Lecture 14: Block Copolymer-Homopolymer Blends

- Analog to Low Molar Mass Surfactants
  - CMC
  - Micelles
  - Micellar Ordering

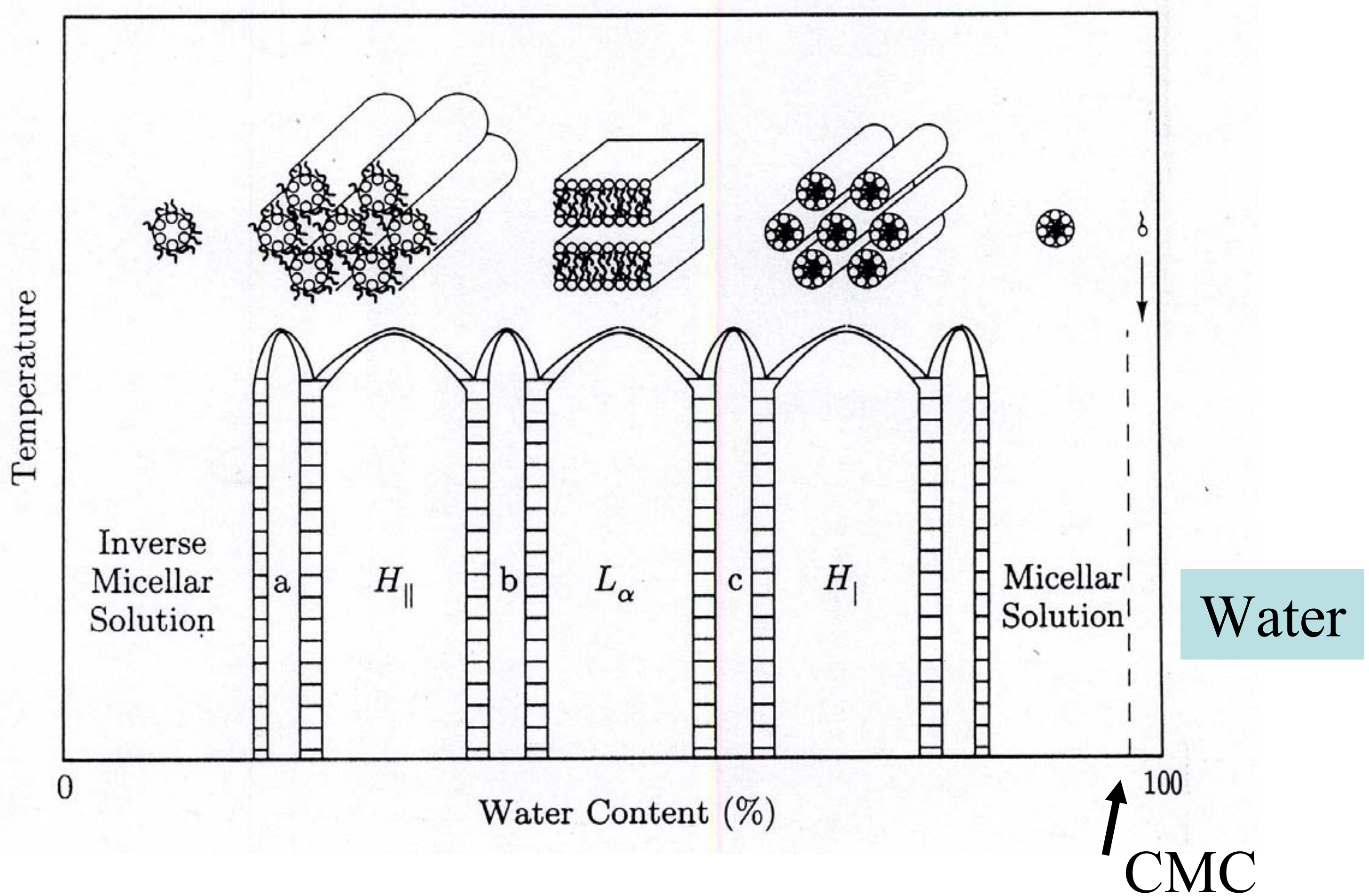
J. Israelachvili's Book: *Intermolecular and Surface Forces*

- BCP Micelles: Dilute diblock in a sea of homopolymer (solvent)
  - Leibler, Orland and Wheeler get it right
  - Micellar Shape Transitions

- Homopolymer Swollen Microdomains in Ordered Phases
  - Manipulating the IMDS: Shape Transitions

Low Molar Mass Amphiphiles

Binary Surfactant - Water Phase Diagram



Phase diagram and schematic representation of phases of aliphatic chains in water showing micellar solutions, lamellar (L_α), and hexagonal columnar $H_{||}$ and $H_|$ phases. (Seddon, 1990)

Ternary Phase Diagram: Oil, Water and Surfactant

Note similarity
to BCP microdomain
structures

Image removed due to copyright restrictions.

