

# **Chemical Engineering 160/260**

## **Lecture 12 - Molecular Engineering with Block Copolymers**

# Molecular Engineering with Block Copolymers

## Objective

To illustrate the structural complexity and the possibility for molecular control of organization in block copolymers.

# Outline

- Block copolymer architecture
- Phase diagram for melts
- Crystallization
- Micellization
- Experimental methods for study of block copolymers

# Motivation

## Compositional Contrast

- Hydrophilic/hydrophobic
- Polar/non-polar
- Charged/uncharged
- Linear/branched

## Conformational Contrast

- Rigid/flexible
- Oriented/unoriented
- Long/short

## MOLECULAR DESIGN WITH BLOCK COPOLYMERS

## Morphological Contrast

- Amorphous/crystalline
- Glassy/rubbery
- Swollen/contracted

## Functional Contrast

- Reactive/unreactive
- Photoresponsive/passive
- Electroactive/passive
- Conducting/nonconducting
- Biocompatible/neutral

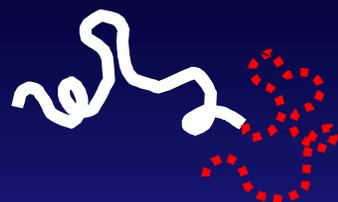
# Motivation:

## Nanoscience and Nanotechnology

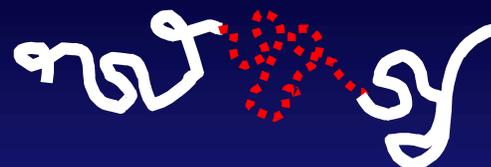
Block copolymers may be the optimum nanomaterials for nanotechnology, either for their intrinsic properties as **self-organized assemblies** or for their ability to **template** other organic, inorganic, semiconducting, metallic, or biologically relevant materials.

# Block Copolymer Architectures

## Linear

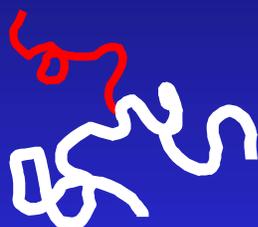


AB Diblock

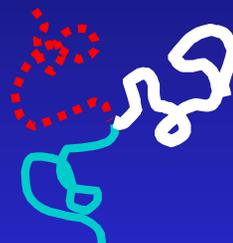


ABA Triblock

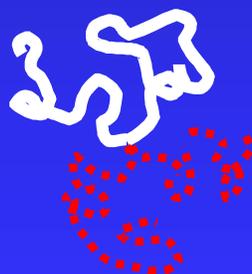
## Star



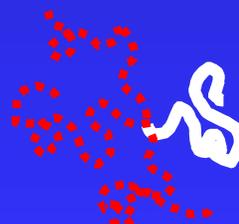
$A_2B$  3-miktoarm



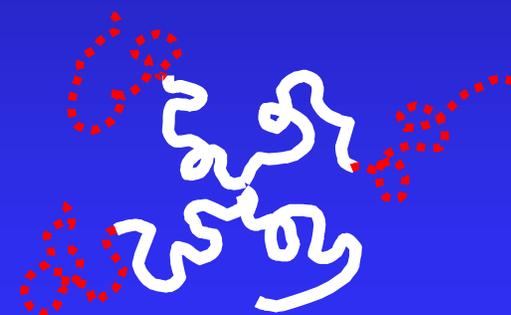
ABC 3-miktoarm



$A_2B_2$  4-miktoarm



$A_3B$  4-miktoarm



$(AB)_4$  4-miktoarm

# Block Copolymer Melts

High temperature: homogeneous mixing

Low temperature: demixing

**The key parameter is  $\chi N$**

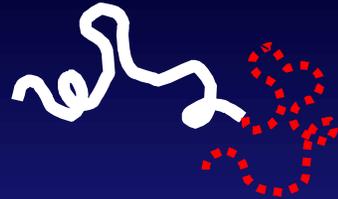
**$\chi$  = Flory-Huggins interaction parameter**

