CHE323/CHE384
Chemical Processes for Micro- and Nanofabrication
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Lecture 68
Directed Self Assembly, part 1

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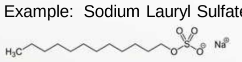
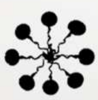
Self-Assembly

- Self-assembly comes about when molecules of a set shape have very different properties on different sides of the molecule
  - Example: polarity (polar on one side, nonpolar on the other)
- Examples of self-assembly can be common (surfactants leading to bubbles) or uncommon (block-copolymers)

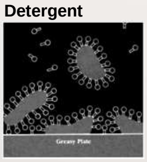
Surfactant – a surface acting agent.
Example: Sodium Lauryl Sulfate



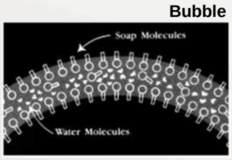


Critical micelle concentration (CMC) - the concentration of surfactants above which micelles form and almost all additional surfactants added to the system go to micelles.

Detergent



Bubble



Copolymers

- **Copolymer** - a polymer derived from two or more monomeric species (vs. a homopolymer where only one monomer is used)

$$[A]_x [B]_y$$

- Generally, the positions of A and B are random, so only the fraction of A and B (f_A, f_B) and molecular weight determine the copolymer
- Three or more monomers can also be used

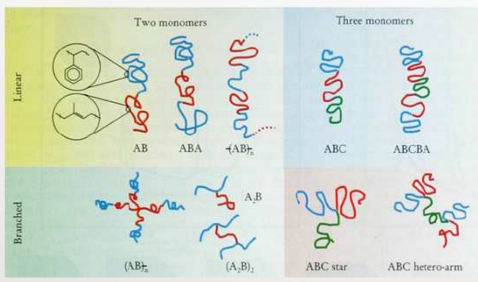
Block Copolymers

- **Block Copolymer** - a copolymer made up of homogeneous blocks of different polymerized monomers

[A]-b-[B] (example diblock copolymer)

- For example, PS-b-PMMA is short for polystyrene-block-poly(methyl methacrylate) and is made by first polymerizing styrene, and then subsequently polymerizing MMA from the reactive end of the polystyrene chains.

Block Copolymer Configurations



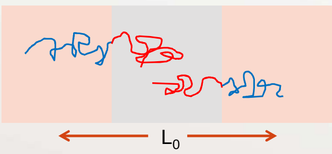
"Block Copolymers—Designer Soft Materials", Frank S. Bates and Glenn H. Fredrickson, *Physics Today*, v52 No. 2 (1999) p. 32.

Microphase Separation

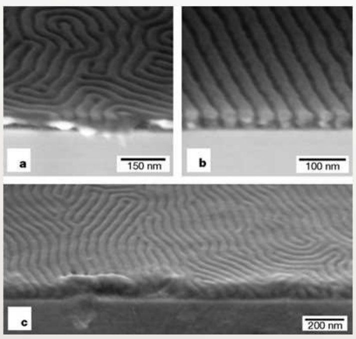
- A and B are necessarily well mixed macroscopically (they are connected!)
- If A and B have a high energy of mixing (they don't like to mix), the block copolymer can exhibit microphase separation
  - Driven by chemical incompatibilities between the different blocks that make up block copolymer molecules
  - Like surfactant, can form micelles and layered films (lamellae)
  - Other, more complex self-organized patterns can result
- Example: PS is nonpolar, PMMA is polar

Microphase Separation

- Basic microphase separation pattern for a diblock copolymer is: A-b-B B-b-A



- The width of one such repeating unit (two copolymer chains) is called the natural period, L_0
- For PS-b-PMMA, L_0 ~ 25 – 80 nm



Microphase separation of a block copolymer

Epitaxial self-assembly of block copolymers on lithographically defined nanopatterned substrates, Sang Ouk Kim, Harun H. Solak, Mark P. Stoykovich, Nicola J. Ferrier, Juan J. de Pablo & Paul F. Nealey, *Nature* **424**, 411-414 (24 July 2003).

