SANS from Polymers

R.M. Briber, University of Maryland

Outline of Talk

Introduction to Polymers and SANS

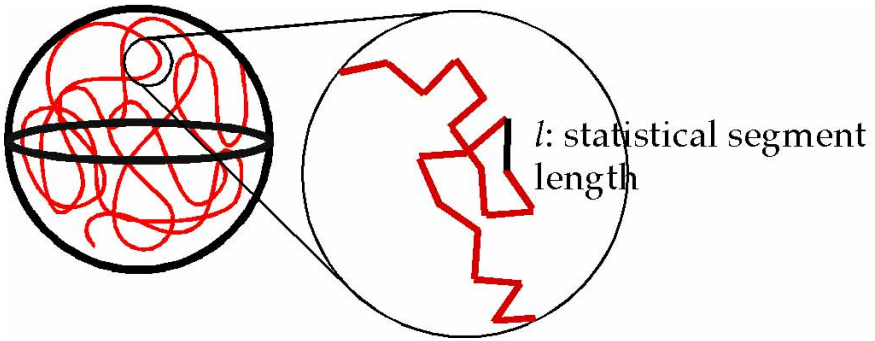
Example Experiments

- Chain conformation
  - Rg in thin films
  - Rg of unusual architecture polymers
- Thermodynamics, phase diagrams and interactions
  - Polymer Blends
  - Block copolymers

Summary

Chain Conformation

Chain Conformation



For a Gaussian Chain

$R_g^2 = Nl^2/6$ (general scaling: $R_g \sim N^v$)

Other conditions

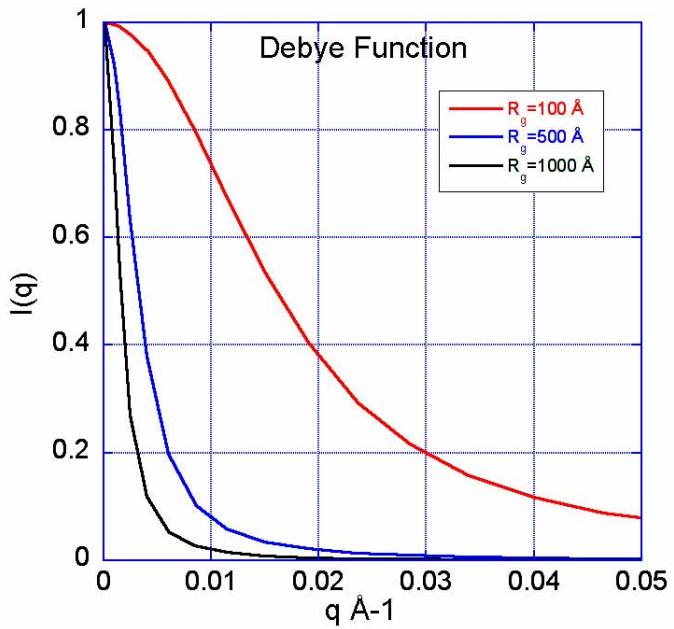
$v =$ 3/5 good solvent
1/2 theta solvent or melt
1/3 collapsed (constant density)

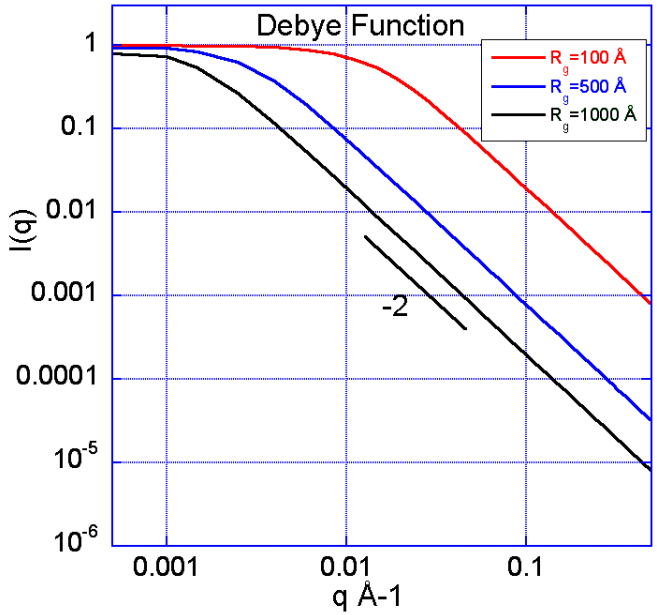
- R_g controls many structural features in polymers
- Typical R_g for most polymers 50-500Å -perfect size scale for SANS

Chain Conformation -cont.

Scattering from a Gaussian chain (Debye function):

$$P(q) = \frac{2}{x^2}\left(\exp(-x) - 1 + x\right) \qquad x = R_g^2 q^2$$





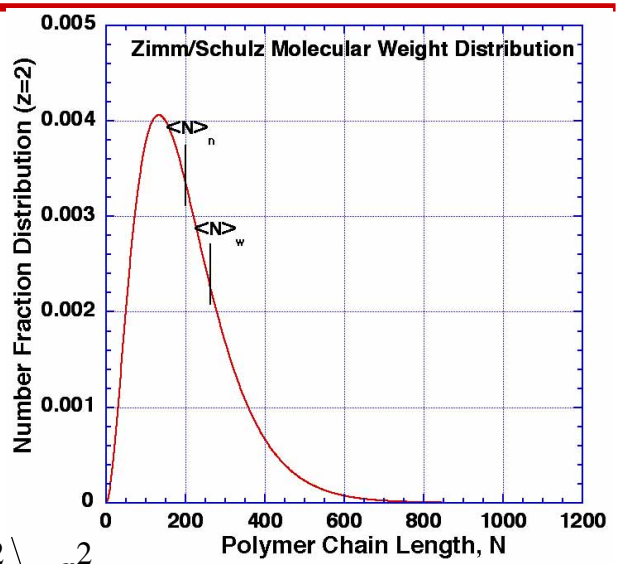
Chain Conformation -cont.

Debye Function with a Zimm-Schulz molecular weight distribution

$$\langle P(q)\rangle_w = \frac{2}{\langle x\rangle_n^2}\left[\langle x\rangle_n - 1 + \left(\frac{h}{h+\langle x\rangle_n}\right)^h\right]$$

where

$$h = \frac{1}{\left[\frac{\langle N\rangle_w}{\langle N\rangle_n} - 1\right]}$$



$\langle N\rangle_n$ number average degree of polymerization

$\langle N\rangle_w$ weight average degree of polymerization

$$\langle x\rangle_n = \langle N\rangle_n l^2 q^2/6 = \langle R_g^2\rangle_n q^2$$

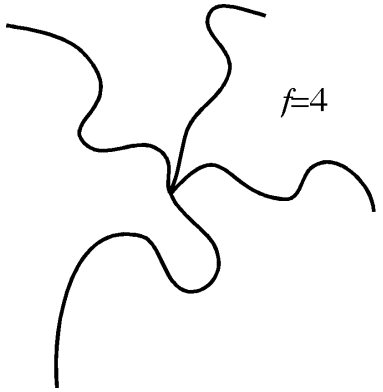
K. Mori, H. Hasegawa, T Hashimoto; *Polymer*, **1989**, 30, 1389

Scattering function for a Gaussian star molecule

$$P(q) = \frac{2}{x^2}\left(\frac{x}{f} - \frac{(1-\exp(-x))}{f} + (1-\exp(-x))^{\frac{2(f-1)}{2f}}\right)$$

$$x = \frac{R_g{}^2 q^2}{f^g} \qquad g = \frac{(3f-2)}{f^2}$$

f is the number of arms



H. Benoit; *J. of Polymer Science*, **1953**, 11, 507-510

Thermodynamics of Polymer Blends

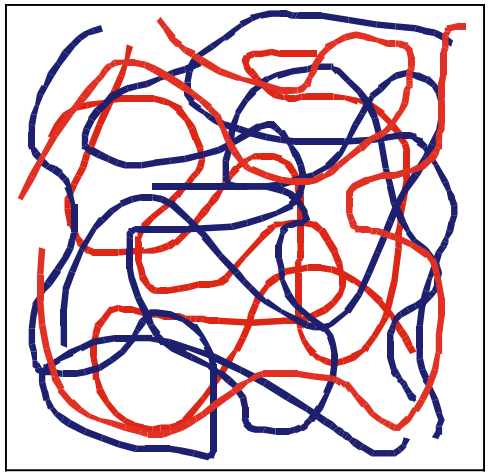
Flory-Huggins Free Energy of Mixing

$$\frac{\Delta f_{mix}}{kT} = \frac{\phi_a ln\phi_a}{N_a} + \frac{\phi_b ln\phi_b}{N_b} + \phi_a\phi_b\chi$$

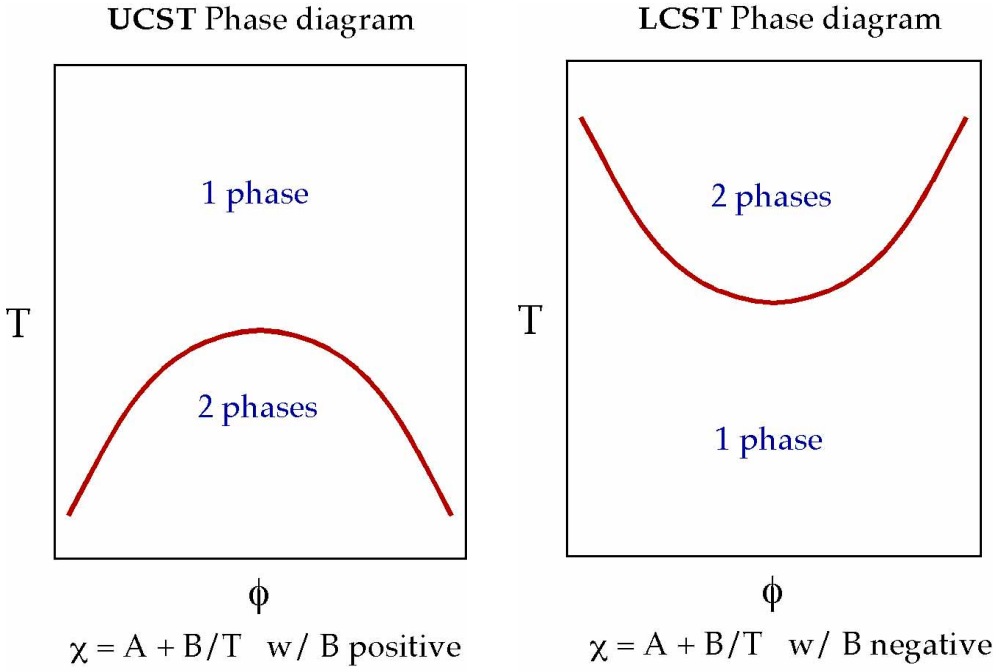
Entropy of mixing — Enthalpy of mixing

χ: Flory interaction parameter

$\chi \sim 1/T$



Miscible binary polymer blend



Thermodynamics of Polymer Blends

de Gennes Random Phase Approximation (RPA) for binary polymer blend

2 identical polymers (one labeled), no interactions (χ=0)

$$I(q) = k_n \phi(1-\phi) N P(q)$$

k_n neutron contrast factor

2 polymers, different molecular weights, with interactions ($\chi \neq 0$)

