SANS Studies of Polymers and Colloids: Past Highlights and Future Directions

George D. Wignall

Center for Neutron Scattering

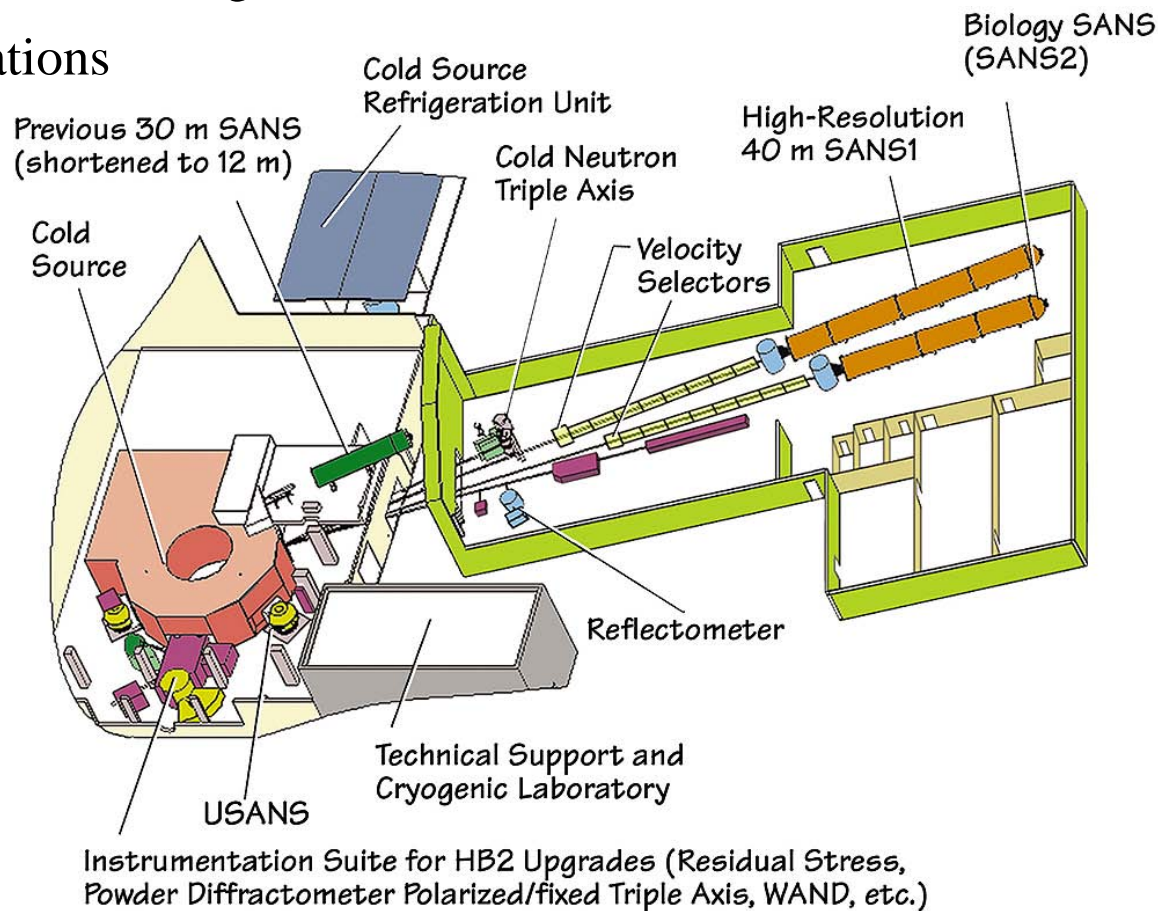*Condensed matter Sciences Division*

Oak Ridge National Laboratory*
Oak Ridge TN 37831-6393

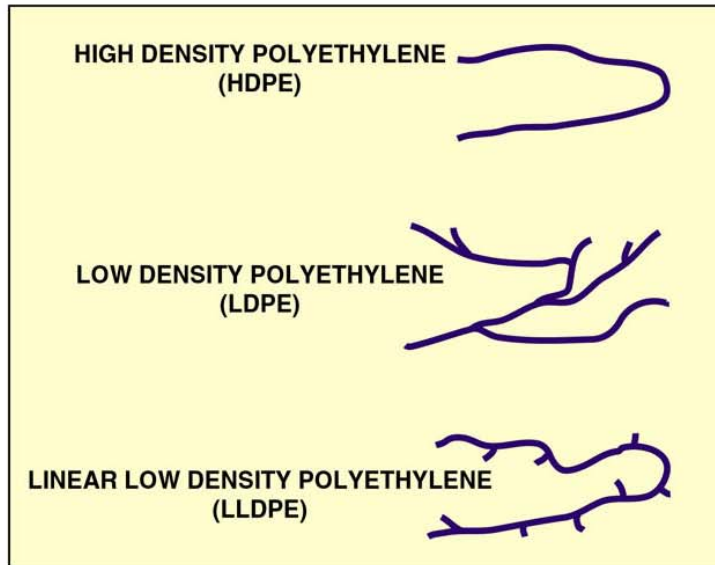SNS/HFIR User Meeting, October 11-13, 2005

Why So Much Time and Money for Small Angle Neutron Scattering?

- Structures on length scales 5 – 2000Å
- Colloidal aggregates in solution (e.g., micelles, microemulsions)*
- Polymer chain configurations
- Polymer blend (alloy) thermodynamics*
- High-temperature superconductivity
- Structure of bone
- Voids in metals
- Composite materials and "filled" polymers*
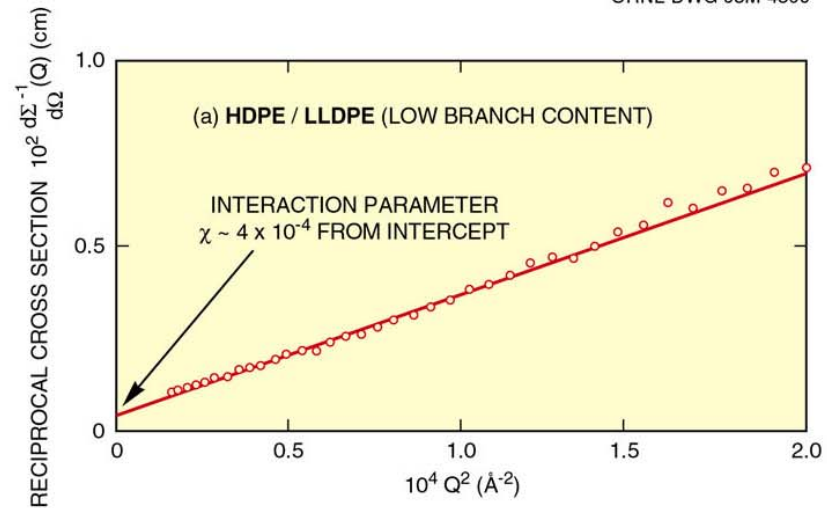- Biological structures
- Supercritical fluids*
- Block co-polymers*

Biology SANS (SANS2)

Cold Source Refrigeration Unit

High-Resolution 40 m SANS1

Previous 30 m SANS (shortened to 12 m)

Cold Neutron Triple Axis

Cold Source

Velocity Selectors

Reflectometer

Technical Support and Cryogenic Laboratory

USANS

Instrumentation Suite for HB2 Upgrades (Residual Stress, Powder Diffractometer Polarized/fixed Triple Axis, WAND, etc.)

ORNL 2005-01734/jcn

Melt Compatibility of Polymer Blends
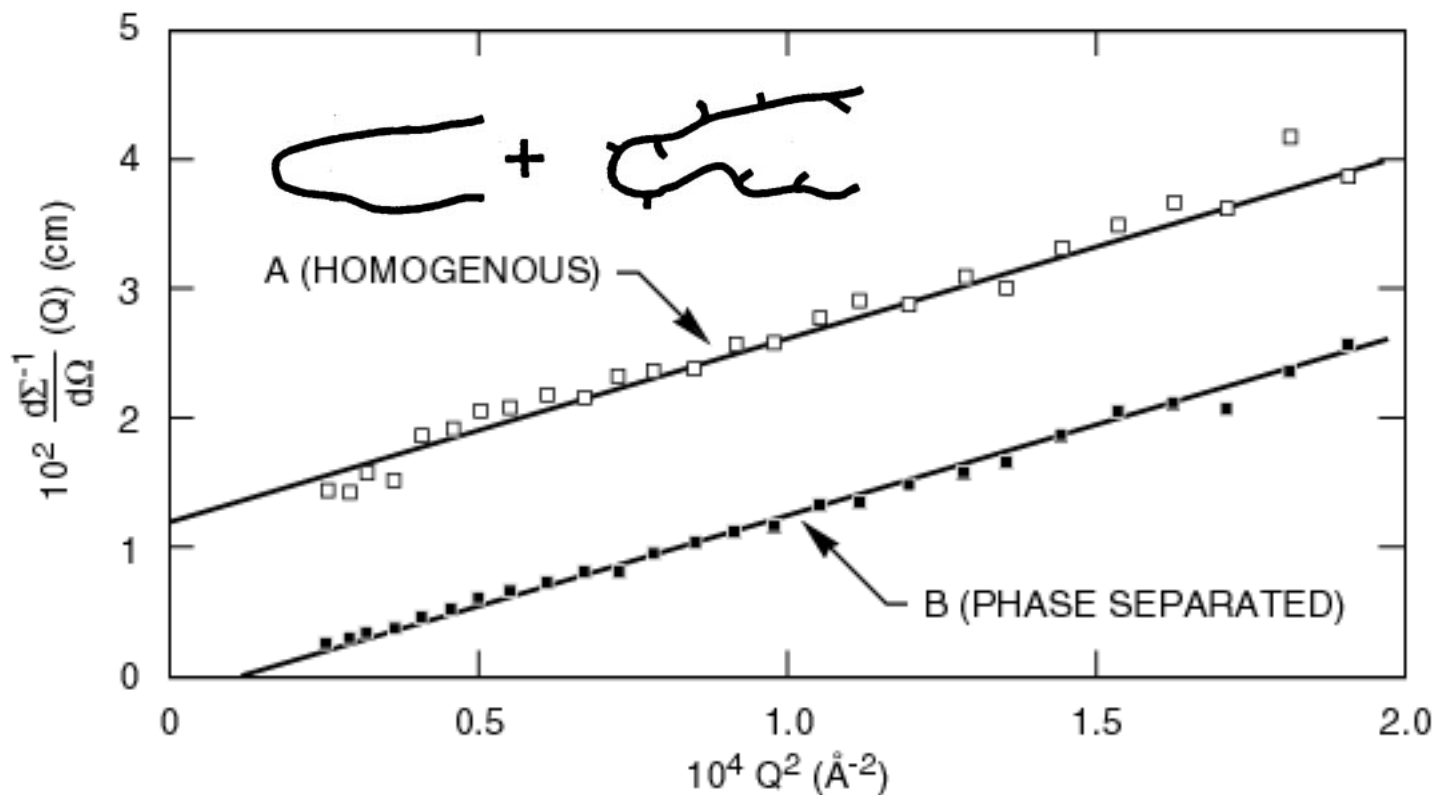

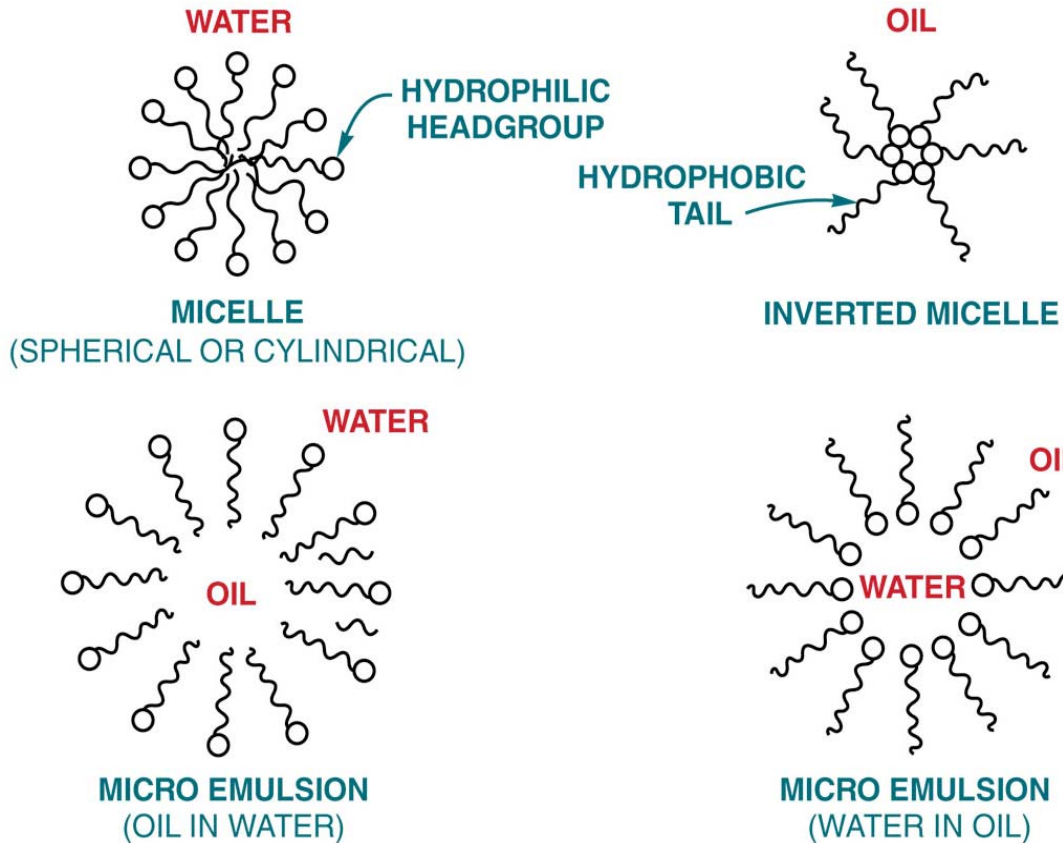Schematic Representation of Different Types of Polyethylenes

- **Blends (alloys) of linear and branched polyolefins (saturated hydrocarbon polymers such as polyethylene) have achieved widespread commercial applications (~10^{11} lbs./yr.) despite the fact that there has been disagreement on the state of mixing in the molten and solid states.**

- **SANS is an ideal technique to probe thermodynamic interactions in blends and indicates that mixtures of high density (HD) and low density (LD) polyethylenes are compatible in the liquid state. Mixtures of HD and linear low density polyethylenes (LLDPE) are homogenous in the melt when the branch content is low, but the phases separate when the branch content is high.**

O-Z PLOTS FOR 50/50 BLENDS OF MODEL POLYETHYLENES (MW ~ 10^5)
AS A FUNCTION OF THE BRANCHING DIFFERENCE BETWEEN COMPONENTS
(A) 2.5 BRANCHES/100 CARBON ATOMS
(B) 7.4 BRANCHES/100 CARBON ATOMS

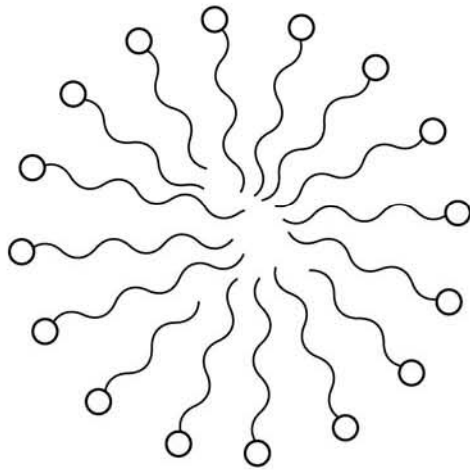Alamo et al., *Macromolecules*, <u>30</u>, 561 (1997).

Schematic Representation of Oil-in-Water or Water-in-Oil Colloidal Aggregates

WATER

HYDROPHILIC HEADGROUP

MICELLE
(SPHERICAL OR CYLINDRICAL)

OIL

HYDROPHOBIC TAIL

INVERTED MICELLE

WATER

OIL

MICRO EMULSION
(OIL IN WATER)

OIL

WATER

MICRO EMULSION
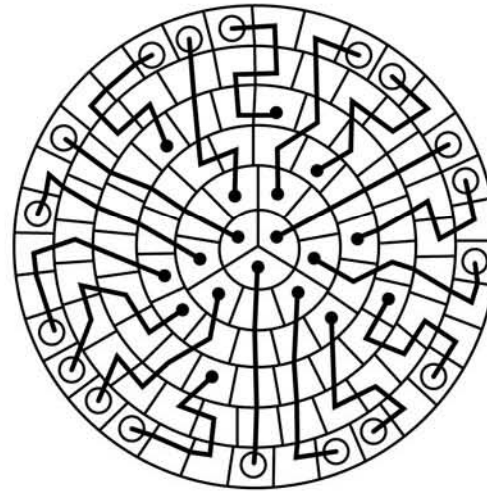(WATER IN OIL)

ORNL-DWG 89M-17194

Applications

- **Detergents, lubricants, emulsions, oil spills, and enhanced oil recovery**
- **Solubilizing and decontaminating toxic materials**
- **Microencapsulation of drugs in pharmaceuticals**

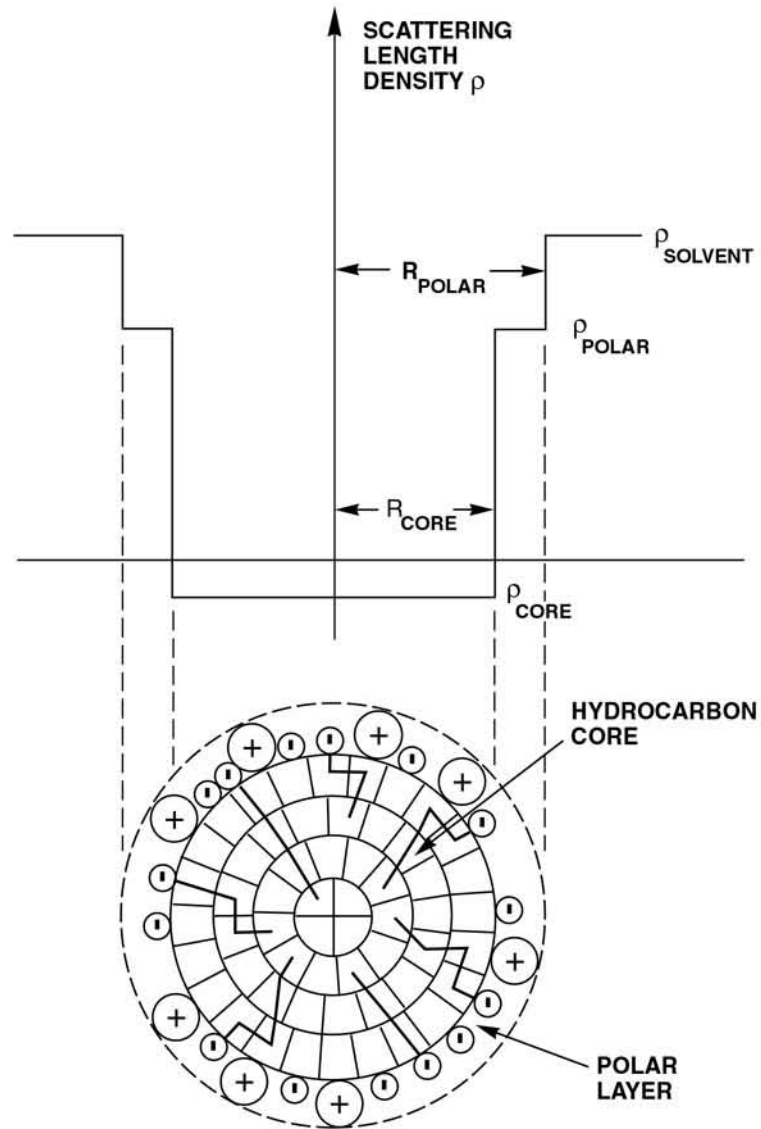# Does Water Penetrate into the Hydrocarbon Core of a Micelle?
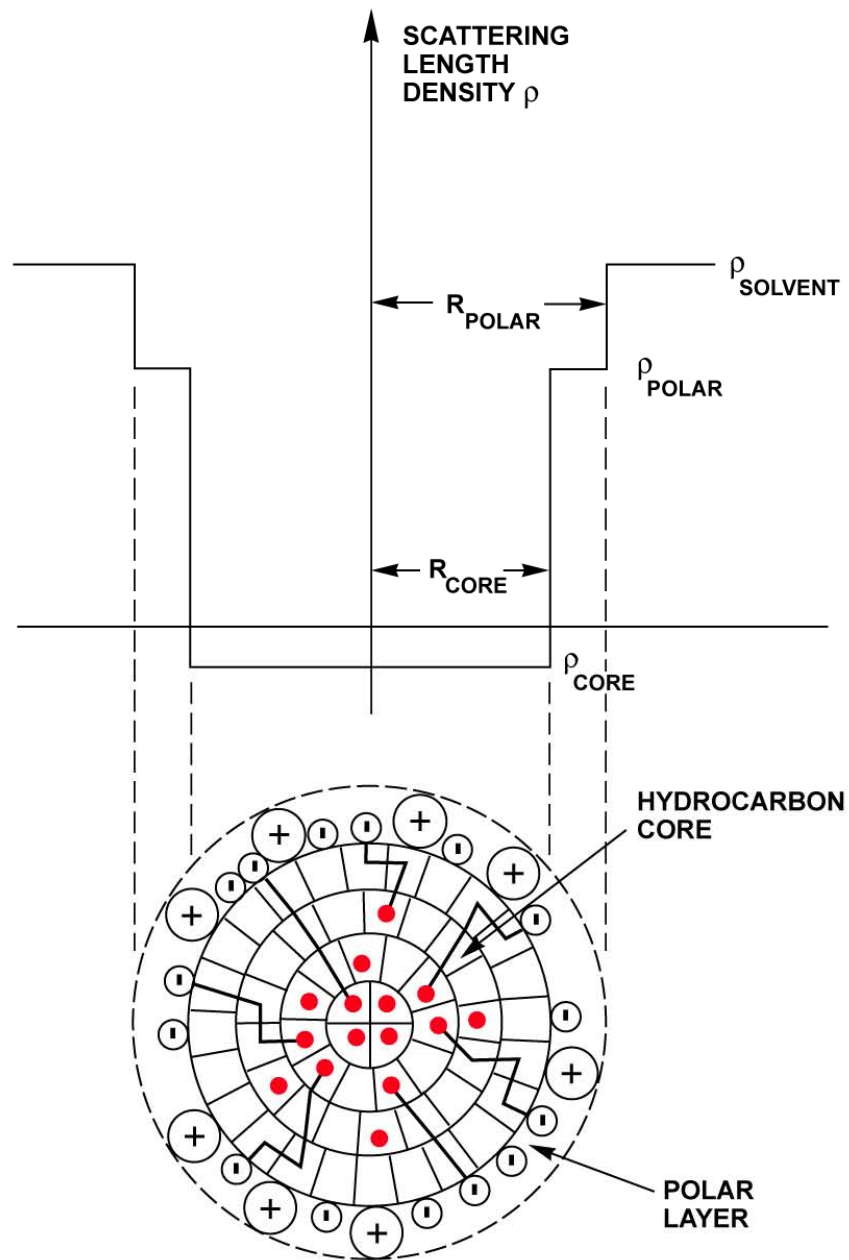

