Lecture 13: Influence of Chain Architecture on Microdomain Characteristics

- Pursuit of New Block Polymer Structures…
  - AB: Diblocks, Rings, Multiblocks, Miktoarm Stars, Star-Diblocks
  - ABC: Terblock, Miktoarm Stars
- Novel Microdomain Patterns Arising:
  - The Theorist's Nightmare: Stadler's Goldmine
  - Processing: a neutral(?) solvent
  - Critical $N\chi_{AB}$ depends on Architecture
  - Architecture can drive block mixing

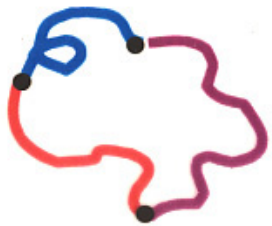
Possible Chain Architectures from an A/B/C Terpolymer

Flexible Coil-Noncrystalline A/B/C Copolymers

- **Linear**

Junctions confined to *surfaces*

- **Rings**



Junctions confined to *surfaces*

- **Miktoarm Stars**

Junction confined to *lines*

Predicting the Future of ABC Polymers

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Please see the final paragraphs of Mogi, Yasuhiro, et al. "Preparation and Morphology of Triblock Copolymers of the ABC Type." *Macromolecules* 25 (1992): 5408-5411.
and
Auschra, Clemens, and Stadler, Reimund. "New Ordered Morphologies in ABC Triblock Copolymers." *Macromolecules* 26 (1993): 2171-2174.

Typical Experimental Procedure

- Films were cast from $CHCl_3$ solutions (~4%wt) over a period of 4 days.

$$\delta_{PS} = 9.1(cal/cm^3)^{1/2}$$
$$\delta_{PI} = 8.2(cal/cm^3)^{1/2}$$
$$\delta_{PMMA} = 9.3(cal/cm^3)^{1/2}$$
$$\delta_{CHCl_3} = 9.3(cal/cm^3)^{1/2}$$

- Films were annealed under vacuum at 140^0C for 5 days.

- The X-ray diffraction patterns (SAXS) were acquired at room temperature at the Time-Resolved Diffraction Facility at the National Synchrotron Light Source at Brookhaven National Laboratory (X12B).

- Thin sections (500-1500 Å) were cryomicrotomed at -90^0C.

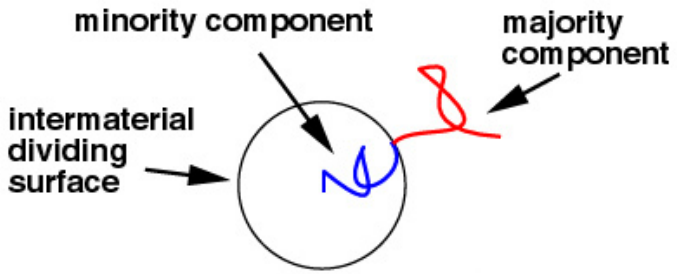
- Sections were stained
  OsO_4 (PI)
  RuO_4 (PS).

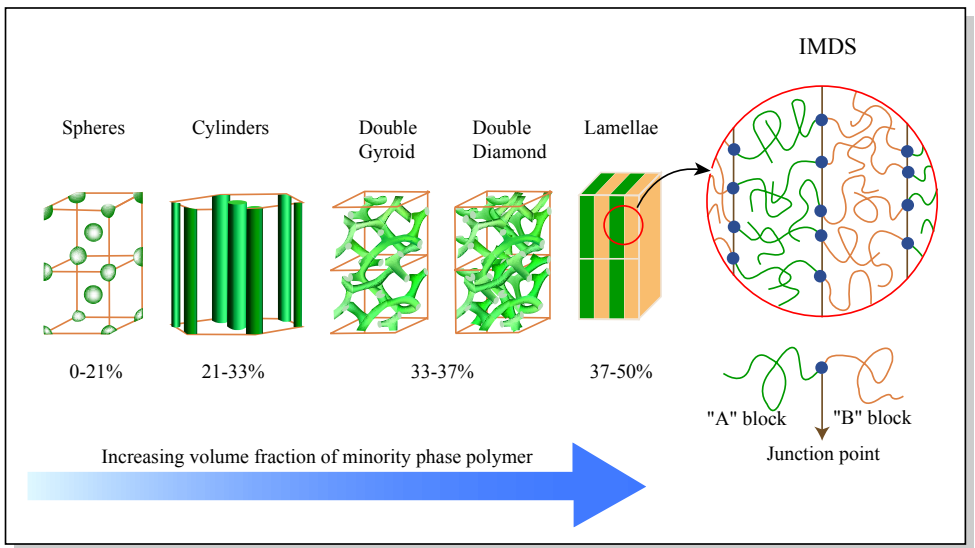
- Bright Field Transmission Electron Microscopy (TEM).