Please see Fig. 4.17 in Allen, Samuel M., and Thomas, Edwin L. *The Structure of Materials*. New York, NY: John Wiley, 1999. ISBN: 0471000825

Langmuir
Blodgett
Films

Langmuir
Blodgett
Films

Ordered Surfactant Phases

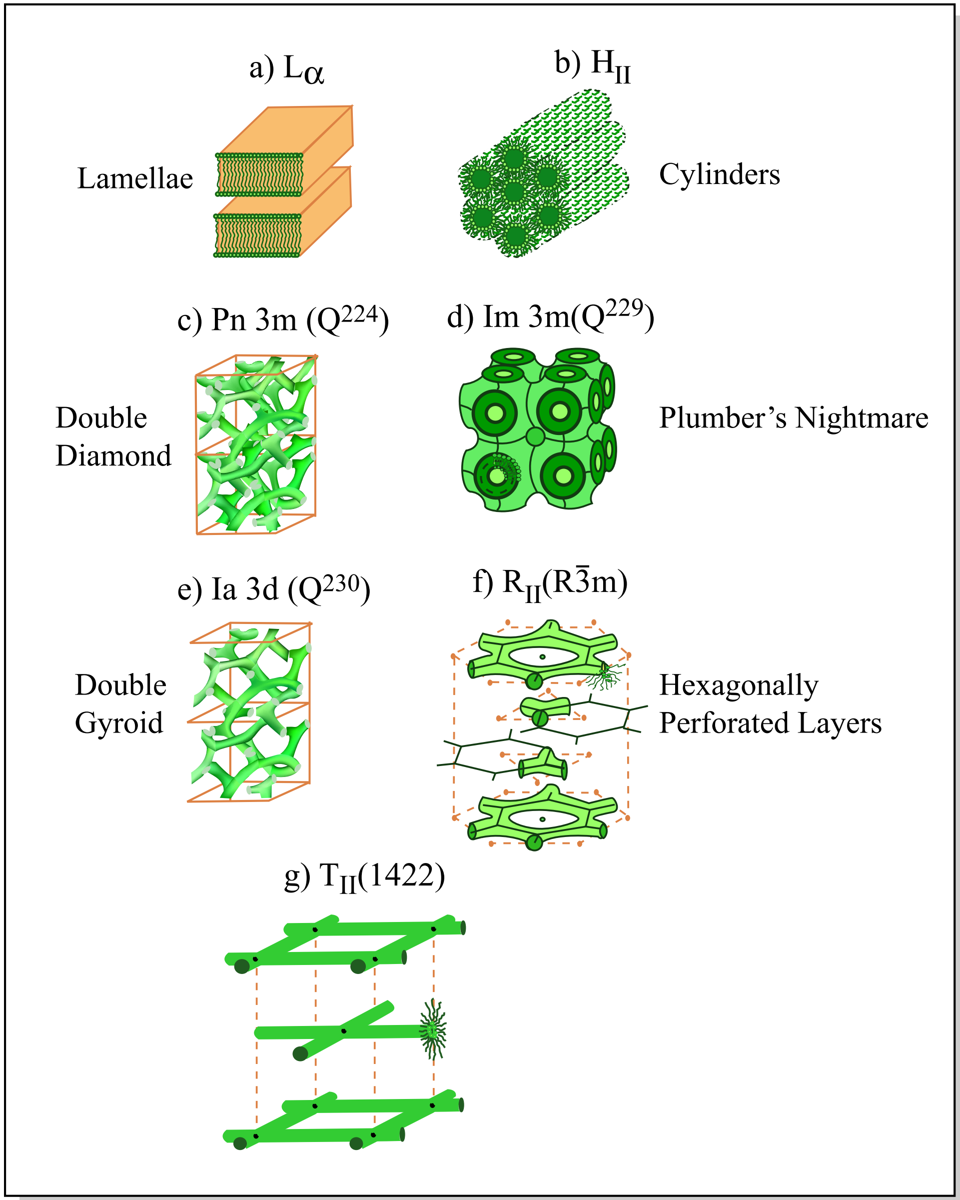


Figure by MIT OCW.