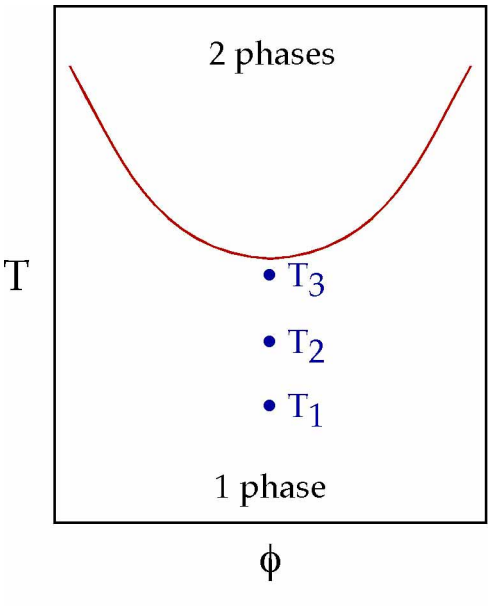
$$\frac{k_n}{I(q)} = \frac{1}{N_a \phi_a P_a(q)} + \frac{1}{N_b \phi_b P_b(q)} - 2\chi$$

q=0 limit

$$\lim\left[\frac{k_n}{I(q \to 0)}\right] = \frac{1}{N_a \phi_a} + \frac{1}{N_b \phi_b} - 2\chi = \frac{\partial^2 \Delta f / kT}{\partial \phi^2}$$

Flory-Huggins Δf
Equation of the spinodal line

Thermodynamics of Polymer Blends



Measure SANS at T_1, T_2, T_3

RPA eq.

$$\frac{k_n}{I(q)} = \frac{1}{N_a\phi_a P_a(q)} + \frac{1}{N_b\phi_b P_b(q)} - 2\chi$$

Expand *P(q)* in small q limit and RPA form reduces to O-Z form (Lorentzian)

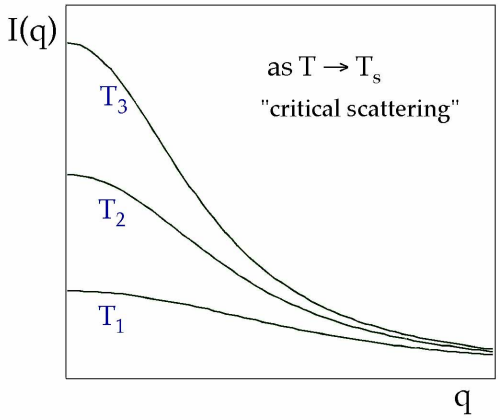
$$I(q) = \frac{K\,I(0)}{1+\xi^2 q^2} \quad \text{with}$$

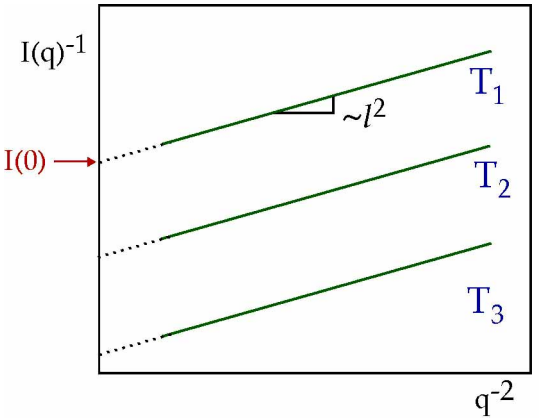
$$\xi^2 = \frac{\overline{l^2}}{36}\left[\phi_a\phi_b(\chi_s - \chi)\right]^{-1}$$ correlation length

$$\overline{l^2} = \phi_a\phi_b\left(\frac{l_a^2}{\phi_a} + \frac{l_b^2}{\phi_b}\right)$$ average statistical step length

$$\chi_s = \frac{1}{2}\left(\frac{1}{N_a\phi_a} + \frac{1}{N_b\phi_b}\right)$$ value of χ parameter at spinodal

RPA scattering (~Lorentzian shape)

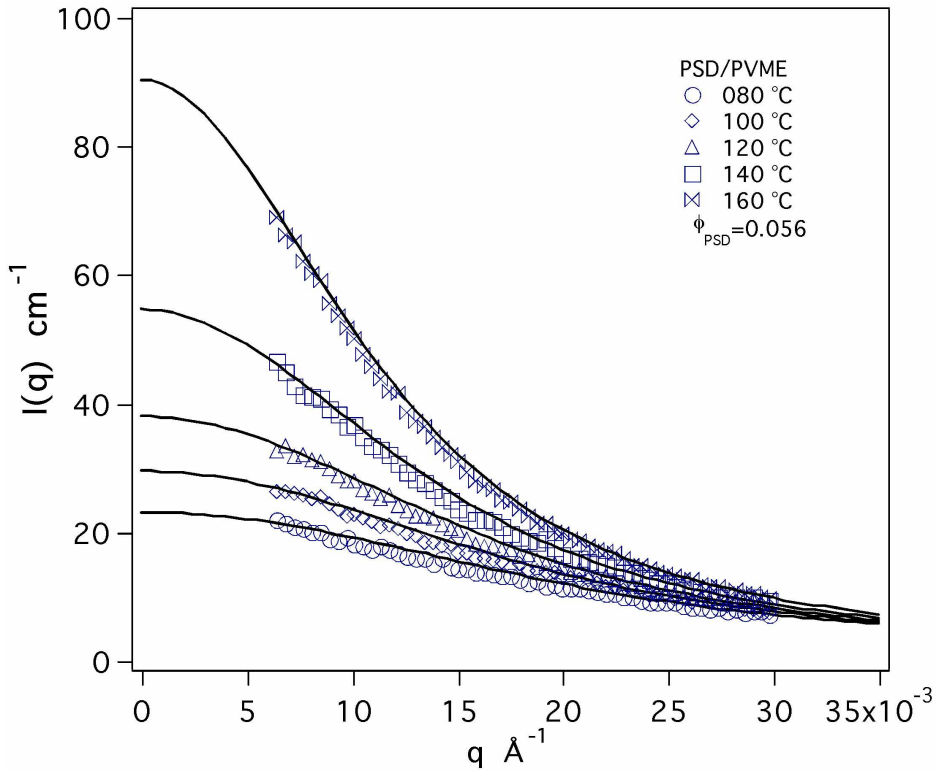




Linearized scattering (O-Z or Zimm plot)

Thermodynamics of Polymer Blends

SANS data from a polymer blend



Fit the data with RPA equation

$$\frac{k_n}{I(q)} = \frac{1}{N_a \phi_a P_a(q)} + \frac{1}{N_b \phi_b P_b(q)} - 2\chi$$

Known parameters

N_i chain length
ϕ_2 composition

Fitting parameters:

$\bar{l}$ average segment length
χ Flory interaction parameter

Calculated parameters:

ξ concentration fluctuation correlation length
I(0) zero angle scattering

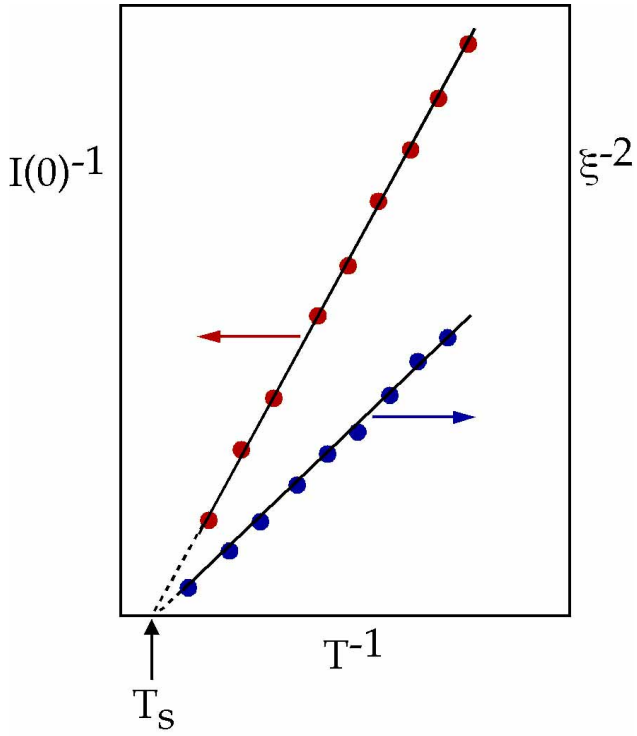
Thermodynamics of Polymer Blends

Determine Phase Diagram

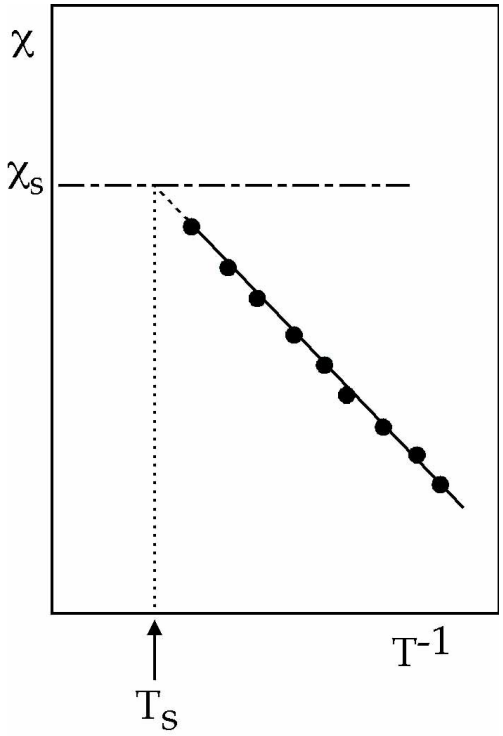
Mean-field scaling of ξ and I(0)

