

# Microstructure of High Pressure Polyolefin/*n*-Alkane Solutions

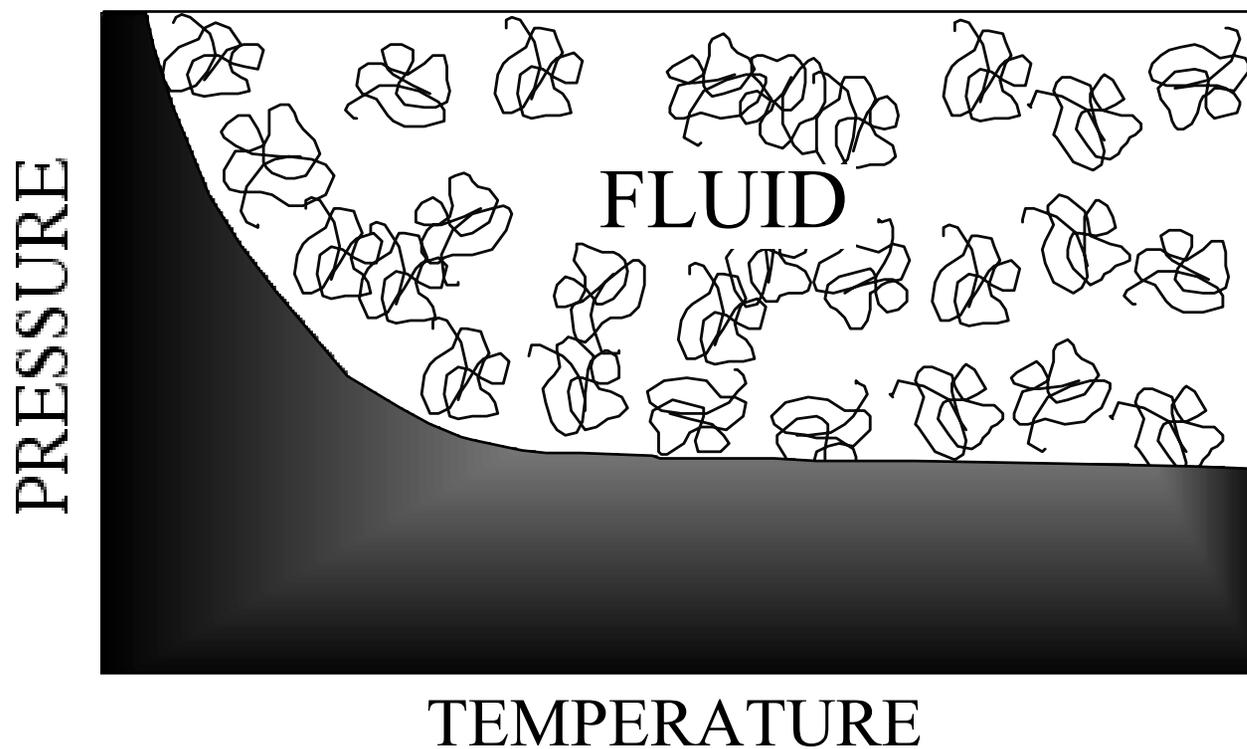
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Highlight macroscopic & microscopic aspects of  
polymer solution phase behavior



Macroscopic Phase Behavior  
SCF – Polymer architecture

Microscopic Solution Structure  
Coil size,  $R_g$  -- Solution stability,  $\xi$

Kirby & M<sup>c</sup>Hugh, Chem Rev, **99**, 565 (1999)

DiNoia, et al., Macromolecules, **33**, 6321 (2000)