Effect of Concentration of Diblock on the Organization of Diblock/Homopolymer Blends

Please see Fig. 2 in Kinning, David J., et al. “Morphological studies of micelle formation in block copolymer/homopolymer blends.” *Journal of Chemical Physics* 90 (May 15, 1989): 5806-5825

Block Polymer Micelles in Homopolymer Fluids

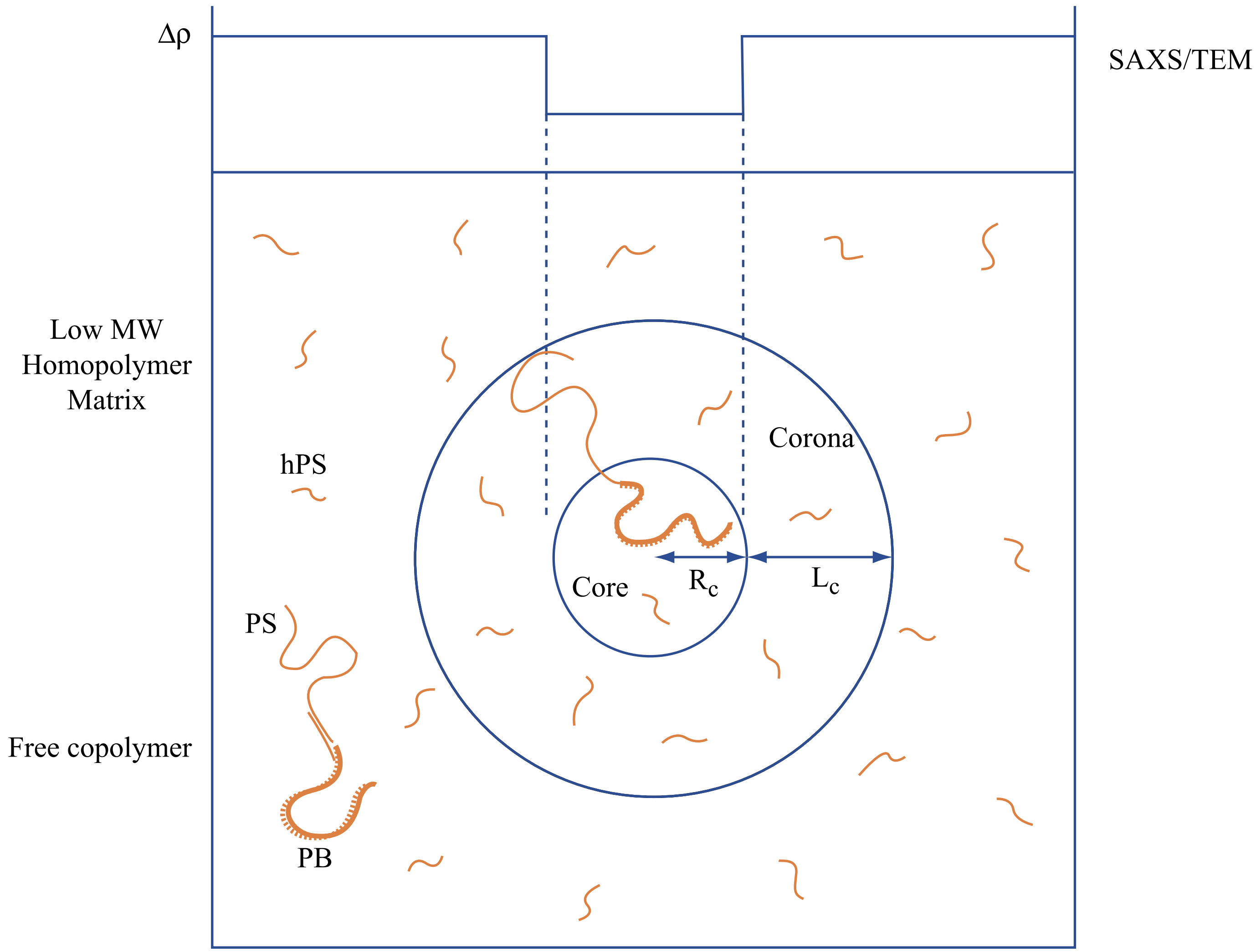


Figure by MIT OCW.