Complex Morphologies in ABC BCPs

Formation of Ordered Microdomains by **Self Assembly**

Linear AB Copolymer





Linear ABC Terpolymer

Image removed due to copyright restrictions.

Please see Bates, F. S., and Fredrikson, G. H. "Overview of ABC Structures and Thermodynamics." *Physics Today* 52 (February 1999): 32

Figure by MIT OCW.

MORPHOLOGY DIAGRAM FOR TERPOLYMERS

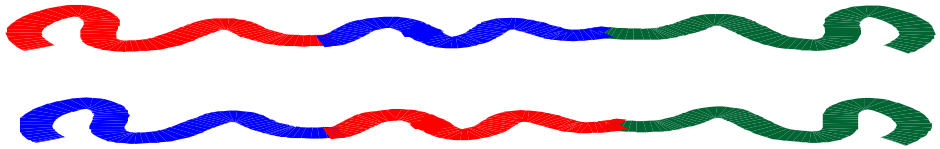
Ternary-like
Morphology Diagram

Image removed due to copyright restrictions.

Please see Fig. 9d in Tschierske, Carsten. "Non-conventional soft matter." Ch. 6 in *Annual Report on Progress in Chemistry C: Physical Chemistry* 97 (2001): 191-267.

"Stadler's Goldmine"

Sequence Matters: A/B/C



Images removed due to copyright restrictions.

Please see Fig. 2 in Gido, Samuel P., et al. "Observation of a Non-Constant Mean Curvature Interface in an ABC Triblock Copolymer." *Macromolecules* 26 (1993): 2636-2640.

ISV vs SIV 1:1:1

Concentric cylinders of P2VP, surrounded by a PI annulus in a matrix of PS

SIV

ISV

33/33/33 = Lamellae or Coaxial Cylinders

S.P. Gido, D.W. Schwark, E.L. Thomas, M.C. Goncalves, *Macromolecules*, 26, 2636 (1993)

Note: Noncircular IMDS

Why? Chi parameter and avoiding segment-segment contact

“Knitting Pattern” Microdomain Morphology

PS-PEB-PMMA

Linear triblock

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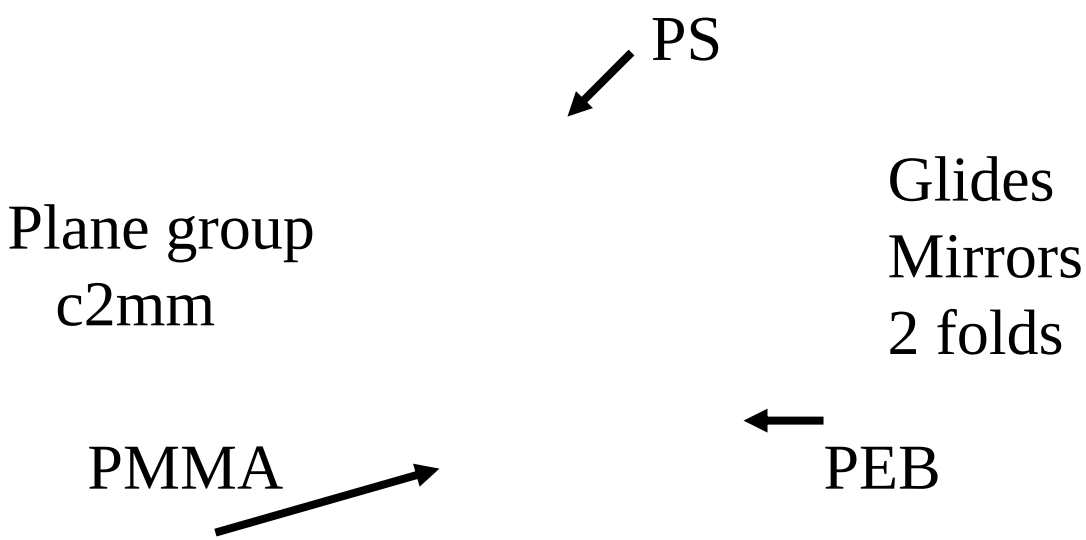
Please see Fig. 1 and 4e in Breiner, Ulrike, et al. “Structural Characterization of the ‘Knitting Pattern’ in Polystyrene-*block*-poly(ethylene-*co*-butylene)-*block*-poly(methyl methacrylate) Triblock Copolymers.” *Macromolecules* 31 (1998): 135-141.