## Nonpolar Polymer

**Poly(ethylene-co-1-butene) (PEB<sub>10</sub>)**

**$M_w = 233,000$        $M_w/M_n = 1.01$**

**Ethyl branch/5 repeat groups**

## Nonpolar Solvents

**Pentane & Ethane**

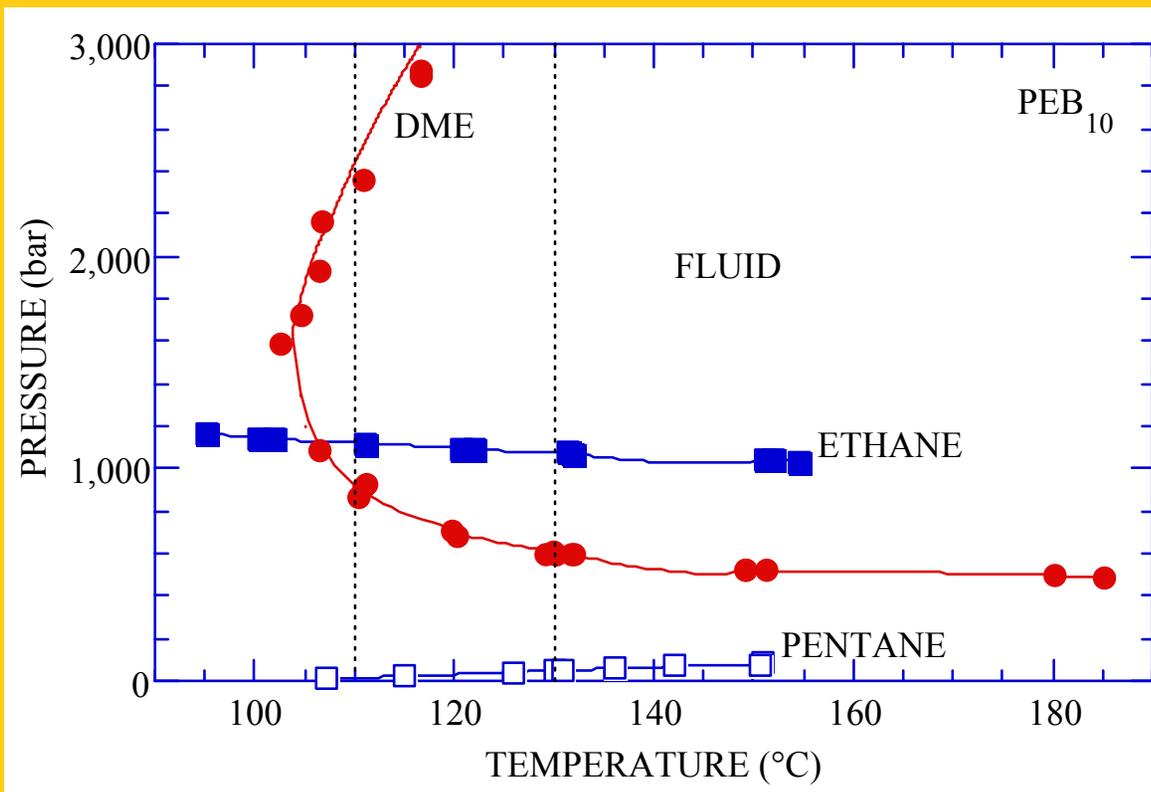
## Polar Solvent

**Dimethyl Ether (DME)**

Lew Fetters (Cornell University & KFA Julich)

Pam Wright (Exxon/Mobil)

# PEB<sub>10</sub> in SCF Ethane, DME, & Liquid Pentane



$$\Gamma_{ij} \approx -C_1 \frac{\alpha_i \alpha_j}{r^6} - C_2 \frac{\mu_i^2 \mu_j^2}{kTr^6}$$

Interchange Energy

$$\Gamma_{ij} = \frac{1}{2} [\Gamma_{ii} + \Gamma_{jj}]$$

	$T_c$ (°C)	$P_c$ (bar)	$\alpha$ (Å <sup>3</sup> )	$\mu$ (Debye)
Ethane	32.3	48.8	4.5	0.0
Pentane	196.6	33.7	9.6	0.0
DME	126.8	53.0	5.2	1.3

## Challenge

**Get radiation into and out of the cell without distortion**

Ruler:  $q(\text{\AA}^{-1}) = \frac{4\pi\eta}{\lambda_o} \sin\left(\frac{\theta}{2}\right)$

$\eta$ , refractive index (T, P,  $\lambda$ )

$\theta$ , need large unsupported window area to get large  $\theta$

How do window properties change with pressure?

## Approach

**Small Angle Neutron Scattering**

$\lambda \sim 5$  to  $10 \text{ \AA}$  -- small unsupported window area,  $\eta \sim 1.0$

# SANS Data Analysis

Scattering intensities corrected for

- Dark-noise/detector efficiency; cell/sapphire window scattering; sample transmissions
- Change in path length with pressure

Absolute differential cross-section per unit volume

- $d\Sigma/d\Omega$  (cm<sup>-1</sup>) -- silica & water standards

Background scattering

- Measured in C<sub>5</sub><sup>o</sup> and estimated for C<sub>2</sub><sup>o</sup>
- Problem with incoherent scattering from H

# SANS Data Analysis

High Concentration Isotopic Labeling Technique

$$I(q) = Nz^2K \cdot S_s(q) + Nz^2L \cdot S_t(q)$$

- $S_t(q)$  fit to Ornstein-Zernike equation -- low  $q$

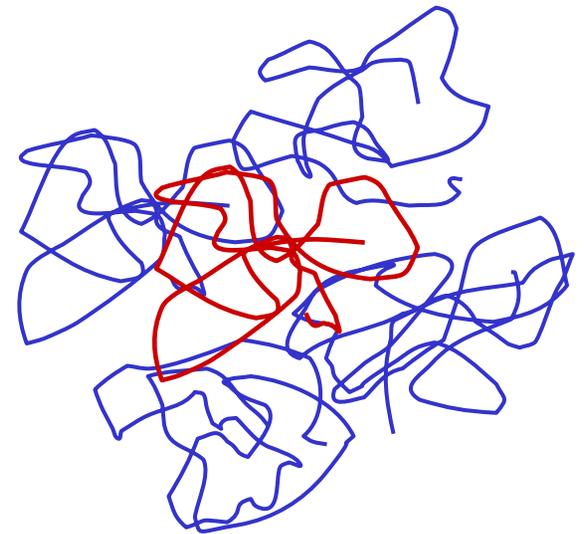
$$S_t(q) = \frac{S(0)}{(1 + q^2 \xi^2)}$$

