Anionic polymerization of monomers containing functional groups, 11

Anionic polymerizations of alkynyl methacrylates

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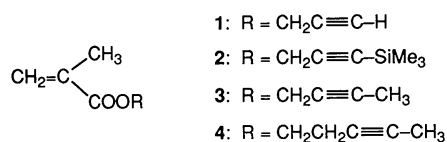   Asahikawa 071, Japan

SUMMARY: Anionic polymerization of 2-propynyl methacrylate (**1**), 3-trimethylsilyl-2-propynyl methacrylate (**2**), 2-butynyl methacrylate (**3**), and 3-pentynyl methacrylate (**4**) was carried out in tetrahydrofuran at −78 °C for 1 h. The employed initiator systems were (diphenylmethyl)potassium/diethylzinc (Et$_2$Zn) and 1,1-bis(4′-trimethylsilylphenyl)-3-methylpentyllithium/lithium chloride (LiCl). Although poly(**1**) was obtained quantitatively with each initiator system, the observed molecular weights were always higher than the predicted values and the molecular weight distributions were rather broad ($\overline{M}_w/\overline{M}_n > 1.3$), indicating a side reaction at the acidic acetylenic proton. On the other hand, the polymerization of **2**–**4**, i.e., methacrylate monomers having no terminal acetylenic protons in the ester moieties, proceeded quantitatively under similar conditions. The resulting poly(**2**–**4**)s were found to possess the predicted molecular weights and narrow molecular weight distributions ($\overline{M}_w/\overline{M}_n < 1.1$), indicating the living character of the polymerization systems. The trimethylsilyl protecting group of poly(**2**) was completely removed to form a poly(**1**) having well-defined chain structures by treating it with potassium carbonate in a mixed solvent of THF and methanol at room temperature for 1 h.

Introduction

The anionic polymerization of alkyl (meth)acrylates has met serious problems as to the yields and the molecular characteristics such as molecular weights and the distributions[1], since an inherent ester carbonyl attack of the anionic initiators and the propagating chain ends occasionally takes place. Moreover, the exothermic instantaneous propagation and the partially aggregated propagating species also cause a broadening of the molecular weight distribution (MWD) of the polymer from kinetic reasons, besides the difficulties in the thorough purification of the monomers[2]. It has been already revealed that the selection of initiator, countercation, solvent, and polymerization temperature is essential for the quantitative and controlled polymerization of alkyl (meth)acrylates[1]. The use of sterically hindered initiators such as 1,1-diphenylhexyllithium and polar solvents such as tetrahydrofuran (THF) has been recommended for the high efficiency of the initiator and the fine control of MWD[3]. Very low polymerization temperature such as −78 °C is preferable to suppress the intramolecular termination known as a back-biting carbonyl attack of the propagating enolate anions[3–5]. In addition, a sufficient purification of methacrylates is almost achieved by distillation in the presence of trialkylaluminium to eliminate the impurities in the monomers[2].

Furthermore, a number of efforts have been intensively dedicated to overcome the above-mentioned drawbacks in recent years[6–16]. These researches succeeded in the controlled anionic polymerization of alkyl (meth)acrylates by developing new polymerization systems to control the primary structure of the resulting polymers such as $\overline{M}_n$s, MWDs, and in some cases the stereoregularities. One of the most striking example is the binary initiator system of bulky organolithiums and LiCl, which was developed by Teyssié et al.[8, 9] This initiator system enables us to produce the well-defined poly(*tert*-butyl acrylate)[8] and poly(methacrylate)s[9] having extremely narrow MWDs. We recently found that the simple addition of Et$_2$Zn to organopotassiums in THF induced the living anionic polymerization of alkyl methacrylates to produce a stabilized propagating species[16]. It is believed that the added Et$_2$Zn acts as a Lewis acid to dissociate the aggregated propagating carbanions and to form a single active species after shifting the equilibrium state in accordance with the combination of organolithium and trialkylaluminium[7]. The undesirable back-biting might be also eliminated to form stable and less nucleophilic active

1: R = $CH_2C\equiv C-H$

$CH_2=C\diagdown^{CH_3}_{COOR}$

2: R = $CH_2C\equiv C-SiMe_3$

3: R = $CH_2C\equiv C-CH_3$

4: R = $CH_2CH_2C\equiv C-CH_3$

chain ends. Retardation of the propagation reaction was apparently observed after addition of Et_2Zn even in a polar basic solvent as THF.

In the present study, we focus on the anionic polymerization of alkyl methacrylates containing reactive carbon-carbon triple bonds (acetylene moieties) in the alkyl side chain by using the above-mentioned initiating systems. The first monomer attempted is 2-propynyl methacrylate (**1**, propargyl methacrylate)[a,17], which has an acidic terminal acetylene proton on the alkyl group. In the anionic polymerization of **1**, the most probable side reactions are the abstraction of the acetylene proton and the nucleophilic addition of the carbanionic species toward the $C\equiv C$ bond. The acidity of the terminal acetylene proton ($pK_a = 25$)[18] is indeed comparable to that of ethyl acetate ($pK_a = 24-25$; corresponding to the active chain ends) and, more seriously, it is much higher than that of diphenylmethane ($pK_a = 34$, conjugated acid of the initiator used here). This suggests the high feasibility of the proton abstractions from the acetylene moieties during the course of and, especially, at the initial stage of the polymerization of **1**. In addition, terminal acetylene moieties ($C\equiv CH$) are known to show higher reactivities toward addition reactions and polymerizations compared with those of inner acetylene moieties.

