Self Organization

Order

Homogeneous state $\Longrightarrow$ Structurally ordered state

Disorder

Order $\Longrightarrow$ Structurally ordered state
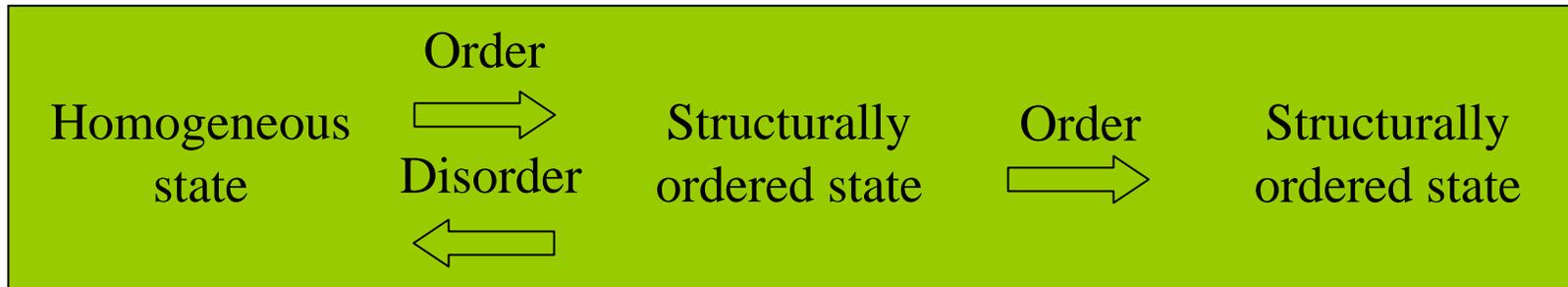
- Competing interactions: Enthalpy (H) vs. Entropy (S)

- Free energy landscape: entropic frustration, multiple pathways

- Order forming processes
  - (Macro)Phase separation
  - Microphase separation
  - Mesophase formation
  - Adsorption/complexation
  - Crystallization

- Selection of symmetries and characteristic lengths
  - Chemical affinities (long range correlations)
  - Interfacial tension

Muthukumar, M., Ober, C.K. and Thomas, E.L., "Competing Interactions and Levels of Ordering in Self-Organizing Materials," *Science,* 277, 1225-1237 (1997).

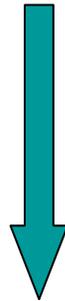# Competing Interactions and Levels of Ordering in Self-Organizing (Soft) Materials

Materials
- liquid crystals
- block copolymers
- hydrogen bonded complexes
- nanocrystals

Structural order over many length scales
- atomic
- molecular
- mesogens
- domains
- grains

increasing size scale

Outcome:

Precise shapes, structures and functions

- **Synthetic design strategy**
    - Intramolecular shapes and interaction sites (molecular docking, etc)
    - Control multistep processing to achieve long range order
- **Interactions**
    - sequential   <u>Reduction of disorder</u>   (S $\downarrow$)
    - simultaneous
    - synergistic   <u>Strengthening of intra- and</u>   (H $\uparrow$)
    - antagonistic   <u>inter-molecular interactions</u>
- **Structural design strategy**
    - organize starting from initially homogeneous state
    - organize from largest to smallest length scale

  (induce a global pattern, followed by sequential development of finer details)
- **Selection of growth directions**
    - applied bias field(s)
    - substrate patterning
- **Prior-formed structures impose boundary conditions**
    - commensuration of emergent and prior length scales
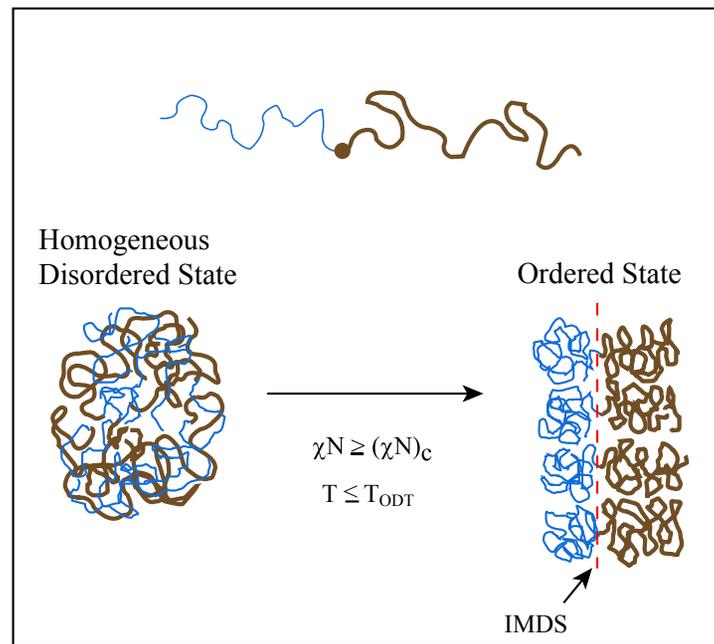   - compatibility of structures across interfaces

