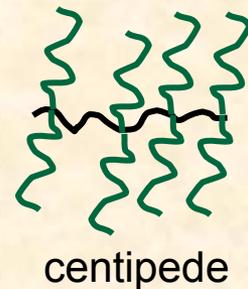
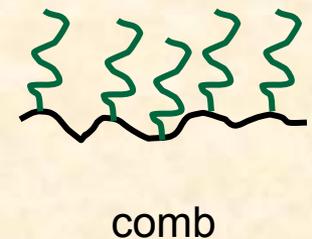
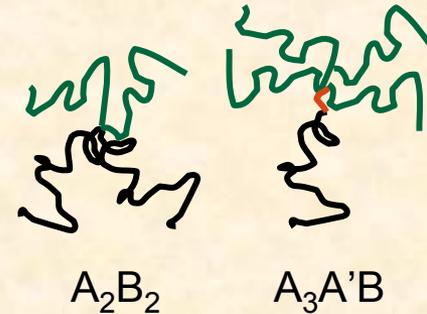
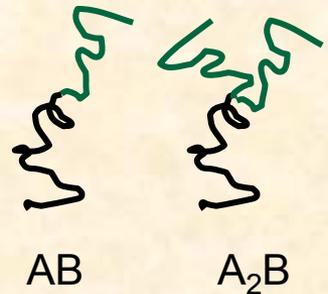


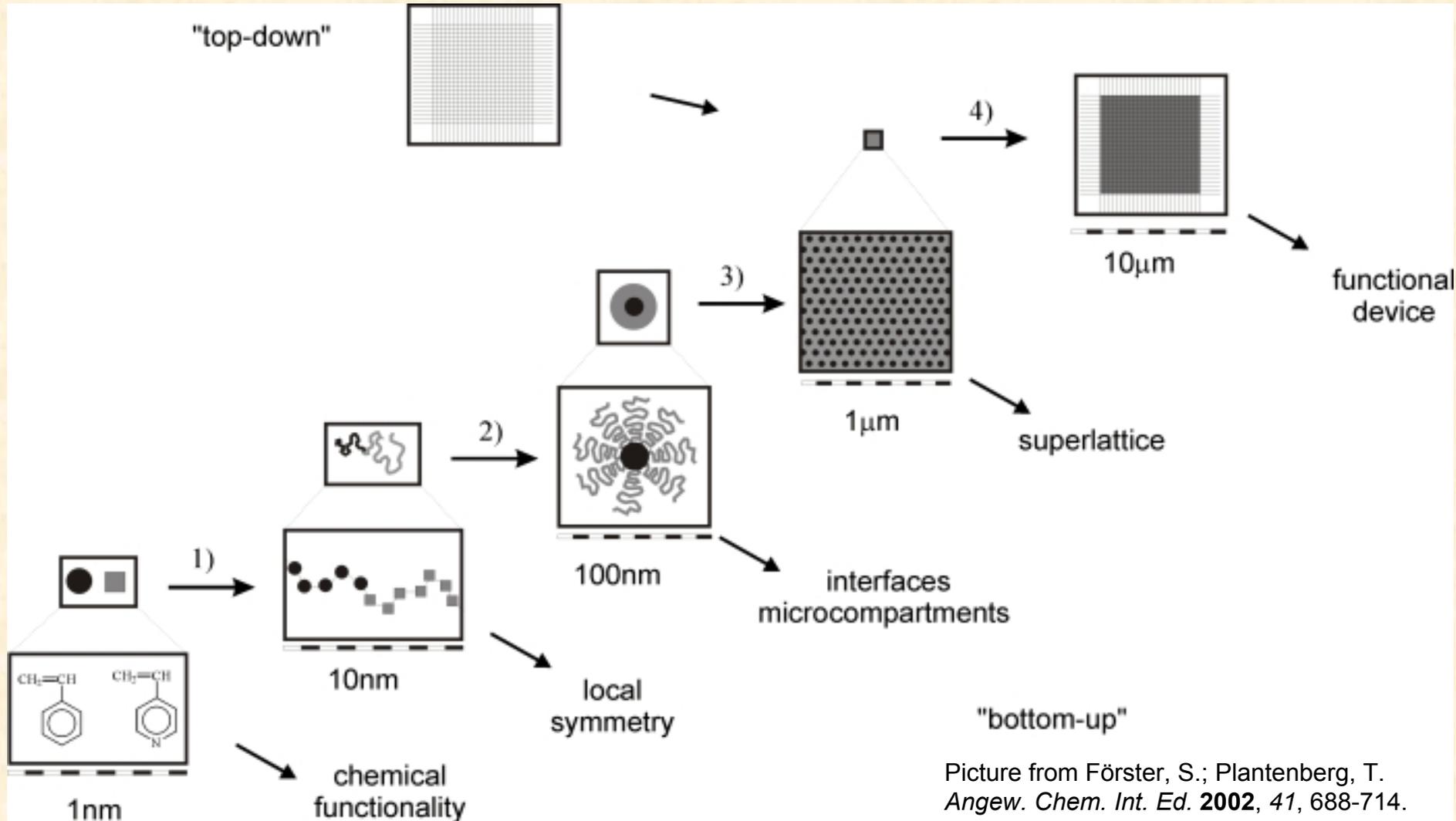
Synthesis and Characterization of Novel Polymer Architectures

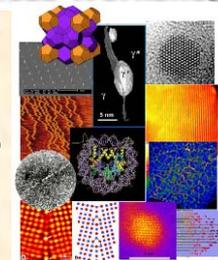
Phillip F. Britt

Center for Nanophase Materials Sciences
Chemical Sciences Division
Oak Ridge National Laboratory



Material Science at the Nanoscale



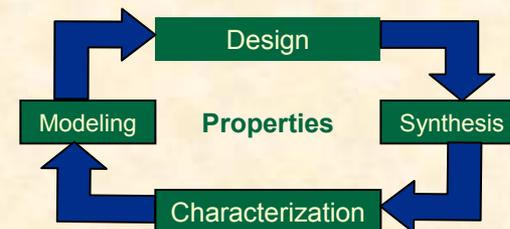


Results from CNMS Planning Workshops

Synthetic and Bio-Inspired Macromolecular Materials

● Scientific Grand Challenges

- To design and control the nanoscale organization of macromolecular materials to achieve novel functionality



● Key Issues

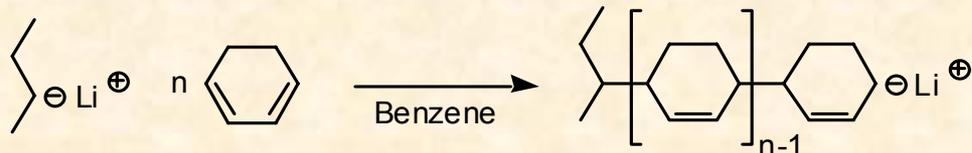
- Design and synthesize complex macromolecular architectures
- Develop directed self-assembly strategies
- Generate biological function by hierarchical structures to achieve material properties
- Understand the effect of nanoscale confinement on structure, dynamics, and properties of macromolecular systems
- Understand and control the nature of interfaces in nanophase macromolecular systems
- Develop a theoretical understanding and predictive capabilities to achieve the above

● Unstated Grand Challenge: Characterization of materials

Controlled Polymer Synthesis

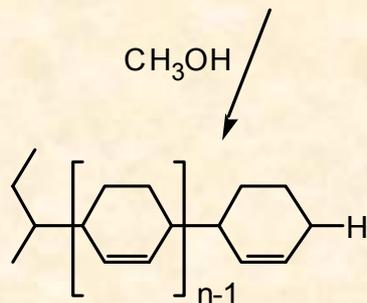
- Living anionic techniques
 - High degree of control over block length, architecture (reactive anions remain at chain ends), and low polydispersities ($M_w/M_n = 1 + X_n^{-1}$)
 - However, very labor intensive - extensive reagent purification
 - Not compatible with electrophilic or acidic groups
- Living (controlled) free-radical techniques
 - Atom Transfer Radical Polymerization (ATRP)
 - Stable Free Radical Polymerization (SFRP)
 - Reversible-Addition Fragmentation Transfer (RAFT)
 - Potentially simpler method to make reasonably well-defined blocks with polydispersities (M_w/M_n) 1.1-1.3
 - Applicable to a wide variety of monomers
 - Complex polymer architectures possible (reactive end groups)
- Cationic Polymerization
 - Limited monomers

Synthesis of Poly(1,3-Cyclohexadiene)

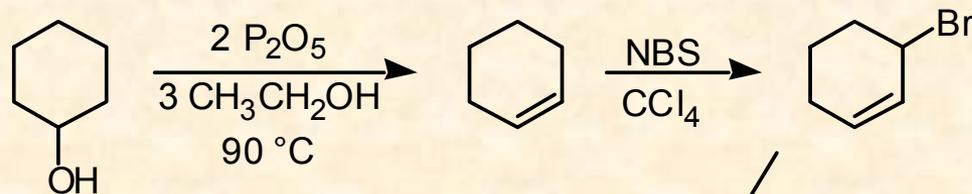


H: $M_n = 7.8 \text{ K}$
PDI = 1.07

D: $M_n = 8.7 \text{ K}$
PDI = 1.06

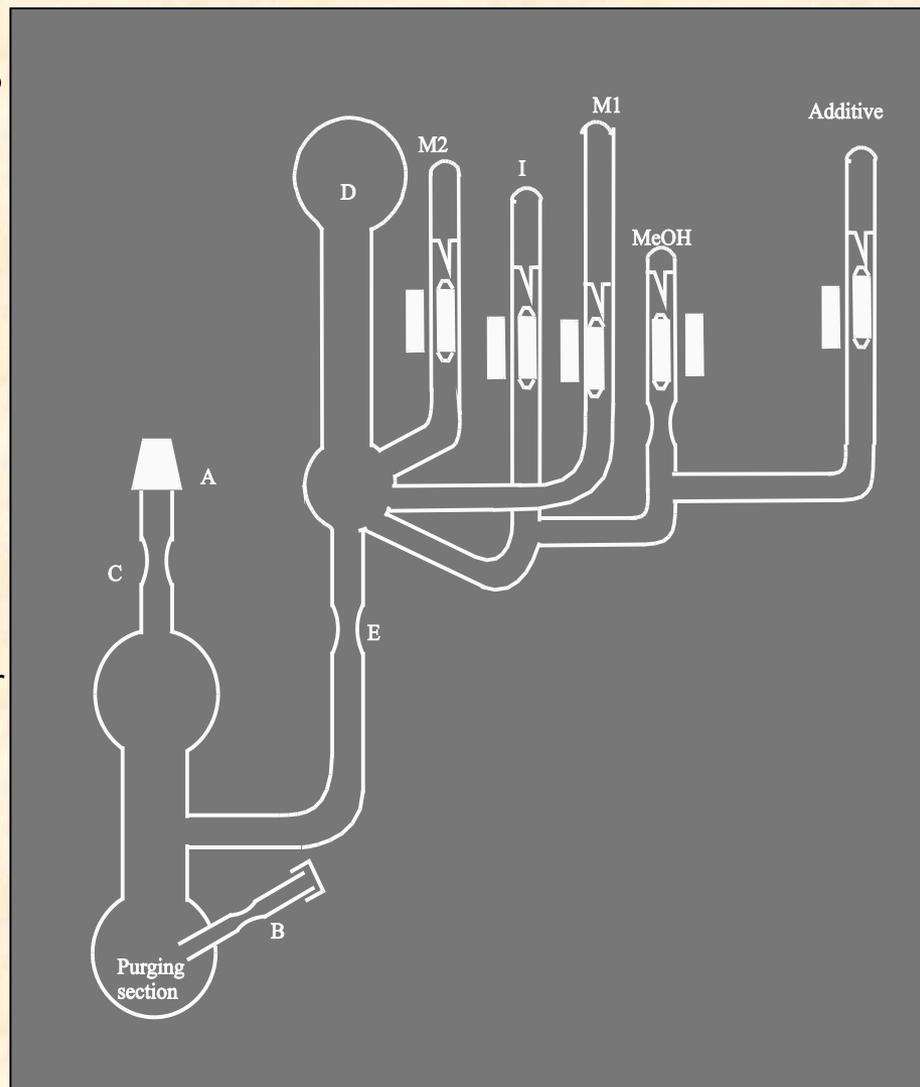
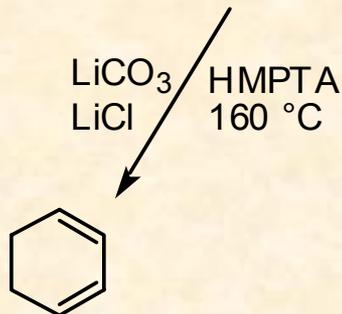