The other monomers employed in this study are 3-trimethylsilyl-2-propynyl methacrylate (**2**), 2-butynyl methacrylate (**3**), and 3-pentynyl methacrylate (**4**). These monomers possess disubstituted inner $C\equiv C$ functions that are less reactive than the terminal $C\equiv CH$. We have recently reported the living anionic polymerization of (trimethylsilylethynyl)styrenes[19] and 4-(4′-trimethylsilyl-3′-butynyl)styrene[20]. Even in case of the styrene derivatives, which produce strongly nucleophilic propagating carbanions, no side reactions concerning the nucleophilic addition toward disubstituted $C\equiv C$ bonds were observed, while in the latter case an abstraction of the methylene proton adjacent to the $C\equiv C$ groups occurred to some extent at elevated polymerization temperature. Since the enolate-type propagating carbanions of methacrylates are much less nucleophilic and basic than those derived from styrenes, the coexistence of the inner carbon-carbon triple bond and the propagating species derived from **2**–**4** are highly expected.

In this paper, we attempt the anionic polymerization of four alkynyl methacrylates, **1**-**4**, to expand the range of functional monomers capable of a controlled polymerization, since it is still an important area for the design of new functional macromolecules having precisely designed chain architecture. The versatility of the binary initiator systems (organolithium/LiCl[8,9] and organopotassium/Et_2Zn[16]) will be demonstrated for the controlled polymerization of functional methacrylates.

Results and discussion

As described in the Introduction, great progress both on the formation of long-lived growing species and on the precise control of the molecular weights and the MWDs has been recently attained in the anionic polymerization of alkyl (meth)acrylates, particularly by the two binary initiating systems[8,9,16]. In these systems, the added $LiCl$[8,9] and Et_2Zn[16] interact with the propagating chain ends as a common-ion salt or a Lewis acid to shift the ionic association equilibrium to the nonassociated species during the course of propagation[10]. The slower propagation rate and the reduced nucleophilicity of the resulting single active species play a very important role to regulate the molecular weights and the MWDs.

Anionic polymerization of **1**

Anionic polymerization of **1** was first investigated in THF at $-78\,°C$ for 1 h, as shown in Tab. 1. The employed initiators were 1,1-bis(4′-trimethylsilylphenyl)-3-methylpentyllithium, **5**, prepared from *sec*-butyllithium and 1,1-bis(4′-trimethylsilylphenyl)ethylene[21], and (diphenylmethyl)potassium (Ph_2CHK). These sterically hindered initiators, **5** and Ph_2CHK, were used either in the presence or in the absence of $LiCl$ and Et_2Zn, respectively.

The initiation reaction of **1** with **5** seemed to be instantaneous, since a rapid color change of the reaction system was observed. The poly(**1**) was obtained in quantitative yield and all the polymeric product was soluble in common organic solvents. The chemical structure of poly(**1**) was characterized by ^1H, ^{13}C NMR and IR spectroscopies (see Experimental part). The pendant propargyl moiety was found to be intact under the polymerization conditions. These are contrasting results to the early finding of D'Alelio and Evers[17], who reported that an insoluble material was partially formed along with a soluble polymer. The SEC curve of the resulting polymer was almost unimodal but showed a tailing toward low molecular weight region and the polydispersity index, $\overline{M}_w/\overline{M}_n$, was

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[a] Although the anionic polymerization of **1** has been previously reported in this report, the yields of the polymers obtained with organolithiums were not always quantitative and the product contained an insoluble polymer in a proportion of 10–30%. For this explanation, they suggested that the metal acetylides formed by the proton abstraction also initiated the polymerization of **1** to result in cross-linking and formation of insoluble products along with the usual propagation to afford a linear polymer.

Tab. 1. Anionic polymerization of **1**–**4** in THF at $-78\,^{\circ}$C for 1 h

Exp. no.	Monomer (amount in mmol)	Initiator (amount in mmol)	Additive (amount in mmol)	Additive/ Initiator (mole ratio)	Yield in %	$10^{-3} \cdot \bar{M}_{\mathrm{n}}$			$\bar{M}_{\mathrm{w}}/\bar{M}_{\mathrm{n}}$ [a]
						calc.	SEC[a]	NMR[b]	
1	**1** (4.76)	*sec*-BuLi (0.0699)/TMS$_2$DPE[c] (0.0754)	–	–	100	10	19	–	1.24
2	**1** (4.66)	*sec*-BuLi (0.0686)/TMS$_2$DPE (0.144)	LiCl (0.231)	3.4	100	8.8	18	16	1.17
3	**1** (3.83)	Ph$_2$CHK (0.0524)	–	–	65	5.9	9.6	–	1.58
4	**1** (4.08)	Ph$_2$CHK (0.0490)	Et$_2$Zn (0.755)	15	100	11	26	–	1.27
5	**2** (2.84)	*sec*-BuLi (0.0468)/TMS$_2$DPE (0.0993)	–	–	100	12	12	–	1.17
6	**2** (3.00)	*sec*-BuLi (0.0584)/TMS$_2$DPE (0.140)	LiCl (0.244)	4.2	100	10	11	11	1.06
7	**2** (3.45)	*sec*-BuLi (0.0318)/TMS$_2$DPE (0.0888)	LiCl (0.189)	5.9	100	22	26	23	1.04
8	**2** (5.07)	*sec*-BuLi (0.0266)/TMS$_2$DPE (0.0734)	LiCl (0.110)	4.1	100	38	50	47	1.04
9	**2** (2.43)	Ph$_2$CHK (0.0460)	–	–	100	11	18	–	1.87
10	**2** (3.89)	Ph$_2$CHK (0.0713)	Et$_2$Zn (0.927)	13	100	11	11	–	1.08
11	**3** (6.81)	*sec*-BuLi (0.0885)/TMS$_2$DPE (0.137)	–	–	100	11	12	–	1.12
12	**3** (4.12)	*sec*-BuLi (0.0718)/TMS$_2$DPE (0.132)	LiCl (0.270)	3.8	100	8.3	11	12[d]	1.05
13	**3** (7.29)	*sec*-BuLi (0.0430)/TMS$_2$DPE (0.0915)	LiCl (0.226)	5.3	100	24	29	26[d]	1.09
14	**3** (4.56)	Ph$_2$CHK (0.0566)	–	–	100	11	14	–	1.28
15	**3** (4.65)	Ph$_2$CHK (0.0582)	Et$_2$Zn (0.729)	13	100	11	12	–	1.06
16	**4** (4.36)	*sec*-BuLi (0.0636)/TMS$_2$DPE (0.110)	LiCl (0.277)	4.4	100	11	15	13	1.08
17	**4** (4.08)	Ph$_2$CHK (0.0529)	Et$_2$Zn (0.580)	11	100	12	15	–	1.09