$I(0)^{-1} \rightarrow 0$ as $T \rightarrow T_s$

$\xi^{-2} \rightarrow 0$ as $T \rightarrow T_s$



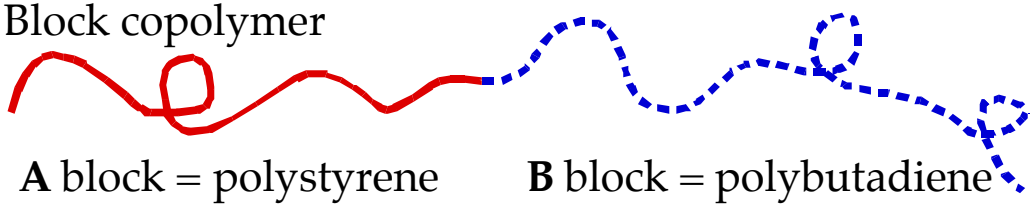
$\chi \rightarrow \chi_s$ as $T \rightarrow T_s$



Thermodynamics of Block Copolymers

Block Copolymer Morphology

A/B Block copolymer



A block = polystyrene **B** block = polybutadiene

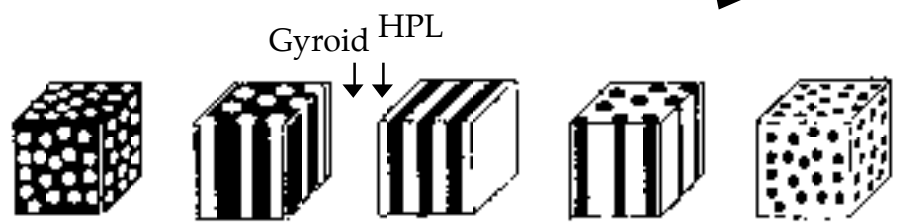
A & **B** are thermodynamically incompatible

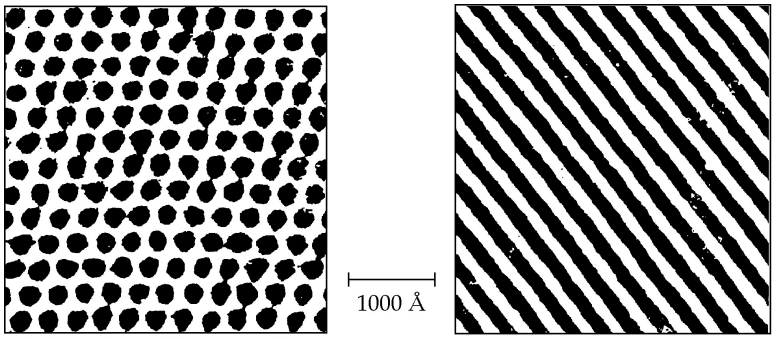
A-B junction between blocks leads to **MICROPHASE SEPARATION**

Microphase separation: phase separation constrained by size of blocks

Microphase separation morphology

Increasing **A** block content (f)





End-on view of hexagonally packed cylinders

Lamellar morphology

TEM Micrographs

Thermodynamics of Block Copolymers

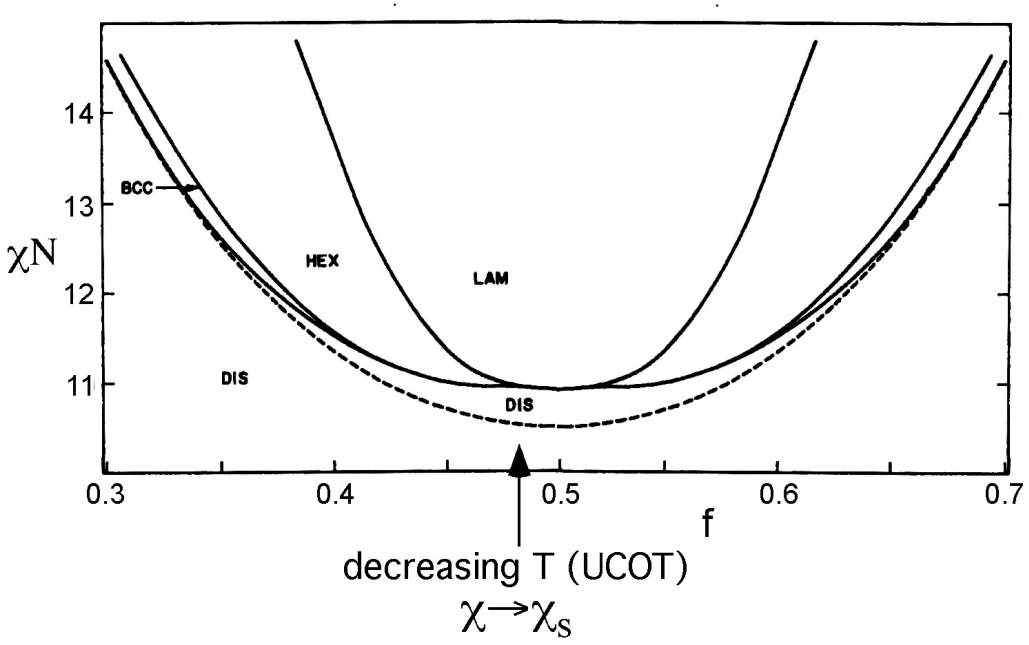
Leibler Scattering function for a diblock copolymer (single phase region)

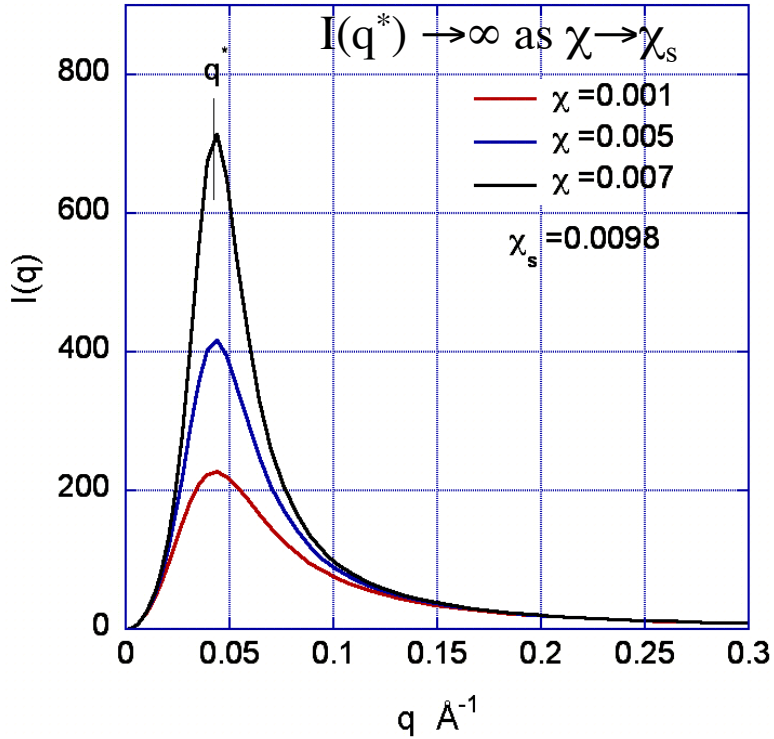
$$\frac{k_n}{I(q)} = \left(P_{aa} + P_{bb} + P_{ab}\right) \Big/ \left(P_{aa}P_{bb} - P_{ab}^2\right) - 2\chi$$

with

$$P(f,x) = \frac{2}{x^2}\left(fx + \exp(-fx) - 1\right)$$

$$x = R_g^2 q^2 \qquad f = N_a / N_a + N_b$$



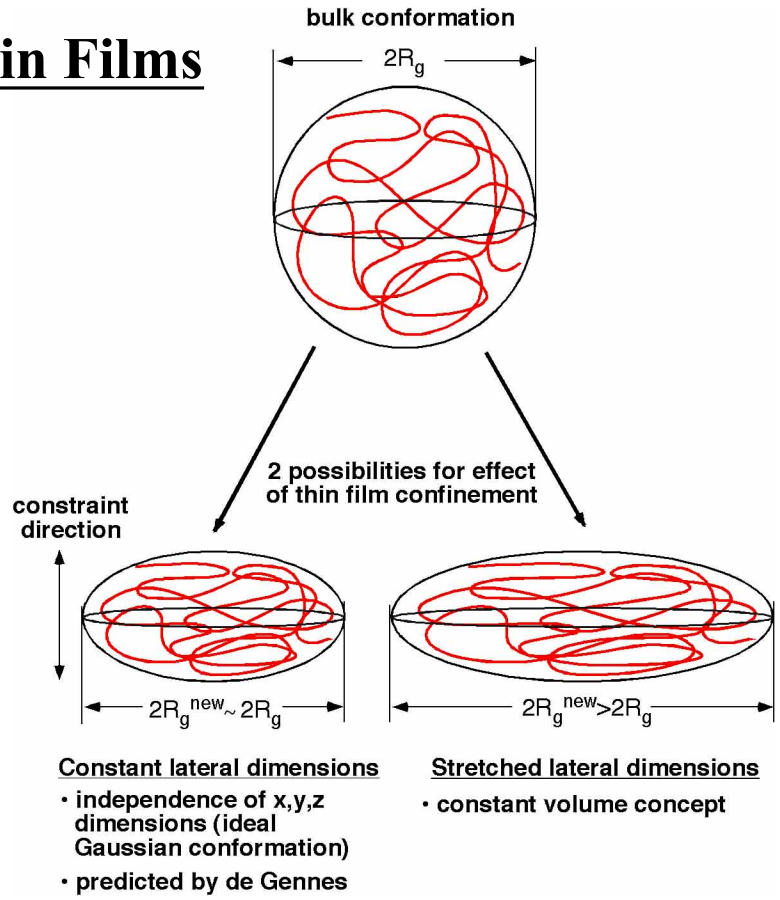


L. Leibler; *Macromolecules*, **1980**, 13, 1602-1617
G.H. Fredrickson, E.Helfand, *J. Chem. Phys.*, **1987**, 8791), 697