Synthesis of deuterated monomer



H: 58% yield

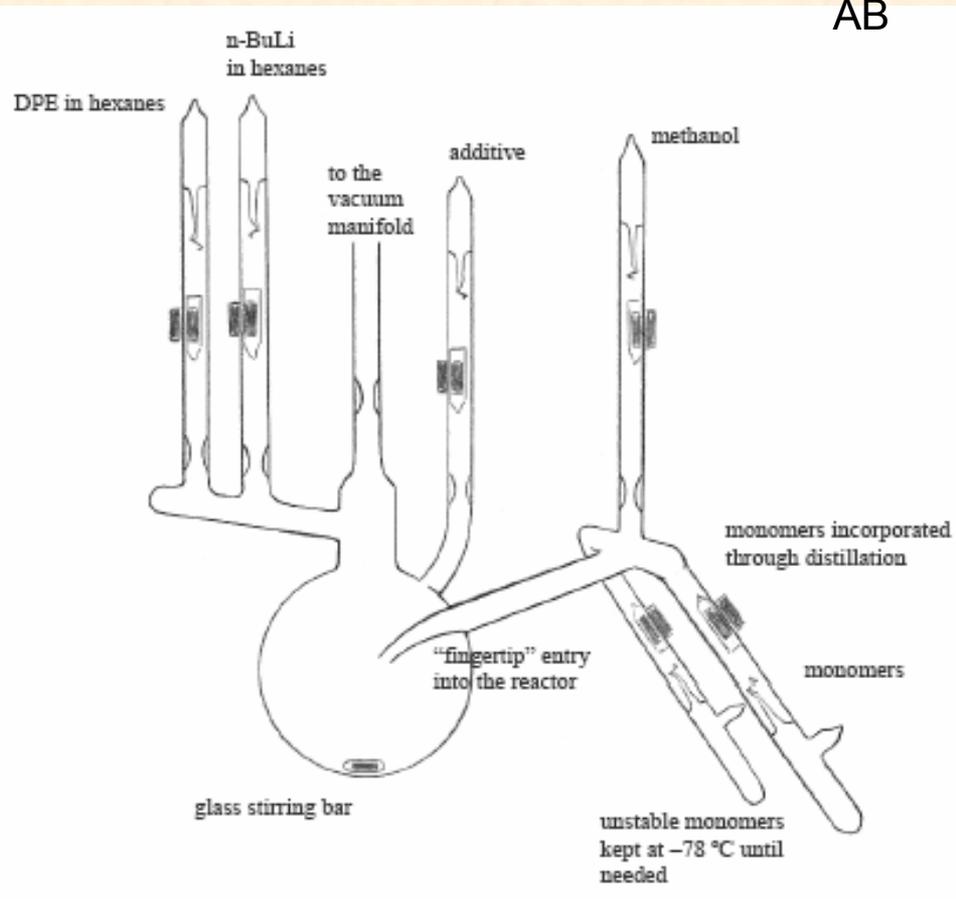
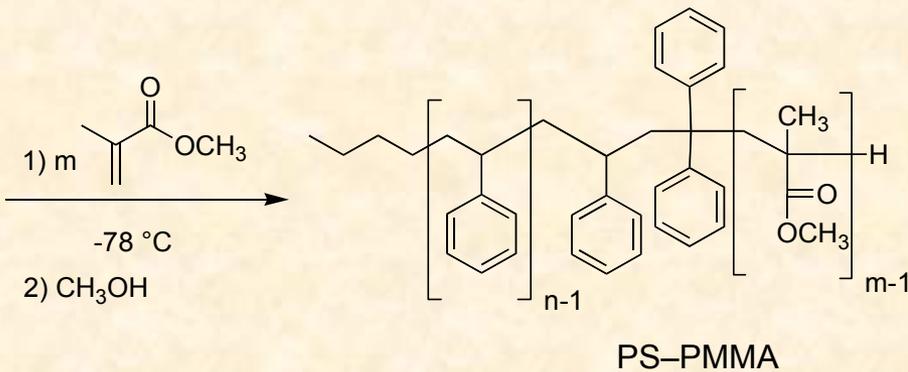
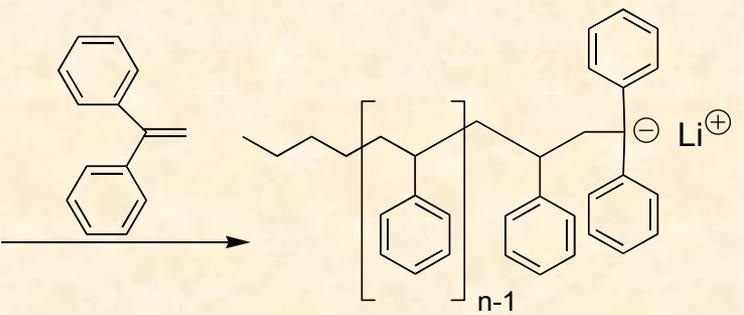
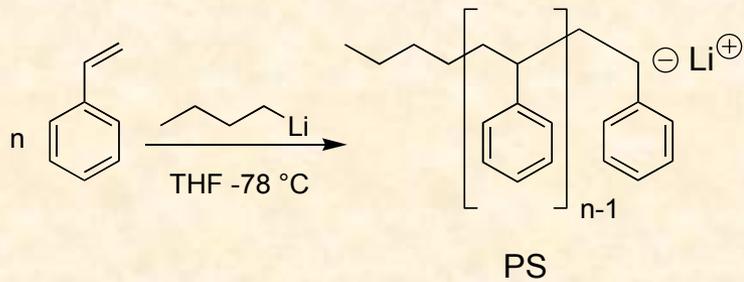
D: 32% yield
99.7% pure
%D > 94%



Synthesis of Polystyrene-*block*-Poly(methyl Methacrylate)

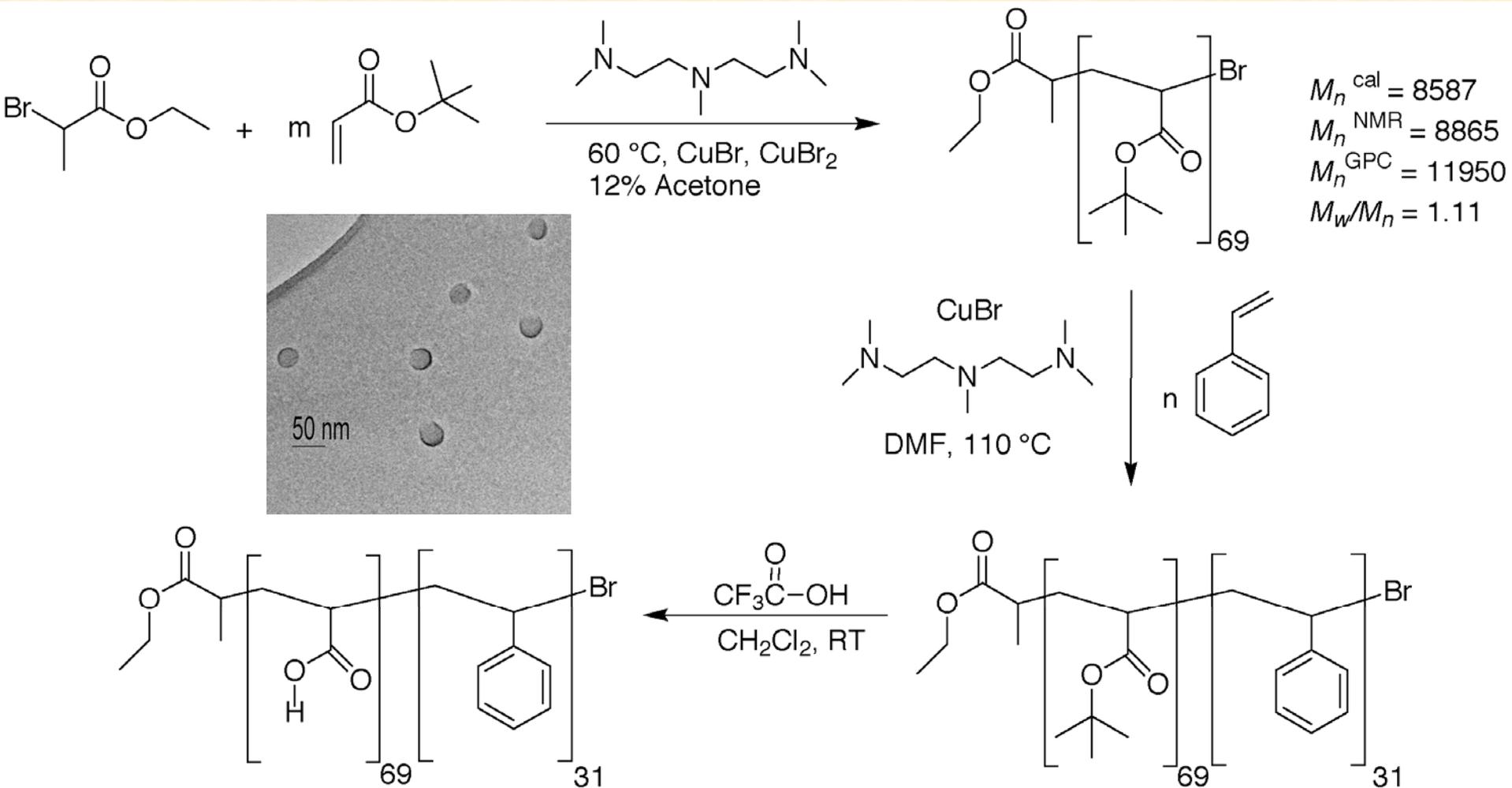
Wang

AB



$M_w = 41 \text{ K}$
 $\text{PDI} = 1.1$
 $\phi_{\text{PS}} = 29$

Synthesis of PAA-PS



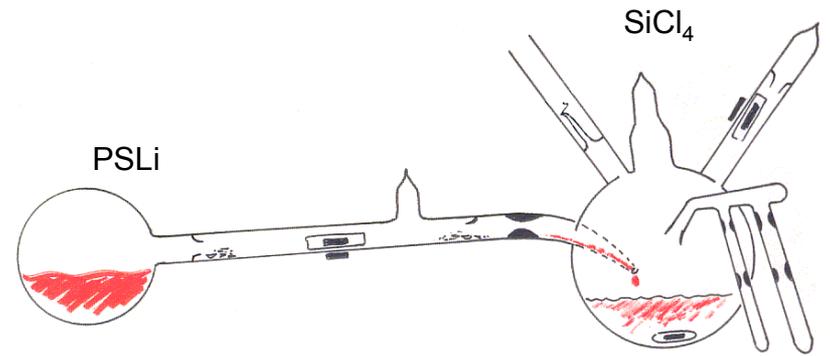
Effect of Polymer Architecture on Ordering

- **Sam Gido, University of Massachusetts, Amherst**

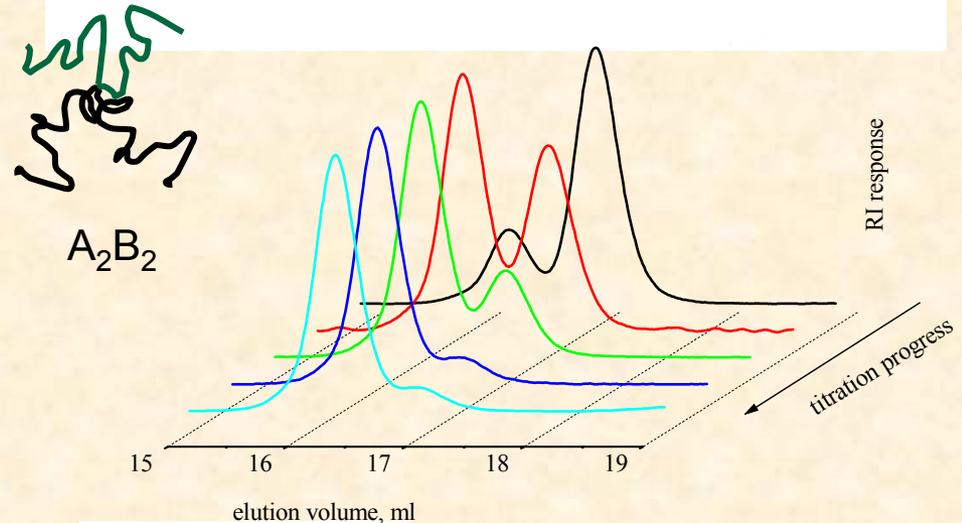
- Synthesize A_nB_n family of star copolymers with spherical domains
- $A=PS$, $B=PI$, $n=1,2,4,8,16$
- Study kinetics of ordering by neutron scattering and reflectivity and morphology by TEM

High-vacuum titration technique

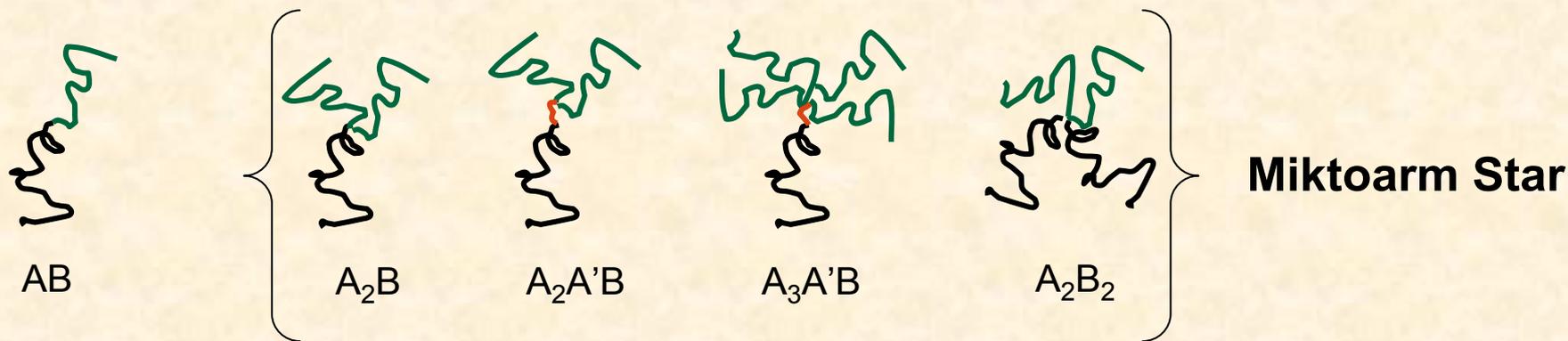
All-glass reactor, BuLi-washed, benzene rinse



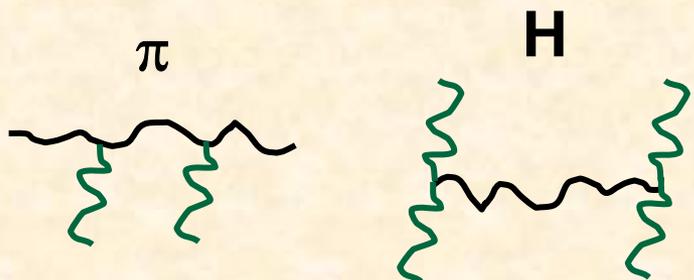
$(PS)_2(PI)_2$ Reaction Scheme



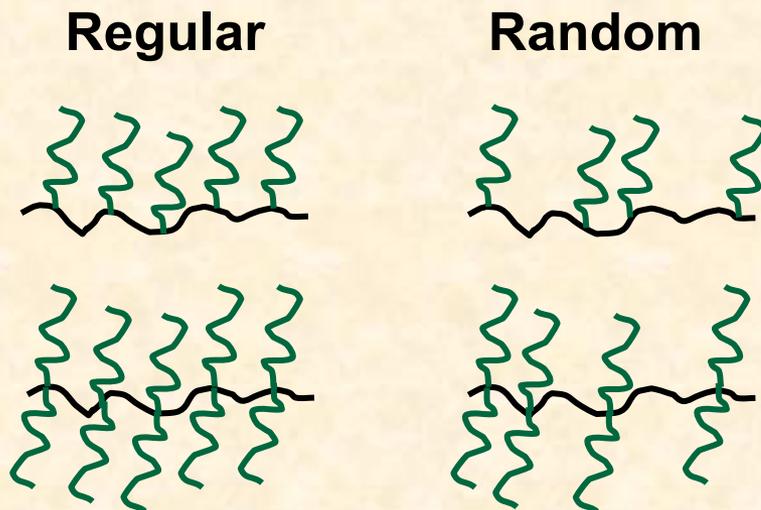
Miktoarm Star and Graft Molecular Architectures



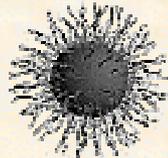
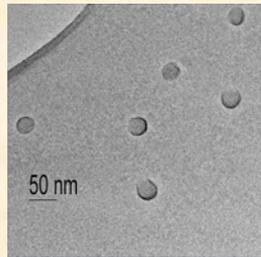
Double Graft Architectures



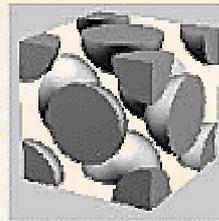
Multigraft Architectures



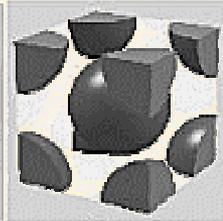
Morphologies of Diblock Copolymers



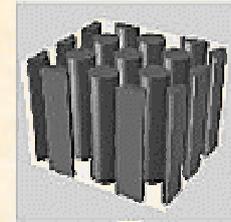
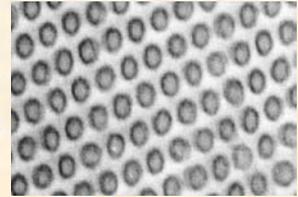
micelle



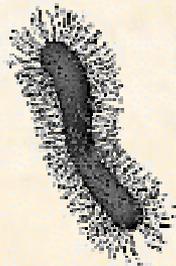
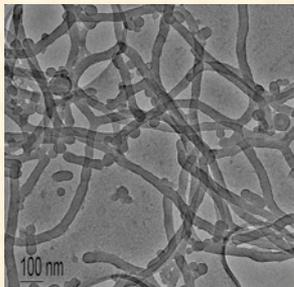
F



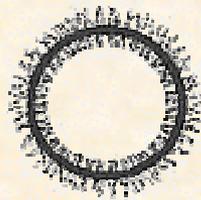
B



H



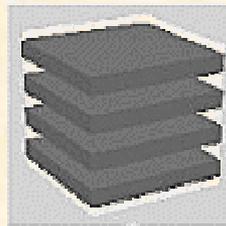
cylindrical micelle



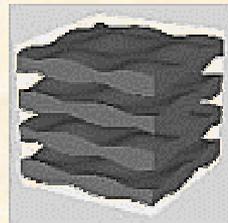
vesicle



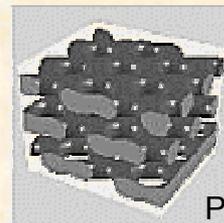
gyroid



L



ML



PL

Picture from Förster, S.; Plantenberg, T. *Angew. Chem. Int. Ed.* **2002**, *41*, 688.

