solvents were removed under reduced pressure at room temperature. The crude white product was dissolved in 150 ml. of petroleum ether, filtered, and precipitated by dropwise addition of this solution to 2000 ml. of acetone. The yield of white, sticky copolymer was 17.9 g. (85%) after drying in a vacuum oven at 40°C. for 16 hr. The inherent viscosity of the product was 0.42 (determined in 0.5% toluene solution at 30°C.). The NMR spectrum in carbon tetrachloride solution showed singlets at 8.62 τ(—CH_2—) and at 8.93 τ(—CH_3).

ANAL. Calcd. for a 40:1 monomer ratio: C, 85.66%; H, 14.34%. Found: C, 85.54%; H, 14.36%.

Polyisobutylene Glycol. Isobutylene-2,5-dimethyl-2,4-hexadiene copolymer (13.7 g., prepared from a 40:1 mole ratio of monomers) was dissolved in 600 ml. of cyclohexane and was ozonized for 1 hr. at room temperature. Oxygen was passed through the solution for 30 min. to remove dissolved ozone, and a suspension of 5 g. of lithium aluminum hydride in 100 ml. of ether was added over a 10-min. period. Stirring was continued for 19 hr., after which the mixture was poured onto about 1000 ml. of cracked ice to decompose excess hydride. After acidification with 10% sulfuric acid, the organic layer was washed with 5% sodium bicarbonate solution and water and was dried over magnesium sulfate. Filtration, removal of solvents under reduced pressure, and drying in a vacuum oven at 40°C. gave 13.0 g. (95%) of white polyisobutylene glycol. The inherent viscosity was 0.15 (determined in toluene solution at 30°C.). Hydroxyl endgroup titration gave a molecular weight of 2190. Singlets appeared in the NMR at 8.60 τ(—CH_2) and 8.93 τ(—CH_3).

ANAL. Calcd. for a molecular weight of 2190: C, 84.84%; H, 14.25%. Found: C, 84.47%; H, 14.15%.

The copolymers and glycols described in Table I were obtained by similar procedures.

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