Modern Techniques in Polymerization: 4582-605

Instructor: Jeff Pyun

Aspects of Step-Chain-Living Polymerizations

International Union of Pure and Applied Chemistry (IUPAC)

1) Polycondensation: condensation + step-reaction

   Formation of low-mol-wt byproduct
   Step-reaction polymerization

2) Polyaddition: addition + step-reaction

   No byproducts
   Step-reaction polymerization

3) Chain polymerization: addition + chain polymerization

   No byproducts
   Chain-reaction polymerization

4) Condensative chain polymerization: condensation + chain-reaction

   Formation of low-mol-wt byproduct
   Chain-reaction polymerization

1.7 Nomenclature

IUPAC name

1) The smallest constitutional repeating unit (CRU) is identified

2) Substituent groups are assigned the lowest possible numbers

3) The name is placed in parenthesis, and prefixed with poly

1.7.1 Vinyl polymers

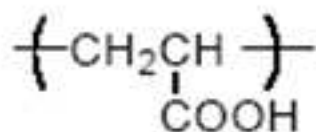poly + monomer name

	Source name = common name	IUPAC name
$-(CH_2CH_2)-$	polyethylene	poly(methylene)
$-[CF_2CF_2]-$	polytetrafluoroethylene	poly(difluoromethylene)
$-(CH_2-CH)-$ (phenyl)	polystyrene	poly(1-phenylethylene)

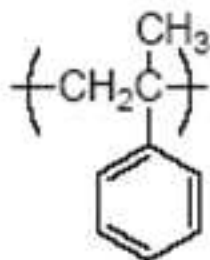poly + (monomer name)

more than one word or letter or number

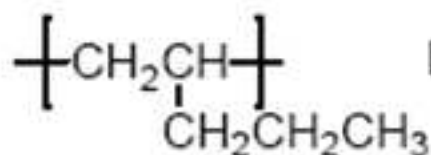|	Source name = common name	IUPAC name

 poly(acrylic acid) poly(1-carboxylatoethylene)

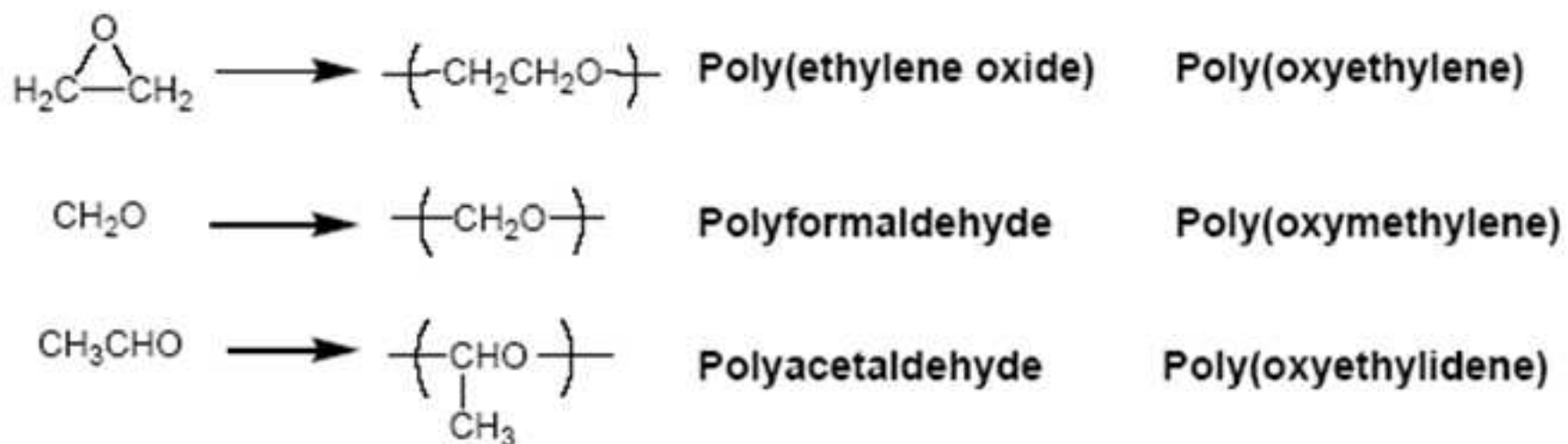 poly(α-methylstyrene) poly(1-methyl-1-phenylethylene)

 poly(1-pentene) poly[1-(1-propyl)ethylene]
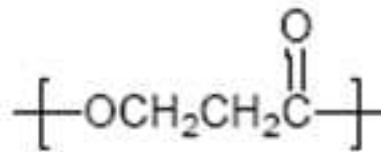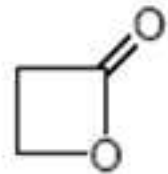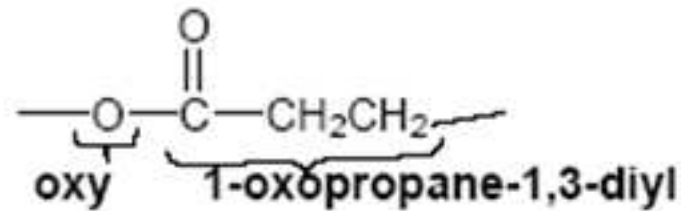
1.7.3. Nonvinyl Polymers

Polyethers, polyesters, polyamides

Heteroatoms Seniority: O, S, N, P

1) Polyethers

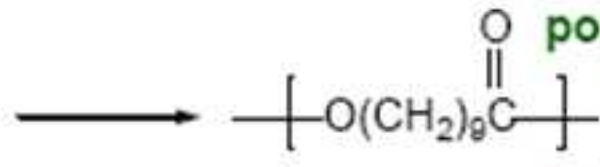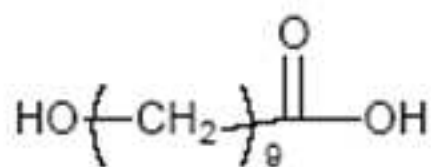|	Source name	IUPAC name
$H_2C\overset{O}{\overset{\diagup\diagdown}{-}}CH_2 \longrightarrow -(CH_2CH_2O)-$	Poly(ethylene oxide)	Poly(oxyethylene)
$CH_2O \longrightarrow -(CH_2O)-$	Polyformaldehyde	Poly(oxymethylene)
$CH_3CHO \longrightarrow -(\underset{CH_3}{CHO})-$	Polyacetaldehyde	Poly(oxyethylidene)

2) Polyesters

oxy   1-oxopropane-1,3-diyl

poly(β-propiolactone)
= poly(3-propionate)

poly[oxy(1-oxopropane-1,3-diyl)]

poly(10-decanoate)

$HO(CH_2)_9OH$

poly[oxy(1-oxodecane-1,10-diyl)]

$HOCH_2CH_2OH$

+

HO_2C — — CO_2H
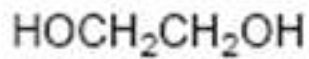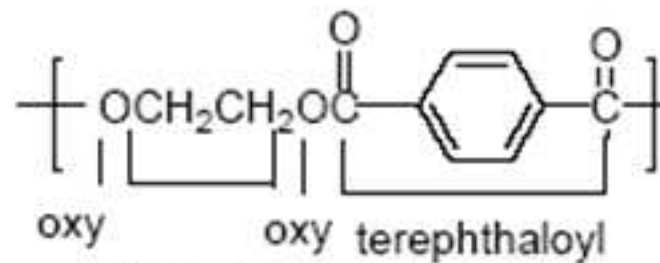
oxy   oxy   terephthaloyl
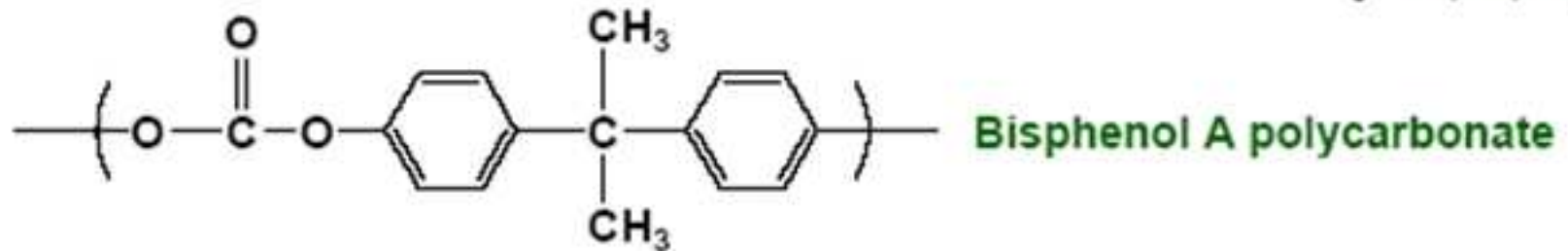ethylene   poly(ethylene terephthalate)

poly(oxyethyleneoxyterephthaloyl)
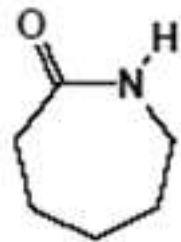
3) Polycarbonate

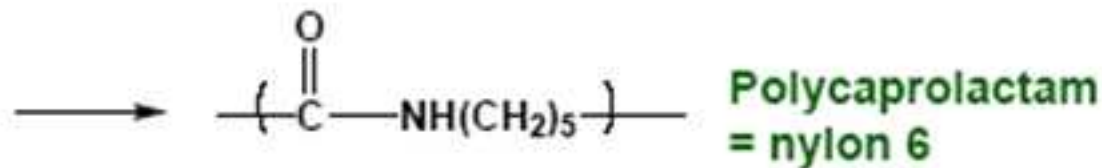Heteroatoms Seniority: O, S, N, P

Bisphenol A polycarbonate

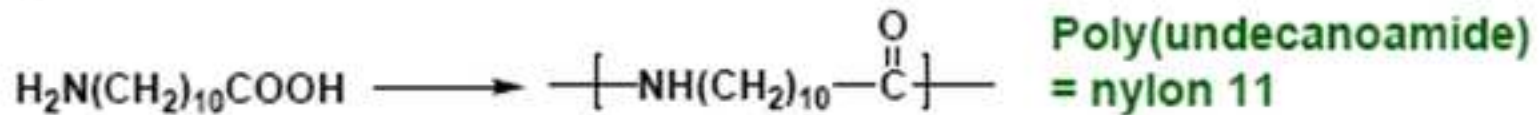poly(oxycarbonyloxy-1,4-phenyleneisopropylene-1,4-phenylene)

4) Polyamide

caprolactam

Polycaprolactam
= nylon 6

Poly[imino(1-oxohexane-1,6-diyl)]

$H_2N(CH_2)_{10}COOH$ →

Poly(undecanoamide)
= nylon 11

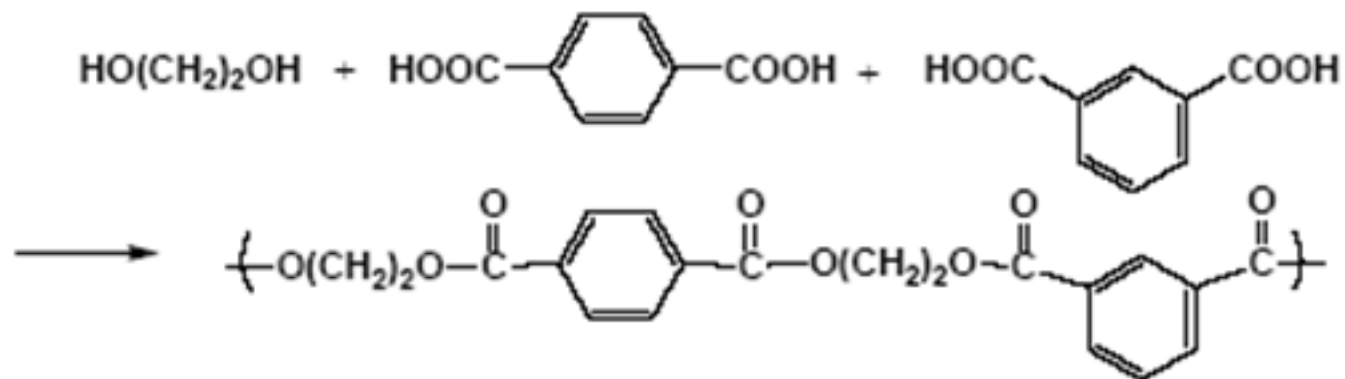11-aminoundecanoic acid

Poly[imino(1-oxoundecane-1,11-diyl)]

1.7.4 Nonvinyl copolymers

IUPAC source-based nomenclature for nonvinyl copolymers

2:1:1 – molar ratio of the monomers
ethylene glycol, terephthalic acid, and isophthalic acid

⟶ poly(ethylene terephthalate-co-ethylene isophthalate)

$HO(CH_2)_2OH$ + HOOC—⟨C$_6$H$_4$⟩—COOH + HOOC—⟨C$_6$H$_4$⟩—COOH

⟶ $+O(CH_2)_2O-\overset{O}{\underset{||}{C}}-$⟨C$_6H_4$⟩$-\overset{O}{\underset{||}{C}}-O(CH_2)_2O-\overset{O}{\underset{||}{C}}-$⟨C$_6H_4$⟩$-\overset{O}{\underset{||}{C}}+$

6-aminohexanoic acid + 11-aminoundecanoic acid

⟶ poly[(6-aminohexanoic acid)-co-(11-aminoundecanoic acid)]

poly[(6-hexanoamide)-co-(11-undecanoamide)]

$H_2N(CH_2)_5COOH$ + $H_2N(CH_2)_{10}COOH$

⟶ $-(HN(CH_2)_5CO-NH-(CH_2)_{10}CO-)-$
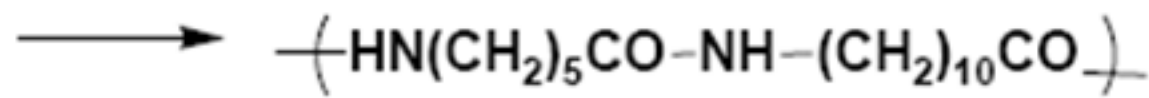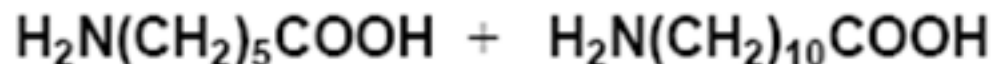
1.7.2. Vinyl Copolymers

IUPAC recommends source-based nomenclature for copolymers.

| Systematic	Concise
Poly[styrene-*co*-(methyl methacrylate)]	Copoly(styrene/methyl methacrylate)
Poly[styrene-*alt*-(methyl methacrylate)]	Alt-copoly(styrene/methyl methacrylate)
Polystyrene-*block*-poly(methyl methacrylate)	Block-copoly(styrene/methyl methacrylate)
Polystyrene-*graft*-poly(methyl methacrylate)	Graft-copoly(styrene/methyl methacrylate)
Poly(styrene-*co*-ethylene-*co*-propylene)	Copoly(styrene/ethylene/propylene)

MW Evolution of Step vs. Chain Growth Polymerization
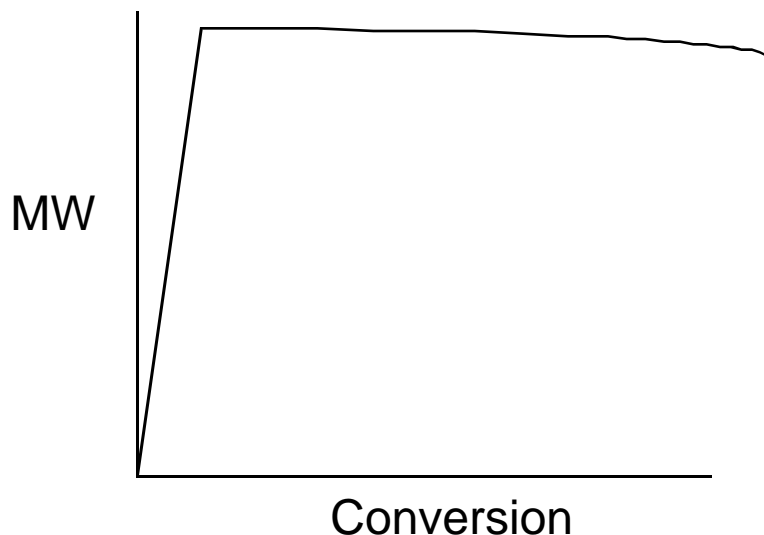
MW

Conversion

MW
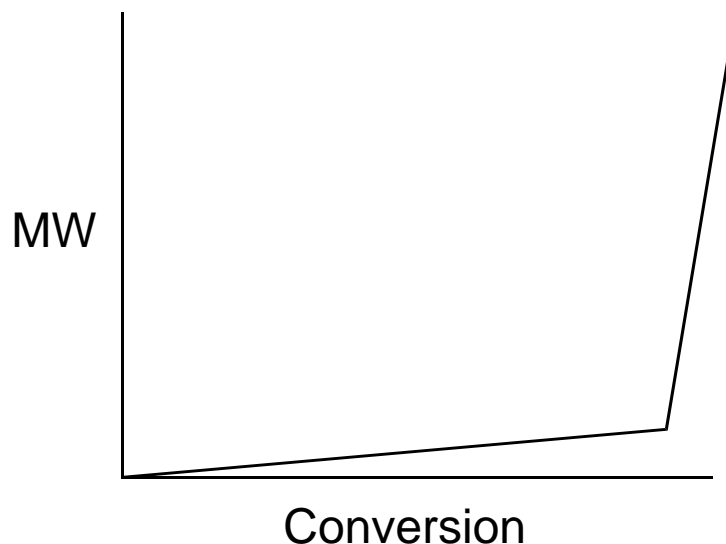
Conversion

Step Growth Evolution of MW

Reaction of difunctional monomers
With complementary functional groups
($A_2 + B_2$)

High polymer formed only at very high
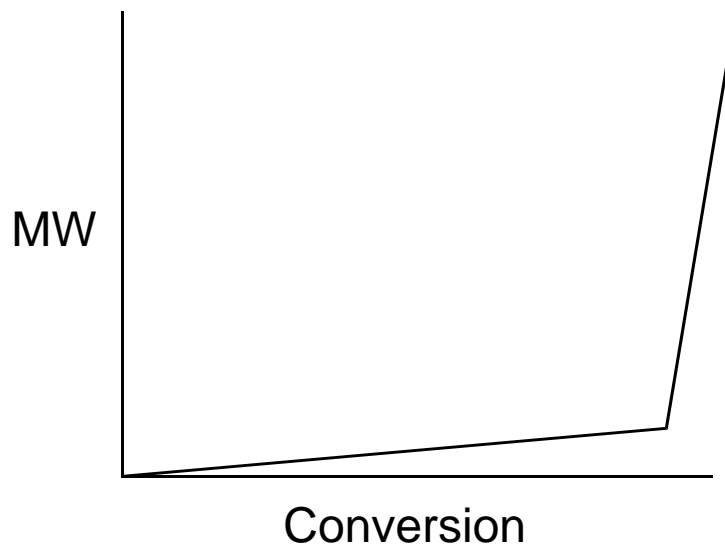conversion

Heteroatom backbones

Chain Growth Evolution of MW

4-Elementary reactions (initiation, propagation,
termination, transfer) of reactive monomer + initiator
(vinylic- π -systems, strained rings)

High polymer formed at low conversion

C-C bonds for vinylic monomers,
Heteroatom backbones for cyclic monomers

Requirements for Step-Growth Polymerization

MW

Conversion

High polymer formed only at very high conversion!!!

99 +

➢High monomer purity
➢Difunctionality
➢Stoichiometry
➢Quantitative conversion of monomer to polymer!
➢No side Reactions

Step Growth/Condensation Polymerization

TABLE 2.1 *A schematic illustration of the fundamental differences in reaction mechanism between step polymerization and chain polymerization**

Formation of	Step polymerization	Chain polymerization
Dimer	o + o → o-o	I + o → I-o I-o + o → I-o-o
Trimer	o-o + o → o-o-o	I-o-o + o → I-o-o-o
Tetramer	o-o-o + o → o-o-o-o o-o + o-o → o-o-o-o	I-o-o-o + o → I-o-o-o-o
Pentamer	o-o-o-o + o → o-o-o-o-o o-o + o-o-o → o-o-o-o-o	I-o-o-o-o + o → I-o-o-o-o-o
Hexamer	o-o-o-o-o + o → o-o-o-o-o-o o-o + o-o-o-o → o-o-o-o-o-o o-o-o + o-o-o → o-o-o-o-o-o	I-o-o-o-o-o + o → I-o-o-o-o-o-o
Heptamer	o-o-o-o-o-o + o → o-o-o-o-o-o-o o-o + o-o-o-o-o → o-o-o-o-o-o-o o-o-o + o-o-o-o → o-o-o-o-o-o-o	I-o-o-o-o-o-o + o → I-o-o-o-o-o-o-o
Octomer	o-o-o-o-o-o-o + o → o-o-o-o-o-o-o-o o-o + o-o-o-o-o-o → o-o-o-o-o-o-o-o o-o-o + o-o-o-o-o → o-o-o-o-o-o-o-o o-o-o-o + o-o-o-o → o-o-o-o-o-o-o-o	I-o-o-o-o-o-o-o + o → I-o-o-o-o-o-o-o-o

* Definition of symbols used : o, molecule of monomer; -, chemical link; I, initiator species

[Young & Lovell, "Introduction to Polymers" 2nd ed.]
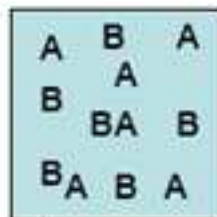
Time zero:
6 A monomers
6 B monomers
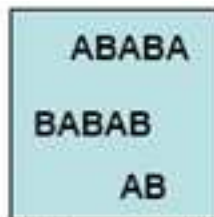
75% conversion
6/24 functional groups left
oligomers

92% conversion
2/24 functional groups left
polymer

Monomer Functionality and Polymer Architecture

Step-Growth

Difunctional monomers:
linear polymers

$A_2 + B_2$; AB monomers

multifunctional monomers:
branched, network polymers

$A_3 + B_2$; $A_2 + B_3$; $A_x + B_x$ -gelation
AB_2; AB_x monomers: (hyper)branched

For multifunctional monomers
Onset of gelation strongly dependent
on functionality of crosslinkers

Chain-Growth

monofunctional monomers:
linear polymers

Vinylic: styrene, acrylates

Di-, multifunctional monomers:
Crosslinked-networks

Dimethacrylates, divinylbenzene

multifunctional initiators:
In living processes with fast
Controlled initiation

Stars, branched polymers

Carother's Theory for Molar Mass Prediction in Step-Growth Polymerization

$$\overline{X_n} = \frac{N_o}{N} \quad (eq. 1)$$

$$p = \frac{\text{\# of functional groups that have reacted}}{\text{\# of functional groups initially present}}$$

$$p = \frac{N_o - N}{N_o} \qquad \frac{N_o}{N} = \frac{1}{1-p}$$

$$(eq. 2)$$

Combine (eq's.1&2)

$$\boxed{\overline{X_n} = \frac{1}{1-p}} \quad \textit{Carothers Eq.}$$

$\overline{X_n}$ Defined as number average degree of polymerization

N_o Number of molecules present initially at $T = 0$ (i.e., monomers)

N Number of molecules present initially at $T = t$ (both polymer and monomers)

p Extent of reaction (fractional, 100% = 1.0) *AND* the probability that any functional group has reacted (i.e., formed bonds)

Theory applicable to polymerizations of: $A_2 + B_2$; AB, A_2-with stoichiometric balance

Requires perfect stoichiometric balance; high MW only at very high conversion!

MW distributions for Step-Growth

Carother's theory only provides X_n, M_n average values, no MW distributions!

Flory developed statistical theory to derive both number and weight fraction distributions

Mole fraction distributions

$P(x)$ = probability distribution = number fraction distribution = mole fxn distrib. "probability of a molecule possessing **x** monomer units at some time = t and _p_, where _p = extent of reactioni and probability of functional group reacted_

$$P(x) \equiv \frac{\text{\# of polymers of } X_n = x}{\text{total \# of macromolecules}}$$

1000 total polymer chains
10 trimeric molecules
P(trimer) = 0.010

Weight fraction distributions

$$W(x) \equiv \frac{\text{total mass polymers of } X_n = x}{\text{total mass of macromolecules}}$$

1000g polymer chains
10g trimeric molecules
W(trimer) = 0.010

Most Probable Distributions: Number Fraction

p = extent of reaction and probability that functional groups have reacted
p = probability of finding bonds between monomers
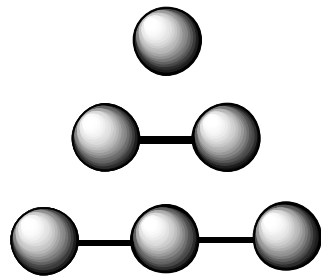
Probability of "finding" a monomer: $\quad$ **P(1) = 1 - p**
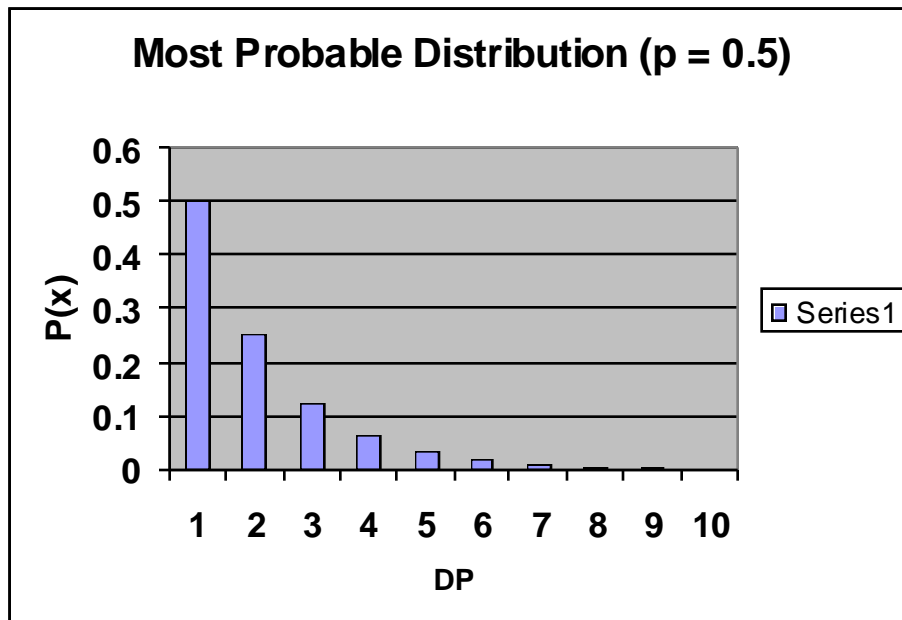
Probability of "finding" a dimer: $\quad$ **P(2) = p(1 − p)**

Probability of "finding" a trimer: $\quad$ **P(3) = p^2(1 − p)**

Probability of "finding" an x-mer: $\quad$ **P(x) = p^{x-1}(1 − p)**

*This type of MW distribution referred to as a "most probable distribution"
or "Flory-Schulz distribution"*

Most Probable Distribution (p = 0.5)

(bar chart: P(x) vs DP, bars at DP 1 through 10 with values approximately 0.5, 0.25, 0.125, 0.0625, 0.03, 0.016, 0.008, ...; legend: Series1)

P(x) decreases monotonically with DP
Characteristic of step-growth polym.