BCP Micelles

Molecular Variables

Copolymer Composition
Copolymer Concentration
Copolymer Molecular Weight
Homopolymer Molecular Weight

Micelle Characterization

Amount of Free Copolymer
CMC
Aggregation Number in Micelle
Core Size and Polydispersity
Corona Size
Amount of Homopolymer in Corona
Amount of Homopolymer in Core

Micelle Scaling Rules with Molecular Parameters

$$R_c \sim M_{PS}^{\alpha} \; M_{PB}^{\beta} \; M_{hPS}^{\gamma}$$

$$L_c \sim M_{PS}^{\delta} \; M_{hPS}^{\varepsilon}$$

PB Core
PS Corona
hPS Matrix

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Please see Fig. 1 in Kinning, David J., et al. "Morphological studies of micelle formation in block copolymer/homopolymer blends." *Journal of Chemical Physics* 90 (May 15, 1989): 5806-5825

Sample Preparation

- Cast films (1mm thick) from a 3 wt% solution of PS/PB in hPS in toluene (neutral solvent) over a 1 week period followed by drying at 40 C, vacuum drying for 1 week then anneal at 115C for 1 week, then quench in LN2.

- 1mm films to SAXS
- Cryoultramicrotome films (500 A thick), OsO_4 stain, TEM

Experimental Approach

- SAXS
  - CMC available from I(q, q -> 0) vs diblock conc.
  - R_C, R_{HS} from Percus-Yevick Hard Sphere Fluid Modeling of SAXS patterns
  - Ordering transition from appearance of Bragg peaks
  - Free copolymer content from SAXS invariant analysis
- TEM
  - CMC available from # micelles/area vs conc.
  - R_C from images (size distribution, shape transitions)
  - Ordering transition from images
  - Check for any macrophase separation

Anionic synthesis by L. J. Fetters

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Please see Table 1 in Kinning, David J., et al. "Morphological studies of micelle formation in block copolymer/homopolymer blends." *Journal of Chemical Physics* 90 (May 15, 1989): 5806-5825

Please see Table 2 in Kinning, David J., et al. “Morphological studies of micelle formation in block copolymer/homopolymer blends.” *Journal of Chemical Physics* 90 (May 15, 1989): 5806-5825

TEM of OsO_4 stained PB Micelle Core regions: Visual Determination of the CMC

PS/PB 20K/20K in 3.9K hPS

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Please see Fig. 3 in Kinning, David J., et al. “Morphological studies of micelle formation in block copolymer/homopolymer blends.” *Journal of Chemical Physics* 90 (May 15, 1989): 5806-5825

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Please see Fig. 4 in Kinning, David J., et al. “Morphological studies of micelle formation in block copolymer/homopolymer blends.” *Journal of Chemical Physics* 90 (May 15, 1989): 5806-5825

CMC

Dependence of CMC on Size of the Diblock and the Homopolymer

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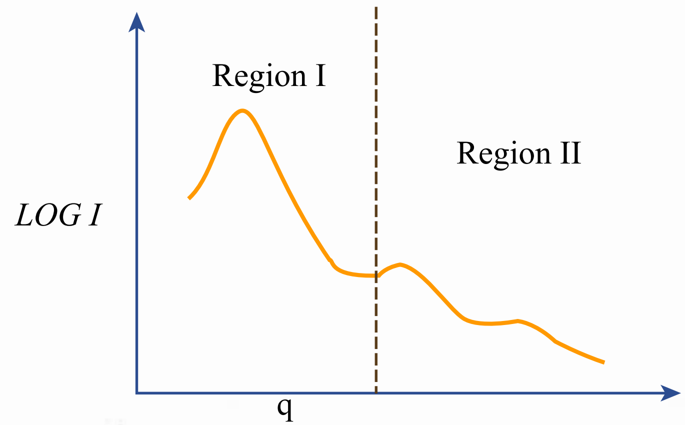
Please see Fig. 10 in Kinning, David J., et al. "Morphological studies of micelle formation in block copolymer/homopolymer blends." *Journal of Chemical Physics* 90 (May 15, 1989): 5806-5825