Contains a significant enthalpic component and is governed by incompatibility of the monomers

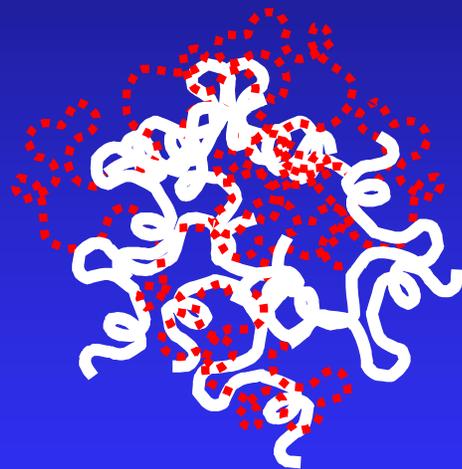
**$N$  = copolymer degree of polymerization**

Reflects the  $N$ -dependent translational and configurational entropy

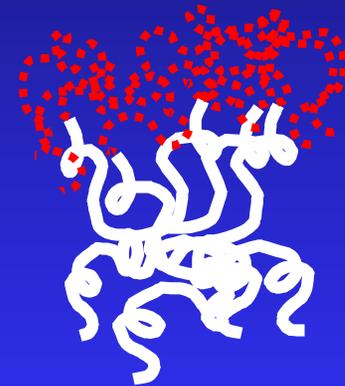
# Microphase Separation



Macroscopic phase separation is prevented by the covalent bond between the blocks.



**Order-Disorder  
Transition**



Creation of an interphase  
boundary region

Microphase separation takes place on the nanometer scale.

# Order-Disorder Transition for a Symmetric Diblock Copolymer

For a symmetric ( $f = 0.5$ ) diblock copolymer with equal segment sizes, the critical order-disorder transition is predicted by mean field theory to occur at  $(\chi N)_{\text{ODT}} = 10.5$ .

The ordered phase that is formed will depend upon the copolymer composition, which determines the curvature of the interface between blocks and their packing density.

# Phase Separation Regimes

## Weak segregation regime

$$\chi N \approx 10$$

Composition profile is sinusoidal about a mean value.