$\xi$  -- correlation length for concentration fluctuations

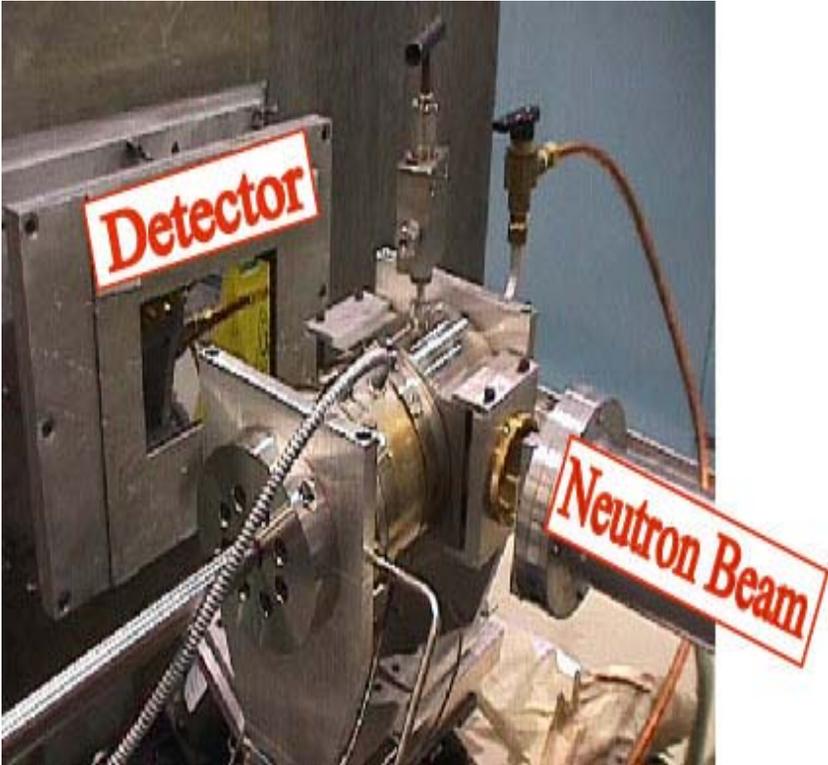
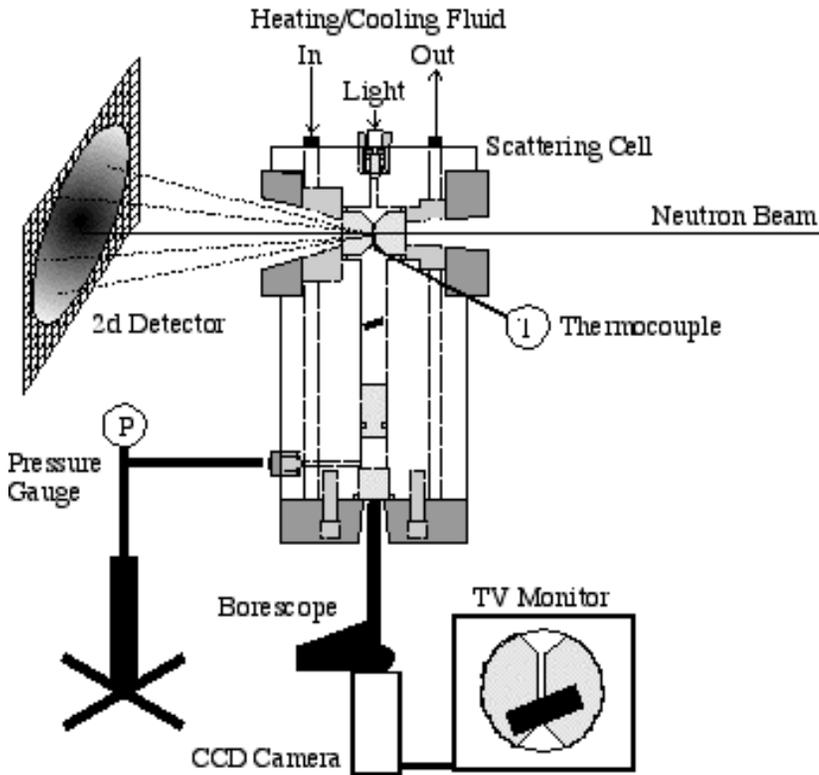
- $S_s(q)$  fit to Debye equation -- low  $q$