Theorist's Nightmare, Uli's Knitting

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Please see Fig. 4b in Breiner, Ulrike, et al. "Structural Characterization of the 'Knitting Pattern' in Polystyrene-*block*-poly(ethylene-*co*-butylene)-*block*-poly(methyl methacrylate) Triblock Copolymers." *Macromolecules* 31 (1998): 135-141.

PS-PEB-PMMA

Linear triblock

ABC Terpolymer Microstructure

Image removed due to copyright restrictions.

Please see Fig. 4a in Breiner, Ulrike, et al. "Structural Characterization of the 'Knitting Pattern' in Polystyrene-*block*-poly(ethylene-*co*-butylene)-*block*-poly(methyl methacrylate) Triblock Copolymers." *Macromolecules* 31 (1998): 135-141.

Grain Boundaries & Defects

Non-CMC IMDS in PS/PEB/PMMA Triblock

Junction Distribution

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Please see Fig. 5a and 4b in Breiner, Ulrike, et al. "Structural Characterization of the 'Knitting Pattern' in Polystyrene-*block*-poly(ethylene-*co*-butylene)-*block*-poly(methyl methacrylate) Triblock Copolymers." *Macromolecules* 31 (1998): 135-141.

No Junctions

On IMDS!

2 differently shaped PEB domains

TEM Image

RuO_4 PS Staining

●

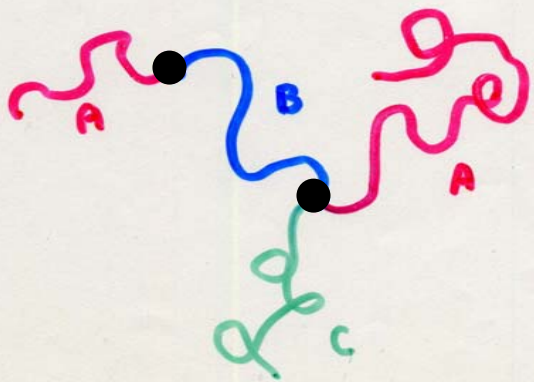
■

Q: Influence on Mechanicals?