Morphological Characterization of Block Copolymers

- What Do We Want to Know???

- In the bulk
 - Geometry of the microphase separated domains (i.e. spheres, cylinders, lamella, perforated lamella, bicontinuous structure, etc.)
 - Kinetics of phase separation
 - Lattice type and crystallographic space group if the structure has long range order
 - Dimensions of the lattice and of the domains ordered on the lattice
 - Possibly information on defects, long range order, etc.
- In solution
 - Geometry of polymer aggregates (spherical micelles or rod)
 - Size of aggregates

Important to Obtain Both Real Space (microscopy) and Reciprocal Space (Scattering) Information:

- **Transmission electron microscopy (TEM) is the most common microscopy technique**
 - **Care in casting/annealing to get equilibrium morphology**
 - **Polymers usually require heavy element staining or the presence of crystallinity to give contrast**
 - **Need very thin sections (typically <100 nm) - ultramicrotoming at cryogenic temperatures is often required with especially with low T_g materials**
 - **Must avoid beam damage (many polymers are readily degraded by electrons) – special microscopes are useful (200 KV energy filtered electron microscope)**
 - **TEM provides direct visual information on the material but its sampling statistics are poor (probes very small portion of sample) – must couple with scattering**

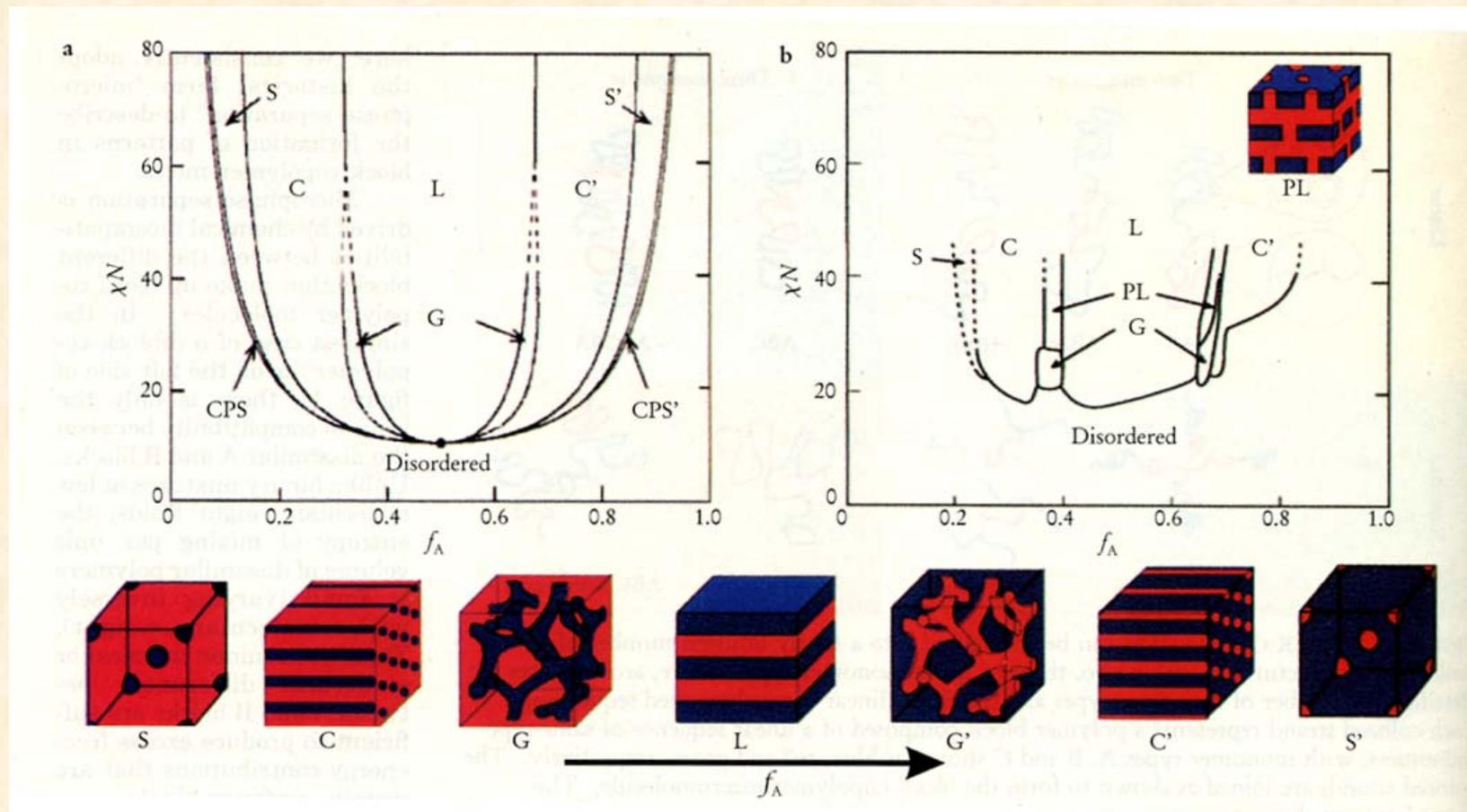
Small-Angle X-ray and Neutron Scattering are the Reciprocal Space Methods of Choice

- Scattering methods yield excellent statistics and accurate dimensions but data may be difficult to interpret without visual clues from TEM images
 - Samples a huge volume compared to TEM
 - Staining not required but selective deuteration greatly enhances contrast in SANS (CNMS has deuteration capabilities as well as a deuteration facilities for *in vivo* H/D labeling of biological molecules at the Center for Structural Molecular Biology at ORNL in partnership with Dean Myles)
 - X-rays and neutrons do not damage polymer samples so time resolved or temperature resolved experiments are possible
 - Interpretation is model dependent (straightforward for simple morphologies but not for complex ones!)

Neutron Scattering of Macromolecular Materials

- Neutron scattering has played a major role in the understanding of the **conformation** (or structure) and **dynamics** of polymers and copolymers in the **bulk solid** and in **solution** for almost 35 years
 - Length ($0.1-10^5$ Å) and time scales (μs -fs) accessed by neutrons
 - Capability of manipulating contrast by H-D substitution (without changing structure)
- Examples of information gained by neutron scattering
 - Molecular conformation of bulk polymers, polymer blends, and copolymers
 - Molecular weight, radius of gyration, and conformation of a single molecule in dilute or concentrated solution
 - Polymer-polymer thermodynamics
 - Morphology of block copolymers in solution and solid state
 - Polymer chain behavior in deformation, shear, extrusion, etc
 - Interface structure and depth profile of polymers
 - Conformational changes upon swelling or stretching of networks

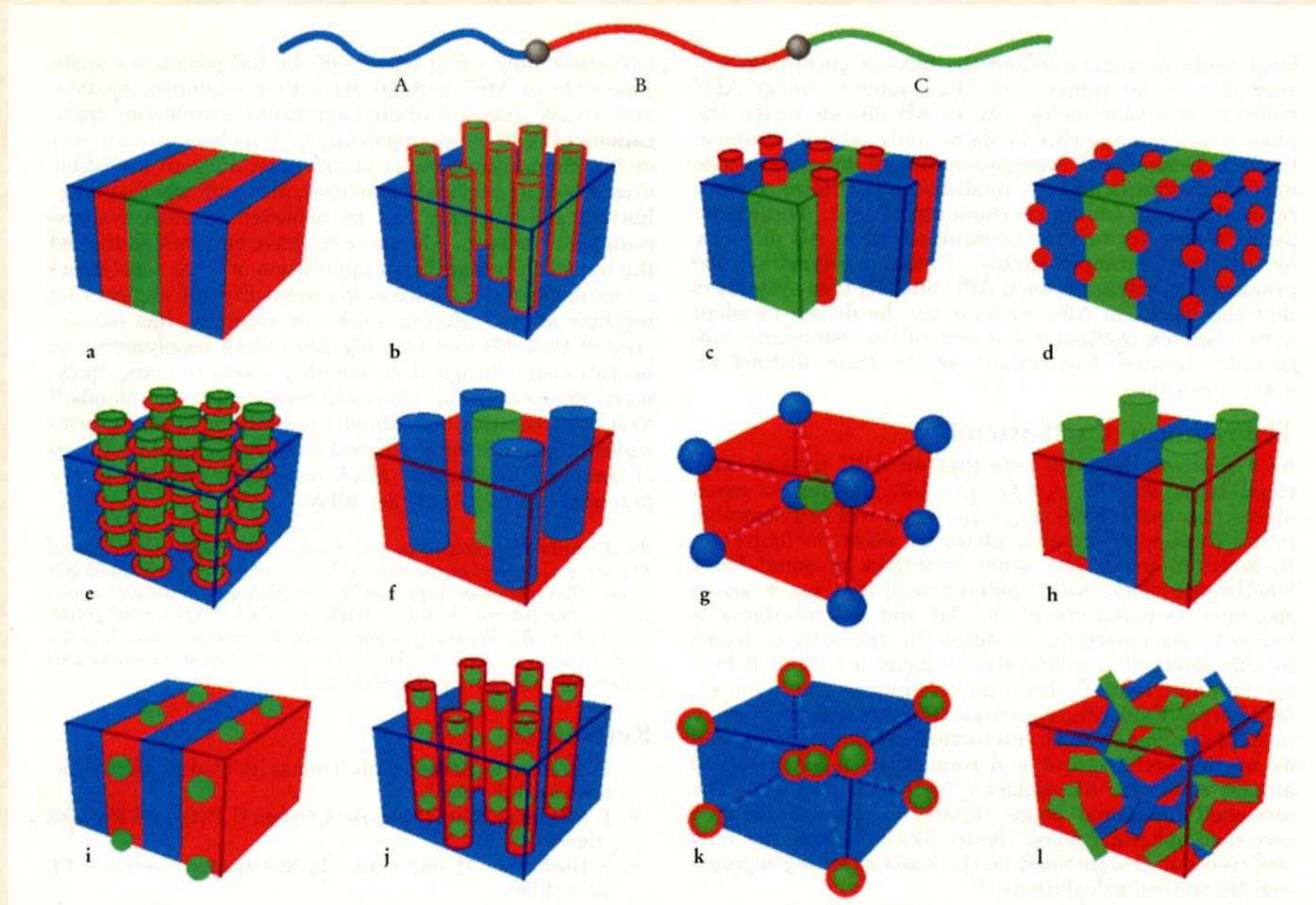
Linear Diblock Copolymer Morphology for Polystyrene-Polyisoprene



In the strong segregated regime ($\chi N > 10.5$), morphology strictly depends on composition; structure controlled by changing N and/or Φ

Bates, F. S., Fredrickson, G. H. *Physics Today* 1999, 52, 32

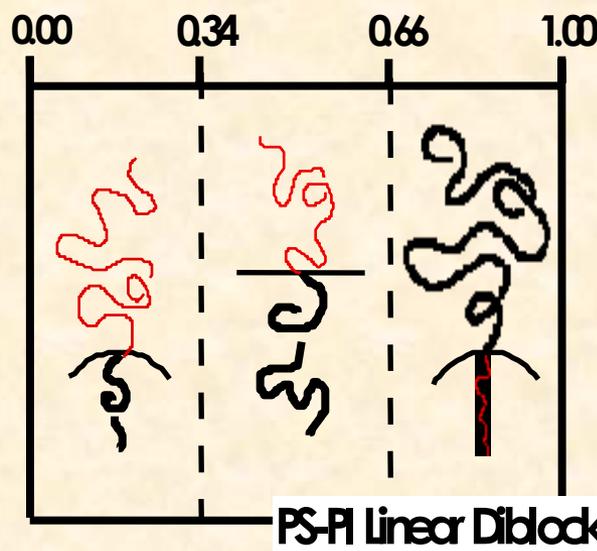
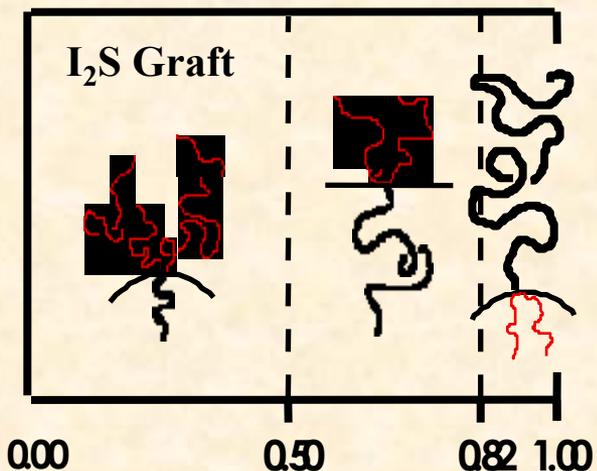
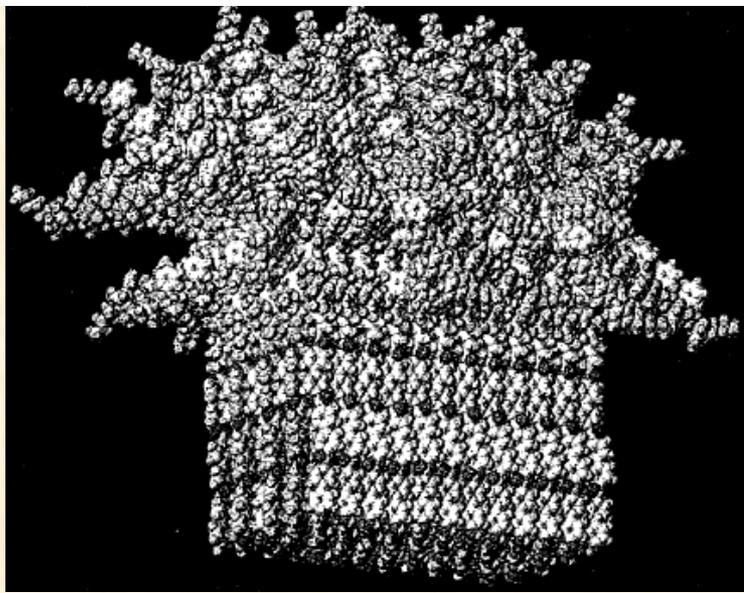
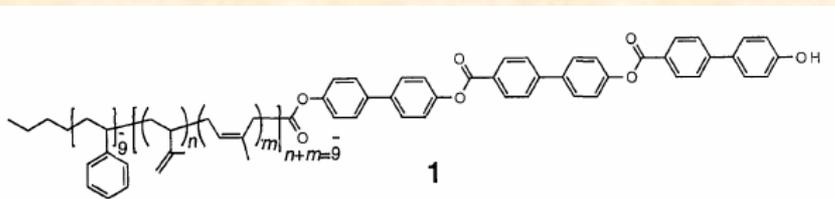
Morphologies for Triblock Copolymers



