Self-Assembly of Block Copolymers (BCPs)

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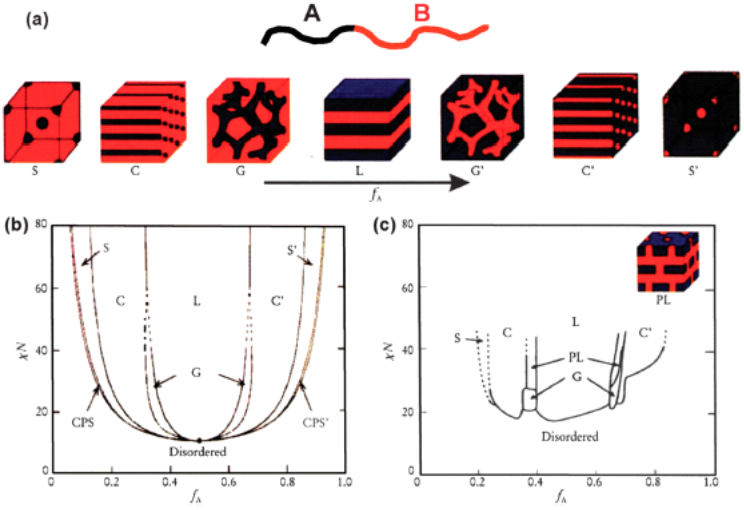
Process Interactions

- Composition *(f)*, number of repeating units (N), and Flory-Huggins interaction parameter (χ) determine morphologies (e.g. sphere, cylinder, gyroid, lamellae) [Feng 2017]
  - Number of repeating units = *degree of polymerization*
  - Mechanical/electrical fields may affect interactions
  - Limited phase separation due to the connected nature of polymer blocks → local segregation of blocks with similar affinity
- Annealing, or heating, followed by slow cooling allows enough time for polymer chains to reach thermodynamically preferred alignments

Expected Outcomes - BCP only

- Morphologies of a linear diblock BCP, as a function of *f* and χN: [Feng 2017]
  - (a)
    S and S' = body-centered-cubic spheres
    - Micelles minimize free energy by aggregating less soluble block away from solvent [Chaparro 2016]
    - Spherical micelles only form above the threshold critical micelle concentration [Li 2011]
      - Concentration of BCP proportionate to the number of micelles

    C and C' = hexagonally packed cylinders
    G and G' = bi-continuous gyroids
    L = lamellae
  - (b) represents a **theoretical** phase diagram of AB diblocks
  - (c) represents the **experimental** phase diagram of polystyrene-b-polyisoprene



- Film thickness h_s at multiples of lamellar thickness L_0 → smooth films [Smith 2001]
  - $h_s = \left(m + \frac{1}{2}\right) L_0$
  - $h \neq h_s$ → hole and island patterns
  - $L_0 \sim M^{0.66}$, where M is molecular mass
  - Explained well on https://www.coursera.org/learn/high-throughput/lecture/5qC8e/physical-structure-of-polymers (5:00)

Expected Outcomes - BCP tethered nanoparticle [Chan 2006]

- "AB tadpole" = spherical nanoparticle head (B) and homopolymer tail (A)
  - 55% tail and 45% sphere → hexagonally close-packed cylinders

- **Linear di-BCPs exhibit lamellar morphology with same molecular composition**

- "ABB tadpole" = spherical nanoparticle head (B) and di-BCP tail (A)
  - 60% A and 40% B → lamellae
  - Analogous to ABC linear tri-BCP, with nanoparticle (C) and diblock copolymer tether (B-A) resulting in three Flory-Huggins forces χ_{AB}, χ_{BC}, χ_{AC}
  - Self-assembled structures for tethered nanocubes:

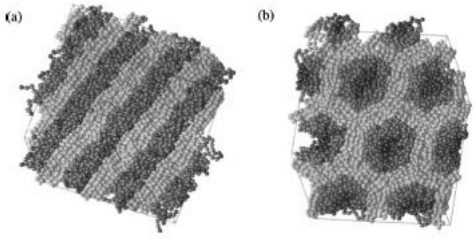
f_B[a]	Selective good solvent for cubes	Neutral poor solvent	Selective poor solvent for cubes
0	Lamellae	Lamellae	Lamellae
0.125	Lamellae	Lamellae	Lamellae
0.25	Lamellae	Lamellae	Lamellae
0.375	hcp core-shell cylinders	Lamellae	Lamellae
0.50	hcp core-shell cylinders	Lamellae	Lamellae
0.625	hcp core-shell cylinders	Lamellae	Lamellae
0.75	hcp core-shell cylinders	Lamellae	Lamellae
0.875	Lamellae	Lamellae	Lamellae