Examples -Chain Conformation

Polymer Chain Conformation in Ultra thin Films

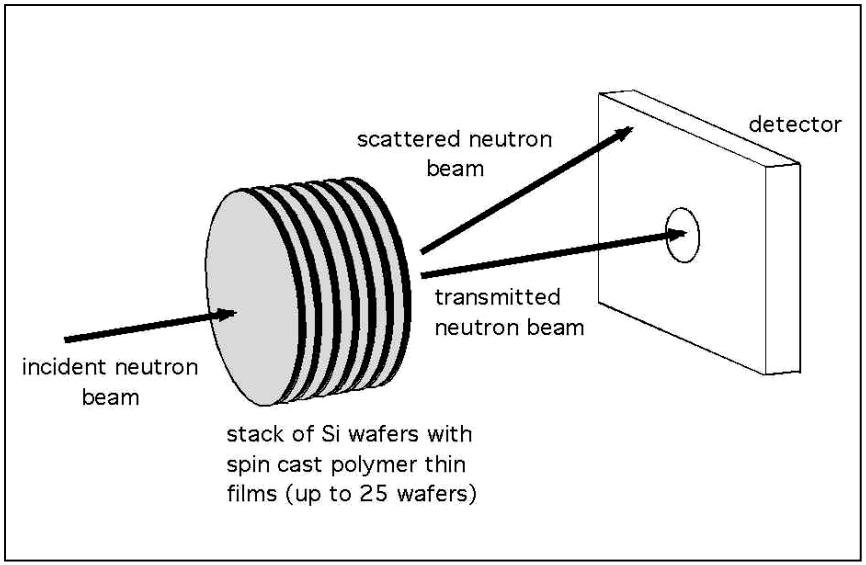
- **Objective:** Characterize polymer chain conformation in ultra thin films (film thickness < 2Rg)
  - **Polymer chain conformation in ultra thin films is a fundamental physical question which remains open**
  - **Development of the technique of small angle neutron scattering (SANS) for the study of thin polymer films**
  - **Polymer conformation plays a critical role in film wetting, adhesion and coatings**



R.L. Jones, S.K. Kumar, D.L. Ho, R.M. Briber, T.P. Russell, *Nature*, 1999, 400, 146

Examples -Chain Conformation

- **Approach**
  - Use SANS to measure the radius of gyration (Rg) of the polymer chain in ultra thin films on Si wafers (neutron transmission of Si ~ 0.999+)
  - Mixtures of deuterated polystyrene and normal polystyrene. Deuterium labeling provides neutron contrast. 25 d-PS/75 h-PS composition.



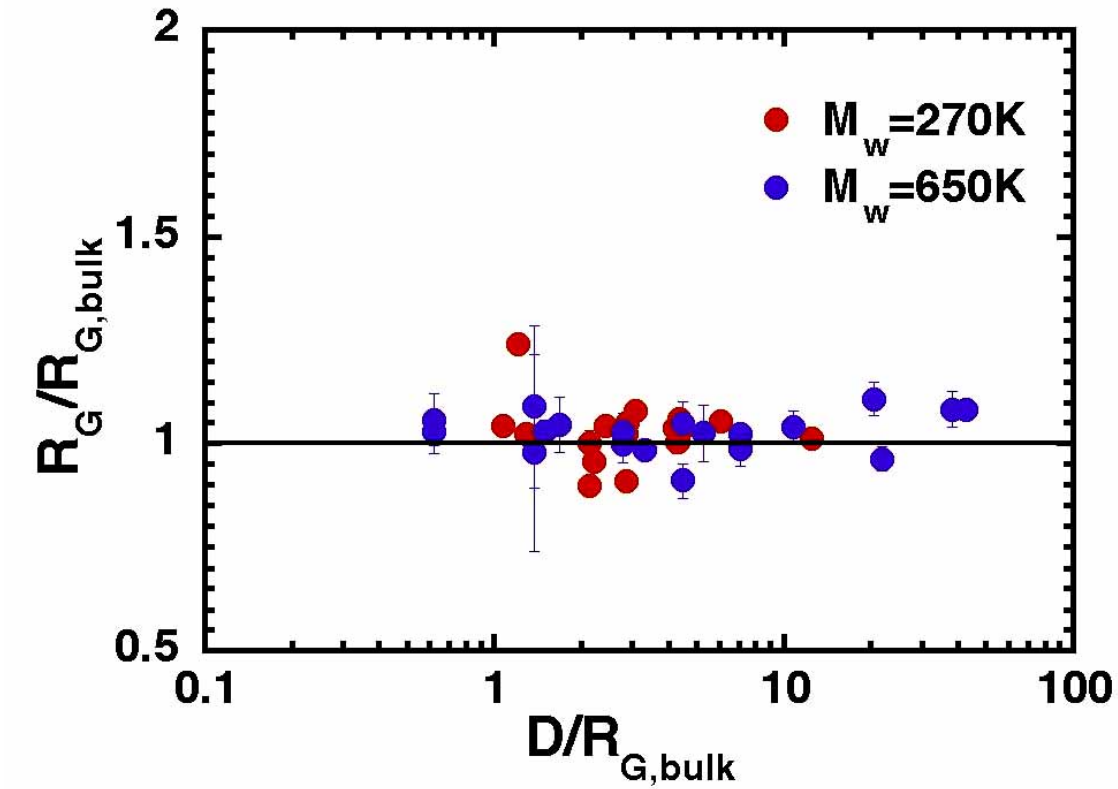
Thin films are spun on 1" Si wafers (0.75" neutron beam diameter)

For stacks of 25 wafers with a film thickness of 10nm total polymer sample is ~ 0.2 mg

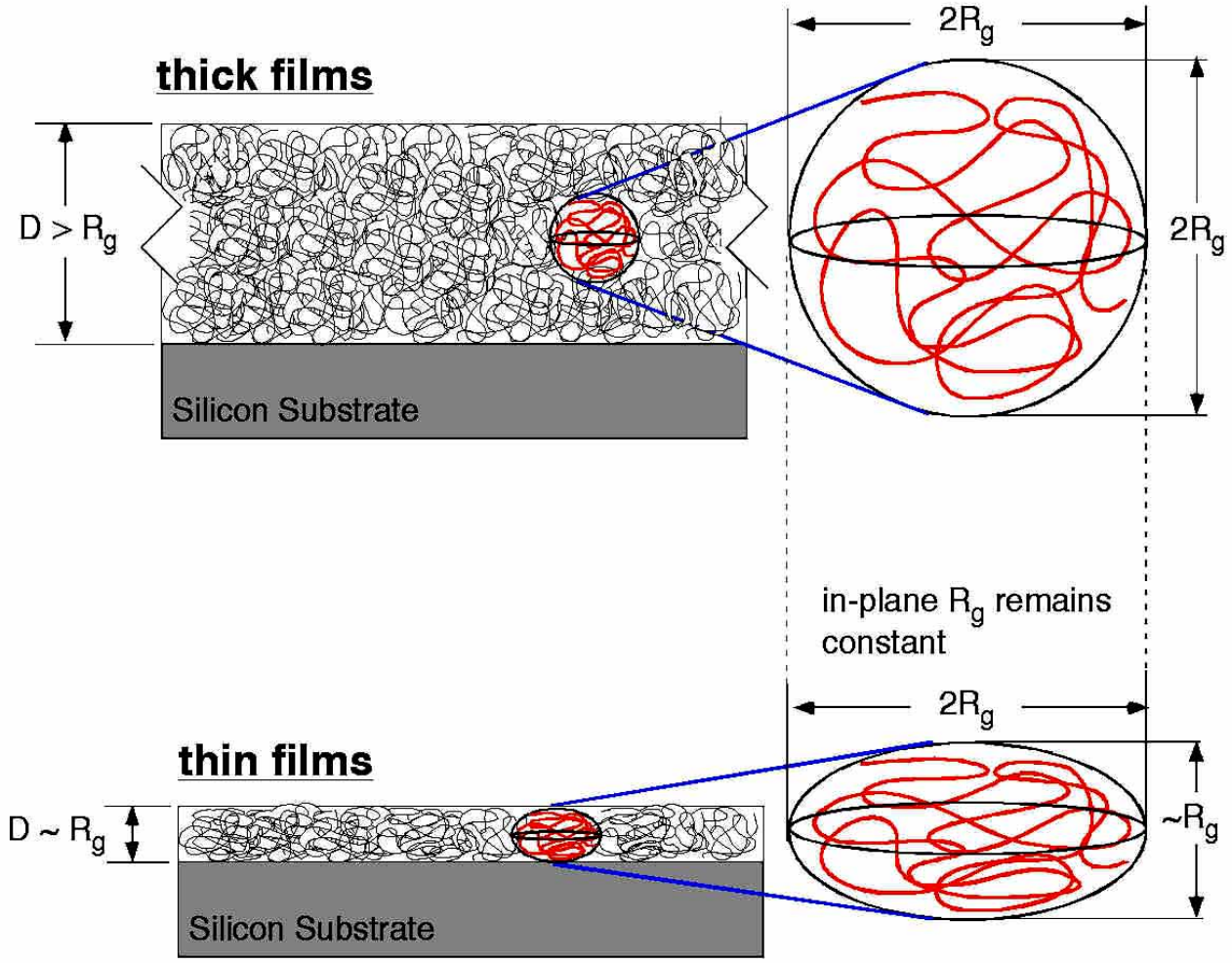
Examples -Chain Conformation

Results:

Rg in plane of film remains unchanged down to film thickness ~1/2 Rg!



