Fundamentals:

Basics for Designing Organic Nanomaterials

Chapter 1. Characteristics of Nanomaterials

Chapter 2. Methodology of Nanomaterials

- **2.1 Template Method**
  - **2.1.1. Microemulsion**
  - **2.1.2. Nanostructured Polymer (Copolymer, Dendrimer, DNA)**
  - **2.1.3. Nanostructured Ceramics (AAO, Porous Silica, Zeolite)**

- **2.2. Non-template Method**
  - **2.2.1. Sol-gel Method**
  - **2.2.2. Vapor Deposition (Physical, Chemical)**
  - **2.2.3. Electrospinning**

Chapter 3. Structure, Property, and Applications of Organic Nanomaterials

- **3.1. 0-D Organic Materials**
- **3.2. 1-D Organic Materials**
- **3.3. 2-D Organic Materials**
- **3.4. 3-D Organic Materials.**

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1. **Microstructure Based on Block Copolymers**
   - 1.1. Definition of Copolymers
   - 1.2. Synthesis Methods for Block Copolymers
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2. **General Theories of Block Copolymers**
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    - 3.2. Host-Guest Chemistry with Dendrimers
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5. **Self-assembled nanostrucutres based on DNA**
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    - 5.3. DNA-templated synthesis

1. Microstructure based on block copolymers

1.1 Definition of copolymers

: polymer having more than two different repeat units.

~ABABABABABAABABABABA~

(Alternating copolymer)

~AABABBABAAABBABBBAAB~

(Random copolymer)

~AAAAAAAAAAAAAAAAAAAAA~
B
B
B
B
B
B
B
~

(Graft copolymer)

~AAAAAAAAAABBBBBBBBBB~

(Block copolymer)

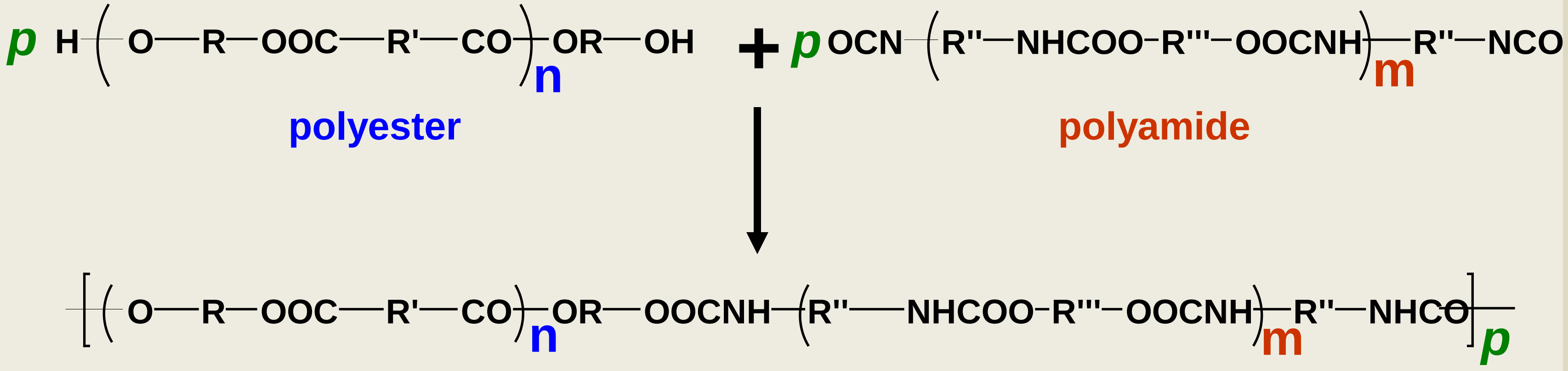
A_mB_p	**diblock**
$A_mB_pA_m$	**triblock**
$A_mB_pA_mB_p$	**tetrablock**
$(A_mB_p)_n$	**multiblock**

A, B: repeating units

1. Microstructure based on block copolymers

1.2 Synthesis Methods for Block Copolymers

- **Step copolymerization**
  → The reaction between two different functional end groups of polymers



$$p\ \mathrm{H{-}\!\left(O{-}R{-}OOC{-}R'{-}CO\right)_{n}\!{-}OR{-}OH} + p\ \mathrm{OCN{-}\!\left(R''{-}NHCOO{-}R'''{-}OOCNH\right)_{m}\!{-}R''{-}NCO}$$

polyester

polyamide

$$\downarrow$$

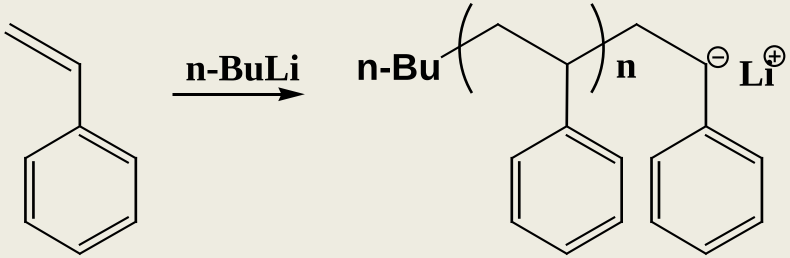
$$\mathrm{\left[\left(O{-}R{-}OOC{-}R'{-}CO\right)_{n}\!{-}OR{-}OOCNH{-}\!\left(R''{-}NHCOO{-}R'''{-}OOCNH\right)_{m}\!{-}R''{-}NHCO\right]_{p}}$$

1. Microstructure based on block copolymers

CNDL

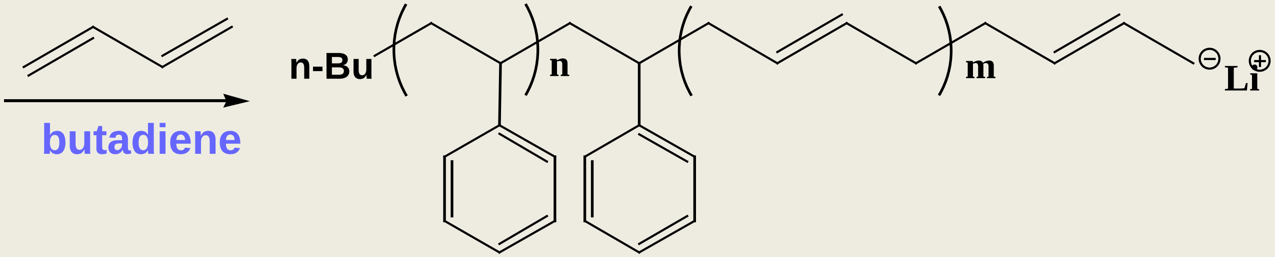
❖ **Sequential polymerization (Anionic polymerization)**

→ A polymer is synthesized by anionic polymerization. Another monomer is then added to the living polymer carbanions.



styrene

Polystyrene



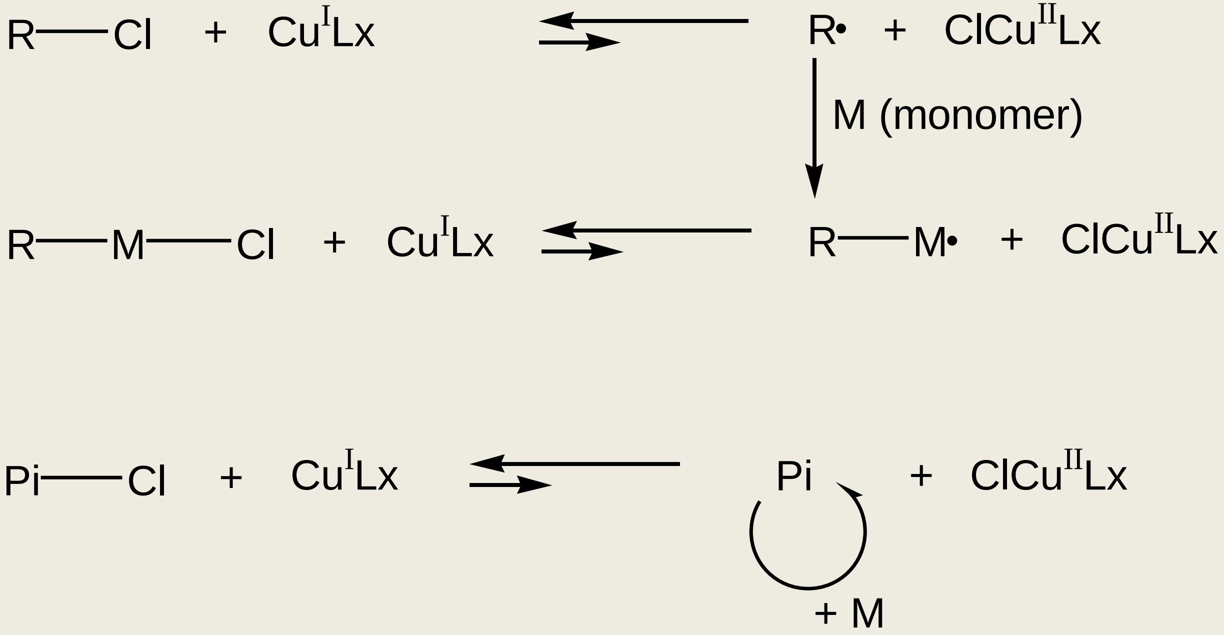
butadiene

Polystyrene-block-Poly(1,4-butadiene)

1. Microstructure based on block copolymers

- **Sequential polymerization (Living radical polymerization)**

  - **ATRP (Atom transfer radical polymerization)**



$$R\text{—}Cl + Cu^{I}Lx \rightleftharpoons R\bullet + ClCu^{II}Lx$$

$$R\bullet \xrightarrow{\text{M (monomer)}} R\text{—}M\bullet$$

$$R\text{—}M\text{—}Cl + Cu^{I}Lx \rightleftharpoons R\text{—}M\bullet + ClCu^{II}Lx$$

$$Pi\text{—}Cl + Cu^{I}Lx \rightleftharpoons Pi\bullet + ClCu^{II}Lx$$

+ M

  - **Copolymerization via ATRP**

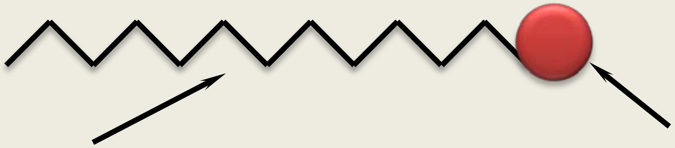
$$R\text{—}X \xrightarrow{\text{A, CuX}} R\text{—}A_n\text{—}X \xrightarrow{\text{B}} R\text{—}A_n\text{—}B_m\text{—}X$$

A, B ; monomer

1. Microstructure based on block copolymers

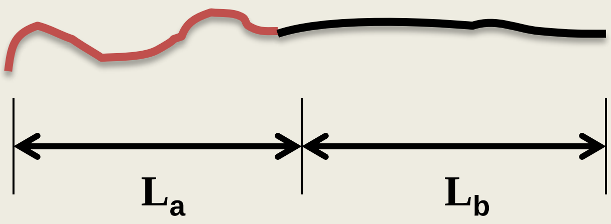
1.3. Block Copolymer Aggregate and Self-assembly

Surfactant



≒

Block copolymer



More than two polymeric units
(different solubility)

HLB value (hydorphilic-liphophilic balance)
Geometrical factor (size)
→ ref. microemulsion chapter

Length and ratio of polymer segments

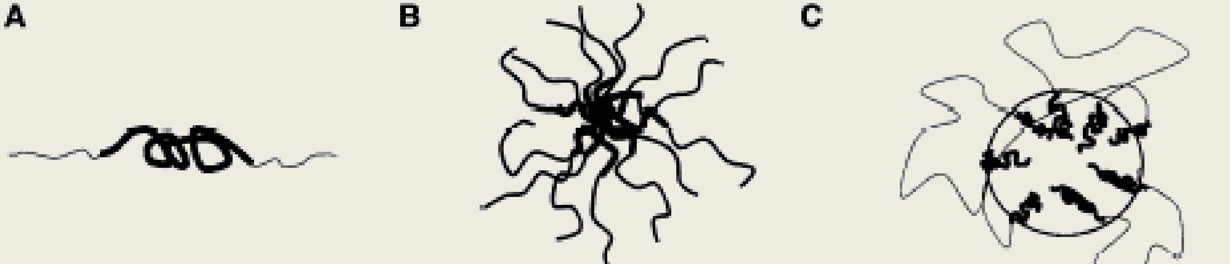
Like surfactant, block copolymers can form various aggregates as varied polymer segments.

