SANS AS A TOOL FOR STUDYING PROPERTIES OF SOFT MATTER AND COMPLEX FLUIDS

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EXAMPLES OF SOFT MATTER SUBSTANCES:

Liquid crystals
Polymer gels
Emulsions
Colloids
Foams
Glues

CHARACTERISTIC STRUCTURES AND RANGE OF INTERACTIONS ARE ~ 10 – 1000 Å, I.E. IDEALLY SUITED FOR SANS

- **COMMON FEATURES OF SOFT MATTER SUBSTANCES:**
- **Large number of internal degrees of freedom**
- **Week interactions between structural elements**
- **Delicate balance between entropic and enthalpic contributions to F**

RESULTING LARGE THERMAL FLUACTUATIONS LEAD TO A WIDE VARIETY OF EQUILIBRIUM STRUCTURES AND THEIR SENSITIVITY TO (RELATIVELY WEEK) EXTERNAL PERURBATIONS

THE OBJECTIVE OF A SANS EXPERIMENT IS TO DETERMINE THE DIFFERENTIAL CROSS-SECTION WHICH CONTAINS ALL INFORMATION ON THE SHAPE AND INTERACTIONS OF THE SCATTERING BODIES IN THE SAMPLE

$$\frac{d\sigma}{d\Omega}(Q) = N_P V_P^2 k_n P(Q) S(Q) + B_{inc}$$

N_P AND V_P: CONCENTRATION AND VOLUME OF SCATTERING BODIES

k_n: NEUTRON CONTRAST FACTOR

$P(Q)$: FORM FACTOR

$S(Q)$: STRUCTURE FACTOR

Q: SCATTERING VECTOR

B_{inc}: INCOHERENT BCGR

NON-INTERACTING BODY (SHAPE/SIZE/MOL. WEIGHT)

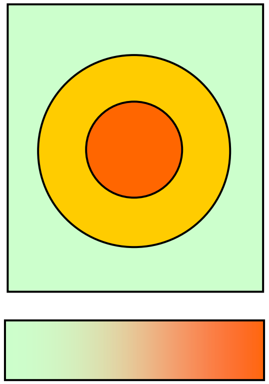
STRONGLY INTERACTING BODIES (SPACE ARRANGEMENTS)

CONTRAST IS PROPORTIONAL TO THE DIFFERENCE BETWEEN SCATTERING POWER OF THE COMPONENTS

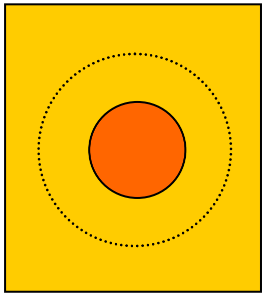
ATOM	NUCLEUS	SCATTERING LENGTH b_{coh} (10^{-12} cm)
HYDROGEN	^{1}H	-0.374
DEUTERIUM	^{2}H (D)	0.667
CARBON	^{12}C	0.665
NITROGEN	^{14}N	0.94
OXIGEN	^{16}O	0.580

$$\text{CONTRAST} \sim \left[\frac{\Sigma b_i}{V_i} - \frac{\Sigma b_j}{V_j}\right]^2$$

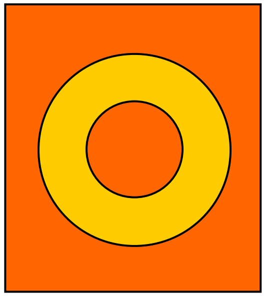
CONTRAST VARIATION: COATED LATEX SPHERE IN A SOLVENT



SLD OF THE SOLVENT (E.G. MIXTURE OF (H_2O+D_2O)