The min - max principle:

- *Minimiz*e interfacial area
- *Maximize* chain conformational entropy

Result:

- Morphology highly coupled to molecular characteristics
- Morphology serves as a sort of molecular probe

Gas of junctions

Homogeneous
Disordered State

Ordered State

$\chi N \geq (\chi N)_c$

$T \leq T_{ODT}$

IMDS

Junctions on
Surfaces

Figure by MIT OCW.

Microdomain Morphologies and Symmetries - Diblock Copolymers

IMDS

Spheres   Cylinders   Double Gyroid   Double Diamond   Lamellae

0-21%   21-33%   33-37%   37-50%

Increasing volume fraction of minority phase polymer

"A" block   "B" block

Junction point
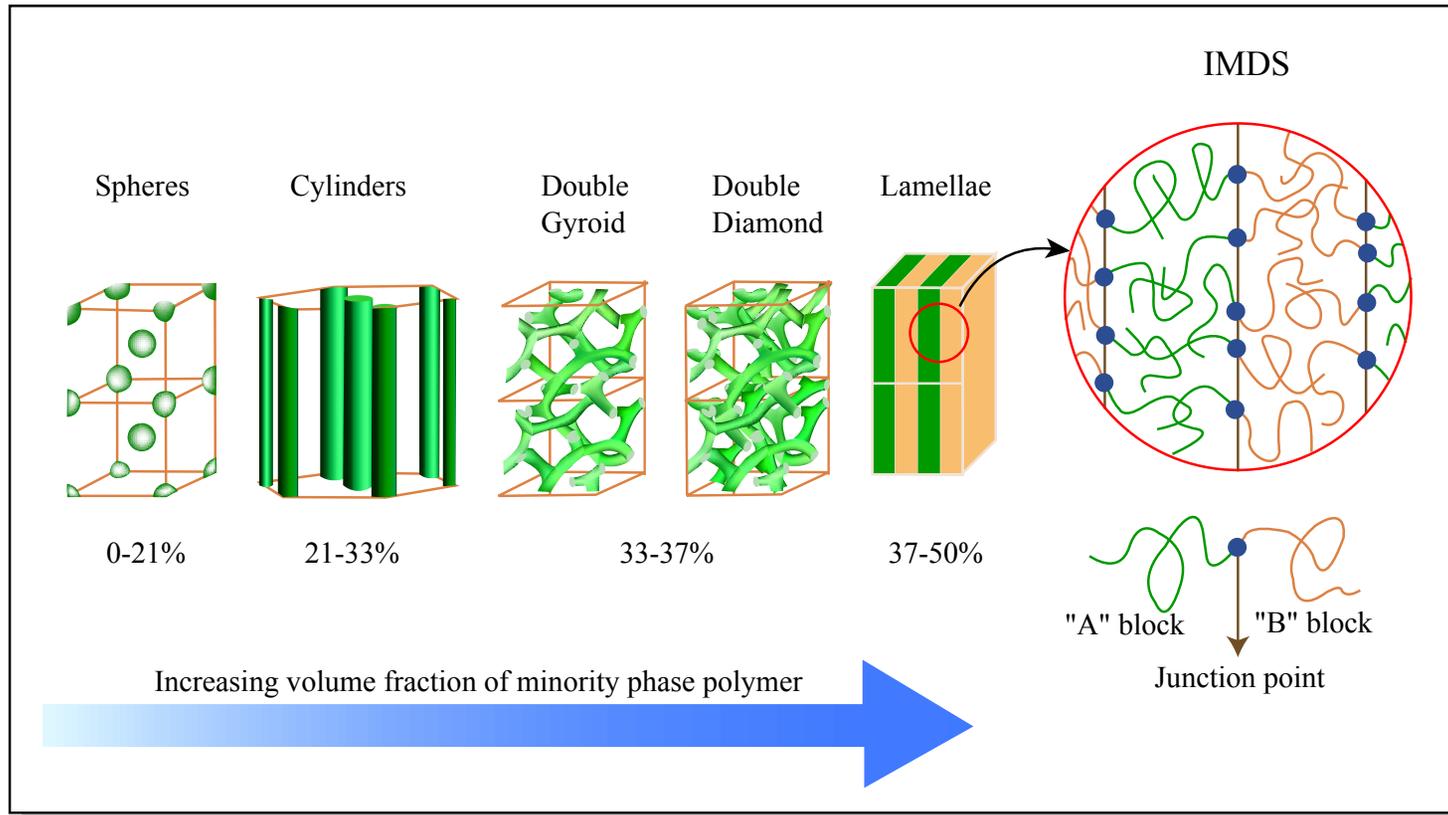
Figure by MIT OCW.