Examples -Chain Conformation



Implications

-Chain conformation in x,y,z directions are independent

- Higher segment density inside coil volume for thin films (D<2Rg)

-Less entanglements per chain in thin films

- Different chain dynamics in thir films

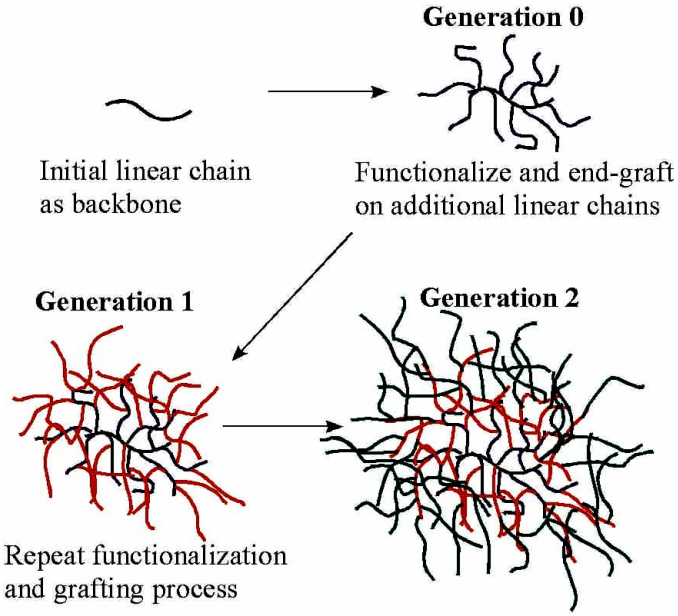
R.M. Briber 3/01

Examples -Chain Conformation

Characterization of Arborescent Graft Polymers

- **Objective: Characterize the behavior of arborescent graft polymers in solutions and in blends with linear polymers**
  - **Arborescent graft polymers are new molecules with an unusual chain architecture. The goal is to use small angle neutron scattering to measure the size and shape in solutions and blends.**
  - **The characterization of the size, shape and density profile of arborescent graft polymers will provide insight useful for tailoring them to meet end use requirements as unimolecular micelles, drug delivery vehicles and flow modifiers.**

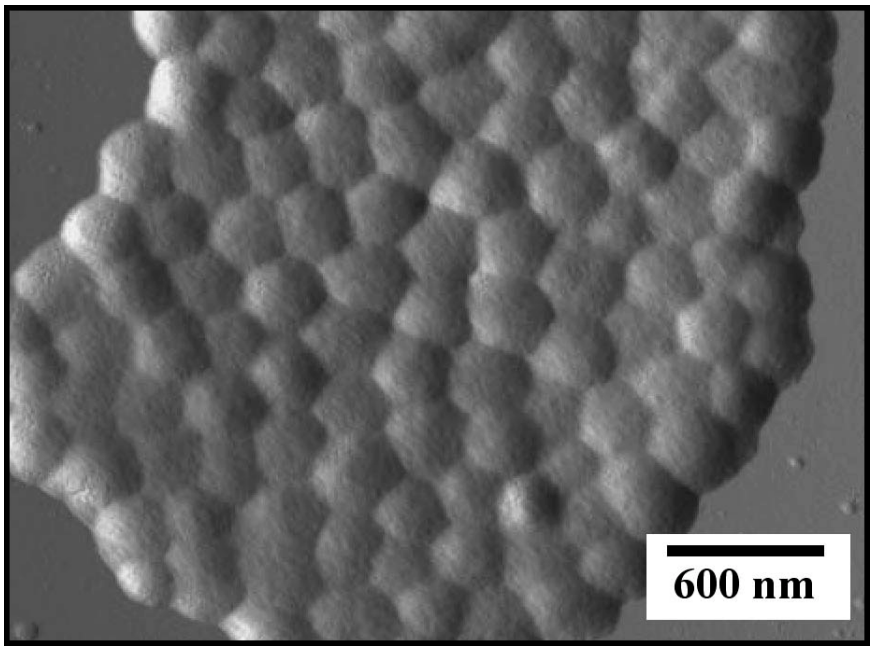
Synthesis of Arborescent Graft Polymers



Notes
- very high grafting density (~0.15-0.2 grafts/monomer)
- Molecular weight increases exponentially

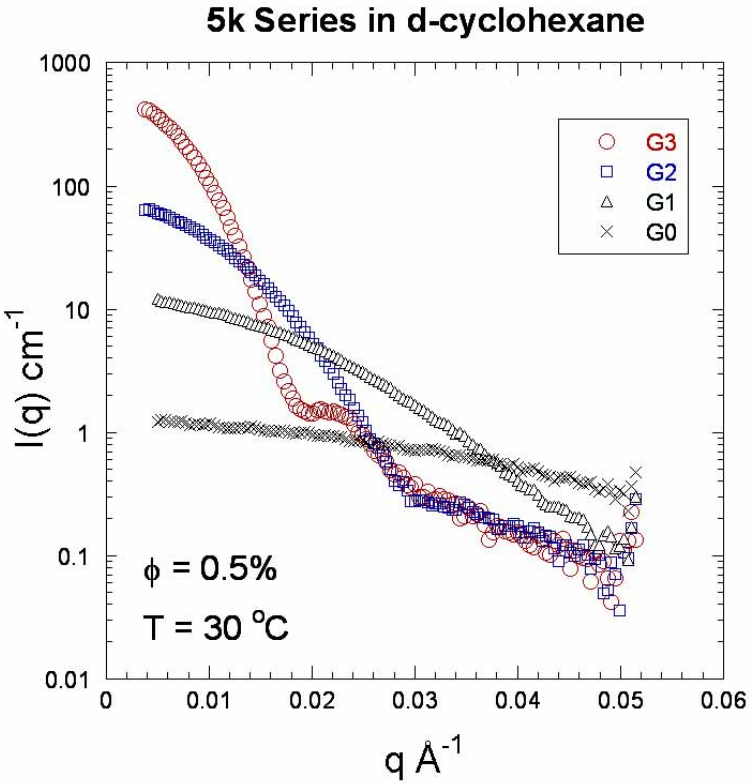
Examples -Chain Conformation

AFM Image



AFM micrograph of a film of 3rd generation AGP molecules synthesized from 30k M_w PS branches.

- **Approach:**
  - **Use small angle neutron scattering to measure Rg and ρ(r) in solutions and blends.**
  - **Deuterated solvents and linear polymers are used to provide neutron contrast.**



Examples -Chain Conformation

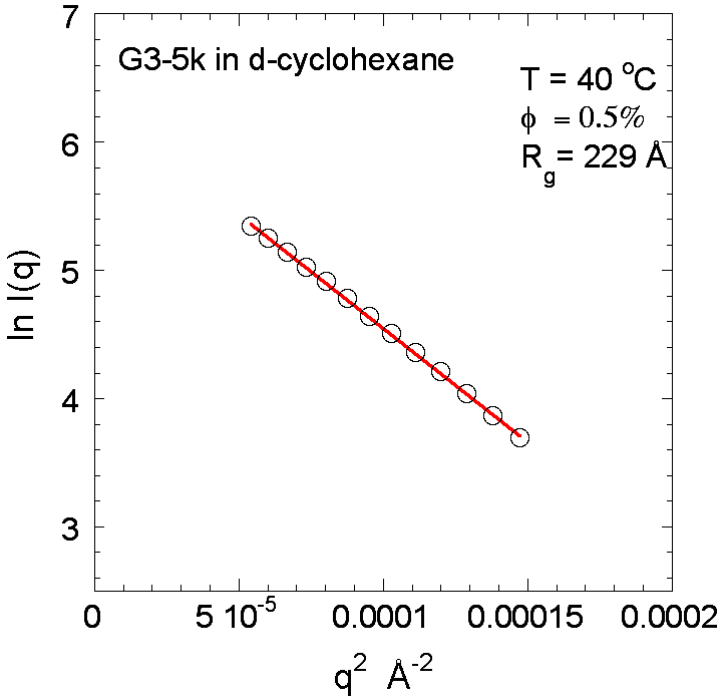
Dilute Solution: -R_g of AG polymer from Guinier Analysis