[a] $\bar{M}_{\mathrm{n}}$ (SEC) and $\bar{M}_{\mathrm{w}}/\bar{M}_{\mathrm{n}}$ were obtained from SEC calibration using poly(methyl methacrylate) standards.

[b] $\bar{M}_{\mathrm{n}}$ (NMR) was determined from end group analysis using ^{1}H NMR spectroscopy.

[c] 1,1-Bis(4'-trimethylsilylphenyl)ethylene.

[d] $\bar{M}_{\mathrm{n}}$ was obtained by VPO.

1.24. The molecular weight determined by the SEC calibration using poly(methyl methacrylate) standards was significantly larger than the calculated value based on the molar ratio of **1** to **5**. Similar result was observed in the polymerization of **1** with a binary initiator system of **5** and LiCl, although the polydispersity index became slightly narrower, from $\bar{M}_{\mathrm{w}}/\bar{M}_{\mathrm{n}}$ = 1.24 to 1.17. On the other hand, the polymerization of **1** with Ph$_2$CHK did not proceed quantitatively and gave poly(**1**) only in 65% yield. The polymer possessed quite broad MWD and ill-controlled $\bar{M}_{\mathrm{n}}$ value (run 3). Yield as well as MWD was improved by addition of Et$_2$Zn to the system. Quantitative yield was obtained within 1 h, and the polydispersity index decreased from 1.58 to 1.27.

The deviation in $\bar{M}_{\mathrm{n}}$ value could be well accounted for by the loss of initiator at the initial stage, probably due to the acetylene proton abstraction. The acetylenic proton abstraction during the propagation could be almost suppressed by using the recently developed initiating systems, although the acetylene proton is considered to be sufficiently acidic (pK_{a} = 25)[18] against the enolate-type propagating carbanion derived from methacrylate monomers. It is surprising that the polymerization of **1**, possessing an acidic terminal acetylene proton, quantitatively gives a linear soluble polymer, while the control of $\bar{M}_{\mathrm{n}}$ and MWD is not perfect due to the side reactions.

Anionic polymerization of **2**

Similar to the successful anionic polymerization of styrenes having C≡CSiMe$_3$ moieties[19, 20], we herein designed the novel protected monomer **2** to synthesize poly(**1**) having well-defined chain structures through the living anionic polymerization of **2** and the subsequent deprotection of the resulting polymer. The terminal acetylene proton of **1** was purposefully masked with a trimethylsilyl protecting group.

In each polymerization, rapid initiation was observed and the complete consumption of **2** was achieved within 1 h at $-78\,^{\circ}$C to give a soluble polymer in 100% yield. The trimethylsilyl protecting group of the resulting poly(**2**) was stable and intact during the course of polymerization and the polymer isolation. No removal of the protecting group was observed on the spectroscopic analyses after several reprecipitations. The spectroscopic analyses revealed that the vinyl polymerization proceeded exclusively on the methacrylate unsaturation of **2**. The SEC curves of poly(**2**) showed unimodal and symmetrical peaks. In most cases, the $\bar{M}_{\mathrm{w}}/\bar{M}_{\mathrm{n}}$ values of the poly(**2**)s were less than 1.1. Furthermore, the most $\bar{M}_{\mathrm{n}}$ values showed good agreement with the calculated values, indicating the high initiator efficiency in the anionic polymerization of **2**. The $\bar{M}_{\mathrm{w}}/\bar{M}_{\mathrm{n}}$ of poly(**2**) produced with organo-