$$S_s(q) = \frac{2}{q^4 R_g^4} [q^2 R_g^2 - 1 + \exp(-q^2 R_g^2)]$$

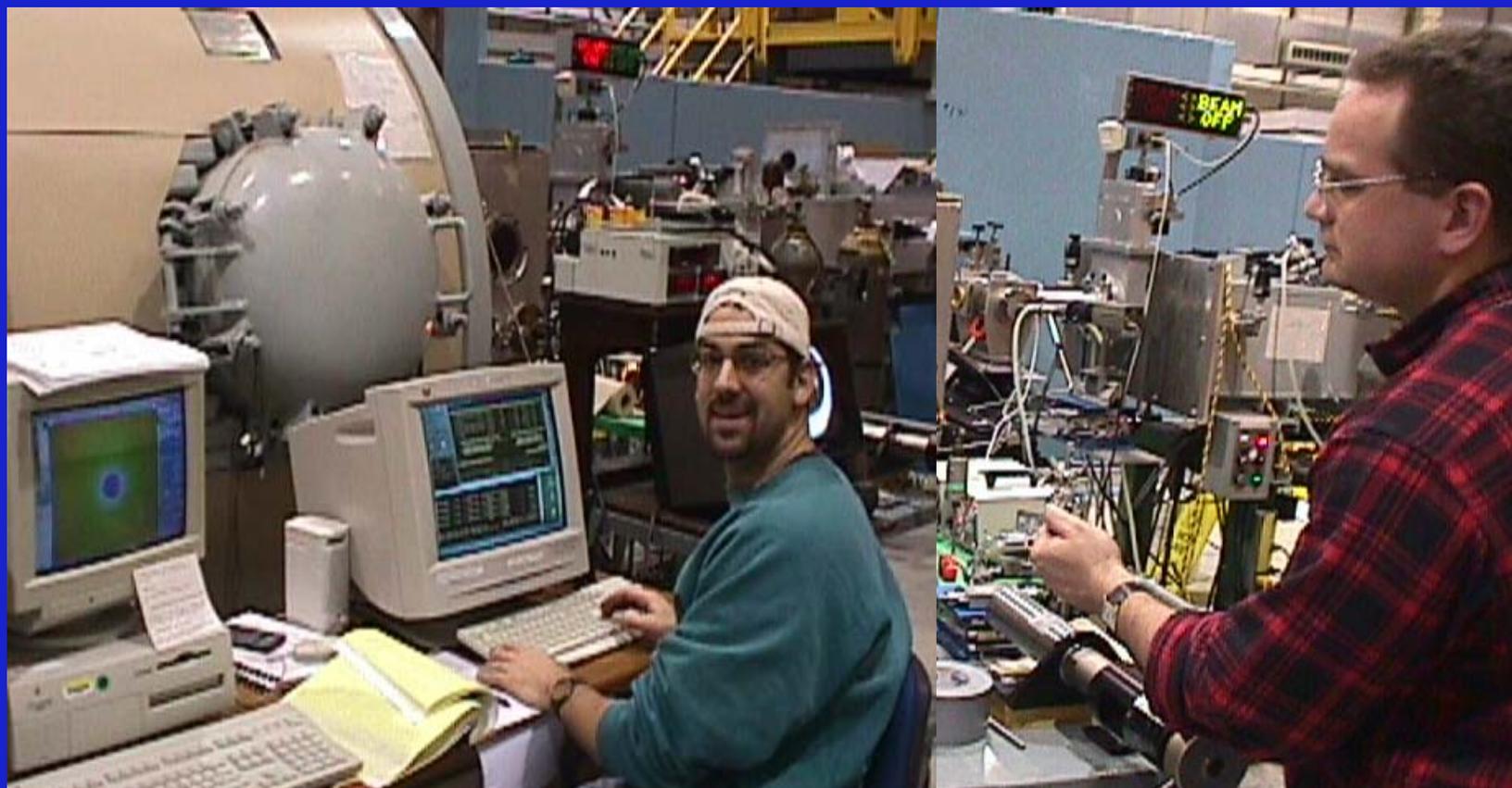
$R_g$  -- polymer coil dimension



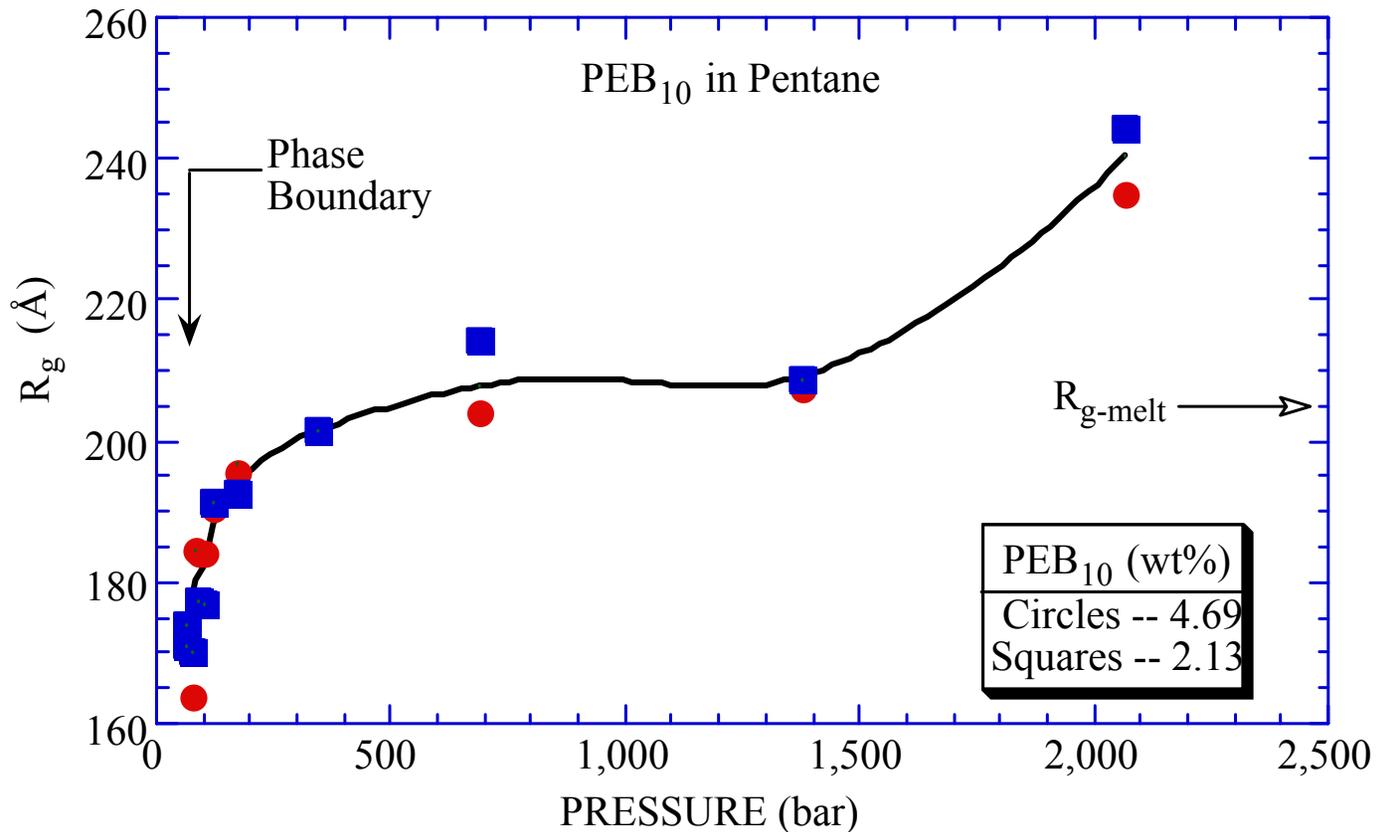
# Unibody High-Pressure SANS Cell



REACTOR ON