P(x) = p^{x-1}(1 − p) *is discrete distr.*

$P(x) = (1/X_n)e^{-x/X_n}$ continuous form

Most Probable Distributions with Higher Conversion

Most Probable Distribution (p = 0.1)

P(x) vs DP (1–10), with Series1

Most Probable Distribution (p = 0.5)

P(x) vs DP (1–10), with Series1

Most Probable Distrbution (p =0.9)

P(x) vs DP (1–64), with Series1

Most Probable Distribution (p = 0.999)

P(x) vs DP (1–469)
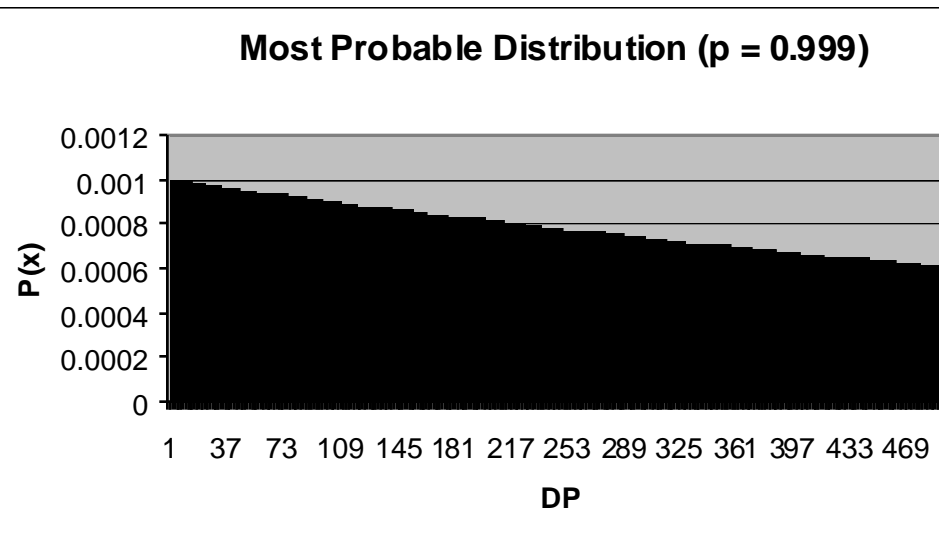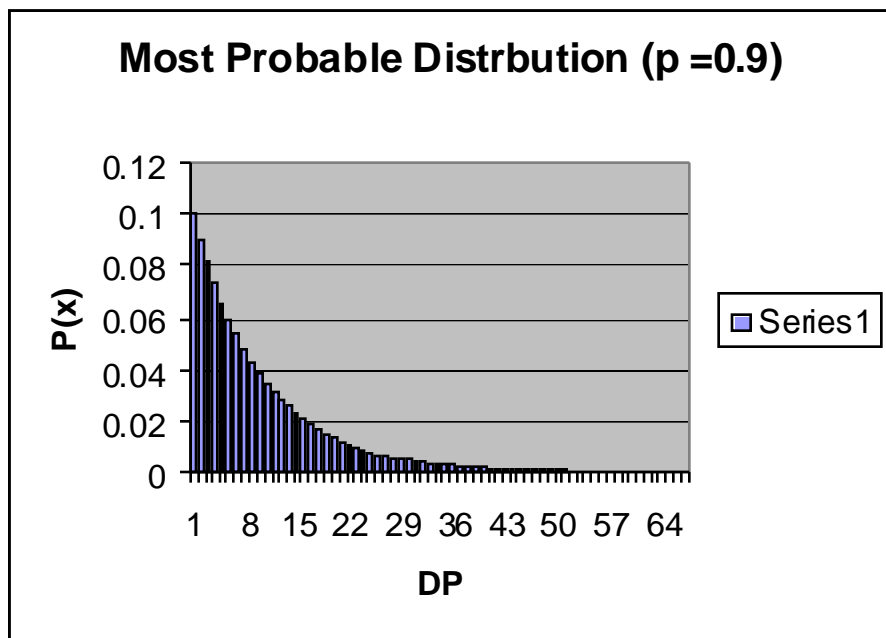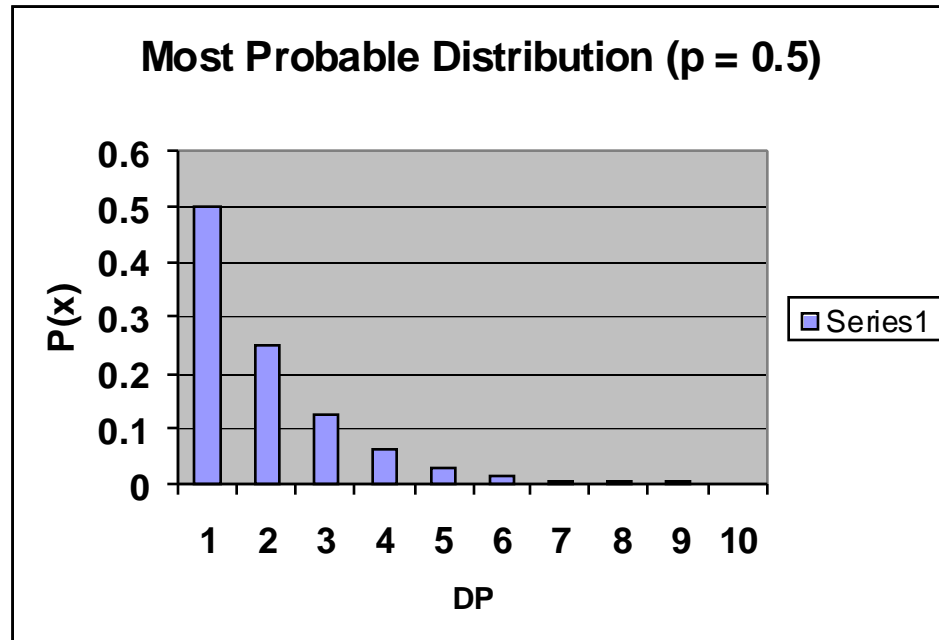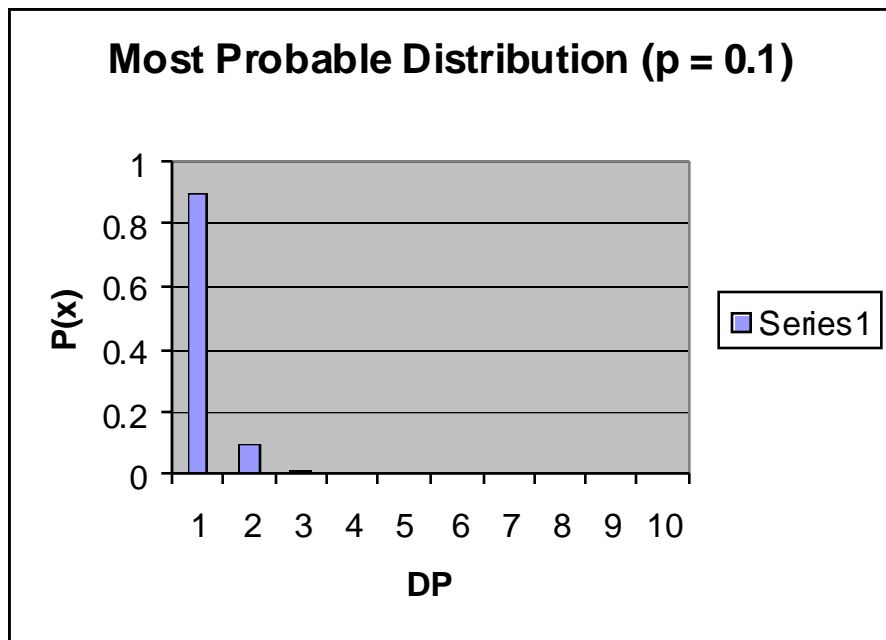
Most Probable Distributions: Weight Fraction

Probability Distribution-Mole Fraction Distribution

$$P(x) = p^{x-1}(1 - p)$$ $$P(x) = \text{mole fraction} = \frac{N_x}{N}$$

N_x = total number of X-mers

N = total number of molecules (monomer & polym) at some Time = t

$$N_x = N (1 - p) \, p^{x-1}$$

However, **N** is cumbersome to determine

$$N = N_o (1 - p)$$ N_o = total number of molecules at T = 0

$$N_x = N_o(1 - p)^2 \, p^{x-1}$$

$$W(x) \equiv \frac{\textit{total mass polymers of } X_n = x}{\textit{total mass of macromolecules}} = \frac{N_x(x \, \overline{M_o})}{N_o \, \overline{M_o}}$$

$\overline{M_o}$ = ave. MW of repeat unit

$$W(x) = \frac{x \, N_x}{N_o} = x \, (1 - p)^2 \, p^{x-1}$$

Other eq. which defines Flory-Schulz Distribution!

Polydispersity in Step-Growth Polym.

Polydispersity $= M_w/M_n$ index for MW distribution

$$\overline{M}_n = \Sigma\, P(x)\, \overline{M}_x = \Sigma\, x\, \overline{M}_o\, (1-p)\, p^{x-1}$$

remember
$P(x) = (1-p)\, p^{x-1}$
$M_x = x\, M_o$

$$\Sigma\, x\, p^{x-1} = (1-p)^{-2} \text{ when } p < 1$$

$$\overline{M}_n = \frac{\overline{M}_o}{(1-p)} = \overline{X}_n\, \overline{M}_o$$

remember
$X_n = 1/(1-p)$

$$\overline{M}_w = \Sigma\, W(x)\, \overline{M}_x = \Sigma\, x^2\, \overline{M}_o\, (1-p)^2\, p^{x-1}$$

remember
$W(x) = p^{x-1}\, x(1-p)^2$
$M_x = x\, M_o$

$$\Sigma\, x^2\, p^{x-1} = (1+p)(1-p)^{-3} \text{ when } p < 1$$

$$\overline{M}_w = \overline{M}_o\, \frac{(1+p)}{(1-p)}$$

$$\boxed{\frac{\overline{M}_w}{\overline{M}_n} = 1 + p}$$

Examples of Step-Growth Polymers
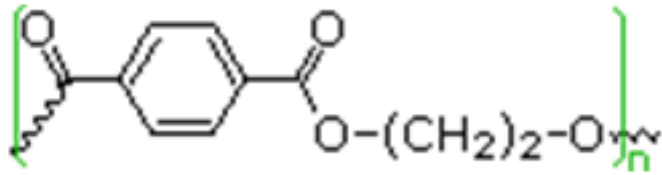
Polyester
Dacron, Mylar

~[CO(CH2)4CO-NH(CH2)6NH]n~
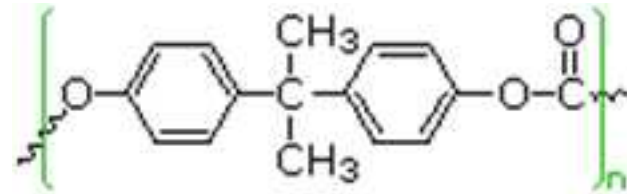
Polyamide
Nylon 6,6

polycarbonate
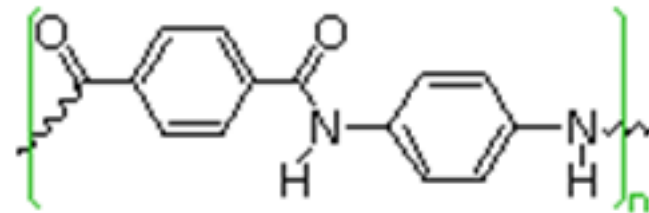
Polyaromatic amide
Kevlar
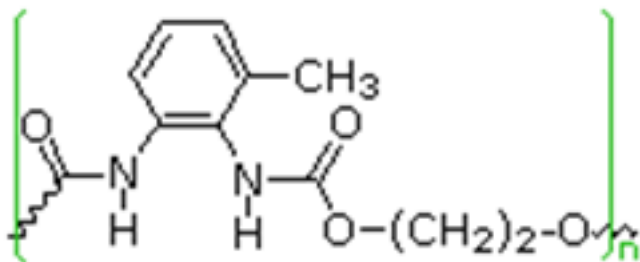
Polyurethane
Spandex

Key Features of Step-Growth Polymers
More expensive than chain-growth poylmers
Improved mechanical properties
Wider range of optical, electronic magnetic properties

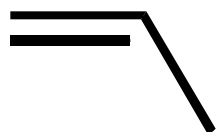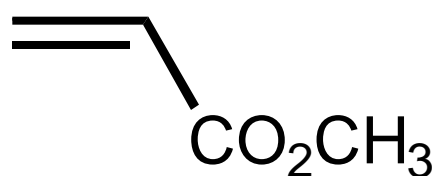# Examples of Monomers Chain-Growth Polymerization

Ethylene
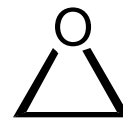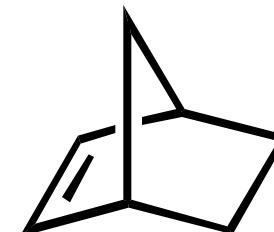
Propylene

Vinyl chloride

$F_2C{=}CF_2$

Tetrafluoroethylene

Styrene

Ph

Methyl methacrylate

CO_2CH_3

Isoprene

Ethylene oxide

O

ε-Caprolactone

O

Norbornene

Lactide

O
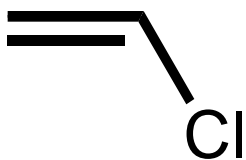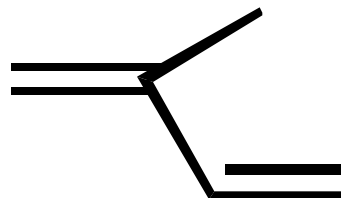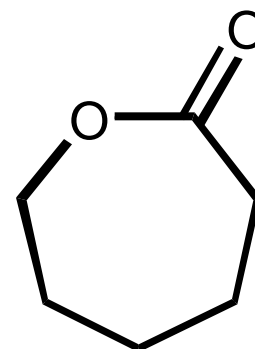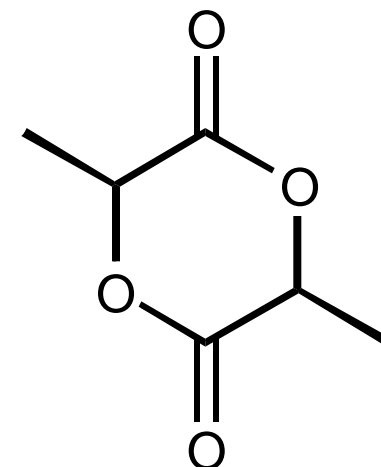
Definition and Criteria for Living Polymerizations

$Ln \frac{[M]_o}{[M]}$ vs. Time

MW vs. Monomer Conversion (Low Initiation Efficiency)
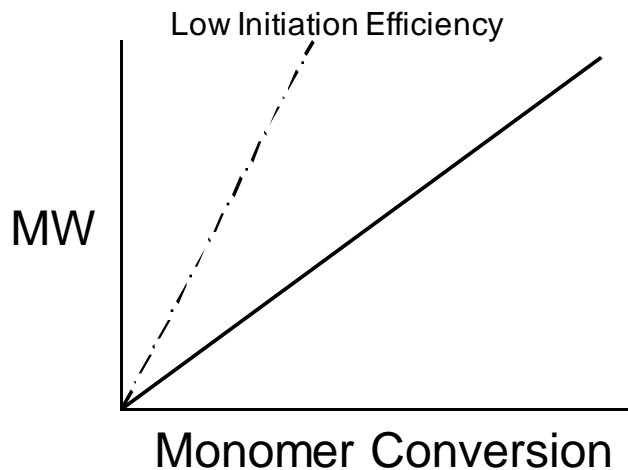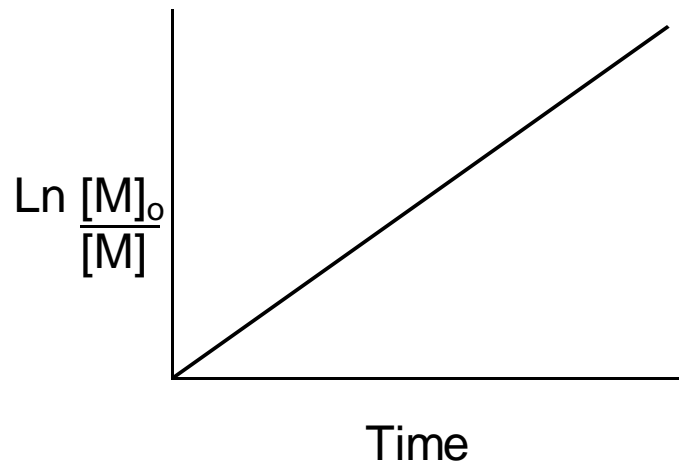
Definition: Chain polymerization that proceeds in the absence of chain breaking processes (termination, transfer

Criteria*: (Quirk et al., Polym. Int. **1992**, *27*, 359)
1) Polymerization proceeds until all monomer consumed, further addition of monomer results in chain extension
2) Number average MW (M_n, X_n) linear relationship with monomer conversion
3) # of initiator molecules = # of polymer chains, which is constant throughout reaction
4) DP = $[M]_o/[I]_o$ x conversion
5) Polymers of low polydispersity formed
   $M_w/M_n = 1 + 1/DP_n$
6) Block Copolymers formed from sequential monomer addition to living polymer chain
7) Facile chain end functionalization
8) Linearity of $Ln([M]_o/[M])$ vs. time (constant # of active centers
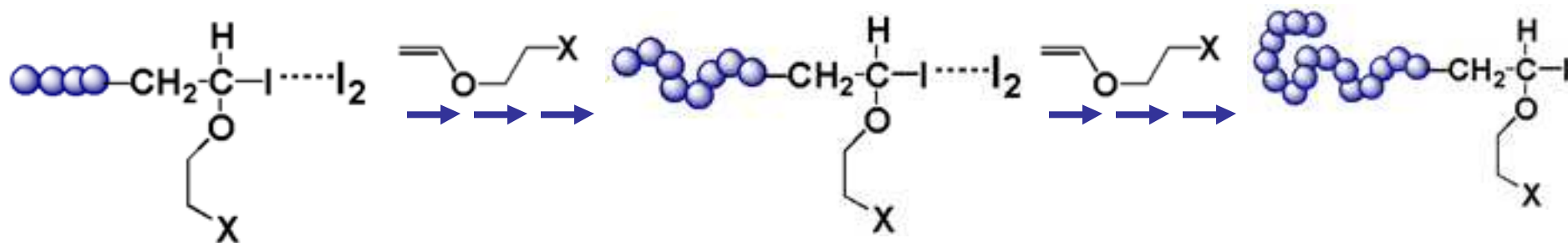
Controlled/Living Polymerizations

Living polymerization: a chain growth process without chain-breaking reactions (termination, transfer)
Anionic, Insertion (ROMP)

Features: precise DP_n ($\Delta[M]/[I]_o$)
Low polydispersity
Active chain ends-Blocks
Control of architecture
Stringent reaction conditions
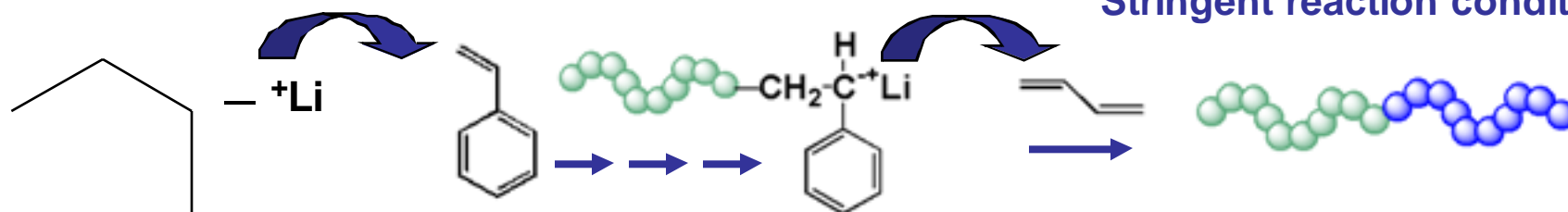
Controlled/"Living" polymerization: a chain growth process with chain-breaking reactions
$R_{propagation} \gg R_{termination}, R_{transfer}$
Reversible deactivation

Features: precise DP_n ($\Delta[M]/[I]_o$)
Low polydispersity*
Active chain ends-Blocks
Control of architecture

Free Radical Chemistry: 1990's

**Greater functional group tolerance
Range of monomers**

Controlled/Living Polymerizations

Living Anionic Polymerization

Initiators: ex. organolithium compounds (sec-butyl lithium; n-butyl lithium)
Grignard reagents, alkali bases

Monomers: ex. *Styrenes, dienes, (meth)acrylates, pyridines, epoxides:*
Functional monomer require protecting groups; alkyl esters cannot be polym

Features: exquisite control of MW, block copolymers, low functional group
tolerance

Controlled Cationic Polymerization

Initiators: ex. Alkyl halides, acetates, inorganic/organic acids, water

Monomers: ex. *Vinyl ethers, alkenes(butylene), styrene, cyclic ethers*
Functional monomer require protecting groups; alkyl esters cannot be polym

Features: highly reactive cation species susceptible to chain transfer
Controlled MW, block copolymers

Controlled Radical Polymerization

Initiators: ex. Alkyl halides, alkoxyamines, thioesters

Monomers: ex. *(meth)acrylates, (meth)acrylamides, styrenes, acrylonitrile,*
Pyridines, dienes,

High functional group tolerance, widest scope of polymerizable monomers

Features: controlled MW, blcck copoylmers, functionality, bimolecular termination

Ring-Opening Polymerization

Coordination-Insertion Polym.

Ring-opening metathesis Polymerization (ROMP)

Initiators/catalysts:
Transition metal alkyldenes (Ru, Mo)

Monomers:
Cyclic alkenes (norbornylene Cyclooctadiene, dicyclopenta-dienes)

Controlled/Living Polymerizations: Materials
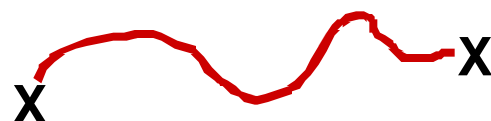
Block copolymers & Functionalization
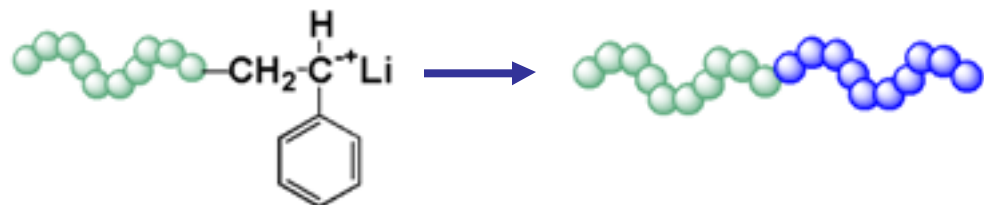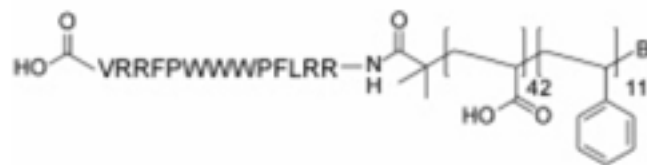

Living Polymer Chain

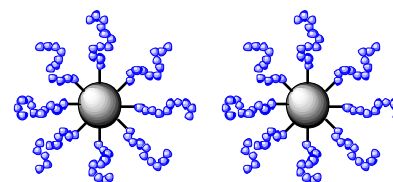Block Copolymer

End-Functional Polym.