Bates, F. S., Fredrickson, G. H. *Physics Today* 1999, 52, 32

Manipulation of Polymer Architecture Allows Morphology to be Independent of Composition

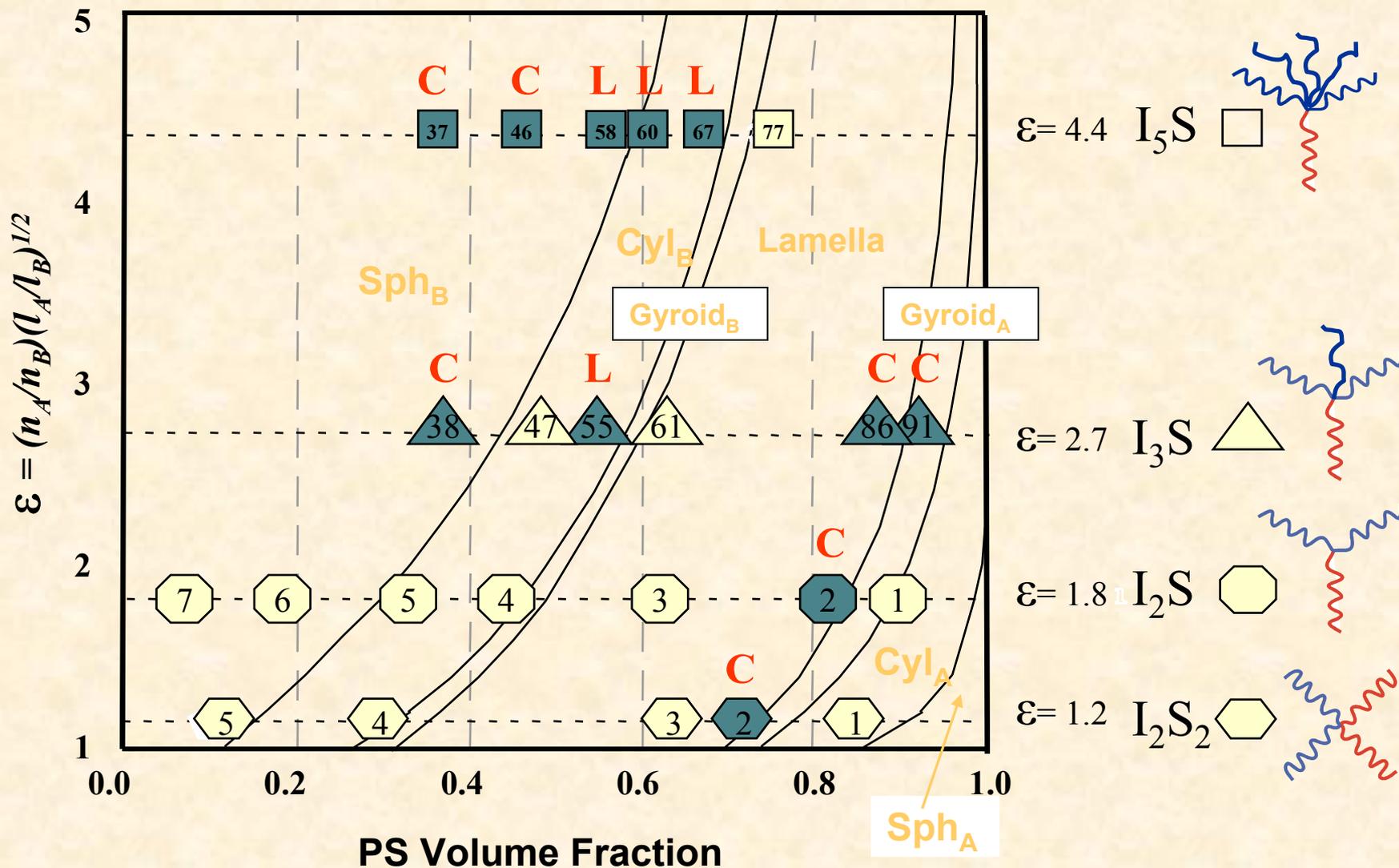
- Configuration asymmetry
 - Branching
 - Dendrimers, brushes, or hyperbranched
- Conformation asymmetry
 - Rigid rod polymers



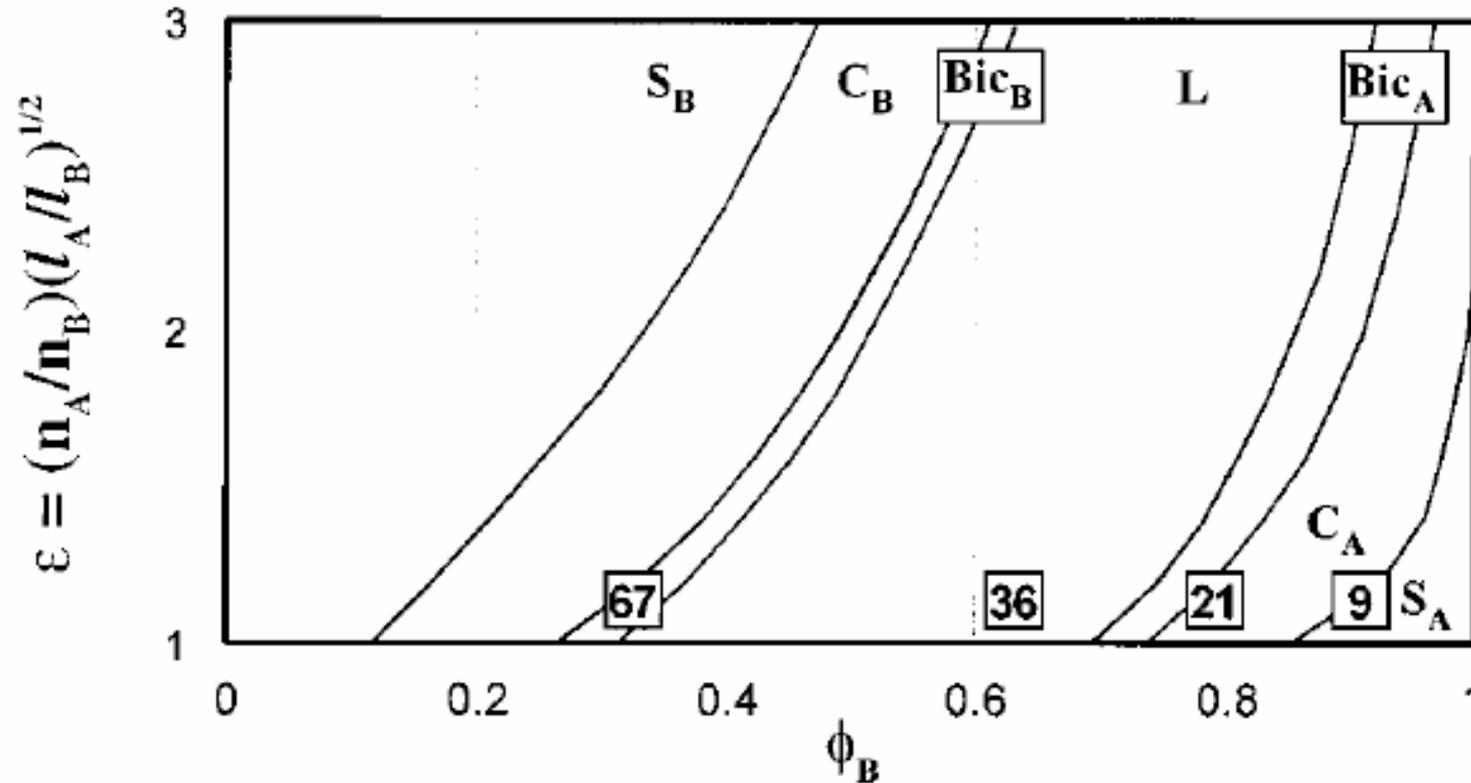
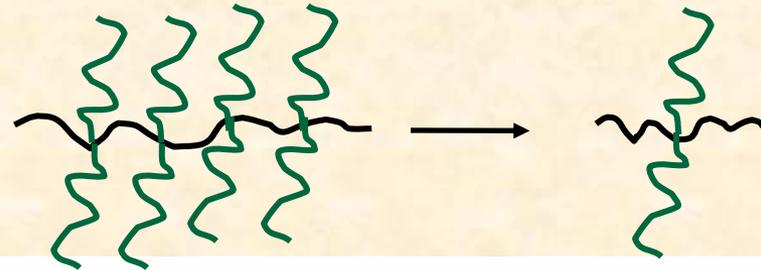
Stupp, S. I. et al.
Science 1997, 276, 384

Gido, Mays, et al.
Macromolecules, 29, 5091 (1996)

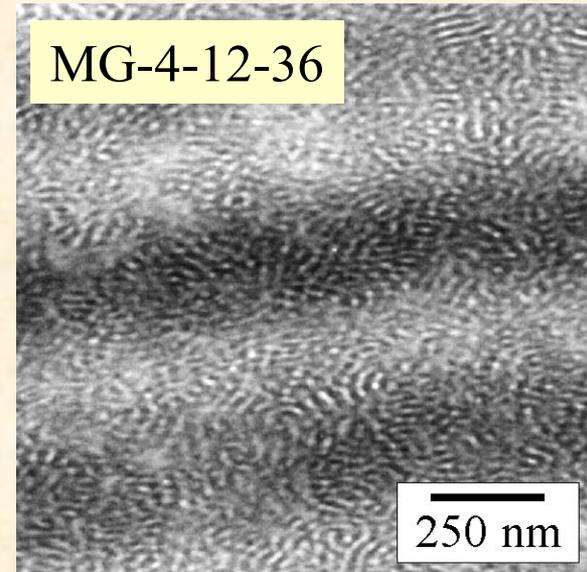
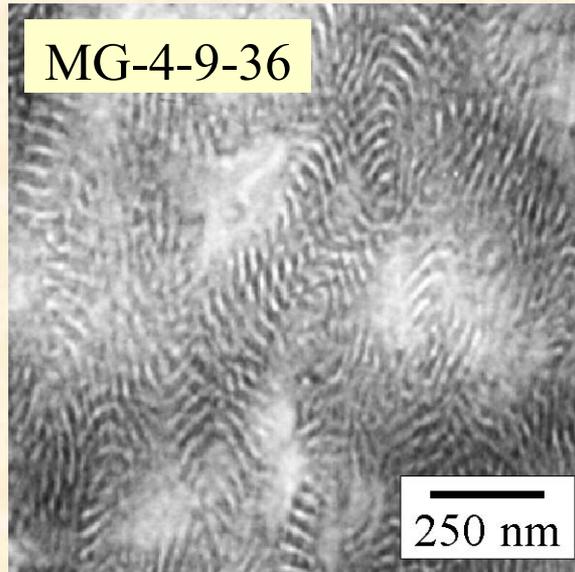
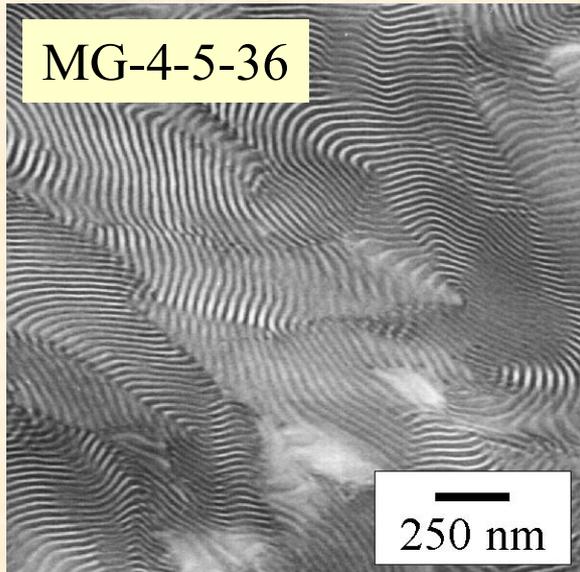
Summary of I_nS Mikotoarm Star Morphology



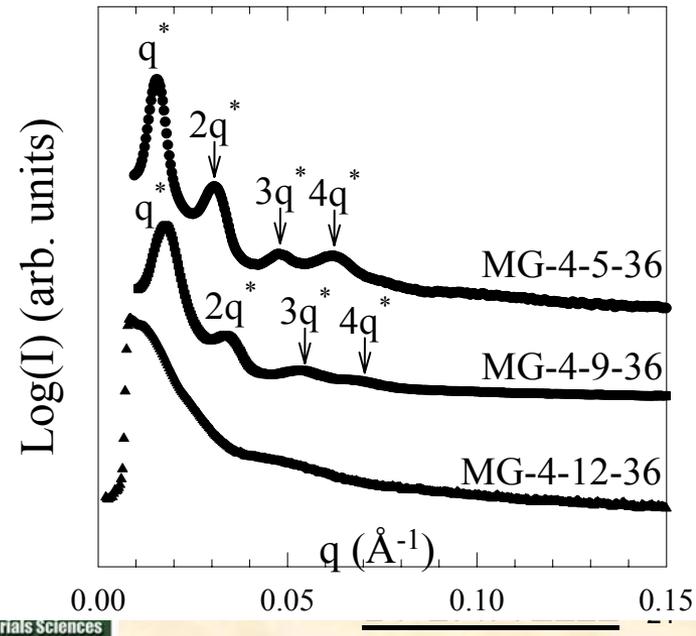
Tetrafunctional Multigraft Behavior Polyisoprene and Polystyrene



SAXS of Multigraph Polymer



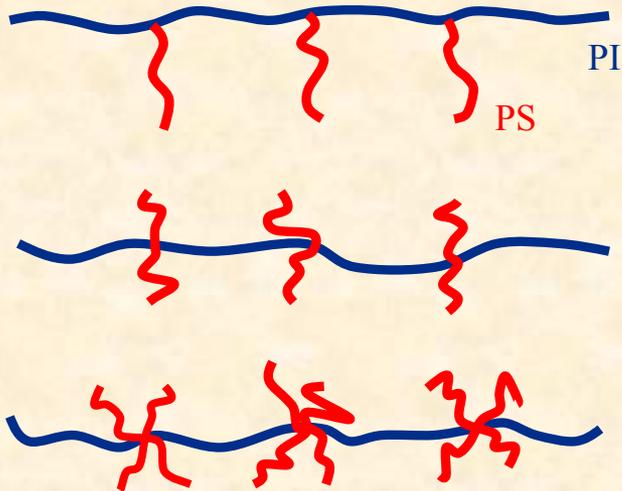
- Lamellae formed
- Agrees with model
- Decrease in order w/ increase in # junction points
- Can quantify grain size dependency