## Intermediate segregation regime

$$\chi N \approx 10 - 100$$

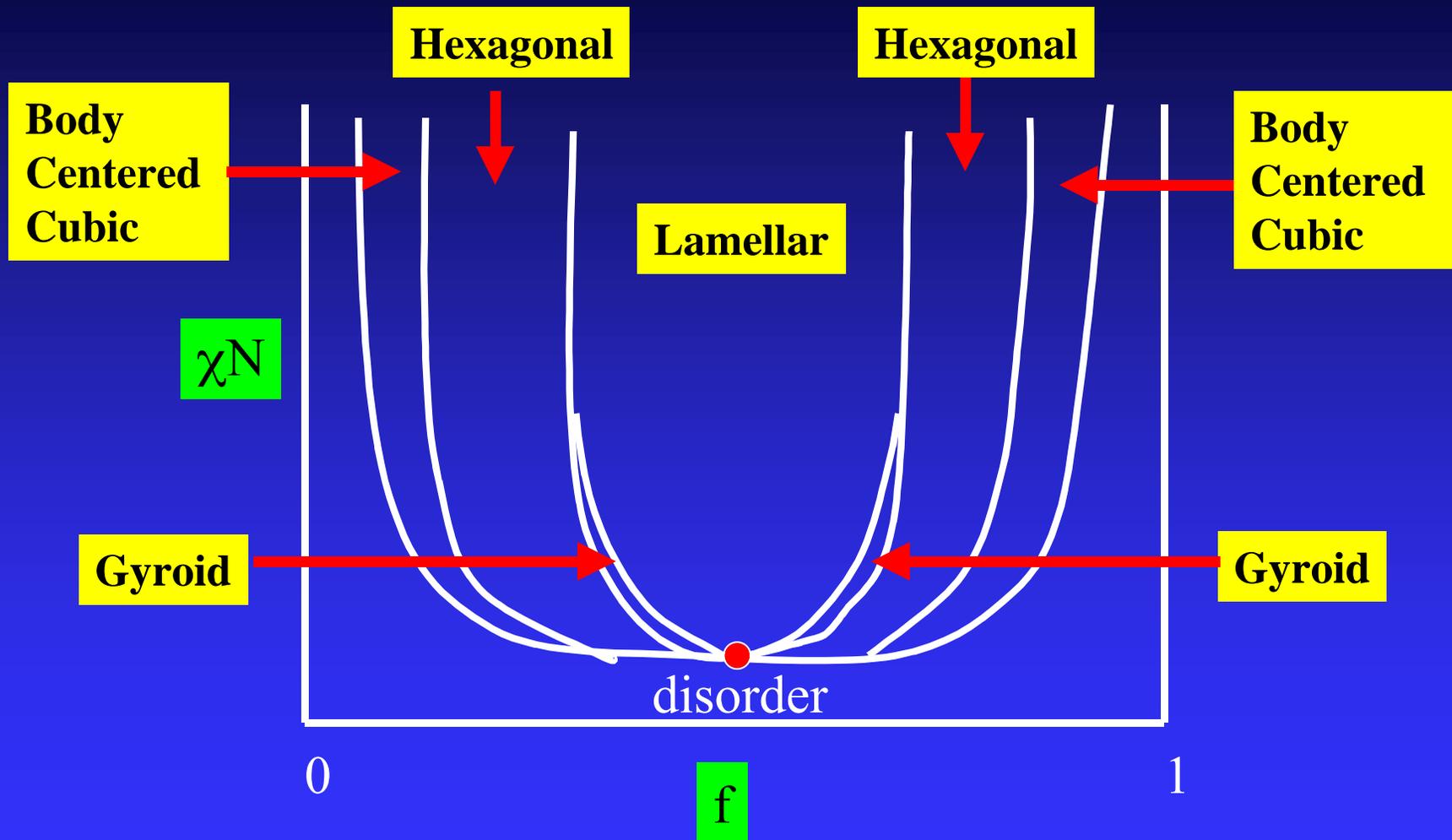
Profile sharpens with interphase between blocks becoming narrower.