1. Microstructure based on block copolymers

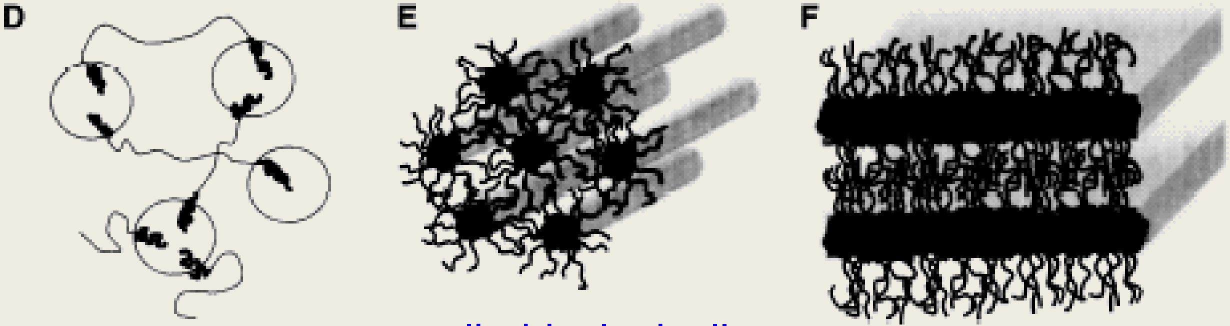
❖ **Micelle formation of block copolymer**

; A solvent that is good for one of the units but poor for the other(s) leads to an amphiphilic behavior. (similar to low-molecular-weight surfactant solution)

; Block copolymer micelles are aggregates that resemble many properties of micelles formed by low-molecular weight surfactants.



copolymer unimer   spherical micelle   spherical micelle



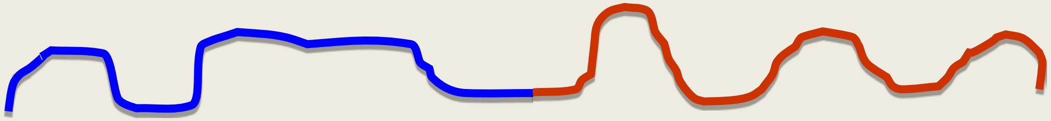
spherical micelle   cylindrical micelle   lamellar structure

1. Microstructure based on block copolymers

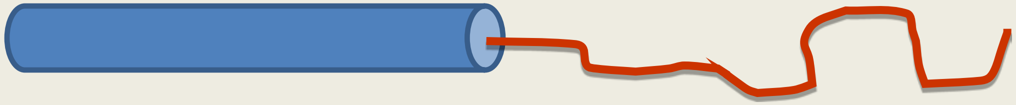
❖ **Self-assembly of Block copolymer based on type of polymer segments**

; The types of polymer segments can affect block copolymer aggregation. (self-assembly)

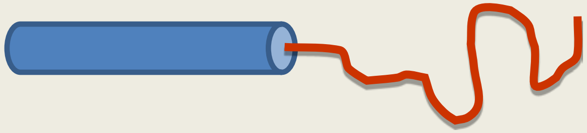
; Three different classes of diblock copolymer type will be discussed in this section.



Coil-coil diblock copolymer



Rod-coil diblock copolymer
(Total MW > 20,000 g/mol)



Rod-coil diblock oligomer
(Total MW < 20,000 g/mol)

1. Microstructure based on block copolymers

- **Coil-coil diblock copolymers**

; Block copolymers comprised of two flexible, chemcally incompatible and dissimilar blocks can microphase separated into a variety of morphologies.
eg) Polystyrene-*b*-Polyisoprene

; The degree of microphase separation is determined by χN.
→ χ : Flory interaction parameter,
a measure for the incompatibility between the two block,
be written in terms of solubility parameter(δ)

→ N : Total degree of polymerization, $N=N_A+N_B$

$$\chi = \frac{V_0}{kT}(\delta_A - \delta_B)^2 \qquad \delta_A = \sqrt{\frac{\Delta E_A}{V_A}}$$

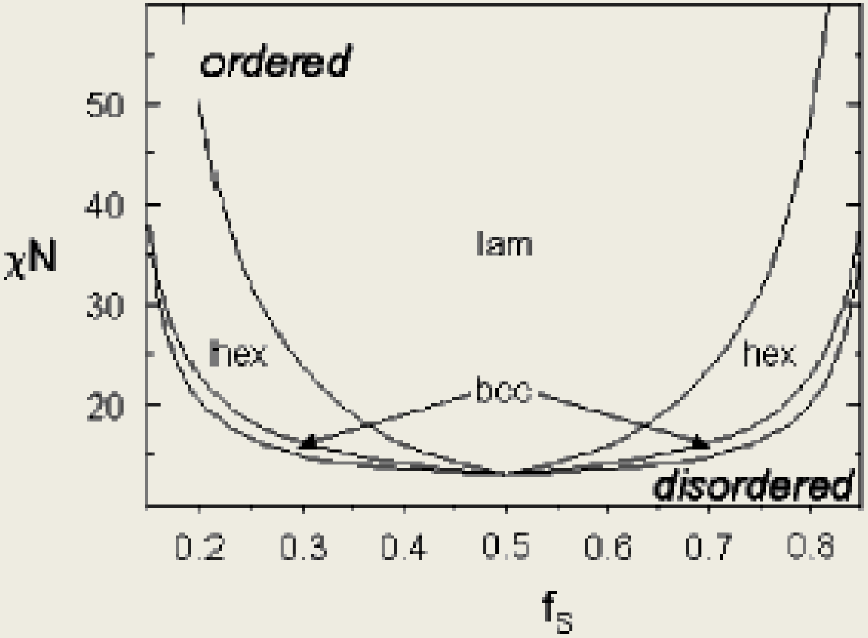
V_o : the lattice site volume
k : Boltzmann constant
T : temperature
ΔE_A : the evergy of vapourization of A molecule
V_A : molecular volume of A units

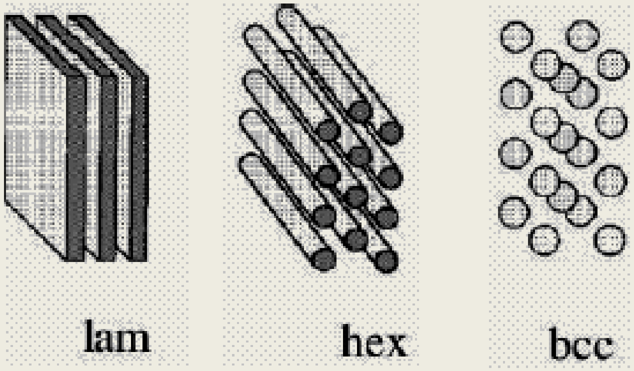
※ Solubility parameter ↔ cohesive energy density, interaction energy per unit volume between the molecules

1. Microstructure based on block copolymers

; Separated morphology can be varied from spheres via lamellae to inverse spheres by changing the volume fractions of the blocks (*f*).

※ Experimental phase diagram for polystyrene-b-polyisoprene





→ f_s : volum fraction of styrene segment

$\chi N \le 10$, weak-segregation limit

$10 < \chi N \le 50$, intermediate segregation region

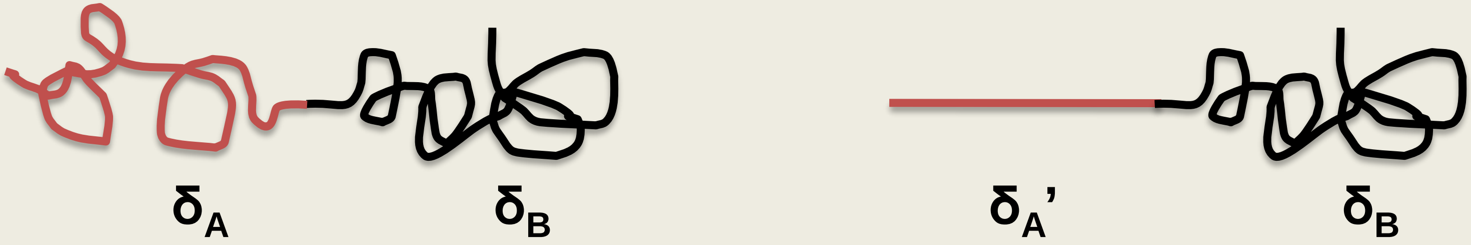
$\chi N \to \infty$, strong segregation limit

1. Microstructure based on block copolymers

- **Rod-coil diblock copolymers**

; Replacing one of the blocks of a coil-coil diblock copolymer by a stiff, rigid segment results in a rod-coil type diblock copolymer.
eg) poly(*p*-phenylene)-*b*-poly(styrene), poly(phenylquinoline)-*b*-poly(styrene),
poly(heyl isocyanate)-*b*-poly(styrene)

; The self-assembly is no longer solely determined by phase-separation, but is also affect by several other process.
→ aggregation of the rigid segments into (liquid-)crystalline domains
→ increase in the Flory interaction parameter due to stiffness asymmetry

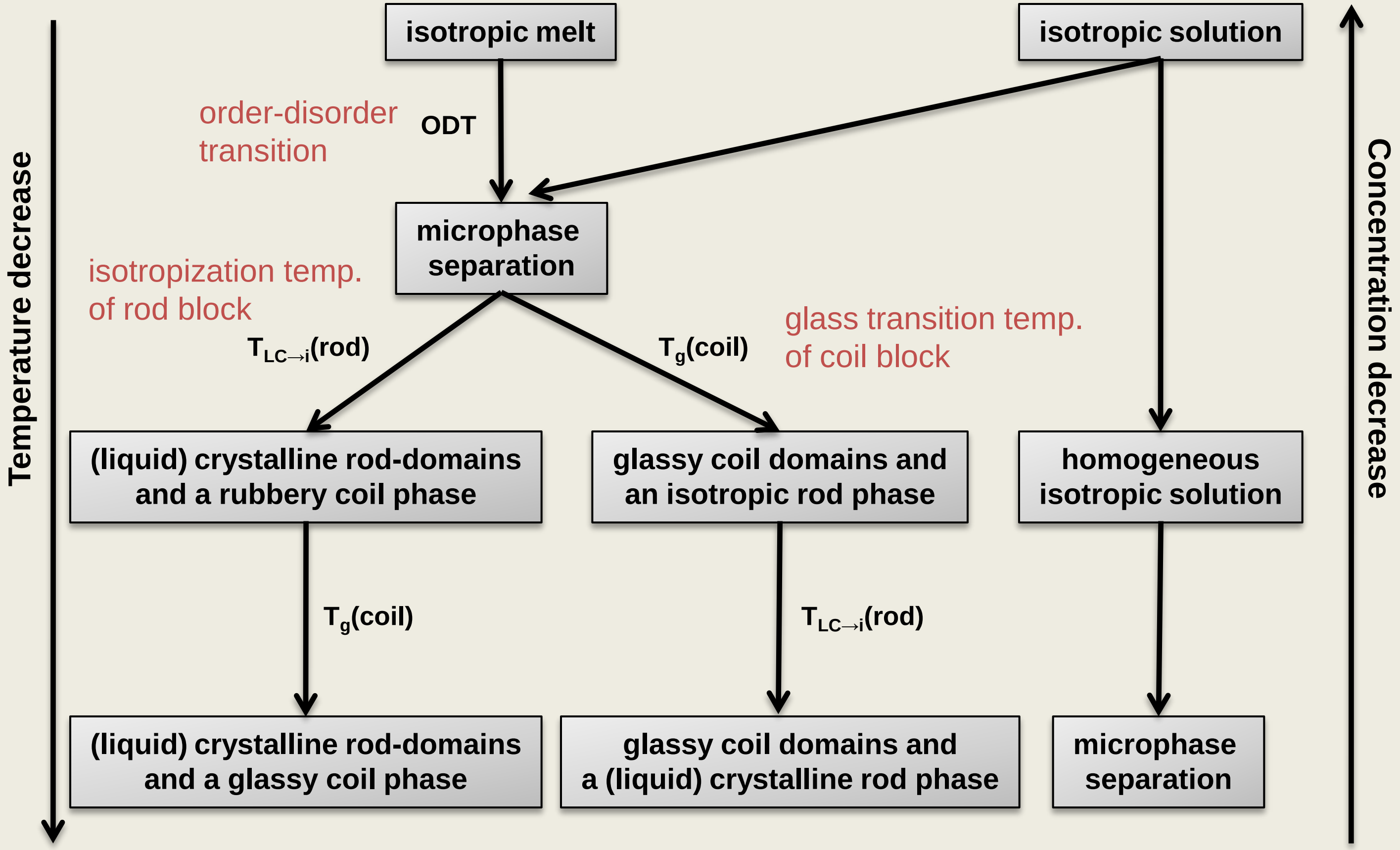


$(\delta_A' - \delta_B)^2 > (\delta_A - \delta_B)^2$ ∴ χ is increased in rod-coil diblock copolymers

1. Microstructure based on block copolymers

CNDL

※ **Possible routes for the self-assembly of rod-coil type diblock copolymer**



Temperature decrease

isotropic melt

isotropic solution

order-disorder transition

ODT

microphase separation

isotropization temp. of rod block

$T_{LC \rightarrow i}$(rod)

T_g(coil)

glass transition temp. of coil block

(liquid) crystalline rod-domains and a rubbery coil phase

glassy coil domains and an isotropic rod phase

homogeneous isotropic solution

T_g(coil)

$T_{LC \rightarrow i}$(rod)

(liquid) crystalline rod-domains and a glassy coil phase

glassy coil domains and a (liquid) crystalline rod phase

microphase separation

Concentration decrease

Ref. Klok et al. *Advanced materials*, **13** (2001) 1217

1. Microstructure based on block copolymers

; Cooling from an isotropic melt

1) The system passes ODT and undergo microphase separation

2) If $T_{LC\rightarrow i}$ of rod > T_g of coil,
further cooling 1 - formation of (liquid-)crystalline domains
surrounded by a layer of rubbery coils
further cooling 2 - (liquid-)crystalline domains of rod segments
surrounded by glassy phase of coil segments

If $T_{LC\rightarrow i}$ of rod < T_g of coil,
further cooling 1 - formation of glassy matrix
further cooling 2 - crystallization of rod blocks can only take place in confined
domains imposed by the glassy matrix formed by the coils

1. Microstructure based on block copolymers

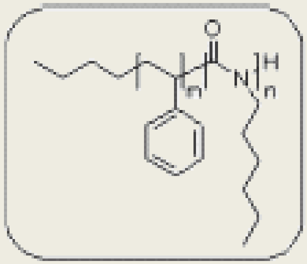
; Evaporation of the solvent from isotropic solution

1) If a good solvent for both blocks is used,
microphase separation will continuously complete with crystallization of the rod segments during the evaporation of solvent until a stable structure is obtained.