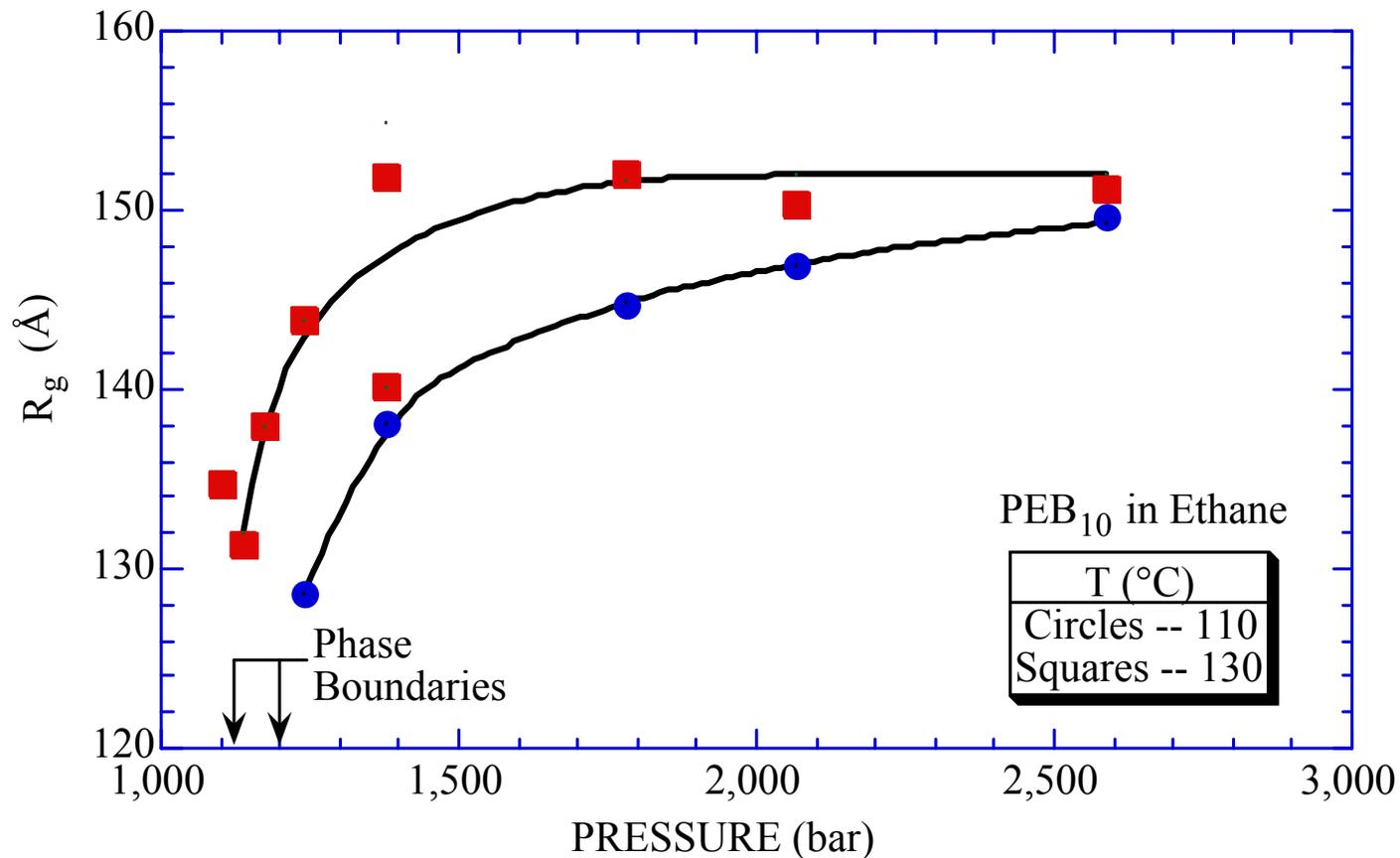
# PEB<sub>10</sub> in Pentane @ 130°C



$R_g$  collapses on *close* approach to boundary &  
at modest pressures  $R_g \approx R_{g\theta\text{-melt}}$

Behavior not observed with normal liquid solvents!