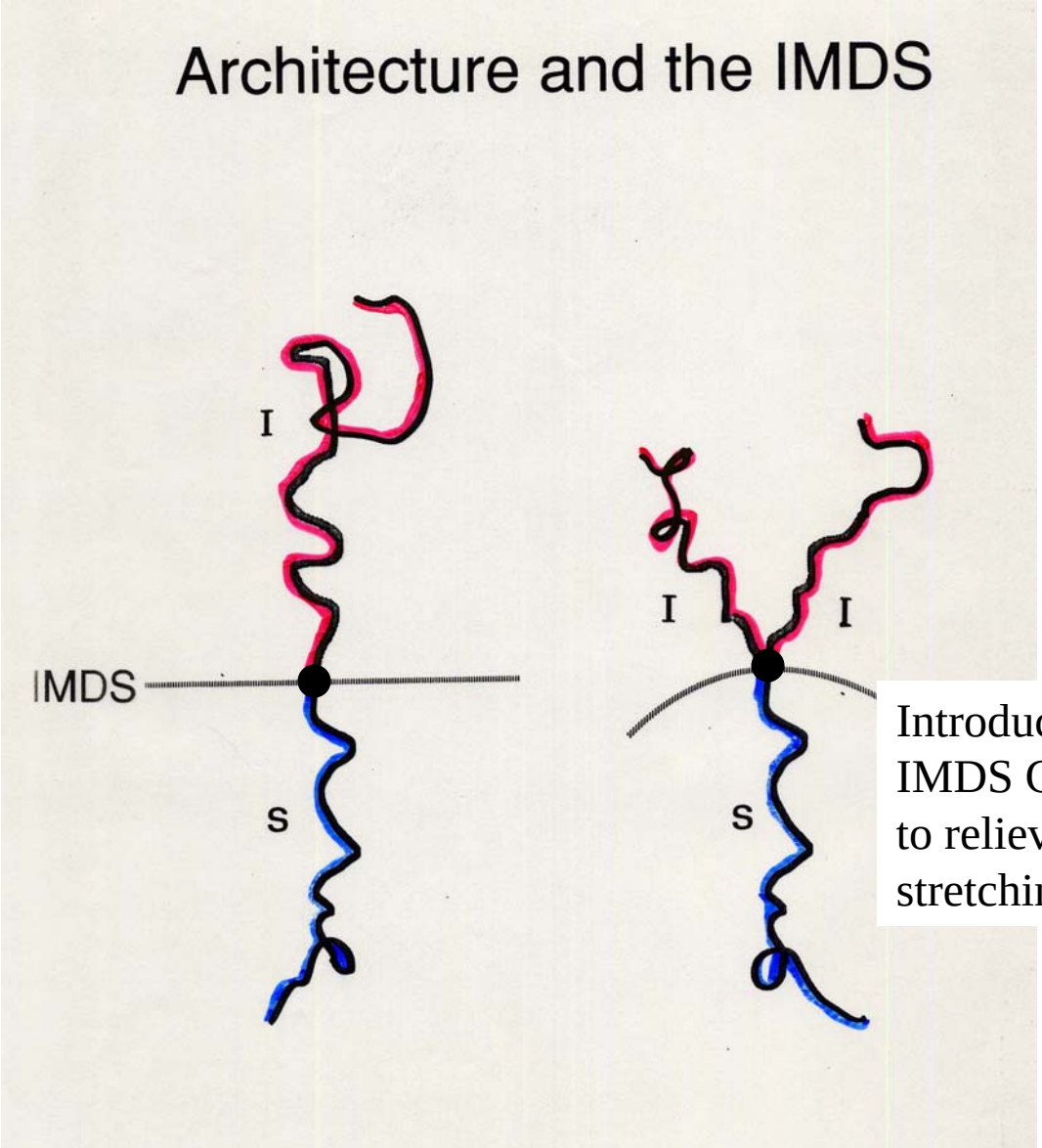
Types of Junctions

Junctions

- Number and Type of Junctions per copolymer interior/exterior ●
- Functionality of the Junction
- Compositional Bias across the Junction
- Chain Packing -Statistical Segment Differences
- Interface Area of the Junction
- Preferred Local Interface Curvature C_1 and C_2