RADIAL CHAIN MICELLE

INTERPHASE LATTICE MODEL (DILL AND FLORY)

ORNL-DWG 89M-17196

- **NMR indicates contact between hydrocarbon segments and H_2O**
- **The chain end-groups are concentrated in the center, or spread out over the whole volume for the two proposed structures**

SCATTERING LENGTH DENSITY ρ

$\rho_{SOLVENT}$

R_{POLAR}

ρ_{POLAR}
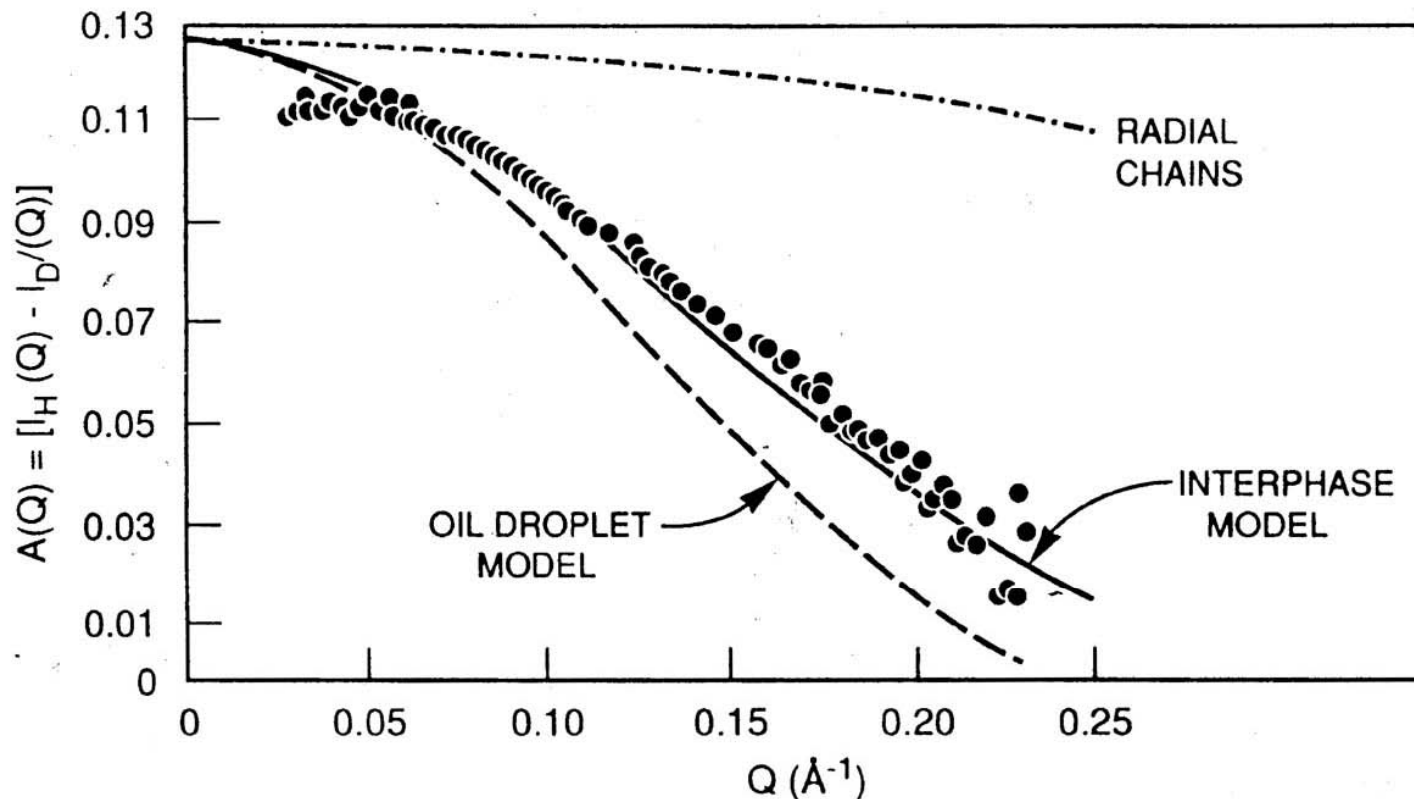
R_{CORE}

ρ_{CORE}

HYDROCARBON CORE

POLAR LAYER

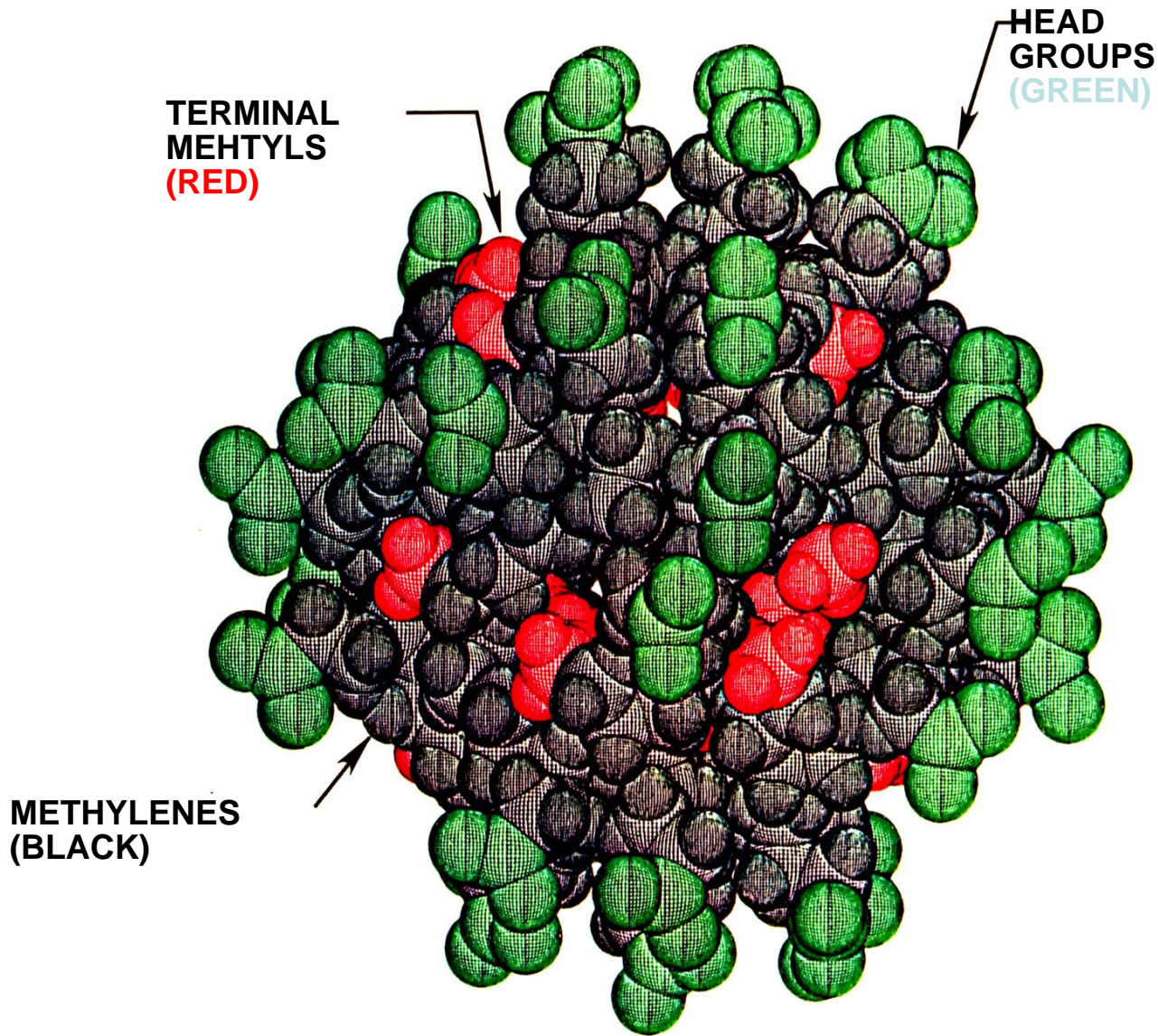**Label End Groups to Observe Distribution of Terminal Methyls**

Difference amplitude between LDS with protonated and deuterated end groups for various models of micelle structure assuming no water penetration of core.

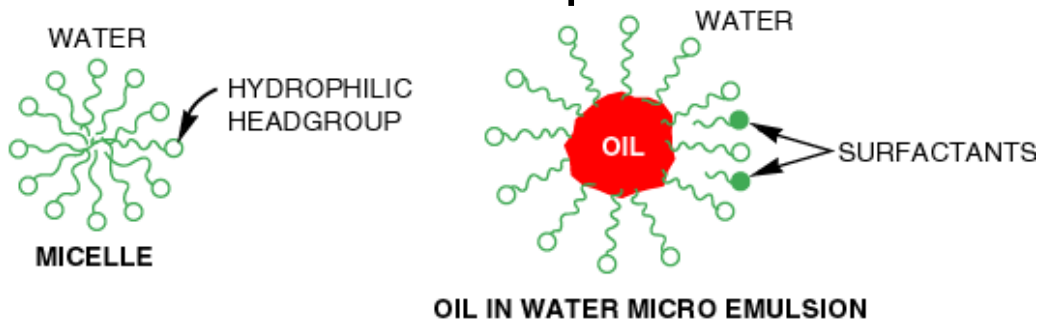Chen, Koehler *J. Phys. Chem.*, (1983); Dill, Flory, *Nature*, (1984)

Outside Surface

TERMINAL
MEHTYLS
(RED)
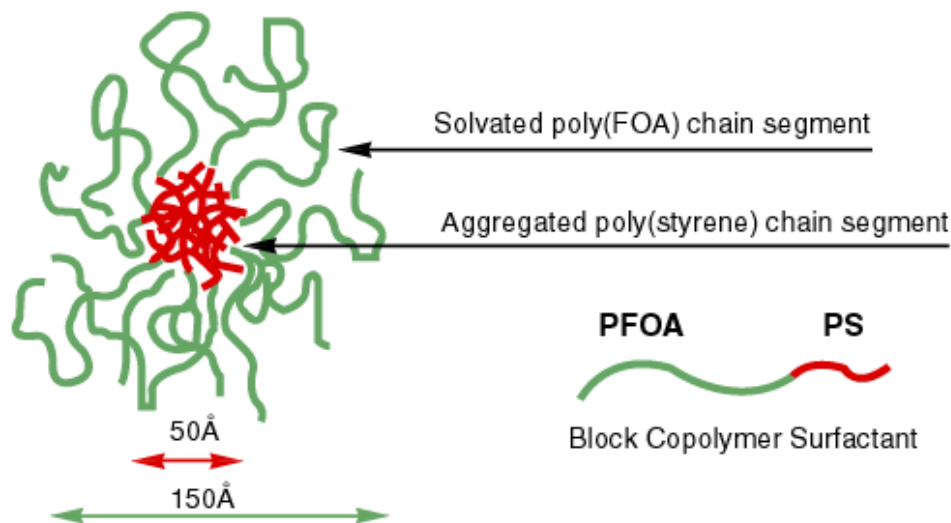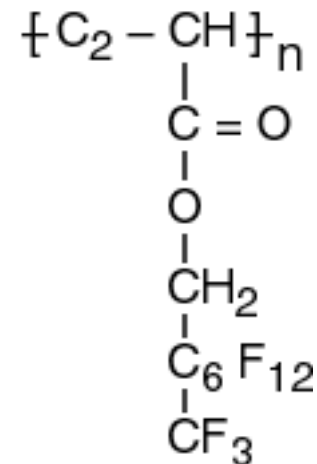
HEAD
GROUPS
(GREEN)

METHYLENES
(BLACK)

Configuration of 38 Chain Decanoate Micelle [Dill et al. Nature 309, 42 (1984)]

Schematic Representation of Colloidal Aggregates in Water and Supercritical Carbon Dioxide
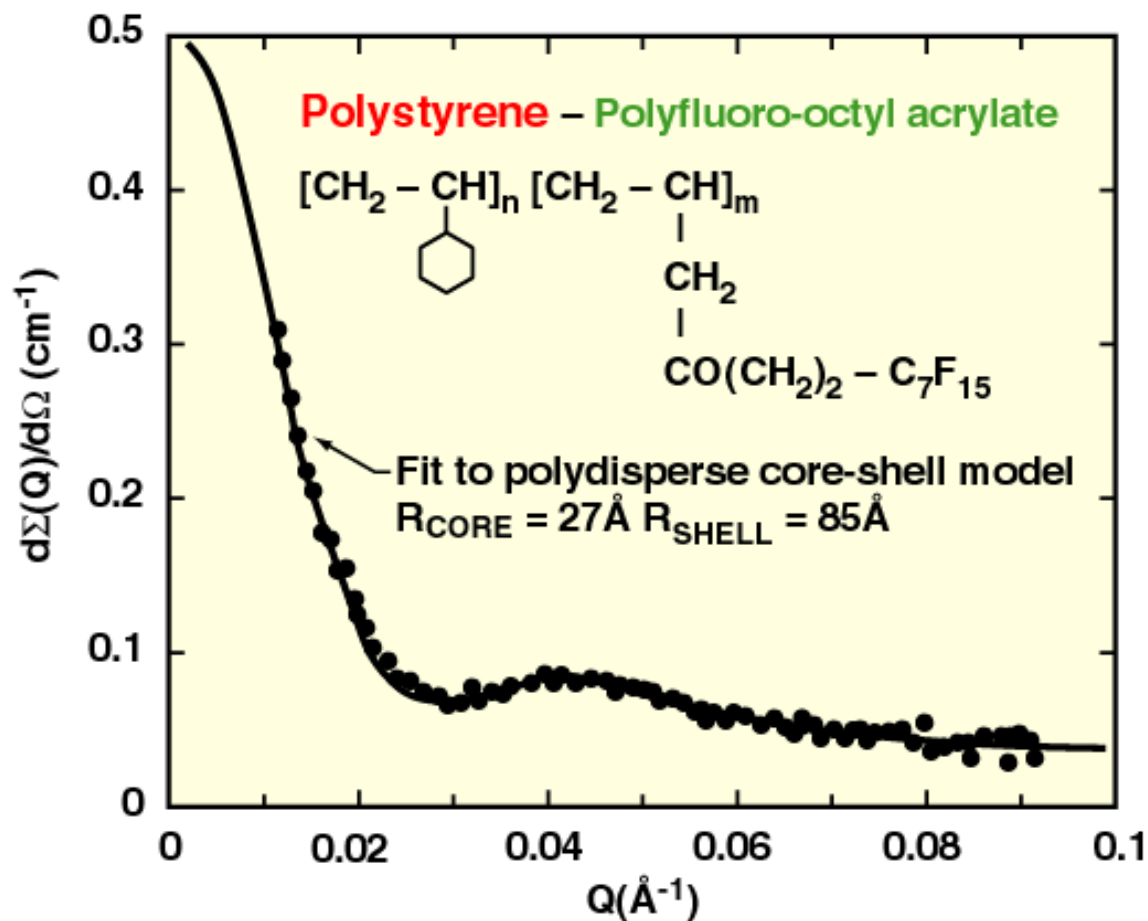

WATER

HYDROPHILIC HEADGROUP

MICELLE

WATER

OIL

SURFACTANTS

OIL IN WATER MICRO EMULSION

POLYFOA

$$\left[C_2 - CH \right]_n$$
$$| $$
$$C = O$$
$$| $$
$$O$$
$$| $$
$$CH_2$$
$$| $$
$$C_6 F_{12}$$
$$| $$
$$CF_3$$

Solvated poly(FOA) chain segment

Aggregated poly(styrene) chain segment

PFOA   PS

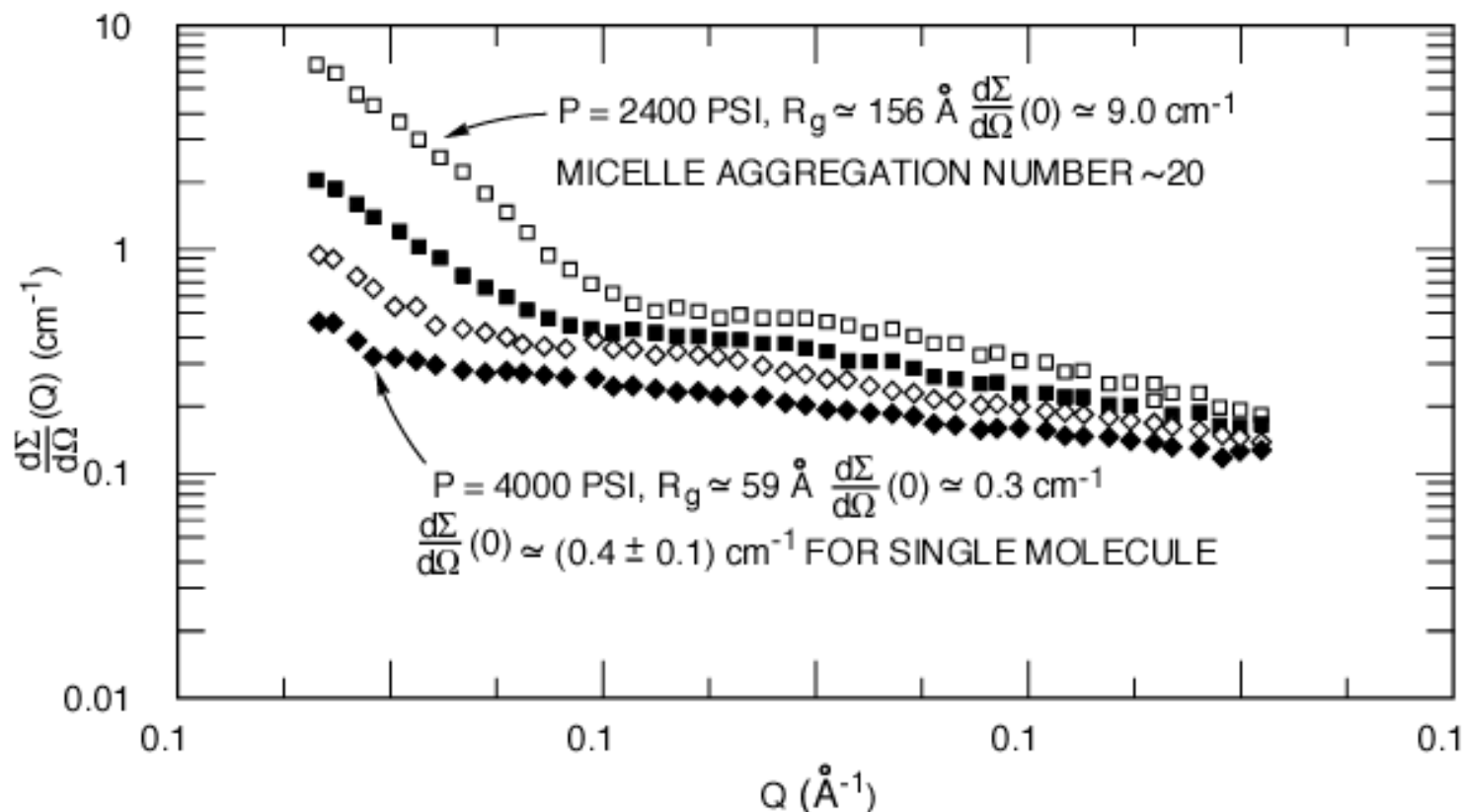Block Copolymer Surfactant

50Å

150Å

MODEL OF POLY(FOA-b-STYRENE) MICELLE IN SUPERCRITICAL CO$_2$

SANS Characterization of Block Copolymer Micelle in Supercritical CO_2

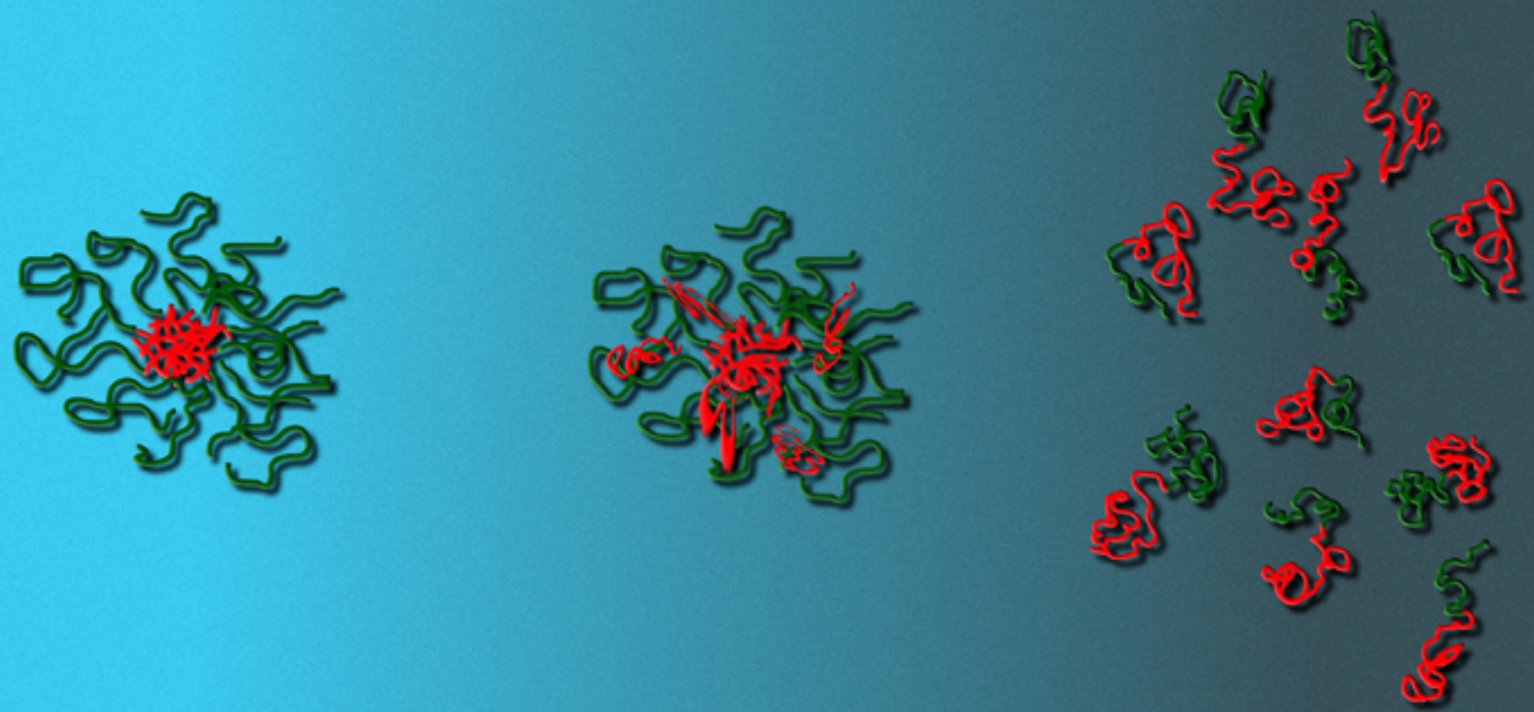McClain et al., Science, **274**, 2049 (1996)