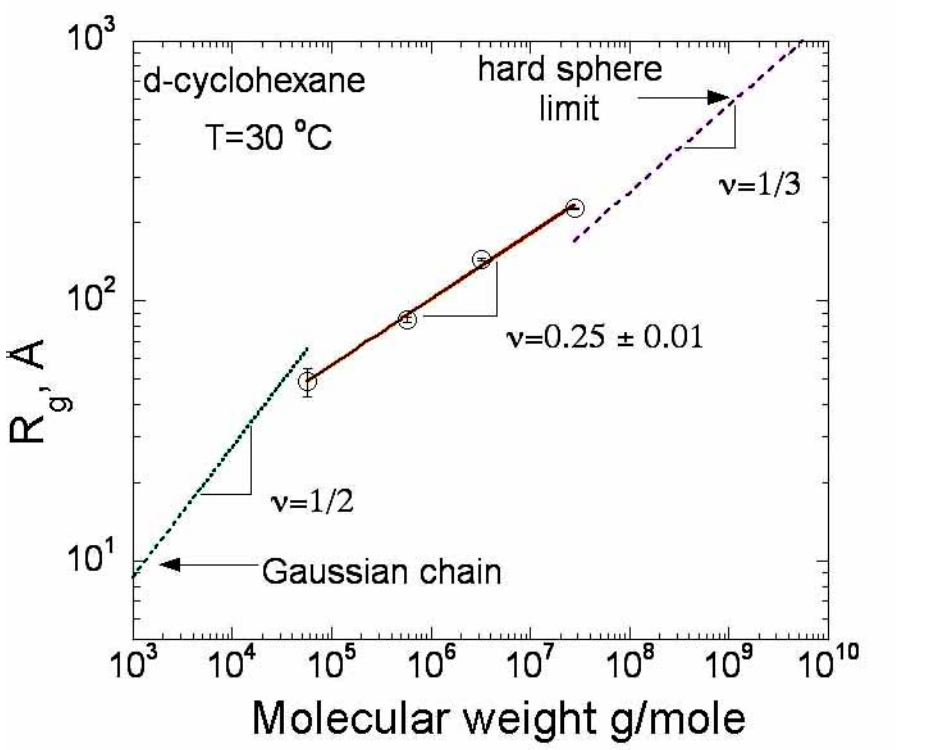
$$I(q) = k_n \phi(1-\phi) N P(q)$$

In the small q limit, $P(q) \rightarrow exp(-R_g^2 q^2/3)$

$$I(q) = k_n \phi(1-\phi) \exp\left(-\frac{R_g^2 q^2}{3}\right)$$

Plot ln $I(q)$ vs. q^2



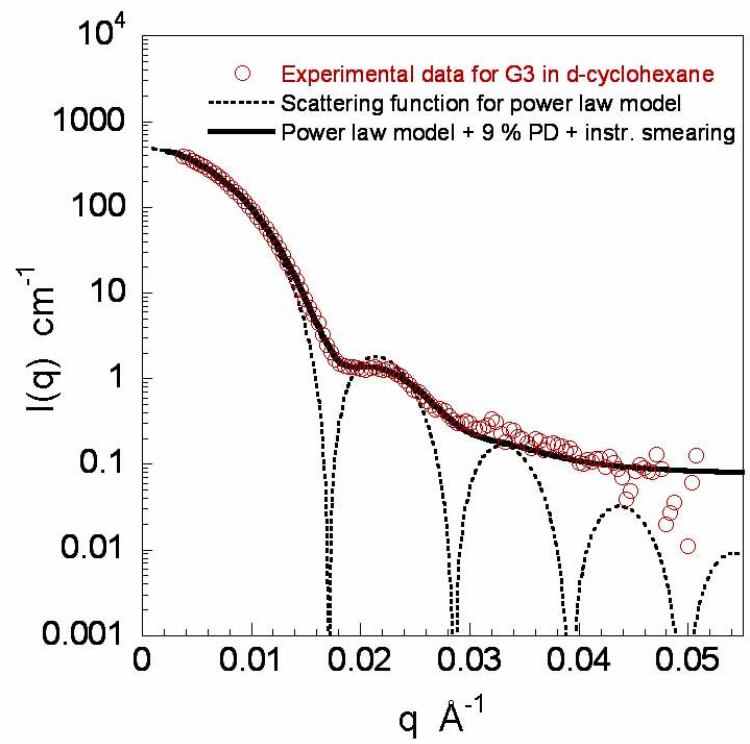


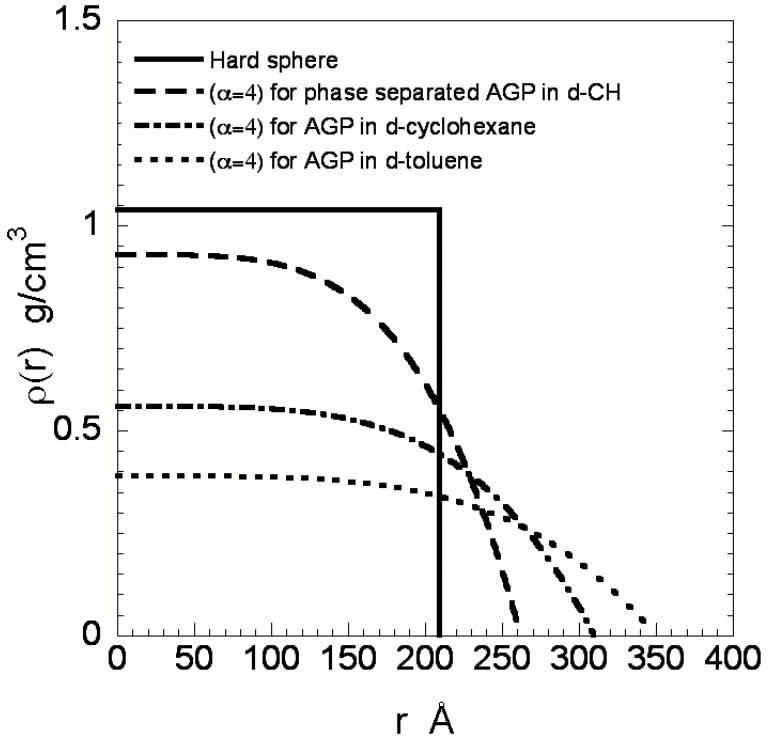
Scaling of Rg with M_w of the form $Rg \sim M^{\nu}$ with ν=0.25 which indicates that arborescent graft polymers become more dense with increasing size (molecular weight).

Examples -Chain Conformation

Model density profile $$\rho(r) = 1 - \left(\frac{r}{R_{\max}}\right)^{\alpha}$$

Calculate scattering (with instrumental and size distribution smearing) $$I(q) = \left[\int \rho(r) \frac{\sin(qr)}{qr} r^2 dr\right]$$



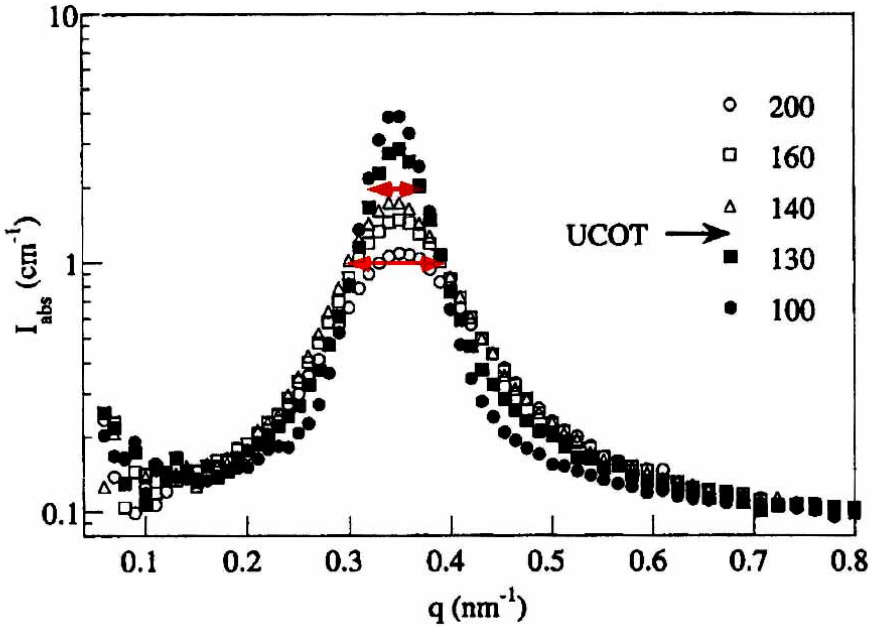


S. Choi, R.M. Briber, B.J. Bauer, D.-W. Liu, M. Gauthier; *Macromolecules*, **2000**, 33(17), 6495-6501

Examples -Block Copolymers

Phase mixing on heating (UCOT)

27K PS-*b*-poly(octylmethacrylate)



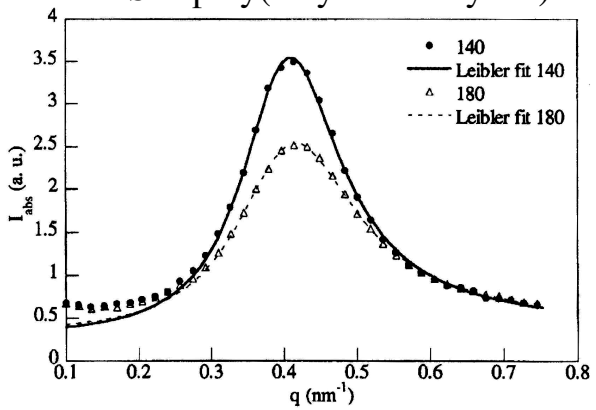
$I(q^*) \rightarrow \infty$ as $\chi \rightarrow \chi_s$ (not reliable)

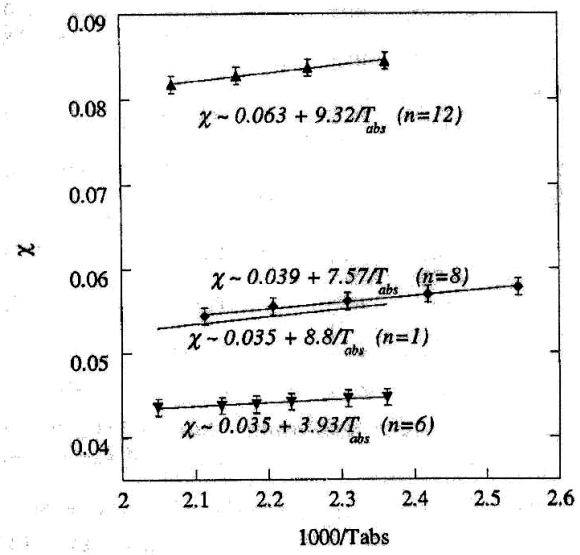
FWHM broadens in single phase

A.-V. Ruzette, A.M. Mayes, M. Pollard, T.P Russell, R. Jerome, T. Slawecki, R. Hjelm, P. Thiyagarajan, *Macromolecules*, **1998**, 31, 8509-8516

Fit to Leibler scattering function with χ, l as fit parameters

23K PS-*b*-poly(octylmethacrylate)