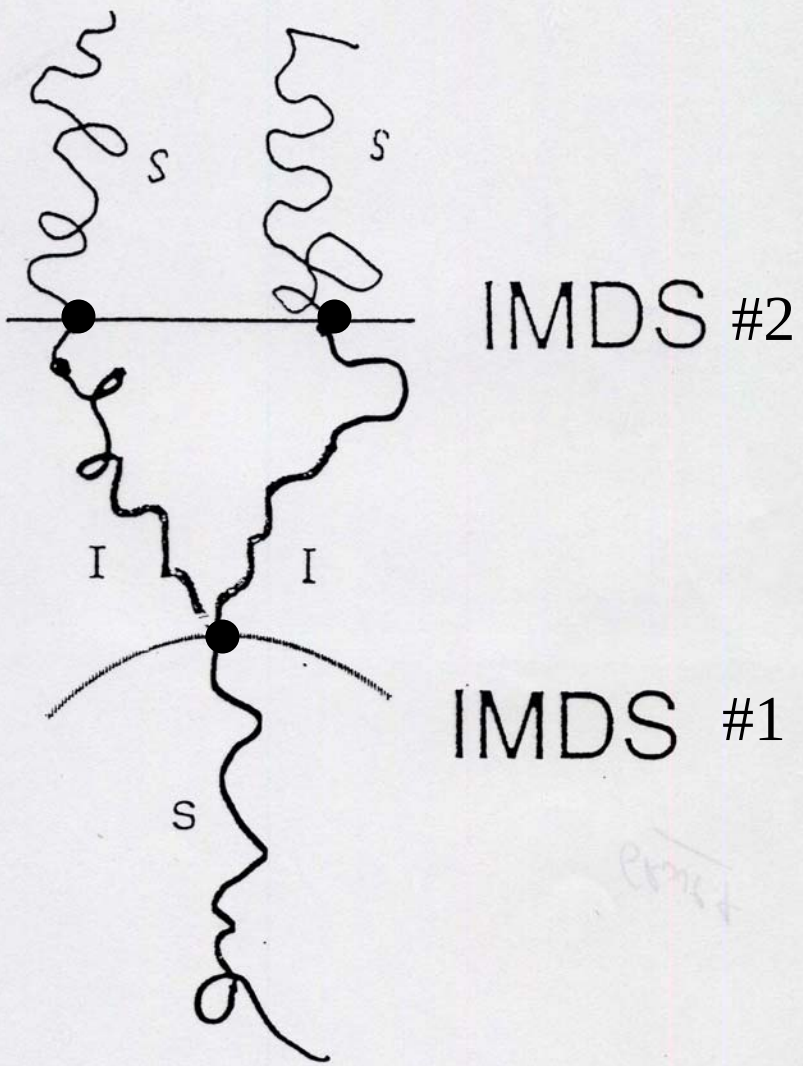
Architecture: Manipulating the IMDS At fixed Composition