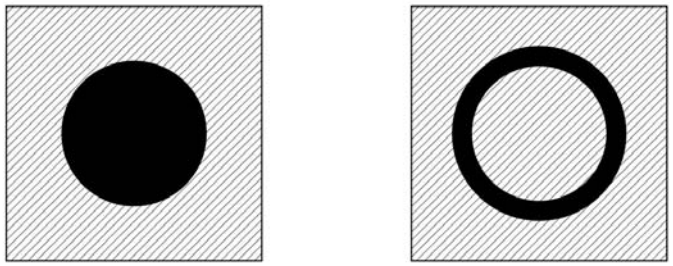


CONTRAST-MATCHED SHELL



CONTRAST-MATCHED CORE

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

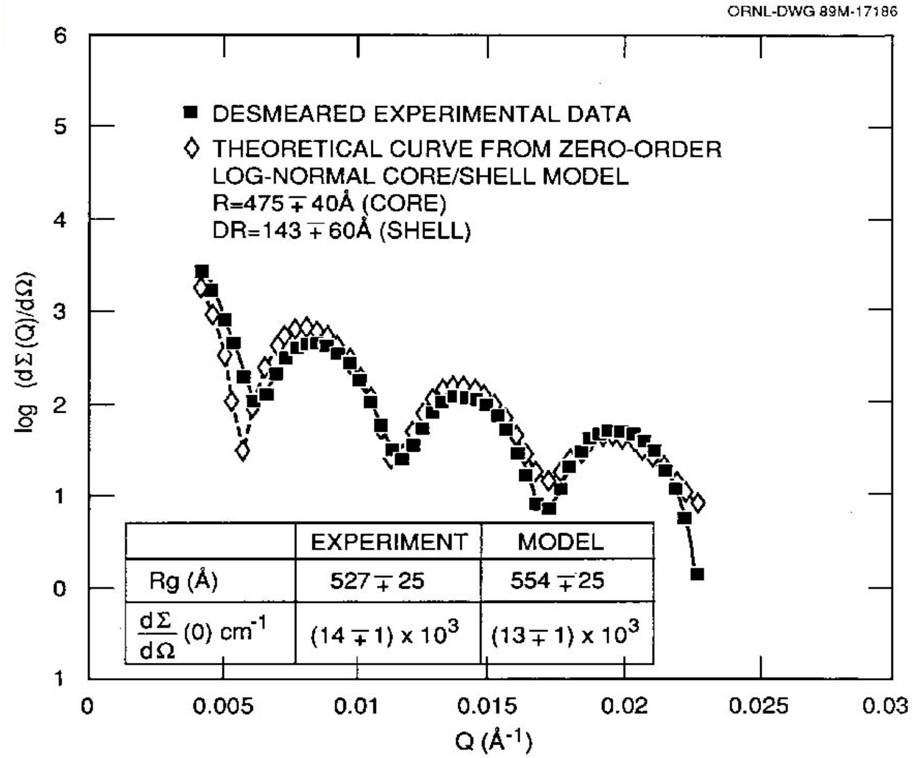
$$P(Q) = \frac{9}{(QR)^6}\,[\sin QR - QR\cos QR]$$