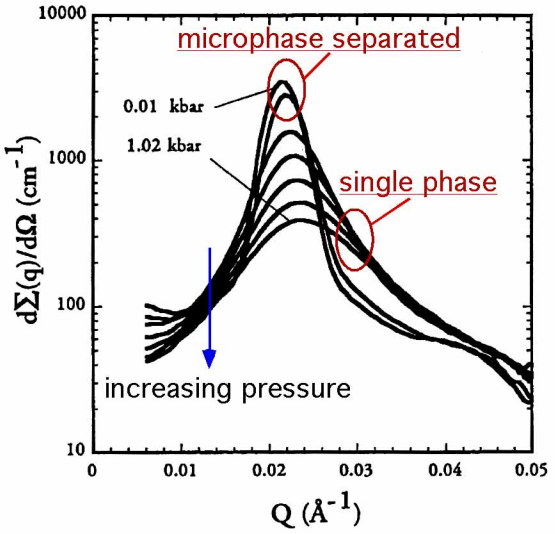


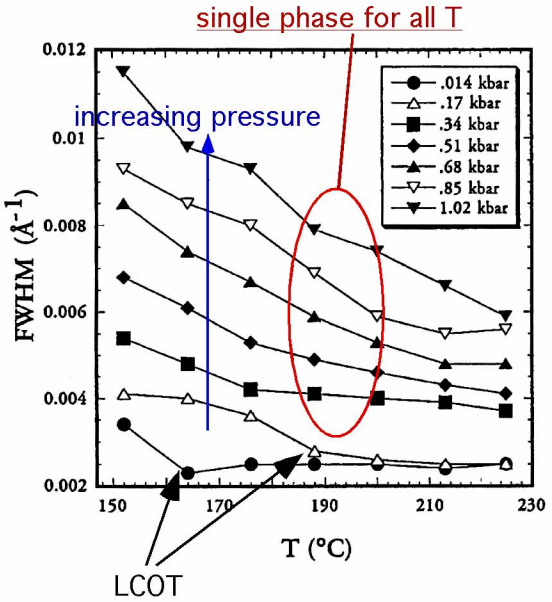
Examples -Block Copolymers

Pressure Effects on the Ordering Transition in Block Copolymers

- **LCOT block copolymer disorders with increasing pressure**
- **Allows for the intelligent design of a baroplastic elastomer**

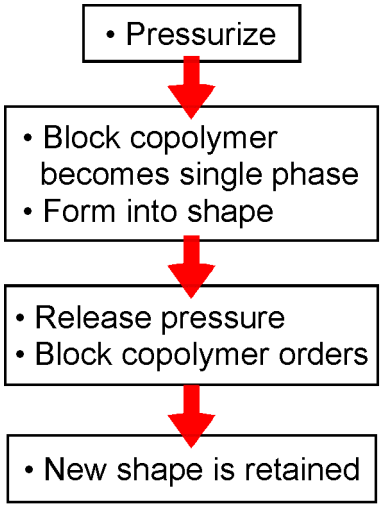
85K d-PS-*b*-poly(*n*-butyl methacrylate)





M. Pollard, T.P Russell, A.-V. Ruzette, A.M. Mayes, Y. Gallot, *Macromolecules*, **1998**, 31, 6493-6498

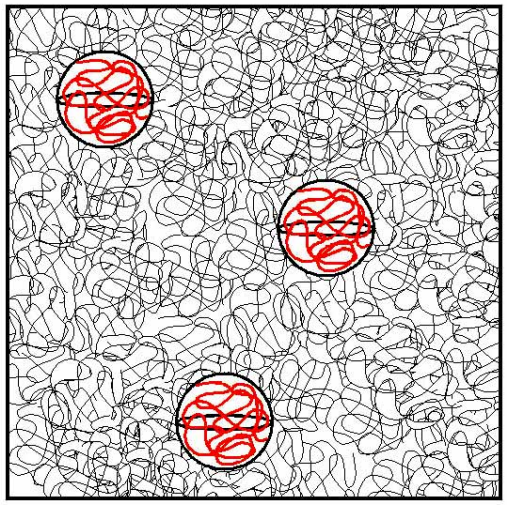
Baroplastic Elastomer



Examples -Polymer Blends

Chain Conformation in Dilute Polymer Blends

Polymer Blend with one species dilute



Questions

- $R_g \sim f(T)$
- Collapse transition in blends

Simulations of $R_g \sim f(T)$ in dilute blends

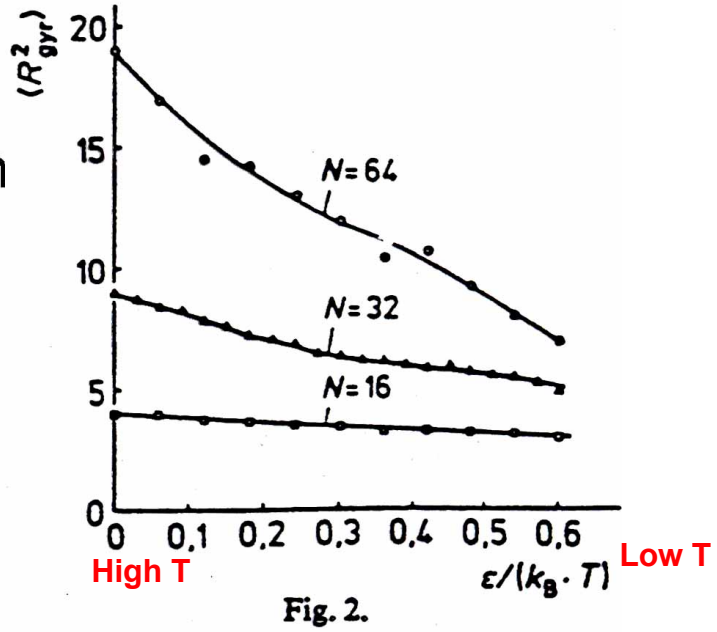
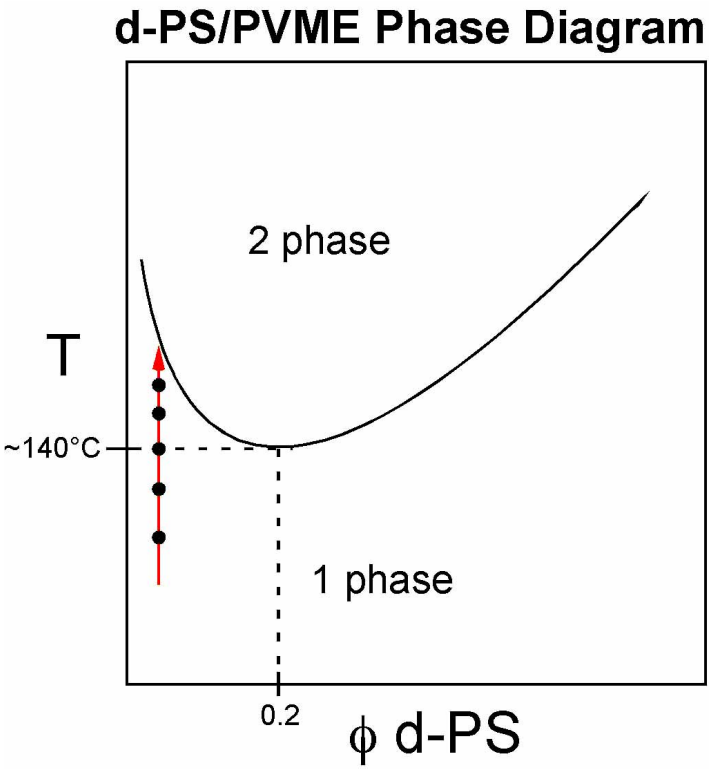
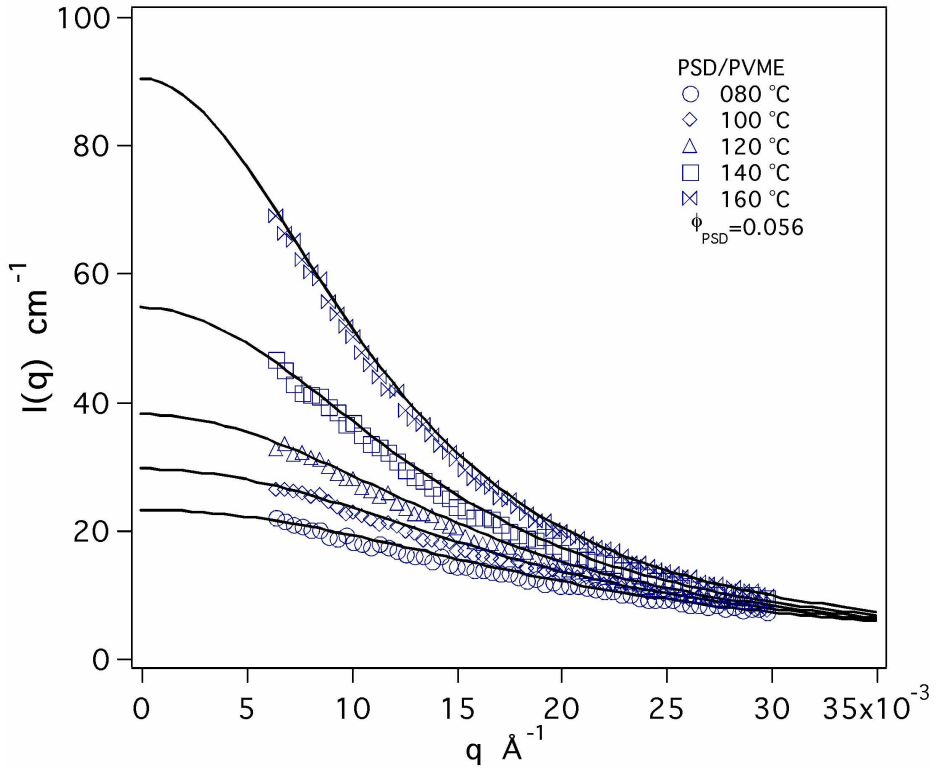


Fig. 2.