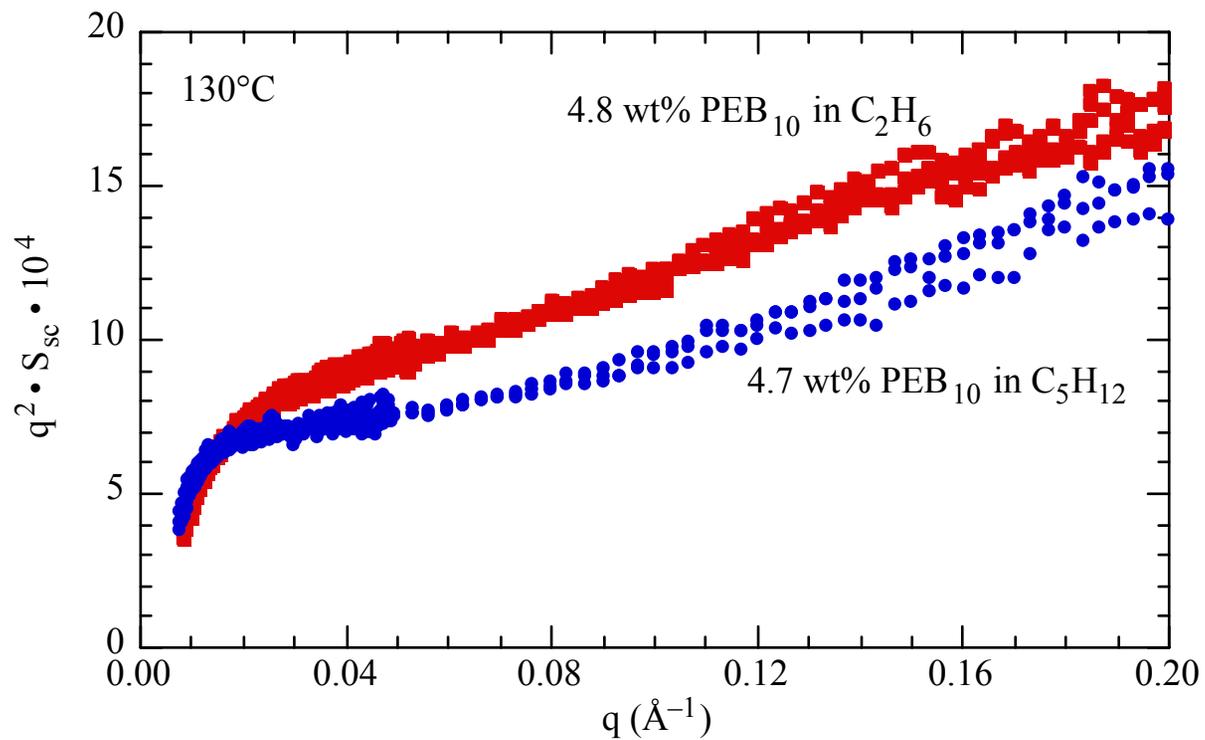
# PEB<sub>10</sub> in Ethane @ 130 & 110 °C



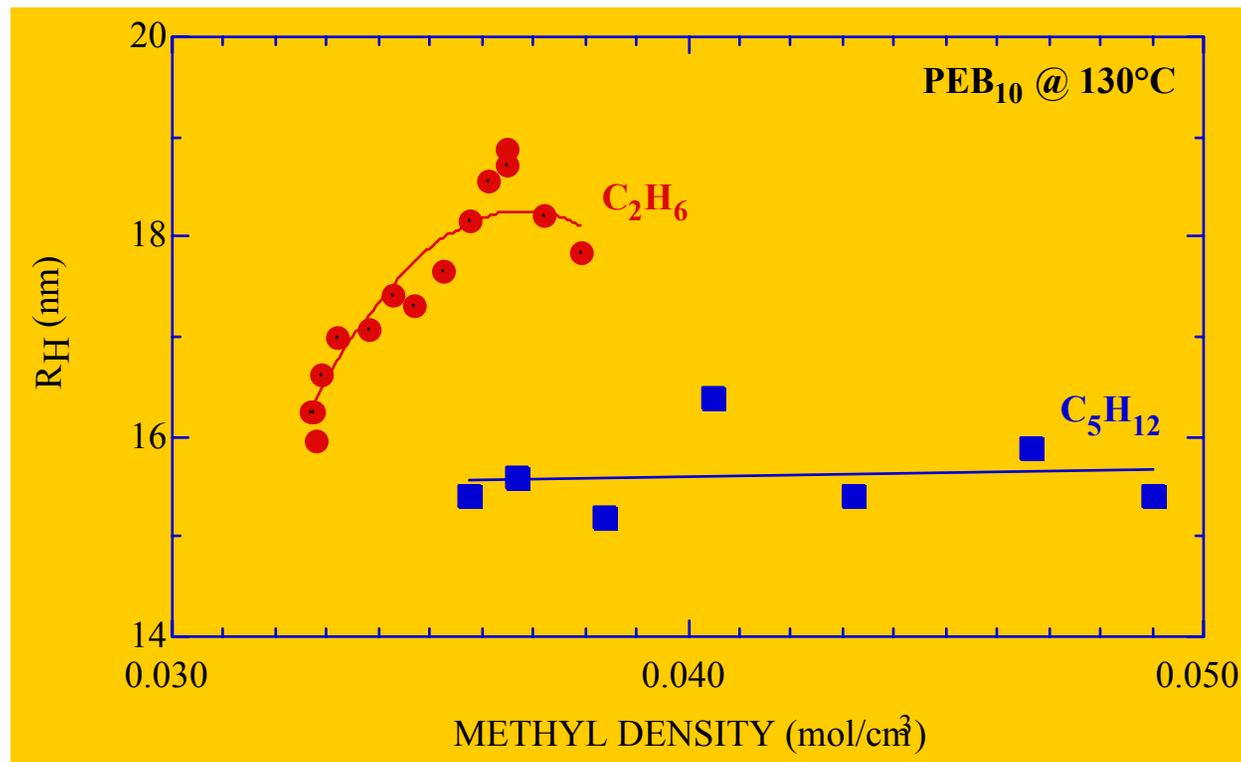
$R_g$  collapses on *approach* to boundary