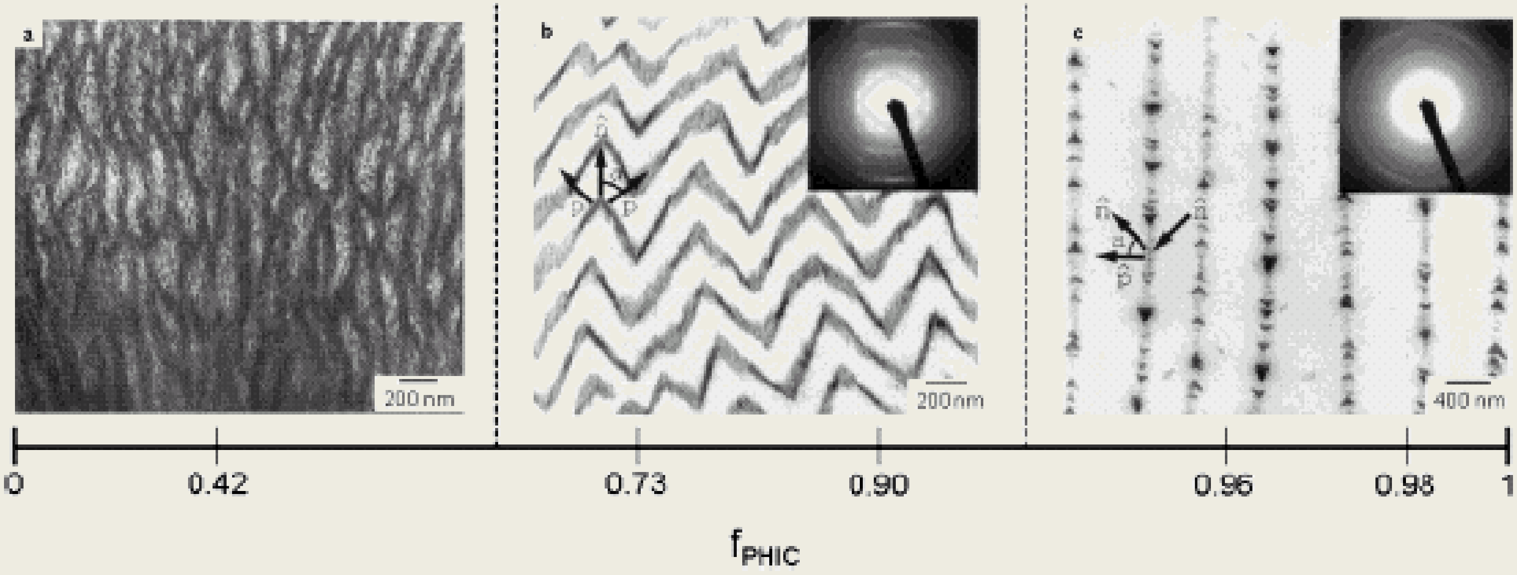
2) If a good solvent for only one block is used,
the rod-coil block copolymers can already be pre-assembled into a particular supramolecular structure prior to film casting and evaporation of the solvent.

1. Microstructure based on block copolymers

※ Self-assembly of Poly(styrene)-*b*-poly(hexyl isocynate) with the volume fraction of hexyl isocynate segment (Rod portion)



PS-*b*-PHIC


a
200 nm
b
200nm
c
400 nm
0
0.42
0.73
0.90
0.96
0.98
1
f_PHIC

1. Microstructure based on block copolymers

- **Rod-coil diblock oligomers**

; Like rod-coil diblock copolymer, the oligomers also indicates the competition between microphase separation of the blocks and aggregation of the rigid rods.

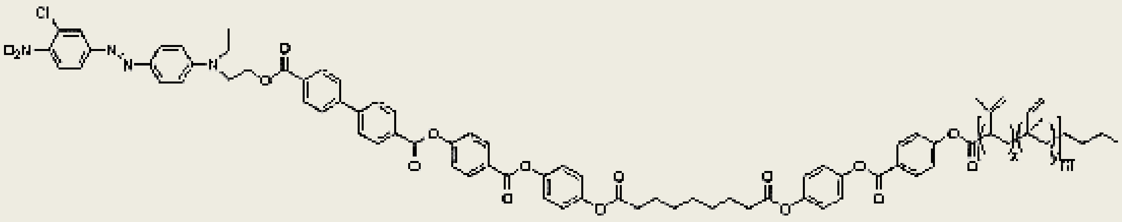
→ increase in the Flory interaction parameter due to their stiffness-asymmetry
→ Rod-coil diblock oligomers can allow access to phase-separated morphologies with domain sizes that can not be attained with traditional coil-coil diblock copolymers.

; Rod-coil diblock copolymers can be divided into two major classes.

→ i) perfectly monodisperse rod-segments, ii) polydisperse rigid rod
→ Diblock oligomers can be simply synthesized by organic reactions, so monodisperse rod-segments can be obtained.
cf) Polymer's MW is polydisperse

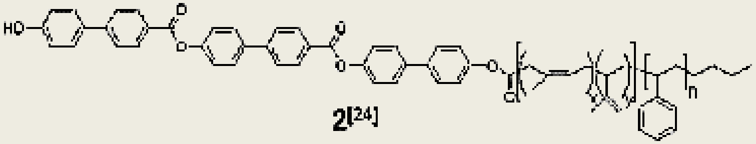
※ Polydispersity (MW) is known to have a strong influence on the liquid crystalline properties of rod-like macromolecules.

1. Microstructure based on block copolymers



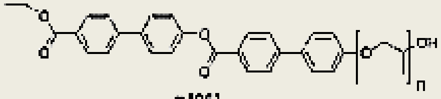
1[23]

$\bar{m}$ ≈ 50 - 110 $\bar{m}$ = x + y



2[24]

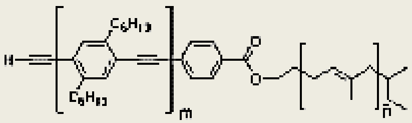
$\bar{m}$ ≈ 9; $\bar{n}$ ≈ 9 $\bar{m}$ = x + y



3[25]

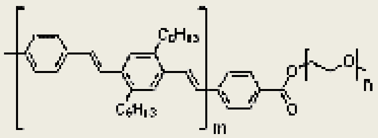
n = 7, ..., 20

※ **Example of rod-coil oilgomers**



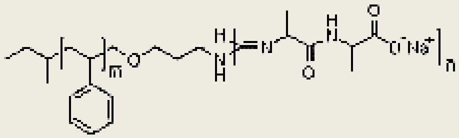
4[26]

m = 2; $\bar{n}$ ≈ 100



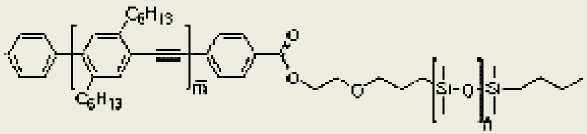
5[27]

m = 4, 6; $\bar{n}$ ≈ 45 - 110



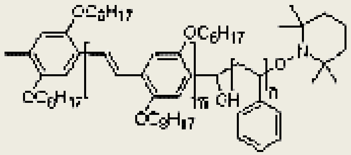
6[31]

$\bar{m}$ ≈ 40; $\bar{n}$ ≈ 10, 20, 30



7[32]

$\bar{m}$ ≈ 12; $\bar{n}$ ≈ 15



8[34]

$\bar{m}$ ≈ 8; $\bar{n}$ ≈ 115

Ref. Klok et al. *Advanced materials*, **13** (2001) 1217

2. General Theories of Block Copolymers

2.1 Copolymer Composition

- We begin our discussion of copolymers by considering the free-radical polymerization of a mixture of two monomers, M_1 and M_2.
  → Growth mechanisms can be responsible for copolymer formation

- The polymerization mechanism: four distinctly different propagation reactions

$$-M_1\cdot + M_1 \xrightarrow{k_{11}} -M_1M_1\cdot \qquad -M_2\cdot + M_1 \xrightarrow{k_{21}} -M_2M_1\cdot$$

$$-M_1\cdot + M_2 \xrightarrow{k_{12}} -M_1M_2\cdot \qquad -M_2\cdot + M_2 \xrightarrow{k_{22}} -M_2M_2\cdot$$

- The rate laws governing these four reactions

k_{11}

repeat unit in growing radical

adding monomer

$$R_{p,11} = k_{11}[M_1\cdot][M_1] \qquad R_{p,21} = k_{21}[M_2\cdot][M_1]$$

$$R_{p,12} = k_{12}[M_1\cdot][M_2] \qquad R_{p,22} = k_{22}[M_2\cdot][M_2]$$

2. General Theories of Block Copolymers

- The customary assumption
  : the kinetic constants are independent of the size of the radical
  : the concentration of all radicals are indicated whatever their chain length, ending with the M_1 repeat unit by the notation $[M_1\cdot]$
  → only the nature of the radical chin end influences the rate constant for propagation

  - the rate of monomer M_1, M_2 conversion to polymer

$$-\frac{\mathrm{d}[M_1]}{\mathrm{dt}} = k_{11}[M_1\cdot][M_1] + k_{21}[M_2\cdot][M_1]$$

$$-\frac{\mathrm{d}[M_2]}{\mathrm{dt}} = k_{12}[M_1\cdot][M_2] + k_{22}[M_2\cdot][M_2]$$

  - the relative rates of the two monomer additions and the ratio of the two kinds of repeat units in the copolymer

$$\frac{\mathrm{d}[M_1]}{\mathrm{d}[M_2]} = \frac{k_{11}[M_1\cdot][M_1] + k_{21}[M_2\cdot][M_1]}{k_{12}[M_1\cdot][M_2] + k_{22}[M_2\cdot][M_2]}$$

2. General Theories of Block Copolymers

- The stationaty-state approximation (total concentration of radicals is constant) ; $R_{p,\,21} = R_{p,\,12}$

$$k_{12}\left[M_1\cdot\right]\left[M_2\right]=k_{21}\left[M_2\cdot\right]\left[M_1\right] \quad \text{or} \quad \frac{\left[M_1\cdot\right]}{\left[M_2\cdot\right]}=\frac{k_{21}\left[M_1\right]}{k_{12}\left[M_2\right]}$$

$$\frac{\mathrm{d}\left[M_1\right]}{\mathrm{d}\left[M_2\right]}=\frac{\left[M_1\right]}{\left[M_2\right]}\frac{\left(k_{11}/k_{12}\right)\left[M_1\right]+\left[M_2\right]}{\left(k_{22}/k_{21}\right)\left[M_2\right]+\left[M_1\right]}$$

$$r_1=\frac{k_{11}}{k_{12}} \quad r_2=\frac{k_{22}}{k_{21}}$$

$$\frac{\mathrm{d}\left[M_1\right]}{\mathrm{d}\left[M_2\right]}=\frac{\left[M_1\right]}{\left[M_2\right]}\frac{r_1\left[M_1\right]+\left[M_2\right]}{r_2\left[M_2\right]+\left[M_1\right]}=\frac{1+r_1\left[M_1\right]/\left[M_2\right]}{1+r_2\left[M_2\right]/\left[M_1\right]}$$

- Defining F_i as the mole fraction of the ith component in the polymer and f_i as the mole fraction of component i in the monomer solutions