Self-assembled structures for linear ABC tri-BCP:

f_B[a]	Selective good solvent for *C* block	Neutral poor solvent	Selective poor solvent for *C* block
0	Lamellae	Lamellae	Lamellae
0.125	Lamellae	Lamellae	Lamellae
0.25	Lamellae	Lamellae	Lamellae
0.375	hcp core-shell cylinders	Lamellae	Lamellae
0.50	Perforated lamellae	Lamellae	Lamellae
0.625	Perforated lamellae	Lamellae	Lamellae
0.75	hcp core-shell cylinders	Lamellae	Lamellae
0.875	Lamellae	Lamellae	Lamellae

*f_b represents the relative volume fraction of the B block on the di-BCP tether
*hcp = hexagonal close-packed
*Selective poor solvent favors one polymer block over the other

  - Selective Good Solvent for Cubes (Non-BCP head)
    - Cubes are solvophilic, tethers are solvophobic
    - Lamellar (flat) structures (a) @ very low and very high f_b
      - Meanwhile, micelles and cylinders (curved) for di-BCP at these values
    - Core-shell cylindrical structures (b) @ intermediate and high f_b
      (A = black core, B = dark gray shell, C = light gray matrix)



    - Rigid cube prevents micelle morphologies
  - Poor Solvent for Nanocube
    - Cubes are solvophobic, tethers are solvophilic
    - Lamellar phases over entire range of relative tether block fractions
    - ABCCBA pattern observed (a) in neutral poor solvent
    - Selective poor solvent (b) forms unique layer in which A blocks and B blocks are mixed

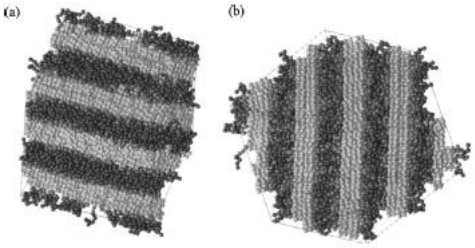
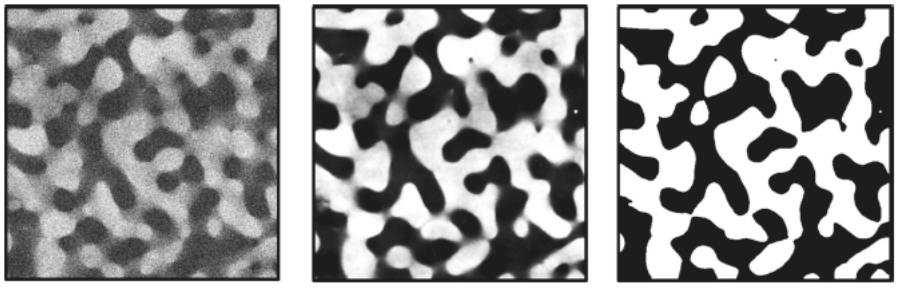


Image Analysis Reconstruction [Lopez-Barron and Mocosko 2009]

- 2D images obtained with Laser Scanning Confocal Microscopy (a)
  - Out-of-focus blur was reduced by applying deconvolution technique (b)
  - Noise was removed using image filters from Adobe Photoshop (c)



  - Images were stacked to generate 3D image
  - Nonstructuring meshing method (marching cubes algorithm?) was used to generate triangular mesh representation
  - Interfacial area (Q) obtained by summing areas of all triangles
  - Surface topology and local curvature obtained as well

Applications [Feng 2017]

- Thermoplastic elastomers for adhesives and food packaging (good vibration damping material)
- Micelles and vesicles for drug delivery with resistance to protein adsorption and cellular adhesion to protect hydrophobic drug against hydrolysis and enzymatic degradation
- Soft lithography in bit patterned media for hard disk drives and microelectronics