Mays and Gido

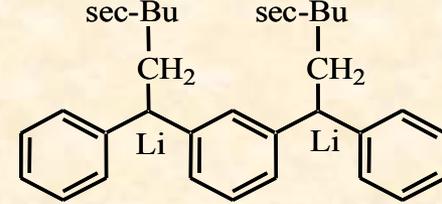
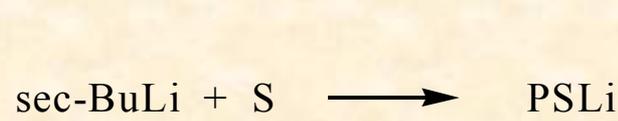
Synthesis and Mechanical Properties of Multigraft Copolymers

- Goal - determine the influence of molecular architecture on mechanical properties
- Multi-branch copolymers have superior properties compared to commercial thermoplastic elastomers

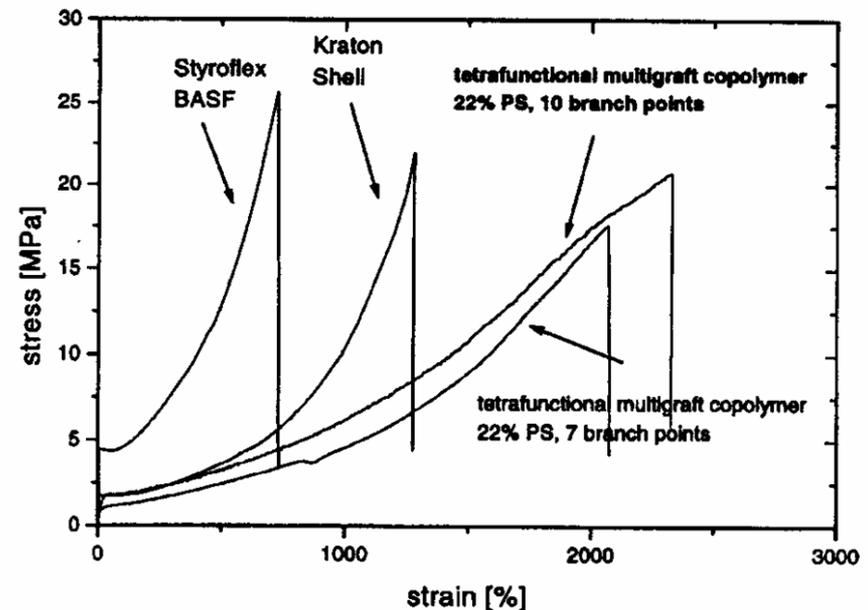


Branch points determined by selection of chlorosilane linker

OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY

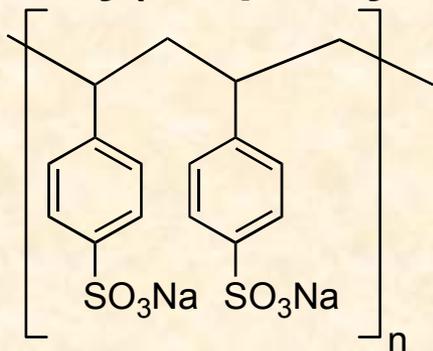


DLI

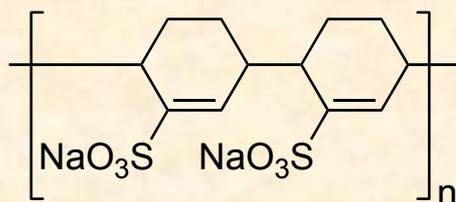


Synthesis and Characterization of Polyelectrolytes

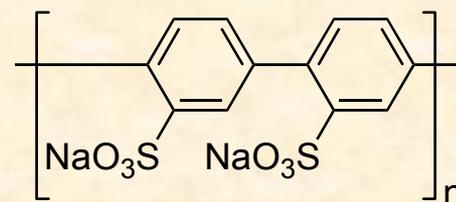
- Mike Simonson, Oak Ridge National Laboratory
- Systematic investigation of the nanoscale structures formed by polyelectrolytes in solution
- **Goal:** Investigate the effect of chain stiffness on polyelectrolyte conformation and counterion interactions in solution by neutron, X-ray, and light scattering techniques
- **Approach:** Synthesis of a series of polymers and deuterated polymers (of similar DP) with different backbone stiffnesses:
 - Poly(styrene sulfonate) - flexible (PSS)
 - Poly(1,3-cyclohexadiene sulfonate) - semiflexible (PCHDS)
 - Poly(1,4-phenylene sulfonate) - rigid rodlike (PPS)



PSS



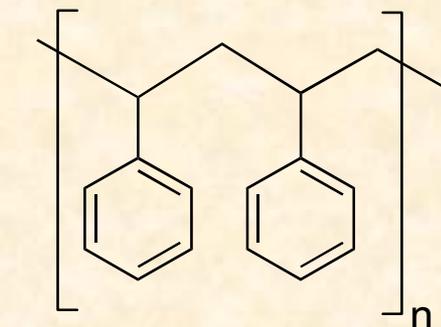
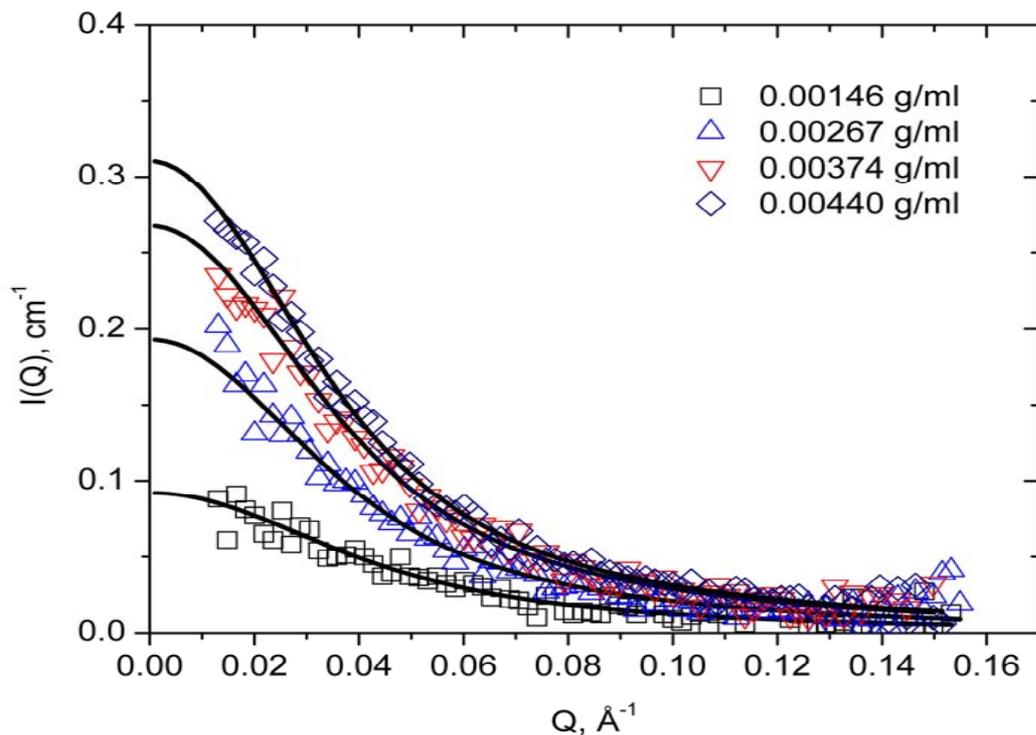
PCHDS



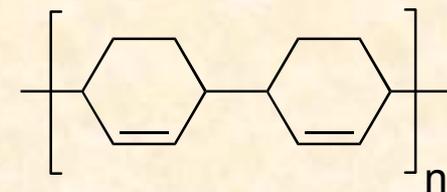
PPS

SANS of Deuterated Poly(1,3-Cyclohexadiene)

- SANS shows a statistical segment length (in THF):
 - PCHD 0.83 nm while polystyrene 0.67 nm
- PCHD has a stiffer polymeric chain than polystyrene
- For sulfonated PCHD, studying the effect of aggregation as a function of molecular weight, concentration, degree of sulfonation, salt concentration, and temperature



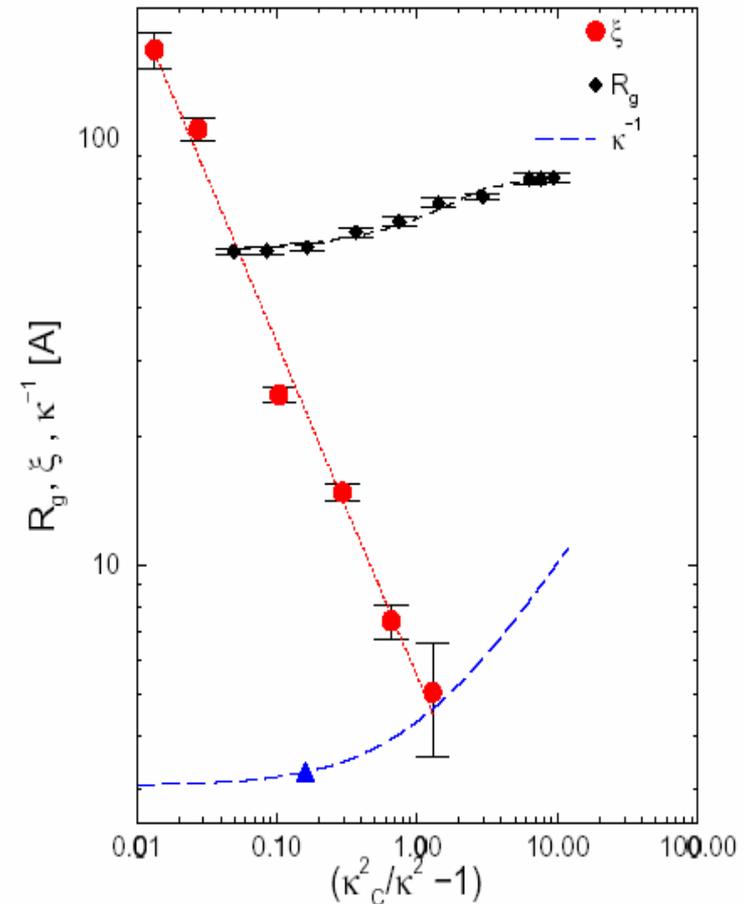
PS



PCHD

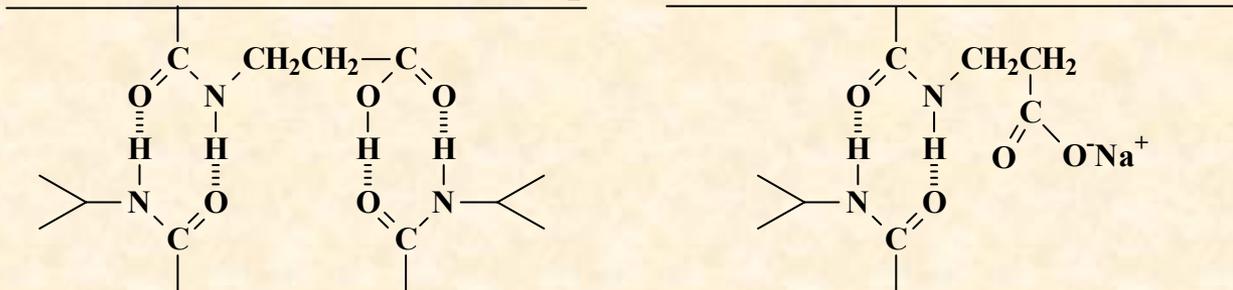
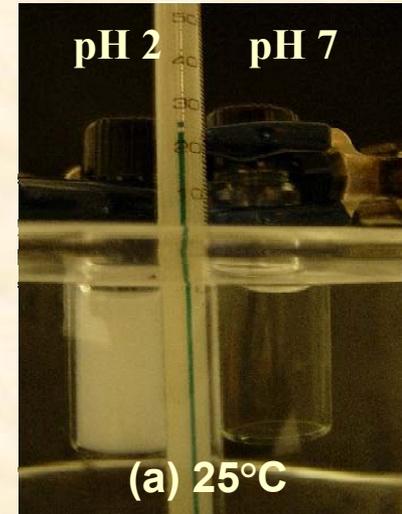
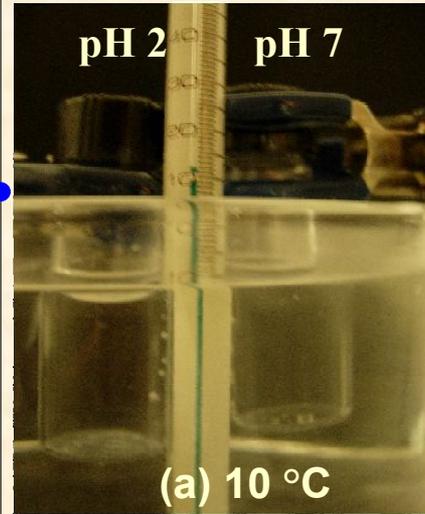
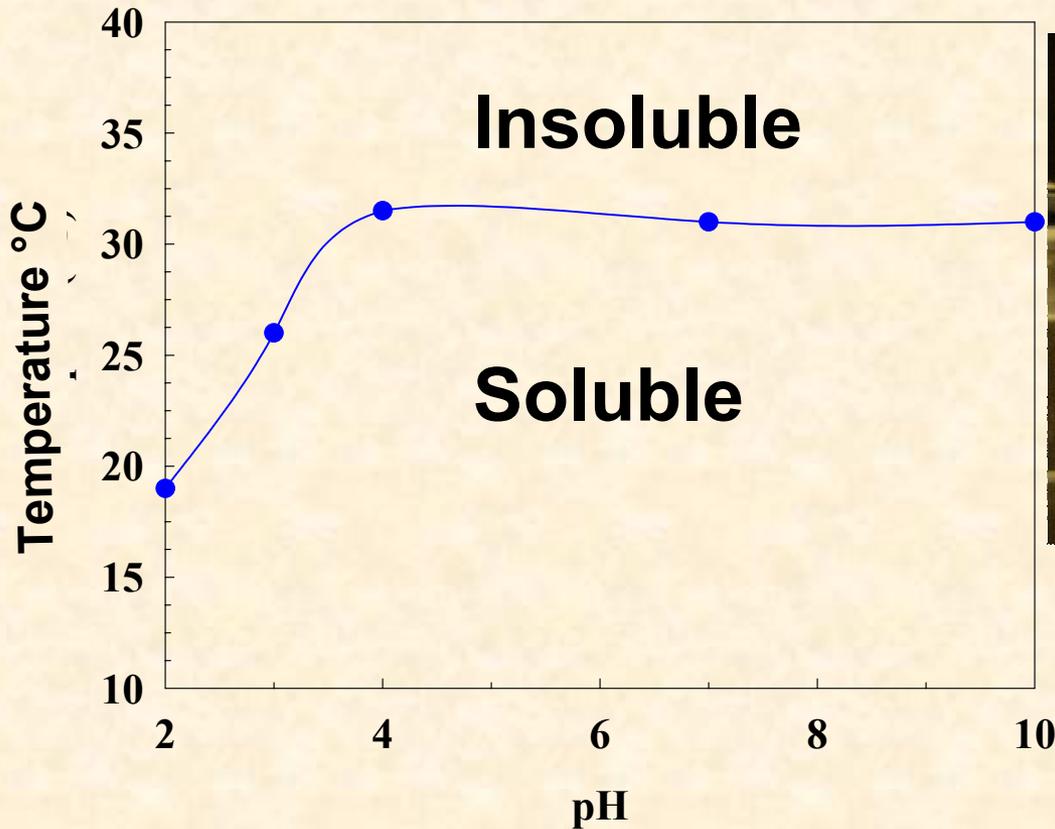
Chain Dimensions and Concentration Fluctuations in Polyelectrolyte Solutions

- Biological macromolecules carry electrical charges and their organization can be approached by studying model solutions of polyelectrolytes (PE).
- Isotopic labeling gives information on their dimensions (R_g) and interactions, as a function of their molecular weight (M_w), ionic strength, concentration (C_p) and temperature (T).
- For low ionic strength semidilute PE- solutions the correlation length (ξ) scales as $\xi \sim C_p^{-0.47 \pm 0.02}$ and $R_g \sim C_p^{-0.24 \pm 0.01} M_w^{0.53}$, in agreement with scaling theory (Muthukumar). ξ diverges as a function of added salt and T as the phase boundaries are approached and the critical value of the Debye screening length (κ^{-1}) is $\kappa_C^{-1} = 3.0 \text{ \AA}$. At the “ θ -salt” condition, $\kappa^{-1} = 3.28 \text{ \AA}$ and $R_g = 57 \text{ \AA}$ [Polymer, 42, 8935 (2001); JCP, 119, 1 (2003)].