lithium initiator **5** in THF was 1.17. As expected from the previous reports[8–10], MWDs of the poly(**2**)s were satisfactorily narrowed to be within 1.1 (runs 6–8), when a 3–5 fold molar excess of LiCl was added to the initiator system of **5**. As discussed later, the trimethylsilyl protecting group of poly(**2**) is readily removed by treating with tetrabutylammonium fluoride in THF/methanol, while the trimethylsilyl groups on the initiator residue of **5** is intact under the same conditions. After the deprotection, the $\overline{M}_n$ values of three poly(**2**) samples (runs 6–8) were determined by end group analysis using ^{1}H NMR spectroscopy as previously reported[b, 21]. The molecular weights thus obtained agreed with the calculated values, supporting the quantitative initiator efficiencies and the fine $\overline{M}_n$ control by the molar ratios of **2** to **5**. The poly(**2**) formed by the direct initiation with Ph₂CHK in THF at $-78\,^\circ$C possessed very broad MWD ($\overline{M}_w/\overline{M}_n = 1.87$) and higher $\overline{M}_n$ value than the calculated one, although a complete conversion of **2** was observed after 1 h reaction. By the addition of 12 equivalents of Et₂Zn to the polymerization system with Ph₂CHK, the $\overline{M}_w/\overline{M}_n$ value of the resulting poly(**2**) was dramatically reduced from 1.87 to 1.08 (Fig. 1) and the observed molecular weight agreed well with the calculated value. Thus, Et₂Zn apparently induces the controlled anionic polymerization of **2** in conjunction with Ph₂CHK as an initiator. This is consistent with our results previously observed for other (meth)acrylates such as *tert*-butyl acrylate[22] and methyl, isopropyl, and *tert*-butyl methacrylates[16]. The protection of an acidic proton of C≡CH with trimethylsilyl group is essential and effective for the controlled polymerization of methacrylate derivative having a C≡CH group.
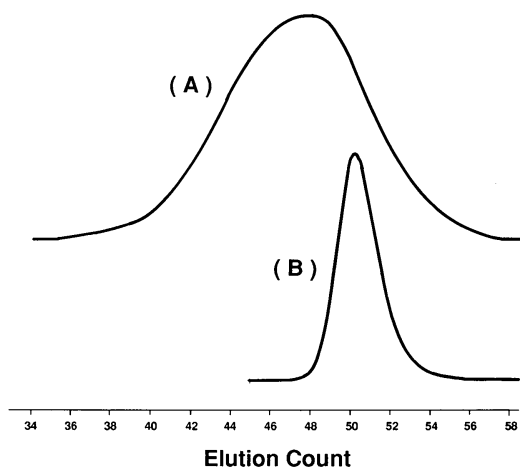

Fig. 1. SEC curves of poly(**2**) obtained at $-78\,^\circ$C with Ph₂CHK (A), $\overline{M}_w/\overline{M}_n = 1.87$ (Tab. 1, run 9), and with Ph₂CHK/Et₂Zn (B), $\overline{M}_w/\overline{M}_n = 1.08$ (Tab. 1, run 10)

*Deprotection of trimethylsilyl group from poly(**2**)*

The trimethylsilyl group on poly(**2**) was quantitatively removed in order to regenerate the terminal acetylene group by the reaction of poly(**2**) with potassium carbonate in a mixed solvent of THF and methanol at room temperature for 3 h (Scheme 1)[23]. The deprotection reaction

Scheme 1 :
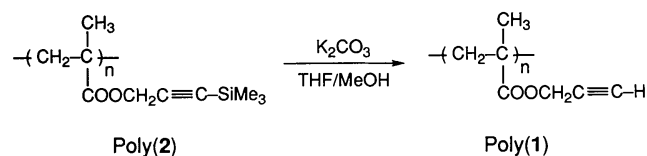
proceeded homogeneously, and a white powder of polymer was obtained after pouring the mixture into a large excess of water. The resulting polymer was characterized by the ^{1}H, ^{13}C NMR and IR spectroscopies, and SEC measurement. In the ^{1}H NMR spectrum of the polymer after deprotection, the strong signal at 0.16 ppm due to the trimethylsilyl groups completely disappeared and a new signal corresponding to the terminal acetylene proton appeared at 2.49 ppm. As shown in Fig. 2, the ^{13}C NMR spectra show that the strong signal of SiCH₃ at -0.1 ppm completely disappears after the deprotection. In addition, the two carbon signals due to protected C≡CSi at 92 and 99 ppm disappear and alternatively the signals for C≡CH are newly observed at 75 and 77 ppm. In the IR spectrum of poly(**2**), the absorptions due to the δ_{Si-C} and the $\nu_{C≡CSi}$ at 1252 cm^{-1} and 2187 cm^{-1}, respectively, diminished after deprotection. Two characteristic absorptions derived from terminal acetylene function alternatively appeared at 2130 cm^{-1} ($\nu_{C≡C}$) and 3298 cm^{-1} ($\nu_{≡CH}$). These spectroscopic analyses confirm the complete removal of trimethylsilyl protecting group from poly(**2**) without unexpected side reactions such as hydrolysis and ester exchange reaction. All the spectra here observed and the solubility of the polymer after deprotection were in good accordance with those of authentic poly(**1**) obtained directly by the anionic polymerization of **1**, also supporting the formation of poly(2-propynyl methacrylate). Furthermore, the SEC curve of the deprotected polymer shifts toward low molecular weight side while keeping the narrow MWD, as can be seen in Fig. 3. This strongly indicates the absence of chain degradation and cross-linking during the course of deprotection reaction under the conditions mentioned above. We thus substantiate the tailored synthesis of poly(**1**) through the controlled anionic polymerization of **2** and the subsequent deprotection reaction of the resulting polymer.