FITTING OF EXPERIMENTAL SAXS CURVES WITH PY THEORY

$$I(q) = P(q)\ S(q)$$

Where P(q) is the Interference factor and S(q) is The form factor

Use P-Y theory for P(q) and S(q) for a sphere



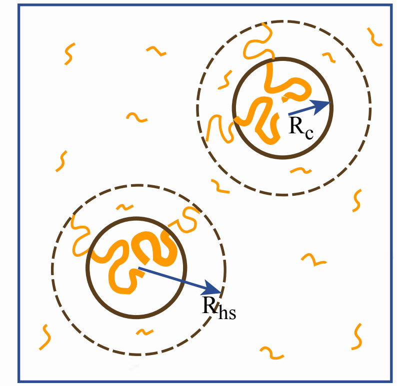


Figure by MIT OCW.

$$R_c,\ R_{hs},\ \eta,\ \varphi_c$$

- R_{core} and polydispersity in core (and subsequently corona) size determined by fitting the data in Region II.
- R_{hs} chosen by fitting the data in Region I.

$$\eta = (R_{hs}/R_{core})^3\ \phi_{core}$$

η = volume fraction of micelles

ϕ_{core} = volume fraction of micelle cores

Kinning, D.J. and Thomas, E.L., "Hard Sphere Interactions Between Spherical Domains in Diblock Copolymer Systems," *Macromolecules* 17, 1712-1718 (1984).

Percus-Yevick SAXS Modeling: Micelle Parameters

5.5 wt%
PS/PB 20/20
in
3.9K hPS

Data ……..
PY Model ___

Please see Fig. 5 in Kinning, David J., et al. "Morphological studies of micelle formation in block copolymer/homopolymer blends." *Journal of Chemical Physics* 90 (May 15, 1989): 5806-5825

Micelle-Micelle Interaction at Higher BCP Concentration

11.7 wt%
PS/PB 20/20
in
3.9K hPS

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Please see Fig. 5 in Kinning, David J., et al. "Morphological studies of micelle formation in block copolymer/homopolymer blends." *Journal of Chemical Physics* 90 (May 15, 1989): 5806-5825

Primitive Cubic Lattice Formation: Disorder (Liquid) to Order (Crystal) Transition

Bragg Peaks

24.9 wt%
PS/PB 20/20
in
3.9K hPS

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Please see Fig. 5 in Kinning, David J., et al. “Morphological studies of micelle formation in block copolymer/homopolymer blends.” *Journal of Chemical Physics* 90 (May 15, 1989): 5806-5825

LRO is primitive cubic
not body centered
cubic!

Disordered Micellar Fluid to Ordered Microdomain Lattice Transition

PS/PB 20/20 in 3.9 HPS

5.5% 11.9% 15.5%

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Please see Fig. 6 in Kinning, David J., et al. "Morphological studies of micelle formation in block copolymer/homopolymer blends." *Journal of Chemical Physics* 90 (May 15, 1989): 5806-5825