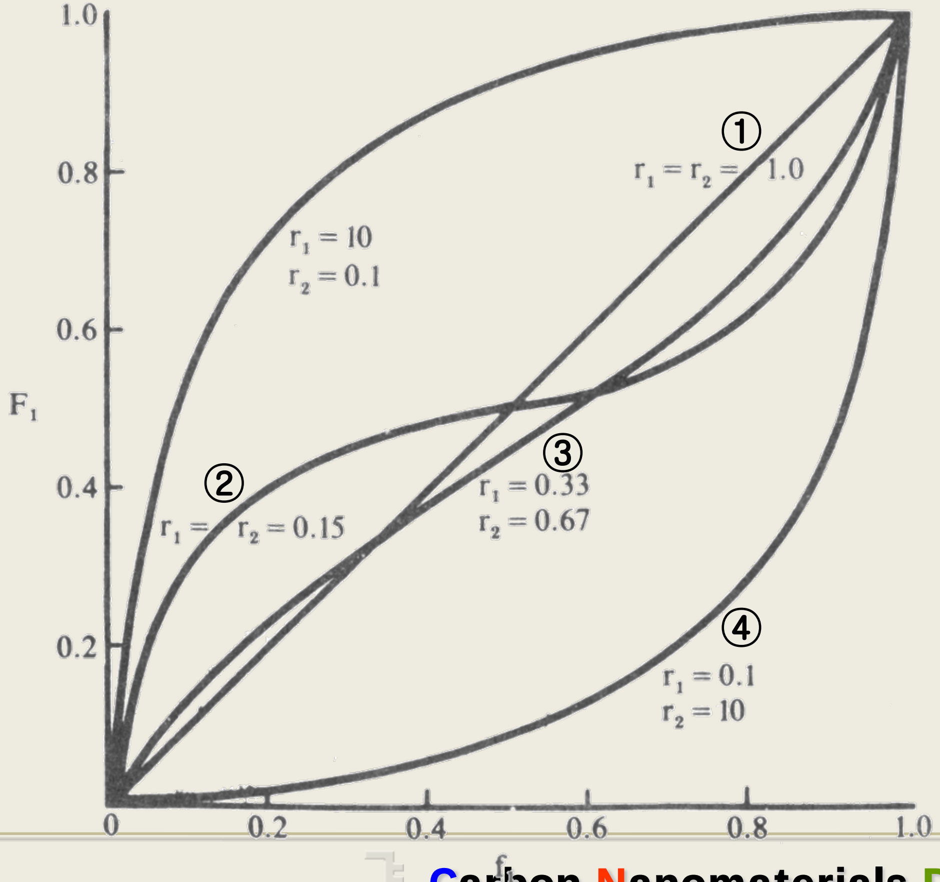
$$F_1=1-F_2=\frac{\mathrm{d}\left[M_1\right]}{\mathrm{d}\left[M_1\right]+\mathrm{d}\left[M_2\right]}$$

$$f_1=1-f_2=\frac{\left[M_1\right]}{\left[M_1\right]+\left[M_2\right]}$$

2. General Theories of Block Copolymers

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}$$

→ This equation relates the composition of the copolymer formed to the instantaneous composition of the feedstock and to the parameters r_1 and r_2 which characterize the specific system.



① $r_1 = r_2 = 1$

: copolymer and the feed mixture have the same composition at all times : $F_1 = f_1$

② $r_1 = r_2$

: copolymer and the feed mixture have the same composition at f=0.5 : $F_1 = 0.5$

③ $r_1 \neq r_2$

: The monomer ratio at crossover point

: For $r_1 = 0.33$, $r_2 = 0.67$ → $f_1 = 0.33$

④ $r_1 = 1/r_2$

2. General Theories of Block Copolymers

2.2 Reactivity Ratios

- The parameters r_1 and r_2 are the vehicles by which the nature of the reactants enter the copolymer composition equation.
- Several important things to note about radical reactivity ratio.

① $r_1=k_{11}/k_{12}$; $r_1>1$ → $M_1\bullet$ adds M_1 in preference to M_2
; $r_1<1$ → $M_1\bullet$ adds M_2 in preference to M_1
② Although r_1 is descriptive of radical $M_1\bullet$, it also depends on the identity of the other
→ To characterize a system the pair of parameters r_1 and r_2 are both required
→ the product r_1r_2 is used to quantify
③ The reciprocal of a radical reactivity ratio is used to quantitatively express the reactivity of monomer M_2 by comparing its rate of addition to radical $M_1\bullet$
④ The radical reactivity ratio follows the Arrhenius equation with an apparent activation energy. (equal to the difference in the activation energies for the individual constants; $E_{app}^* = E_{p,\,11}^* - E_{p,\,12}^*$)

2. General Theories of Block Copolymers

Table. Values of reactivity ratio r_1 and r_2
and the product r_1r_2 for a few copolymers at 60 ℃

M_1	M_2	r_1	r_2	r_1r_2
Acrylonitrile	Methyl vinyl ketone	0.61	1.78	1.09
	Methyl methacrylate	0.13	1.16	0.15
	A-Methyl styrene	0.04	0.20	0.008
	Vinyl acetate	4.05	0.061	0.25
Methyl methacrylate	Styrene	0.46	0.52	0.24
	Methacrylic acid	1.18	0.63	0.74
	Vinyl acetate	20	0.015	0.30
	Vinylidene chloride	2.53	0.24	0.61
Styrene	Vinyl acetate	55	0.01	0.55
	Vinyl chloride	17	0.02	0.34
	Vinylidene chloride	1.85	0.085	0.16
	2-Vinyl pyridine	0.55	1.14	0.63
Vinyl acetate	1-Butene	2.0	0.34	0.68
	Isobutylene	2.15	0.31	0.67
	Vinyl chloride	0.23	1.68	0.39
	Vinylidene chloride	0.05	6.7	0.34

2. General Theories of Block Copolymers

- The products r_1r_2 lie in the range between 0~1.
- The product r_1r_2 → 0

① $r_1r_2 = 0$ and $r_1=r_2 =0$; the copolymer adds monomers with perfect alternation.
→ No tendency for a radical to add a monomer of the same kind
② when only one of the r's is zero; alternation occurs whenever the radical ends with an $M_1\bullet$ unit → Tendency toward the alternation
∴ Increasing tendency toward alternation as $r_1 \rightarrow 0$ and $r_2 \rightarrow 0$, more succinctly, as the product $r_1r_2 \rightarrow 0$

- The product r_1r_2 → 1

: two monomers have the same relative tendency to add to both radicals
→ If $r_1= 10$, monomer 1 is 10 times as likely to add to $M_1\bullet$ than monomer 2
→ If $r_2= 0.1$, monomer 1 is 10 times as likely to add to $M_2\bullet$ than monomer 2
∴ The radicals exert the same influence; monomers add at random

- Recognition of these difference in behavior points out an important limitation on the copolymer composition equation.
→ *describes the overall composition of the copolymer, but gives no information about the distribution of the different kinds of repeat units within polymer*

2. General Theories of Block Copolymers

- It is possible that copolymers with the same overall composition have very different properties because of differences in microstructure.
  - *Alternating structure* by $r_1 \rightarrow 0$ and $r_2 \rightarrow 0$

    $$M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2$$

  - *Random structure* by $r_1r_2 \rightarrow 1$

    $$M_1M_2M_2M_2M_1M_1M_2M_1M_1M_2M_1M_2M_1M_2M_1M_2M_2M_1$$

  - *Block structure* by $r_1r_2 > 1$

    $$M_1M_1M_1M_1M_1M_1M_1M_1M_1M_2M_2M_2M_2M_2M_2M_2M_2M_2$$

- Each of these polymers has a 50:50 proportion, but differ in properties

What factors in the molecular structure of two monomers govern the kinetics of the different addition steps?

3. A Closer Look at Microstructure

3.1 Block Copolymer Phase Behavior (in the “melt” state)

(1) One-component block copolymer system

- The different blocks of a block copolymer are able to segregate (microphase separation) and form domains with different morphologies.
- The stability of different morphologies
  → From an interplay between enthalpic (contact between chemically different blocks) and entropic (chain stretching, confinement, frustration) contribution to the system free energy.
  → Described in terms of a χN vs *f* phase (Fig)

χ : Flory-Huggins interaction parameter between the different blocks
  → Enthalpic contribution
N : degree of polymerization (copolymer molecular weight)
  → Tendency for block segregation → Entropic contribution
f : volume fraction of one block (composition variable)

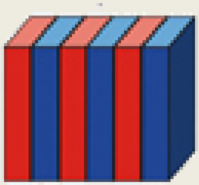
- The higher χN → higher degree of segregation between the different blocks
  → higher tendency for forming ordered microstructures
- Order-disorder transition : at χN≈10.5
- The morphologies (sphere, cylinder, lamellar) depend on the composition *f*

3. A Closer Look at Microstructure

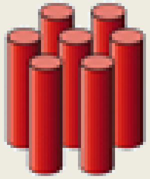
Fig. χN vs f phase diagram for symmetric AB block copolymer, predicted from mean-field theory. L (lamellar), H (hexagonal-packed cylinders), Q_{Ia3d} (gyroid), Q_{Im3m} (bcc spheres), CPS (close-packed FCC spheres), and DIS (disorderd).
Ref. M. W. Matsen and F. S. Bates, Macromolecules, 29 (1996) 478