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[b]   The 18 trimethylsilyl protons of initiator residue derived from **5** provide valuable probes for determining $\overline{M}_n$ by ^{1}H NMR analysis.
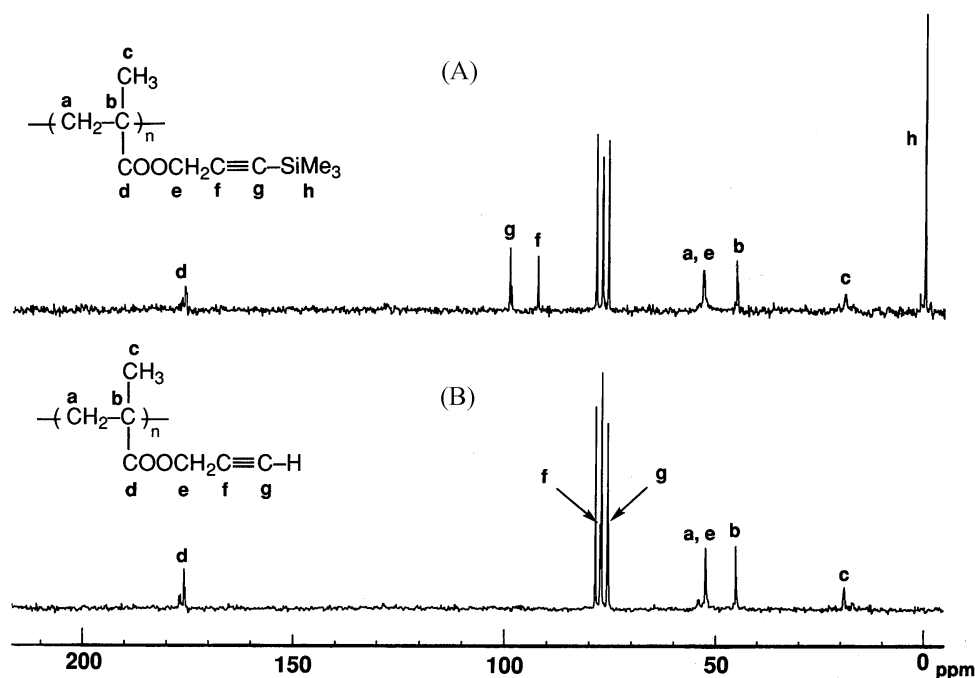
Fig. 2. ^{13}C NMR spectra (CDCl$_3$) of poly(**2**) before deprotection (A) and after deprotection (B)
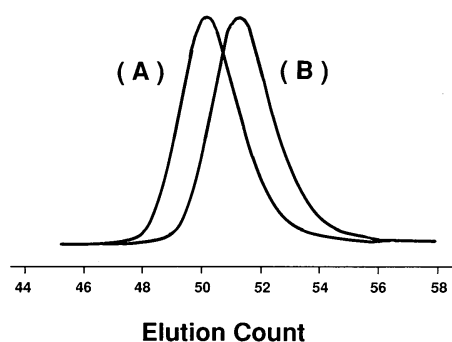
Fig. 3.   SEC curves of poly(**2**) before deprotection (A); $\overline{M}_\mathrm{w}/\overline{M}_\mathrm{n}$ = 1.08 and after deprotection (B); $\overline{M}_\mathrm{w}/\overline{M}_\mathrm{n}$ = 1.10

*Anionic polymerization of **3** and **4***

We have next attempted to polymerize **3** and **4** with the same initiator systems to compare their polymerization behaviors with that of **1**. In monomers **3** and **4**, the acidic terminal acetylene protons are substituted with methyl group. In other words, they possessed inner acetylene functions on the ester alkyl groups. Their anionic polymerizations always proceeded smoothly at −78 °C within 1 h to give polymers in quantitative yields under similar conditions to those of **1** and **2**. The polymerization behaviors of **3** and **4** resembled that of **2** from the viewpoints of molecular weight control. The $\overline{M}_\mathrm{n}$ values were usually regulated well by the molar ratios of monomer to initiators. The $\overline{M}_\mathrm{n}$s of two poly(**3**) samples measured by vapor pressure osmometry were actually close to the calculated values. By addition of LiCl or Et$_2$Zn to the initiator systems, the MWDs of poly(**3**) were always very narrow ($\overline{M}_\mathrm{w}/\overline{M}_\mathrm{n}$ < 1.1), while no addition gave broader MWDs of the polymers. Similarly to the case of **3**, poly(**4**)s of predicted molecular weights and narrow MWDs were obtained by each binary initiator system of **5** and LiCl or Ph$_2$CHK and Et$_2$Zn, respectively.

Thus, we have successfully demonstrated that the controlled anionic polymerizations of **2**–**4**, i.e., alkynyl methacrylates bearing inner acetylene moieties, quantitatively give polymers of well-defined chain structures by the binary initiator systems, **5** and LiCl or Ph$_2$CHK and Et$_2$Zn. The additive effect of LiCl, which leads to the fine control of molecular weight and MWD, has been already confirmed in the anionic polymerization of several methacrylates bearing (protected) functional moieties. The functional monomers include 3-(trialkoxysilyl)pro-pyl[24], 6-[4-(4-methoxyphenyl)phenoxy]hexyl[25], 2-[(tri-alkylsilyl)oxy]ethyl[26], 2-[(methoxymethyl)oxy]ethyl[27], (2,2-dimethyl-1,3-dioxolan-4-yl)methyl[27], glycidyl[28], and (dimethylamino)ethyl[29] methacrylates. The results obtained in this study are consistent with the former successful examples. As described before, we have recently found that the addition of Et$_2$Zn to the organopotassium initiator reduces the rate of propagation and narrows the MWD of the resulting poly(alkyl methacrylate)s dramatically[16]. This new binary anionic initiator is also effective for *N*,*N*-dialkyl-acrylamides to regulate the tacticity of the repeating units along with the M_n control and the

Tab. 2. Solubility of polymers[a]

Solvent	poly(**1**)	poly(**2**)	poly(**3**)	poly(**4**)	PMMA
hexane	I	S	I	I	I
benzene	S	S	S	S	S
toluene	S	S	S	S	S
chloroform	S	S	S	S	S
dichlormethane	S	S	S	S	S
diethyl ether	I	S	I	S	I
1,4-dioxane	S	S	S	S	S
tetrahydrofuran	S	S	S	S	S
ethyl acetate	S	S	S	S	S
acetone	S	S	S	S	S
N,N-dimethylforma-mide	S	S	S	S	S
dimethyl sulfoxide	S	I	S	S	S
pyridine	S	S	S	S	S
ethanol	I	S	I	I	I
methanol	I	S	I	I	I
H_2O	I	I	I	I	I

[a] I: insoluble, S: soluble.