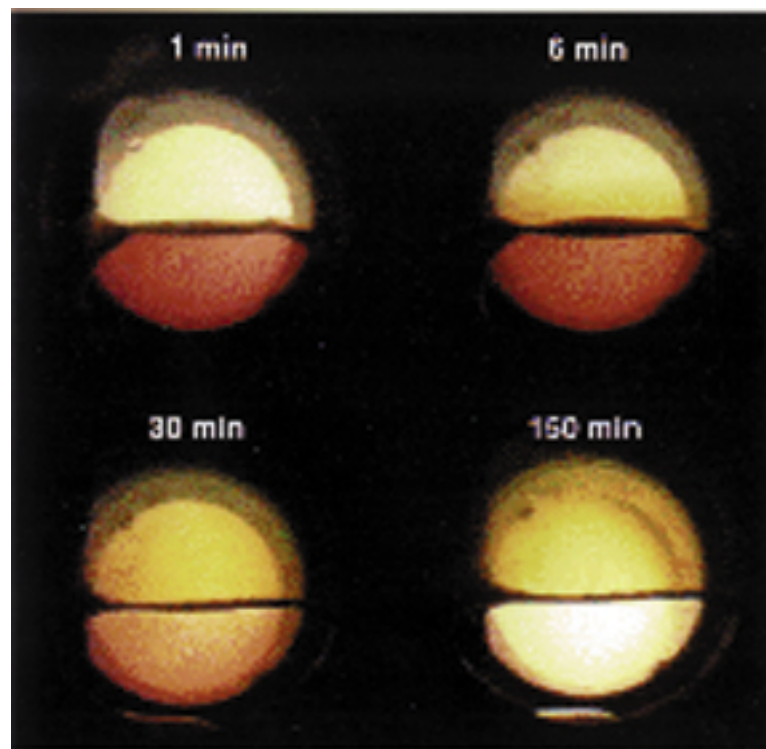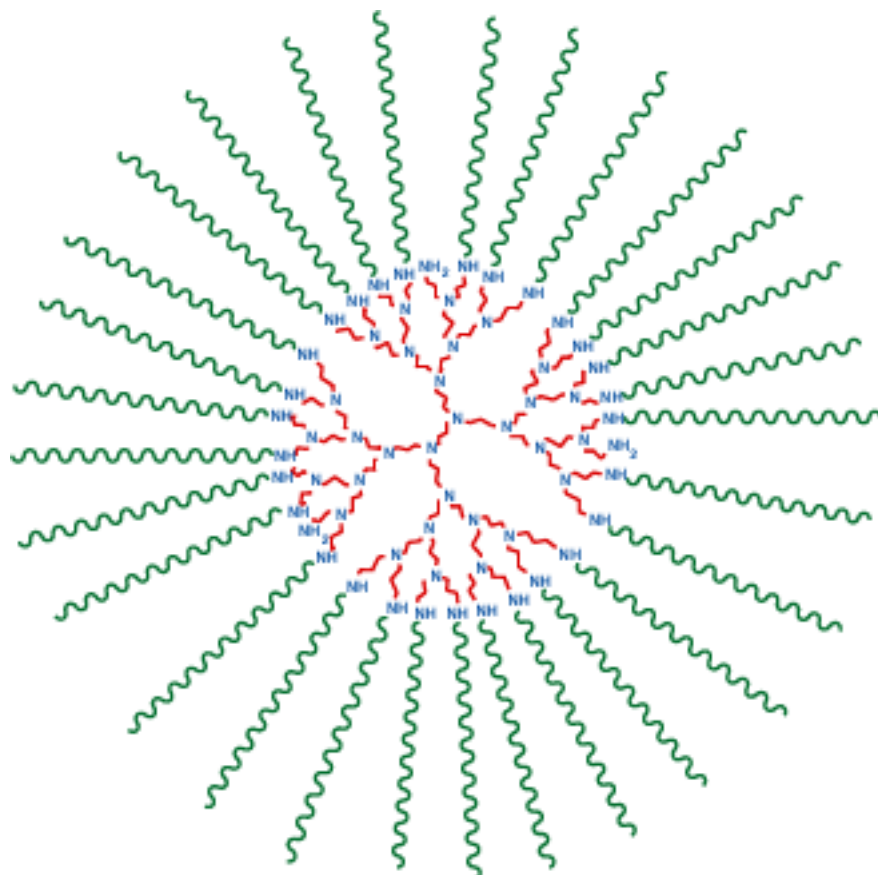# F. Triolo et al., Langmuir, <u>16(2)</u>, 416 (2000)

$\frac{d\Sigma}{d\Omega}$ (Q) FOR 6% (W/V) POLYVINYL ACETATE–b–PFOA BLOCK COPOLYMERS IN CO_2. AT HIGH PRESSURES, THE SCATTERING ARISES FROM SINGLE MOLECULES; AS THE PRESSURE IS LOWERED, MICELLES FORM BELOW A CRITICAL CO_2 DENSITY.

Increasing CO$_2$ Density
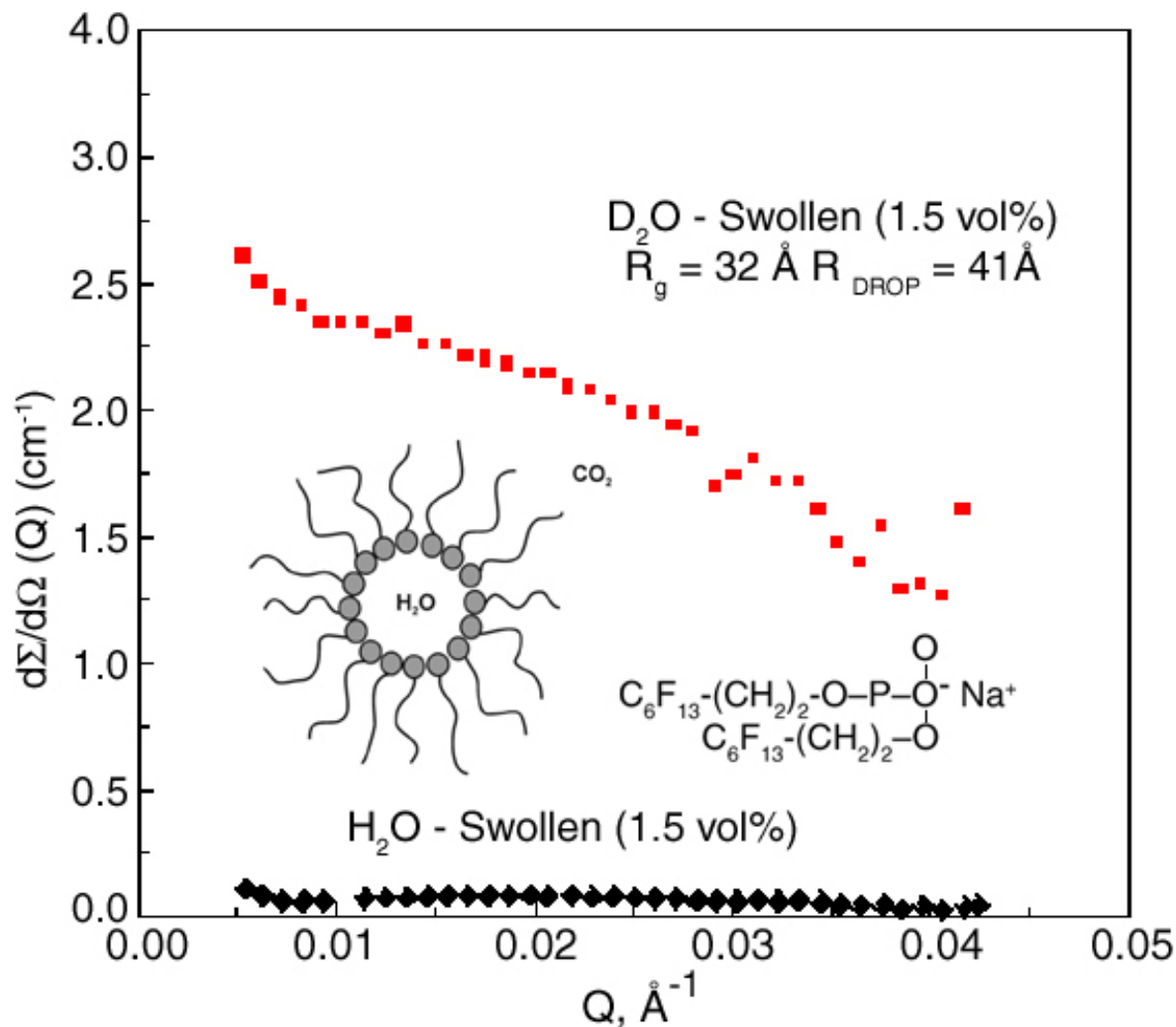
ORNL 98-4607/jpp

UT–BATTELLE

A fourth generation dendrimer with CO_2-soluble (fluorinated) chains forms unimolecular micelles and extracts a CO_2-insoluble (orange) dye from the aqueous phase (below) to the CO_2 phase (above), thus demonstrating its potential in cleanup applications

Nature, <u>389</u>, 368 (1997)

dΣ/dΩ for 7.5 wt. % Phosphate Ester Surfactants Swollen with H_2O & D_2O

[Keiper et al., *JACS*, 124 1834 (2002); *Langmuir*, 20, 1065 (2004);
Xu et al., *J. Chem. Phys.,* 109, 10261 (2005)]

D_2O - Swollen (1.5 vol%)
R_g = 32 Å R_{DROP} = 41Å

CO_2

H_2O

C_6F_{13}-$(CH_2)_2$-O–P–O^- Na$^+$
C_6F_{13}-$(CH_2)_2$–O

H_2O - Swollen (1.5 vol%)

dΣ/dΩ (Q) (cm^{-1})

Q, Å^{-1}

WATER NANODROPLETS IN CO_2-MICROEMULSIONS FORMED BY SELF-ASSEMBLED GRAFT COPOLYMERS AND SURFACTANTS

- Possible Applications:

– extraction of hydrophilic substances [proteins, heavy metals] into CO_2

– heterogeneous reactions

– dry cleaning [commercialized]

- Examples:

– polyethylene oxide-PFOA graft copolymers

   [Fulton (PNWL), McClain (UNC), Triolo (Palermo)]   ~ 0.3   vol% H_2O

– Ammonium carboxylate perfluoroethers

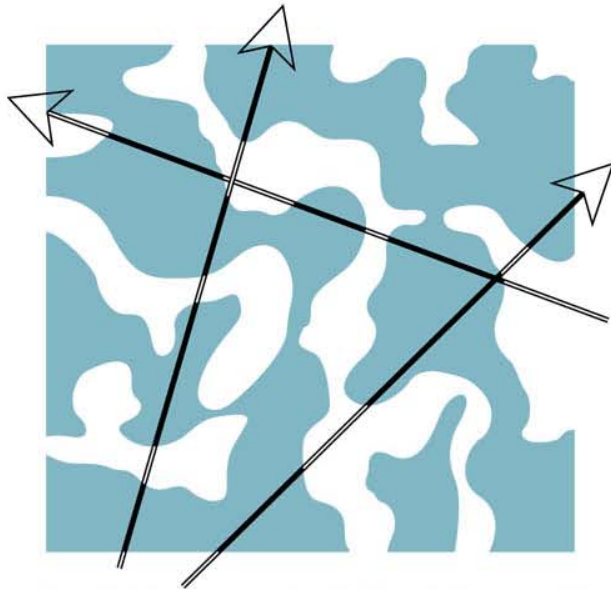   [Johnston (UTEX), Heitz and Bright (SUNY)]   ~ 0.4   vol% H_2O

_ phosphate esters [Keiper, DeSimone (UNC)]   ~ 5   vol% H_2O

– perfluoroethers [Lee, Johnston (UTEX)]   5 –10   vol% H_2O

Debye Bueche Model for Two-Phase System, Each with Random Shape, Uniform Electron or Scattering Length Density and Sharp Boundaries

Mean Chord Intercepts:

$$L_1 = \frac{a}{\phi}$$

$$L_2 = \frac{a}{(1-\phi)}$$
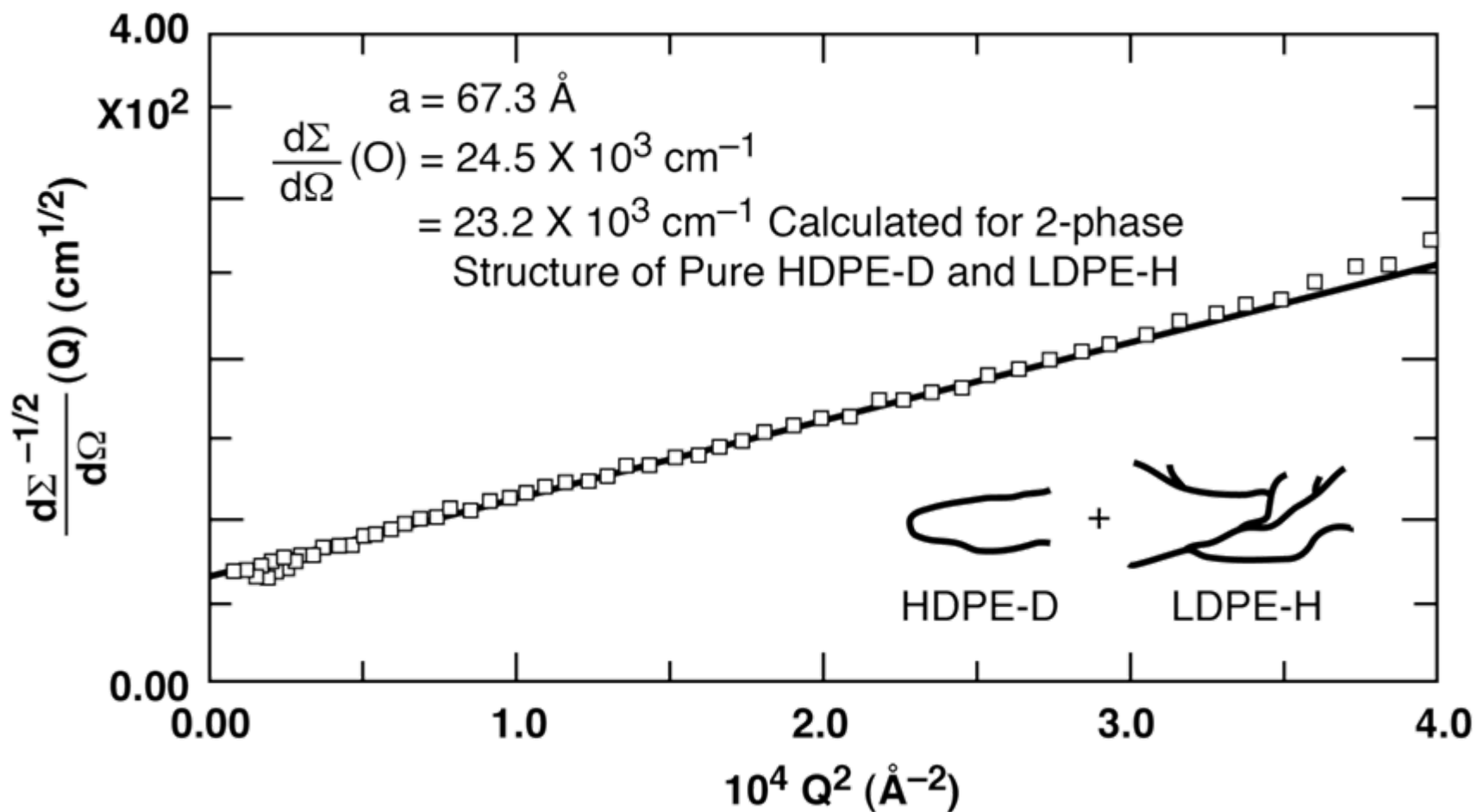
Physical Concept of the Mean Chord or Inhomogeneity Length

The fluctuations in scattering power at two points A and B, distance r apart, can be characterized by $\gamma(r) <\eta^2>_{AV} = <\eta_A\eta_B>_{AV}$. For random two phase system: $\gamma(r) = e^{-r/a}$

$$\frac{d\Sigma}{d\Omega}(Q) = \frac{A}{[1 + Q^2a^2]^2}$$

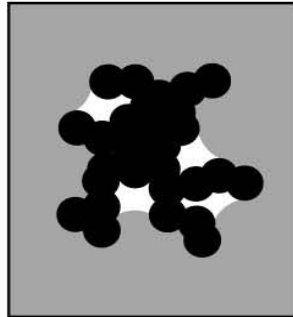J. Appl.Cryst., 28, 679 (1957)

ORNL-DWG 92M-9485

Debye-Bueche Plot for Phase Separated Blend of Deuterated High Density and Protonated Low Density Polyethylenes Slow Cooled from the Melt at 0.75°C/min
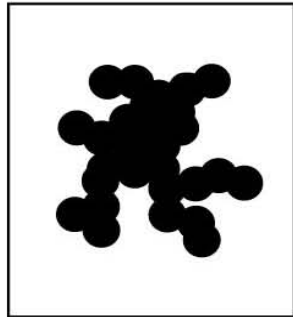R. G. Alamo et al., *Macromolecules*, 27, 411 (1994)

$a = 67.3$ Å

$\frac{d\Sigma}{d\Omega}(O) = 24.5 \times 10^3$ cm^{-1}

$= 23.2 \times 10^3$ cm^{-1} Calculated for 2-phase Structure of Pure HDPE-D and LDPE-H

HDPE-D   +   LDPE-H

Contrast Factors for SAXS and SANS in Carbon Black Filled Polyethylenes

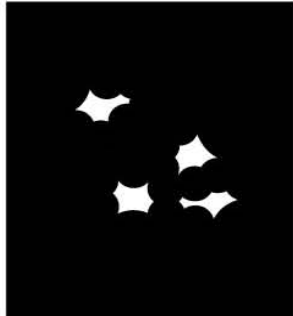|	Electron Density $(10^{23}\ cm^{-3})$ (SAXS)	Scattering Length Density $(10^{10}\ cm^{-2})$ (SANS)
Carbon Black	5.8	6.4
Void	0	0
Polyethylene-H	3.5	-0.36
Polyethylene-D	3.5	8.8

ORNL 97-3941/arb

Contrast Options for SAXS and SANS Studies of Carbon-Polyethylene Composite Materials

SAXS contains contributions from all three phases

SANS from carbon in H-PE gives structure of carbon alone

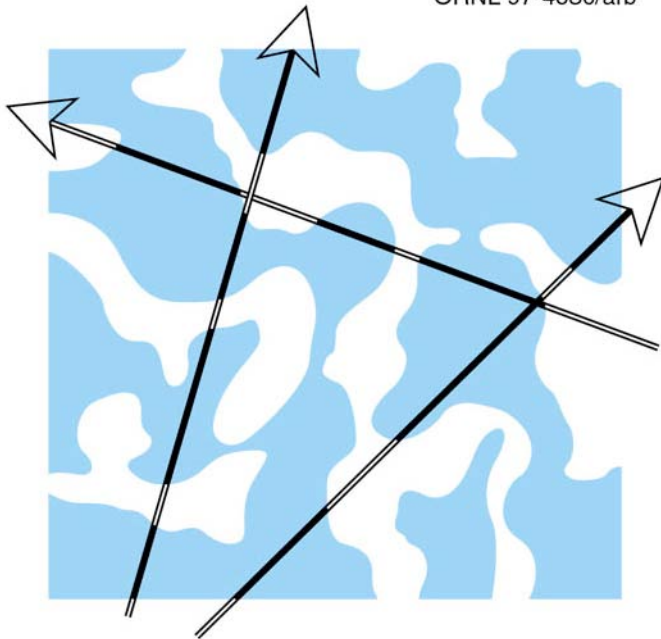**SANS from carbon in D-PE gives structure of voids alone**