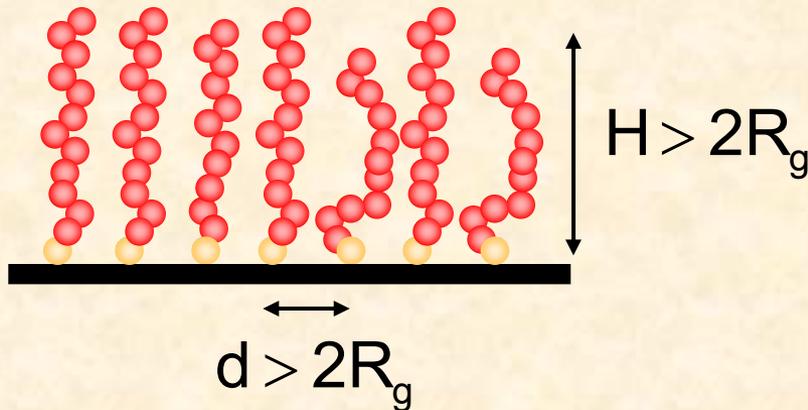


Sodium Polystyrene Sulfonate

Thermo-Responsive Block Copolymers



Brushes from Linear Diblock Copolymers - Well Understood



As the degree of crowding increases, the build-up of osmotic pressure forces the chains to stretch away from the surface to reduce local crowding (chain overlap)

Two competing forces:

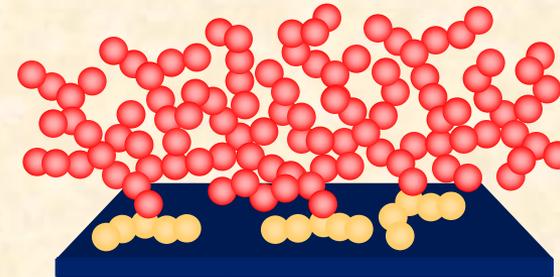
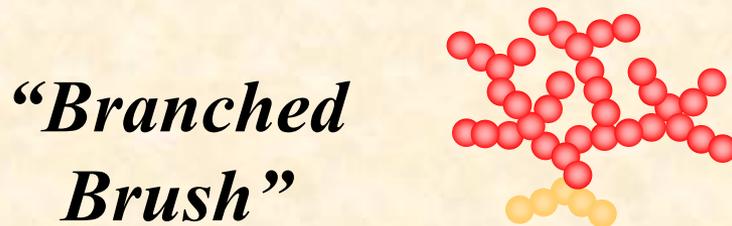
$$\frac{F_{\text{osmotic}}}{kT} \propto C^2 \quad (\text{favors dilution manifested in chain stretching})$$

$$\frac{F_{\text{elastic}}}{kT} \propto \frac{H}{R_g^2} \quad (\text{resists chain stretching})$$

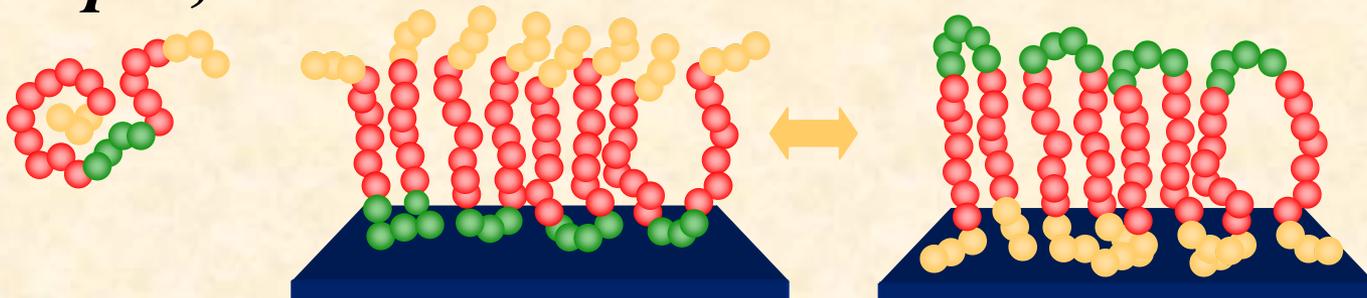
Alexander, 1977;
de Gennes 1980

$$\text{Equilibrium: } F_{\text{osmotic}} = F_{\text{elastic}} \Rightarrow H_{\text{equilibrium}} = 2R_g (\sigma^*)^{1/3}$$

More complex architectures are not understood

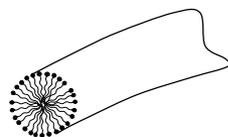
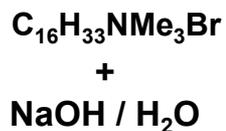


“Loops”, etc.

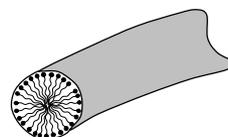


Preparation of Hexagonal Mesoporous Silicas

- Standard templated synthesis
- MCM-41: $C_nH_{2n+1}NMe_3Br$; TEOS $\{Si(OEt)_4\}$; Base
 - Beck, et. al. *J. Am. Chem. Soc.* 1992, 114, 10834
- SBA-15: Pluronic P123 ($EO_{20}PO_{70}EO_{20}$) copolymer; TEOS; Acid
 - Zhao, et. al. *Science* 1998, 279, 548

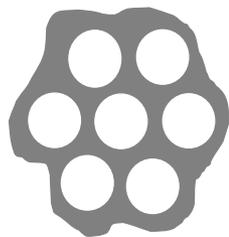


rod-like micelle

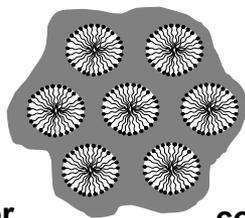


silica encapsulated micelles

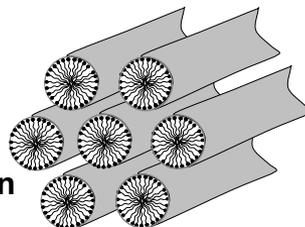
Synthesis of MCM-41



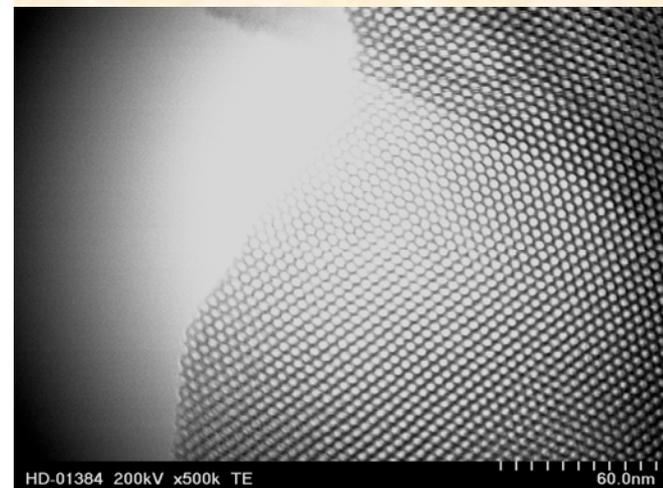
surfactant extraction or calcination



silica condensation



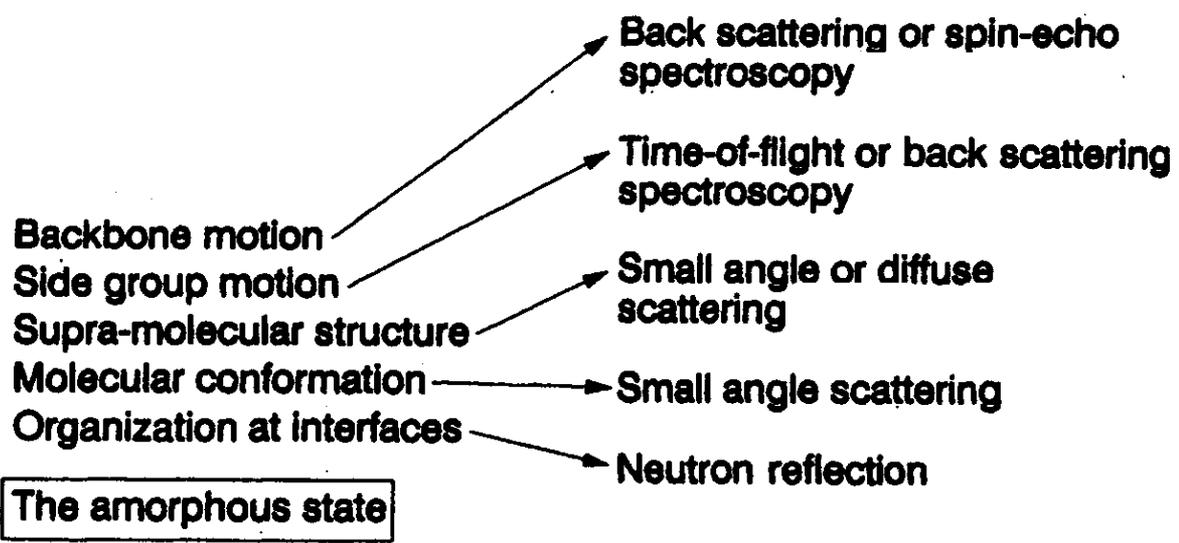
TEM of MCM-41: 2.9 nm pores



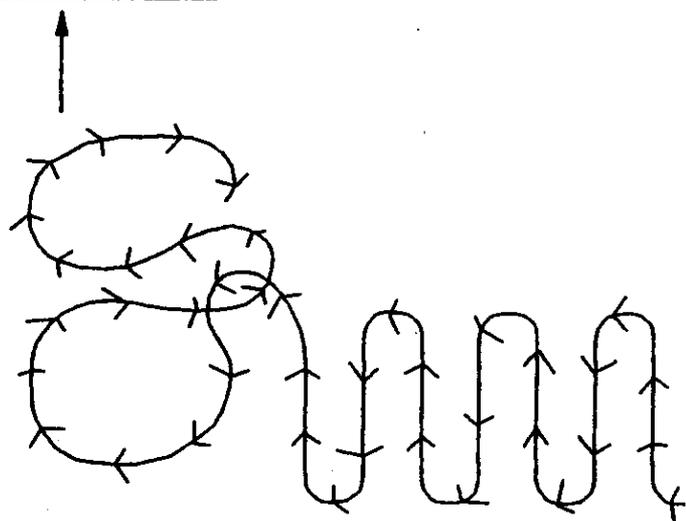
Pluronic = 5.6 nm pores

$C_{16} = 2.9 \text{ nm}$, $C_{14} = 2.2 \text{ nm}$, $C_{12} = 1.7 \text{ nm}$

Relationship Between Neutron Scattering and Structure and Dynamics of a Polymer



The amorphous state



The crystalline state

- Crystal structure
- Crystal morphology
- Crystal vibrations

Neutron diffraction

Small angle scattering

Time-of-flight and triple axis spectrometry

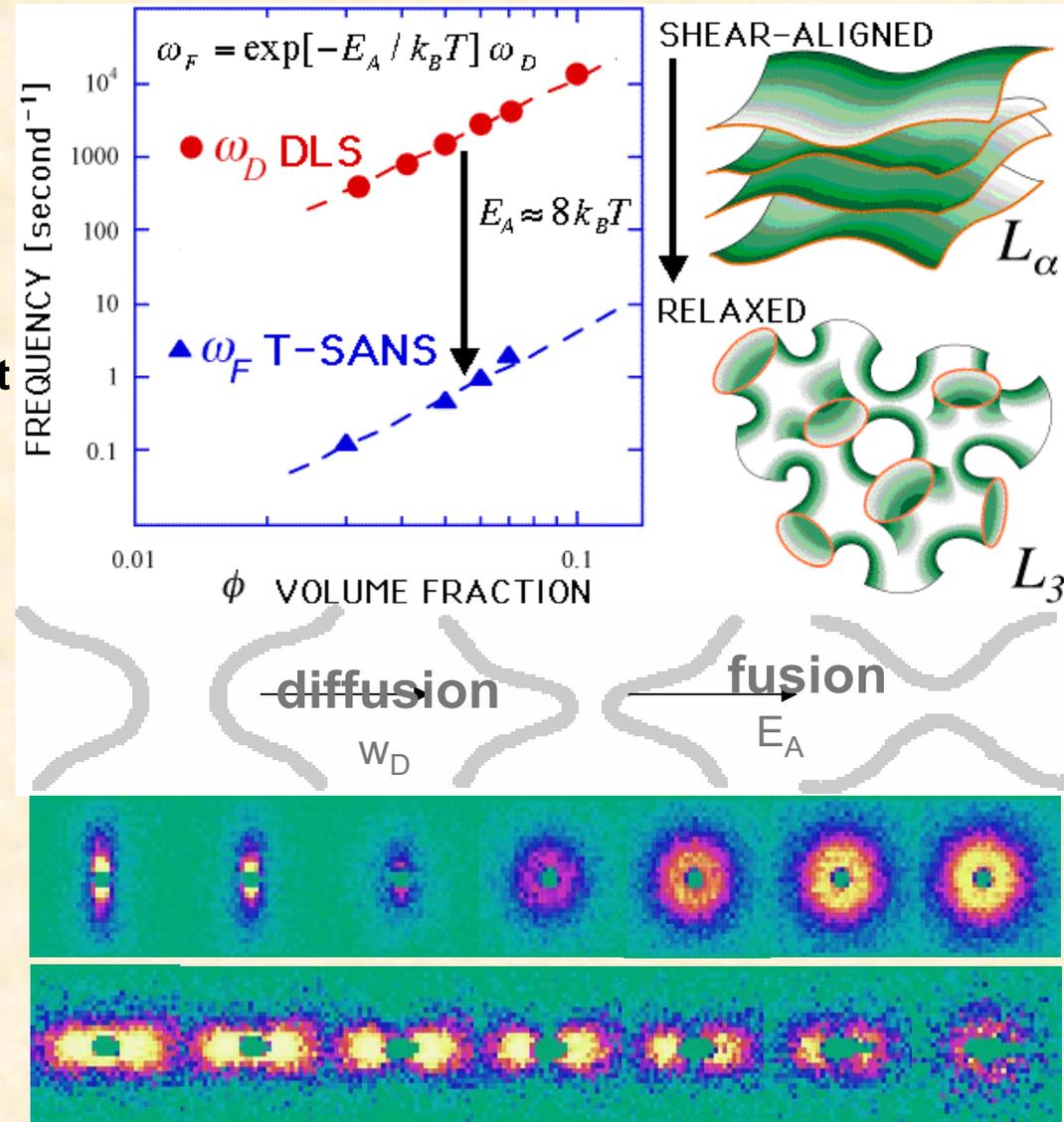
Higgins, J. S.; Benoît, H. C.
Polymers and Neutron Scattering Oxford University Press, New York, 1994; p. 2