Introduce IMDS Curvature to relieve chain stretching

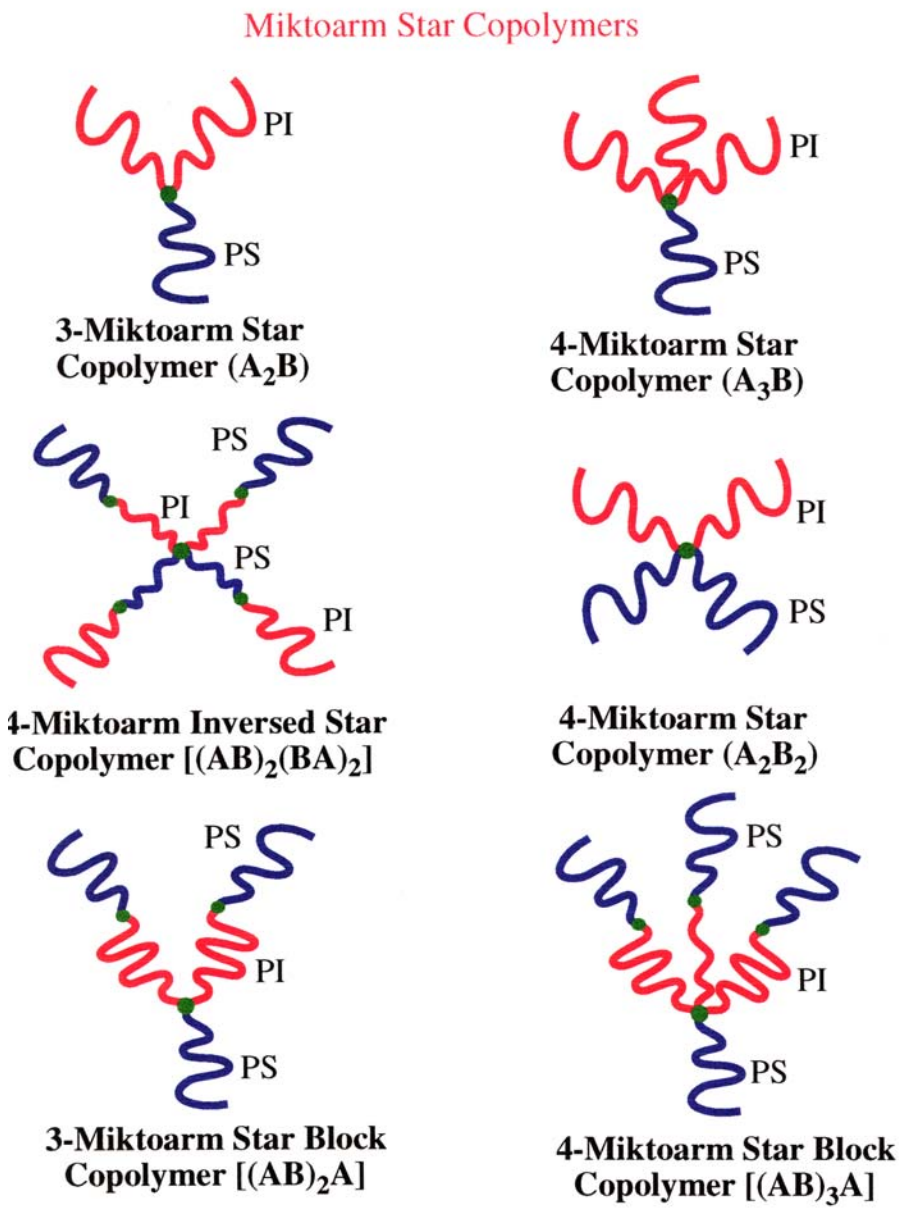
More Complexity: Multiple IMDS

Concept:
Locally preferred
IMDS Curvature



Miktoarm A/B Star Copolymers

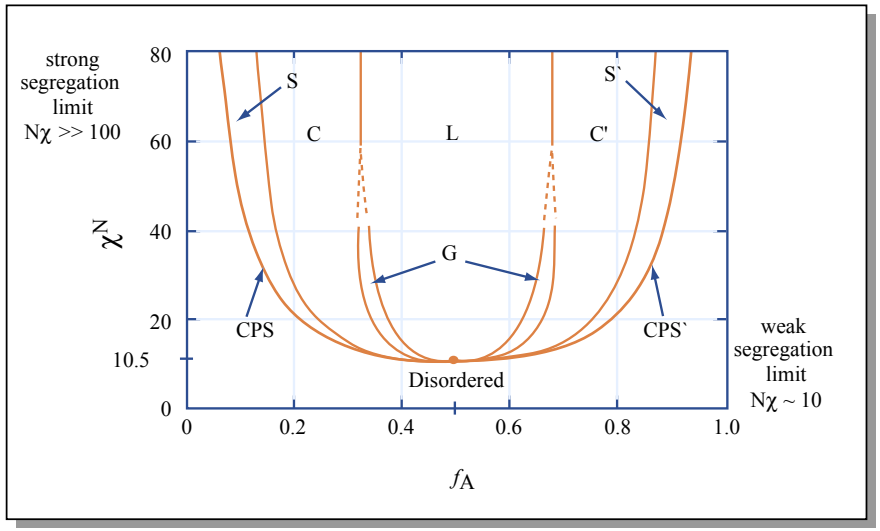
Miktos = mixed



Architectural Influence on the Morphology Diagram

$\varepsilon = 1$

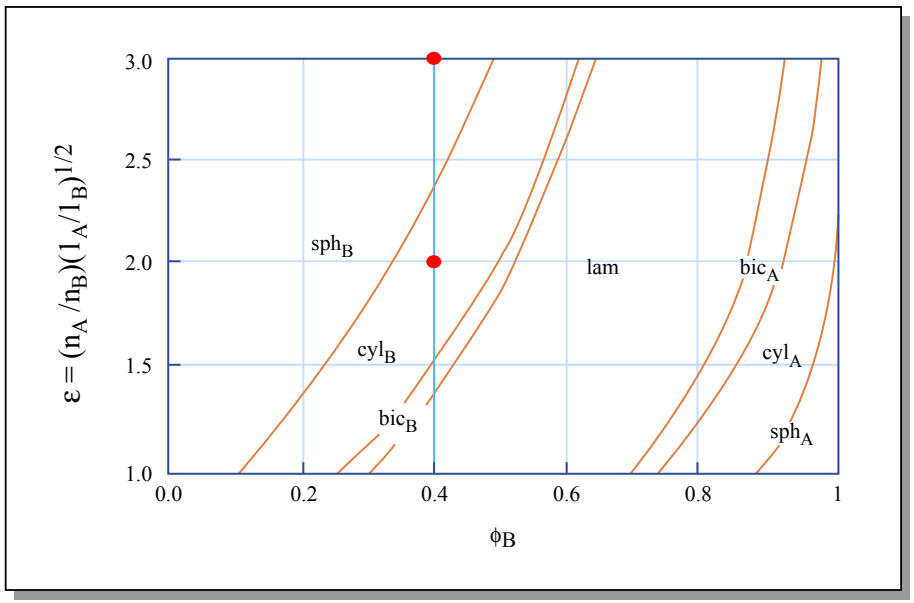
$l_A = l_B$



Leibler, 1980

Matsen and Schick 1996

Figures by MIT OCW.