ORNL 97-3942/arb

D. W. Marr et al., *Macromolecules*, 30, 2120 (1997)

Volume Fraction of Voids and Mean Chords of Carbon and Polythylene Phases

Temperature	Volume of Fraction of Voids	Mean Chords (Å)	
		Carbon	Polyethylene
25°C (solid)	2.1%	580	770
150°C (melt)	0.2%	570	850

ORNL 97-4036/arb

Use methodology of W. L. Wu [*Polymer*, **23**, 1907 (1982)] to estimate volume fraction of third phase (voids)

Macromolecules, **30**, 2120 (1997)

Physical Concept of the Mean Chord Length

POROUS SYSTEM WITH QUENCHED CORRELATED DISORDER: AEROGELS
(see talk by Y. B. Melnichenko; Thursday am)

BASE-CATALYZED AEROGELS ARE DILUTE NETWORKS OF RANDOMLY INTERCONNECTED SiO_2 STRANDS, WITH $\rho_{SiO2} \sim$ 0.1 g/cc, PORE VOLUME ~ 96% AND DIAMETER 60-70 Å

$\nu_{BULK}=0.61 \pm 0.02$

$\nu_{CONF}=0.5 \pm 0.04$

R_P

ξ, Å

τ

In CO_2-saturated aerogels, the correlation length of the density fluctuations (ζ) saturates at the pore radius (R_P). SANS reveals the existence of a compressed adsorbed phase with density > 1 g/cc and the methodology of Wu (1982) may again be used to give the volume fraction (submitted to *J. Chem Phys.*)

Diblock Copolymers

•two polymer segments, covalently joined

•self-assemble on nm length scales

•three parameters govern self-assembly
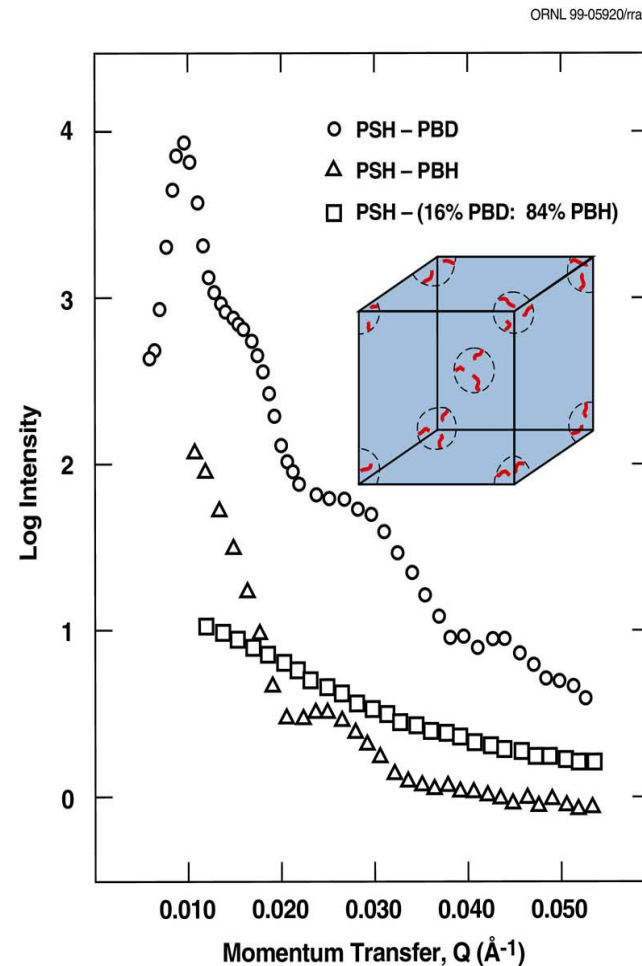
- total polymer length *N*
- interaction parameter χ
- relative block length *f*

•phase separate (*Nχ ~ 10*)

•four stable morphologies
- *short/long: spheres in matrix*
- *~ 20%: cylinders*
- *~33%: gyroid*
- *equal lengths: lamellae*

ORNL 90-12746a/rra

Nanoscale Morphologies Generated by Self-Assembly of Diblock Copolymers

SPHERES (diameter ~ 150 Å)	CYLINDERS	GYROID (DD)	LAMELLAE (spacing ~ 500 Å)
f ~ 0.1	f ~ 0.2	f ~ 0.3	f ~ 0.5

POLYMER A (N_A units)   POLYMER B (N_B units)

BLOCK JUNCTION

$$f = \frac{N_A}{N_A + N_B}$$
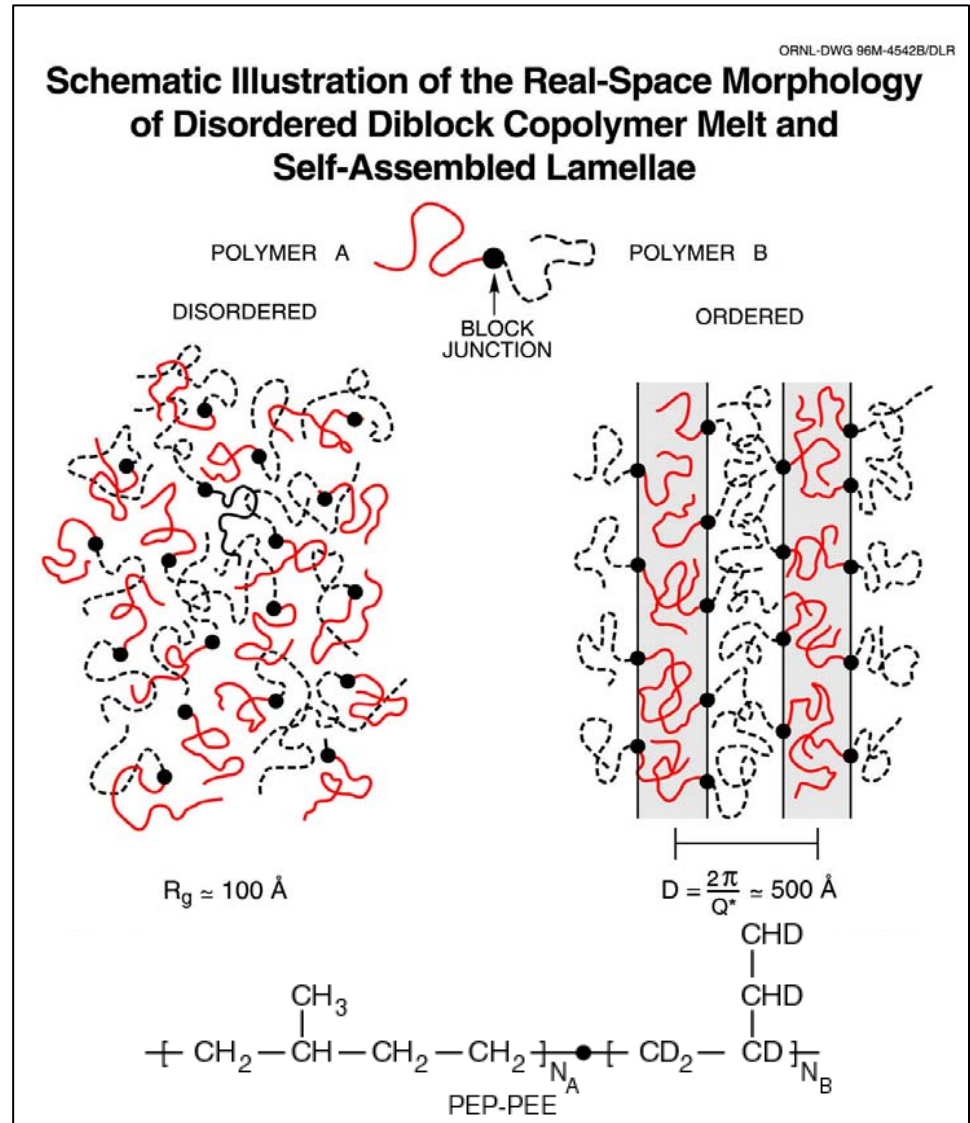
Contrast Variation via Isotopic Substitution

- The neutron refractive index or scattering length density (SLD) difference between protonated polystyrene (PSH) and polybutadiene is larger when the latter is deuterated

- Thus the intensity scattered by PSH-PBD is much higher (30x) that from PSH-PBH

- Both SANS patterns reflect the block-copolymer morphology of spheres (radius ~ 10 nm) on a Bragg lattice (spacing ~ 60nm)

- Blending 84% PBH and 16% PBD matches the SLD of the PS matrix and thus "washes out" the sphere scattering [Polymer, *24,* 519 (1983)]

ORNL 99-05920/rra

○ PSH – PBD
△ PSH – PBH
□ PSH – (16% PBD: 84% PBH)

SANS FROM POLYSTYRENE-POLYBUTADIENE (PS-PB) DI-BLOCK COPOLYMERS.
A BLEND OF PS-PBH AND PS-PBD MATCHES THE NEUTRON REFRACTIVE INDEX
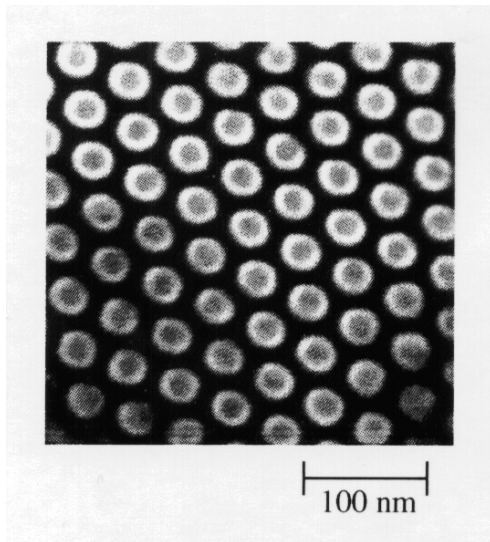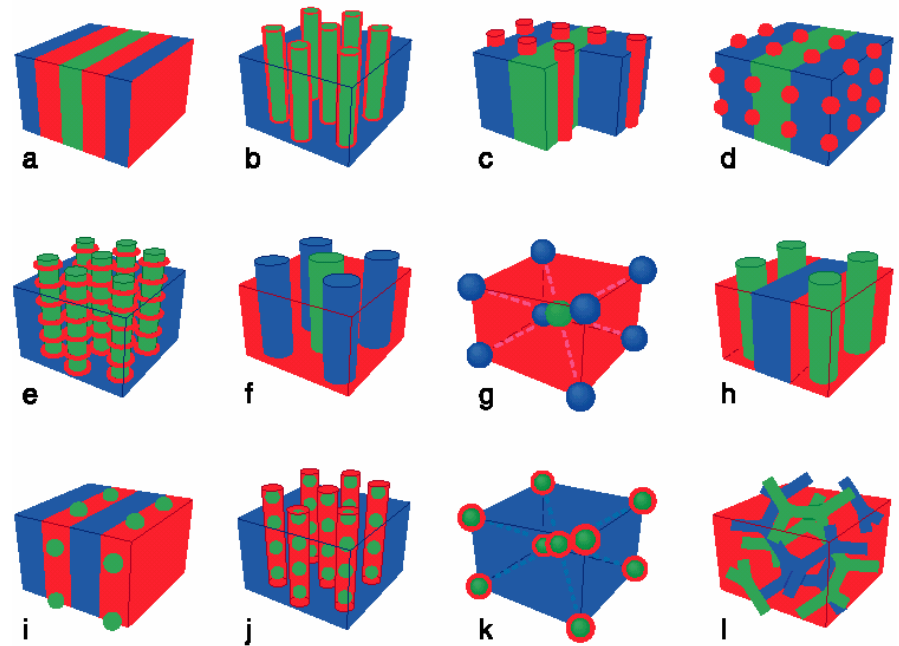OF THE MATRIX AND "WASHES OUT" THE SPHERE SCATTERING

Morphology from SANS

- **In the ordered state, the polymer molecules are stretched, due to total reflection at the domain interface**

- **In the disordered state they may be expected to have unperturbed (random) configurations**

- **SANS reveals a transition between Gaussian coils and stretched coils in the disordered state**

- **The dimensions are probed by SANS via the peak in the scattering curve [Almdal et al., Phys. Rev. Lett., 65, 1112 (1990)].**

ORNL-DWG 96M-4542B/DLR

Schematic Illustration of the Real-Space Morphology of Disordered Diblock Copolymer Melt and Self-Assembled Lamellae

POLYMER A   POLYMER B

DISORDERED   BLOCK JUNCTION   ORDERED

$R_g \approx 100$ Å

$D = \frac{2\pi}{Q^*} \approx 500$ Å

PEP-PEE

Unique Characteristics of Triblocks

- 280+ morphologies - greatly enhanced parameter space

- tailor properties of each phase with polymer block

- selection precise control of feature size with block lengths (1-100 nm)

Core-shell cylinder structure

Some morphologies for linear ABC triblock copolymers. A combination of block sequence, composition and molecular weights provides enormous parameter space for new morphologies.

Shear Alignment of Cylindrical Morphology

- **Shear orientation of quenched SIS results in macroscopically anisotropic stiffness**

- **SIS: poly(styrene-*b*-isoprene-*b*-styrene), "Kraton"**

- **processing is important**
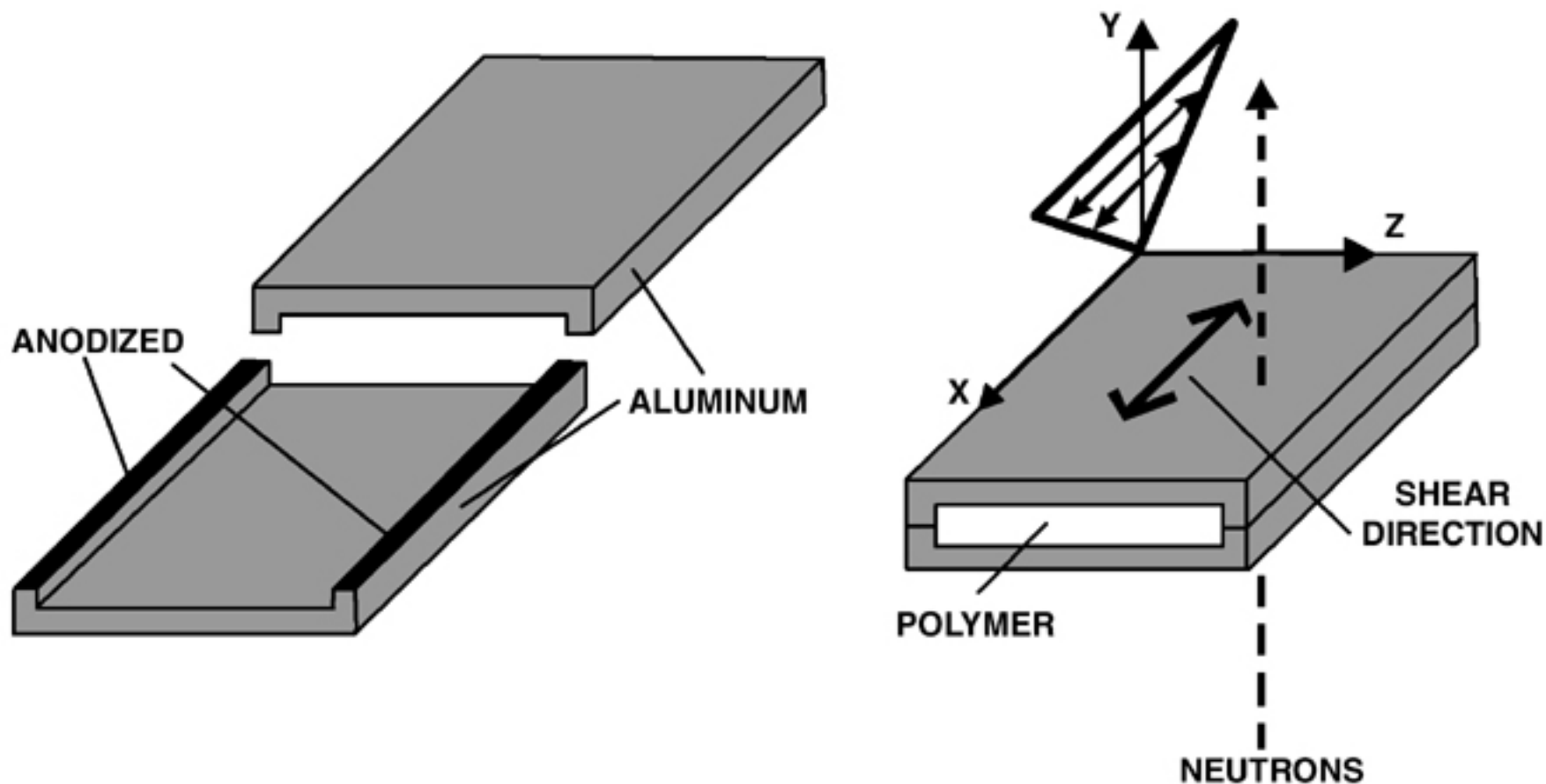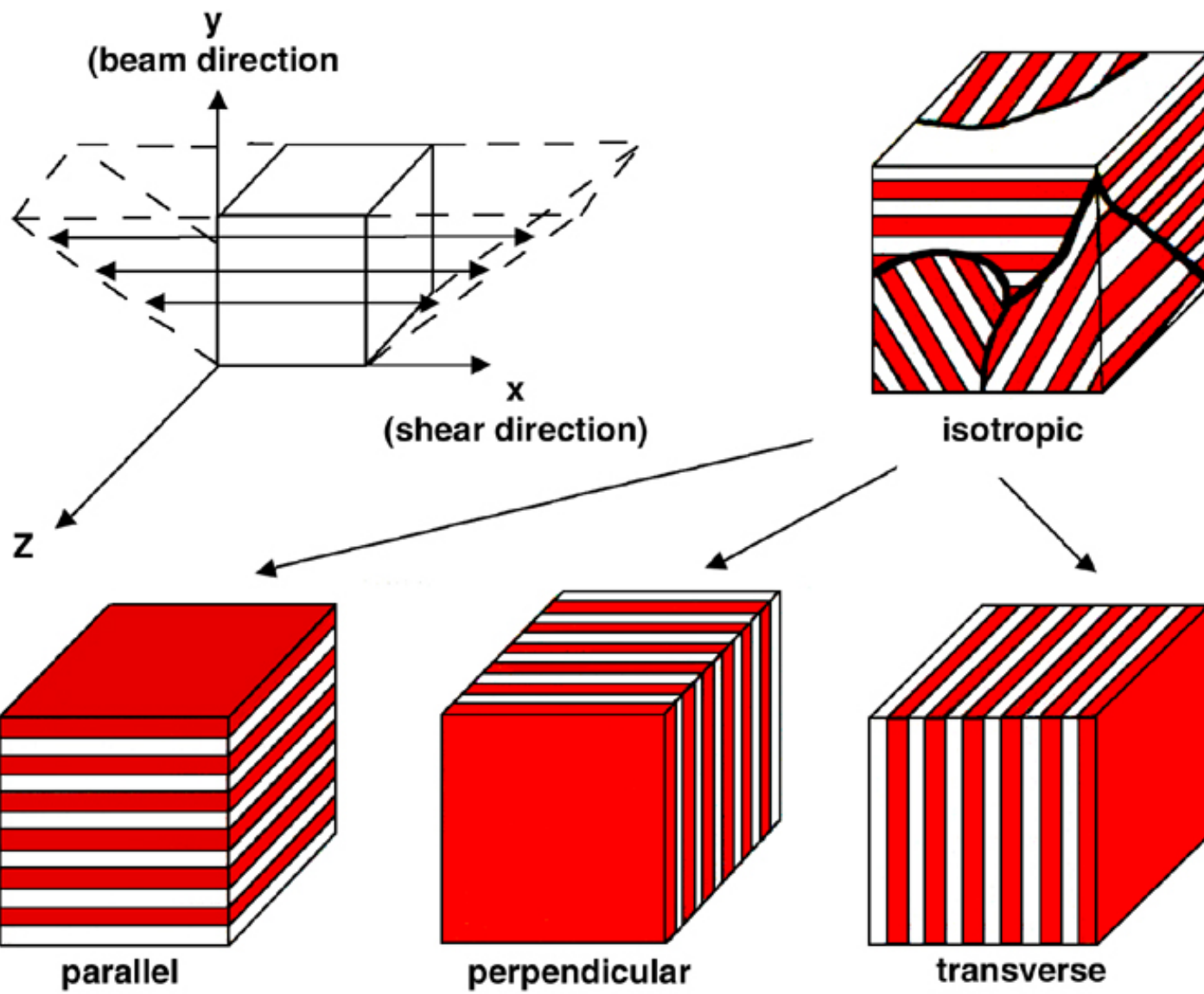