Telechelic

Well-defined initiators: Stars, graft
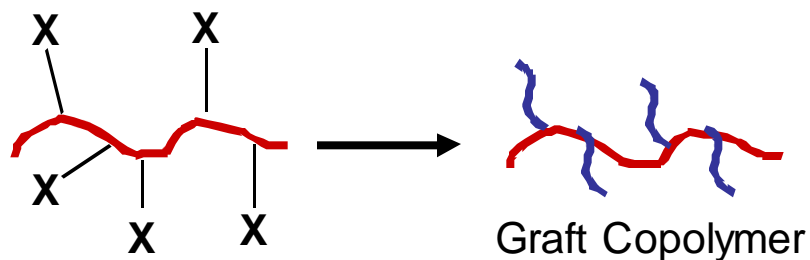

Stars

Graft Copolymer

Biohybrids, Nanocomposites

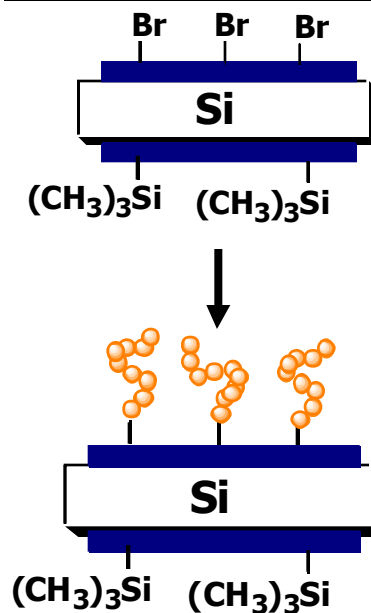

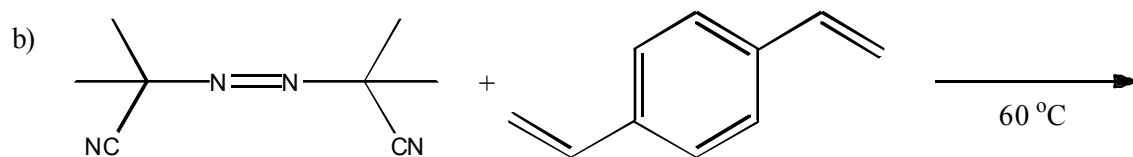Peptide Conjugates

Organic/Inorganic Composite
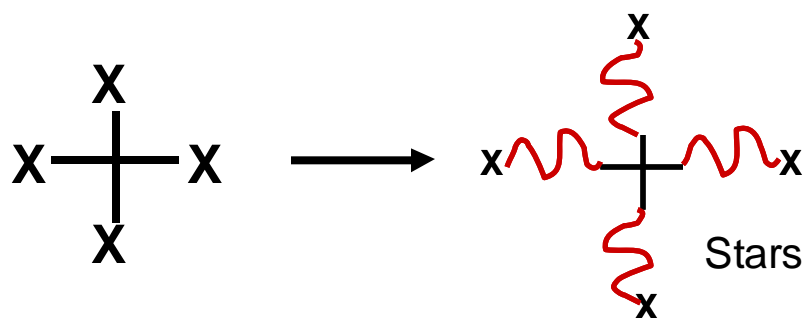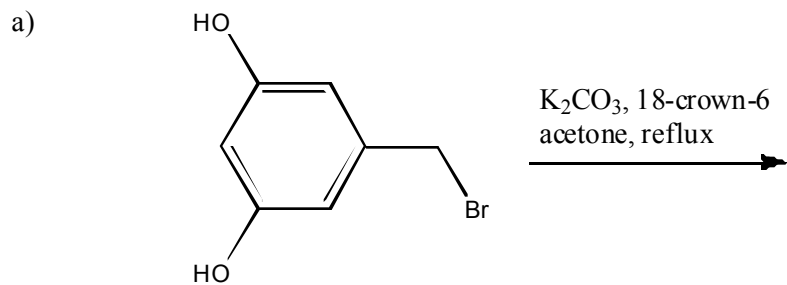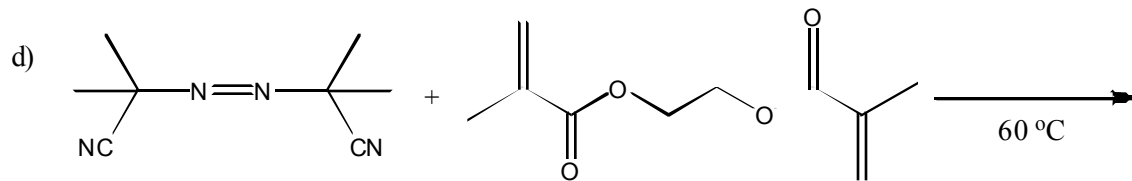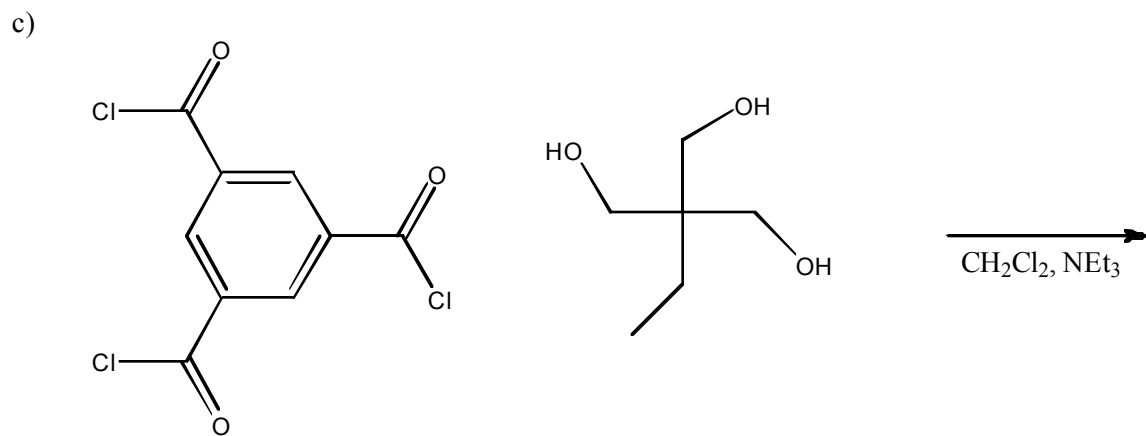
Surface Modification

For the following polymerization reactions, indicate if linear, branched, or crosslinked polymer architectures are formed: (4 pts, ca)

a)

K_2CO_3, 18-crown-6
acetone, reflux

b)

AIBN = free radical initiator

60 °C

c)

CH_2Cl_2, NEt_3

d)

60 °C

AIBN = free radical initiator

Write out the chemical structure of syndiotactic polystyrene

What thermal transitions would you expect for this polymer?

If this polymer were made thru a living polymerization, describe the following:

MW dependence of monomer to initiator stoichiometry

Most probable vs. Poisson distributions

Describe the types of "structural heterogeneities discussed in class.

For each, provide any and all supporting info that was discussed in general terms

Fundamentals of Step-Growth Polymerization

- Polymer nomenclature (traditional versus IUPAC systems)
- Kinetics of Polymerization
  - ***Equal reactivity of functional groups***
  - Kinetics of polyesterification (self versus external catalysis)
  - ***Carother's equation***
  - Nonequilvalence (example of polyurethanes)
  - ***Equilibrium polymerizations (closed versus open-driven systems)***
  - Side reactions: cyclization
- ***Molecular Weight Evolution (M_n vs. conversion) in Step-Growth***
  - Carother's equation
  - MW control from stoichiometic imbalance
- ***Branching and Gelation***
- ***Polyesters and Polyesterification***
  - *Examples and structure-property relationships*
  - Bulk driven systems (direct polyesterification and transesterification)
  - Nonequilibrium polymerizations (acid chloride rxn's, activated polymerizations)
  - Applications

Kinetics of Step-Growth Polymerization: Equal Reactivity of Functional Groups

Simplification of kinetic analysis: assumption of equal functional group reactivity
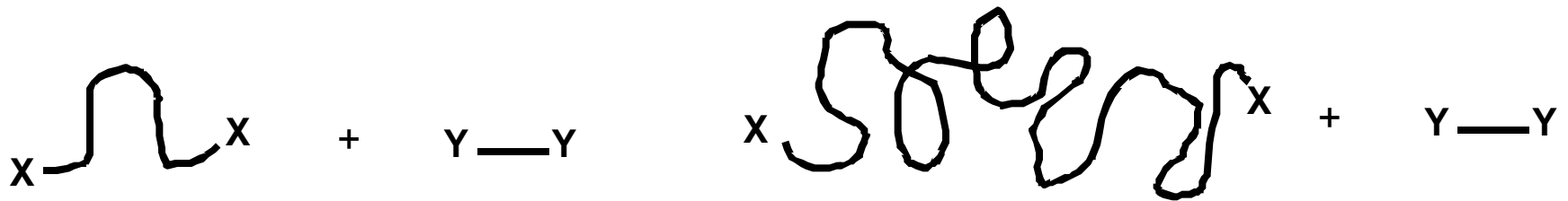
Above critical chain length-reaction rates level off and are comparable

Rate constant independent of chain-length

MW and Step-Growth Polymerization: Carothers and Flory Eq.

$$\overline{X_n} = \frac{\overline{M_n}}{MW_{monomer}} = \frac{[M]_o}{[M]}$$

$$[M] = [M]_o - [M]_o p$$

$$p = \frac{monomer\,\%\,conversion}{100}$$

$$\overline{X_n} = \frac{1}{1-p} \quad \text{Carother's equation}$$

$$[M] = [M]_o (1 - p)$$

$$\overline{X_w} = \frac{1+p}{1-p}$$

$$\overline{M_n} = M_o \overline{X_n} + M_{eg}$$

$$= \frac{M_o}{1-p} + M_{eg}$$

$$\frac{\overline{X_w}}{\overline{X_n}} = 1 + p$$

Theoretical Polydispersity in Step Growth
Process approaches pdi = 2

Mechanism and Kinetics of Polyesterification

Acid Catalyzed Polymerization

$$\text{COOH} \quad + \quad \text{HA} \quad \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \quad \overset{\displaystyle \text{OH}}{\underset{\displaystyle +}{\overset{|}{\text{C}}}} - \text{OH} \ (\text{A}^-)$$

$$k_4 \Big\uparrow \Big\downarrow k_3$$

$$\overset{\displaystyle \text{OH}}{\underset{\displaystyle \overset{|}{\underset{+}{\text{OH}}} \ (\text{A}^-)}{\overset{|}{\text{C}} - \text{OH}}}$$

$$\overset{\displaystyle \text{O}}{\underset{\displaystyle \ }{\overset{||}{\text{C}}}} - \text{O} - \quad \overset{k_5}{\underset{\ }{\rightleftharpoons}}$$
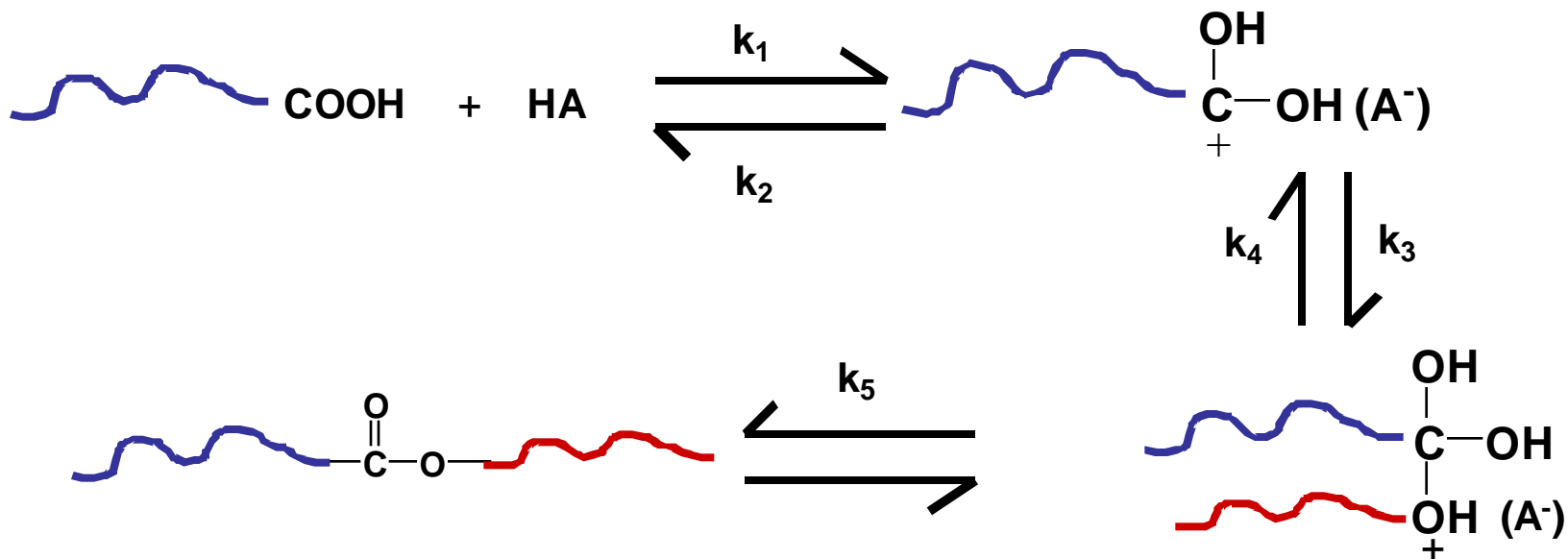
R_p = rate of polymerization $\equiv$ rate of –COOH consumption

$$R = \frac{-d[\text{COOH}]}{dt} = k_3 [\text{C}^+(\text{OH})_2][\text{OH}] \qquad K = \frac{k_1}{k_2} = \frac{[\text{C}^+(\text{OH})_2]}{[\text{COOH}][\text{HA}]}$$

Reactive intermediate
Difficult to measure

$$R = \frac{-d[\text{COOH}]}{dt} = k_3 K \, [\text{COOH}][\text{OH}][\text{HA}]$$

Equilibrium Polymerizations
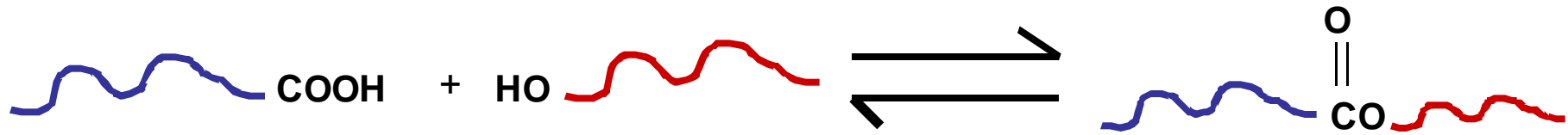
- **Closed system (no removal of byproducts)**

$$K = \frac{p_e^2}{(1 - p_e)^2} \qquad X_n = 1 + K^{1/2}$$

$K_{polyesterification} \sim 1\text{-}10$

$K_{transesterification} \sim 0.1\text{-}1$

$K_{polyamidation} \sim 10^2\text{-}10^3$

Very high K
For reasonble DP

TABLE 2-5 Effect of Equilibrium Constant on Extent of Reaction and Degree of Polymerization in Closed System

Equilibrium Constant (K)	p	$\overline{X}_n$
0.0001	0.0099	1.01
0.01	0.0909	1.10
1	0.500	2
16	0.800	5
81	0.900	10
361	0.950	20
2,401	0.980	50
9,801	0.990	100
39,601	0.995	200
249,001	0.998	500

Odian, "Principles of Polymerization,"

Equilibrium Polymerizations
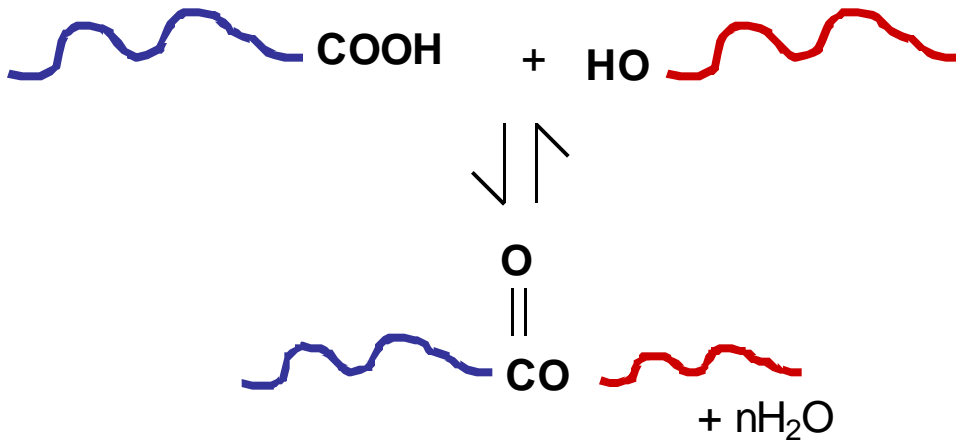
Open-Driven Systems (removal of byproducts)

$$K = \frac{p[H_2O]}{[M]_o(1-p)^2}$$

$$[H_2O] = \frac{K[M]_o}{\overline{X_n}\,(\overline{X_n}-1)}$$

$[H_2O]$ very low for high DP

TABLE 2-6 Effect of Water Concentration on Degree of Polymerization in Open, Driven System

K	$\overline{X_n}$	$[H_2O]^a$ (moles/liter)
0.1	1.32[b]	1.18[b]
	20	1.32×10^{-3}
	50	2.04×10^{-4}
	100	5.05×10^{-5}
	200	1.26×10^{-5}
	500	2.00×10^{-6}
1	2[b]	2.50[b]
	20	1.32×10^{-2}
	50	2.04×10^{-3}
	100	5.05×10^{-4}
	200	1.26×10^{-4}
	500	2.01×10^{-5}
16	5[b]	4.00[b]
	20	0.211
	50	3.27×10^{-2}
	100	8.10×10^{-3}
	200	2.01×10^{-3}
	500	3.21×10^{-4}
81	10[b]	4.50[b]
	20	1.07
	50	0.166
	100	4.09×10^{-2}
	200	1.02×10^{-2}
	500	1.63×10^{-3}
361	20[b]	4.75[b]
	50	0.735
	100	0.183
	200	4.54×10^{-2}
	500	7.25×10^{-3}

[a] $[H_2O]$ values are for $[M]_o = 5$.
[b] These values are for a closed reaction system at equilibrium.

Odian, "Principles of Polymerization,"

Side Reactions in Step-Growth Polymerization

**Cyclization:** **Competition between linear polm. vs. cyclization**

More common in AB monomer homopolymerization

OH-R-COOH $\longrightarrow$ **O-R-COO**
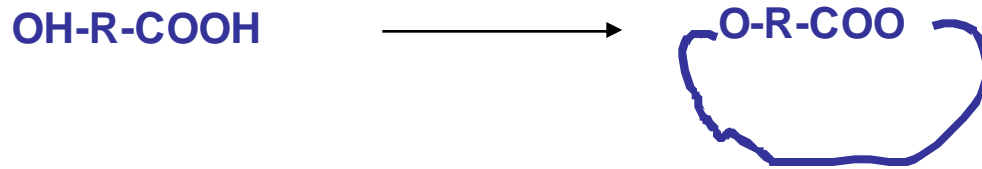
1) Highly dependent on [M]
2) And ring strain of cyclics

Less likely for A_2 + B_2 polymerization

OH-R-OH + HOOC-R_2-COOH $\longrightarrow$ **OOC-R_2-COO-R-O**
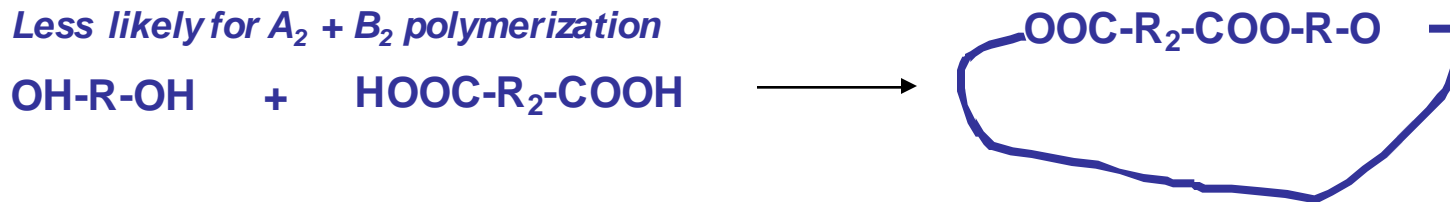
**Interchange: e.g.,Transesterification, transamidation**

$$\underset{\text{C}}{\overset{\text{O}}{\|}}\text{—C—O—}$$

HO

$\longrightarrow$

$$\underset{\text{C}}{\overset{\text{O}}{\|}}\text{—C—O—}$$

HO
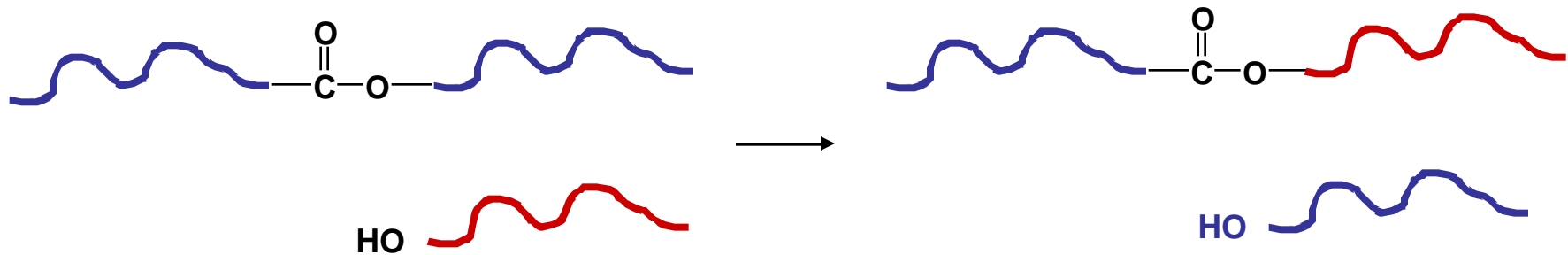
**Scramble composition and MW of (co)polymers in reaction mixture**

Examples of Aliphatic, Aromatic-Aliphatic, Aromatic Polyesters
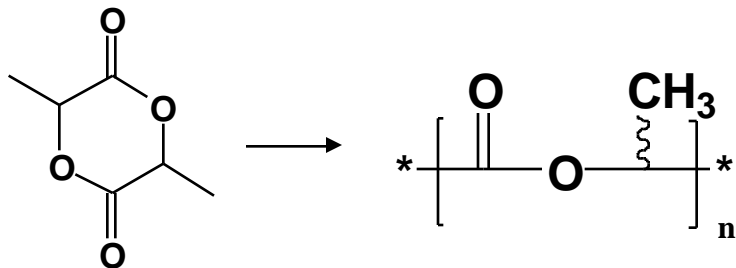
Polylactide (PLA), Natureworks (Cargill-Dow)
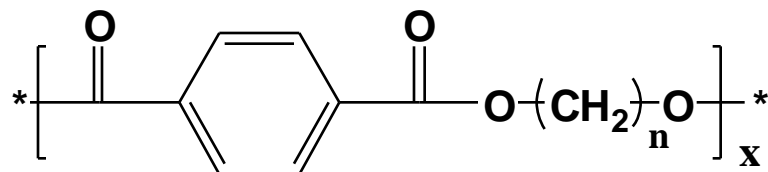
n = 2; poly(ethylene terephthalate), PET, *Rymite, Mylar, Dacron (Dupont)*

n = 3; poly(trimethylene terephthalate), PTT, Corterra (Shell), Sorona (Dupont)
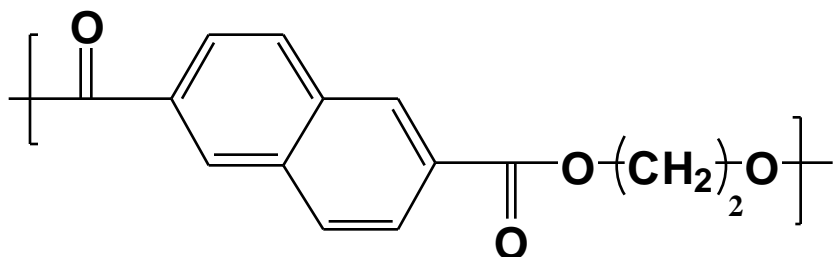
n = 4; poly(butylene terephthalate), PBT, Ektar (Eastman), Pocan (Bayer), Valox (GE), Crastin (Dupont)

Poly(ethylene 2,6-naphthalate), PEN, *Kaladex* (*Dupont*), *Pentex* (Honeywell-Allied Signal)
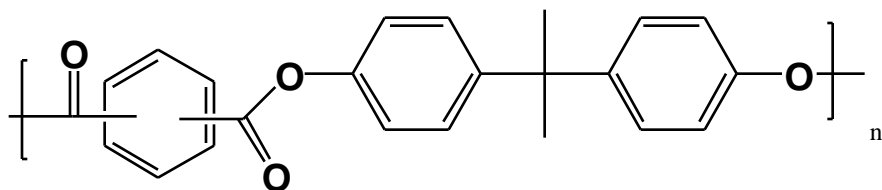
Poly(2,2'-bis(1,4-phenylene)propaneterephthalate-co-isophthalte), PAR *Ardel* (*Amoco*)

Comparisons of Thermal Properties of Poly(alkylene adipate)s Versus Poly(alkylene terephthalate)s

n	T_g	T_m (°C)
1	-	-
2	-63	50
3	-59	45
4	-74	56
6	-73	61
8	-56	80

n	T_g	T_m (°C)
1	101	269
2	69	265
3	35	233
4	17	232
6	-9	154

Poly(alkylene arylate)s

$$* \left[\begin{array}{c} O \\ \parallel \\ C \end{array} - Ar - \begin{array}{c} O \\ \parallel \\ C \end{array} - O - (CH_2)_n - O \right]_X *$$

n	T_g	T_m (°C)	T_g	T_m (°C)	T_g	T_m (°C)
1	101	269	-	340	-	-
2	69	265	117	337	-	>350
3	35	233	73	199	-	263
4	17	232	76	241	-	296
5	10	134	38	135	42	176
6	-9	154	44	211	-	240