Tab. 3. Glass transition temperatures of polymers

Polymer	Countercation	$10^{-3} \cdot \overline{M}_n$ (obs.)	$T_g/°C$
poly(**1**)	K^+	8.3	55
poly(**2**)	Li^+	26	52
poly(**2**)	K^+	11	54
poly(**3**)	Li^+	29	71
poly(**3**)	K^+	12	63
poly(**4**)	Li^+	15	36
poly(**4**)	K^+	15	35

reducing of the MWD[30]. In addition to these reports, the polymerization result in this study shows the versatility of the new binary initiator system comprised of Ph₂CHK and Et₂Zn for the living anionic polymerization of functional (meth)acrylic acid derivatives.

Tab. 2 shows the solubilities of the resulting polymers. The solubilities of poly(**1**) and poly(**3**) resembled that of poly(methyl methacrylate). They were readily soluble in a wide range of organic solvents but insoluble in hexane, diethyl ether, ethanol, methanol, and water. The poly(**4**) also showed similar solubility to poly(**1**) and poly(**3**) but was soluble in diethyl ether, indicating the small effect of alkyl chain length on the solubility. The substitution of the terminal acetylene proton by a trimethylsilyl group remarkably changed the solubility of poly(**2**) from that of poly(**1**). After deprotection of the trimethylsilyl group of poly(**2**), the solubility of the polymer changed and showed good agreement with that of poly(**1**), supporting the formation of a linear poly(propargyl methacrylate).

The glass transition temperatures (T_g) of poly(**1**) to poly(**4**) were measured by differential scanning calorimetry as summarized in Tab. 3. The polymers showed T_g values between 35 and 71 °C, which are apparently lower

than that of poly(methyl methacrylate) ($T_g = 130$ °C). Among the polymers, poly(**4**) showed the lowest T_g around 35 °C, probably due to the mobility of the longer alkyl chain. After substitution of the acetylene hydrogen of poly(**1**) with the methyl group, the T_g slightly increased from 55 to 71 °C for poly(**3**).

In conclusion, it is suggested from the analyses of the molecular weight and its distribution that the anionic polymerization of propargyl methacrylate, **1**, is accompanied with side reactions to some extent, especially in the initiation step. By contrast, the anionic polymerization of **2**–**4**, i.e., alkynyl methacrylates having a trimethylsilyl-protected acetylene moiety or inner C≡C linkages, proceeds in a living fashion in THF at –78 °C by the initiation with Ph₂CHK/Et₂Zn and **5**/LiCl to give polymers having well-controlled chain lengths. Quantitative deprotection of the trimethylsilyl group on the resulting poly(**2**) is attained by treating it with potassium carbonate to give a poly(propargyl methacrylate) bearing a C≡CH moiety in each monomer unit.

Experimental part

Materials

Commercially available methacryloyl chloride, 2-propyn-1-ol, 2-butyn-1-ol, and 3-pentyn-1-ol were used without purification. 3-Trimethylsilyl-2-propyn-1-ol was synthesized from 2-propyn-1-ol according to the reported procedure[31]. Triethylamine was dried and distilled over CaH₂ under nitrogen. Heptane was washed with conc. H₂SO₄ and dried over MgSO₄, and then dried over P₂O₅ for 1 day under reflux. It was then distilled in the presence of BuLi under nitrogen. Diethylzinc (Tosoh-Akzo Co., Ltd.) was distilled under reduced pressure and was diluted with dry THF. Lithium chloride was dried in vacuo for 2 days and used as a THF solution. Trioctylaluminium (Sumitomo Chemical Industry Co., Ltd.) was diluted with dry heptane. THF was refluxed over sodium wire for 6 h and distilled over lithium aluminium hydride, and finally distilled on a vacuum line from sodium naphthalenide solution.

Initiators

Commercially available *sec*-BuLi (1.3 M in cyclohexane, Nacalai Tesque Inc.) was used without further purification. (Diphenylmethyl)potassium was synthesized by the reaction of diphenylmethane and potassium naphthalenide in THF at room temperature for 48 h. The concentration of the initiators was determined by colorimetric titration with 1-octanol in a sealed reactor in vacuo as previously reported[32].

*2-Propynyl methacrylate (**1**)*

Methacryloyl chloride (6.19 g, 59.2 mmol) in ether (10 mL) was added dropwise to a mixture of 2-propyn-1-ol (3.00 g, 53.5 mmol) and triethylamine (14 mL, 100 mmol) in ether

(30 mL) at 0 °C over 30 min under nitrogen. The mixture was stirred at room temperature overnight and filtered to remove triethylamine hydrochloride. The filtrate was washed with 2N HCl, saturated NaHCO$_3$, and water and then dried over anhydrous MgSO$_4$. After concentration of the ether solution, vacuum distillation from CaH$_2$ gave a colorless liquid of 2-propynyl methacrylate (3.39 g, 27.3 mmol, 51%, b. p. 60 °C/33 mmHg (lit.[17]: 83 °C/65 mmHg)).

^{1}H NMR (90 MHz, CDCl$_3$): δ = 1.97 (m, 3H, =C—CH$_3$), 2.49 (t, 1H, ≡C—H, J_4 = 2.4 Hz), 4.76 (d, 2H, OCH$_2$), 5.63 (m, 1H, =CH$_2$ cis), 6.18 (m, 1H, =CH$_2$ trans).