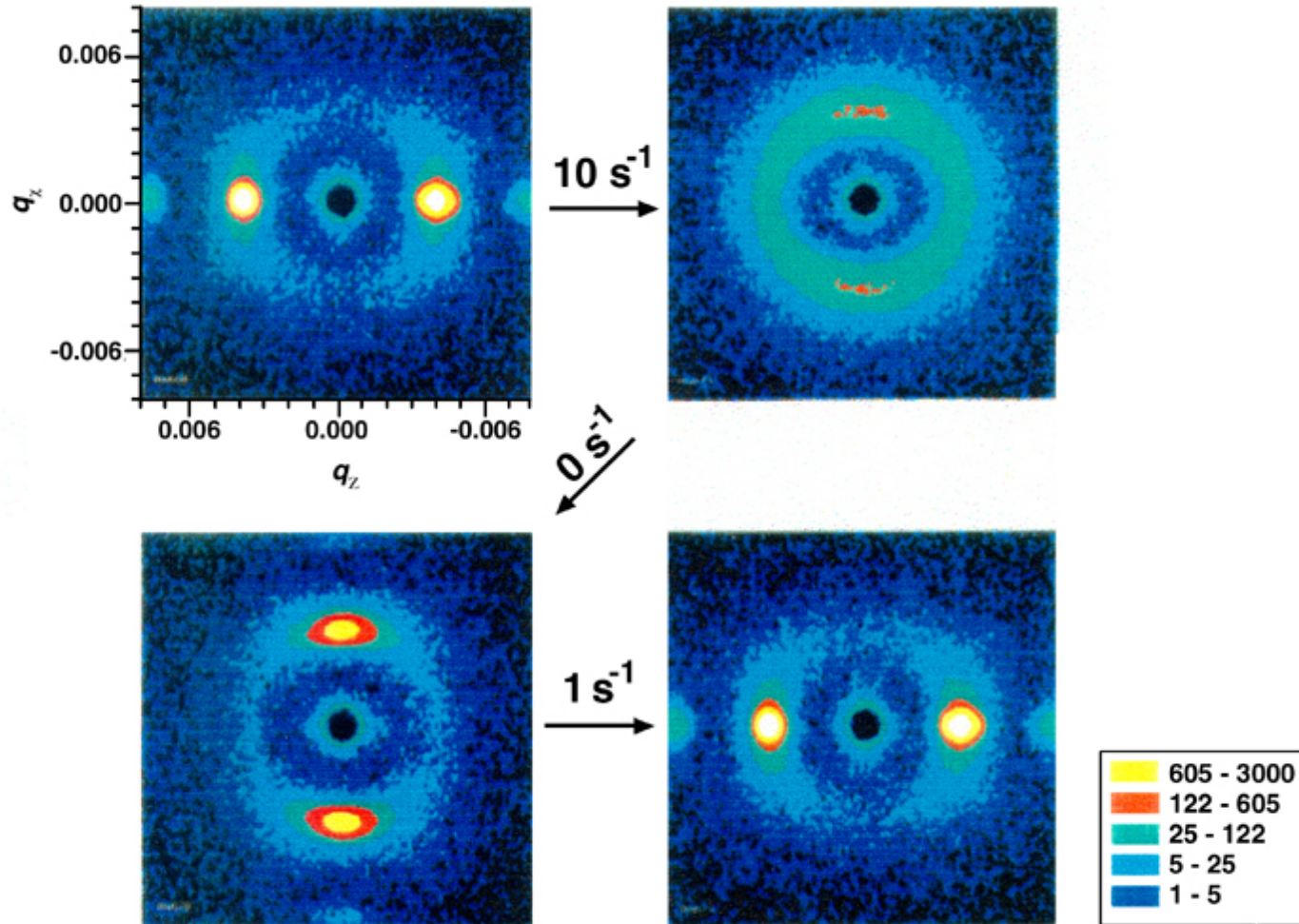Cylinders parallel to fingers

Cylinders normal to fingers

In-situ SANS Shear Cell

y
(beam direction

x
(shear direction)

z

isotropic

parallel

perpendicular

transverse
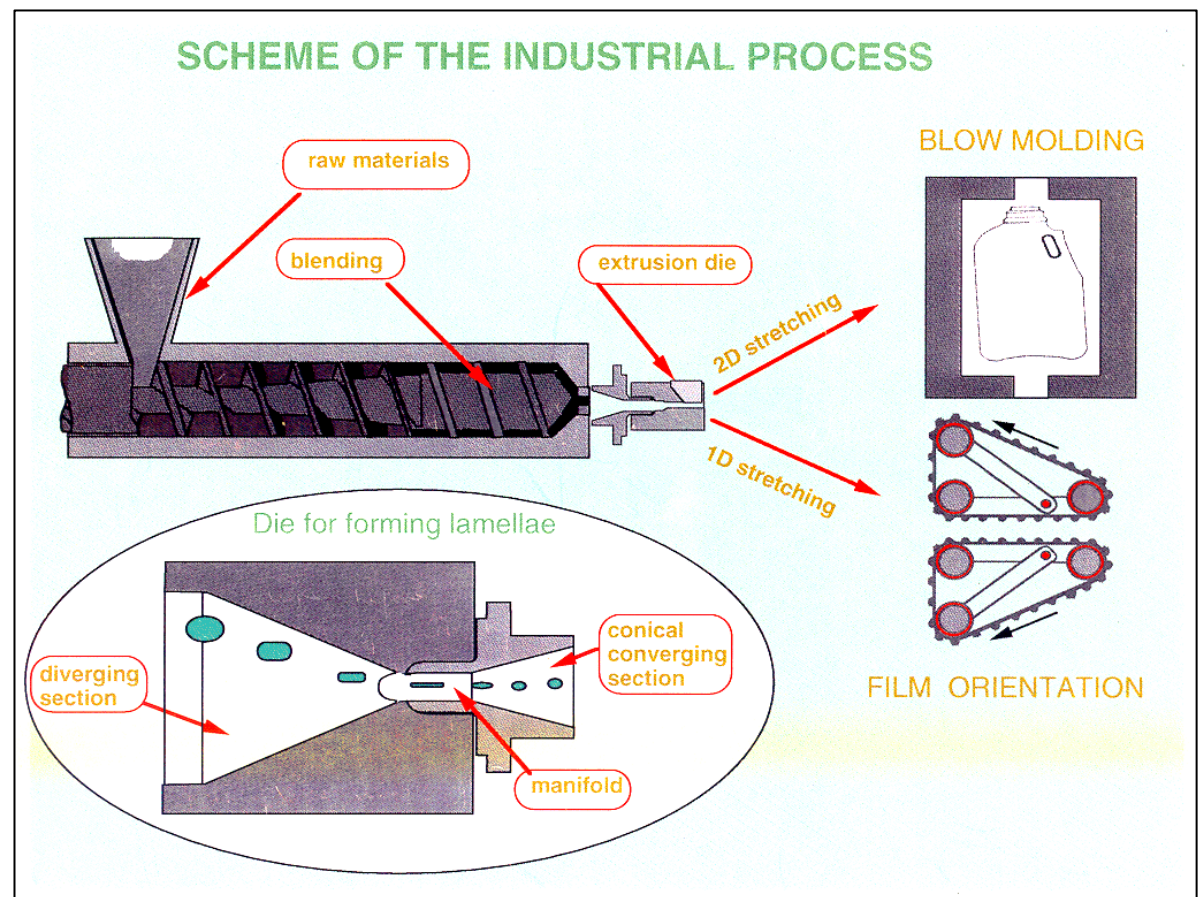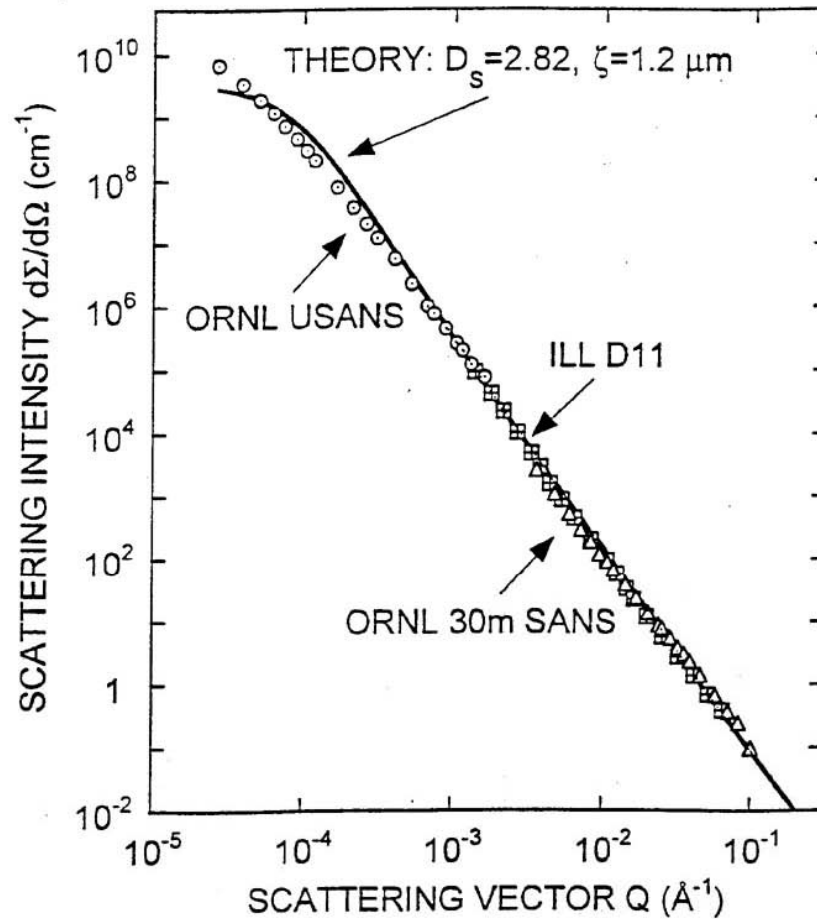
Shear quench + shear, T = 183°C

Koppi et al., *Macromolecules* 34, 951 (2001); *J. Phys. II (France)* 2, 1941 (2002)

An Extruder on a SANS Machine

- processing effects properties
- place extruder in SANS beam

- study evolution of morphology as a function of position and time under industrially relevant conditions

THEORY: $D_s = 2.82$, $\zeta = 1.2$ μm

ORNL USANS

ILL D11

ORNL 30m SANS

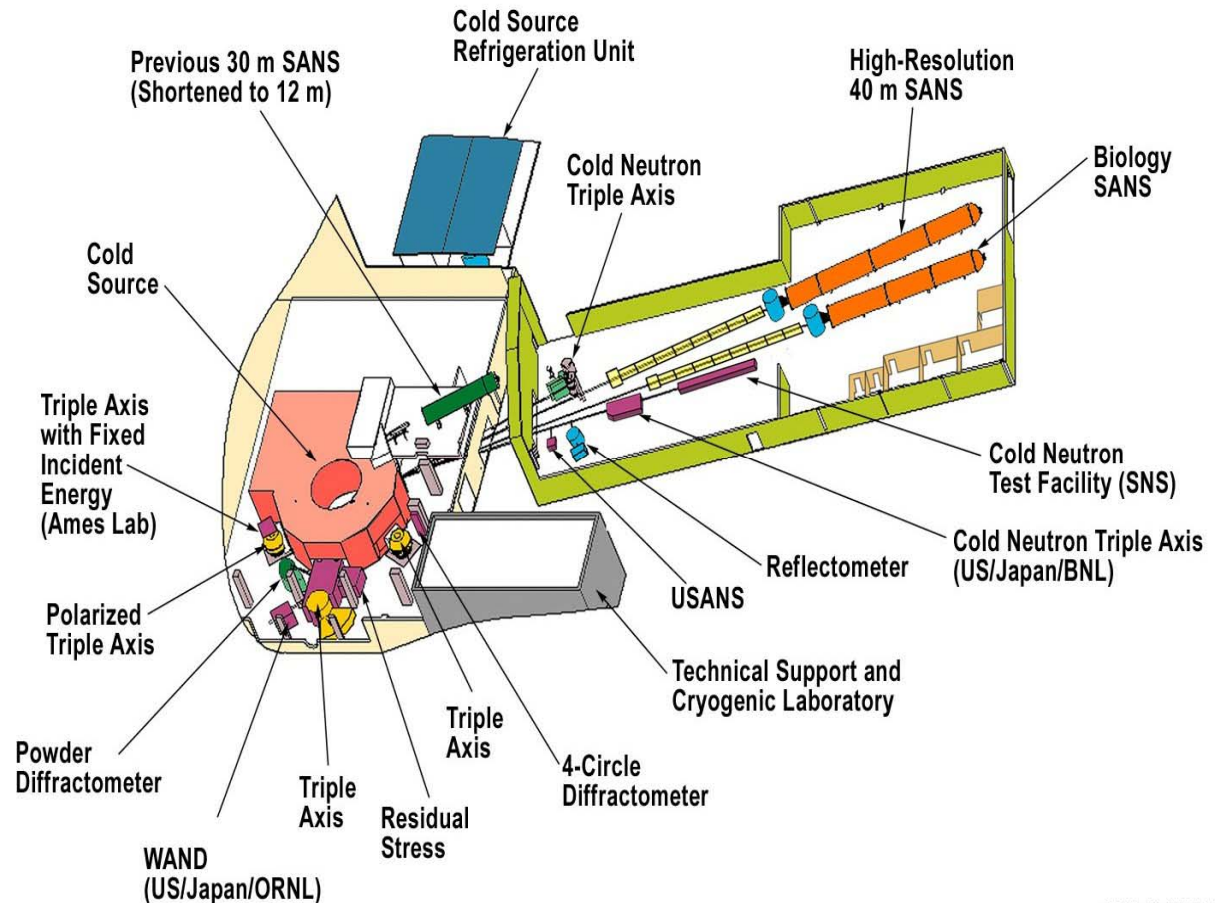SCATTERING INTENSITY dΣ/dΩ (cm^{-1})

SCATTERING VECTOR Q (Å^{-1})

OVERLAP OF ORNL/ILL DATA FROM SEDIMENTARY ROCK SHOWING THAT THE PORE-ROCK INTERFACE IS A SURFACE FRACTAL (D_s = 2.82) OVER TEN ORDERS OF MAGNITUDE IN dΣ/dΩ [RADLINSKI ET AL., PHYS. REV. LETT., 82, 3078 (1999)]

New Small Angle Scattering Instruments

[see talks by Lynn (HFIR-SANS), Zhao (SNS-SANS), Agamalian (USANS)]

- The High Flux Isotope Reactor is one of two worldwide with a core flux exceeding 10^{15} n sec^{-1} cm^{-2}

- The SANS facilities on the HB4 cold source will have fluxes similar to the ILL

- They will also have larger (100 x 100 cm2) area detectors, thus allowing measurements over a wider solid angle range

- The CG4 reflectometer will measure down to R ~ 10^{-8}

Cold Source Refrigeration Unit

Previous 30 m SANS (Shortened to 12 m)

High-Resolution 40 m SANS

Cold Neutron Triple Axis

Biology SANS

Cold Source

Triple Axis with Fixed Incident Energy (Ames Lab)

Cold Neutron Test Facility (SNS)

Cold Neutron Triple Axis (US/Japan/BNL)

Reflectometer

USANS

Polarized Triple Axis

Technical Support and Cryogenic Laboratory

Powder Diffractometer

Triple Axis

Triple Axis

4-Circle Diffractometer

WAND (US/Japan/ORNL)

Residual Stress

ORNL 99-05665c/djr

- A focusing monochromator on CG4 would provide a flux ~ 10^5 n/(cm^2 sec) for a USANS to extend the resolution to Q_{min} ~ 10^{-5} Å^{-1}, at a cost ~ 300 k$. Such upgrades will permit new classes of experiments to be performed.

ORNL Small Angle Neutron Scattering: Future Directions

Flux increases, larger detectors and extended Q-range should make it possible to:
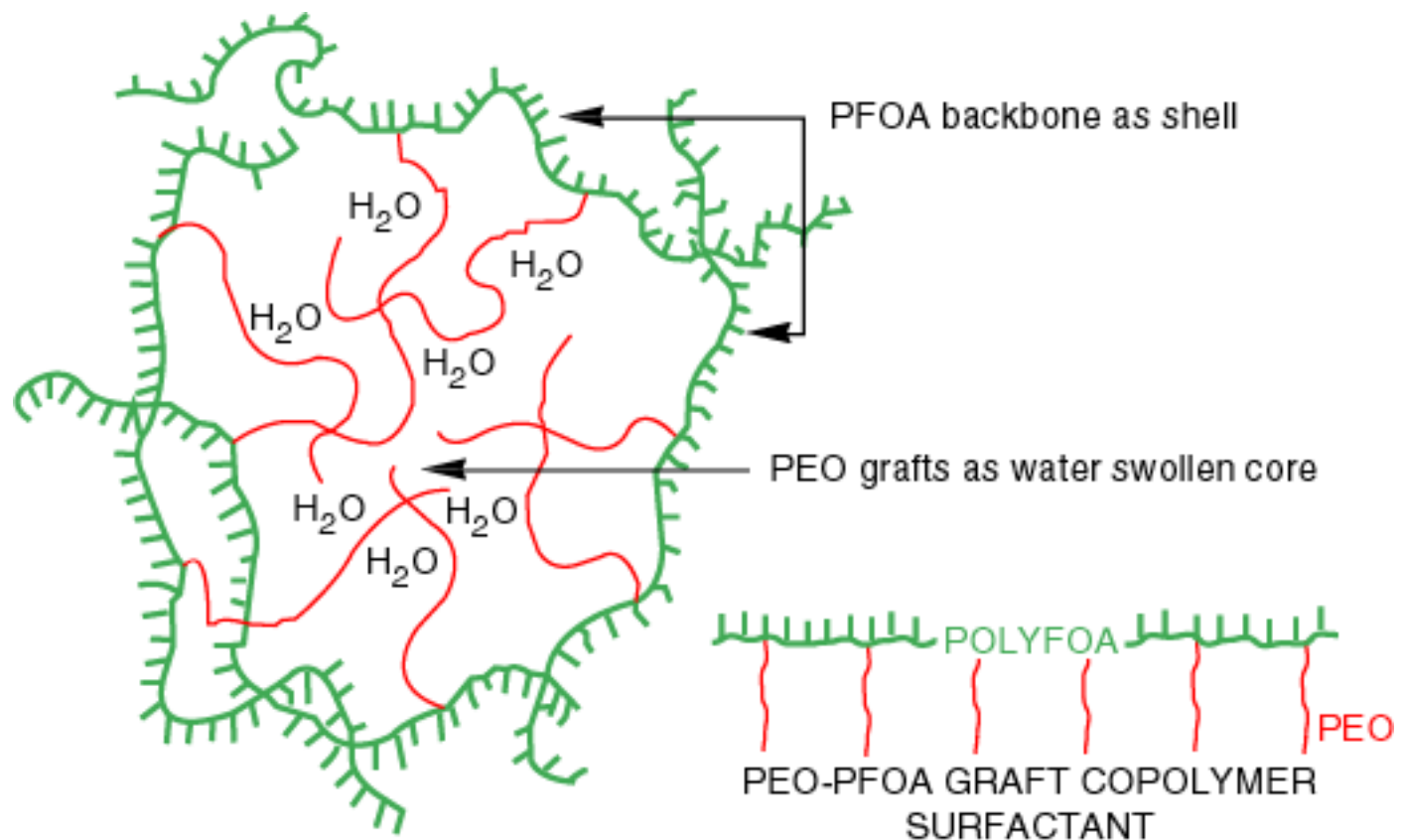
- Explore new directions in soft materials such as *in-situ* processing using a neutron beam to follow structure evolution in industrially relevant equipment (e.g., extruders)

- Study weakly scattering biological materials (cross sections 10^{-1}-10^{-3} cm^{-1})

- Use much smaller samples (1mg vs. 100mg)
  - Pharmaceuticals and developmental polymers available only in small amounts
  - Biological materials, which are often difficult to prepare in bulk
  - Small (~ 1mm^3) crystals of high-T_c superconductors for flux line lattice melting

- Undertake kinetic studies (e.g., phase separation in polymer blends or metallic alloys)

- Use polarized neutrons to explore magnetic materials, spin-glasses, etc.

- Quantify inelastic effects in SANS (currently assumed to be an elastic process)

- Study complicated polydisperse hierarchical structures extended over 4 orders of magnitude in length scale (1 nm < D < 10 μm) by combining SANS & USANS
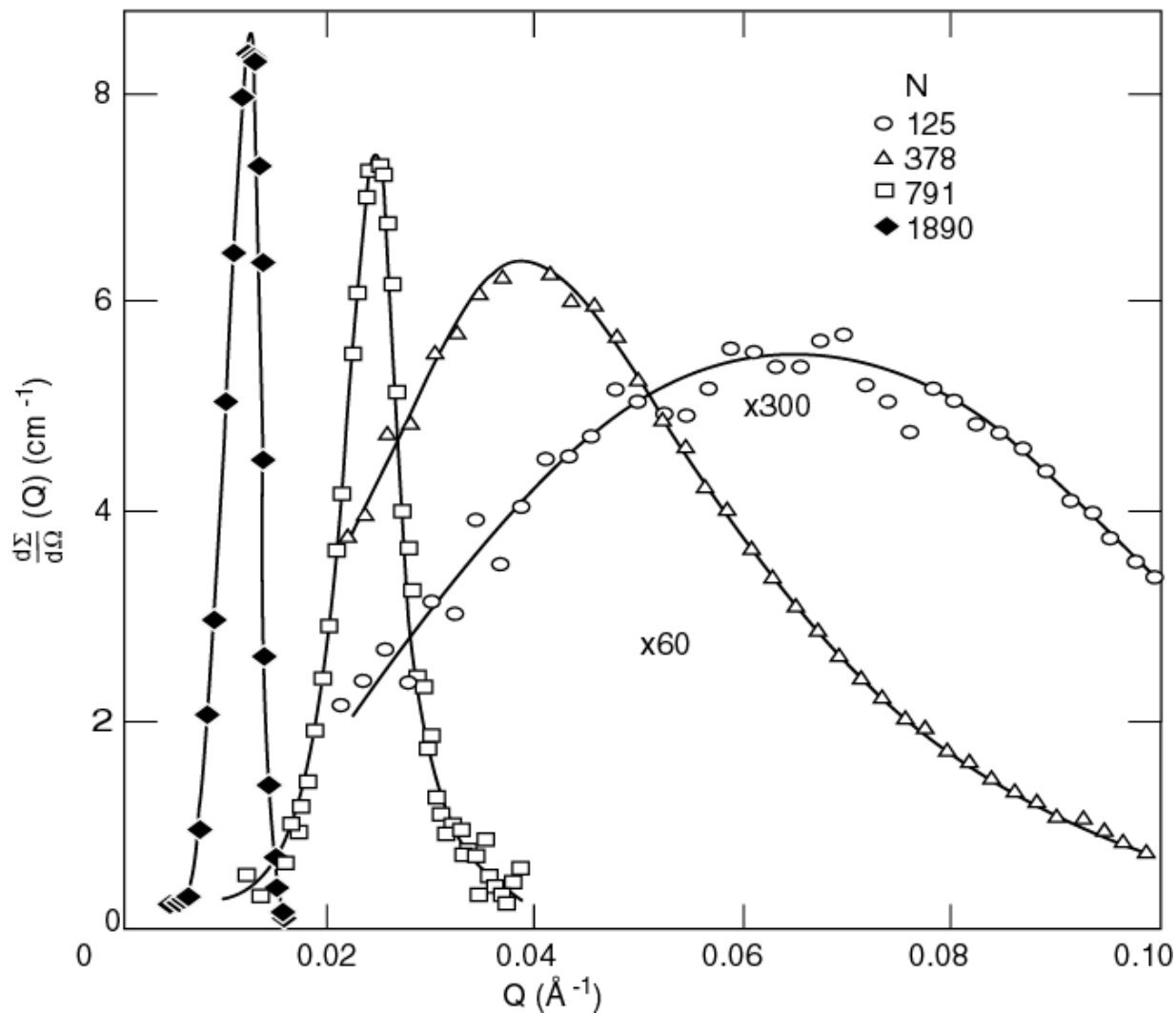
- ???