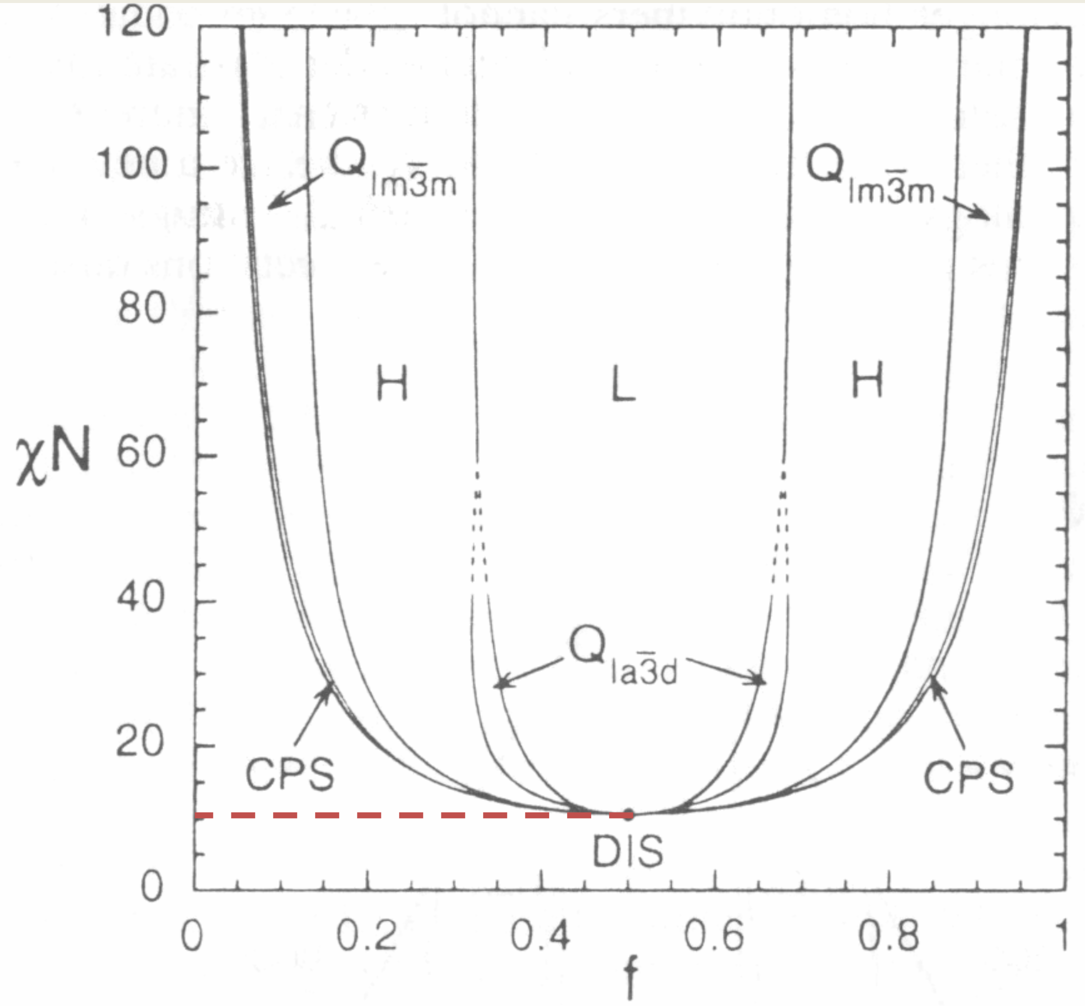
Appendix 1

Lamellar

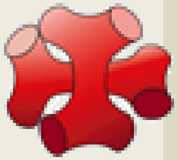


Hexagonal cylinder

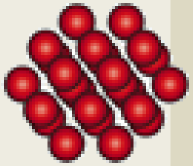




Gyroid



Sphere



3. A Closer Look at Microstructure

(2) Two- and three-component block copolymer system

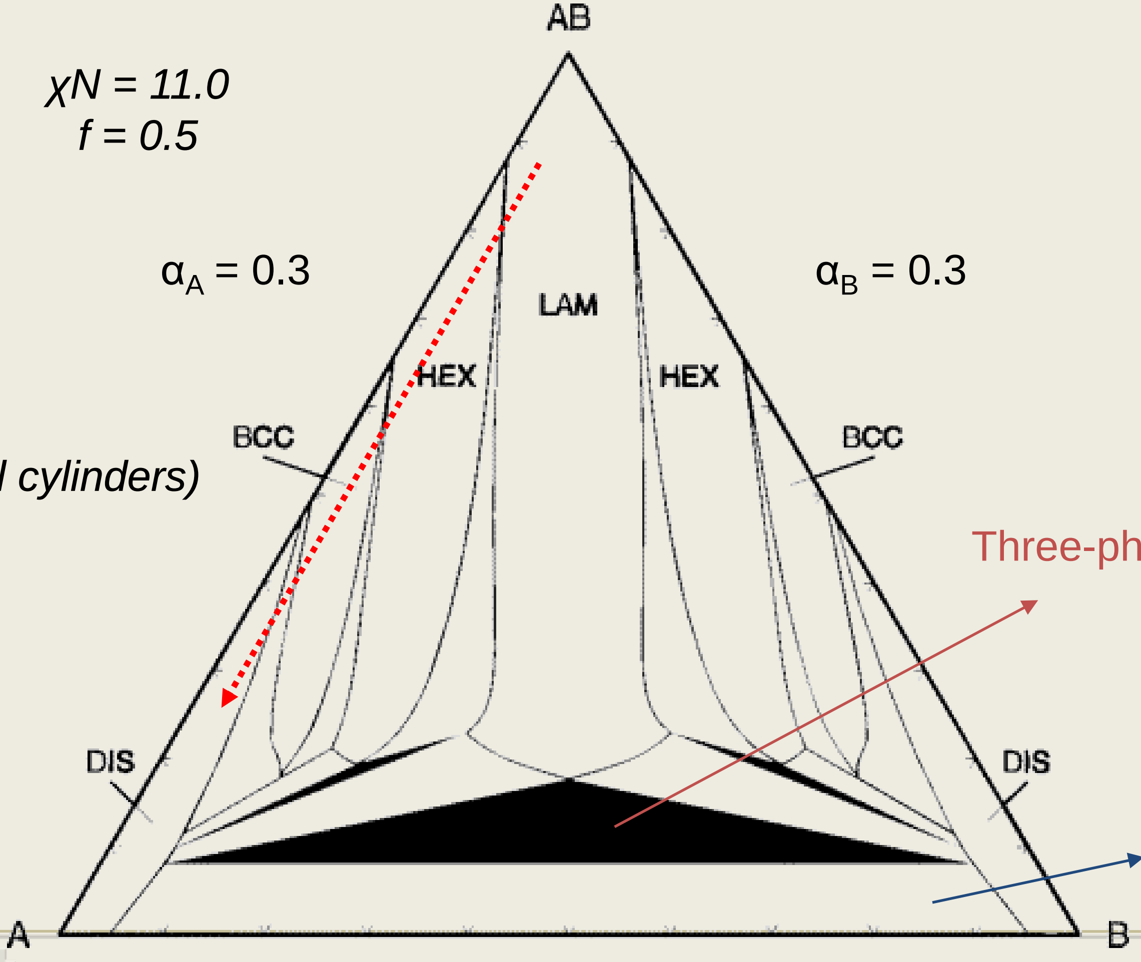
- The interfacial curvature in solvent-free block copolymers → by the composition *f*
  → At given block composition can result in only one type of microstructure
  → For different structures, different composition are required (synthesis of other polymers)
- Multicomponent system: homopolymer or copolymer added to a block copolymer
  → can result into a wide variety of morphologies
- For example, addition of an A-homopolymer to an AB-block copolymer
  → modifying the ratio of A and B: increase of A → shift the phase stability
  → predicting by self-consistent field theory (Appendix 2)

- Fig : isothermal (constant χN) phase diagram
  : AB-block copolymer + A-homopolymer + B-homopolymer
  → Morphologies change: lamellar → cylinder → sphere (red dotted line)

➔ Reducing the need to synthesize a new block copolymer for a specific morphology

3. A Closer Look at Microstructure

Fig. Phase diagram for a symmetric AB-diblock copolymer (N) with an A-homopolymer (0.3N) and a B-homopolymer (0.3N), predicted from mean-field theory.
Three-phase coexistence; shaded and biphasic region; unlabeled
Ref. P. K. Janert and M. Schick, Macromolecules, 30 (1997) 137



$\chi N = 11.0$
$f = 0.5$

$\alpha_A = 0.3$

$\alpha_B = 0.3$

Three-phase coexistence

Biphasic region

LAM (lamellar)
HEX (hexagonal cylinders)
DIS (disorderd).

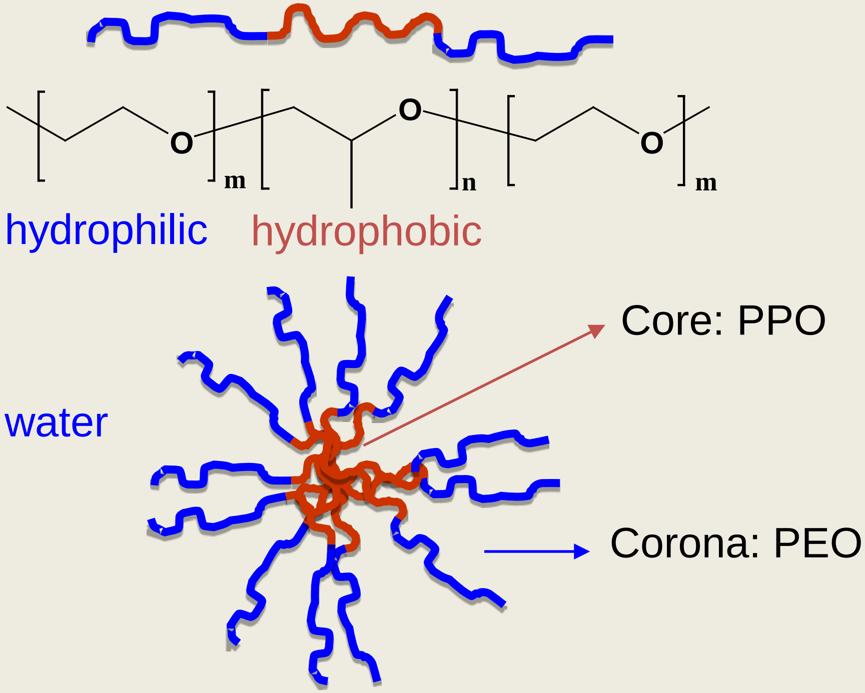
3. A Closer Look at Microstructure

3.2 Amphiphilic Block Copolymers in Mixtures with Water and Oil

: The main features of the self-assembly of block copolymers in binary and ternary systems with solvents and effects on self-assembly of the block copolymer MW and composition

(1) Binary amphiphilic block copolymer - water system

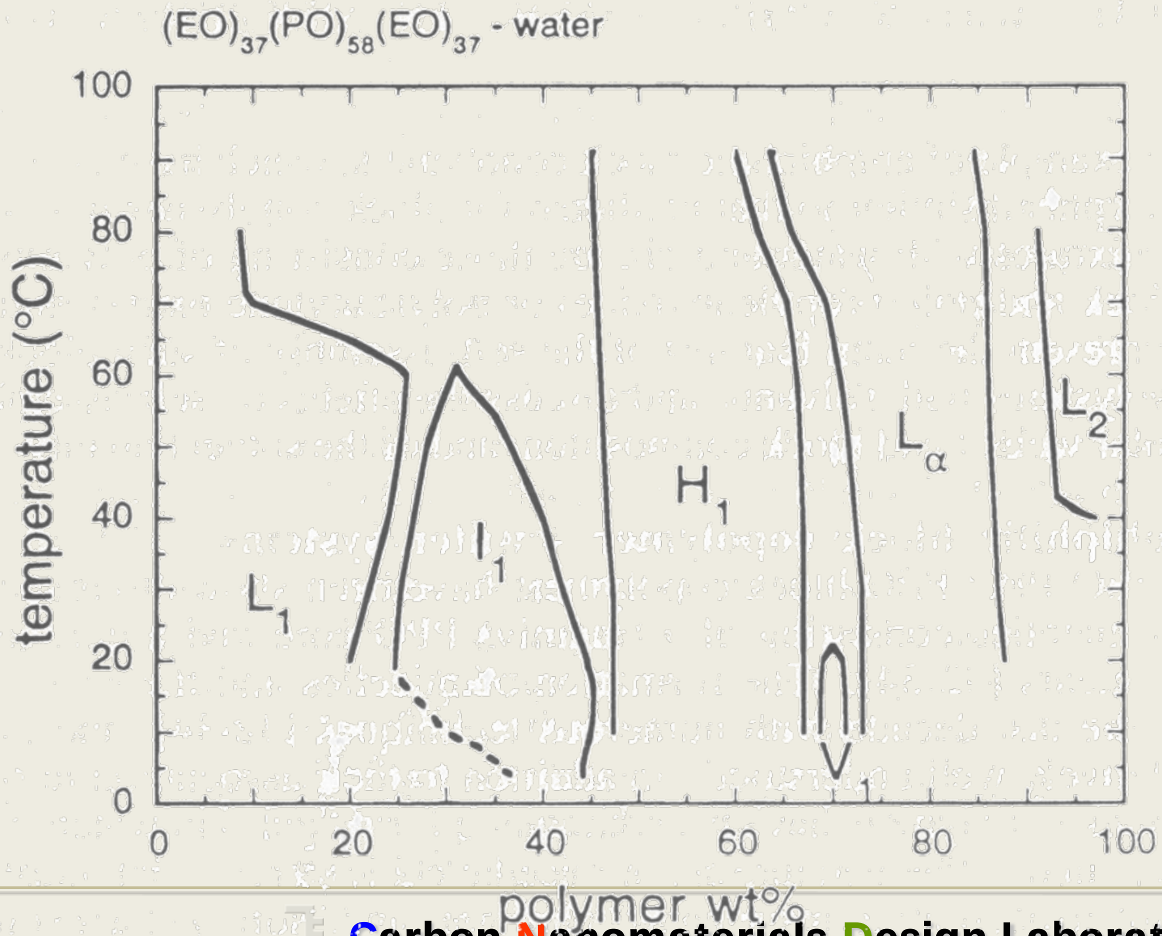
PEO-PPO-PEO



- The temperature effects on the phase behavior of copolymers → understood by invoking the reverse solubility
  (temperature↑ → solubility↓)
- The temp.↑
  → PEO-water and PPO-water interaction parameter χ ↑
  → PEO-PPO interaction parameter χ↓
  → hydrophobicity of the polymer ↑
  → solubility ↓
- At Fig, Lα regions shift to lower polymer concentration as the temp ↑

3. A Closer Look at Microstructure

Fig. The concentration-temperature phase diagram of the $EO_{37}PO_{58}EO_{37}$ (Pluronic P105) block copolymer-H_2O binary system.
Ref. P. Alexandridis, D. Zhou, A. Khan, Langmuir, 12 (1996) 2690