Hierarchical Structure & Length Scales

$+CH_2 - CH = CH - CH2+_n$

Polybutadiene

$+CH_2 - CH+_n$

Polystyrene

-0.5 nm

loop

bridge

-20 nm

-40 nm

-5 µm
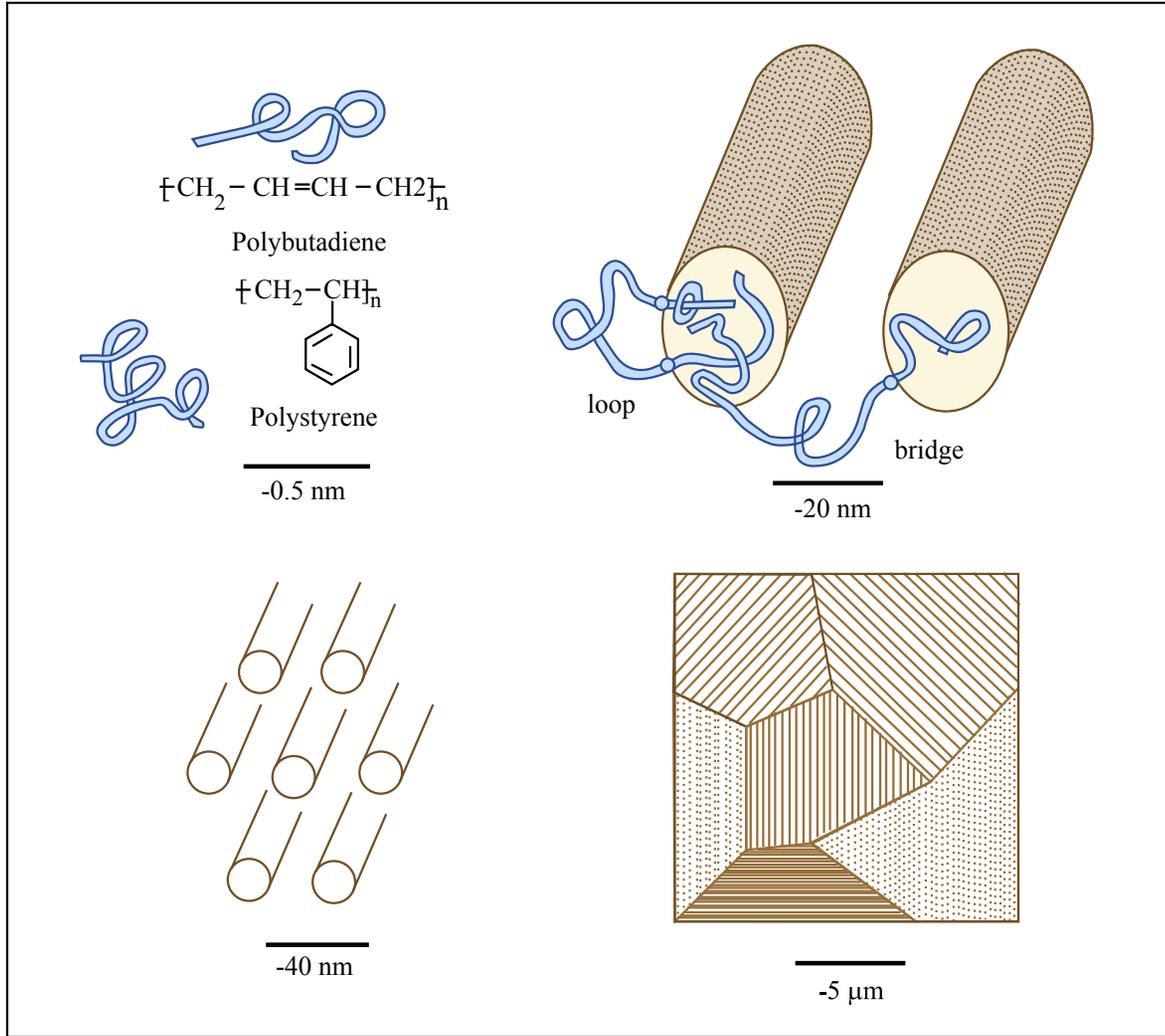
Figure by MIT OCW.