Back-up Slides

Schematic Representation of Reverse Micelle Formed by Self-Assembly of Polyethylene Oxide-PFOA Graft Copolymer in CO_2 [Fulton et al., Langmuir, 11 4241 (1995)]
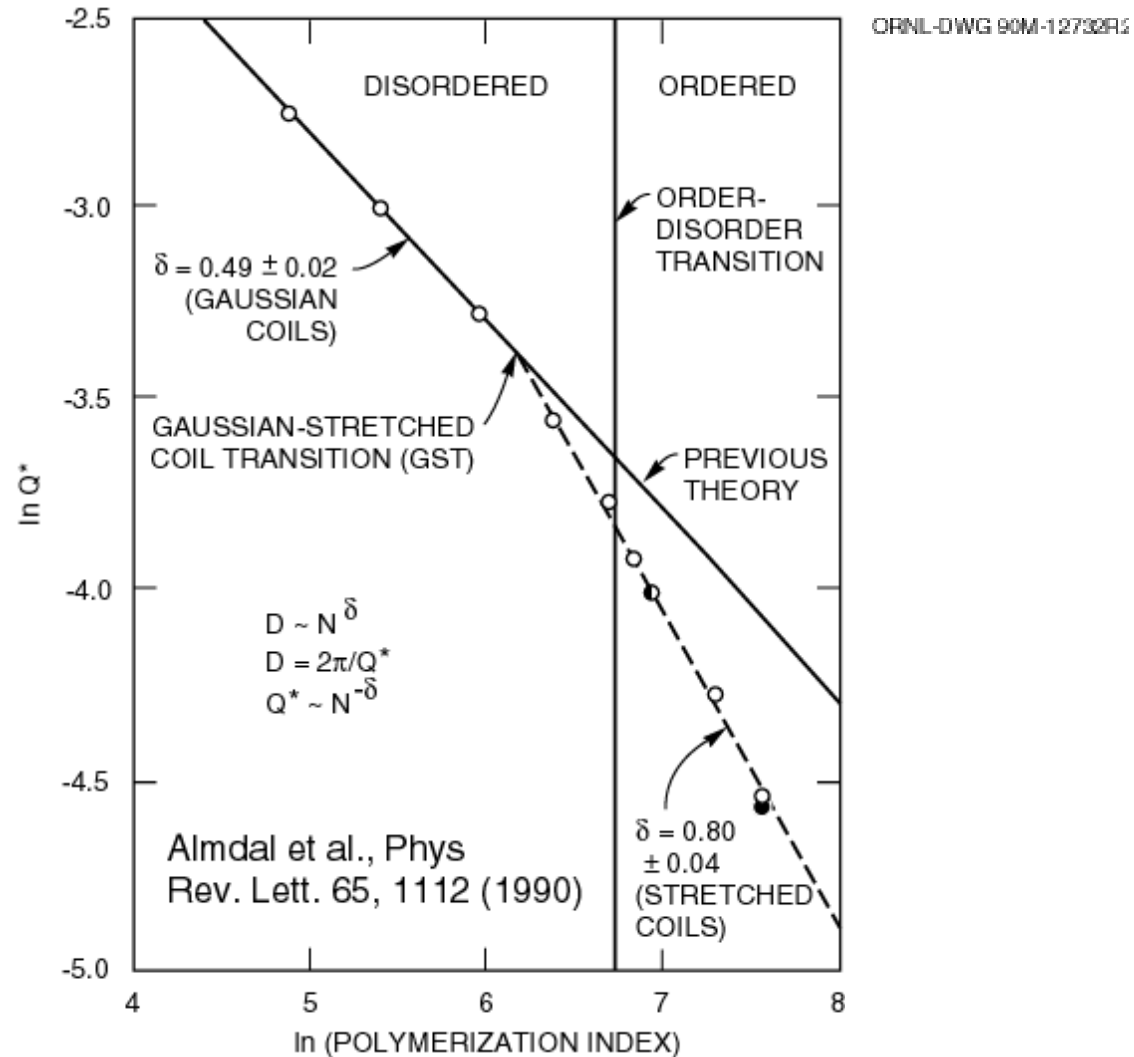

PFOA backbone as shell

H_2O H_2O H_2O H_2O H_2O H_2O H_2O

PEO grafts as water swollen core

POLYFOA

PEO

PEO-PFOA GRAFT COPOLYMER SURFACTANT

Differential Scattering Cross Section for PEP-PEE Block Copolymers as a Function of the Degree of Polymerization, N
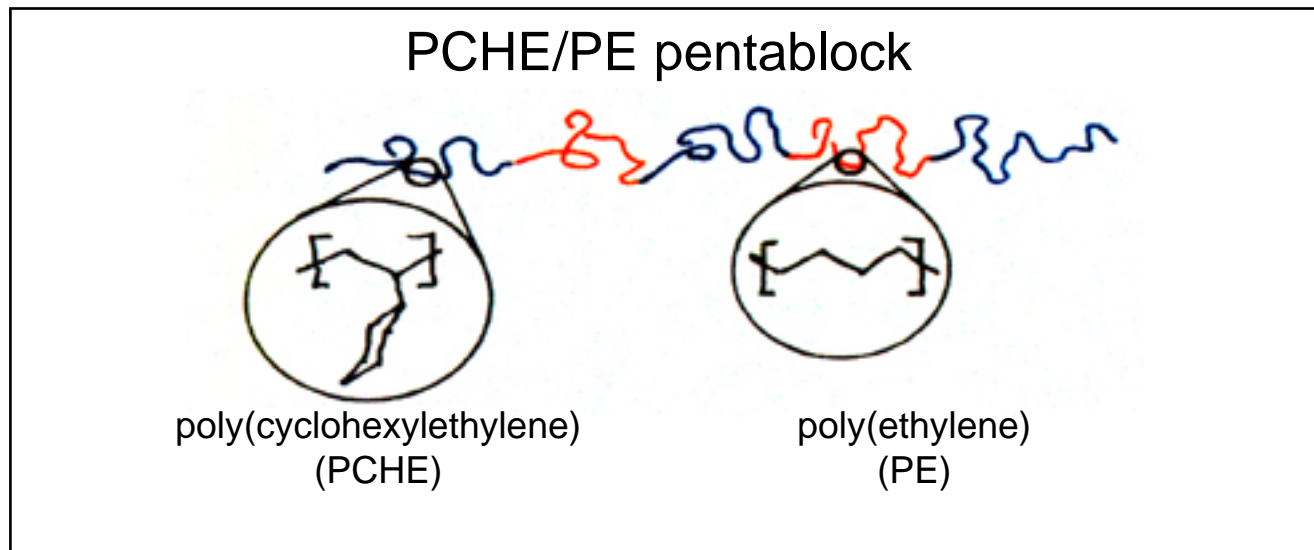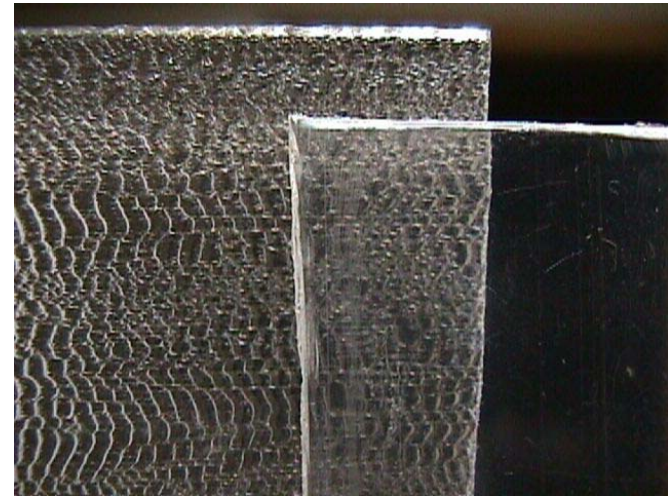
Gaussian-Stretched Coil Transition for PEP-PEE Block Copolymers as a Function of Polymerization Index
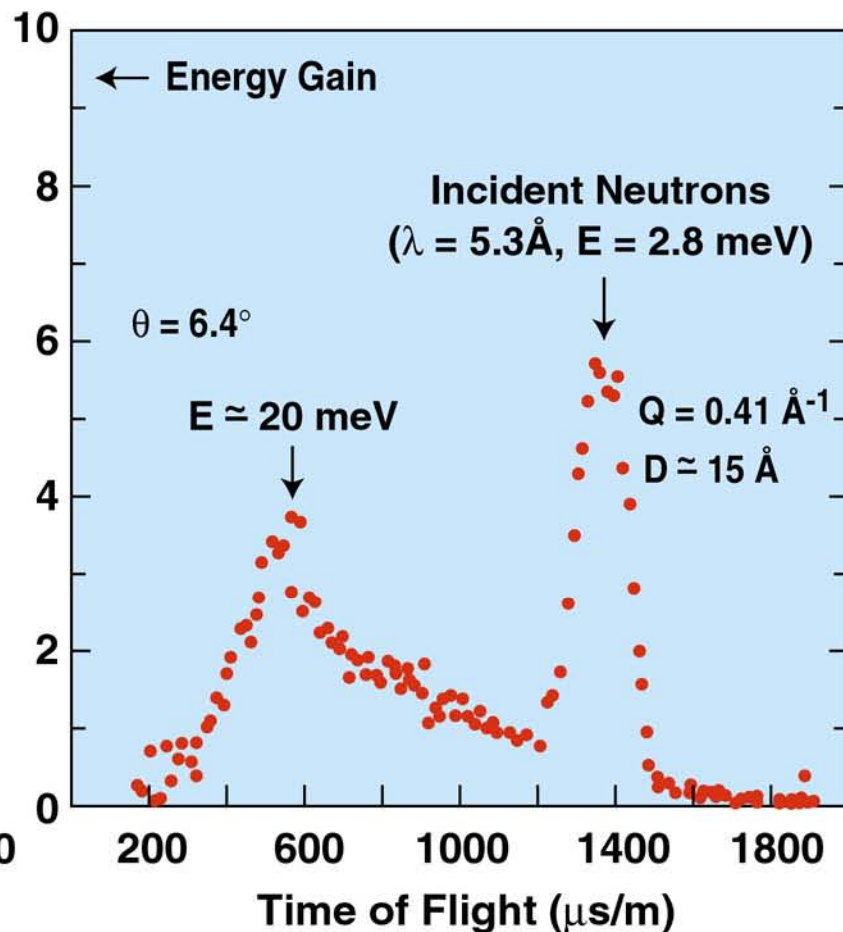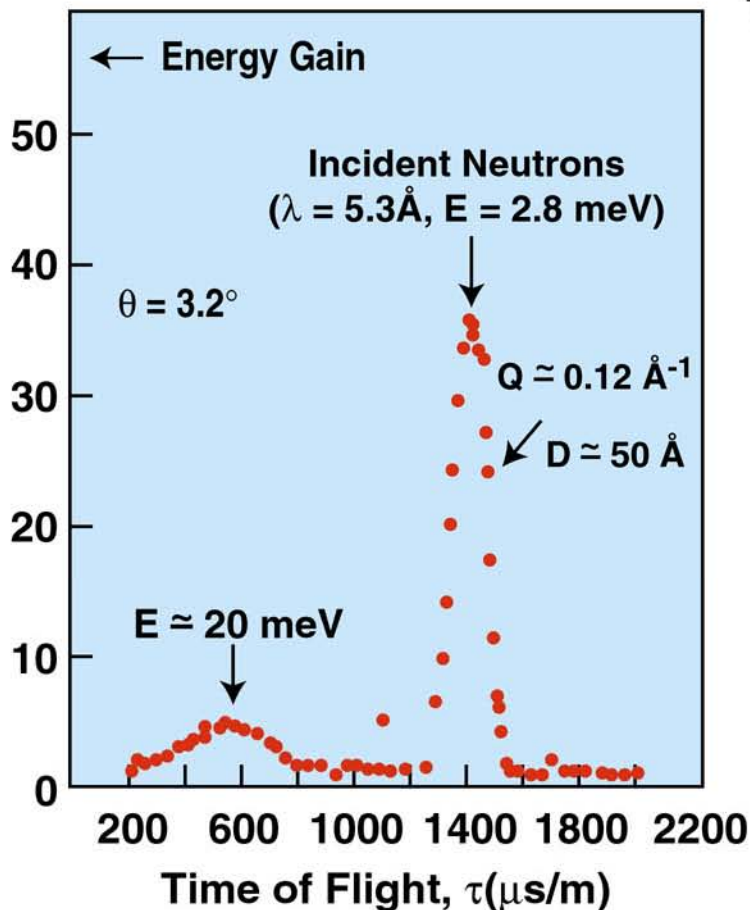
Processing Effects Morphology

- poly(cyclohexylethylene-b-ethylene) pentablock co-polymer extruded sheets

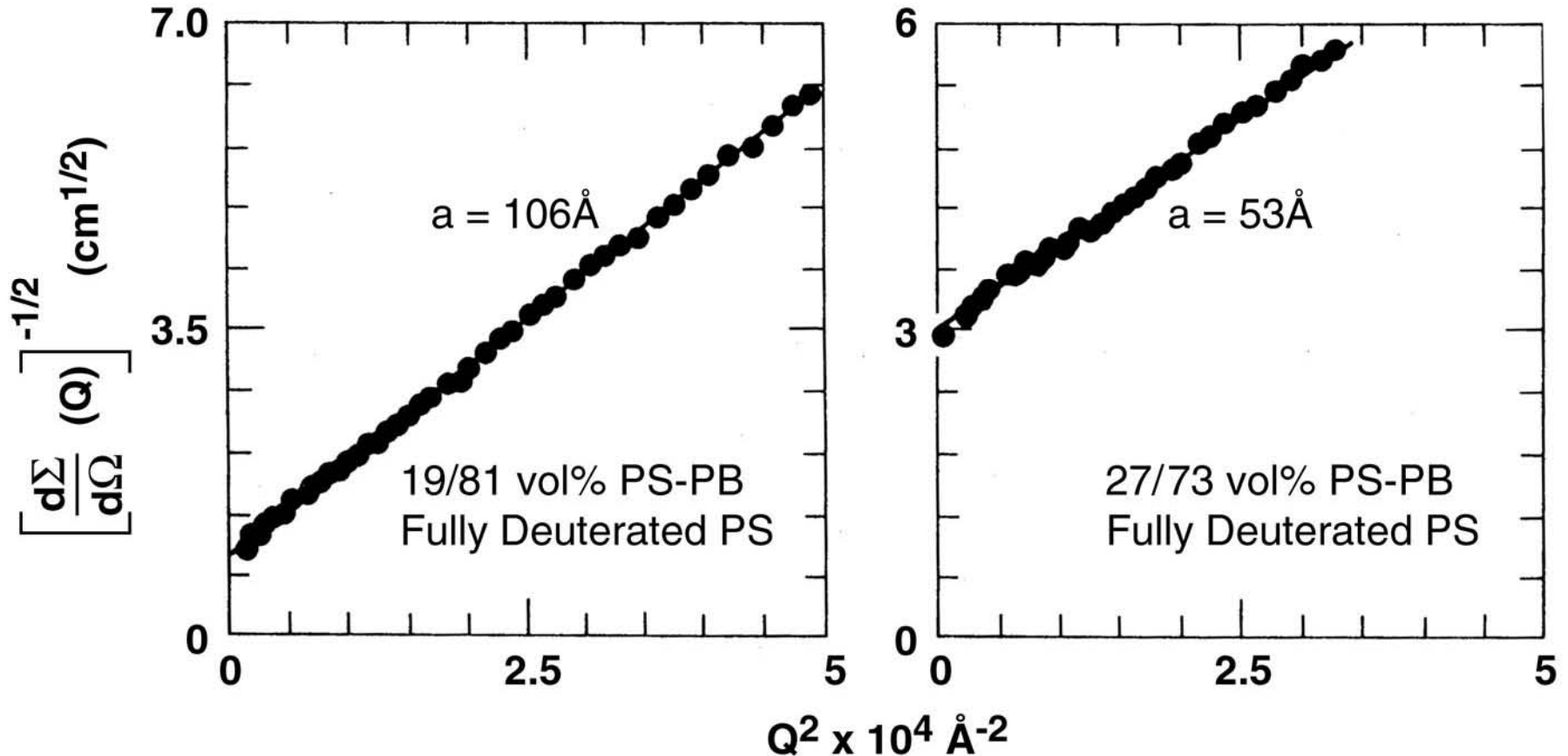- two different molecular architectures result in two lamellar orientations

PCHE/PE pentablock

poly(cyclohexylethylene)
(PCHE)

poly(ethylene)
(PE)
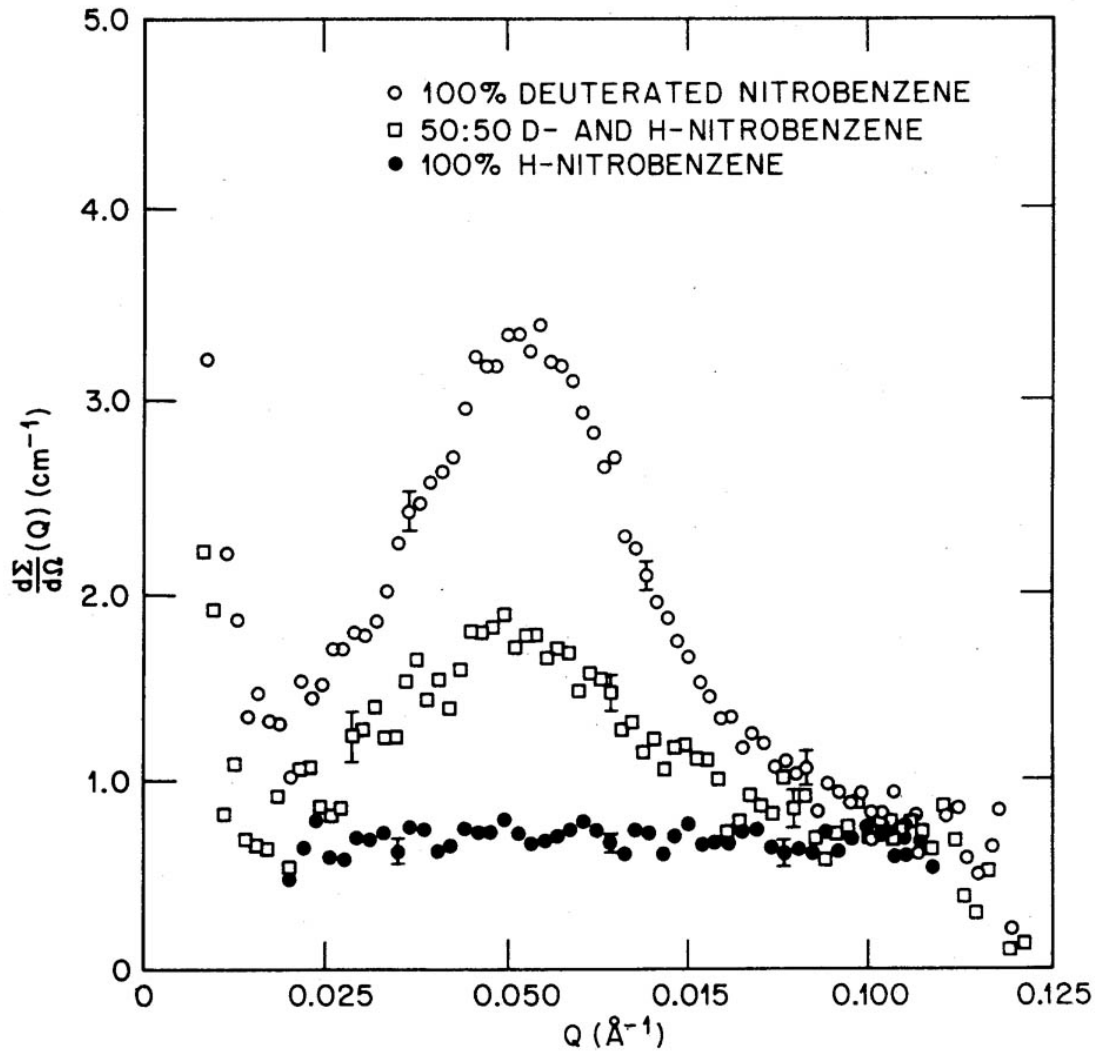
INELASTIC SPECTRUM FROM Bi-Zn SOLUTIONS (646°C)
NEAR THE PHASE BOUNDARY FOR DE-MIXING
[J. Phys. C. 1, 1088 (1968)]

$$\left[\frac{d\Sigma}{d\Omega}(Q)\right]^{-1/2}$$ **VS Q² FOR TWO PHASE-SEPARATED BLENDS OF POLYSTYRENE (PS) AND POLYBUTADIENE (PB)**
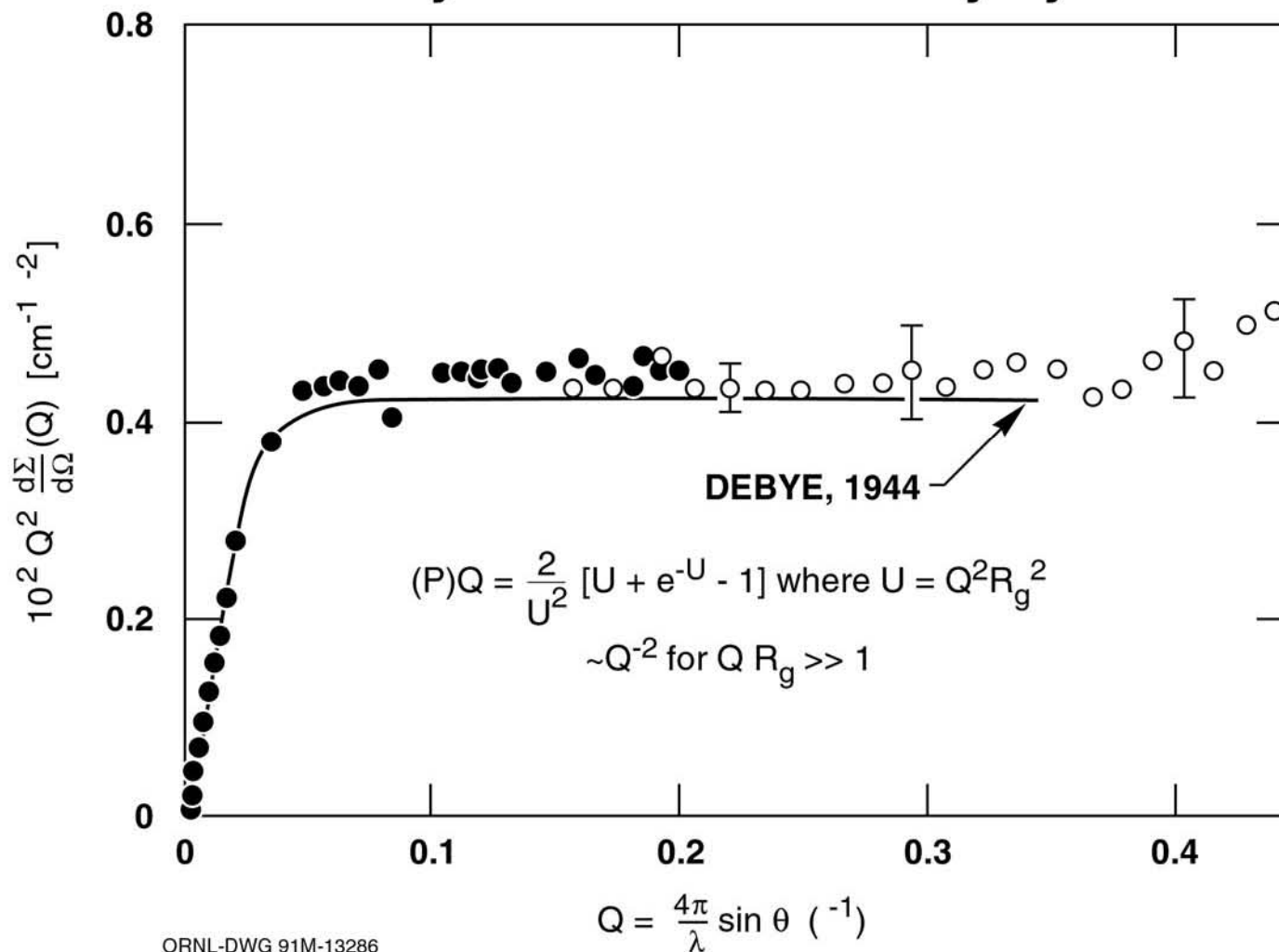
ORNL-DWG 84-16324/rra