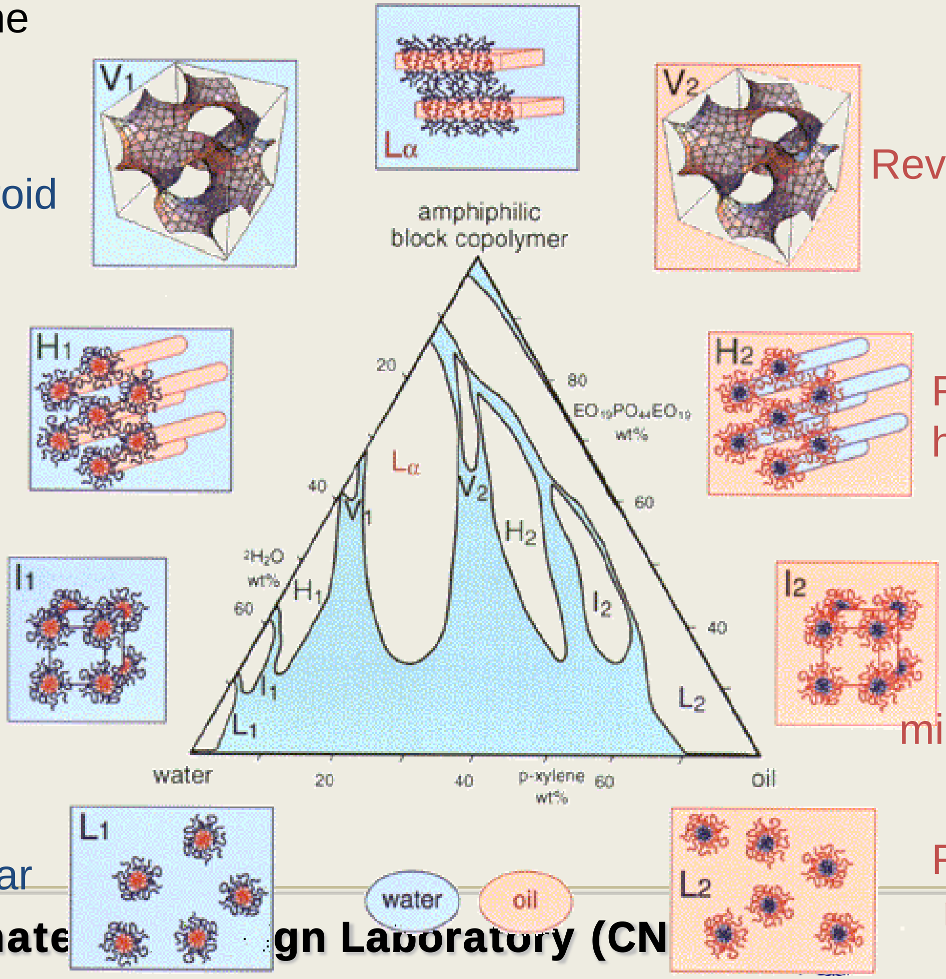
I_1 : micellar cubic
H_1 : hexagonal cylinder
V_1 : gyroid
L_α : lamellar
L_1 : water-rich solutions
L_2 : polymer-rich solutions

3. A Closer Look at Microstructure

(2) Ternary amphiphilic block copolymer – water – oil system

- The lack of “mirror image” symmetry in the phase diagram → due to the different nature of the PEO-water and PPO-xylene interactions

Fig. Phase diagram of the $(EO)_{19}(PO)_{43}(EO)_{19}$ -H_2O- p-xylene ternary system.


Lα
V1
V2
amphiphilic block copolymer
H1
H2
20
80
$EO_{19}PO_{44}EO_{19}$ wt%
Lα
40
60
V1
V2
H2
H_2O wt%
H1
I2
60
40
I1
I1
L2
L1
I2
water
20
40
p-xylene wt%
60
oil
L1
water
oil
L2

Lamellar

Gyroid

Reverse gyroid

Hexagonal

Reverse hexagonal

Micellar cubic

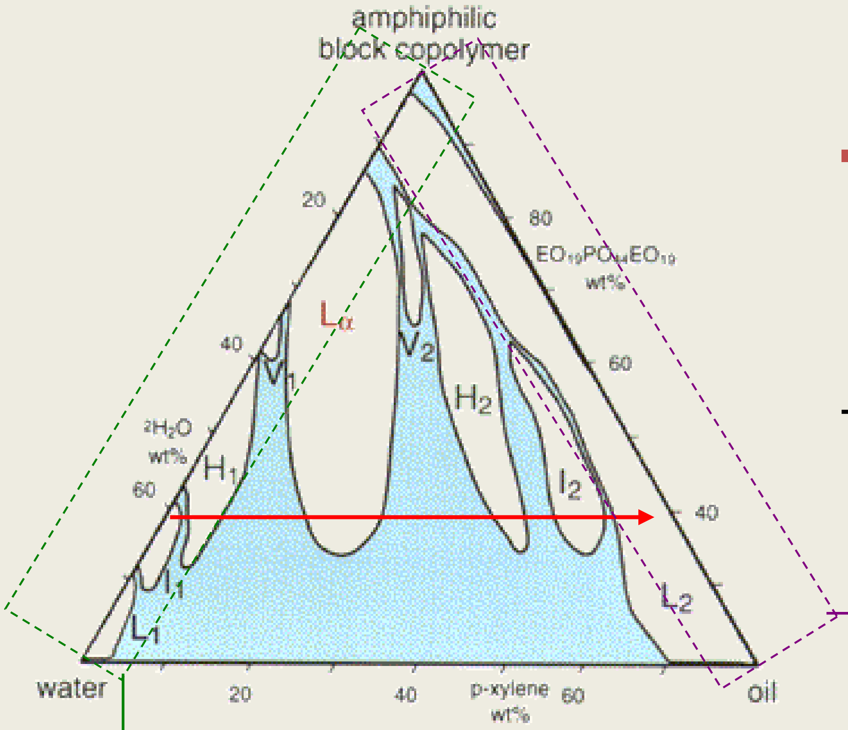
Reverse micellar cubic

Normal micellar

Reverse micellar

3. A Closer Look at Microstructure

(3) Progression of microstructure in block copolymer


amphiphilic
block copolymer
20
80
EO19PO44EO19
wt%
Lα
V2
40
V1
60
H2
2H2O
wt%
H1
60
I2
40
I1
L2
L1
water
20
40
p-xylene
wt%
60
oil

- At constant copolymer content (40 wt%), varying the water/oil ratio → phase changes
  : $I_1 \rightarrow H_1 \rightarrow L_\alpha \rightarrow H_2 \rightarrow I_2 \rightarrow L_2$ ($\longrightarrow$)
  : consistent with a decreasing interfacial mean curvature (H); H=0 in lamellar phase

→ Relates to geometric factor

→ Next page Fig (Right)

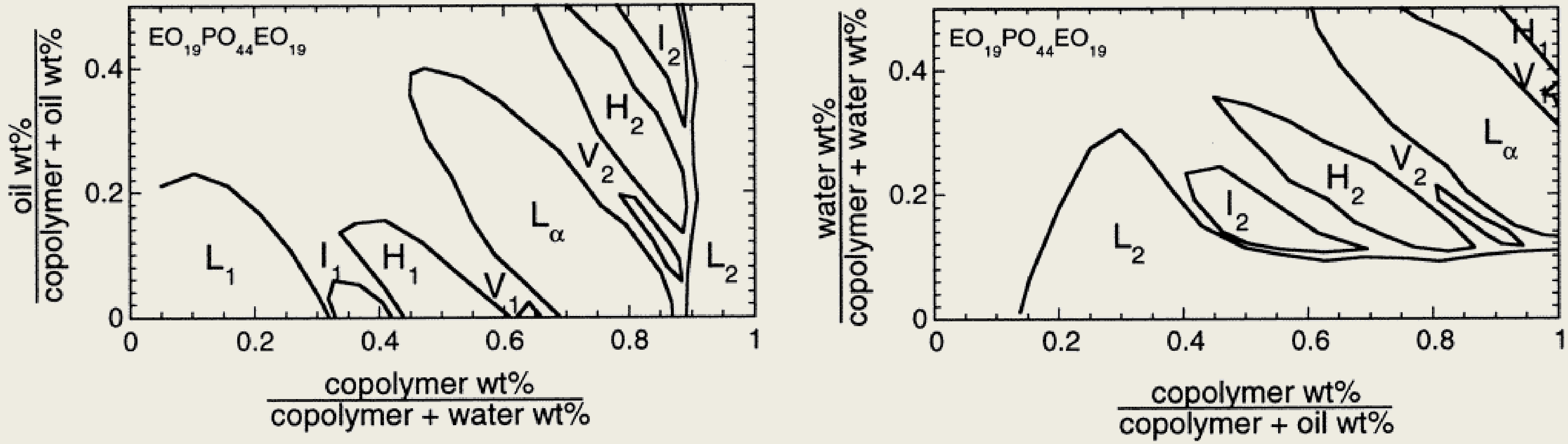
- At constant copolymer/water ratio

↓ Next page Fig (Left)

- At constant copolymer/oil ratio
  : $L_1 \rightarrow I_1 \rightarrow H_1 \rightarrow V_1 \rightarrow L_\alpha \rightarrow L_2$

3. A Closer Look at Microstructure

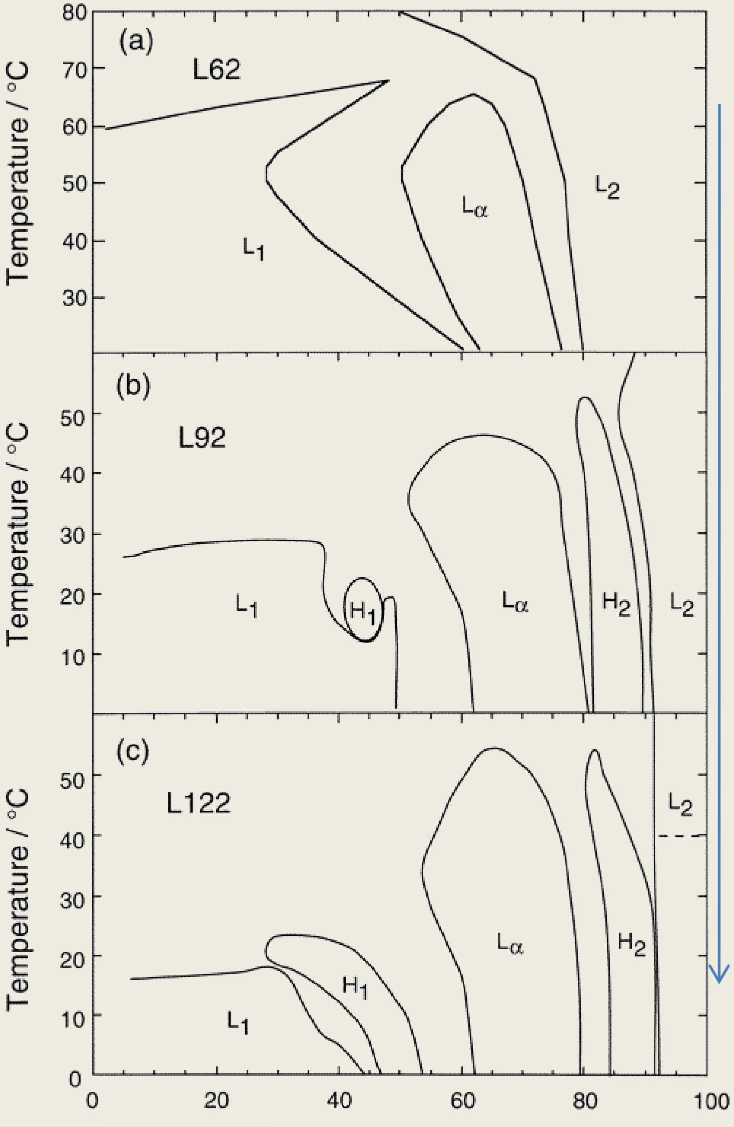
Fig. (Left) Boundaries of the various phases along the copolymer-water side of the ternary phase diagram (x-axis: copolymer weight fraction; y-axis: oil weight fraction). (Right) Boundaries of the various phases along the copolymer-oil side of the ternary phase diagram (x-axis: copolymer weight fraction; y-axis: water weight fraction).



- For a PEO/PPO block copolymer of a given block composition and molecular weight, the types of structures appear to be a function of the volume fraction of the polar (water-like) / apolar (oil-like) components.
- The microstructure in such systems is not tied up to a specific block copolymer molecular weight and block composition, which define a point in the χN vs f phase diagram

3. A Closer Look at Microstructure

(4) Effect of block copolymer molecular weight



- An increase in copolymer MW → increase the block segregation and the tendency for organization
- Figure confirms that a certain minimum MW is required for PEO and PPO blocks to segregate
  (a) only one mesophase L_α
  (b), (c) three mesophase and the increase of the range of the hexagonal regions when L92 → L122

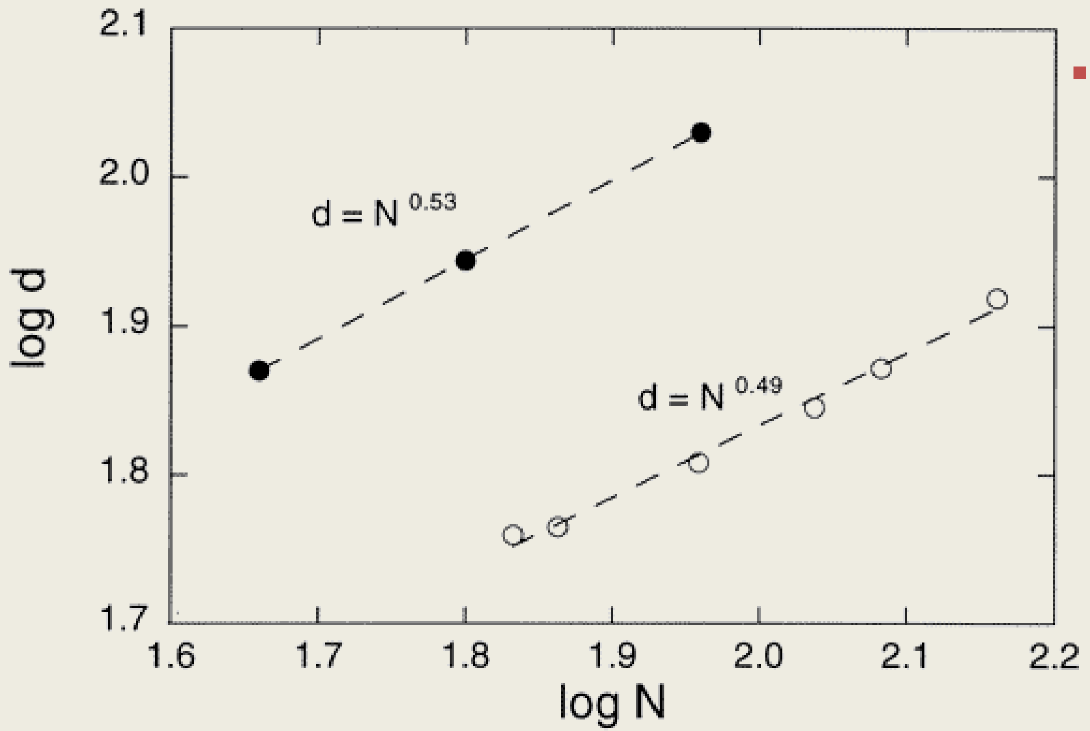
Increase in copolymer MW

Fig. Concentration-temperature phase diagrams for the (a) Pluronic L62/water, (b) Pluronic L92/water, and (c) Pluronic L122/water systems. L62, L92, and L122 have the same EO/PO ratio but different molecular weight (increasing in the order L62<L92<L122).