Computing the characteristic length scale:
Equilibrium Domain Spacing

Min-Max Principle

G = Free Energy per Chain
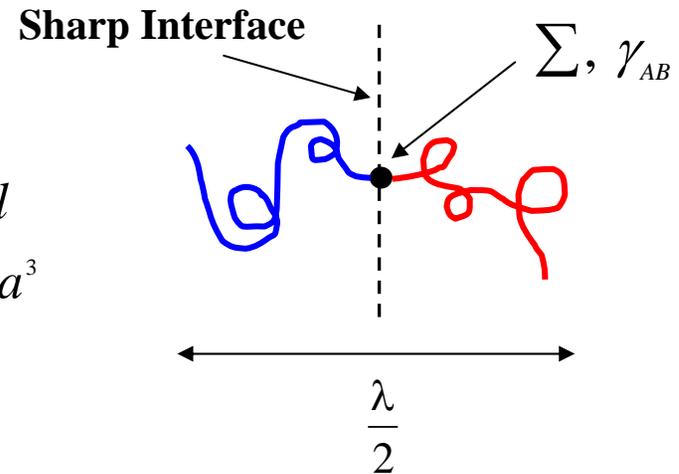
N = # of segments = $N_A + N_B$

a = Step Size $\quad a_A \sim a_B$

λ = Domain Periodicity

Σ = Interfacial Area/Chain

γ_{AB} = Interfacial Energy = $\dfrac{kT}{a^2}\sqrt{\dfrac{\chi_{AB}}{6}}$

Sharp Interface

Σ, γ_{AB}

segmental

volume ~ a^3

$\dfrac{\lambda}{2}$

$$\chi_{AB} = \text{Segment - Segment Interaction Parameter} = \frac{z}{kT}\left[\varepsilon_{AB} - \frac{1}{2}\left[\varepsilon_{AA} + \varepsilon_{BB}\right]\right]$$

Strong Segregation Limit $\rightarrow$ **Nχ very large (high MW and positive χ),**

=> pure A domains & pure B microdomains

Characteristic Period (Lamellae)

State 1   Melt

State 2   Microdomains

IMDS
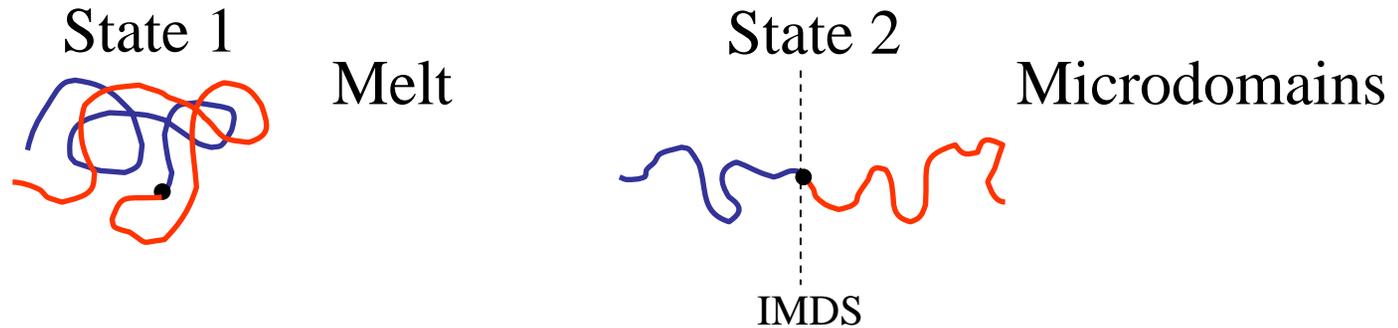
$$\Delta G = \Delta H - T\Delta S$$

$$= \gamma_{AB} \sum \ - \ N \chi_{AB} \phi_A \phi_B kT \ + \ \frac{3}{2} kT \left[\frac{(\lambda/2)^2}{Na^2} - 1 \right]$$

$\underbrace{\qquad\qquad\qquad}_{\textbf{Enthalpic} \text{ Term}}$ $\underbrace{\qquad\qquad\qquad}_{\textbf{Entropic} \text{ Spring Term}}$