$\frac{d\Sigma}{d\Omega}(Q)$ vs Q FOR POLYVINYL CHLORIDE PLASTICISED
WITH 33 wt. % NITROBENZENE

○ 100% DEUTERATED NITROBENZENE
□ 50:50 D− AND H−NITROBENZENE
● 100% H−NITROBENZENE

$\frac{d\Sigma}{d\Omega}(Q)$ (cm^{-1})

5.0

4.0

3.0

2.0

1.0

0

0   0.025   0.050   0.015   0.100   0.125

Q $(\mathring{A}^{-1})$

OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY

UT−BATTELLE

COMPARISON OF MICELLE DIMENSIONS AND AGGREGATION NUMBER (N_{AGG}) BY SAXS AND SANS

REFERENCE		RADIATION	R_{CORE} (Å)	R_{SHELL} (Å)	N_{AGG}
THIS WORK	UNSWOLLEN	SANS	25	39	3
	D_2O–SWOLLEN	SANS	86	130	83
	H_2O–SWOLLEN	SANS	86	126	83
FULTON *et al.* LANGMUIR, 1995	H_2O–SWOLLEN	SAXS	105	125	120

Kratky Plot for Atactic Polystyrene

Add Gaussian Term to Describe Long Range Fluctuations

$$\gamma(r) = f \exp(-r/a_1) + (1-f) \exp(-r^2/a_2^2)$$

$$\frac{d\Sigma}{d\Omega}(Q) = \frac{A_1}{(1 + Q^2 a_1^2)^2} + A_2 \exp\left(\frac{-Q^2/a_2^2}{4}\right)$$
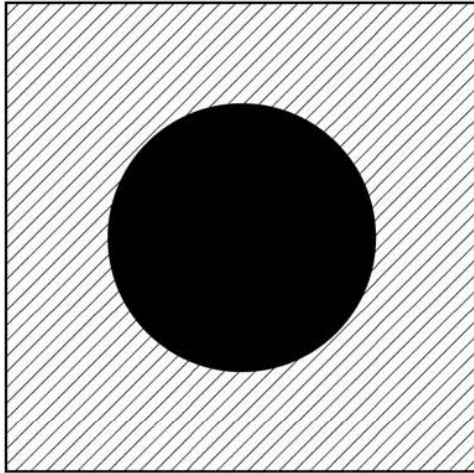
$$A_1 = 8\pi a_1^3 f \phi (1-\phi)(\rho_1 - \rho_2)^2$$

$$A_2 = \pi a^{3/2} a_2^3 (1-f)\phi(1-\phi)(\rho_1 - \rho_2)^2$$

These parameters may be used to calculate surface areas, correlation volume, Porod lengths, etc.
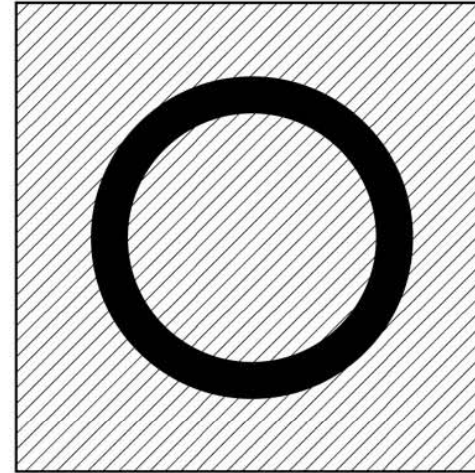
ORNL-WSM 14844/rra

SANS Studies of Polymer Latex Particles in H_2O/D_2O Mixtures

SANS FROM H-LATEXES IN D_2O
GIVES THE CORE MORPHOLOGY
VIA THE THEORETICAL SPHERE
SCATTERING (BESSEL) FUNCTION
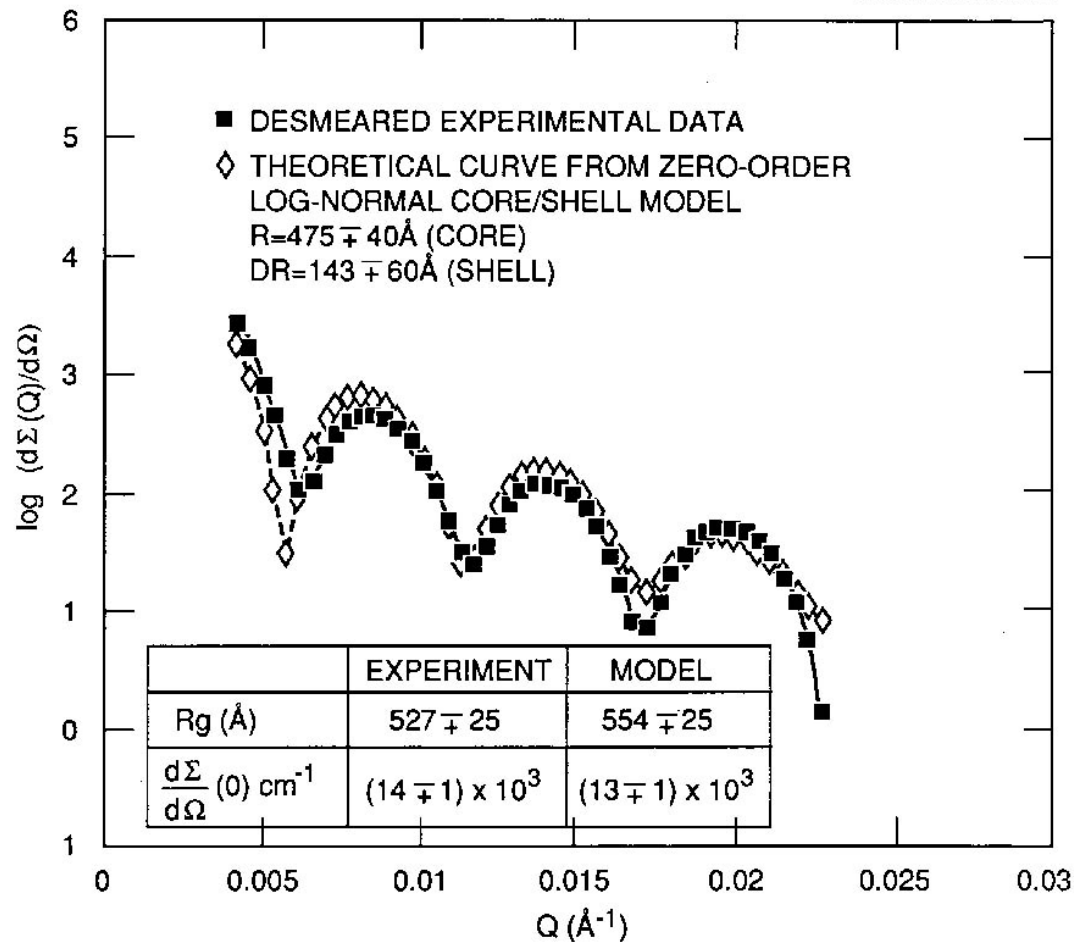
SANS FROM H-LATEXES POLYMERIZED
WITH A D-SECOND MONOMER AND
EXAMINED IN A D_2O/H_2O MIXTURE
CHOSEN TO MATCH THE CORE SLD
SHOWS HOLLOW SHELL SCATTERING
FUNCTION

$$P(Q) = \frac{9}{(QR)^6} \left[\sin QR - QR \cos QR \right]$$

$$P(Q) = \frac{9}{QR^6 (I-L^3)^2} \left[\sin QR - QR \cos QR \right.$$
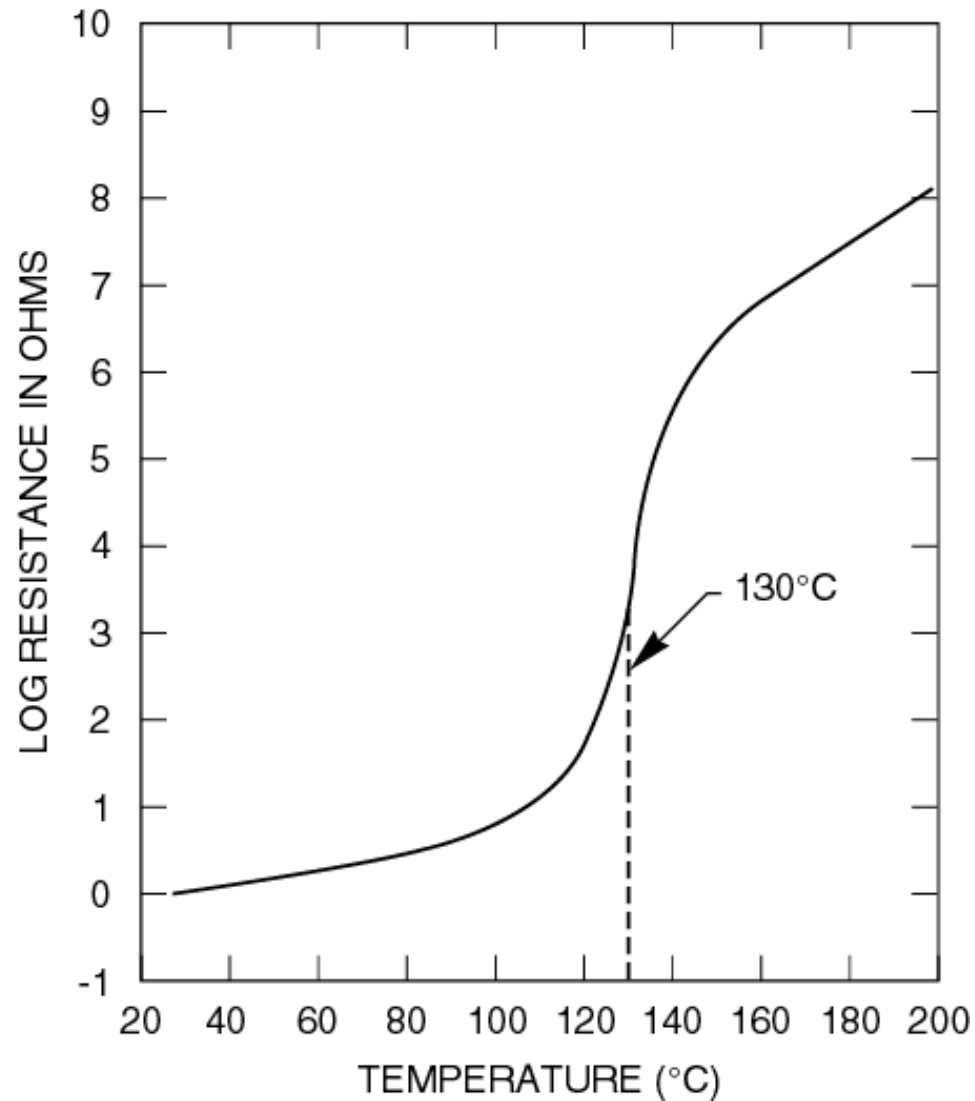$$\left. - \sin QRL - QRL \cos QRL \right]^2$$

$$L = \frac{R_1}{R} = \frac{\text{INNER RADIUS}}{\text{OUTER RADIUS}}$$

ORNL-DWG 90M-12748R

Comparison of experimental Sans data and theoretical scattering function for PS-PMMA-H core latex with PMMA-D3 shell. Core contrast matched in 25:75 % solution of D_2O/H_2O.
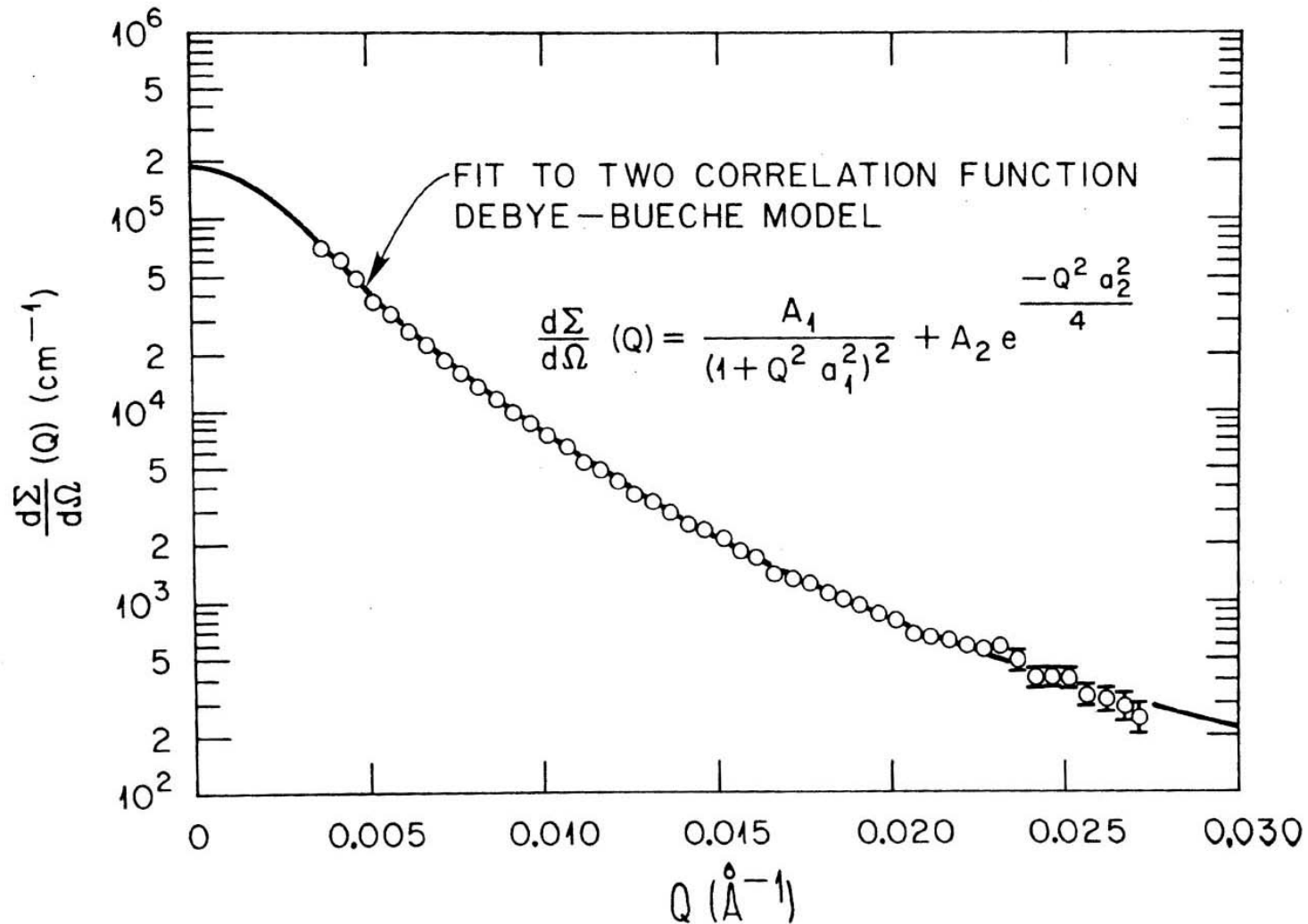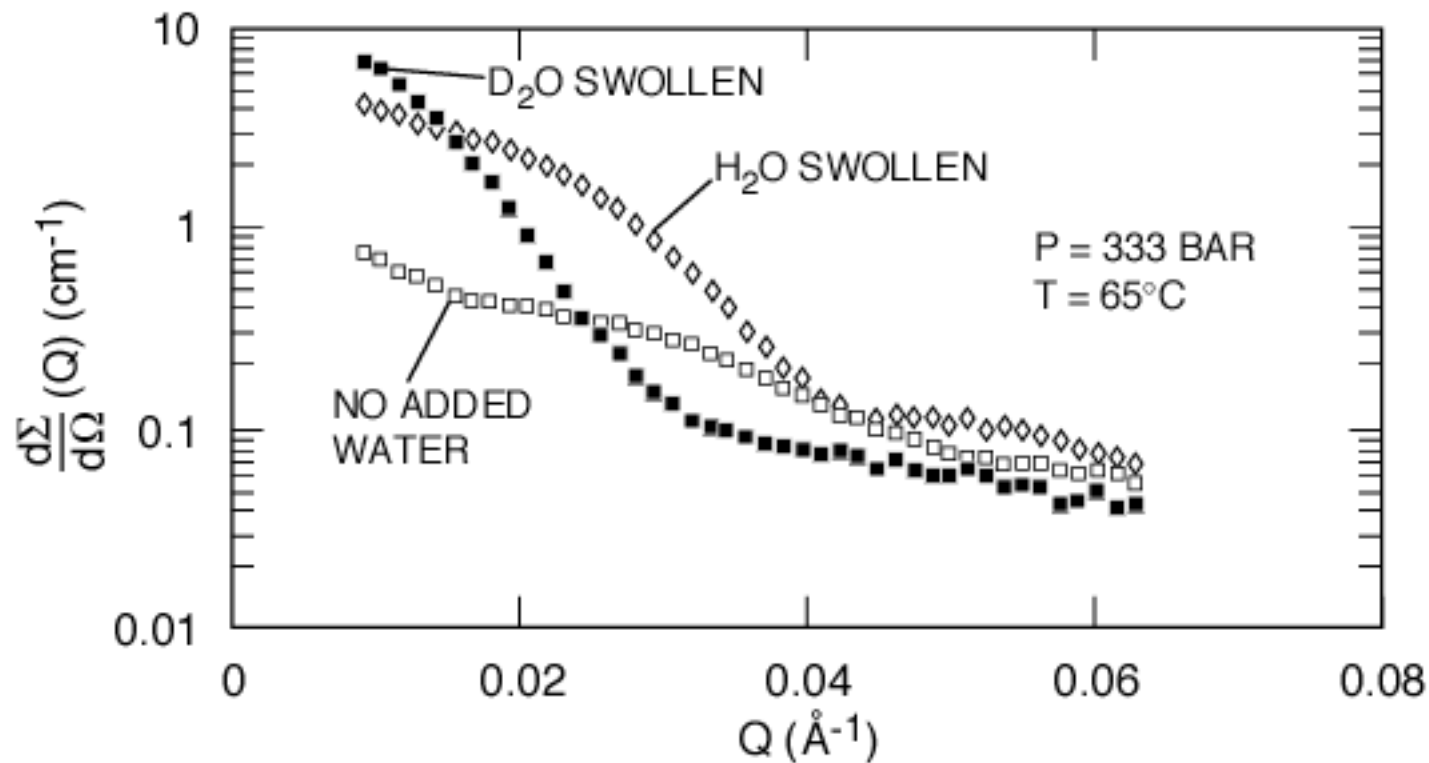
M.P Wai et al. Polymer _28_ , 919, 1987

RESISTANCE AS FUNCTION OF TEMPERATURE FOR CARBON – POLYETHYLENE
COMPOSITE MATERIALS (IEE TRANSACTIONS CHMT4, 372, 1981)