^{13}C NMR (22.5 MHz, CDCl$_3$): δ = 18.1 (=C—CH$_3$), 52.1 (OCH$_2$), 74.7 (C—H), 77.8 (CH$_2$C≡), 126.3 (=CH$_2$), 135.6 (C=CH$_2$), 166.3 (C=O).

IR (KBr): 815, 1163, 1298, 1321, 1640, 1717 (C=O), 2241 (C≡C) cm^{-1}.

3-Trimethylsilyl-2-propynyl methacrylate (2)

By use of a procedure similar with that described for the preparation of 1, 6.66 g (63.7 mmol) of methacryloyl chloride was reacted with 6.24 g (48.7 mmol) of 3-trimethylsilyl-2-propyn-1-ol[31] to afford a colorless liquid of 2 (7.27 g, 37.0 mmol, 76%, b.p 50–51 °C/0.35 mmHg).

^{1}H NMR (90 MHz, CDCl$_3$): δ = 0.16 (s, 9H, SiCH$_3$), 1.94 (m, 3H, =C—CH$_3$), 4.74 (s, 2H, OCH$_2$), 5.59 (m, 1H, =CH$_2$ cis), 6.15 (m, 1H, =CH$_2$ trans).

^{13}C NMR (22.5 MHz, CDCl$_3$): δ = −0.2 (SiCH$_3$), 18.4 (=C—CH$_3$), 53.0 (OCH$_2$), 92.1 (C≡C—SiMe$_3$), 99.3 (C≡C—SiMe$_3$), 126.4 (=CH$_2$), 135.9 (C=CH$_2$), 166.7 (C=O).

IR (KBr): 813, 1154, 1252, 1293, 1316, 1641, 1728 (C=O), 2186 (C≡C) cm^{-1}.

2-Butynyl methacrylate (3)

By use of a procedure similar with that described for the preparation of 1, 23.85 g (228 mmol) of methacryloyl chloride was reacted with 12.42 g (177 mmol) of 2-butyn-1-ol to afford a colorless liquid of 3 (17.39 g, 126 mmol, 71%, b.p. 58–59 °C/4–5 mmHg).

^{1}H NMR (90 MHz, CDCl$_3$): δ = 1.86 (t, 3H, ≡C—CH$_3$, J_5 = 2.4 Hz), 1.96 (m, 3H, =C—CH$_3$), 4.72 (q, 2H, OCH$_2$, J_5 = 2.4 Hz), 5.60 (m, 1H, =CH$_2$ cis), 6.15 (m, 1H, =CH$_2$ trans).

^{13}C NMR (22.5 MHz, CDCl$_3$): δ = 3.5 (≡C—CH$_3$), 18.2 (=C—CH$_3$), 52.9 (OCH$_2$), 73.3 (C≡C—CH$_3$), 82.9 (C≡C—CH$_3$), 126.0 (=CH$_2$), 135.9 (C=CH$_2$), 166.7 (C=O).

IR (KBr): 814, 1157, 1295, 1316, 1640, 1722 (C=O), 2241 (C≡C) cm^{-1}.

3-Pentynyl methacrylate (4)

By use of a procedure similar with that described for the preparation of 1, 6.34 g (60.6 mmol) of methacryloyl chloride was reacted with 4.71 g (56.0 mmol) of 3-pentyn-1-ol to afford a colorless liquid of 4 (4.45 g, 29.2 mmol, 52%, b.p. 43–45 °C/0.8 mmHg).

^{1}H NMR (90 MHz, CDCl$_3$): δ = 1.74 (t, 3H, C—CH$_3$, J = 2.6 Hz), 1.91 (m, 3H, =C—CH$_3$), 2.46 (m, 2H, CH$_2$—C≡C), 4.16 (t, 2H, OCH$_2$, J = 7.1 Hz), 5.53 (m, 1H, =CH$_2$ cis), 6.09 (m, 1H, =CH$_2$ trans).

^{13}C NMR (22.5 MHz, CDCl$_3$): δ = 3.4 (≡C—CH$_3$), 18.2 (=C—CH$_3$), 19.2 (CH$_2$—C≡), 63.0 (OCH$_2$), 74.7 (C≡C—CH$_3$), 77.1 (C≡C—CH$_3$), 125.5 (=CH$_2$), 136.3 (C=CH$_2$), 167.1 (C=O).

IR (KBr): 815, 1163, 1298, 1321, 1640, 1717 (C=O), 2241 (C≡C) cm^{-1}.

Purification of monomers

Monomers were purified by column chromatography (silica gel, hexane/ethyl acetate = 9/1) and fractional distillation in vacuo from CaH$_2$. After careful fractional distillation, the purified methacrylates were sealed off under degassed conditions in an apparatus equipped with a breakseal in the presence of CaH$_2$. The monomer was stirred for 20 h at ambient temperature and then distilled from CaH$_2$ on a vacuum line into ampoules fitted with breakseals. The distilled monomers were treated with 1.5–2 mol-% of 0.4 M trioctylaluminium in heptane for 30 min and again distilled under high vacuum conditions into an ampoule fitted with a breakseal. The monomers were diluted with dry THF and the resulting monomer solutions (0.4–0.7 M) were stored at −30 °C until ready to use for the polymerization.