Chem 542B: Step-Growth Polymerization

University of Arizona

Synthesis of Polyamides-Nylon 6,6
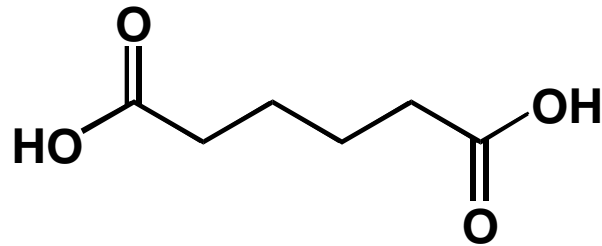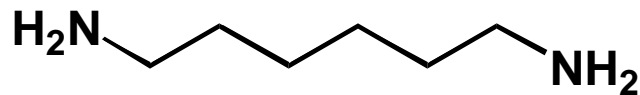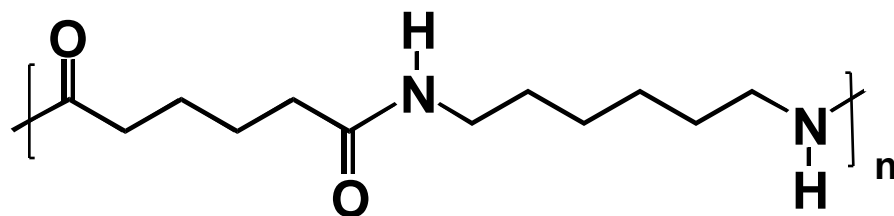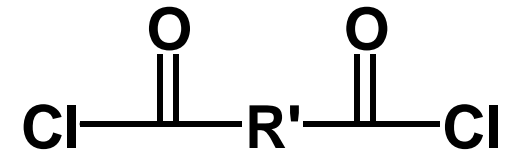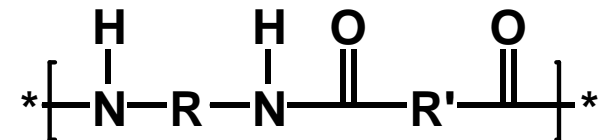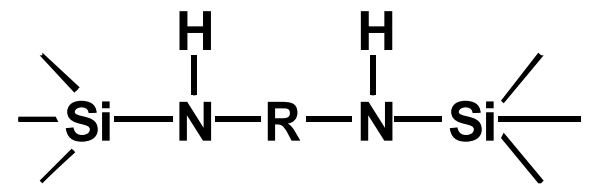
Synthesis of Polyaromatic amides/Aramids
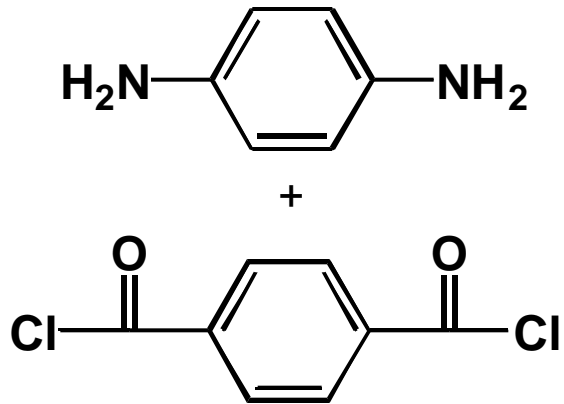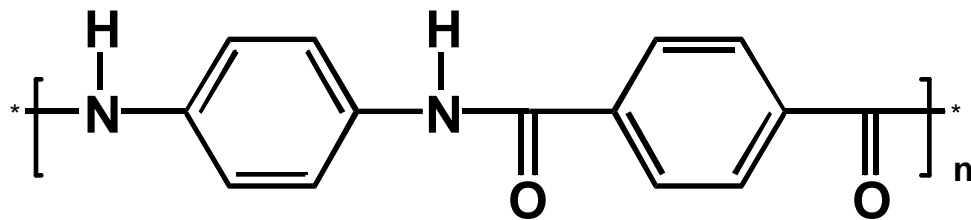
Poly(imino-1,4-phenyleneiminoterephthaloyl)
Kevlar
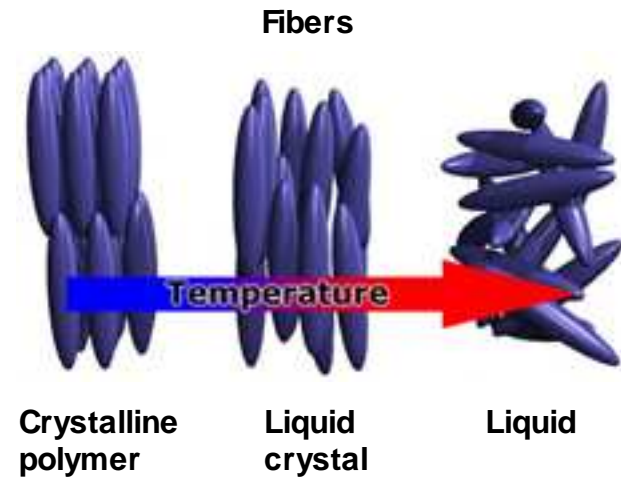
Synthesis of Polyurethanes and Polyureas

n HO—R—OH + n OCN—R'—NCO $\longrightarrow$
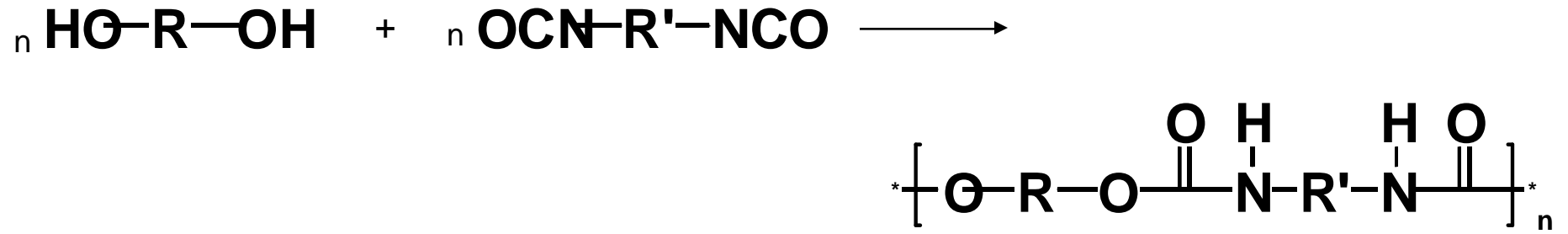
Catalysts: tin (II) ethyl hexanoate (Sn (Oct)$_2$)

2 〰〰〰NCO + H_2O $\longrightarrow$ 〰〰〰N—C(=O)—N〰〰〰

+ CO_2 ↑

Blowing agent
(foams)
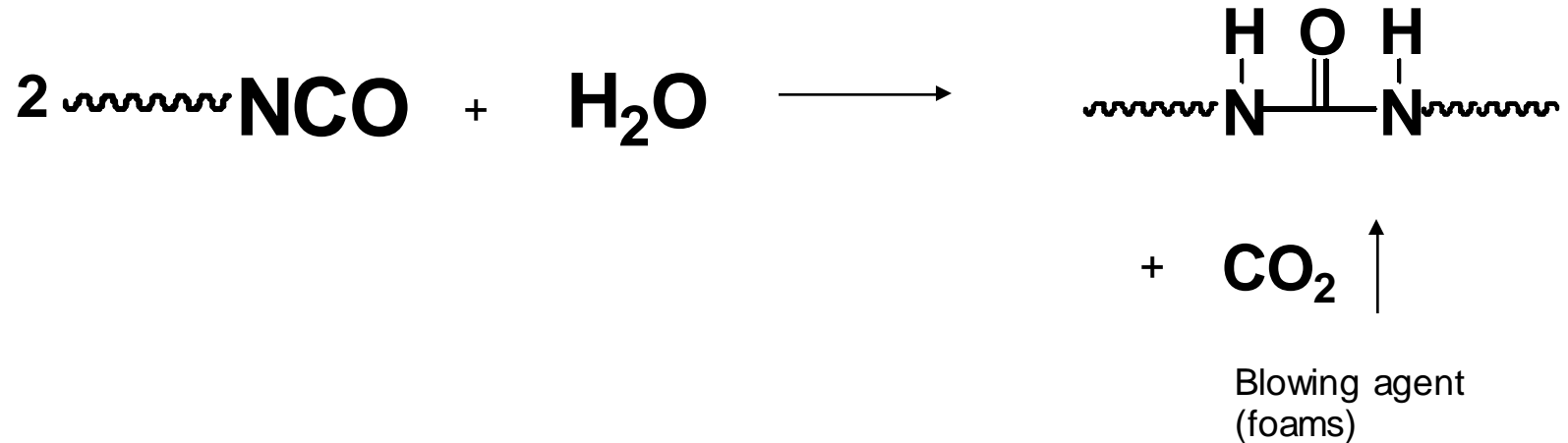
Crosslinking in Polyurethanes and Polyureas

allophanate

biuret

Isocyanurate linkages
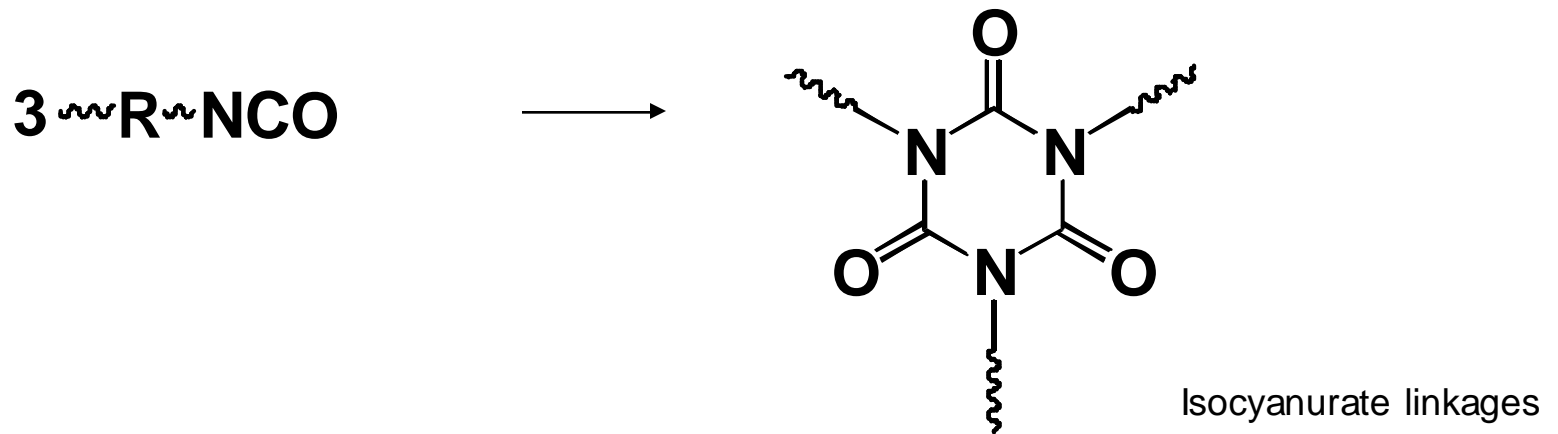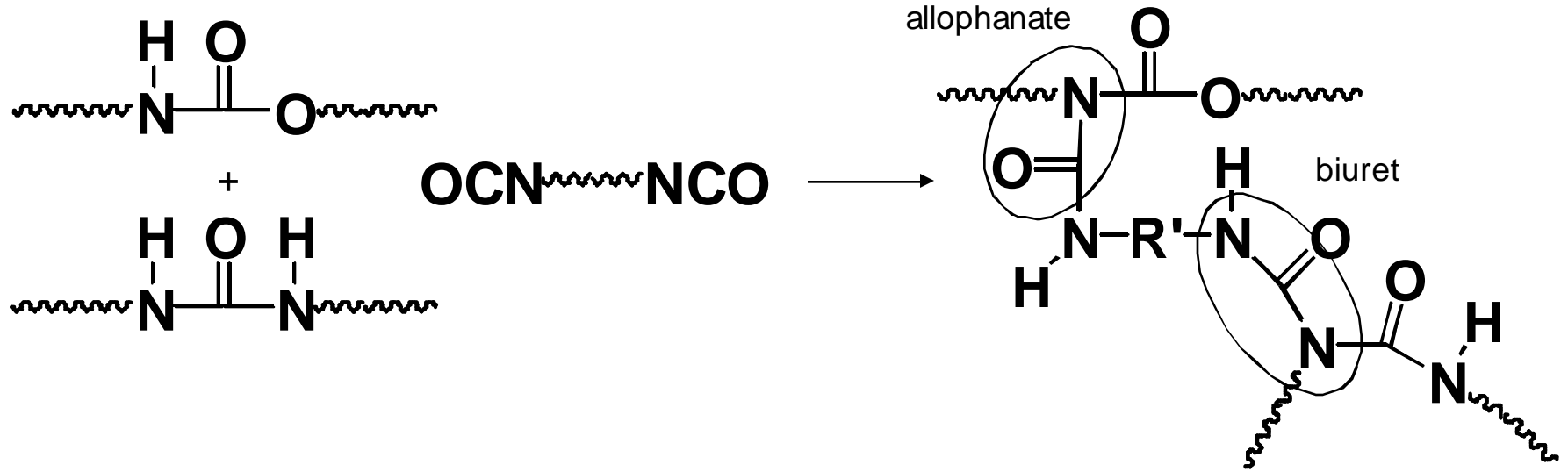
Block Copolymers via Step-Growth Polym: Prepolymer Approach

"Two Prepolymer" Approach:

Separate synthesis of two different prepolymers via polymerization of telechelics thru end-groups.
(e.g., α,ω-macrodiol with α,ω-macrodiisocynate = polyester-*block*-polyurethane)

HO〜〜〜OH   OCN〜〜〜NCO

↓

$$O$$
$$\|$$
HO〜〜〜OCN〜〜〜NCO

+
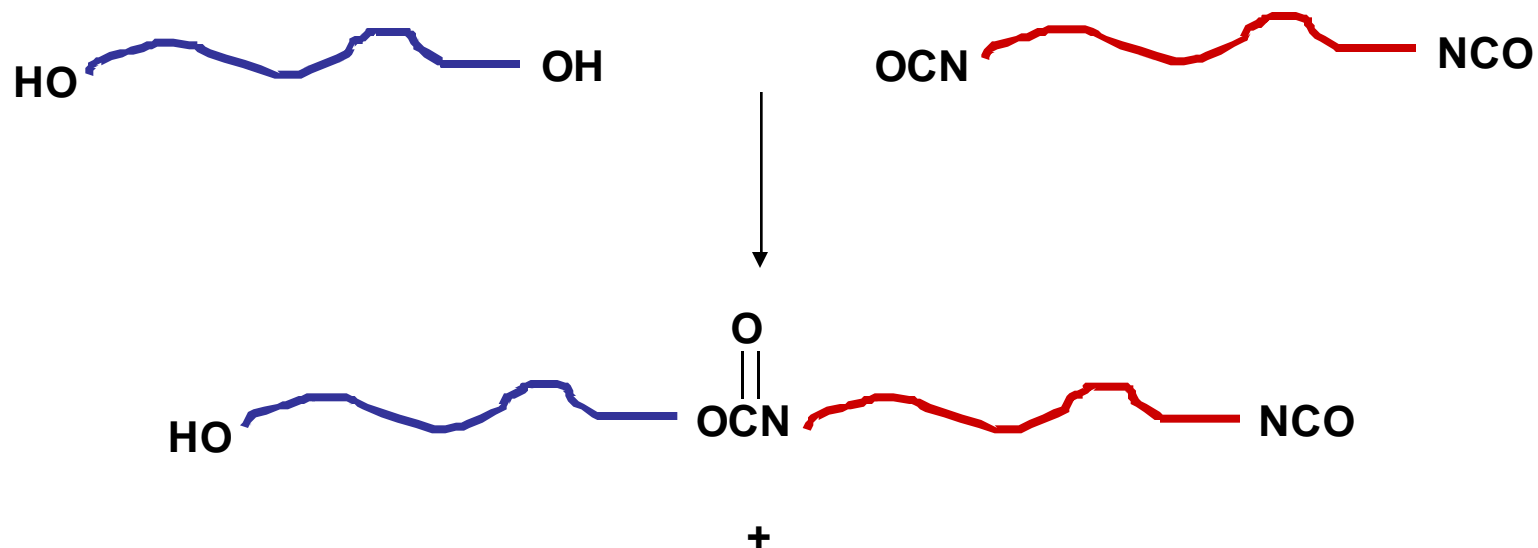
homopolymers and segmented block copolymers
depending on stoichiometry

Polyesterification: Equilibrium and Nonequilibrium Polymerization

Equilibrium Polymerizations

Bulk-Direct Polyesterifications

Polytransesterifications-Ester Interchange

Two-stage processes
Catalysts (Sb_2O_3)
Temperature

Nonequilibrium Polymerizations

Acid chloride reactions

Activated polyesterifications
(carbonyldimidazole, chlorophophates)

Irreversible reactions
High polymer formed
Mild conditions
Expensive monomers

Schotten-Baumann Polymerization: Interfacial Polyamidation

+

Interfacial
Polymerization

Collapsed film

Diamine in water

Polymer film forming
at interface

Diacid chloride in
organic solvent
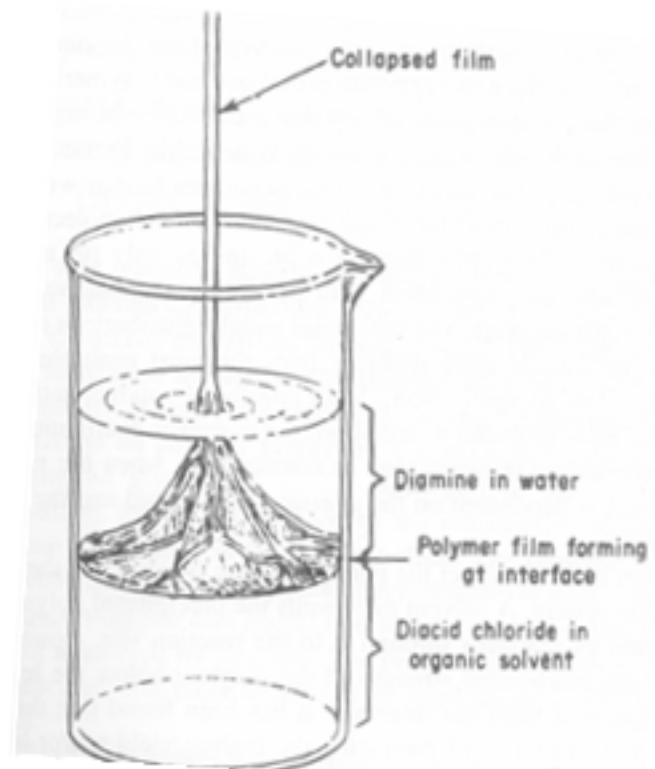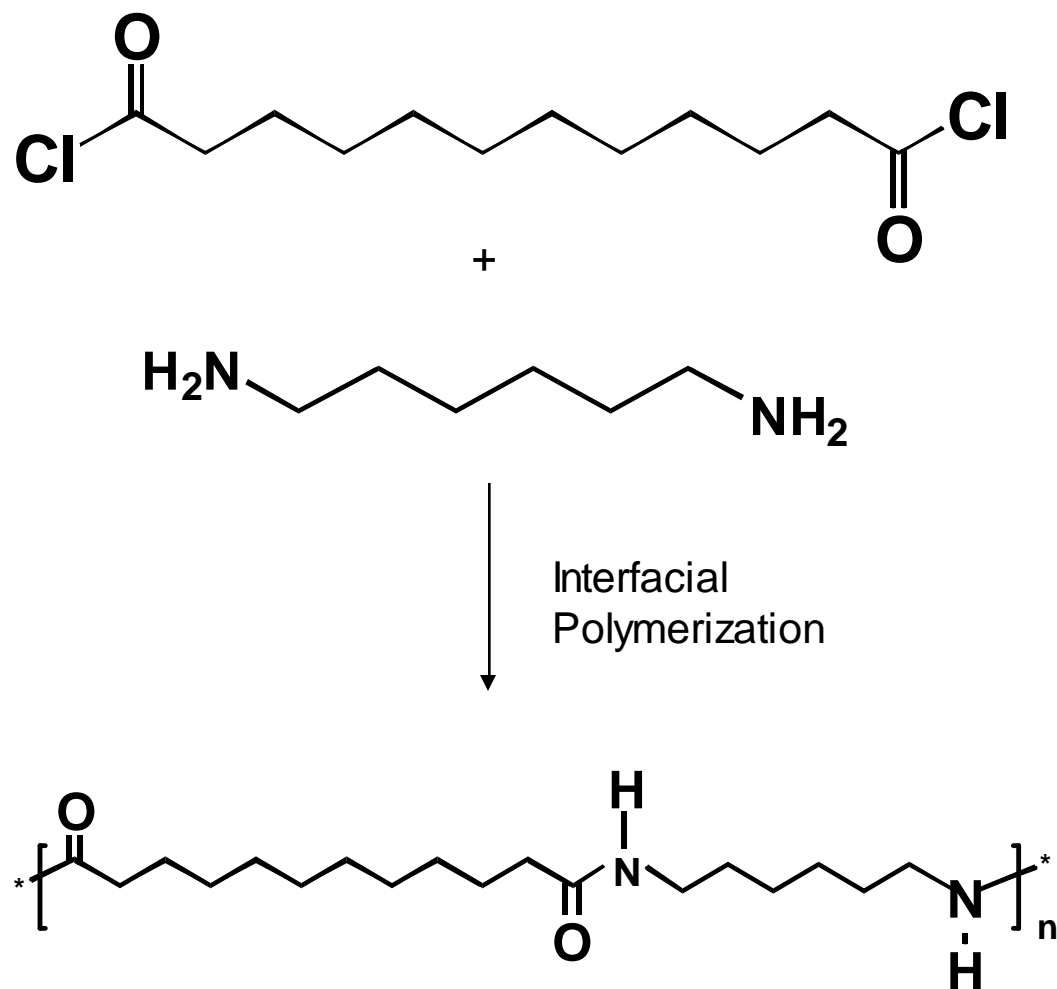
Odian, "Principles of Polymerization"
4th Ed.

Nonequilibrium Polyesterifications: 1,1'-Carbonyldiimidazole
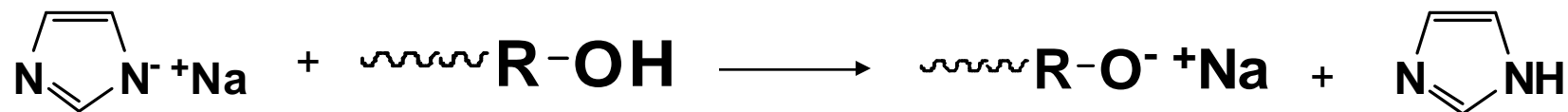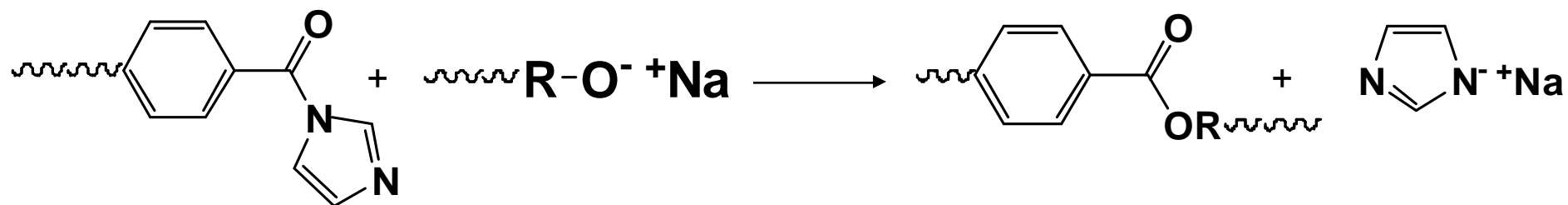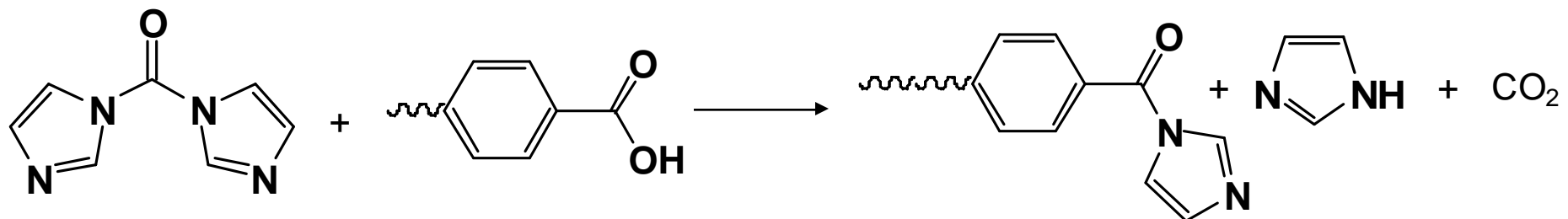
Drug Delivery with Degradable Polyester Microparticles
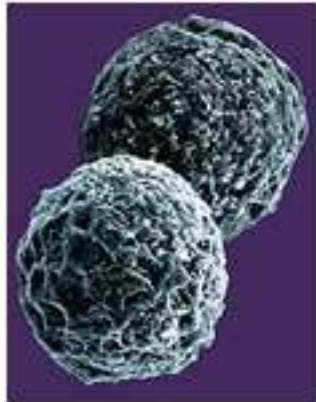
Drug loaded
Microspheres
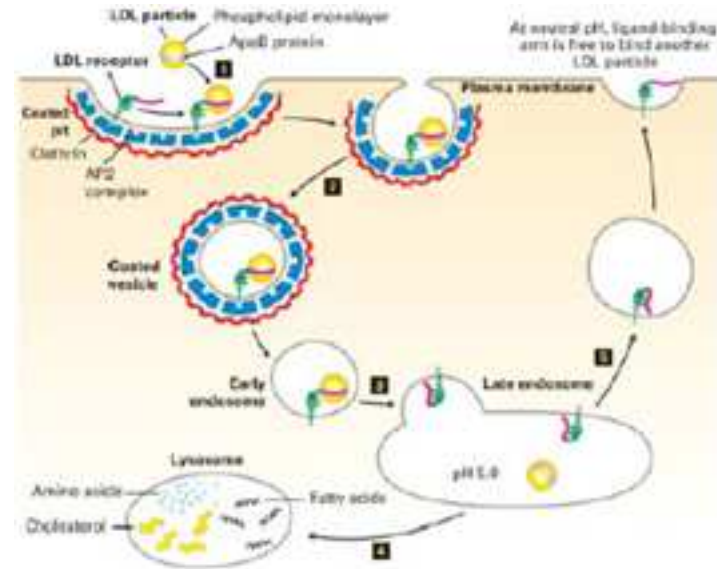
Increased retention in system Due to larger hydrodynamic volume

Cleavable Linkage

drug

Polymer Conjugate

The human urinary system, part of the excretory system, removes nitrogen-containing waste and helps maintain osmotic balance.