## Strong segregation regime

$$\chi N > 100$$

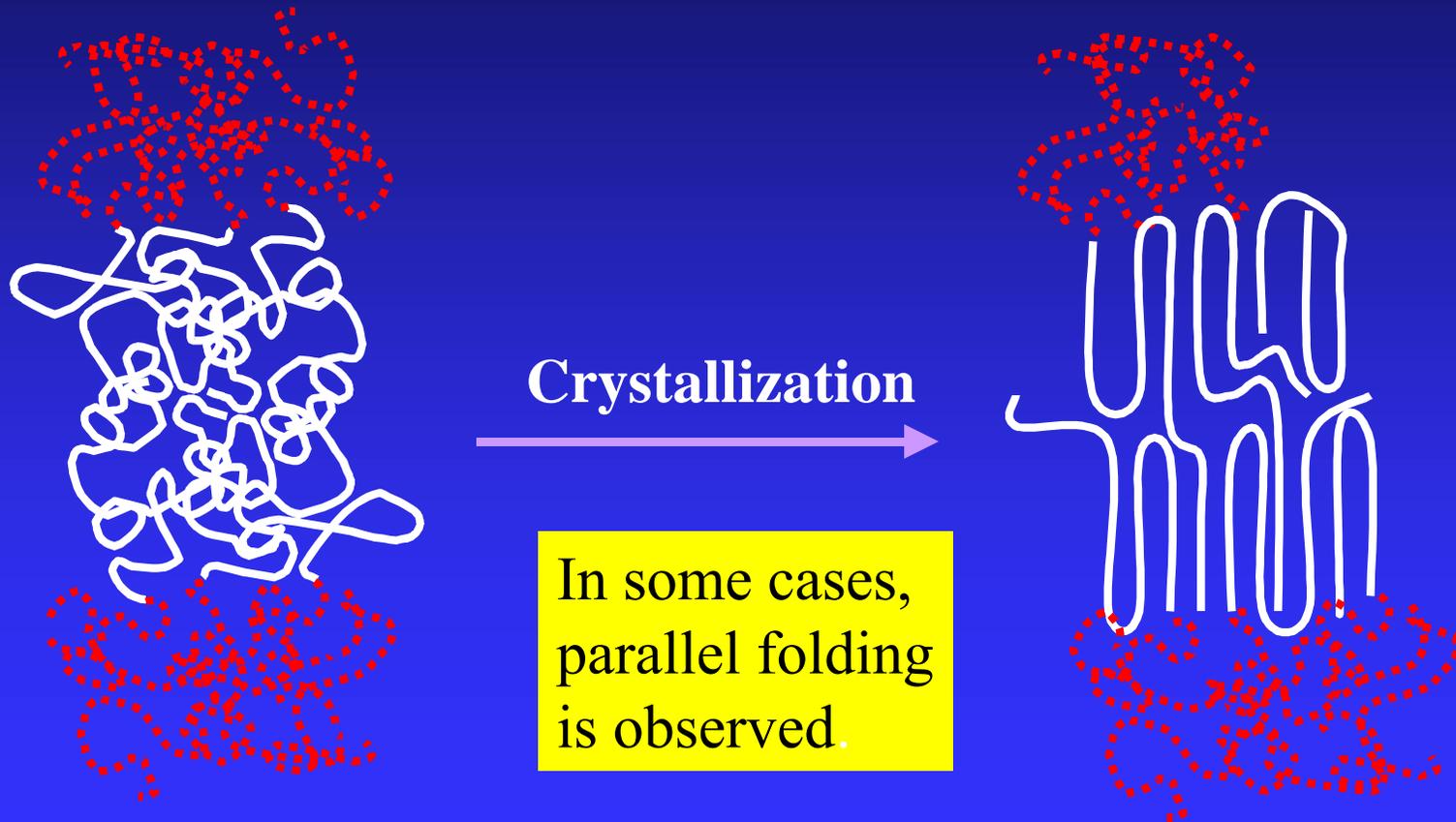
Domains contain essentially pure components.

# Phase Diagram



# Block Copolymers in the Solid State

The structure in block copolymer melts is usually trapped upon vitrification (formation of a glassy state). If one block can crystallize, a lamellar structure usually forms, but this may be a nonequilibrium state.



# Crystallization of Block Copolymers

## Whitmore and Noolandi

- Self-consistent mean field theory applied to diblocks where one block is amorphous and the other one is crystallizable.
- Amorphous regions were modeled as flexible chains, and the crystalline regions as folded chains.

# Crystallization of Block Copolymers

Lamellar thicknesses:

Amorphous:

$$l_a \propto N_a^{7/12}$$

Crystalline:

$$l_c \propto N_c N_a^{-5/12}$$

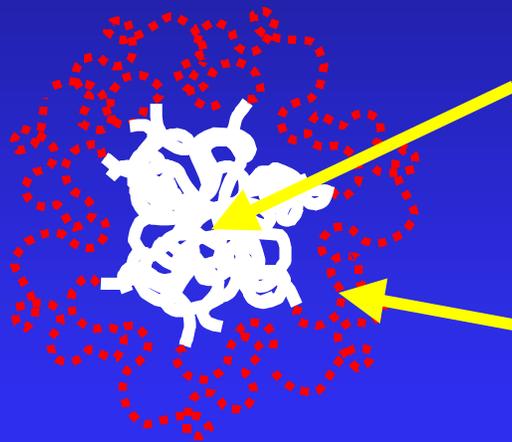
# Block Copolymers as Blend Compatibilizers