Note: $Na^3 = \dfrac{\lambda}{2} \Sigma$

$$\Delta G(\lambda) \ = \ \frac{kT}{a^2} \sqrt{\frac{\chi_{AB}}{6}} \frac{Na^3}{(\lambda/2)} \ - \ N \chi_{AB} \phi_A \phi_B kT \ + \ \frac{3}{2} kT \left| \frac{(\lambda/2)^2}{Na^2} - 1 \right|$$

$$\Delta G(\lambda) \ = \frac{\alpha}{\lambda} - \ const1 + \beta\lambda^2 - const2$$

$$\frac{\partial \Delta G}{\partial \lambda} = 0 \qquad \longrightarrow \qquad 0 \ = \ \frac{-\alpha}{\lambda^2} \ + \ 2\beta\lambda$$

Free Energy of Lamellae con't

Thus, the optimum period of the lamellae repeat unit is :

$$\lambda_{opt} = \sqrt[3]{\frac{\alpha}{2\beta}} \cong aN^{2/3}\chi^{1/6}$$

Important Result: Domain dimensions scale as $\lambda \sim N^{2/3}$
Chains in microdomains are therefore stretched
compared to the homogeneous melt state

$$\Delta G(\lambda_{opt}) = 1.2kTN^{1/3}\chi_{AB}{}^{1/3} - \frac{3}{2}kT$$

Order-Disorder Transition (ODT)

Estimating the Order-Disorder Transition:

$$G_{LAM} \cong G_{Disordered}$$

$$1.2 kT N^{1/3} \chi^{1/3} \approx N \chi_{AB} \phi_A \phi_B kT \qquad \text{since both terms } >> \frac{3}{2} kT$$

For a 50/50 volume fraction, $\phi_A \phi_B = 1/4$ so

$$1.2 N^{1/3} \chi^{1/3} = N\chi / 4$$

The critical $N\chi$ is just $(N\chi)_c = (4.8)^{3/2} \sim 10.5$

$N\chi < 10.5$ **Homogeneous, Mixed Melt**

$N\chi > 10.5$ **Lamellar Microdomains**

Original Order-Disorder Diblock Phase Diagram computed by L. Leibler , *Macromolecules*, 1980

Diblock Copolymer Morphology Diagram

Image removed due to copyright restrictions.

Please see http://people.ccmr.cornell.edu/~uli/images/bc2.jpg
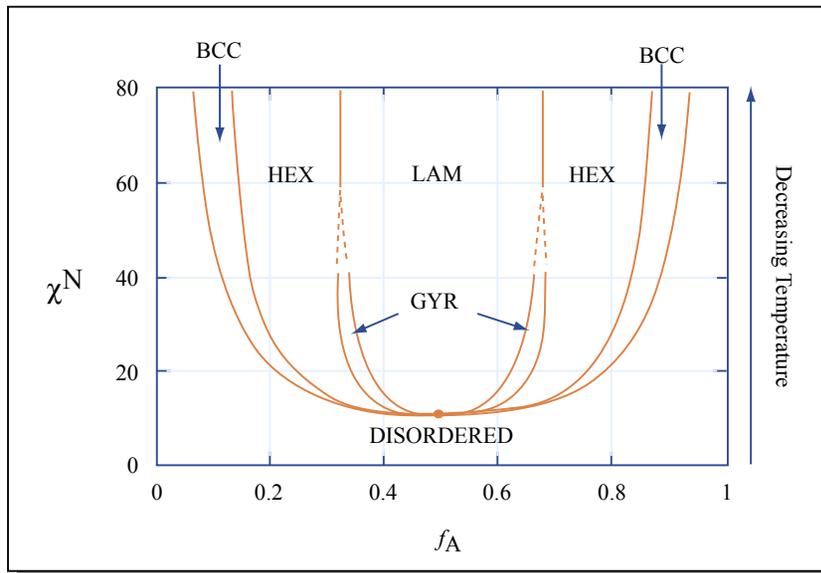
Figure by MIT OCW.

$\chi N \gg 100$
strong segregation limit

$\chi N \sim 10$
weak segregation limit

Diblock Copolymer Morphologies

The Block Copolymer Platform

Key Features:

1, 2, 3D periodic structures in bulk and thin films

Tailorable dimensions: 5-200 nm

Huge variety of patterns, *connected* patterns (some self supporting)

Template for organization of mesogenic or nanoparticle components

- sequestration via covalent, H-bond, miscibility

- excellent etch selectivity (thermal, UV, chemical)

- backfilling

Blocks: large number of chemistries and architectures possible
noncrystalline
liquid crystalline
crystalline

Properties
conductive, electroactive, photoactive
mechanical, optical, gas transport

Templated Self Assembly

PS-PEP in a 95 nm deep and 600 nm wide channels

Images removed due to copyright restrictions.
Please see Fig. 1 and 5 in Cheng, Joy Y., et al. "Templated Self-Assembly of Block Copolymers: Top-Down helps Bottom-Up."
Advanced Materials 18 (2006): 2505-2521.