Aorta
Kidney
Renal artery
Renal vein
Ureter
Urinary bladder
Urethra
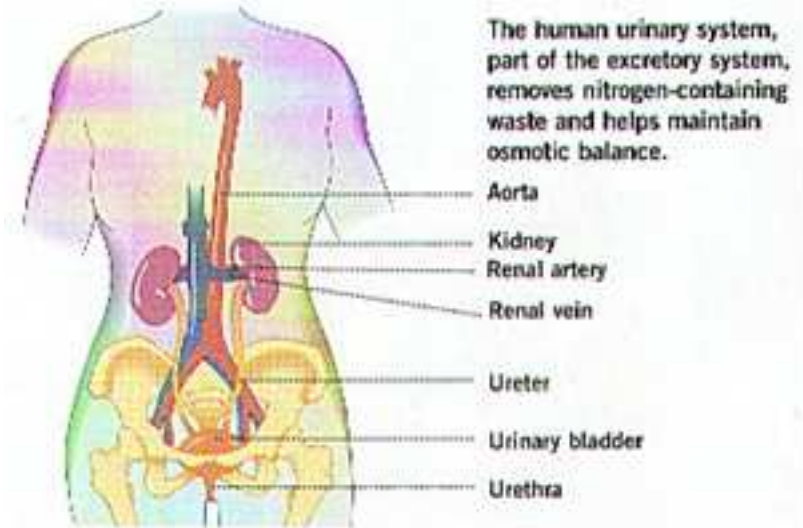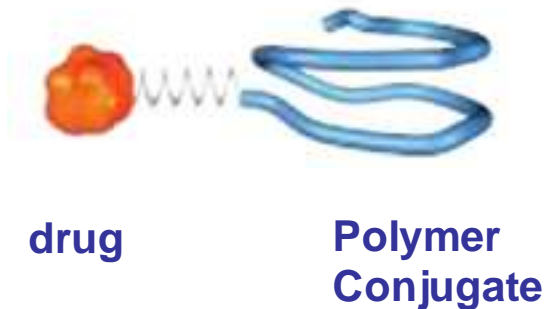
Nonstoichiometric Conditions: MW Control

I. **A-A + B-B** $r = N_A/N_B$ = stoichiomeric imbalance

        excess

II. **A-A + B-B + B'** $r = N_A/(N_B + 2N_{B'})$ = stoichiomeric imbalance

III. **A-B + B'**

$$\overline{X_n} = \frac{1+r}{1+r-2rp}$$

$r = 1 \longrightarrow \overline{X_n} = \frac{1}{1-p}$

$p = 1 \longrightarrow \overline{X_n} = \frac{1+r}{1-r}$

Branching and Gelation

Branching and Star Formation

A—A   A-B $\longrightarrow$ A-B A—AB-A

Crosslinking and gelation

A-A   + B_f $\longrightarrow$

A-A   +   B-B   + B_f $\longrightarrow$ crosslinking

A_f + B_f $\longrightarrow$

Monomer   *gel phase*   **Gel Point**   *Sol phase*   **Crosslinked Network**
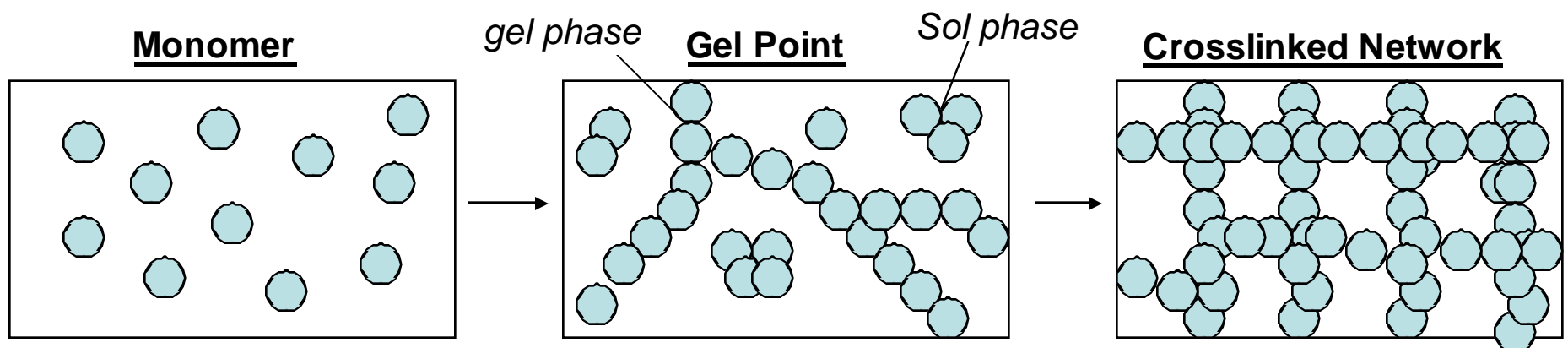
Gelation Theory

Carother's Eq.

$$\overline{X_n} \longrightarrow \infty \qquad f_{avg} = \frac{\Sigma N_i F_i}{\Sigma N_i} \qquad p = \frac{2}{f_{avg}} - \cancel{\frac{2}{\overline{X_n} f_{avg}}}^{\;0}$$

$$p_c = \frac{2}{f_{avg}}$$

Statistical Approach (Flory)

$$\overline{X_w} \longrightarrow \infty \qquad \alpha_{critical} = \frac{1}{(f-1)} \qquad p_c = \frac{1}{\{r[1 + \rho(f-2)]\}^{1/2}}$$

Increasing $f_{avg.}$

MW

Conventional Step-growth

p

$p_{critical}$
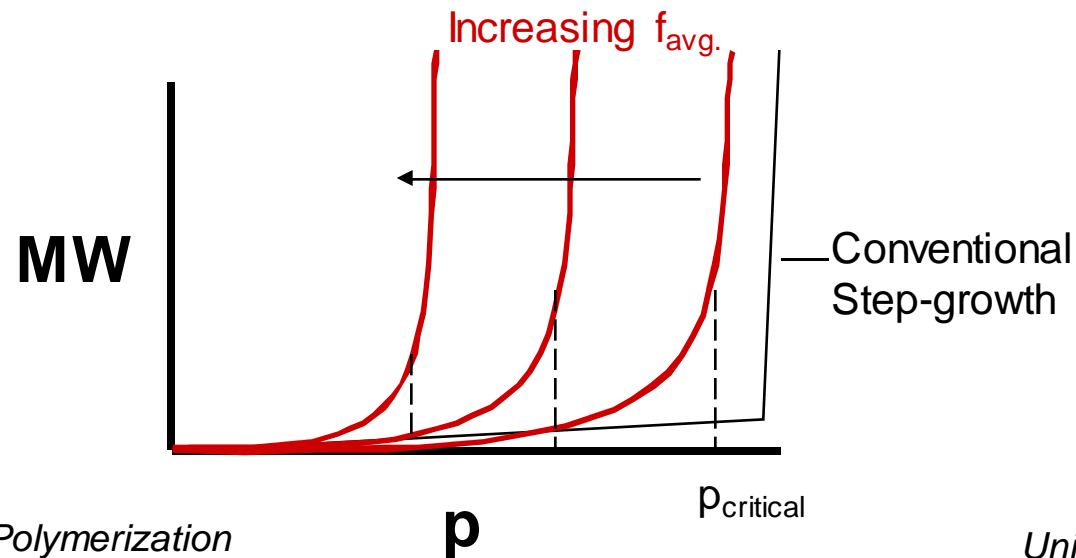
High Temperature Polymers: Replacement Materials for Metals-Ceramics
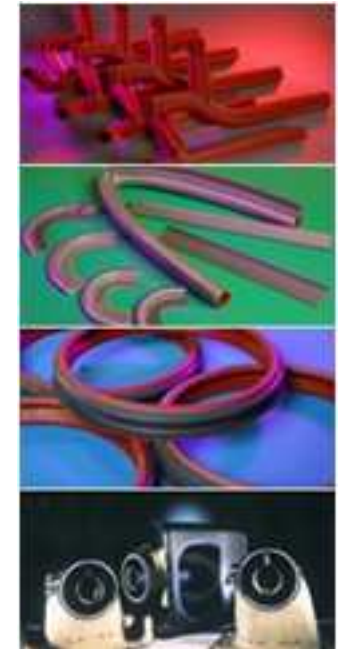
Shape-Persistent Polymers and Low-k Dielectric Materials
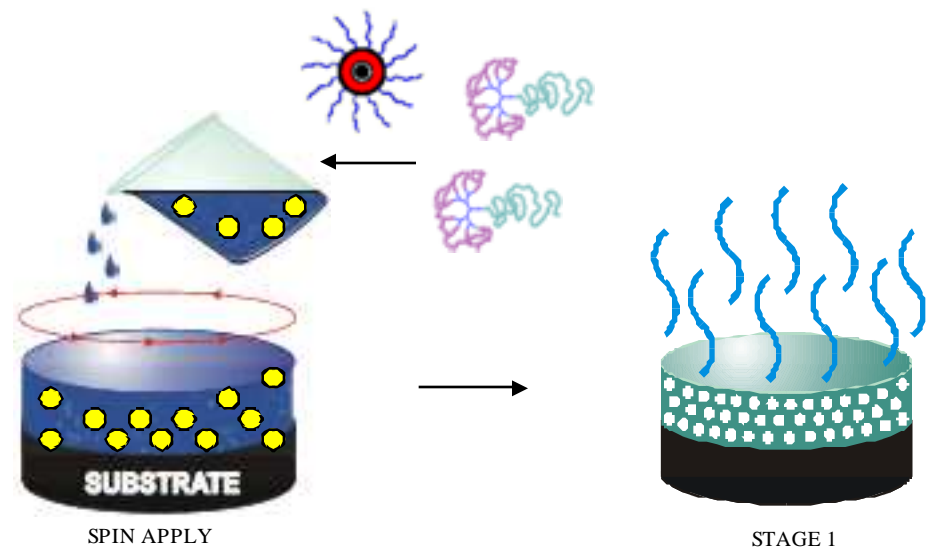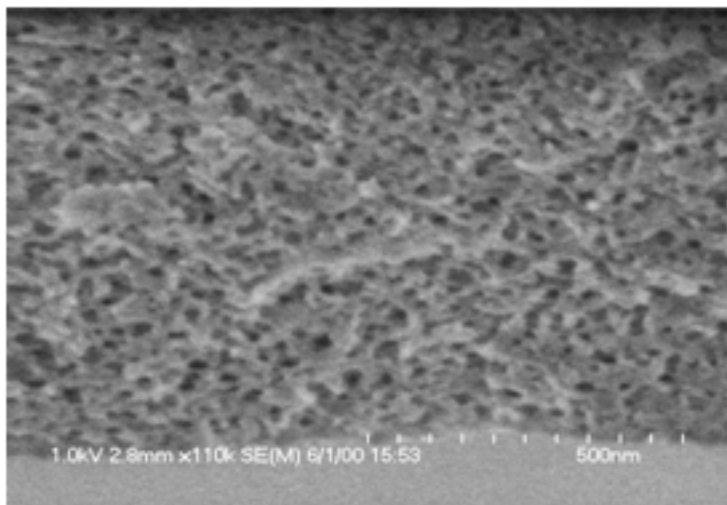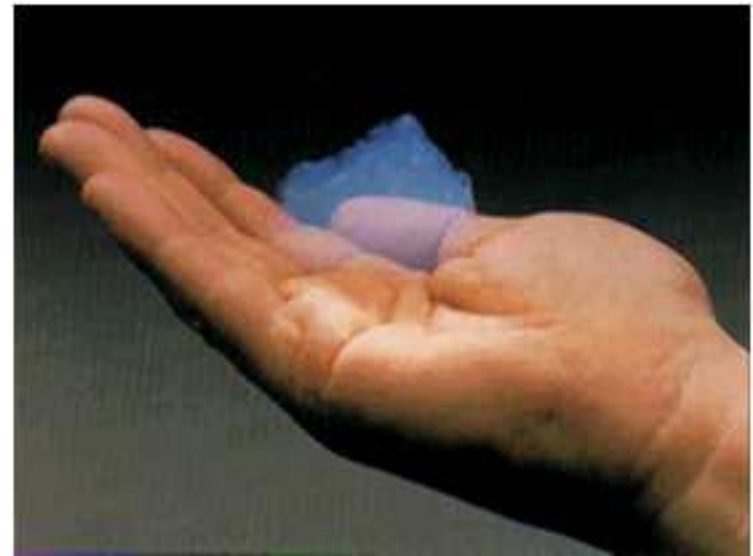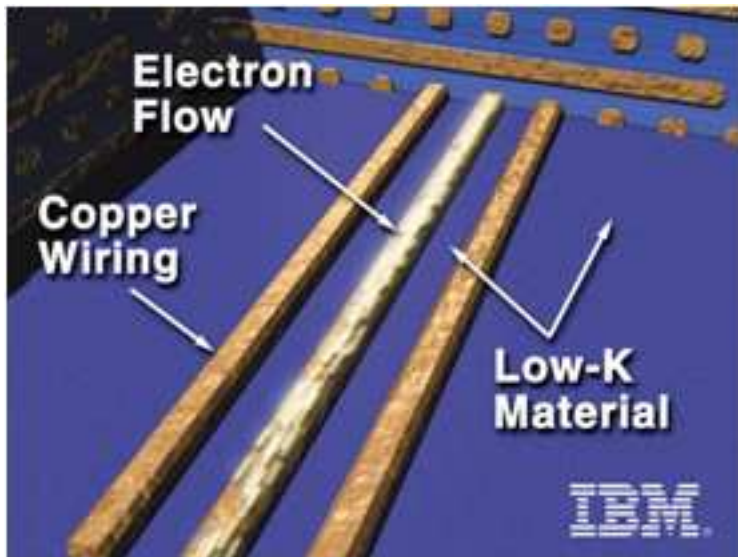
J. Hedrick, C. Hawker, W. Volksen, V. Lee, E. Conner, R. Miller

Synthesis of Polyimides: High Temperature Polymers

T < 70 ℃

NMP
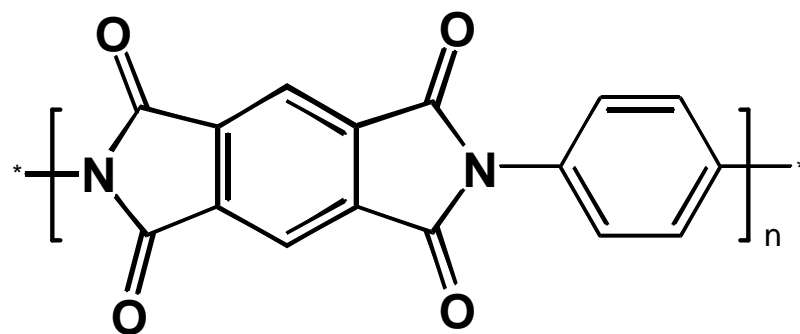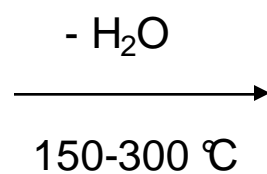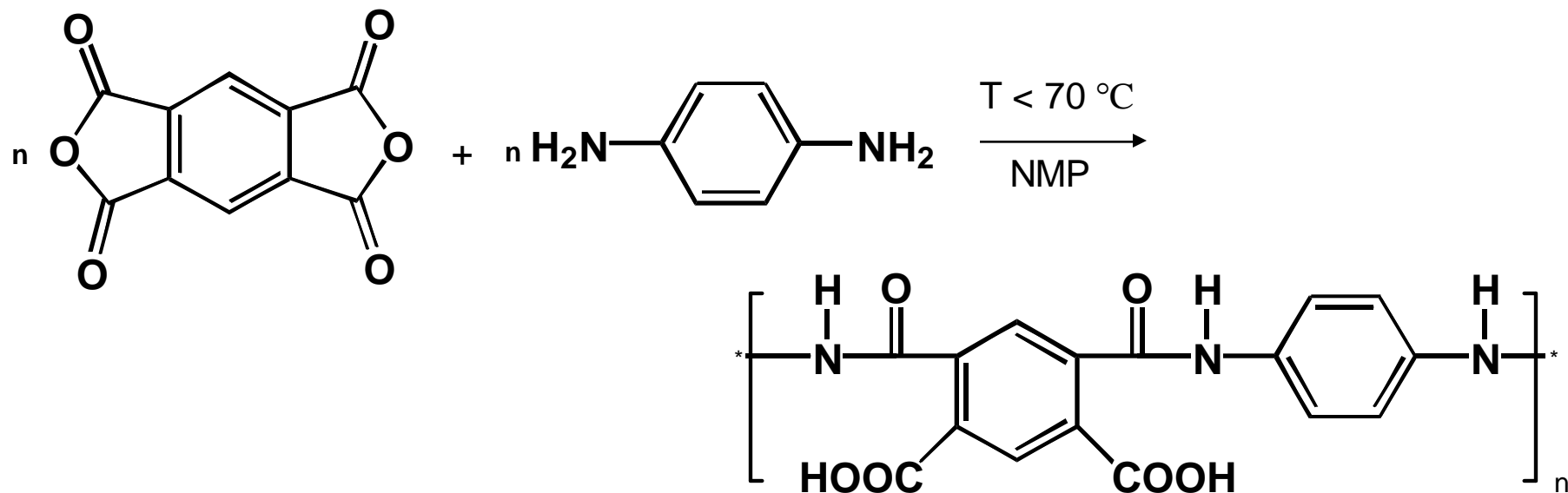
Polyamic acid
Precursor is soluble
In aprotic polar solvents
(NMP, DMAc)

- H$_2$O

150-300 ℃

Polyimides prepared by "setting"
polyamic precursor and annealing

Synthesis of Heterocyclic High Temperature Polymers: Polybenzimidazoles

3,3'-diaminobenzidine

+

diphenylisophthalate

1) 290 °C, $-H_2O$, $-PhOH$

2) Crush foam
   370 - 390°C
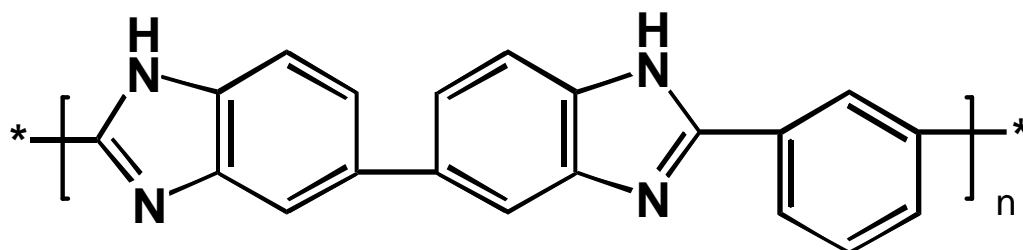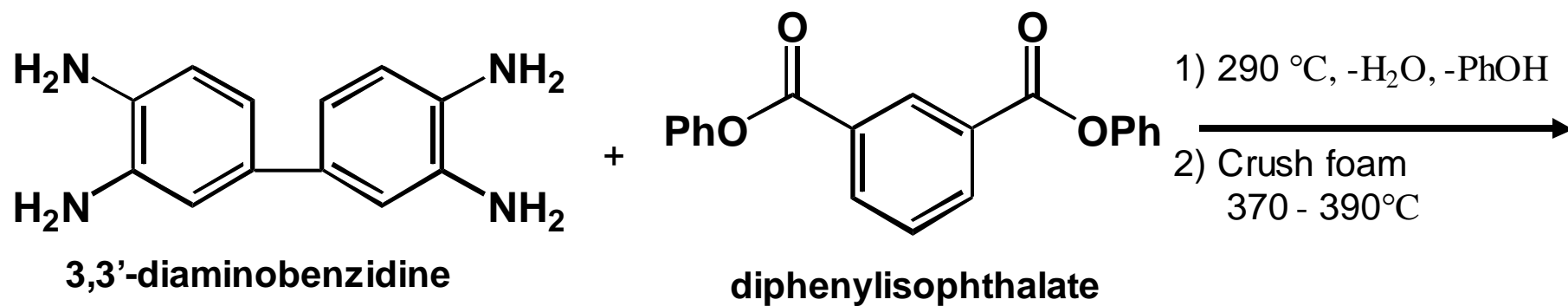
Poly[(5,5'-bi-1H-benzimidazole]-2,2'-diyl)-1,3-phenylene

Polybenzimidazoles: Two Stage Nucleophilic Substitution Mechanism
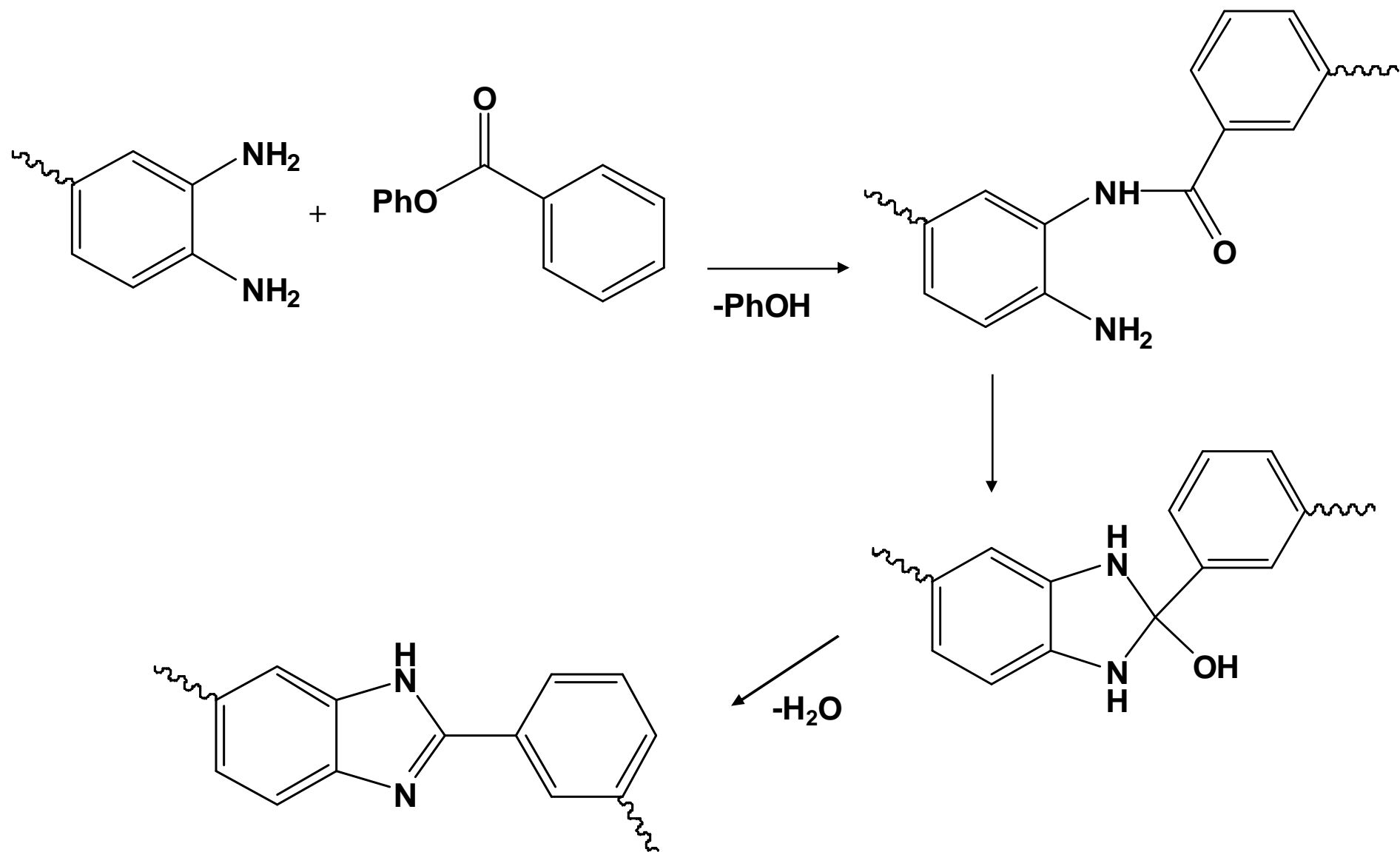
* *NEED K < 2.0!!!!!*
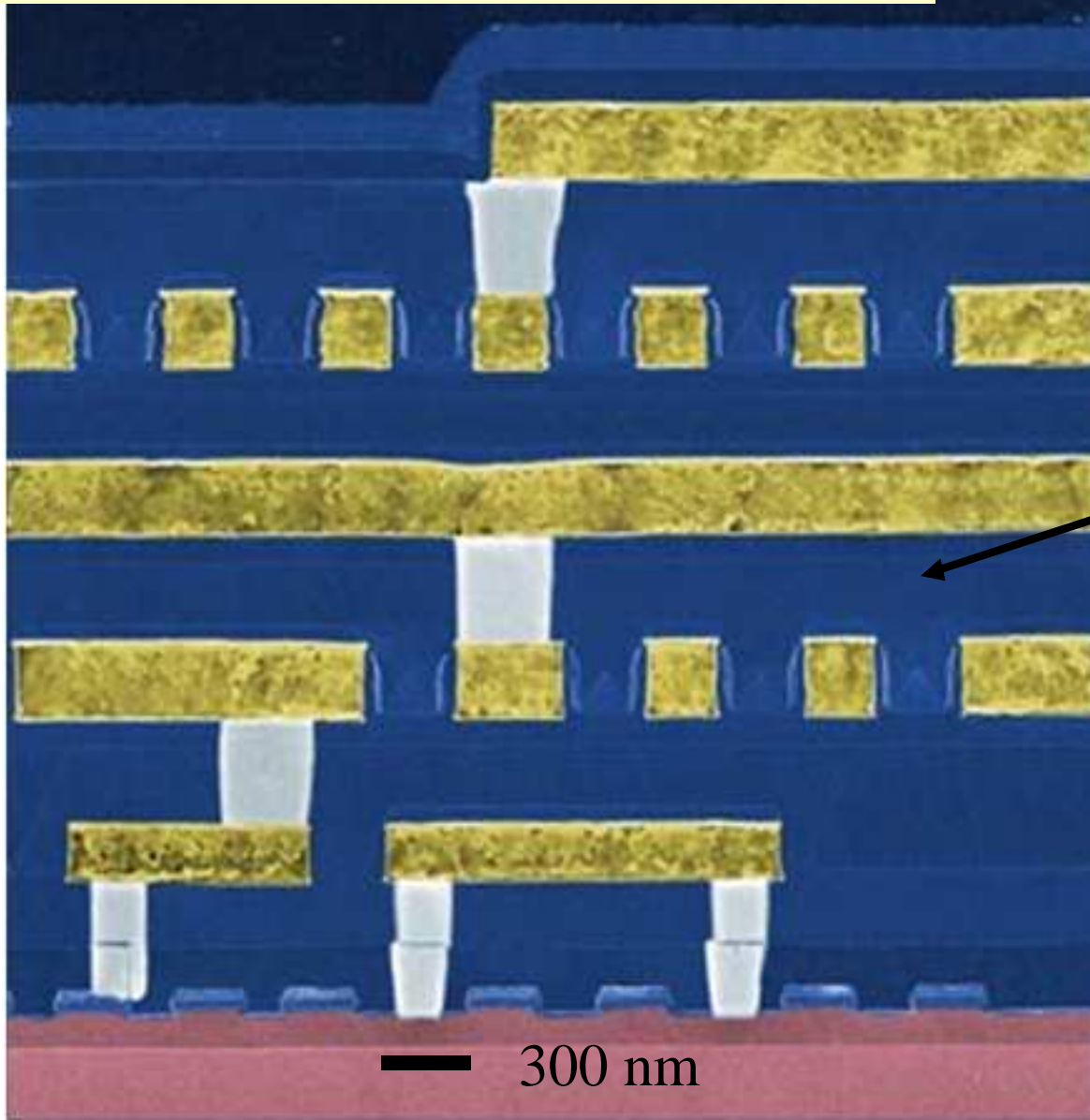
Dielectric materials

SiO$_2$
K = 4.0!!!