# Block Copolymers in Solution

## Micellization

- Forms upon placement of a block copolymer in a selective solvent.
- Typically spherical with aggregation numbers 30 - 100.
- Critical micelle concentration, temperature, and pressure



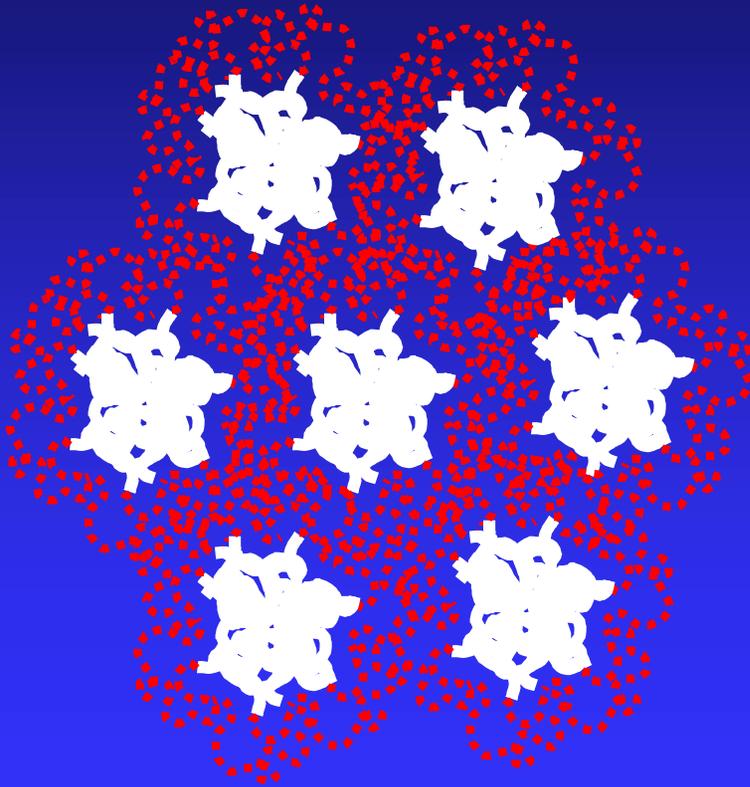
Micelle **core** consists of insoluble or poorly solvated block.

Micelle **corona** consists of selectively solvated block.

Example: Polystyrene-poly(ethylene propylene)  
in decane

# Block Copolymers in Solution

## Gelation



Gels have a finite yield stress;  
i.e. they are Bingham fluids..

# Techniques for Studying Block Copolymers

## Transmission Electron Microscopy

Most direct method for study of morphology in the melt and solid state but sample preparation technique is complex and critical. Misidentification of morphology can arise due to inspection of only a projection.

## Light Microscopy

Examine spherulitic structures of crystalline blocks in the solid and existence of lamellar and hexagonal-packed cylindrical micellar phases.

## Differential Scanning Calorimetry

Follow crystallization and glass transition as well as micellization and gelation in block copolymer solutions

# Techniques for Studying Block Copolymers

## Small-angle Neutron and X-ray Scattering

Excellent methods because the length scales probed are typical of block copolymer microstructures (1 - 100 nm).

## Small-angle Light Scattering

Weight-average molecular weight of block copolymers and of micelles in solution.

## Dynamic Light Scattering

Follow diffusion in polymer solutions and relaxation modes in block copolymer melts.

## Rheology

Locate the ODT through sharp decreases in storage and loss moduli and sol-gel transitions in concentrated block copolymer solutions.

# Techniques for Studying Block Copolymers

## **X-ray and Neutron Reflectivity**

Specular reflectivity measurements, coupled with an appropriate model, yield thicknesses of ultrathin films of block copolymer melts and block copolymers at a liquid-liquid interface.

## **Atomic Force Microscopy**

Chemical force and microscopic friction measurements of block copolymers in ultrathin films.