Flory-Huggins Interaction

- Gibbs Free Energy of Mixing (ΔG_m)

$$\Delta G_m = RT[n_1 ln\phi_1 + n_2 ln\phi_2]$$

  - number of moles n_1 and volume fraction ϕ_1 of solvent
  - number of moles n_2 and volume fraction φ_2 of polymer
- Flory-Huggins solution theory: takes account of the great dissimilarity in molecular sizes in adapting the usual expression for the Gibbs free energy of mixing

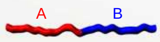
$$\Delta G_m = RT[n_1 ln\phi_1 + n_2 ln\phi_2 + n_1\phi_2\chi_{12}]$$

  - χ - interaction parameter to account for the energy of interdispersing polymer and solvent molecules

Flory-Huggins Interaction

- Flory-Huggins interaction parameter for the two copolymer blocks (A and B)

$$\chi_{AB} = z\Delta w/kT$$



  - Δw = energy change (free energy cost) per A-B interaction compared to A-A and B-B interactions
  - z = coordination number, the number of nearest neighbor monomers for a lattice site
- Positive χ_{AB} indicates net repulsion between species A and B; negative value indicates a free-energy drive towards mixing

Flory-Huggins Interaction

- The strength of the repulsive interaction between copolymer blocks is given by χN, where N is the number of monomers in the diblock copolymer
- Microphase separation can occur when this quantity is greater than ~ 10.5
- The natural period of a diblock copolymer is

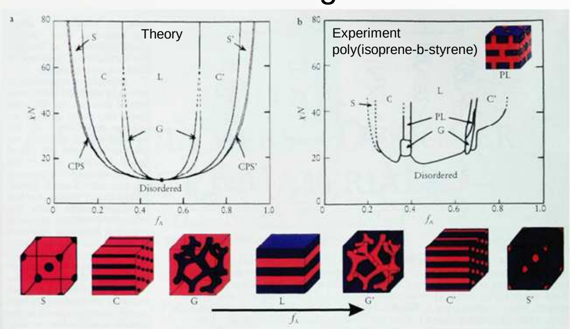
$$L_0 \approx a\chi^{1/6}N^{2/3}$$

a = monomer size

Phase Diagrams

- For a given copolymer, vary N and f_A, find out what "phase" results
  - Disorganized, lamellae, horizontal cylinders, close-packed spheres, gyroids, etc.
- Plot boundaries between phases on χN vs. f_A graph
- Results depend on substrate properties and film thickness

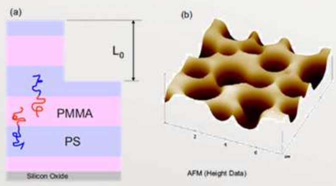
Phase Diagrams



"Block Copolymers—Designer Soft Materials", Frank S. Bates and Glenn H. Fredrickson, *Physics Today*, v52 No. 2 (1999) p. 32

Effect of Film Thickness (t)

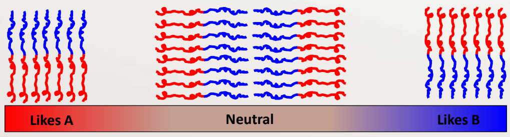
- For t << L_0, microdomain formation is frustrated, giving slow phase separation and complex results
- For t >> L_0, layers of microdomains can form, including surface topography



H.-C. Kim and W. D. Hinsberg, "Surface patterns from block copolymer self-assembly ", *J. Vac. Sci. Technol.* A, Vol. 26, No. 6, Nov/Dec 2008.

Effect of Film Thickness (t)

- For t ~ L_0, microdomain formation is very dependent on interface properties
  - Most common regime for lithography applications
  - The interface with air can also influence orientation



Annealing

- Evaporation-induced self assembly
  - Different solvents, temperatures, and evaporation rates create a wide range of different self-assembled structures (non-equilibrium)
  - Very difficult to control evaporative flux, solvent concentration, interfacial interactions
- Thermal annealing
  - Equilibrium can be well controlled (but slow)
  - Fewer degrees of freedom affecting self-assembly morphologies

Lecture 68: What have we learned?

- Why does molecular self-assembly happen?
- What is a copolymer?
- What is a block copolymer?
- Explain microphase separation
- What is the Flory-Huggins interaction parameter and what does it tell us?
- What are the factors that determine the morphology of self-assembled block copolymers?