Future of Neutron and X-Rays in Nanoscience

- **More intense sources, together with advances in instrument allow access to length and time scales that were previously inaccessible (with smaller samples)**
 - **Opportunities for real-time measurements of (need to build the sample environment):**
 - **Phase/morphology changes (kinetics of change)**
 - **polymer processing (electric, magnetic, shear)**
 - **polymer relaxation processes**
 - **polymer rheology**
 - **chemical reactions of polymers**
 - **Measure of (buried) interfaces (for example composites)**
- **Need better visualization tools and better models to fit complex data – 3D images from scattering data**

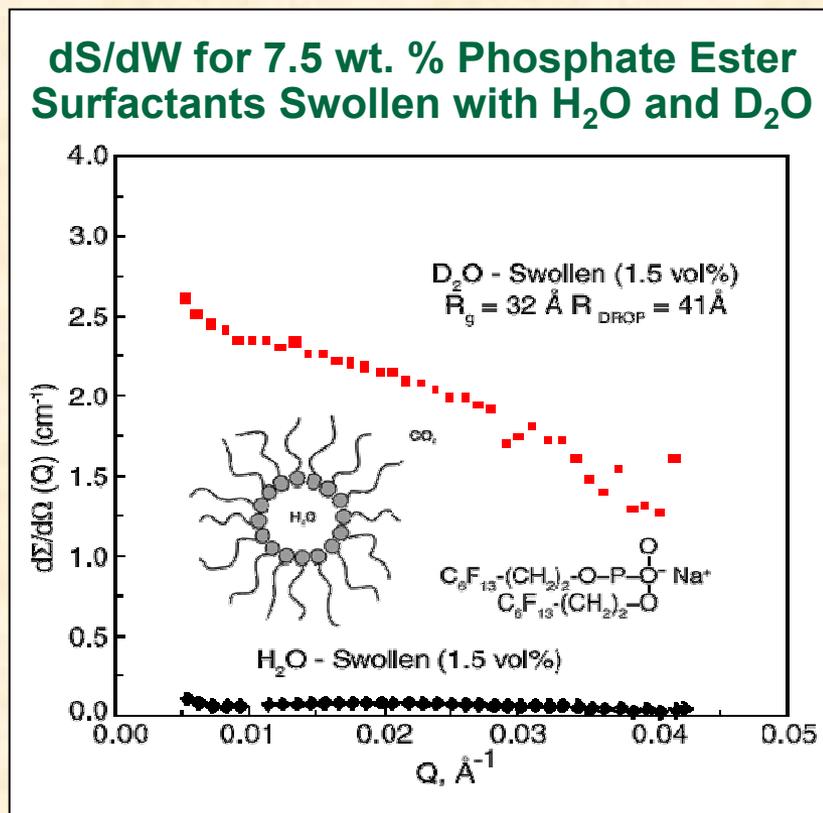
Energetics of passage (re)formation in membrane phases

- **Background:** Our previous work shows how to produce a well characterized shear-induced smectic L_α stacked phase from initial equilibrium L_3 sponge phase
- **Topological relaxation to the sponge phase** requires that the passages that characterize the sponge reform. What are the energetics of this process?
- **SANS relaxation** indicates rate of passage formation, while dynamic light scattering (DLS) gives rate of collision between adjacent membranes
- **Activation energy of passage formation** emerges directly from comparison of characteristic rates determined by each technique



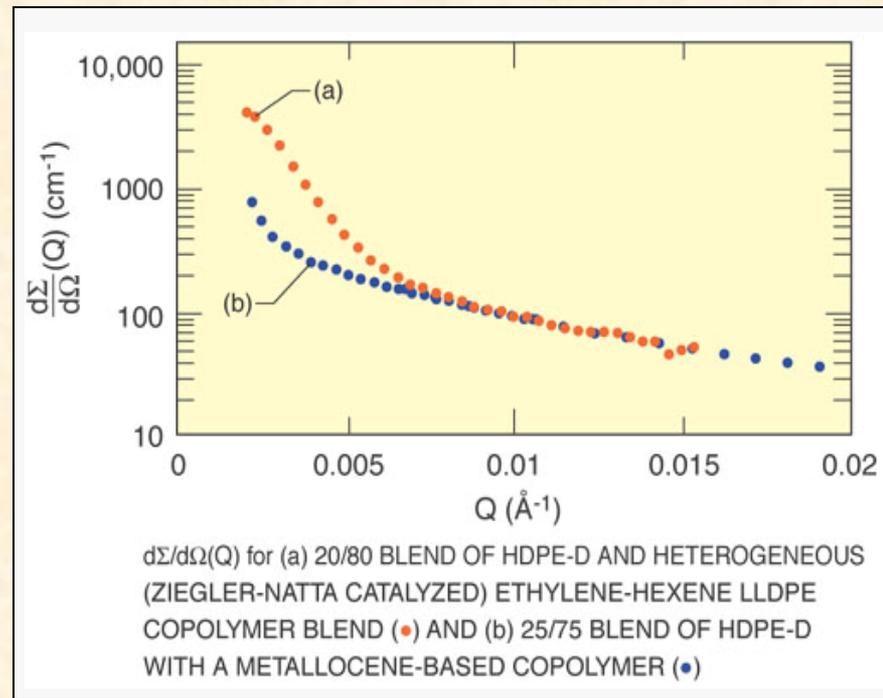
Water Nanodroplets in CO₂-Microemulsions Formed by Novel Phosphate Fluorosurfactants

- The potential of carbon dioxide (CO₂) as an environmentally clean, tunable solvent is limited by its low capacity for solubilizing many materials, including water.
- This issue is being addressed through the use of novel anionic phosphate fluorosurfactants, which aid the dispersion of water-in-CO₂ (W/C) via the formation of W/C microemulsions.
- *The presence of W/C microemulsions was confirmed via SANS, which showed that the majority of the scattering originates from deuterium-labeled nanodroplets, which form the core of the microemulsions.*
- Water loadings range up to ~5 vol%, which is one of the highest concentrations achieved for W/C microemulsion systems [*J. Am. Chem. Soc.* 124; 834 (2002); *Langmuir* 18, 7371 (2002); *Langmuir* in press].



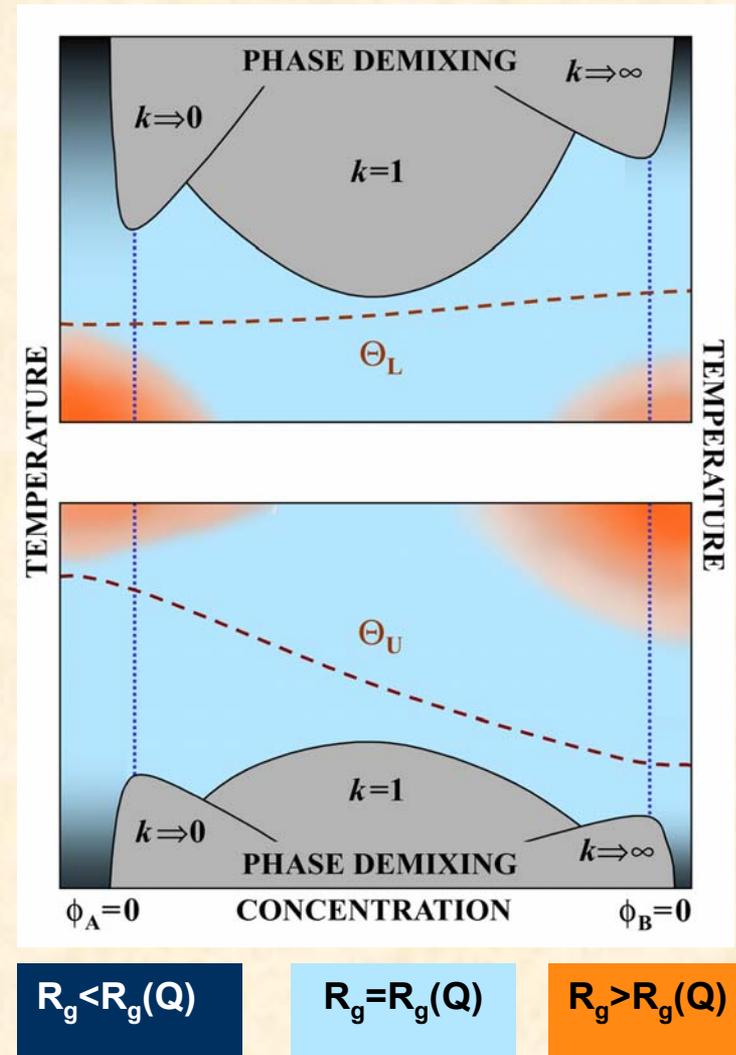
Liquid-liquid Phase Separation in Heterogeneous and Metallocene-based Linear Low Density Polyethylenes

- Polyolefins constitute the largest segment of the polymer market and branched molecules are widely used to modify the properties of linear molecules such as polyethylene.
- Short-chain branched linear low density polyethylenes (LLDPEs) made via traditional (multi-site) catalysts have a wide distribution of branch contents, which act as a "blend" of different species, and when the distribution is broad enough, the highly branched chains phase separate.
- This is manifested in an "upturn" [see (a)] in the SANS data at $Q < 0.01 \text{ \AA}^{-1}$.
- Recently, a new class of copolymer, made with "single-site" (metallocene) catalysts, has been developed with a narrow distribution of branch contents, and SANS has confirmed that the "upturn" (b) is greatly reduced, indicating a single-phase morphology [Macromolecules, 34, 8160 (2001)].



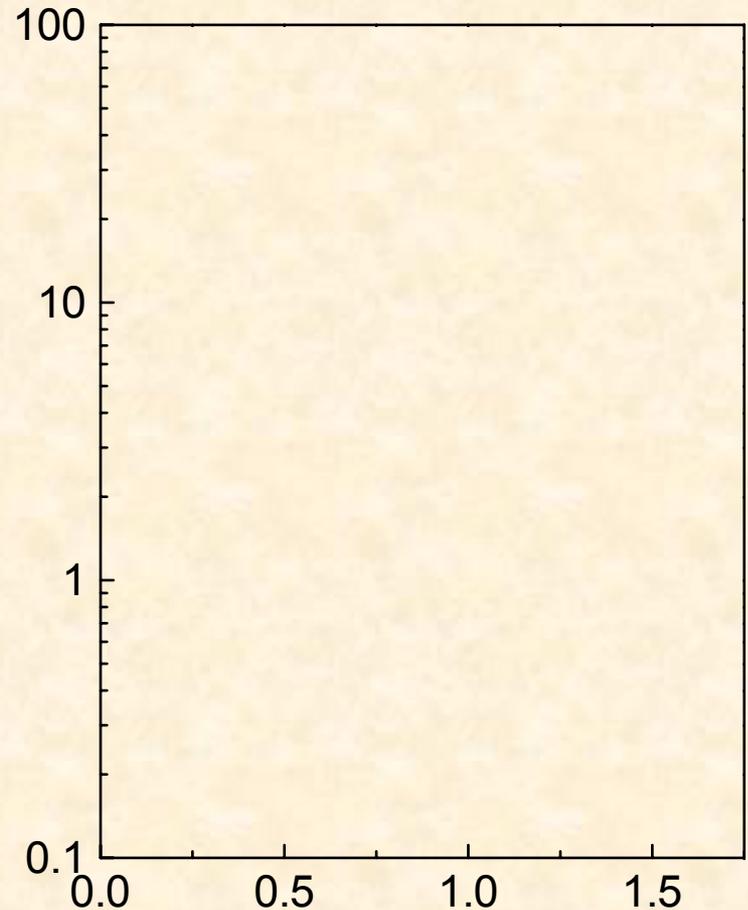
On the Validity of the Random Phase Approximation

- The random phase approximation (RPA) is based on the assumption that the dimensions of polymer chains in a blend is identical to the unperturbed or Θ dimensions for all concentrations and temperatures.
- Recent SANS studies of weakly and strongly interacting polymer blends have demonstrated the existence of both upper and lower Θ temperatures, which separate poor and good solvent domains. The latter occur near the edges of the phase diagram, where the assumption of unperturbed dimensions breaks down, thus delineating the regions of validity of the RPA [*Phys. Rev.*, **E65**, 061802 (2002); *Fluid Phase Equilibria*, **212**, 211 (2003)].