AIR
K = 1.01??

300 nm

Nanoporous Materials – *HOLES!!!*

Copper wires

Dielectric

150 nm

Wafer

50-200 nm pores are TOO BIG!!
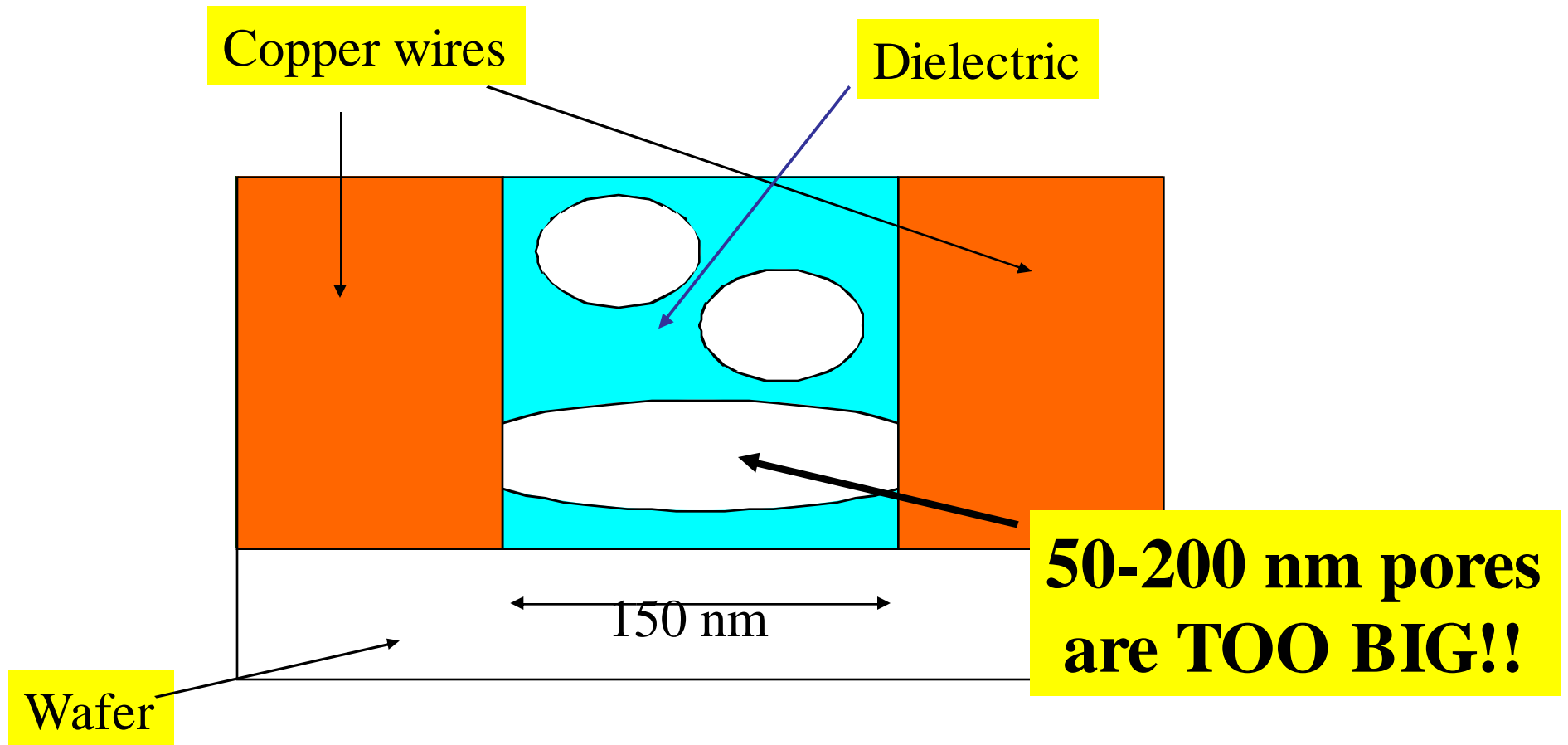
*   Feature/line size is shrinking, ca. 100-200 nm

Nanoporous Materials – *HOLES!!!*

Copper wires

Dielectric

5 nm pores are OK!!!!

150 nm

Wafer
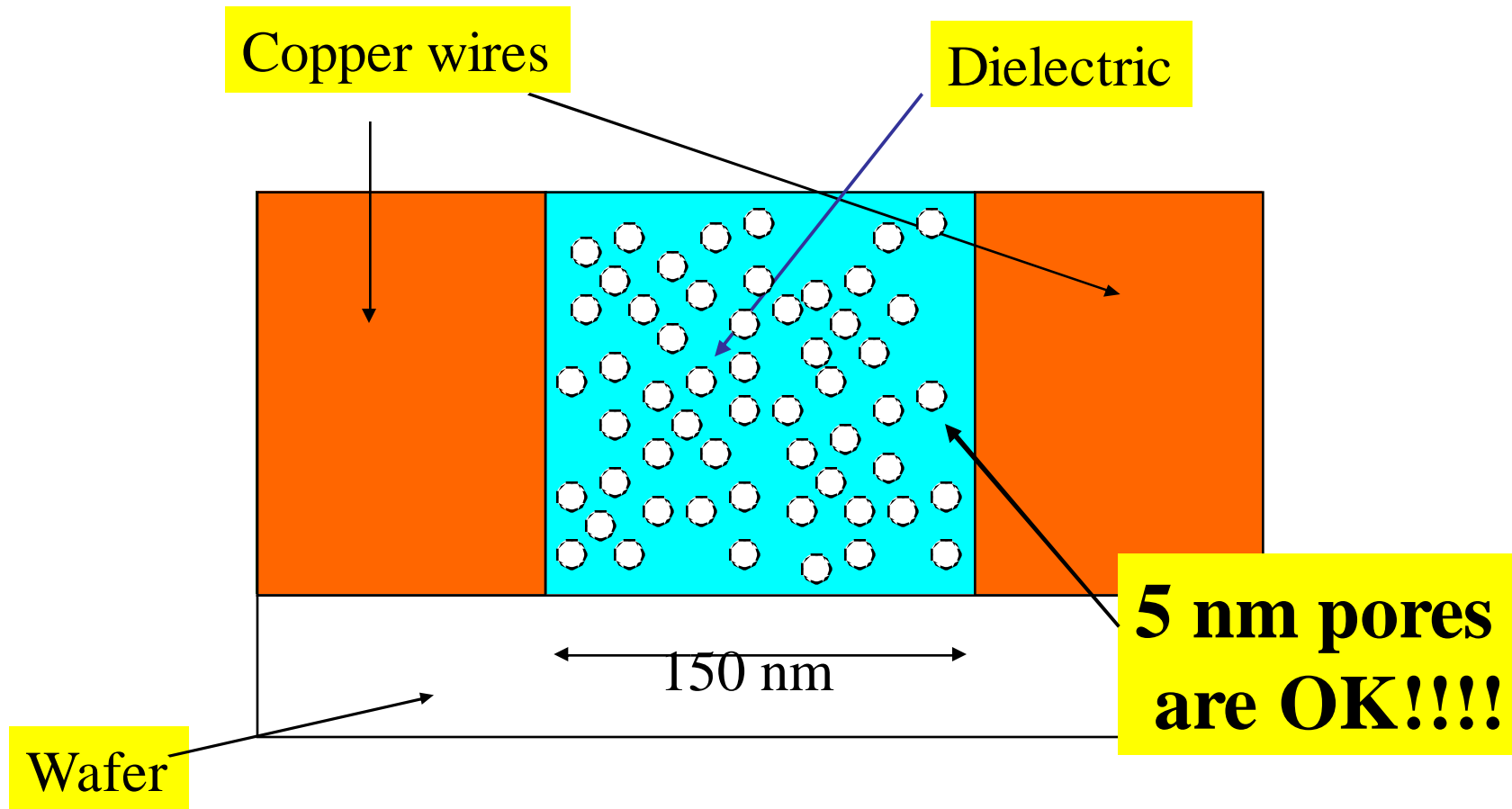
*   Feature/line size is shrinking, ca. 100-200 nm

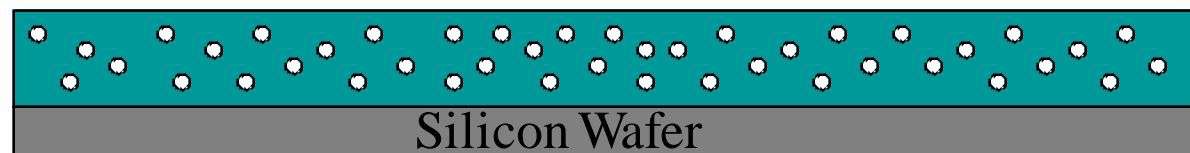# Synthesis of PMMA-*block*-Polyphenylquinoxalines-*block*-PMMA

3,3'diaminobenzidine

Bis(phenylglyoxalyl)benzene

PMMA-*b*-PPQ-*b*-PMMA

Hedrick et al., Polymer 1993, 34, 4717
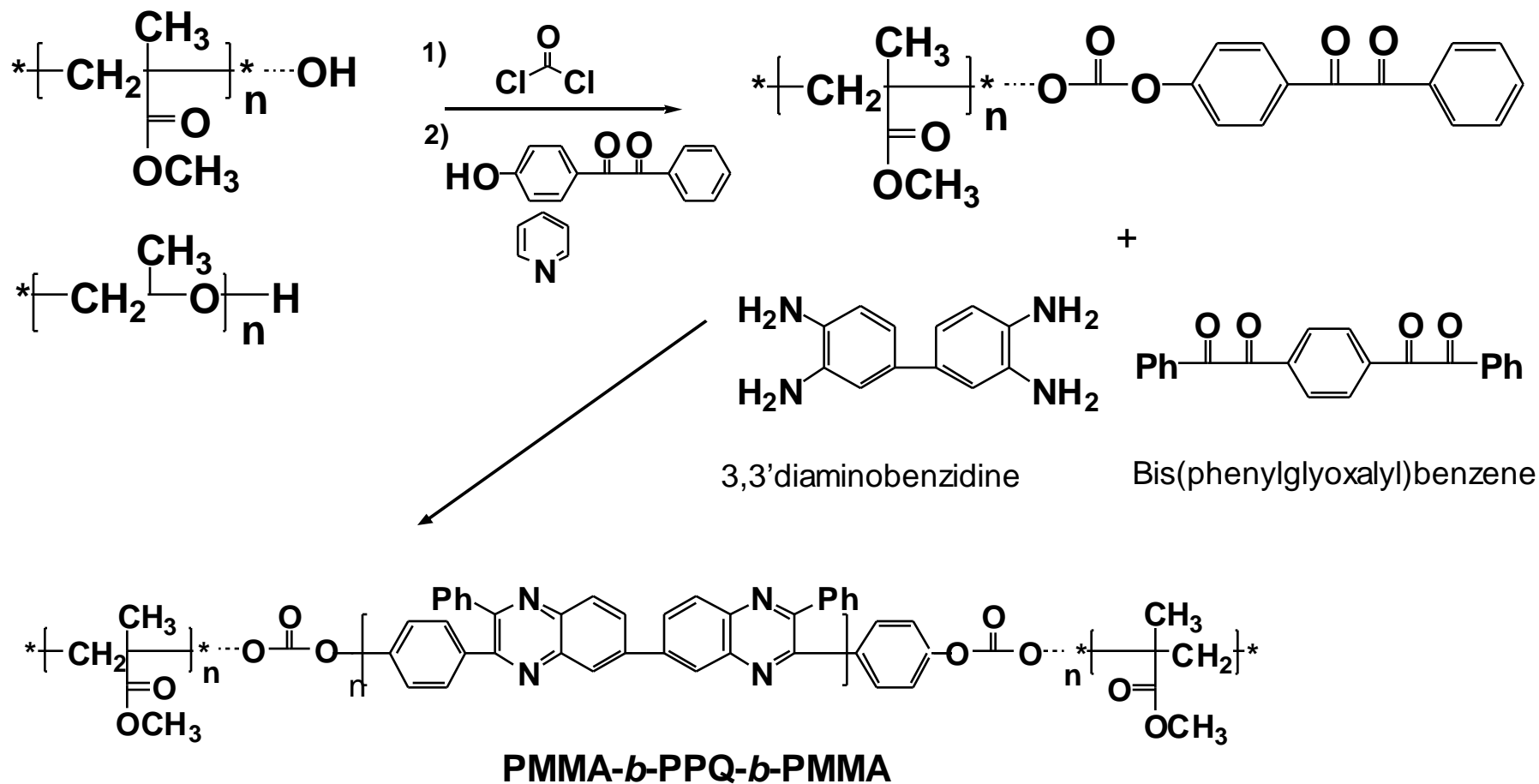
Synthesis of Nanoporous Polyphenylquinoxalines Films
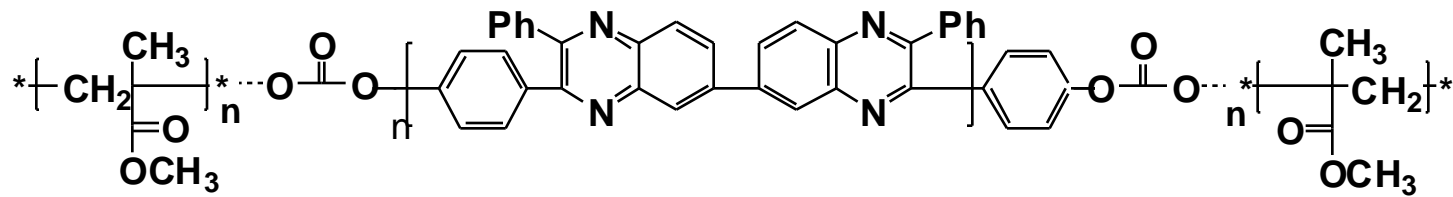
PMMA-*b*-PPQ-*b*-PMMA
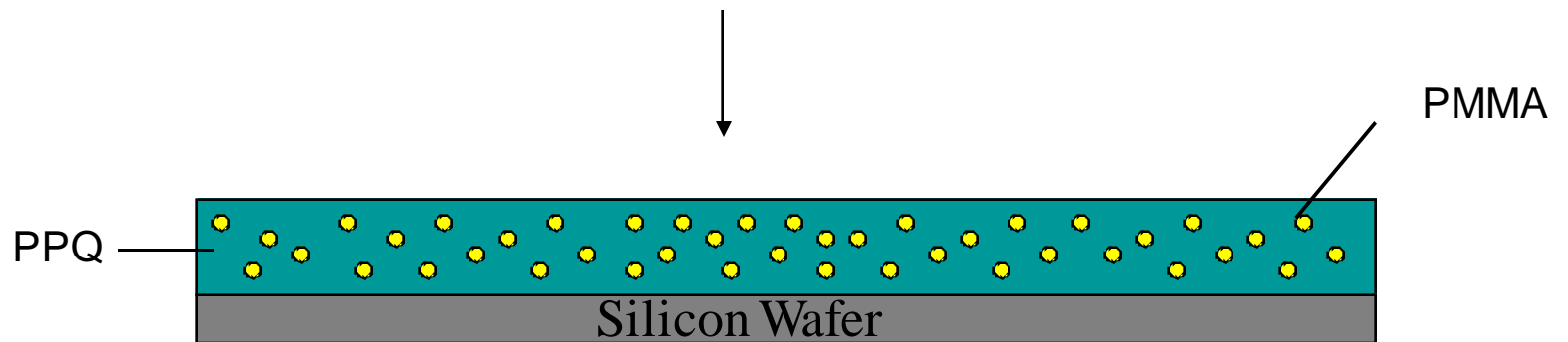
Heat to decomposition

Nanoporous PPQ
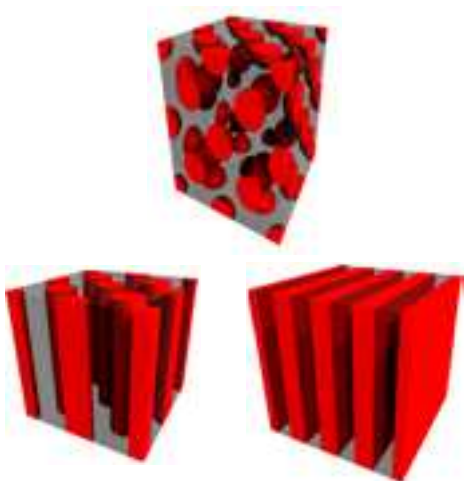
Dielectric Materials Overview

Material	Dielectric Constant	Deposition Technique
Silicon Dioxide	3.9 – 4.1	CVD
Fluorinated Oxide	3.4 – 4.1	CVD
Polyimides	3.0 – 3.6	Spin-on
Spin-on Glasses	2.7 – 3.1	Spin-on
Fluorinated polyimides	2.6 – 2.9	Spin-on
(DLC) Diamond like glass	2.8 – 3.0	CVD
Poly(arylene ethers)	2.6 – 2.9	Spin-on
Poly(arylenes)	2.6 – 2.8	Spin-on
Poly(norbornenes)	2.5 - 2.7	Spin-on
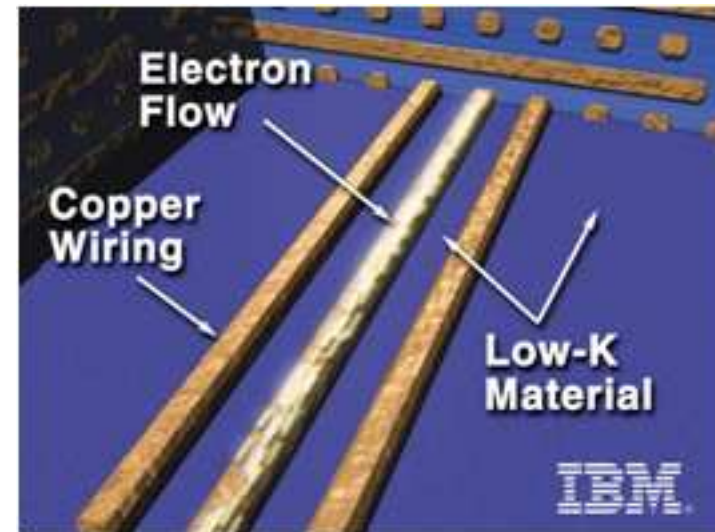
Ultra Low k Materials (< 2.2)

Teflon A-F	1.9 – 2.1	Spin-on
Teflon Microemulsion	1.9 – 2.1	Spin-on

Porous Dielectrics

Polyimide Nanofoams	2.2	Spin-on
Silica Aerogels	1.1 – 2.2	Spin-on
Silica Xerogels	1.5 – 2.2	Spin-on

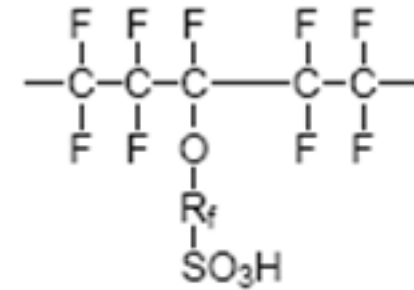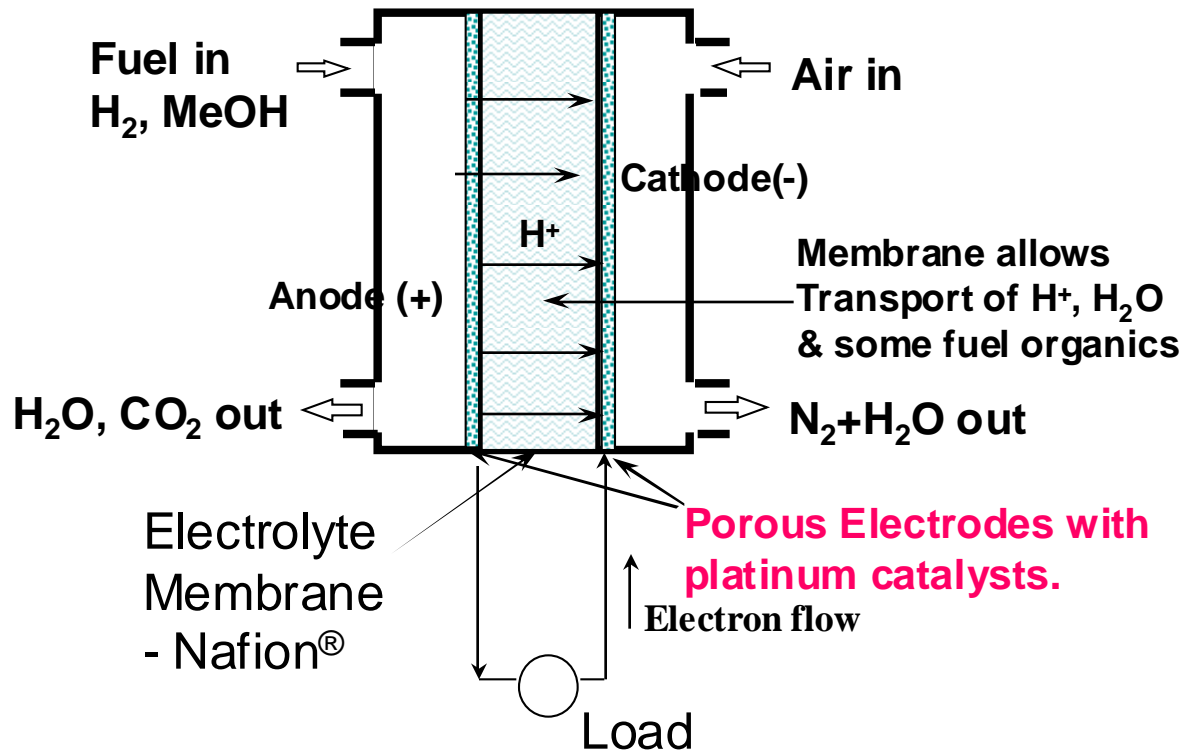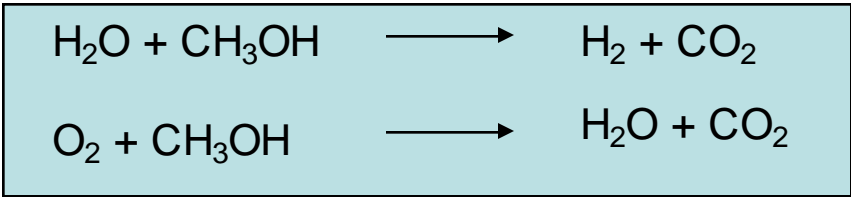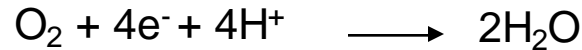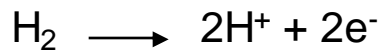➥Concept: Introduction of AIR lowers Dielectric properties

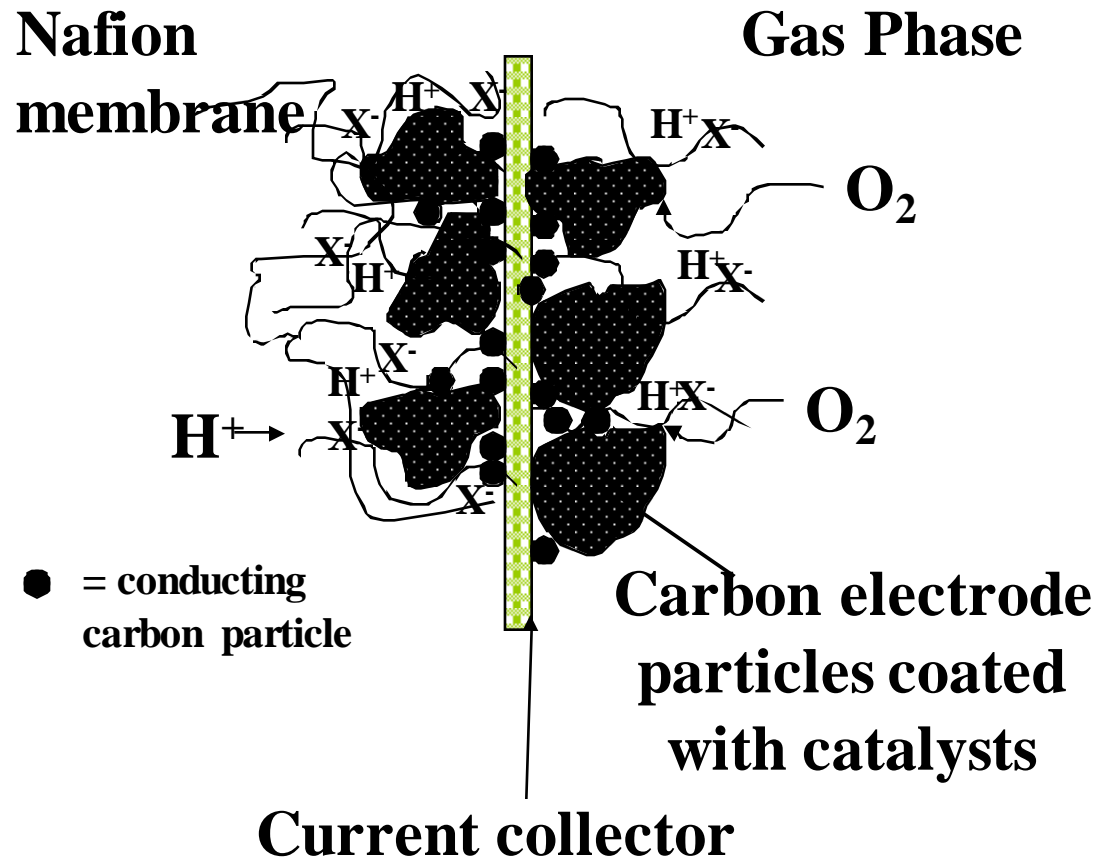# Fuel Cell Applications: Clean Abundant Energy

Fuel Cell Scheme: Role of membranes

Fuel in
H_2, MeOH

Air in

Cathode(-)

H^+

Anode (+)

Membrane allows
Transport of H^+, H_2O
& some fuel organics

H_2O, CO_2 out

N_2+H_2O out

Electrolyte
Membrane
- Nafion®

Porous Electrodes with
platinum catalysts.