**BUT**, at high pressures & near overlap conditions,  $R_g \neq R_{g\theta\text{-melt}}$

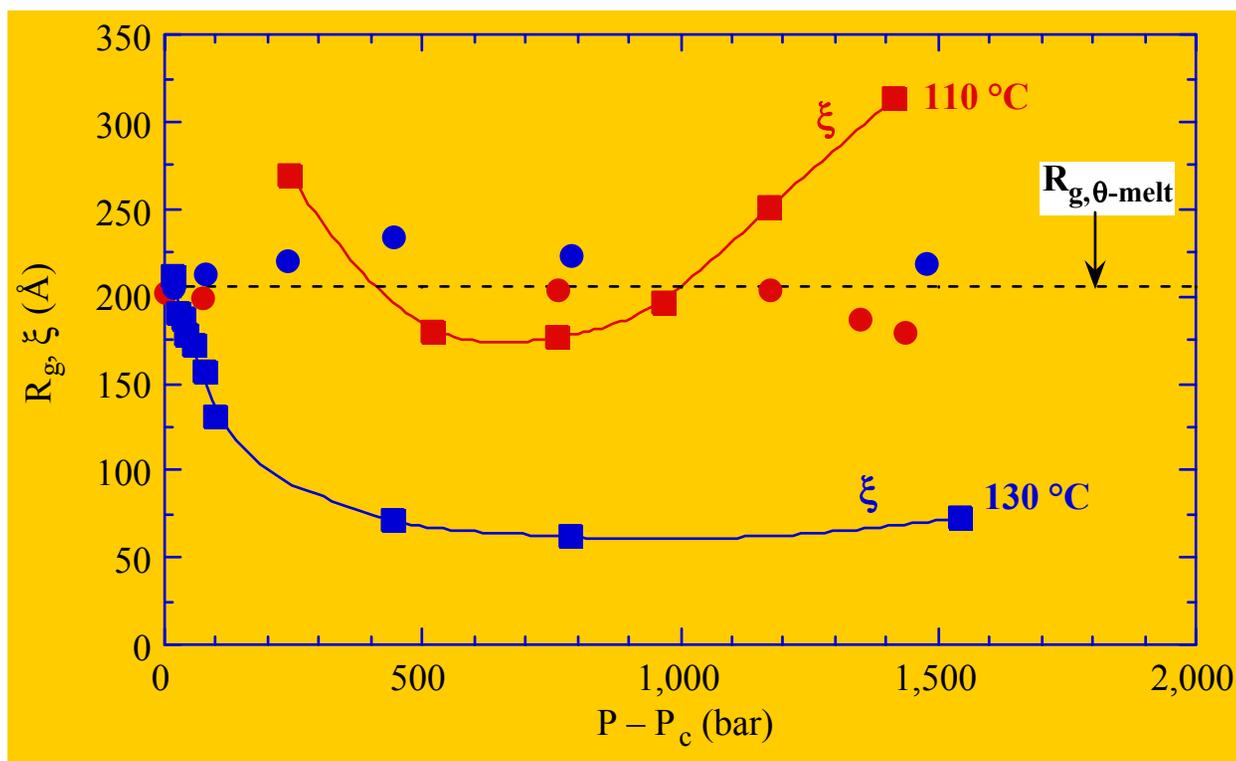
# PEB<sub>10</sub> in Ethane & Pentane @ 130°C