3. A Closer Look at Microstructure

- An important result from the study of MW affects concerns the dependence of the lamellar characteristic spacing on the polymer MW

Fig. Logarithm of the lamellar domain spacing d, vs the logarithm of number of polymer monomers N, for aqueous solution of Pluronic L62, L92, and L122 at 75 wt% (filled symbols) and calculated values from mean field theory (open symbols)



- $d \sim N^{1/2}$
  → characteristic of a random coil
  → the block copolymer chains are in the weak segregation regime

3. A Closer Look at Microstructure

(5) Effect of block copolymer composition

- The block composition is the main determinant of the microstructure observed in solvent-free block copolymers, and the chemical composition of typical surfactants affects their hydrophile/lipophile ratio and self-assembly properties.

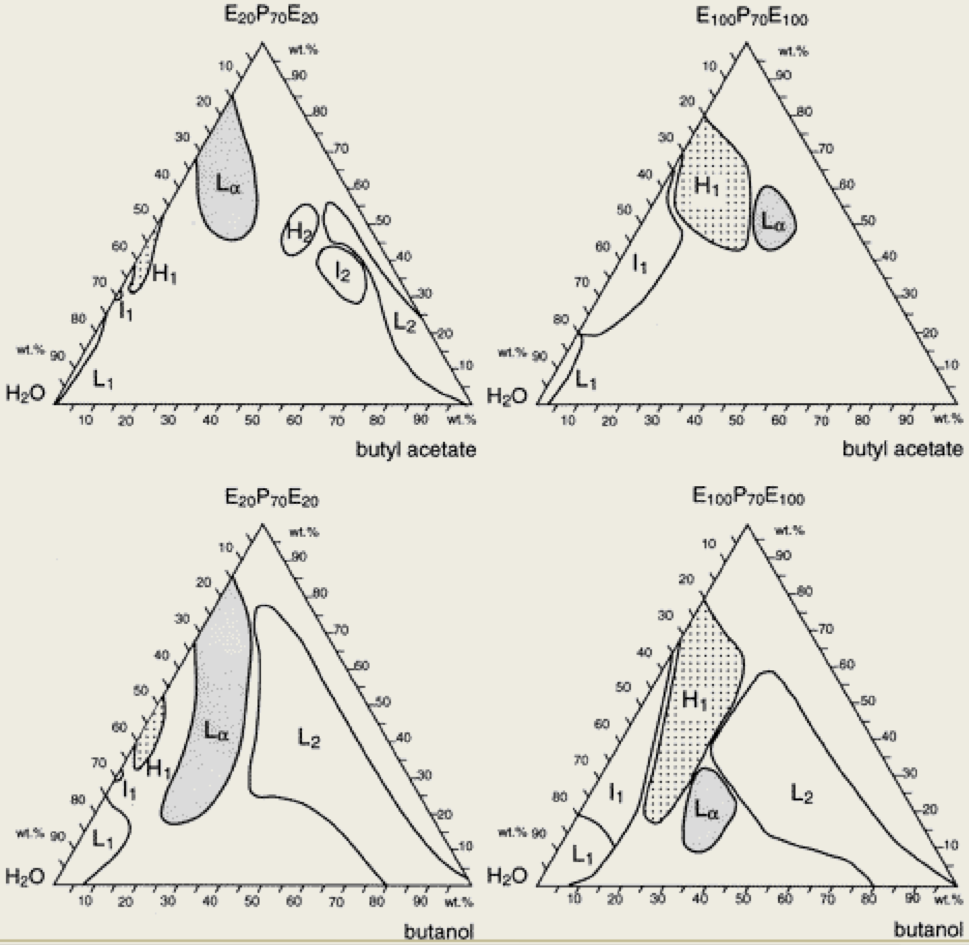
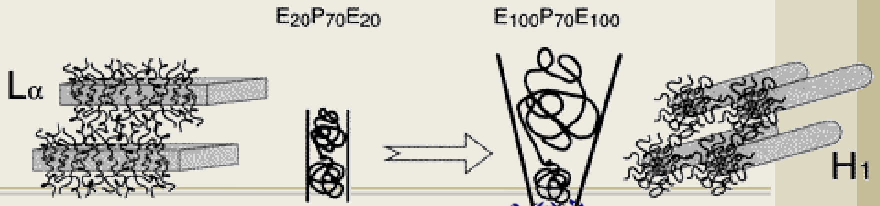


Fig. Phase diagrams of the copolymer-oil-water ternary systems.

The change in phase behavior when

(i) the size of the copolymer E block changes from E_{20} to E_{100}

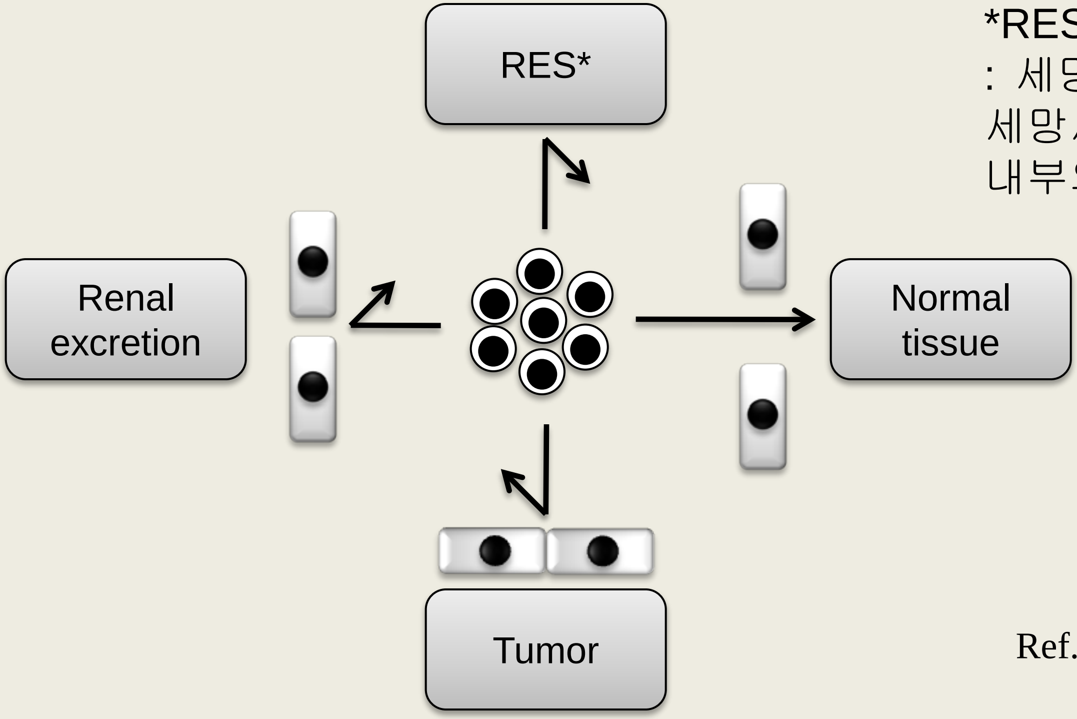
(ii) the "oil“ changes from butyl acetate to butanol (top to bottom). The schematic represents the change of the self-organization of the amphiphilic block copolymers from the lamellar (L) to the normal hexagonal (H_1) structures upon an increase of the E block size and the corresponding increase in the interfacial curvature. The shaded areas represent the apolar domains.



4. Applications of Copolymers

(1) Drug release in target cells

- A block copolymer for use in drug delivery as a microcontainer device must consist of a water-soluble block(hydrophilic), in order to impart blood solubility of the microcontainer, and a water-insoluble block (hydrophobic) compatible with the drug to be carried.



RES*

Renal excretion

Normal tissue

Tumor

*RES (reticuloendothelial system)
: 세망내피계 (림프절 지라 골수 등 속의 세망세포나 간 부신(副腎) 등 특별한 기관 내부의 혈관 내피세포 등의 총칭)

Fig. Accumulation of micelle-forming microcapsules in a tumor utilizing enhanced permeability of tumor vasculature

Ref. *Macromol. Symp.* (1997) **118**, 577.

4. Applications of Copolymers

(2) Nanopatterning

- Sizes less than 30nm are not easily obtained standard lithography (photolithography, electron beam lithography).
- One way to overcome this problem is by using block copolymer

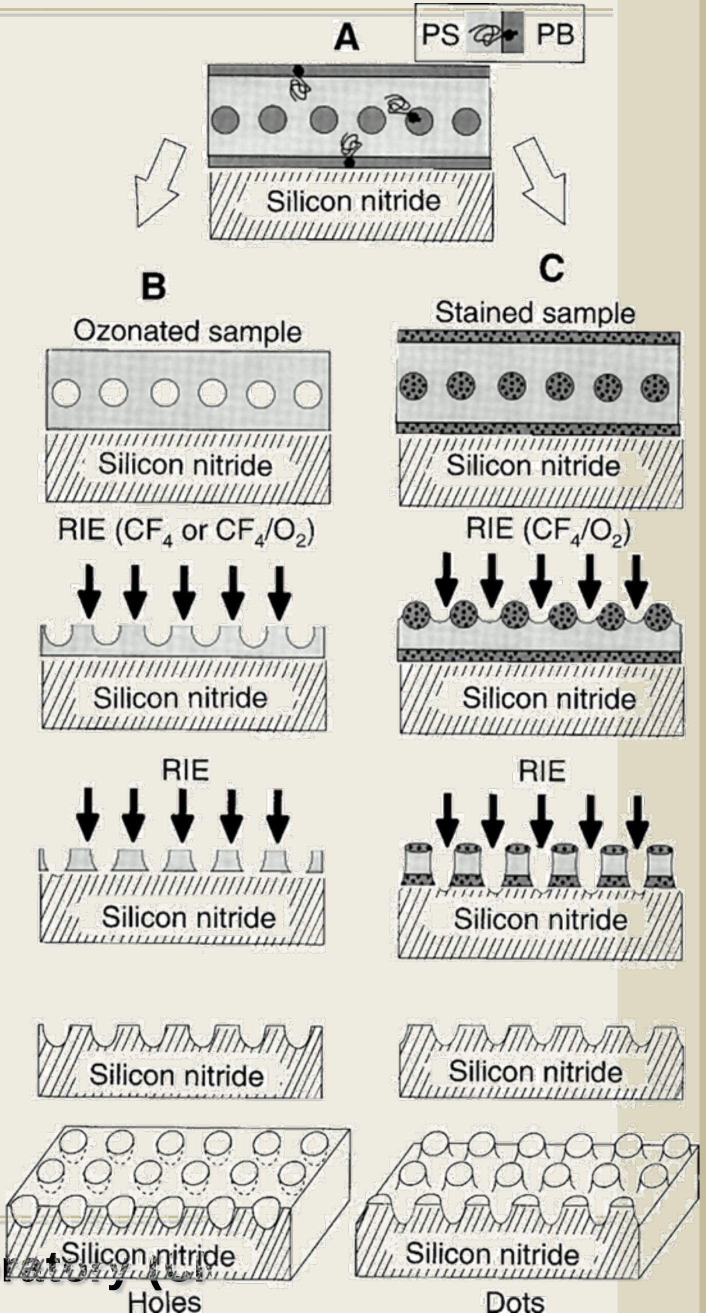

A
PS
PB
Silicon nitride
B
Ozonated sample
Silicon nitride
RIE (CF_4 or CF_4/O_2)
Silicon nitride
RIE
Silicon nitride
Silicon nitride
Silicon nitride
Holes
C
Stained sample
Silicon nitride
RIE (CF_4/O_2)
Silicon nitride
RIE
Silicon nitride
Silicon nitride
Silicon nitride
Dots

Fig. (A) Schematic cross-sectional view of a nanolithography template consisting of a uniform monolayer of PB spherical microdomains on silicon nitride. PB wets the air and substrate interfaces. (B) Schematic of the processing flow when an ozonated copolymer film is used, which produces holes in silicon nitride. (C) Schematic of the processing flow when an osmium-stained copolymer film is used, which produces dots in silicon nitride.