Universal Aspects of Macromolecules in Various Θ Solvents

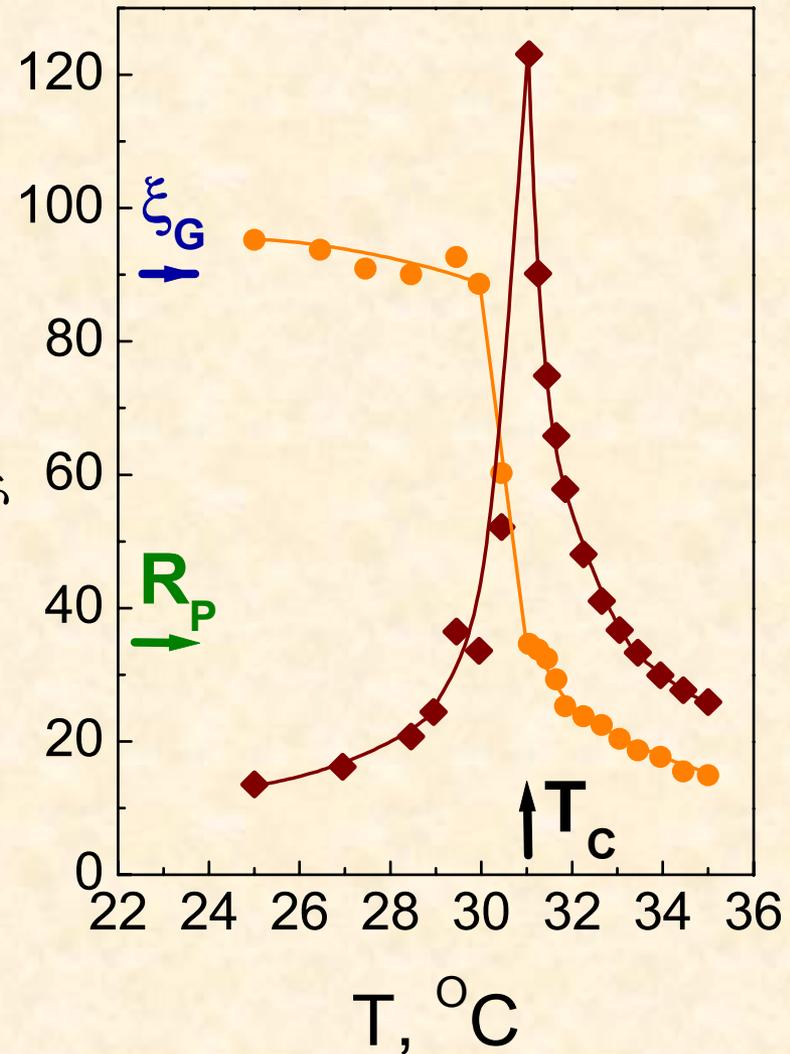
- The existence of the Θ -condition in polymer blends and solutions allows us to develop a general scaling relationship based on the deGennes' scaling variable, $\tau^* = (T - T_c) / (\Theta - T_c)$.
- The correlation length ξ of polymer blends as well as polymer solutions in organic and supercritical solvents normalized to the value, $x(\Theta)$, at the corresponding Θ -temperature collapses onto a single master curve over a wide range of molecular weight, Θ -temperatures, and critical temperatures for all three systems.
- This is the first demonstration of the universality of the structure and thermodynamic properties of polymers in polymeric, liquid and supercritical solvents.



Critical Density Fluctuations in Confined Fluids

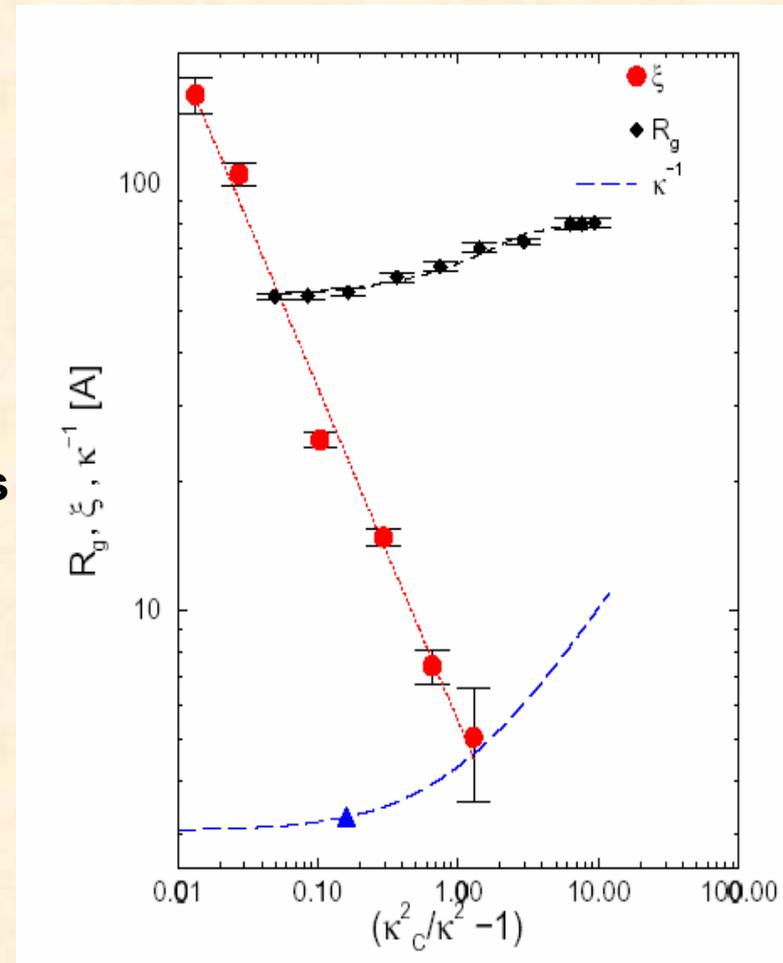
• Two competing theoretical approaches for interpretation of critical behavior of confined fluids are the “single pore” and random field Ising models. Experimental efforts to verify the validity of these models for confined *binary liquid solutions* have been obscured by complications caused by local composition gradients in pores in addition to sluggish kinetics in the liquid-liquid critical region.

• SANS measurements of the correlation length (ξ) of the density fluctuations in a *single-component fluid* (CO_2) confined in a dilute (ϕ_{PORES} ca. 96 %) aerogel indicate that quenched disorder works to suppress density fluctuations in the critical region. The correlation length does not exceed the characteristic pore size, which provides strong evidence in favor of the single pore model [Melnichenko *et al.*, submitted to PRL].



Chain Dimensions and Concentration Fluctuations in Polyelectrolyte Solutions

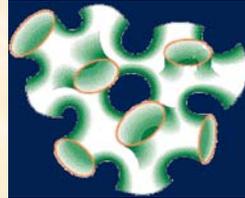
- Biological macromolecules carry electrical charges and their organization can be approached by studying model solutions of polyelectrolytes (PE).
- Isotopic labeling gives information on their dimensions (R_g) and interactions, as a function of their molecular weight (M_w), ionic strength, concentration (C_p) and temperature (T).
- For low ionic strength semidilute PE- solutions the correlation length (ξ) scales as $\xi \sim C_p^{-0.47 \pm 0.02}$ and $R_g \sim C_p^{-0.24 \pm 0.01} M_w^{0.53}$, in agreement with scaling theory (Muthukumar). ξ diverges as a function of added salt and T as the phase boundaries are approached and the critical value of the Debye screening length (κ^{-1}) is $\kappa_C^{-1} = 3.0 \text{ \AA}$. At the “ θ -salt” condition, $\kappa^{-1} = 3.28 \text{ \AA}$ and $R_g = 57 \text{ \AA}$ [Polymer, 42, 8935 (2001); JCP, 119, 1 (2003)].



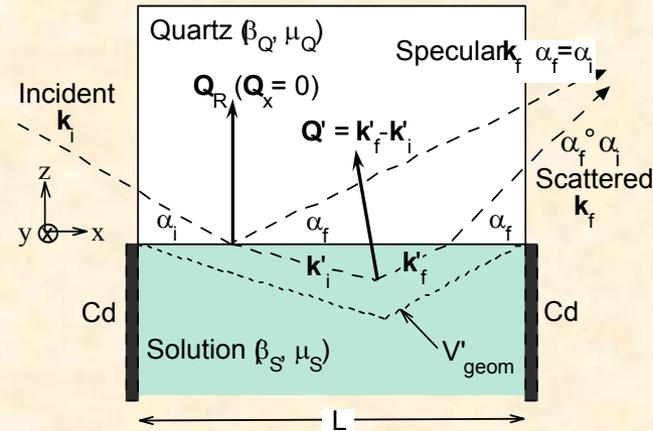
Sodium Polystyrene Sulfonate

Membrane ordering of sponge phases at a solid surface

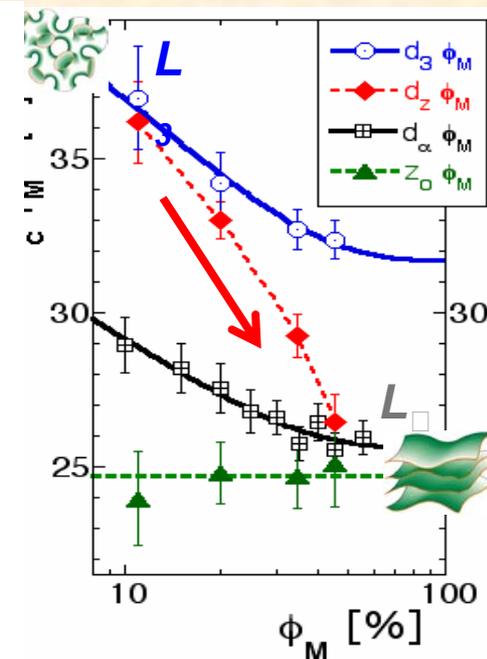
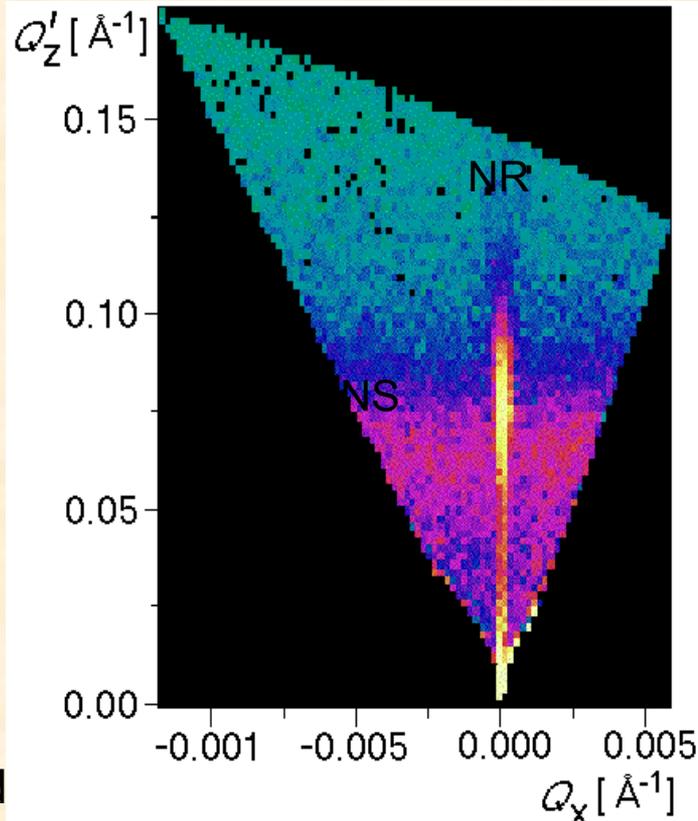
- Bulk transitions between the L_3 “sponge” phase and the stacked lamellar L_α phase reflect competition between fluctuations (entropy) and intrinsic curvature (elasticity)



- Will phase boundaries shift when the manifestly isotropic sponge must conform to the constraint of a proximate surface?



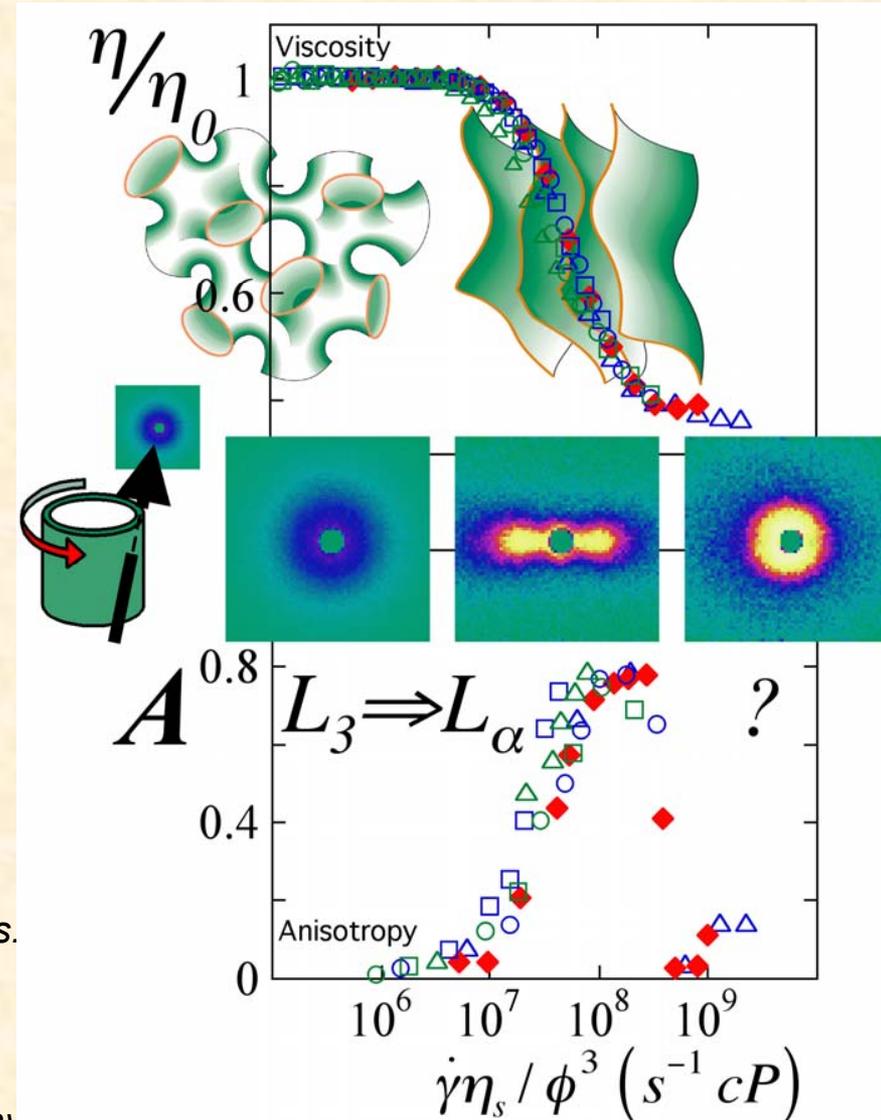
- Neutron reflectivity (NR) shows that a sponge solution’s surface periodicities may differ significantly from bulk solution correlations seen in off-specular “Near-Surface” SANS signals (NS-SANS)



- Geometric constraint induced from L_3 to L_α bulk values with increasing membrane volume fraction

Scaling of membrane phase dynamics

- **Strategy:** use of inert thickener to tune the shear response of membrane phases
- **Master curve response** in both rheology and structure as shear rate parameter is rescaled by two orders of magnitude
- **Shear-induced L_3 sponge to lamellar L_α phase transition**
- **Application:** modification of response and symmetry of membrane phases in chemical templating processes (e.g. protein crystallization)



• L. Porcar, W.A. Hamilton, P.D. Butler and G.G. Warr, *Phys. Rev. Lett.* **89**,168301 (2002) [<http://www.vjbio.org> **4** (2002)]

• *Rev. Sci. Instrum.* **73**, 2345 (2002) *Langmuir* in press)

• P. D. Butler, L. Porcar, W. A. Hamilton, and G. G. Warr, *Phys. Rev. Lett.* **88**, 059601 (2002) - comment

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