Block Copolymer Epitaxy

BCP orientation can be template
via chemical epitaxy

BCPs preferentially orient to
minimize interfacial energy

Images removed due to copyright restrictions.
Please see Fig. 7 and 8 in Cheng, Joy Y., et al. "Templated Self-Assembly of Block
Copolymers: Top-Down helps Bottom-Up." *Advanced Materials* 18 (2006): 2505-2521.

The greater the interfacial energy contrast
of the template the less defects present
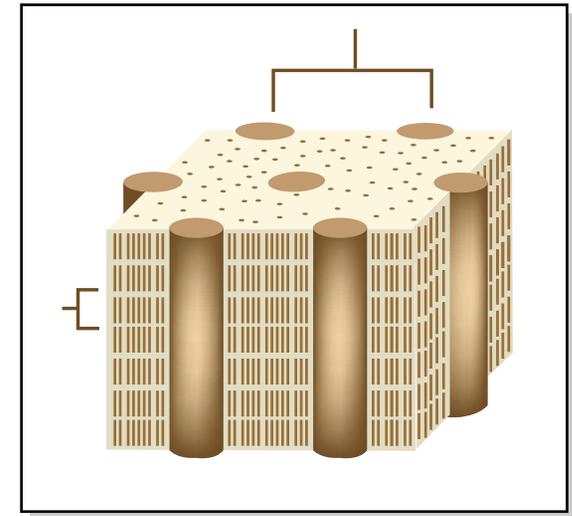
Liquid Crystalline Block Copolymers (LC BCPs)

Amorphous Block

Liquid Crystalline Block
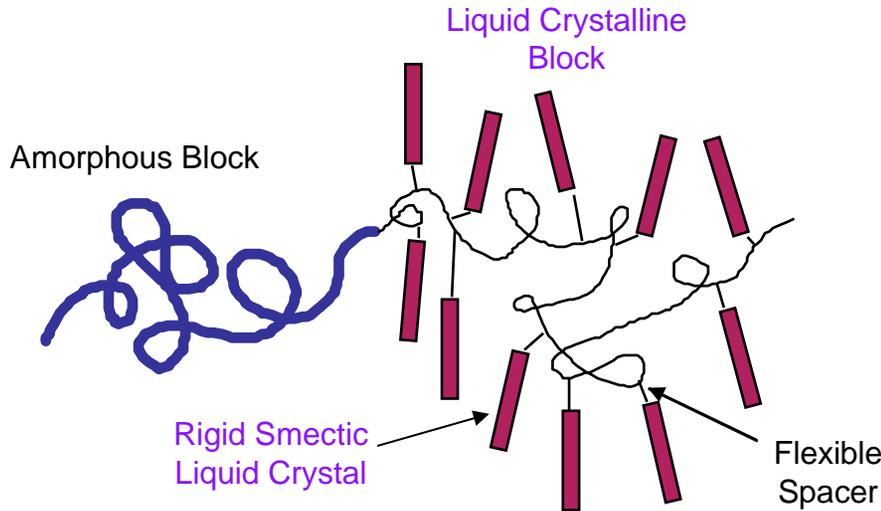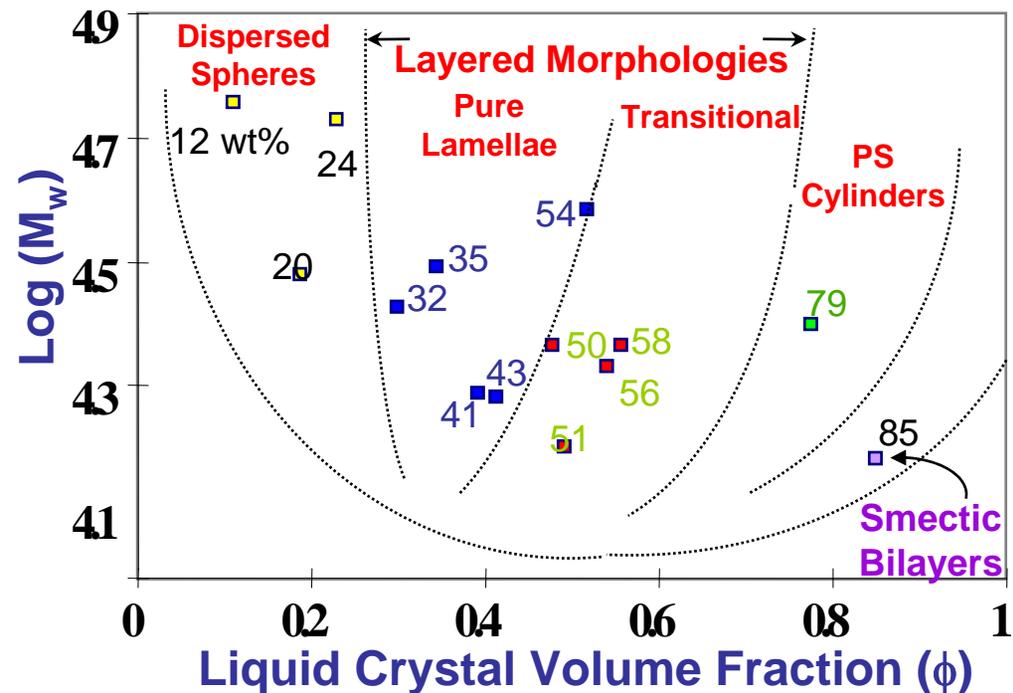
Rigid Smectic Liquid Crystal