24.9% 30.3% 49.4%

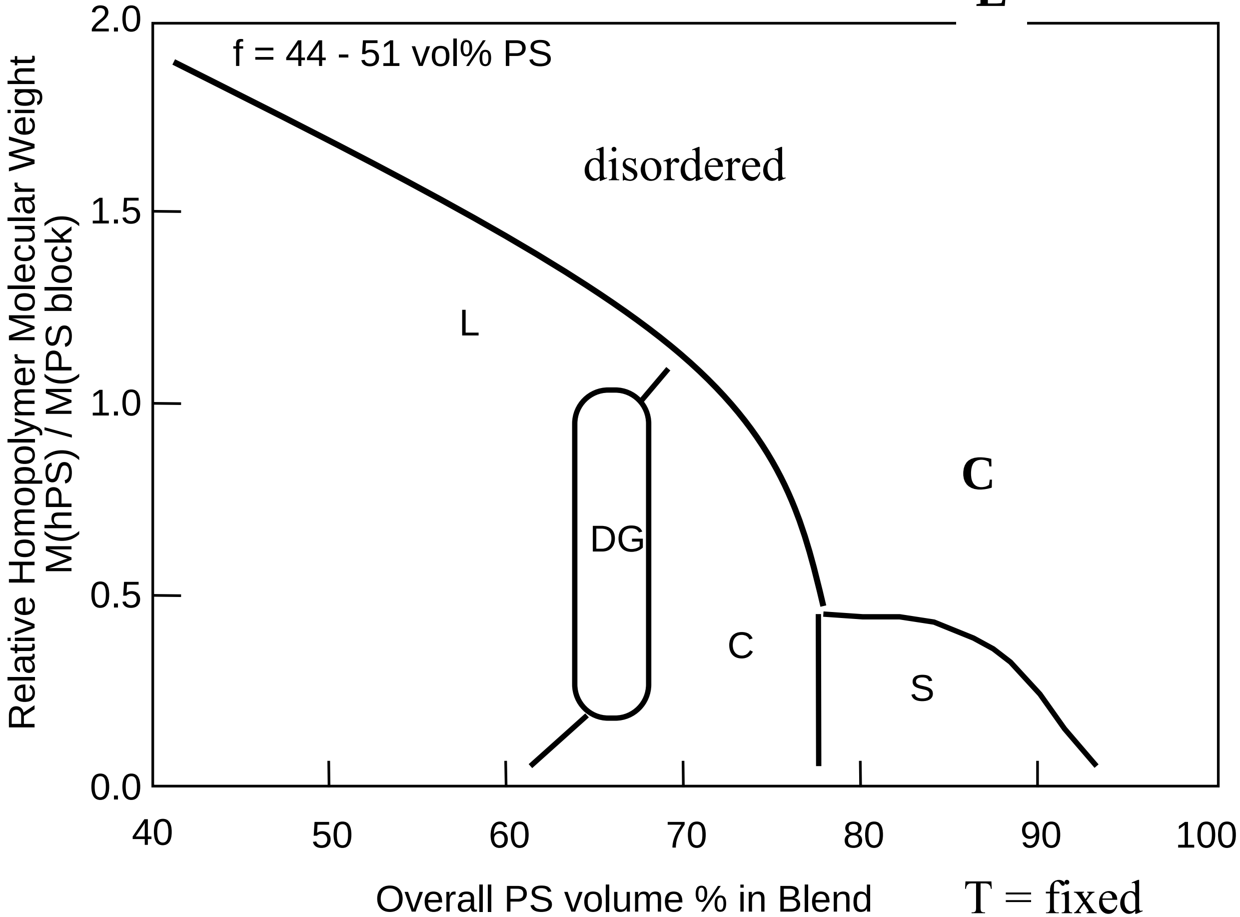
Ordered Spheres Ordered Spheres Cylinders!

Blending a lamellar copolymer with one of its homopolymers gives access to all the other morphologies

Please see Fig. 2 in Winey, K.I., Thomas, E.L. and Fetters, L.J. "Ordered Morphologies in Binary Blends of Diblock Copolymer and Homopolymer and Characterization of their Intermaterial Dividing Surfaces." *Journal of Chemical Physics* 95 (December 15, 1991): 9367-9375.

L

DG



C

S

T = fixed

Free Copolymer Fraction

Leibler, Orland & Wheeler, J. Chem. Phys. 79, 3550 (1983)

Experimentally, the free copolymer concentration continues to increase (slowly) past the CMC