Sariban and Binder, *Mackromol. Chemie*, **1988**, 189, 2357

Examples -Polymer Blends





Fit the data with the RPA equation

$$\frac{k_n}{I(q)} = \frac{1}{N_a \phi_a P_a(q)} + \frac{1}{N_b \phi_b P_b(q)} - 2\chi$$

Fitting parameters:

$\bar{l}$ average segment length

χ Flory interaction parameter

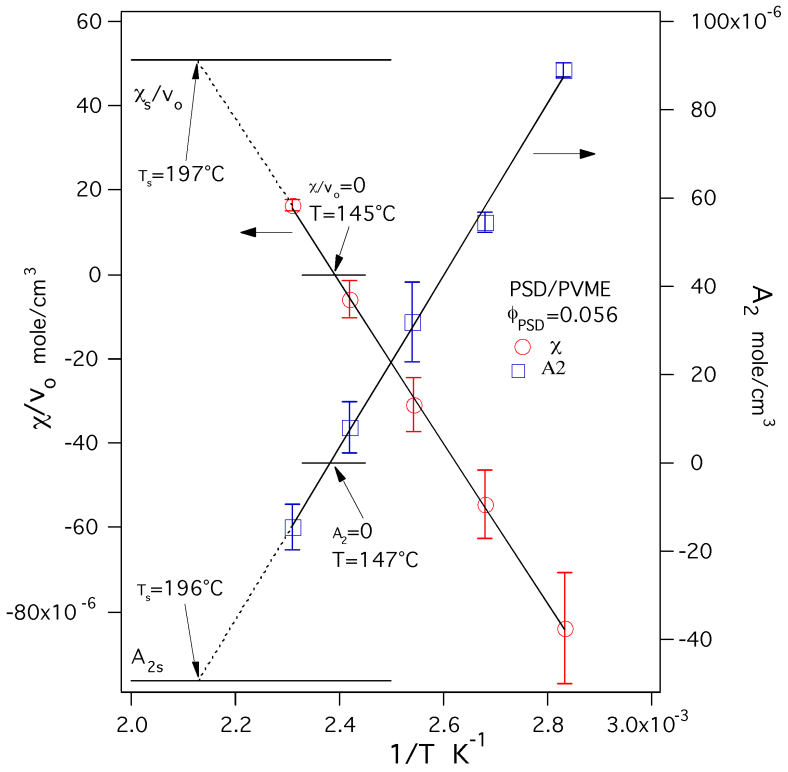
R.M. Briber, B.J. Bauer, B. Hammouda; *J. Chem. Phys.*, **1994**, 101(3), 2592

S. Choi, X. Liu, R.M. Briber; *J. of Polym. Sci., Polym. Phys. Ed.*, **1998**, *36*, 1

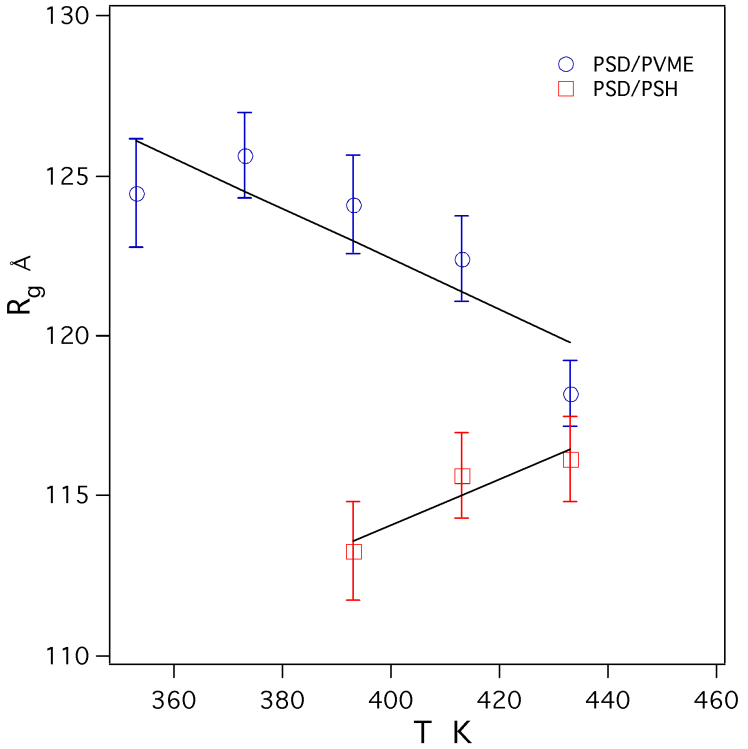
Examples -Polymer Blends

d-PS/PVME Blend

A_2 and χ vs. T

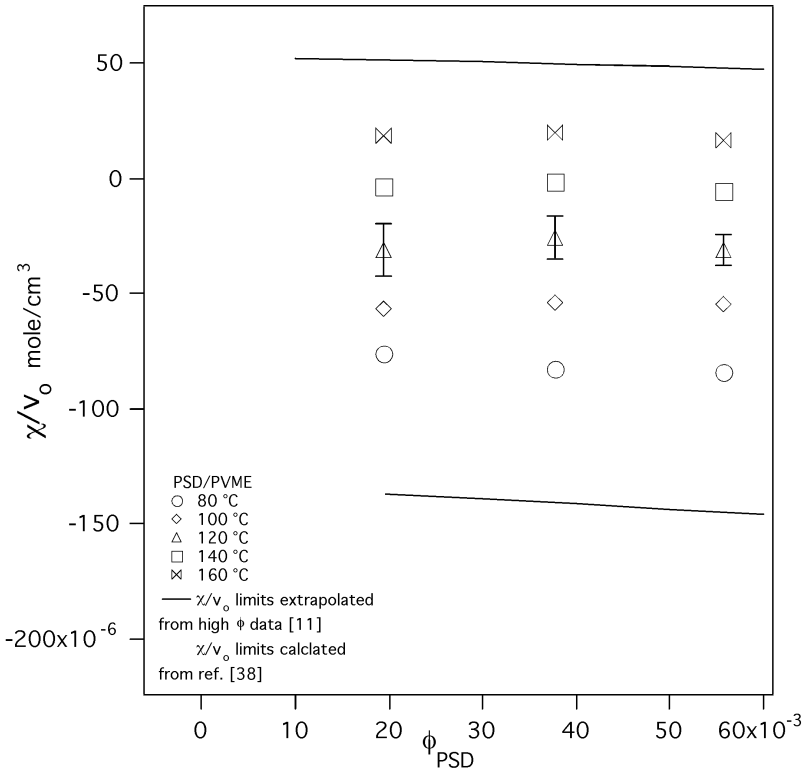


R_g vs. T



Examples -Polymer Blends

χ vs. ϕ



Comparison of SANS data for χ for dilute blends with:

- data extrapolated from separate study at higher concentrations
- calculated values of χ from modified F-H lattice model

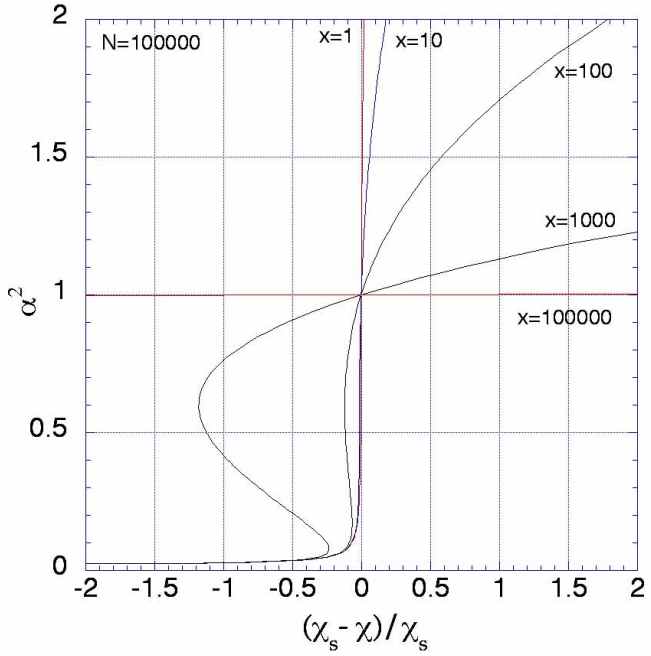
Han, C.C., et al.; *Polymer*, **1988**, *29*, 2002

Dudowicz, J.; Freed, K.; *J. Chem. Phys.*, **1992**, *96*, 1644, 9147

Examples -Polymer Blends

Collapse Transition in Dilute Blends

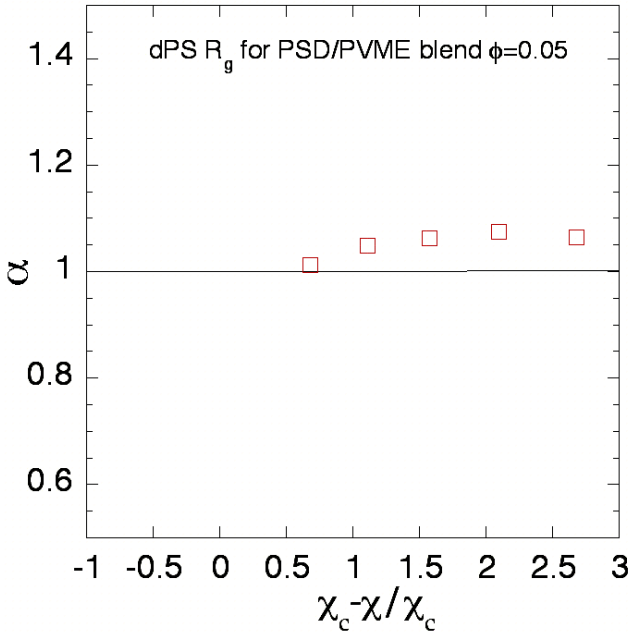
Prediction by Theory



$$\alpha^2 = \frac{\left(R_g\right)^2}{\left(R_g^o\right)^2}$$

N: dilute species
x: matrix species

d-PS/PVME data



Interesting range of prediction not accessed experimentally

Theory shows change in transition from
2nd order→1st order with increasing matrix mol wt. (x)

E.A. Di Marzio, R.M. Briber; *Macromolecules* , **1995**, 28, 4020-4023

Summary

SANS of Polymers

- **q range accessible in SANS matches intrinsic size scale of polymer (R_g) which controls many structural and physical properties**
- **Examples of chain conformation (thin films, arborescent graft polymers)**
- **Examples of thermodynamics (blends, block copolymers)**
- **Comparison of experiments with theory (blends, block copolymers)**