## Self Organization

<table>
<thead>
<tr>
<th>Homogeneous state</th>
<th>Order</th>
<th>Structurally ordered state</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Disorder</td>
<td></td>
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<td>Disorder</td>
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</tr>
</tbody>
</table>

- 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

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

Outcome:
Precise shapes, structures and functions
**Strategic Design** for Materials with Multiple Length Scales

- **Synthetic design strategy**
  - Intramolecular shapes and interaction sites (molecular docking, etc)
  - Control multistep processing to achieve long range order

- **Interactions**
  - sequential Reduction of disorder \( (S \downarrow) \)
  - simultaneous
  - synergistic Strengthening of intra- and inter-molecular interactions \( (H\uparrow) \)
  - antagonistic

- **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
Principles of Self Organization: Microphase Separation Block Copolymers

The min - max principle:
- Minimize interfacial area
- Maximize chain conformational entropy

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

Gas of junctions

Junctions on Surfaces

Figure by MIT OCW.
Microdomain Morphologies and Symmetries - Diblock Copolymers

- Spheres
- Cylinders
- Double Gyroid
- Double Diamond
- Lamellae

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

Increasing volume fraction of minority phase polymer

IMDS

"A" block "B" block

Junction point

Figure by MIT OCW.
Hierarchical Structure & Length Scales

\[ \text{\(CH_2\!-\!CH\!\equiv\!CH\!-\!CH_2\!\)}_n \]
Polybutadiene

\[ \text{\(CH_2\!-\!CH\!}_n \]
Polystyrene

-0.5 nm

-40 nm

-20 nm

-5 \(\mu\)m

Figure by MIT OCW.
Computing the characteristic length scale:
Equilibrium Domain Spacing

Min-Max Principle

\[ G = \text{Free Energy per Chain} \]
\[ N = \# \text{ of segments} = N_A + N_B \]
\[ a = \text{Step Size} \quad a_A \sim a_B \]
\[ \lambda = \text{Domain Periodicity} \]
\[ \Sigma = \text{Interfacial Area/Chain} \]
\[ \gamma_{AB} = \text{Interfacial Energy} = \frac{kT}{a^2} \sqrt{\frac{\chi_{AB}}{6}} \]

\[ \chi_{AB} = \text{Segment - Segment Interaction Parameter} = \frac{Z}{kT} \left[ \epsilon_{AB} - \frac{1}{2} (\epsilon_{AA} + \epsilon_{BB}) \right] \]

**Strong Segregation Limit**  \[ \rightarrow \quad N\chi \text{ very large (high MW and positive } \chi), \]
\[ \rightarrow \quad \text{pure A domains} \& \text{pure B microdomains} \]
Characteristic Period (Lamellae)

\[ \Delta G = \Delta H - T\Delta S \]

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

\[ \text{Enthalpic Term} \quad \text{Entropic Spring Term} \]

Note: \( Na^3 = \frac{\lambda}{2} \Sigma \)

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

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

\[ \frac{\partial \Delta G}{\partial \lambda} = 0 \quad \Rightarrow \quad 0 = -\frac{\alpha}{\lambda^2} + 2\beta\lambda \]
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:

\[ G_{LAM} \cong G_{\text{Disordered}} \]

\[ 1.2kTN^{1/3}\chi^{1/3} \approx N\chi_{AB}\phi_A\phi_BkT \]

since both terms \( >> \frac{3}{2}kT \)

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

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

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

\[ N\chi < 10.5 \quad \text{Homogeneous, Mixed Melt} \]

\[ N\chi > 10.5 \quad \text{Lamellar Microdomains} \]

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Please see http://people.ccmr.cornell.edu/~uli/images/bc2.jpg

\( \chi N \gg 100 \)

strong segregation limit

\( \chi N \sim 10 \)

weak segregation limit

Figure by MIT OCW.
Diblock Copolymer Morphologies

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Please see http://people.ccmr.cornell.edu/~uli/images/bc2.jpg

Fig. 3a in Cheng, Joy Y., et al. "Templated Self-Assembly of Block Copolymers: Top-Down Helps Bottom-Up.”

Fig. 10 in Lammertink, Rob G. H., et al. "Periodic Organic-Organometallic Microdomain Structures in Poly(styrene-block-ferrocenyldimethylsilane) Copolymers and Blends with Corresponding Homopolymers.”

Fig. 1 in Urbas, Augustine, et al. “Bicontinuous Cubic Block Copolymer Photonic Crystals.”
*Advanced Materials* 14 (December 17, 2002): 1850-1853.

Fig. 3 in Lammertink, Rob G. H., et al. "Periodic Organic-Organometallic Microdomain Structures in Poly(styrene-block-ferrocenyldimethylsilane) Copolymers and Blends with Corresponding Homopolymers.”
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

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Block Copolymer Epitaxy

BCP orientation can be template via chemical epitaxy

BCPs preferentially orient to minimize interfacial energy

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

Amorphous – Side chain liquid crystalline block copolymers

Phase diagram has asymmetry introduced
Some morphologies are no longer favorable
a) Cartoon and b) SAXS showing orientation observed for melt fiber drawn PS27-LCP$_{4BPP479}$

Image removed due to copyright restrictions.
Responsive LC BCPs

Stimulus induces change in the LC configuration →

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

Image removed due to copyright restrictions. Please see Fig. 1c in Lehmann, W., et al. "Giant lateral electrostriction in ferroelectric liquid-crystalline elastomers." Nature 410 (March 22, 2001): 447-450.

Images removed due to copyright restrictions. Please see Fig. 5c and 6 in Barrett, Christopher J., et al. "Photo-mechanical effects in azobenzene-containing soft materials." Soft Matter 3 (2007): 1249-1271.

Nanoparticles in Block Copolymers

BCPs can be used to pattern nanoparticles

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 Bockstaller, Michael R., et al. "Size-Selective Organization of Enthalpic Compatibilized Nanocrystals in Ternary Block Copolymer/Particle Mixtures." *JACS* 125 (2003): 5276-5277.

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

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.

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BCPs as Nanopatterning Templates

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Please see Scheme 1, Fig. 1, and Fig. 2 in Guo, Shouwo, et al. "Nanopore and Nanobushing Arrays from ABC Triblock Thin Films Containing Two Etchable Blocks." Chemistry of Materials 18 (2006): 1719-1721.
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

- Spherical micelles, Cylindrical micelles, Vesicles, ect.


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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.