Flexible Spacer

Figure by MIT OCW.

Amorphous – Side chain liquid crystalline block copolymers

Phase diagram has asymmetry introduced

Some morphologies are no longer favorable

Dispersed Spheres

Layered Morphologies

Pure Lamellae

Transitional

PS Cylinders

12 wt%

24

20

35

32

54

79

50 58

56

43

41

51

85

Smectic Bilayers

$\text{Log}(M_w)$

Liquid Crystal Volume Fraction (ϕ)

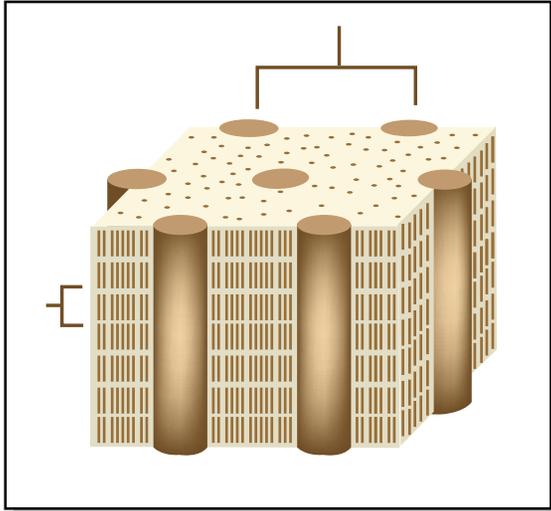# Mechanical Deformation of LC BCPs

a)

Figure by MIT OCW.

Image removed due to copyright restrictions.
Please see Fig. 6b in Verploegen, Eric, et al.
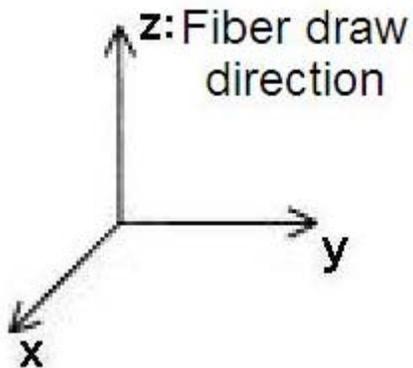"Side Chain Liquid Crystalline Thermoplastic
Elastomers for Actuator and Electromechanical Applications."
In *Electroresponsive Polymers and their Applications*. Edited by
Bharti, Vivek, et al. Warrendale, PA: MRS Proceedings
889, 2006. 0889-W05-09.

z: Fiber draw direction

y

x

b)

a) Cartoon and b) SAXS showing orientation observed for
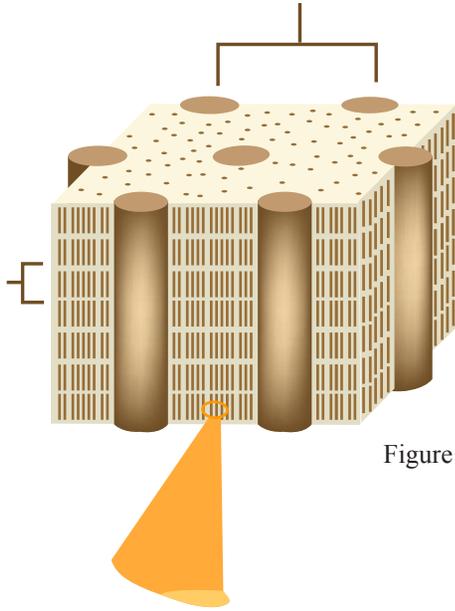melt fiber drawn PS27-LCP$_{4BPP4}$79

Responsive LC BCPs

Figure by MIT OCW.