Anionic polymerization

All polymerization was carried out at −78 °C under high vacuum conditions in an all-glass apparatus equipped with several breakseals[32]. Monomer in THF was rapidly added to a THF solution of initiator with vigorous shaking of the apparatus. The polymerization was quenched with degassed methanol. The reaction mixture of 1 was concentrated by an evaporator, and then poured into a large excess of hexane to precipitate the polymer. Similarly, the polymers of 3 and 4 were precipitated into methanol and the poly(2) was collected after precipitation into water containing a small amount of acetic acid. Polymers collected by filtration were purified by reprecipitations with a THF/methanol system and by freeze-drying from benzene solutions. Poly(1–4) thus obtained were then characterized by ^{1}H, ^{13}C NMR, IR spectroscopies as follows.

Poly(1): ^{1}H NMR (90 MHz, CDCl$_3$): δ = 0.7–1.2 (3H, CH$_3$), 1.7–2.2 (2H, CH$_2$), 2.5 (1H, C—H), 4.6 (2H, OCH$_2$).

^{13}C NMR (22.5 MHz, CDCl$_3$): δ = 17.6 (CH$_3$), 45.2 (quaternary C), 52.3 (OCH$_2$), 54 (CH$_2$), 75.5 (≡C—H), 77.3 (C≡C—H), 176.3 (C=O).

IR (KBr): 734, 991, 1139 (C—O), 1168, 1267, 1448, 1484, 1734 (C=O), 2130 (C≡C), 2941–2993 (C—H), 3298 (C—H) cm^{-1}.

Poly(2): ^{1}H NMR (90 MHz, CDCl$_3$): δ = 0.18 (9H, SiCH$_3$), 0.7–1.2 (3H, CH$_3$), 1.9 (2H, CH$_2$), 4.59 (2H, OCH$_2$).

^{13}C NMR (22.5 MHz, CDCl$_3$): δ = −0.1 (SiCH$_3$), 18.2 (CH$_3$), 45.3 (quaternary C), 53.1 (OCH$_2$), 54.7 (CH$_2$), 92.5 (≡CCH$_2$), 98.8 (SiC≡), 176.1 (C=O).

IR (KBr): 761, 845, 1034, 1137, 1168, 1252, 1359, 1406, 1448, 1484, 1737 (C=O), 2187 (C≡C), 2900–2950 (C–H) cm^{-1}.

*Poly(*3*)*: ^{1}H NMR (90 MHz, CDCl$_3$): δ = 0.5–1.2 (3 H, CH$_3$), 1.5–2.2 (5 H, CH$_3$C≡ and CH$_2$), 4.5 (2 H, OCH$_2$).

^{13}C NMR (22.5 MHz, CDCl$_3$): δ = 3.4 (*C*H$_3$C≡), 17.2 (CH$_3$), 45.1 (quaternary C), 52.9 (OCH$_2$), 54.1 (CH$_2$), 72.9 (≡*C*CH$_2$), 83.4 (CH$_3$*C*≡), 176.6 (C=O).

IR (KBr): 734, 914, 1138, 1232, 1266, 1448, 1484, 1733 (C=O), 2243 (C≡C), 2923–2997 (C–H) cm^{-1}.

*Poly(*4*)*: ^{1}H NMR (90 MHz, CDCl$_3$): δ = 0.6–1.2 (3 H, CH$_3$), 1.6–2.1 (5 H, CH$_3$C≡ and CH$_2$), 2.4 (2 H, CH$_2$C≡), 4.0 (2 H, OCH$_2$).

^{13}C NMR (22.5 MHz, (CD$_3$)$_2$SO): δ = 2.5 (*C*H$_3$C≡), 16.4 (CH$_3$), 17.8 (≡C*C*H$_2$), 44.0 (quaternary C), 53.5 (CH$_2$), 62.8 (OCH$_2$), 74.9 (≡*C*CH$_2$), 76.9 (CH$_3$*C*≡), 176.1 (C=O).

IR (KBr): 735, 1010, 1152, 1175, 1240, 1268, 1448, 1729 (C=O), 2246 (C≡C), 2858–2991 (C–H) cm^{-1}

*Deprotection of trimethylsilyl group of poly(*2*)*

Poly(**2**) (0.48 g, 2.44 mmol based on the monomer unit) and potassium carbonate (0.70 g, 5.1 mmol) were dissolved in a mixed solvent of THF (20 mL) and methanol (5 mL). The mixture was stirred at room temperature for 3 h and then poured into water to precipitate the polymer. The white powder was collected by filtration and purified by the reprecipitations from THF/hexane system and by freeze-drying from benzene solution to afford a white powder of polymer (0.29 g). The resulting polymer was characterized by NMR, IR, and SEC as poly(2-propynyl methacrylate).

Measurements

Size exclusion chromatograms (SEC) for MWD determination were obtained at 40 °C in THF (1.0 mL min^{-1}) with a TOSOH HLC-8020 instrument equipped with a series of polystyrene gel columns (TOSOH G5000H$_{XL}$, G4000H$_{XL}$, and G3000H$_{XL}$) with ultraviolet (254 nm) or refractive index detections. Vapor pressure osmometry (VPO) measurements for $\overline{M}_n$ determination were made with a Corona 117 instrument in benzene. Infrared spectra (KBr disk) were recorded on a JEOL JIR-AQS20M FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q (89.6 MHz ^{1}H and 22.53 MHz ^{13}C) in CDCl$_3$. Chemical shifts were reported in ppm downfield relative to tetramethylsilane (δ 0) for ^{1}H NMR and to CDCl$_3$ (δ 77.1) for ^{13}C NMR as standards. The glass transition temperature of the polymer was measured by differential scanning calorimetry using a Seiko Instrument DSC220 apparatus and analyzed by an SSC5200TA station. The samples were first heated to 120 °C, cooled rapidly to −40 °C, and then scanned again at a rate of 20 °C · min^{-1}.

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