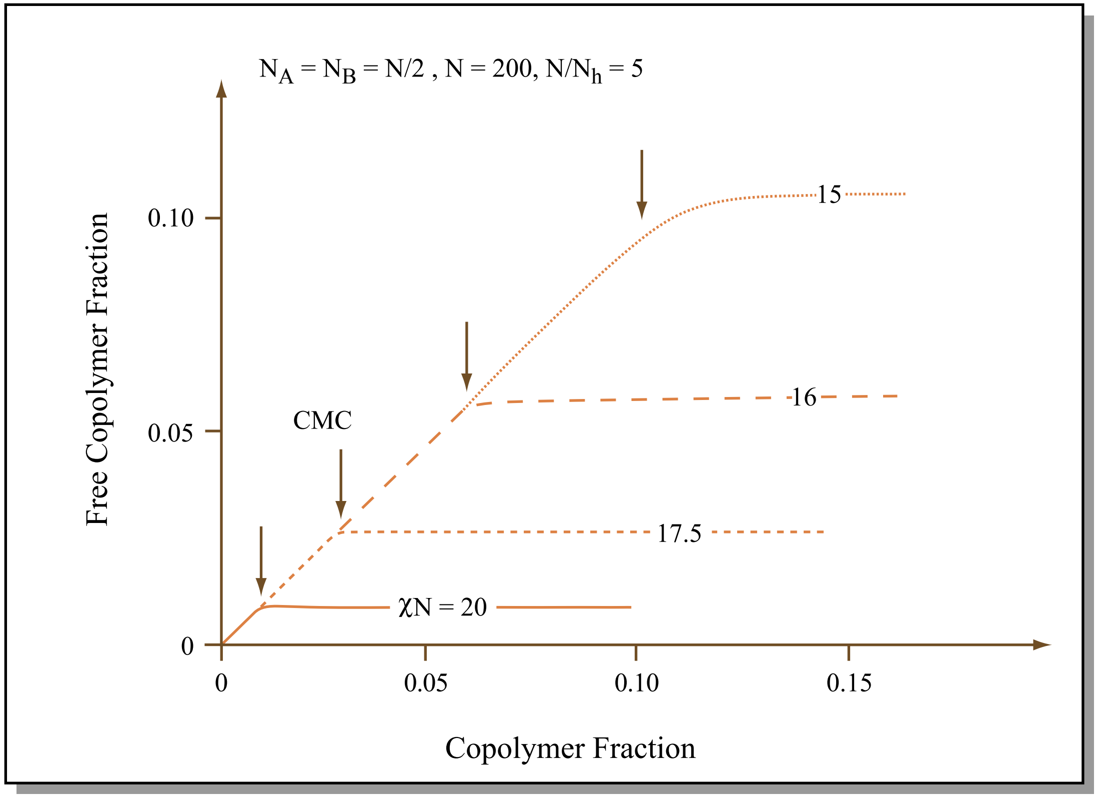


Figure by MIT OCW.

Scaling Rules for Micellar Parameters

$$R_c \sim M_{PS}^{\alpha} M_{PB}^{\beta} M_{hPS}^{\gamma}$$

$$L_c \sim M_{PS}^{\delta} M_{hPS}^{\varepsilon}$$

Homopolymer

Spherical Micelle

Free Copolymer

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Please see Fig. 1 in Kinning, David J., et al. "Morphological studies of micelle formation in block copolymer/homopolymer blends." *Journal of Chemical Physics* 90 (May 15, 1989): 5806-5825

Scaling Exponents

$$R_{CORE} \sim M_{PS}^{\alpha}\, M_{PB}^{\beta}\, M_{hPS}^{\gamma}$$

LOW Theory!

	Exp	Theory
α	-.20 + .05	-.05
β	.60 ± .04	.62
γ	.17 ± .04	.06

Theory *first* and then verified

Good Job!

$$L_{CORONA} \sim M_{PS}^{\delta}\, M_{hPS}^{\varepsilon}$$

	Exp	Theory
δ	.60 ± .04	.60
ε	-.18 ± .07	-.07

Effect of MW of hP on Micelle Structure

homopolymer

Number of copolymer chains per micelle decreases -> core radius decreases

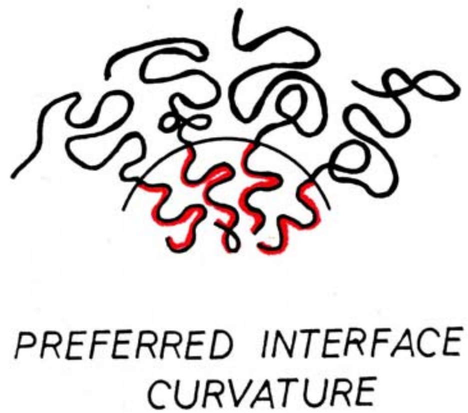
Volume fraction of homopolymer in corona increases -> corona thickness increases

Understanding the role of MW of the matrix

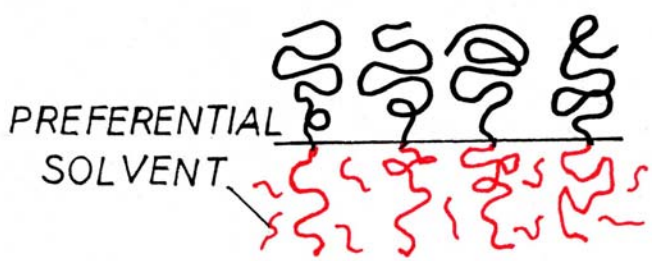
$$\varepsilon < 0$$

$$\gamma > 0$$

Manipulating the IMDS by Blending



Compositional Asymmetry



Preferred Swelling

Micelle Shape Change: Spheres to Cylinders

Please see Fig. 3 in Kinning, David J., et al. "Structural Transitions from Spherical to Nonspherical Micelles in Blends of Poly(styrene-butadiene) Diblock Copolymer and Polystyrene Homopolymers." *Macromolecules* 21 (1988): 3502-3506.

All Spheres

Mixture of Spheres and Cylinders