Electron flow

Load

Nafion

$$H_2 \longrightarrow 2H^+ + 2e^-$$

$$O_2 + 4e^- + 4H^+ \longrightarrow 2H_2O$$

$$H_2O + CH_3OH \longrightarrow H_2 + CO_2$$

$$O_2 + CH_3OH \longrightarrow H_2O + CO_2$$

Fuel Cell Composite Electrodes

Nafion membrane

Gas Phase

H+ X-
X- H+ X-
X- H+
X- H+
H+ X-
H+→ X-
X-

H+ X-
H+ X-
O₂
H+ X-
H+ X-
O₂

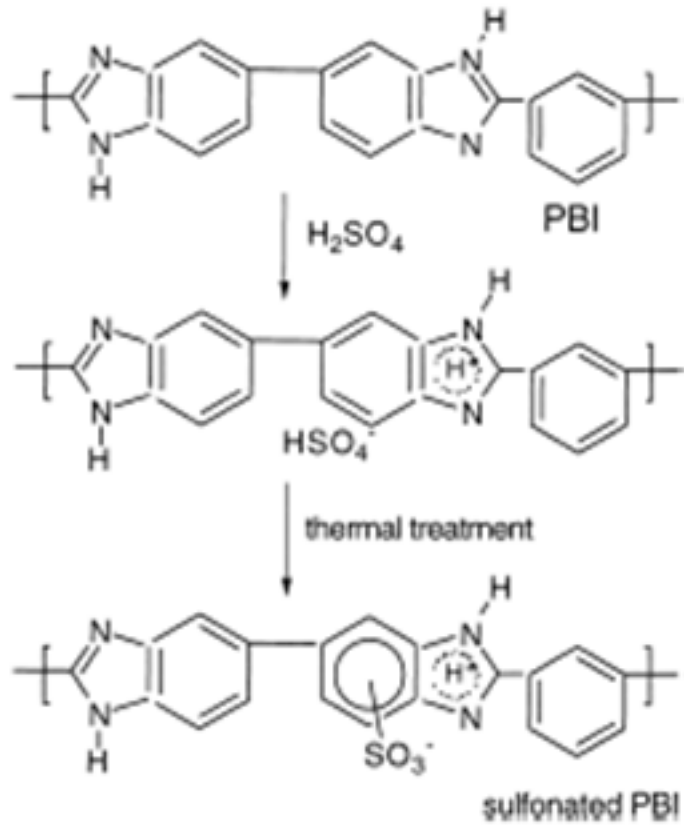● = conducting carbon particle

Carbon electrode particles coated with catalysts

Current collector

- Transport of gases and ions through crowded polymer-solid interfaces where the electrolyte mobility is restricted.
- Polyelectrolytes close to glassy phase
- Poor ion transport and dis-bondment.
- Ion activity?

Sulfonated Polybenzimidazoles
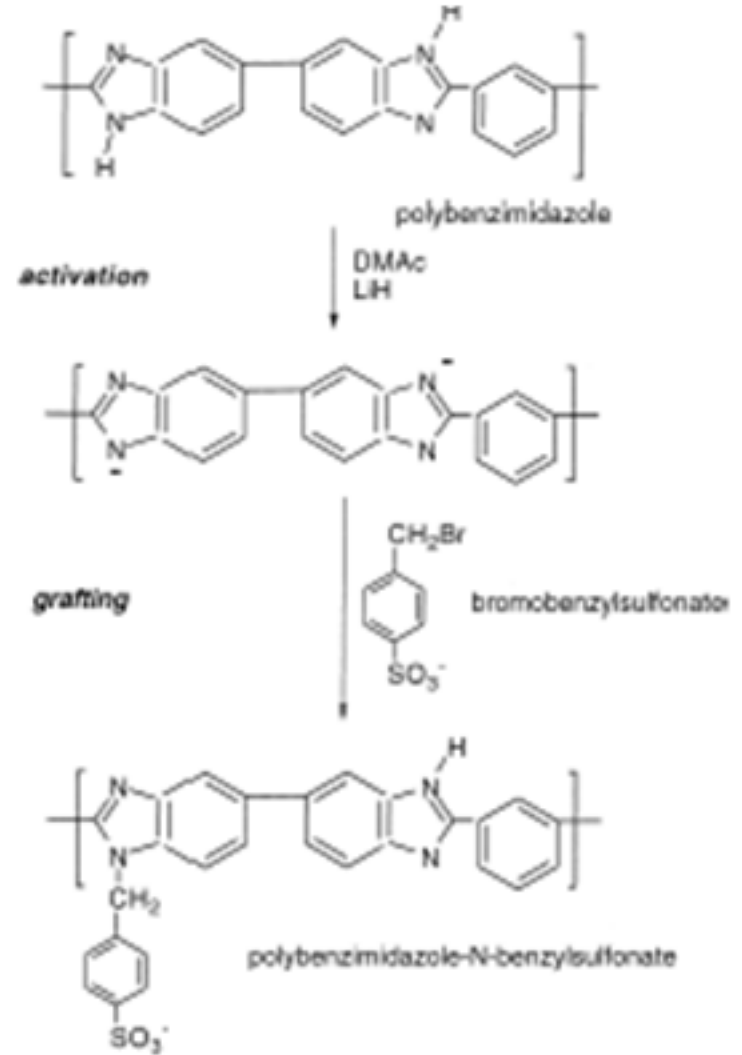
Ionic Conductivity Sulfonated Polybenzimidazoles
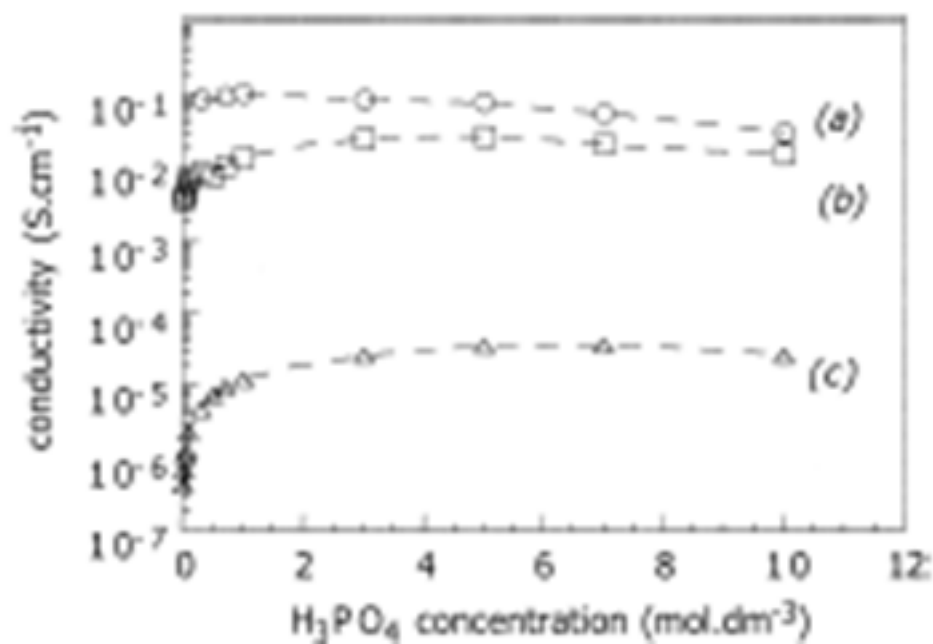
Fig. 3. Conductivity at 25°C of: (a) Nafion™-117, (b) benzyl-sulfonate-grafted PBI and (c) PBI as a function of the H₃PO₄ concentration (immersion time 8 h) [46,47].
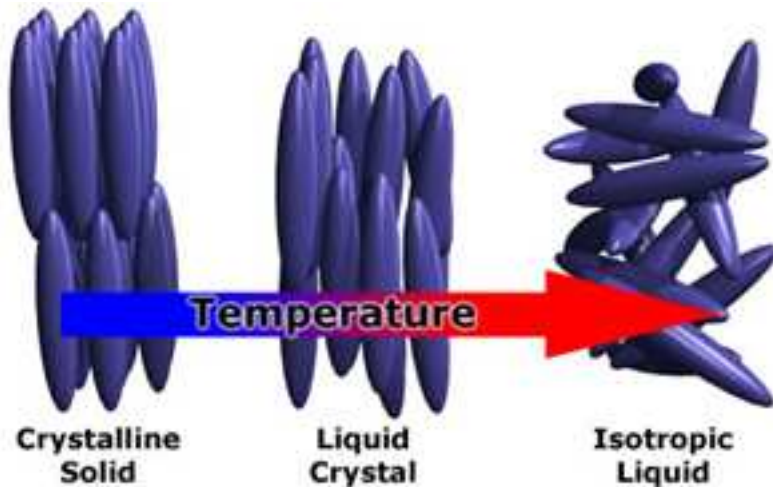
Desirable Membrane Properties

Materials-maximum ionic conducivity

Selectively permeable to H⁺ Impermeable to MeOH other ions

Capable of higher use temperatures

Suppression of CO catalyst Poisoning of Pt electrodes

Jones et al., J. Membrane Sci. **2001**, *185*, 41

Liquid Crystals and Liquid Crystalline Polymers

crystal: 3D-order solid
LC: 1D, or 2D ordered liquid
Isotropic liquid: disordered

LC's are *anisotropic*
i.e., properties dependent on direction
of measurement

Small molecule LC and
Liquid Crystalline Polymers

Mesogens in LC polymers

Main-chain mesogens
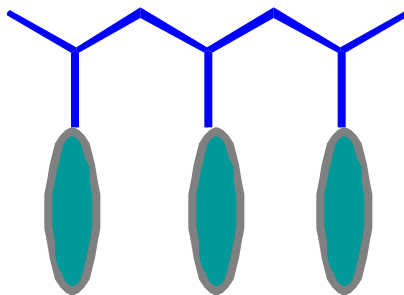
Side-chain mesogens

Mesogen: rigid or rod-like groups
that point along a common axis

In presence of solvent, or when heated
Tendency of mesogens to align along
One-axis gives rise to the mesogenic state,
Or "liquid crystallinity"

Certain proteins, viruses, cellulose are
LC due to rigid helical conformations

Nematic and Cholesteric Phases of LC's

nematic

No positional order
But tend to point along
Same axis

├─ 1/2 Pitch distance ─┤
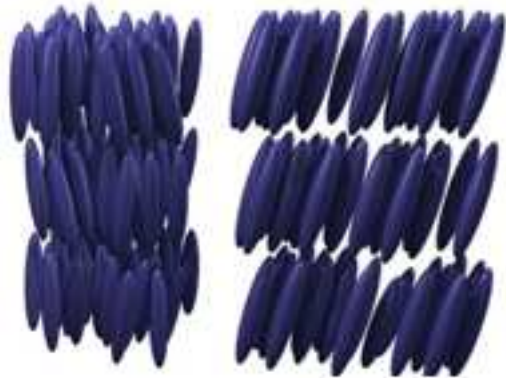
**Cholesteric
(chiral nematic)**
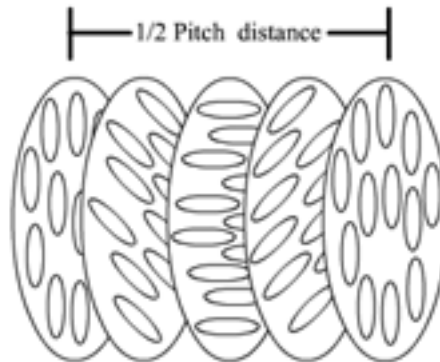
Typically composed of nematic
Mesogen with chiral center
Produced intermolecular forces
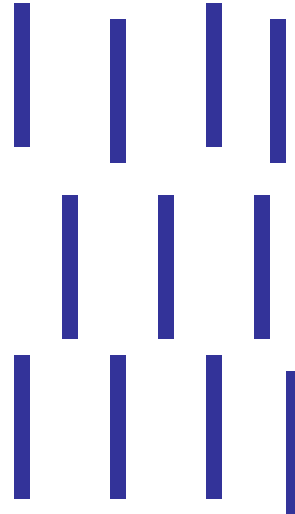Aligning molecules at slight angles

thin nematic sheets angled to
each layer

"pitch" = distance for one full turn
of helix

Smectic and Discotic Phases of LC's

smectic

Molecules maintain general alignment similar to nematic but tend to align in layers,or planes

Discotic Nematic

Discotic Columnar

Mesogens are disc-like instead of rigid-rod like

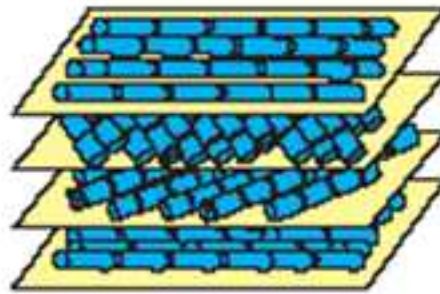Stacking of columns yields 2-D crystalline array
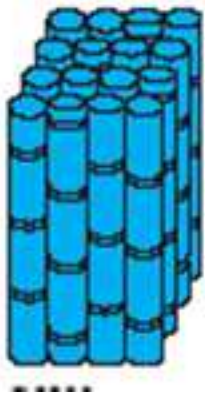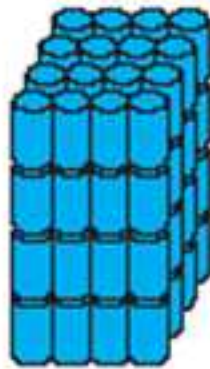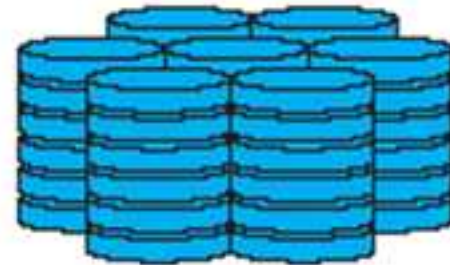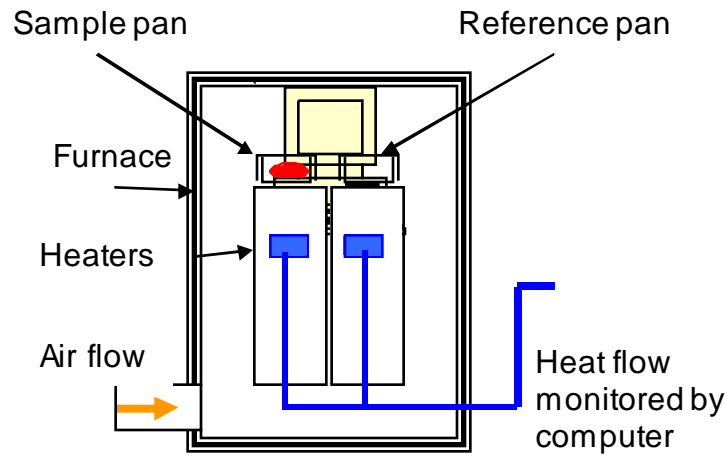
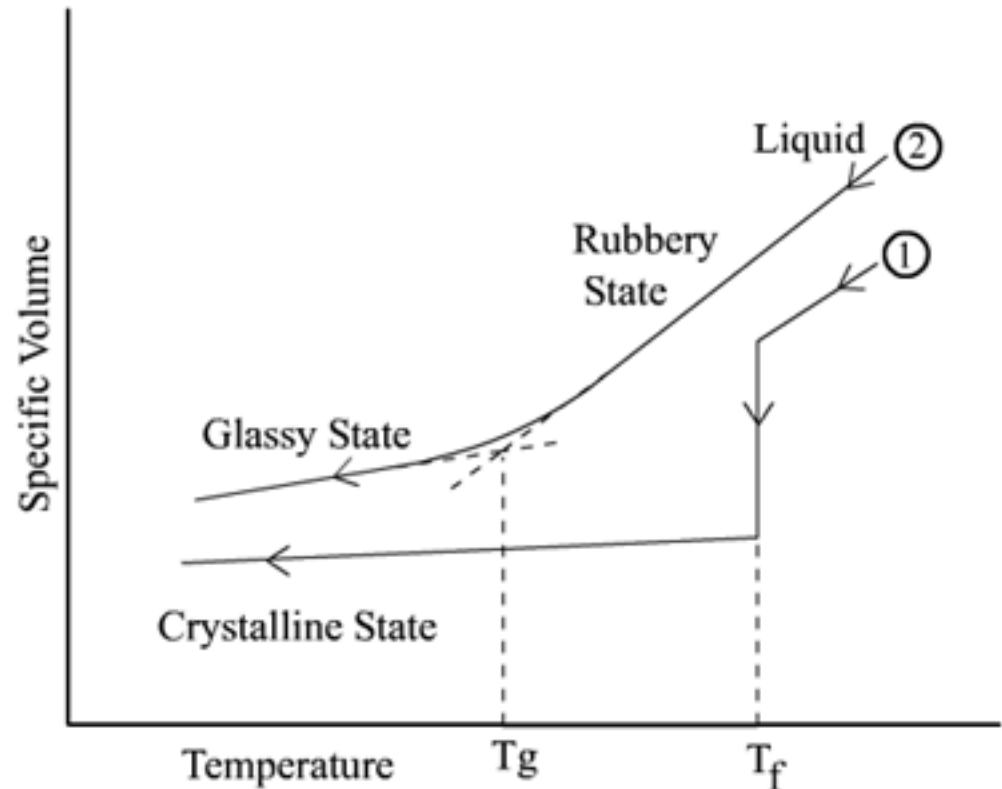Nematic   Smectic   Cholesteric   Columnar

Characterization of LC Materials

- X-ray diffraction: characteristic scattering of different mesostructures clearly identifies LC phase

- Differential Scanning Calorimetry (DSC): monitors each thermal transition

  crystalline solid to smectic phase to nematic phase to isotropic liquid

- Birefringence: measure of different refractive indices from anisotropy from LC

- Microscopy: optical images of different crystal phases and morphology from polarized optical microscopy

# General concept of DSC and Review of Thermal Transitions

Sample pan   Reference pan

Furnace

Heaters

Air flow

Heat flow monitored by computer

Schematic diagram of a DSC instrument

Specific Volume

Liquid ②

Rubbery State

①

Glassy State

Crystalline State

Temperature   Tg T_f

2 = amorphous glassy polymer

1 = crystalline solid (not crystalline polymer!)
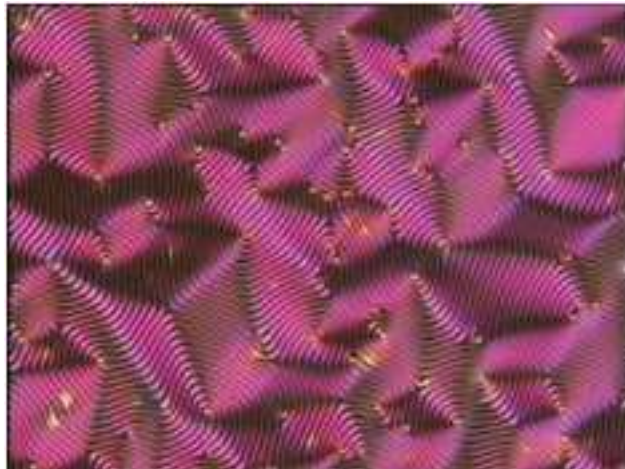
DSC of Thermotropic Liquid Crystal
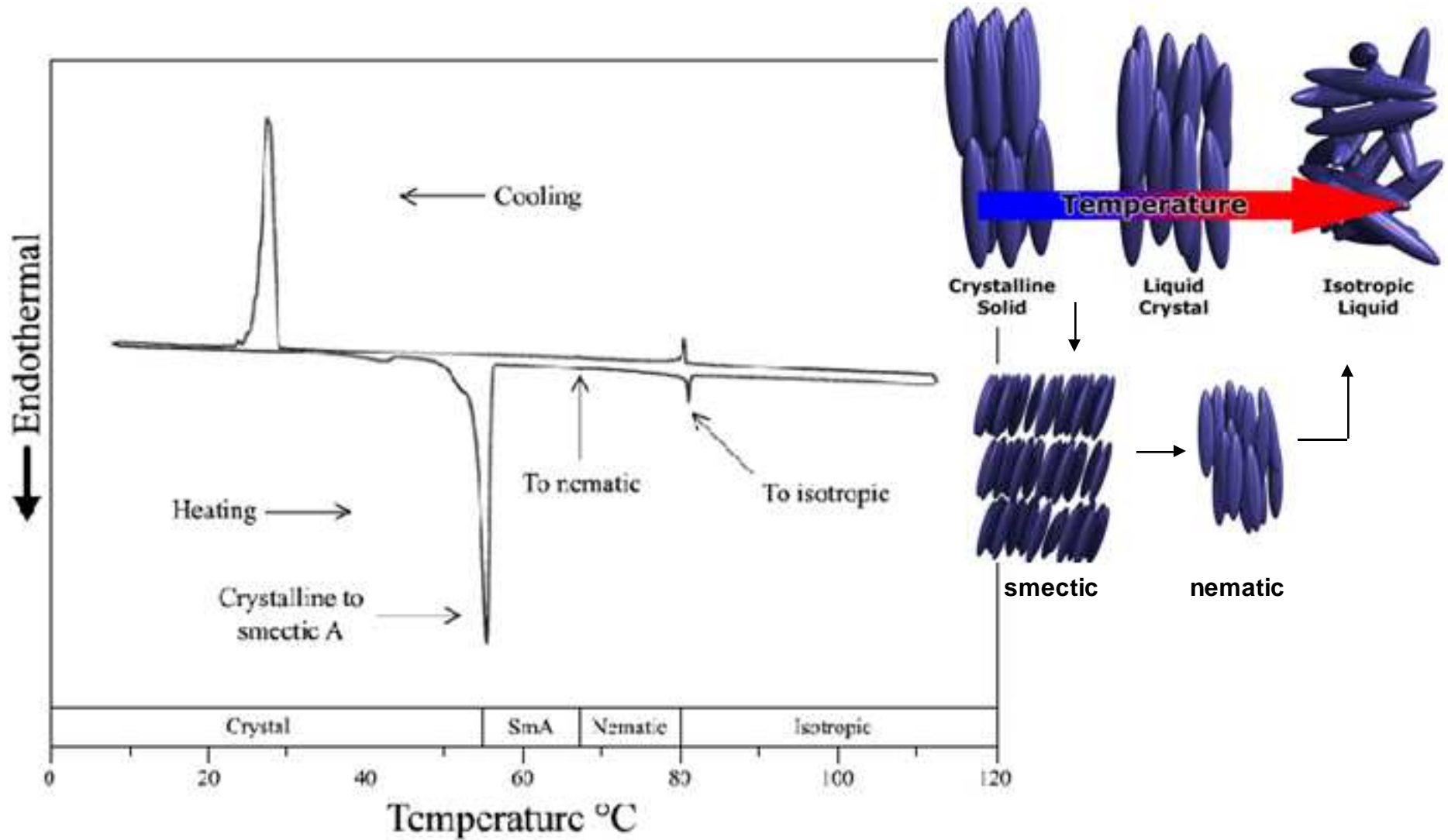
Examples of LC Textures from Optical Microscopy

Spherulite texture of a crystalline phase

Schlieren texture of a nematic phase

Cholesteric fingerprint texture

SmA fan-shaped texture

Possible Thermal Transitions on LC's
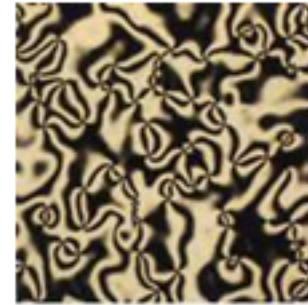

Crystalline solid   Smectic phase   nematic phase   Isotropic liquid
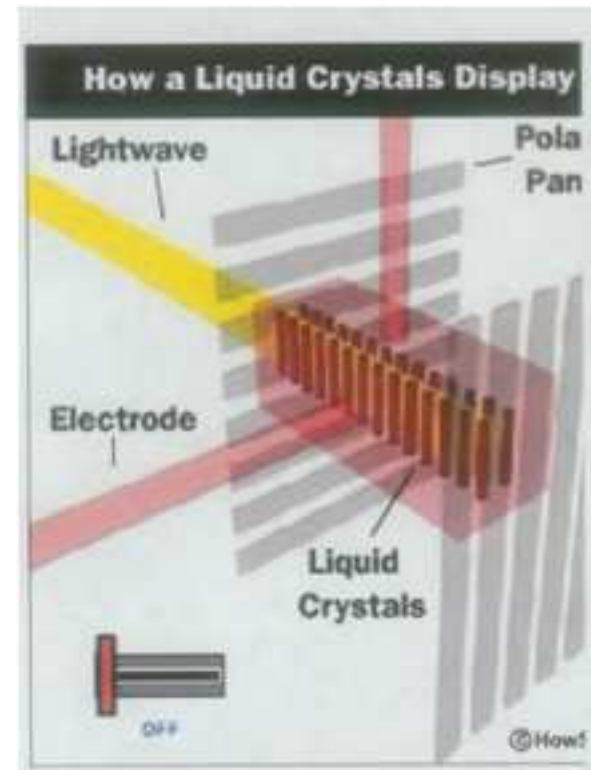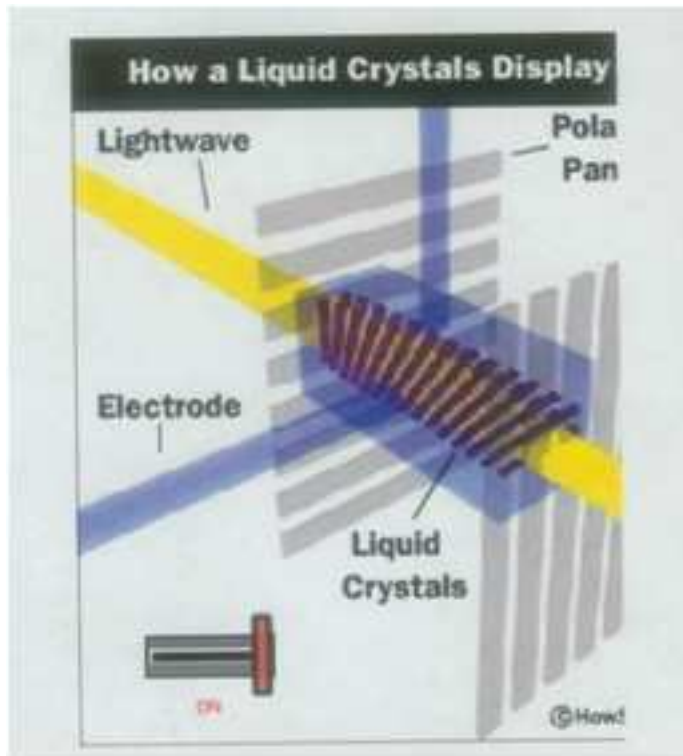
decreasing temperature
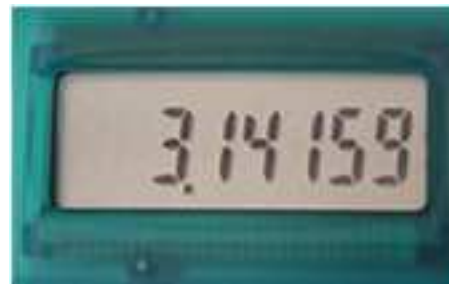
Increasing temperature