Ref. *Science* **276** (1997) 1401

4. Applications of Copolymers

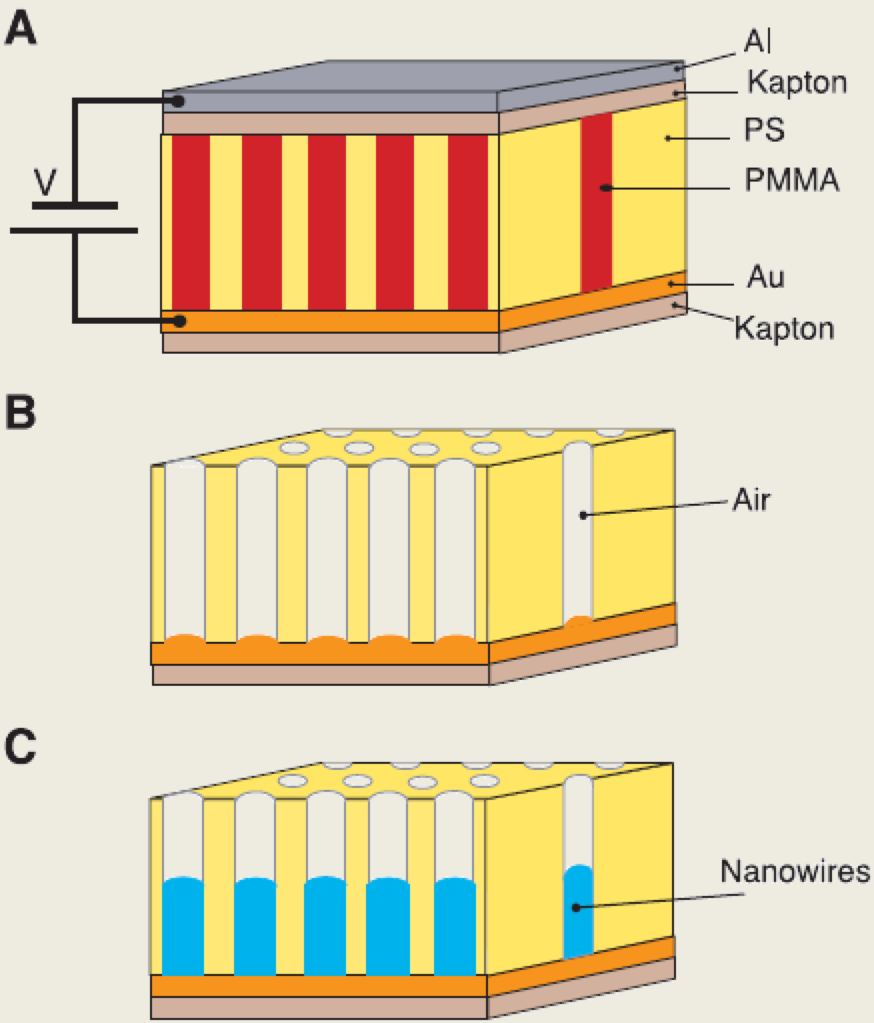


Fig. A schematic representation of high density nanowire fabrication in a polymer matrix.
(A) An asymmetric diblock copolymer annealed above the glass transition temperature of the copolymer between two electrodes under an applied electric field, forming a hexagonal array of cylinders oriented normal to the
film surface. **(B)** After removal of the minor component, a nanoporous film is formed. **(C)** By electrode position, nanowires can be grown in the porous template, forming an array of nanowires in a polymer matrix.

Ref. *Science* **290** (2000) 2126.

4. Applications of Copolymers

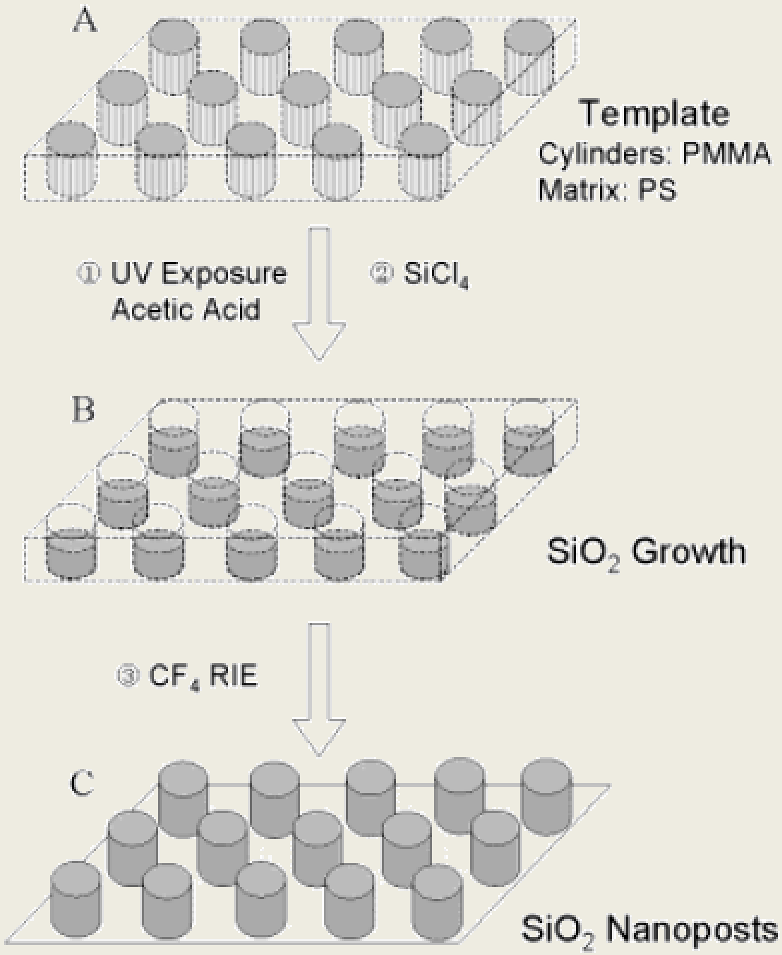

A
Template
Cylinders: PMMA
Matrix: PS
① UV Exposure
Acetic Acid
② SiCl$_4$
B
SiO$_2$ Growth
③ CF$_4$ RIE
C
SiO$_2$ Nanoposts

Fig. Schematic diagram of the steps required to generate SiO_2 nanoposts. A) Block copolymer films having cylindrical microdomains oriented normal to the surface. B) Growth of SiO_2 within the nanopores generated by selective elimination of PMMA cylinders. C) Array of SiO_2 nanoposts after removing PS matrix with CF_4 RIE.

Ref. *Adv. Mater.* **13** (2001) 795.

4. Applications of Copolymers

(3) Organic-inorganic hybrid mesostructures

- By using an amphiphilic block copolymer as a structure-directing agent, organic-inorganic hybrid materials with nanoscale structures can be prepared.

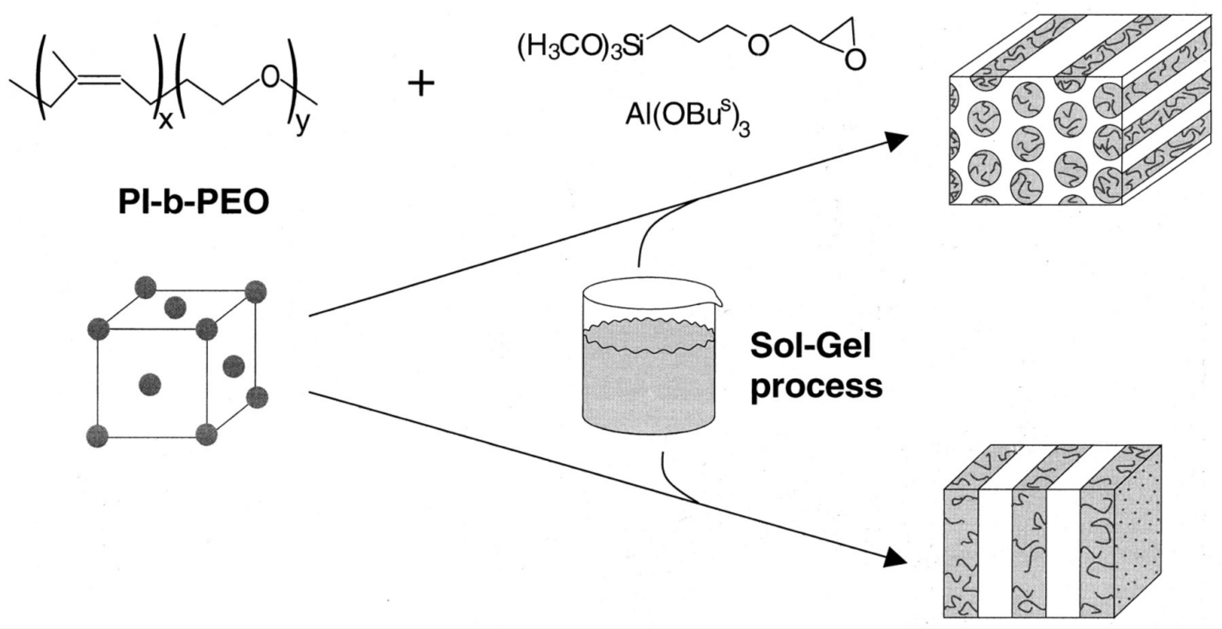


Fig. Schematic drawing of our approach for synthesizing organically modified silica mesostructures.

Ref. *Science* **278** (1997) 1795.

4. Applications of Copolymers

- By thermal treatment, single ceramic nanoobjects of different shapes and sizes can be prepared.

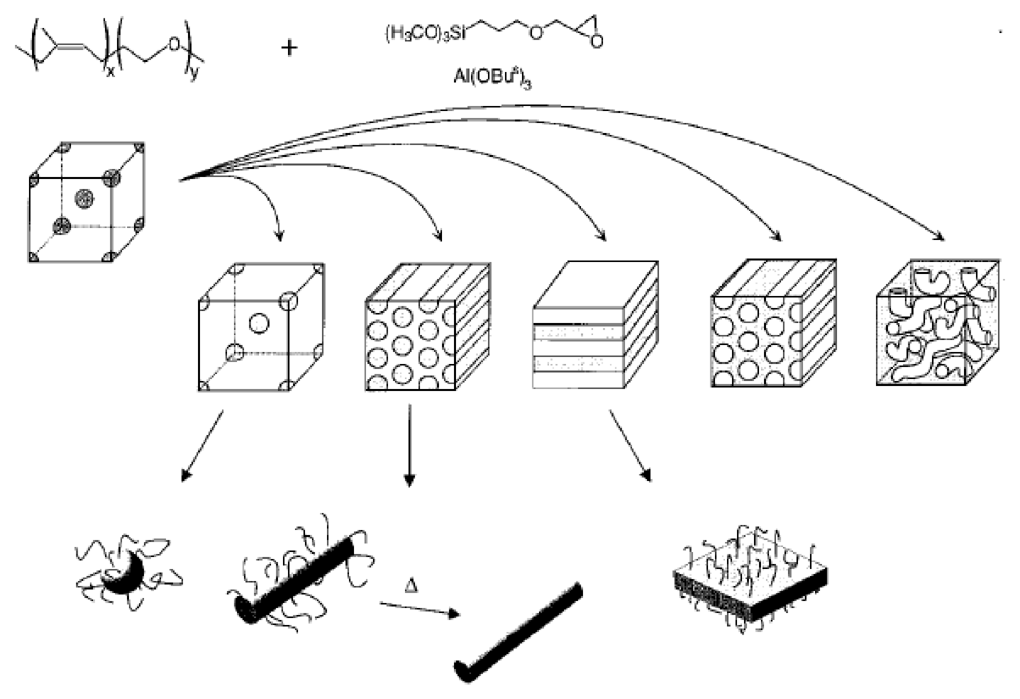


Fig. Schematic drawing of our approach for synthesis of single nano-objects with controlled shape, size, and composition. In the upper part all morphologies obtained from PI-b-PEO and different amounts of metal alkoxides are shown. As displayed in the lower part of the figure, the single “hairy” hybrid nano-objects of different shape are isolated by dissolution.

Ref. *Adv. Mater.* (1999) 11, 141