COHERENT SANS CROSS SECTION FROM 34.8
VOL % CARBON BLACK IN POLYETHYLENE

FIT TO TWO CORRELATION FUNCTION
DEBYE—BUECHE MODEL

$$\frac{d\Sigma}{d\Omega}(Q) = \frac{A_1}{(1+Q^2 a_1^2)^2} + A_2 e^{\frac{-Q^2 a_2^2}{4}}$$

$\frac{d\Sigma}{d\Omega}$ (Q) FOR PFOA–g–PEO GRAFT COPOLYMER IN CO_2 BEFORE AND AFTER SWELLING WITH H_2O AND D_2O
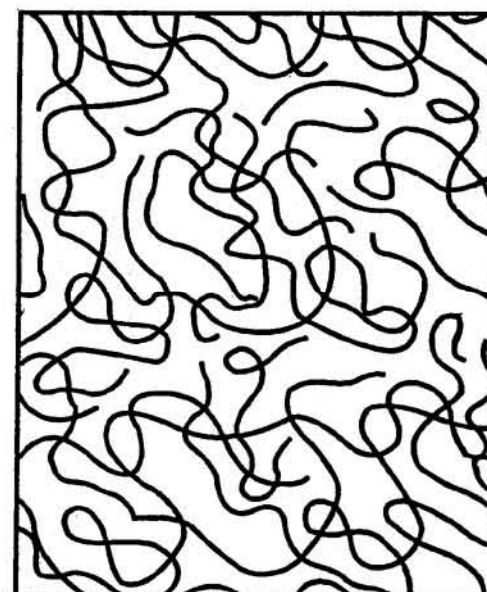
SCHEMATIC REPRESENTATION OF VARIOUS MODELS FOR POLYMER CHAIN CONFORMATION IN AMORPHOUS POLYMERS
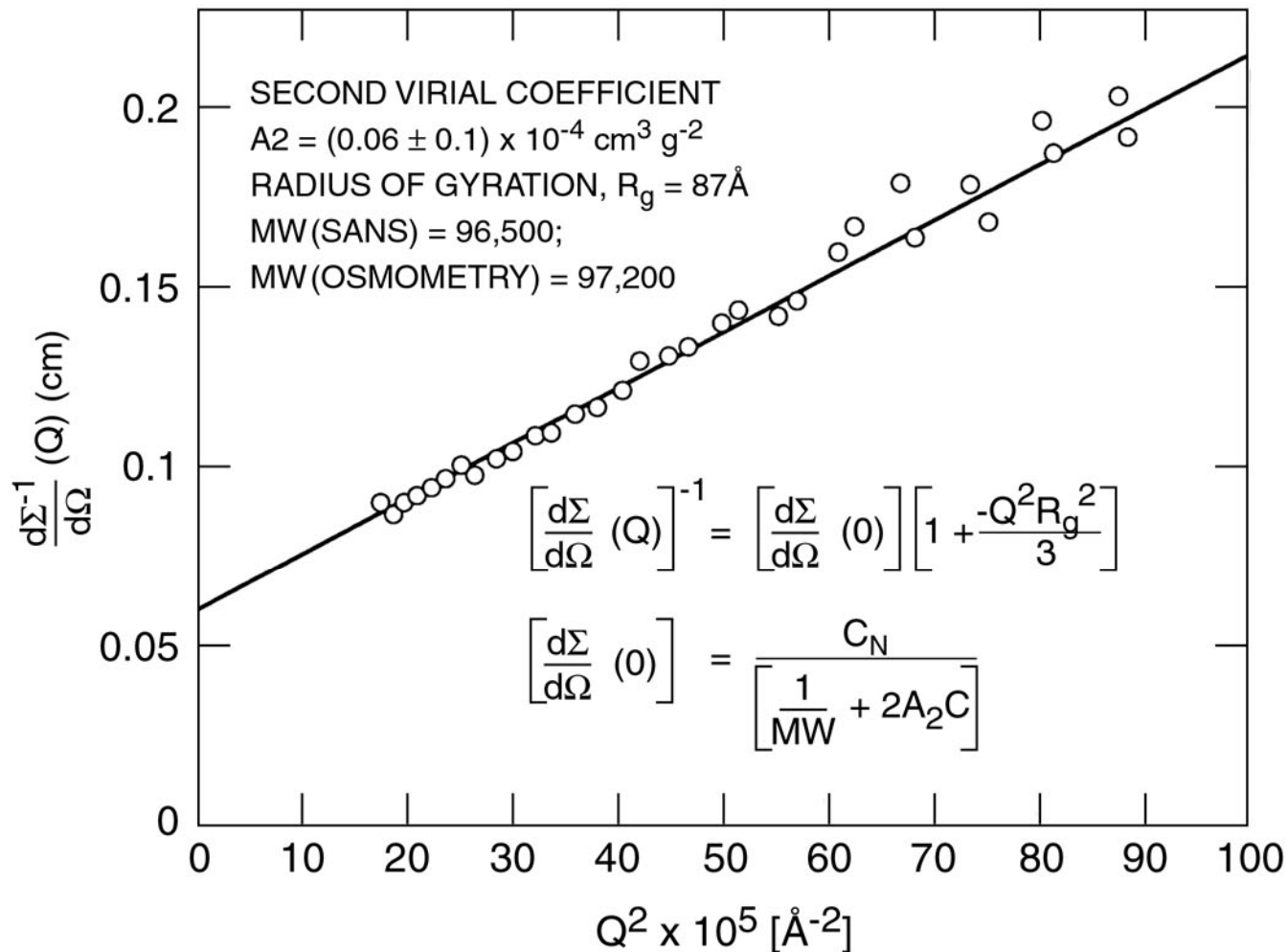
FOLD-CHAIN FRINGED-MICELLAR GRAIN MODEL (YEH, 1972)

MEANDER MODEL (PECHOLD, 1968) CHAINS HAVE QUASI-PARALLEL PACKING

RANDOM COIL MODEL (FLORY, 1951) CHAIN HAS SAME CONFIGURATION AS IN THETA SOLVENT ($A_2 = 0$); $R_g/M_w^{0.5} = 0.27$Å FOR PS IN CYCLOHEXANE (T = 38°C) AND IN CONDENSED STATE!

SECOND VIRIAL COEFFICIENT
$A2 = (0.06 \pm 0.1) \times 10^{-4}$ cm^3 g^{-2}
RADIUS OF GYRATION, $R_g = 87$Å
MW (SANS) = 96,500;
MW (OSMOMETRY) = 97,200

$$\left[\frac{d\Sigma}{d\Omega}(Q)\right]^{-1} = \left[\frac{d\Sigma}{d\Omega}(0)\right]\left[1 + \frac{-Q^2R_g^2}{3}\right]$$

$$\left[\frac{d\Sigma}{d\Omega}(0)\right] = \frac{C_N}{\left[\dfrac{1}{MW} + 2A_2C\right]}$$
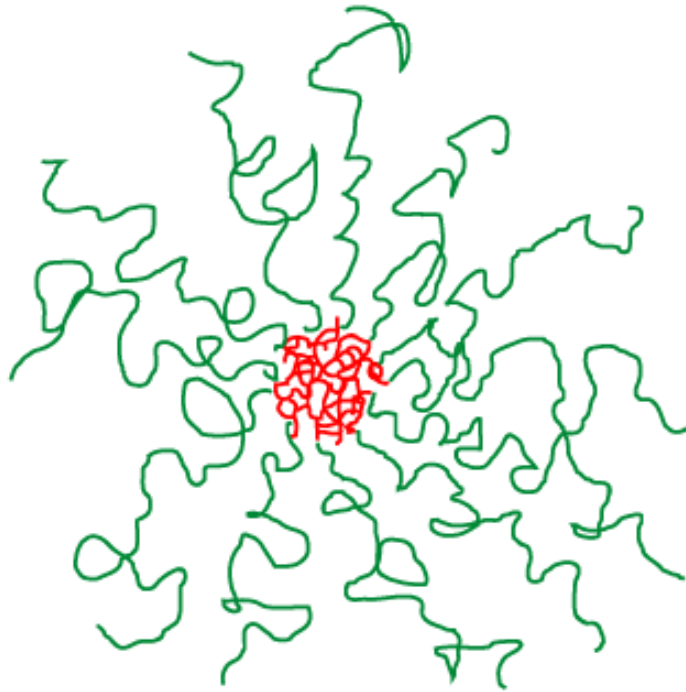
$\dfrac{d\Sigma^{-1}}{d\Omega}$ (Q) VS Q^2 FOR SAMPLE CONTAINING 5 wt % LABELED PSD MOLECULES IN POLYSTYRENE (PSH)
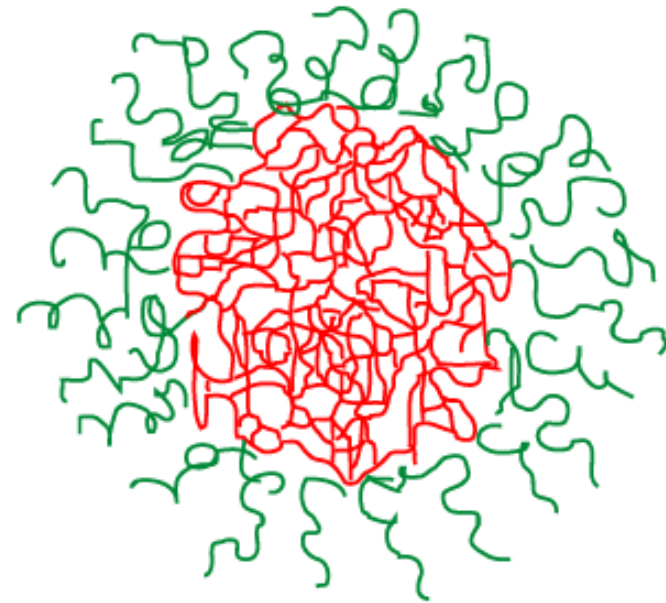
Molecular Dimensions in Bulk Amorphous Polymers

Polymer	State	$R_g/M_w^{1/2}$ ($gm^{-1/2}$)	
		Bulk	**θ Solvent**
Polystyrene	Glass	0.275	0.275
Polystyrene	Melt	0.280	0.275
Polyethylene	Melt	0.46	0.45
Polyvinyl chloride	Glass	0.40	0.37
Poly-butylene	Glass	0.31	0.30
Polymethyl-Methacrylate	Glass		
(Atactic)		0.275	0.275
(Syndio)		0.289	0.243
(Isotactic)		0.297	0.28
Polyethylene-Terepthalate	Glass	0.385	0.39-0.42
	Melt	0.35	0.34-0.42
Polybutadiene	Melt	0.35	0.34-0.42
Polyethylene Oxide	Melt	0.35	0.34

Gaussian (Random) Coils, $R_g \sim M_w^{1/2} \sim N^{1/2}$ (N = Number of units on chain)

(a) "HAIRY" MICELLE

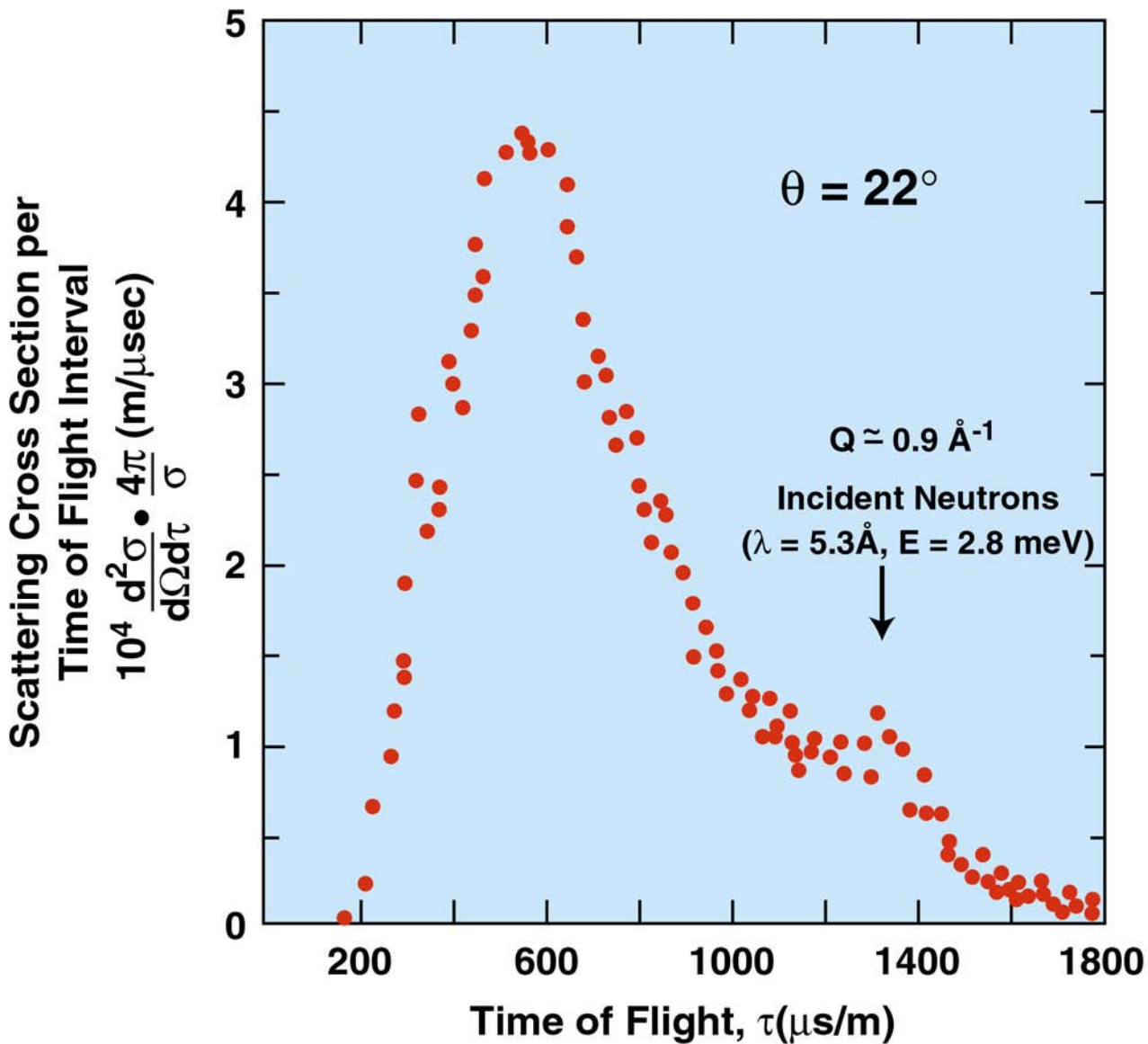(b) "CREWCUT" MICELLE

POSSIBLE STRUCTURES OF BLOCK COPOLYMER MICELLES
[HALPERIN *et al.*, Advances in Polymer Science, 100 31 (1992)]

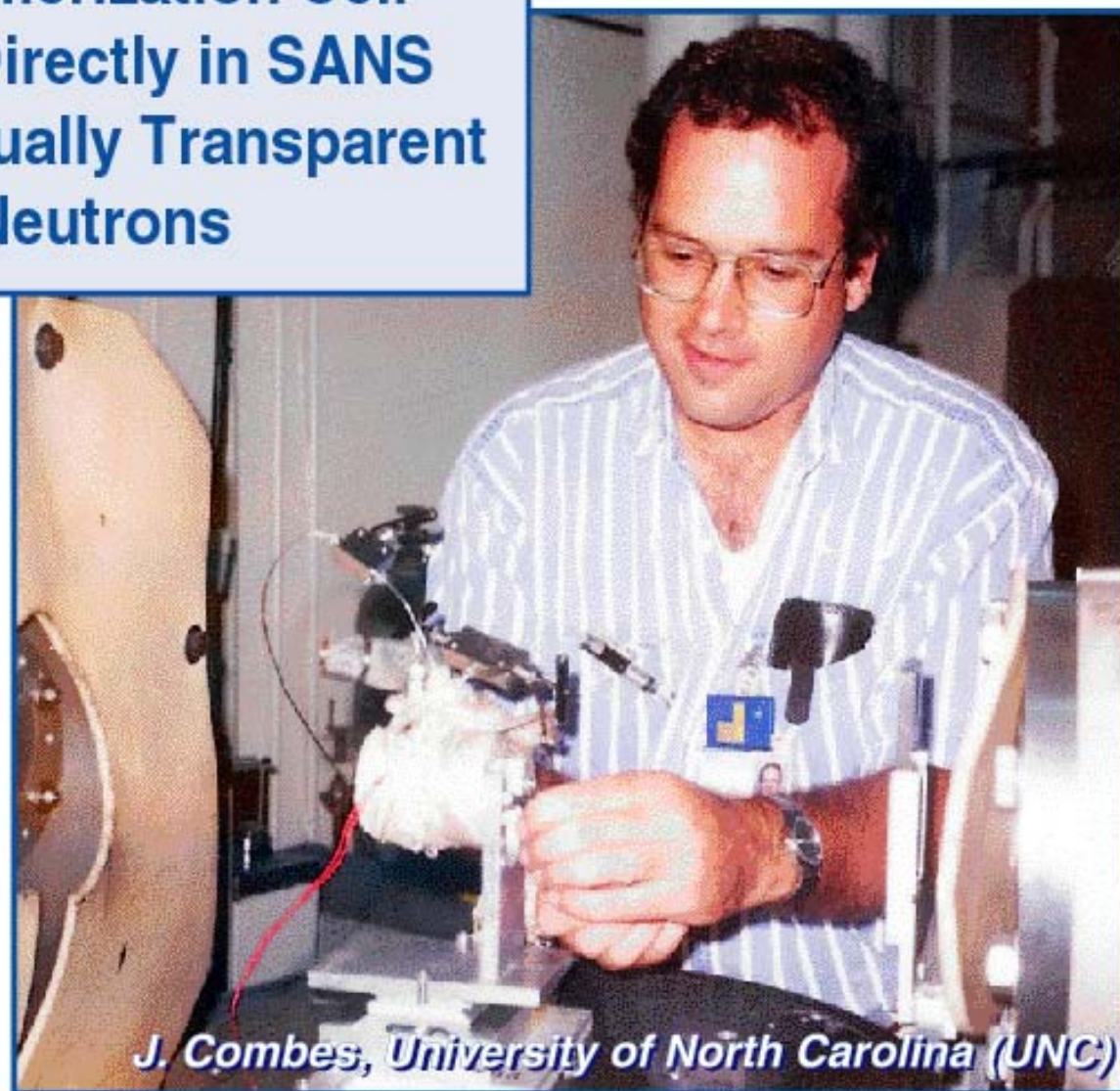# THE AGGREGATION NUMBER IS INDEPENDENT OF THE CORONA BLOCK LENGTH FOR BOTH LIMITING STRUCTURES

AGGREGATION NUMBER (N_{agg}) FOR PS–PFOA BLOCK COPOLYMER MICELLES AS A FUNCTION OF THE CORONA BLOCK LENGTH

Surfactant	N_{agg}	R_{core} (Å)	R_{total} (Å)	N_{CO2}	Z_{core}
3.7^k–b–16.6^k	7	27	85	40	10
3.7^k–b–27.5^k	11	30	80	10	8
3.7^k–b–40.0^k	7	27	89	16	8
3.7^k–b–61.2^k	6	26	100	17	8

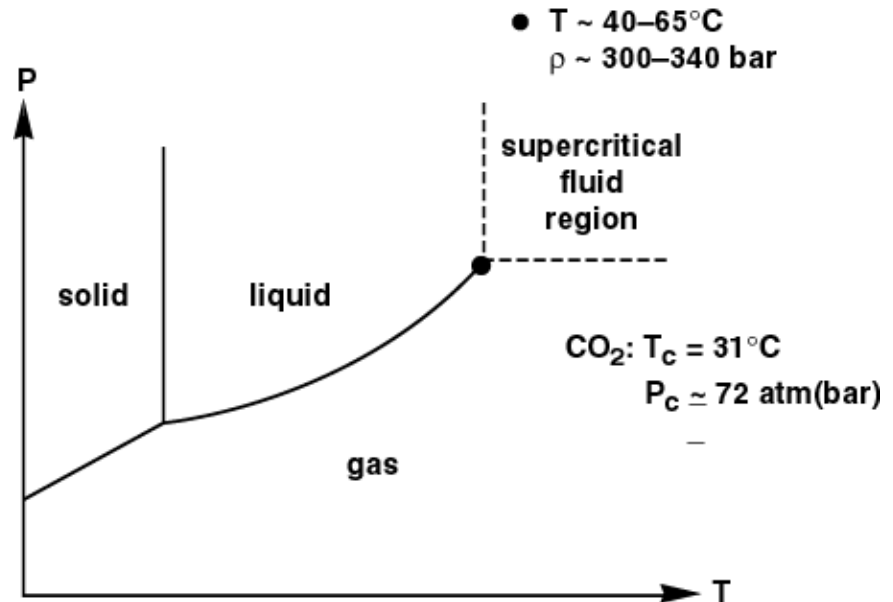INELASTIC SPECTRUM FROM Bi-Zn SOLUTION (646°C)
AT HIGHER-Q [$Q_{elastic} \cong 0.9\text{Å}^{-1}$)

SCF Polymerization Cell Mounted Directly in SANS Beam is Virtually Transparent to Neutrons

J. Combes, University of North Carolina (UNC)

ORNL 98-3887/vlb

Supercritical Fluids in Colloidal Science

Schematic Phase Diagram

Advantages of CO_2:

– nontoxic

– nonflammable

– environmentally benign

– tunable solvent

● T ~ 40–65°C
ρ ~ 300–340 bar

supercritical
fluid
region

CO_2: $T_c = 31°C$

$P_c \simeq 72$ atm(bar)

Phase	Density (g/cm^3)	Diffusion coeff. (cm^2/s)	Viscosity $(g/cm/s)$
gas(STP)	10^{-3}	10^{-1}	10^{-4}
SCF	0.3–0.8	10^{-3}–10^{-4}	10^{-4}–10^{-3}
liquid	1	$<10^{-5}$	10^{-2}