n = number of arms

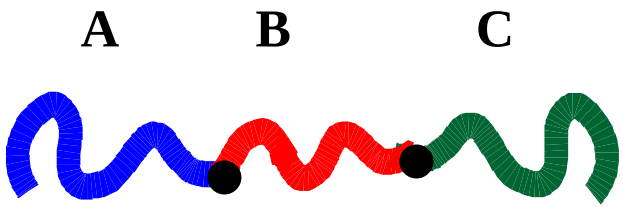
l = statistical segment

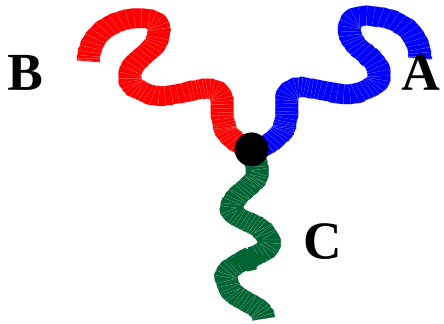
$\varepsilon = n_A/n_B\,(l_A/l_B)^{.5}$

Milner, 1994

ABC Polymers

Many Macromolecular Architectures...





Two junctions

Confined to IMDS ***Surfaces***

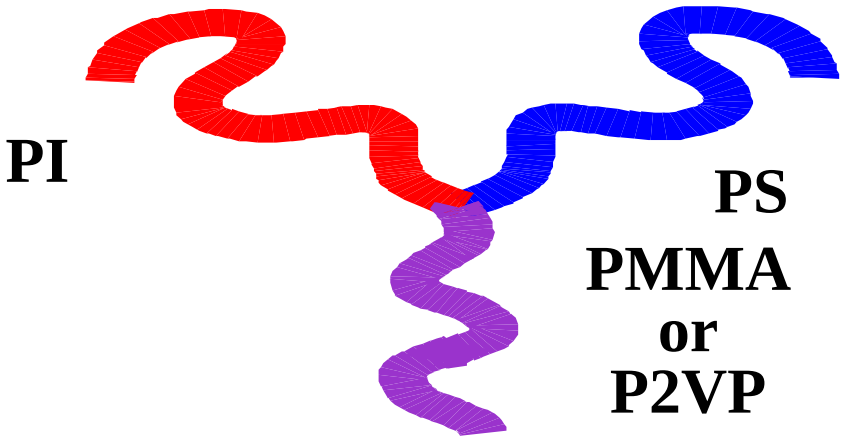
Dependence on the block sequence

One junction

Confined to ***Lines***

All blocks interact

SYNTHESIS AND PHASE SEPARATION OF MODEL 3-MIKTOARM STAR TERPOLYMERS



Synthesis *(Anionic Polymerization, Controlled Chlorosilane Chemistry)*

Molecular Characterization *(SEC, MO, LALLS, NMR)*

Morphology *(TEM, SAXS)*

ABC Miktoarm *Star* Terpolymers

ABC Miktoarm Star Block Copolymers

For 2 dimensional periodic structures, the components form domains which partition the material into polygonal structures, with all 3 arm components contacting at every vertex of the structure.

Junctions are confined to periodic lines which are orthogonal to and pass through the vertices of the tiling.

In 2 dimensions, the condition to minimize interfacial boundary length at fixed area favors formation of constant curvature domain boundaries: segments of circular arcs or straight lines.

References:

A/B Chain Architecture and Asymmetry Effects on the Morphology Diagram
S. T. Milner, Macromolecules 27, 2227 (1994)

Theoretical ABC Morphology Diagrams for Strong Segregation
W. Zheng and Z-G Wang, Macromolecules 28, 7215 (1995)

Overview of ABC Structures and Thermodynamics
F. S. Bates and G. Fredrickson, Physics Today, 32, Feb (1999)