Liquid Crystals Displays

"on state" = current on

"off State" = current off

Numbers appear
when electrodes
induce twisting
of LC

Blank screen with zero current

Only small molecule LC's have fast enough dynamics for LCD's
Polymers rearrange to slowly on longer time scales
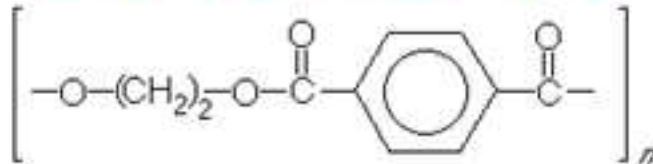
Main-Chain Thermotropic LC Polymers

Without flexible spacer

Poly(4-oxybenzoly)

PHNA poly(hydroxynapthoic acid)
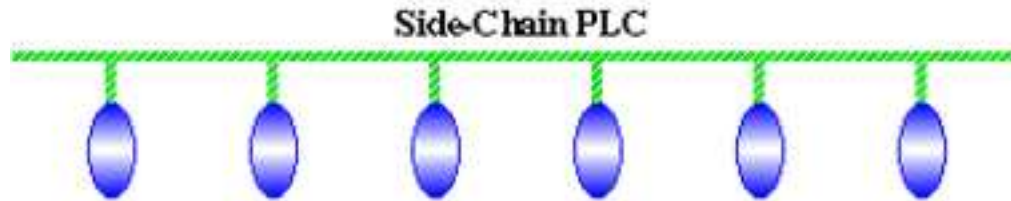
With flexible spacer
Mesogens are "decoupled"

PET poly(p-phenyleneterephthalate)

Processability improved with copolymerization with:
Asymmetric monomers (*ortho*, -*meta* functional monomers)
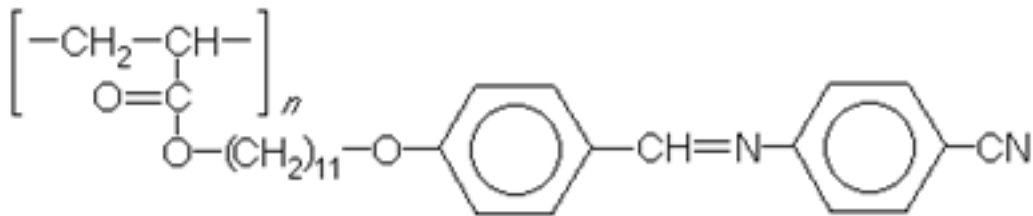Monomers with longer spacers

Side-Chain Thermotropic LC Polymers

Side-Chain PLC
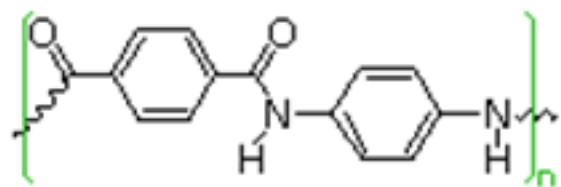
Polymer Backbone
Mesogen
Spacer

Optimization of each
Structural parameter
affect final properties

Ex. Of Side Chain Thermotropic LC
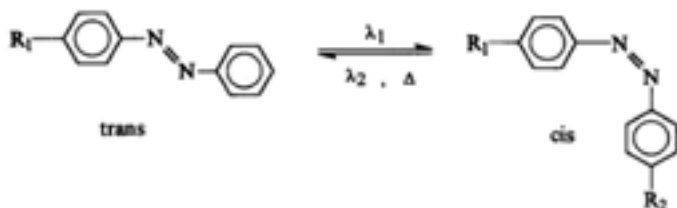
Applications of Thermotropic LC Polymers

- ## High Strength Fibers: Kevlar

**Polyaromatic amide
Kevlar**

- ## Photonics: Optical Storage Media

λ_1

λ_2 , Δ

trans

cis

R_1

R_2

High T_g of LC polymers allows "memory" of optical data

McGrath Group-University of Arizona

Classifications of LC's : Thermotropic vs. Lyotropic

- **Thermotropic LC's:** the liquid crystalline state is induced thermally form bulk material
  - Enatiotropic LC: LC state can be reached by either heating solid, or cooling liquid
  - Monotropic: LC state can be reached by heating solid, or cooling liquid, but not both
- **Lyotropic LC's:** LC stated occurs from influence of solvent, micellar structures from solvent induced aggregation
  - Lyotropic mesogens usually amphiphilic with both lyophilic (solvent attracting) and lyophobic (solvent repelling) segments
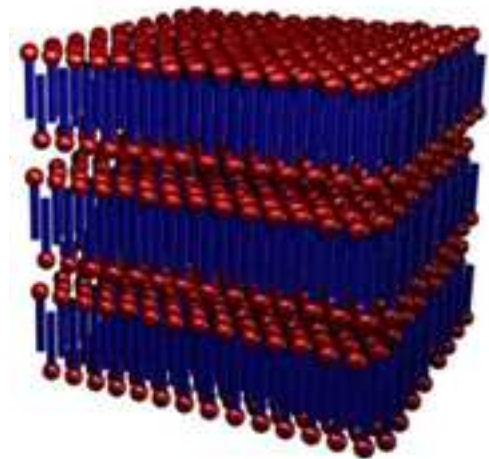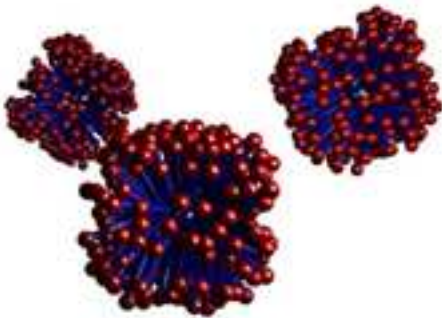
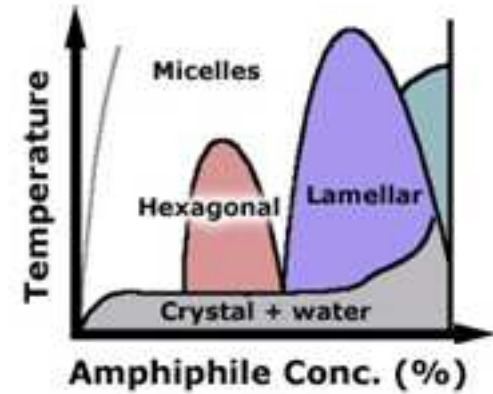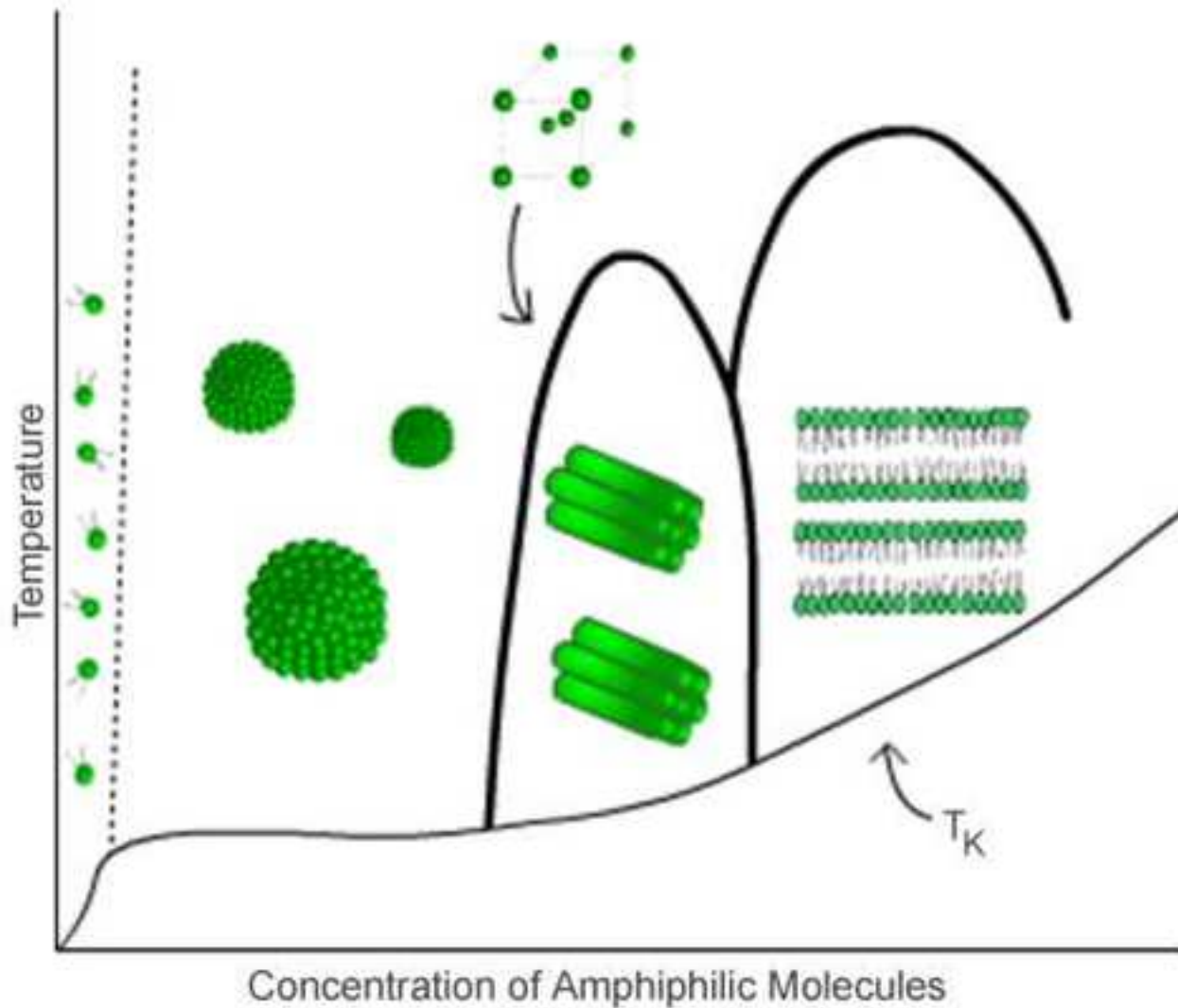# Lyotropic LC Polymers

Lyotropic LC's
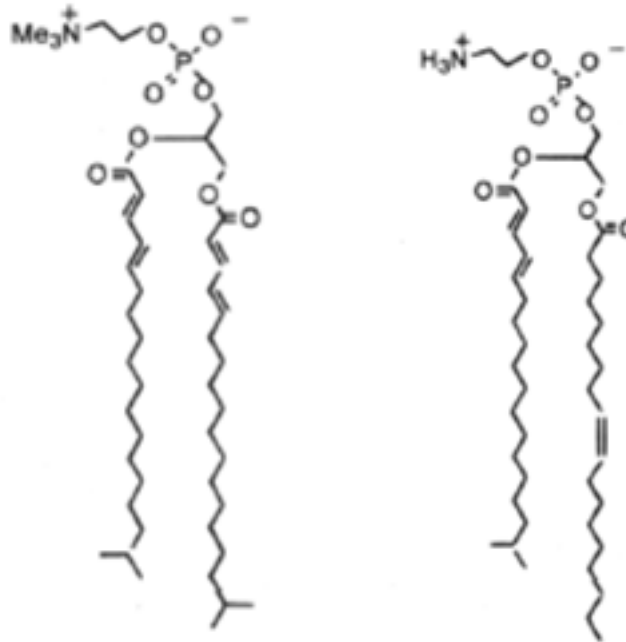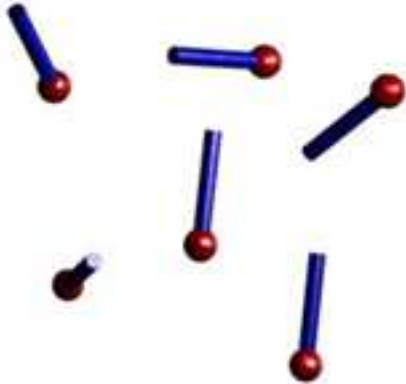
O'Brien et al.,
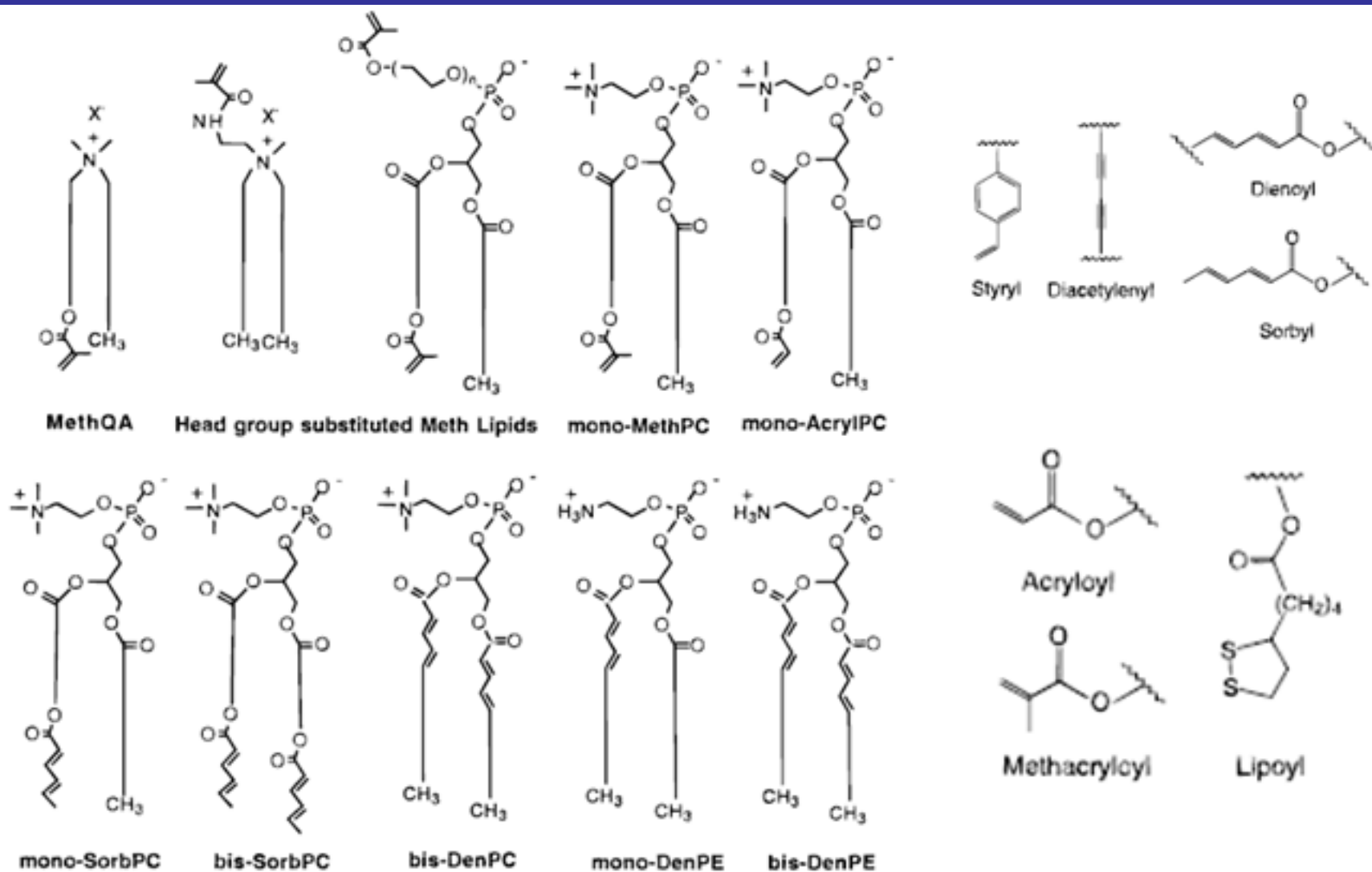*J. Am. Chem. Soc.*
1995, *117*, 5573

Lyotropic LC phases

Concentration Dependent Lyotropic Phases

Examples of Lyotropic LC Phases

"lamellar"

Multilamellar
vesicles

Curvature of hydrocarbons
In lyotropic LC

Non-
lamellar

Lipid phase determined from:
1) Curvature energy
2) Geometric-dependent
   energy: packing, vander
   Waals (attractive),
   electrostatics (replusive)
   hydration (replusive)

O'Brien et al., J. Am. Chem. Soc. **1995**, *117*, 5573; O'Brien et al., *Acc. Chem. Res.* **1998**, *31*, 861; O'Brien et al., *Chem. Rev.* **2002,** *102*, 727
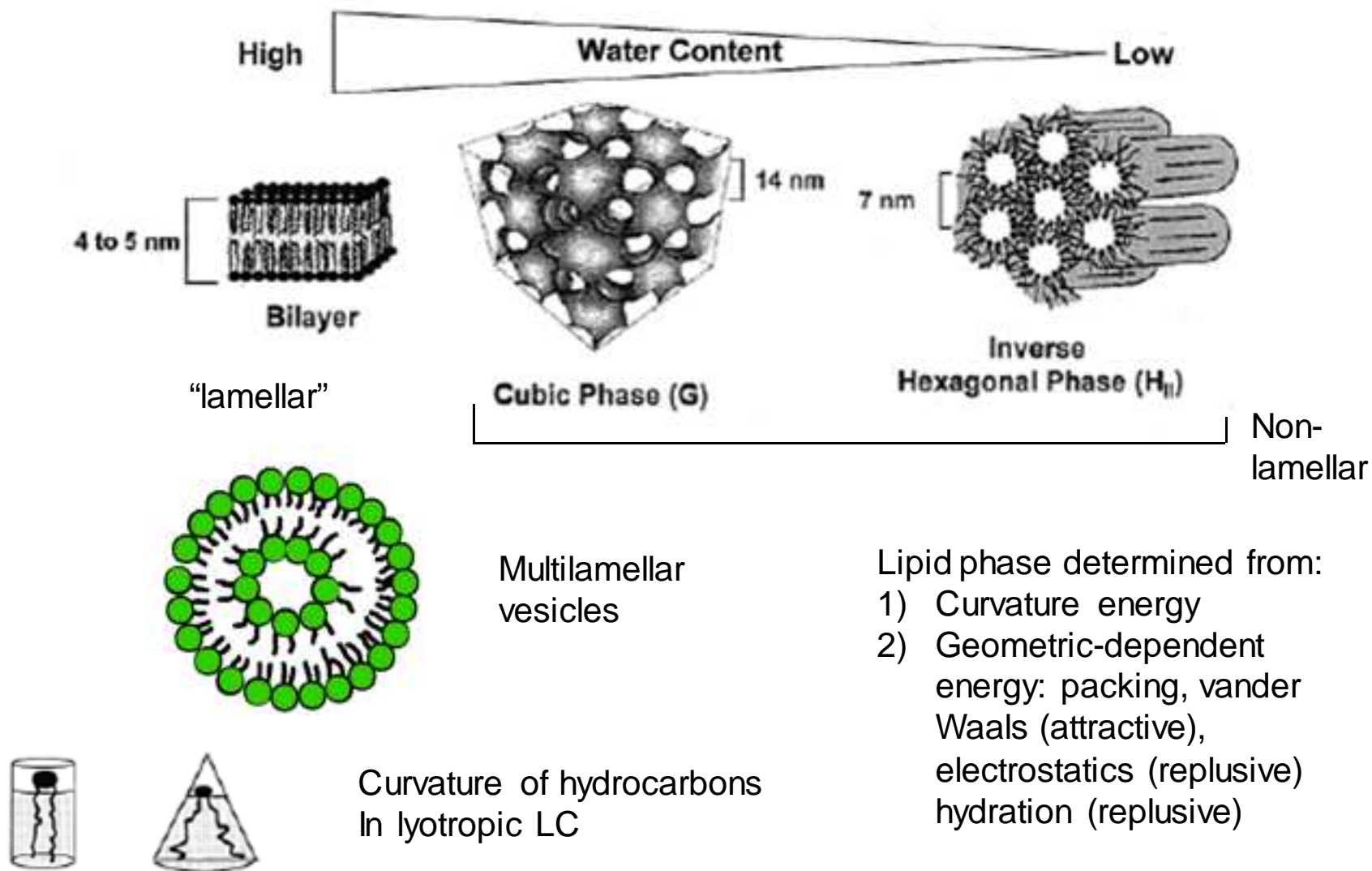
Examples of Polymerizable Lipids

MethQA   Head group substituted Meth Lipids   mono-MethPC   mono-AcrylPC

Styryl   Diacetylenyl

Dienoyl

Sorbyl

mono-SorbPC   bis-SorbPC   bis-DenPC   mono-DenPE   bis-DenPE

Acryloyl

Methacryloyl   Lipoyl

O'Brien et al., J. Am. Chem. Soc. **1995**, *117*, 5573; O'Brien et al., *Acc. Chem. Res.* **1998**, *31*, 861; O'Brien et al., *Chem. Rev.* **2002,** *102*, 727

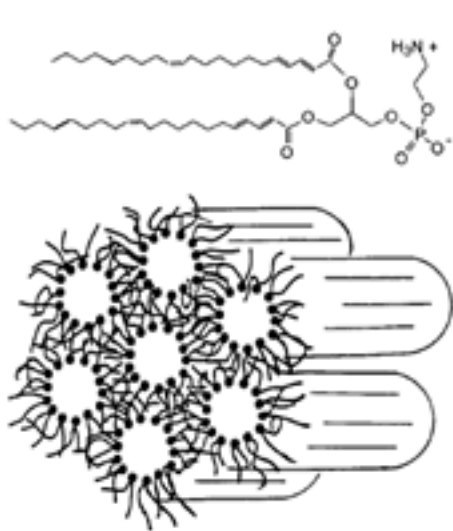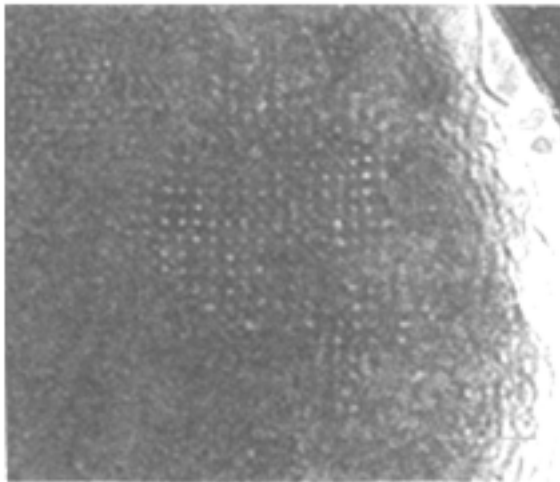# Polymerized of Hexagonal Lipid Assemblies

FIGURE 6. A polymerizable phosphatidylethanolamine used to form and polymerize the H$_{II}$ phase (bottom). Note the disordered tails of the lipids and the headgroups surrounding a water channel.
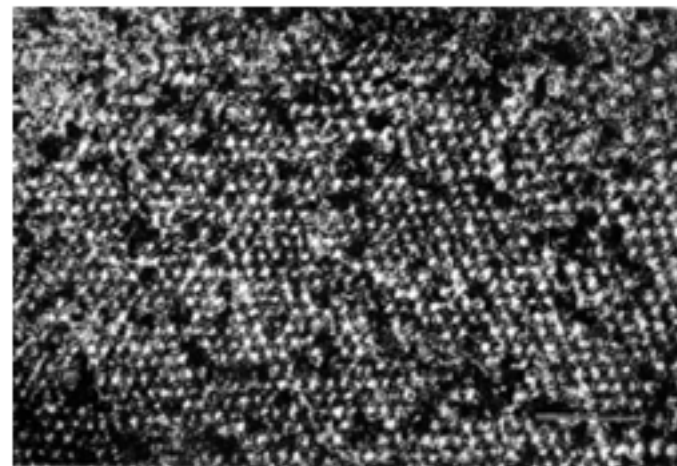
mono-isoMeDenPE

bis-isoMeDenPC

Phosphatidyl ethanolamine

Phosphatidyl choline

O'Brien et al., J. Am. Chem. Soc. **1995**, *117*, 5573; O'Brien et al., *Acc. Chem. Res.* **1998**, *31*, 861; O'Brien et al., *Chem. Rev.* **2002,** *102*, 727