Stimulus induces change in the LC configuration →

Change in the film thickness and/or self-assembly behavior

Modified from: Lehmann et al. Nature 410, 447 (2001), Yu, Y.L. et al., Angew. Chem, 2006. 45(33): p. 5416

Nanoparticles in Block Copolymers

BCPs can be used to pattern nanoparticles

Image removed due to copyright restrictions.
Please see Fig. 2 in Bockstaller, Michael R., et al. "Size-Selective
Organization of Enthalpic Compatibilized Nanocrystals in Ternary Block
Copolymer/Particle Mixtures." *JACS* 125 (2003): 5276-5277.
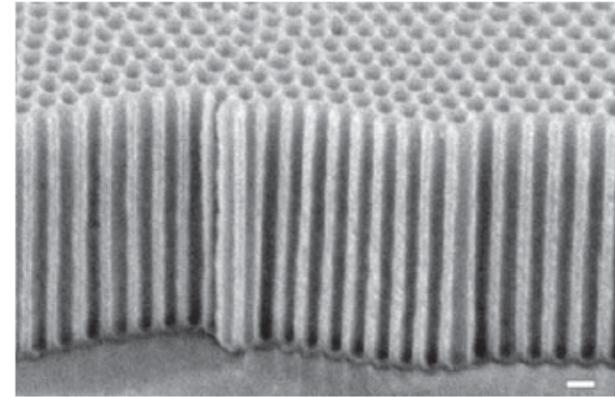
Remove on block leaving extremely high surface

Place nanoparticles at the surface for catalytic applications

Image removed due to copyright restrictions.
Please see Fig. 2 in Urbas, Augustine, et al.
"Bicontinuous Cubic Block Copolymer Photonic Crystals."
Advanced Materials 14 (December 17, 2002): 1850-1853.

Triblock Copolymers

Image removed due to copyright restrictions.
Please see http://people.ccmr.cornell.edu/~uli/images/triblk2.jpg

As the number of blocks increases so does the complexity of the structures that can be designed

Theoretical simulations are often used to predict the conditions under which specifically interesting morphologies will self-assemble

http://people.ccmr.cornell.edu/~uli/

BCPs as Nanopatterning Templates

BCPs and Micelle formation

- Use of polymers for drug therapy
  - Protects drug from degradation
  - Polymer properties vs. drug properties
  - Alters biodistribution of drug
  - Deliver hydrophobic drug in a hydrophilic environment

Can form a variety of self assembled structures

formation of micelles

amphiphilic diblock copolymer

block copolymer micelle
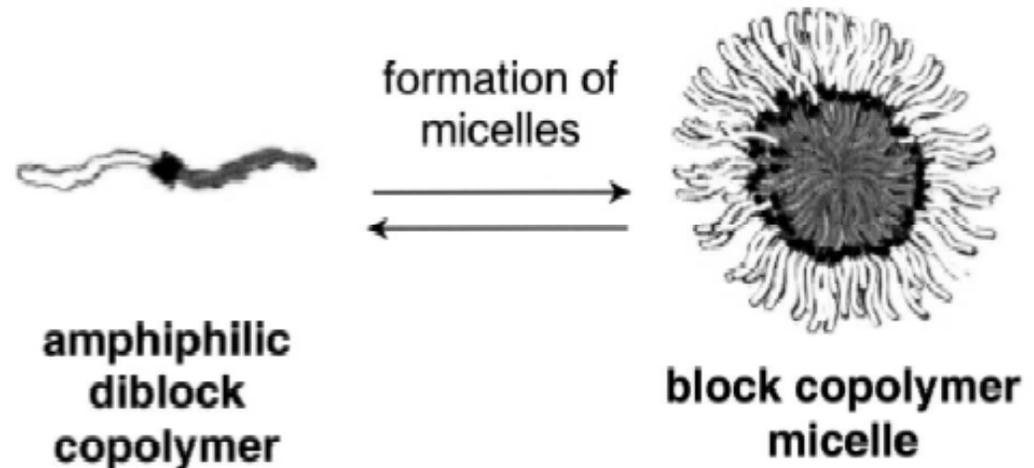
  - Spherical micelles, Cylindrical micelles, Vesicles, ect.

Rösler, A., et al., *Adv. Drug. Del. Rev.*, **53**: 95-108 (2001).

Multi-Compartment Micells

Images removed due to copyright restrictions.

Please see Fig. 1, 4d, 6b, 8a, and 8b in Li, Zhibo, et al. "Control of Structure in Multicompartment Micelles by Blending mu-ABC Star Terpolymers with AB Diblock Copolymers." *Macromolecules* 39 (2006): 765-771.