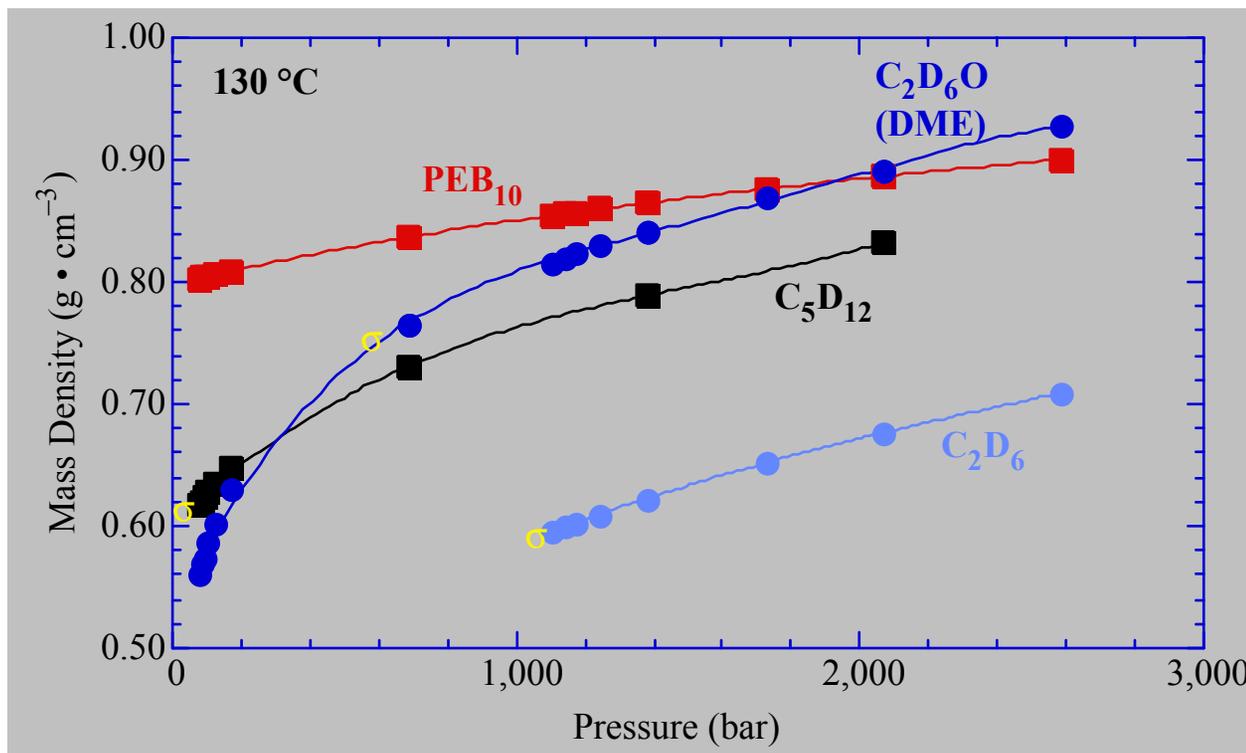
# PEB<sub>10</sub> R<sub>H</sub> in Ethane & Pentane @ 130°C



# PEB<sub>10</sub> in Dimethyl Ether @ 110 & 130 °C



# Density & Sedimentation Effects



# Conclusions

- ①  $R_g$   $\uparrow$  at high density,  $\downarrow$  at low density in alkanes;  
 $R_g$  is unaffected by density in DME  
“solvent quality” is sensitive to both interactions & packing
- ② While solvent chemical potential depends on both P & T,  
 $\uparrow$ P may lead to structural solvent effects that affect polymer  
conformation via solvent-solvent interactions
- ③ Challenge to theorists/simulators to model these  
“*simple*” systems?



Chris Kloxin

Mobil/Exxon Res. & Eng  
Low Fetters, Pamela Wright

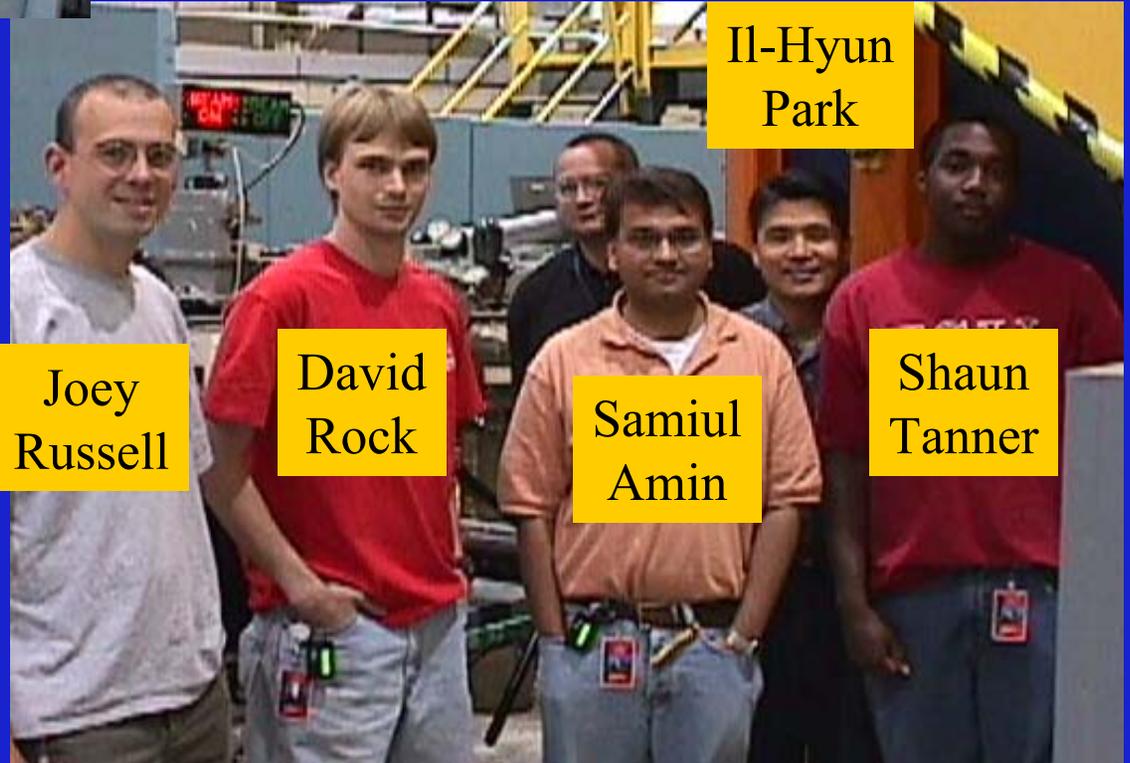
JHU PhD Graduates  
Chris Kirby  
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Dr. Steve Kline

NSF



Alberto Garach



Il-Hyun Park

Joey Russell

David Rock

Samiul Amin

Shaun Tanner