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

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

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

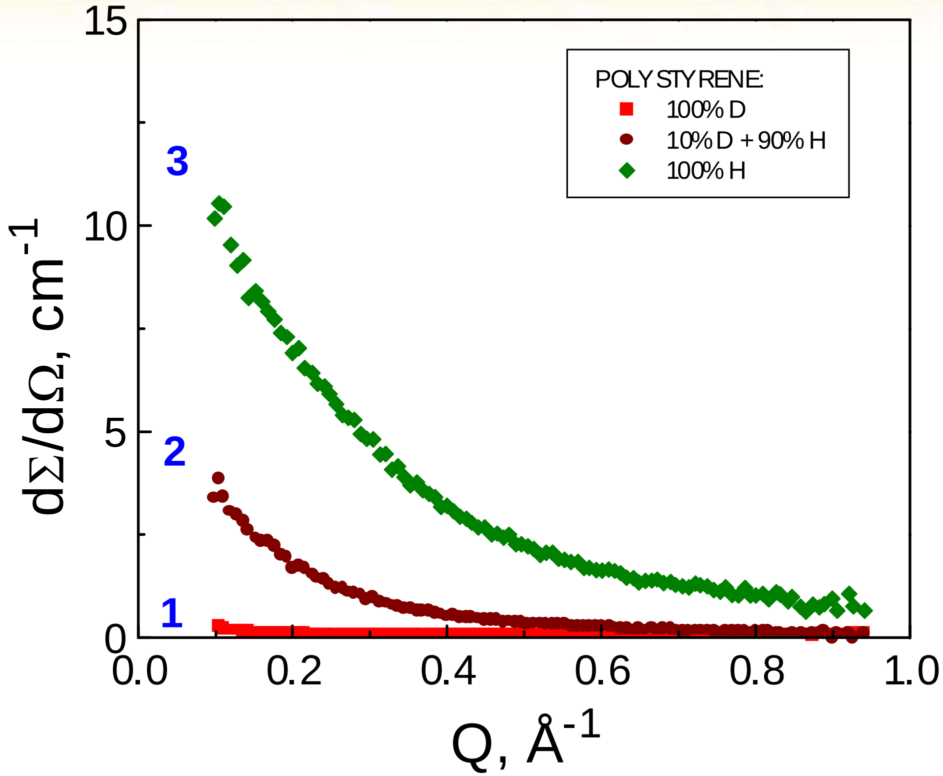
ORNL-DWG 90M-12748R

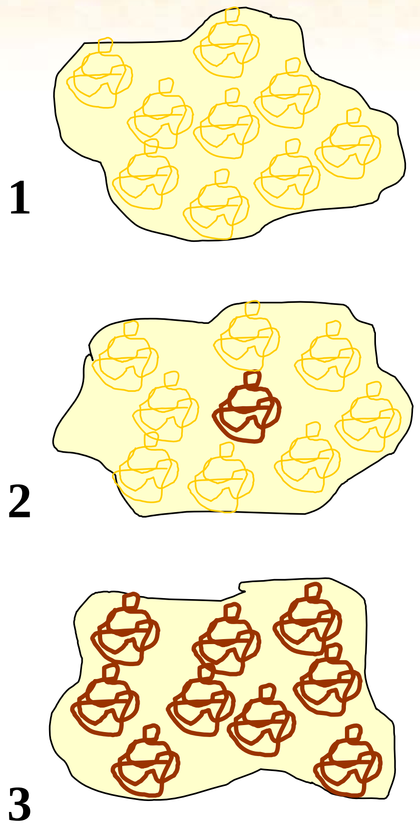


COMPARISON OF EXPERIMENTAL SANS DATA AND THE THEORETICAL SCATTERING FUNCTION FOR PS-PMMA-H CORE LATEX WITH PMMA-D SHELL. CORE CONTRAST MATCHED IN 25/75% SOLUTION OF D_2O/H_2O

SOLUTION OF POLYSTYRENE IN DEUTERATED CYCLOHEXANE

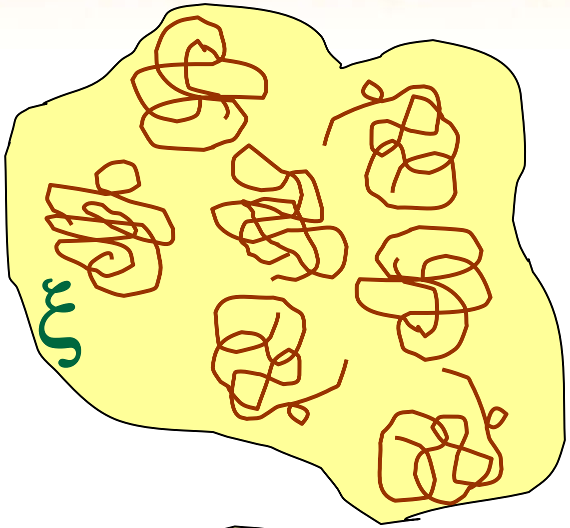
M_W(PS)=115,000, ϕ=8.6% (T=Θ=40 ^{O}C)





ISOTOPE SUBSTITUTION OF ~ 1% POLYMER CHAINS INCREASES THE INTENSITY OF NEUTRON SCATTERING BY AN ORDER OF MAGNITUDE

DIMENSION OF POLYMER COILS NEAR CRITICAL DEMIXING POINT



FULL NEUTRON CONTRAST: H-POLYMER MIXED WITH D-SOLVENT

$$d\sigma/d\Omega_{total}$$

GIVES CORRELATION LENGTH (ξ) OF THE CONCENTRATION FLUCTUATIONS

PARTIAL CONTRAST: MIXTURE OF (H + D) POLYMER WITH D- SOLVENT

$$d\sigma/d\Omega = \boxed{d\sigma/d\Omega_{total}} + d\sigma/d\Omega_{chain}$$

GIVES THE RADIUS OF GYRATION (R_g) AT ZERO AVERAGE CONTRAST CONDITION

NEUTRON CROSS SECTION OF THE THREE_COMPONENT SYSTEM (H+D) POLYMER IN A D-SOLVENT

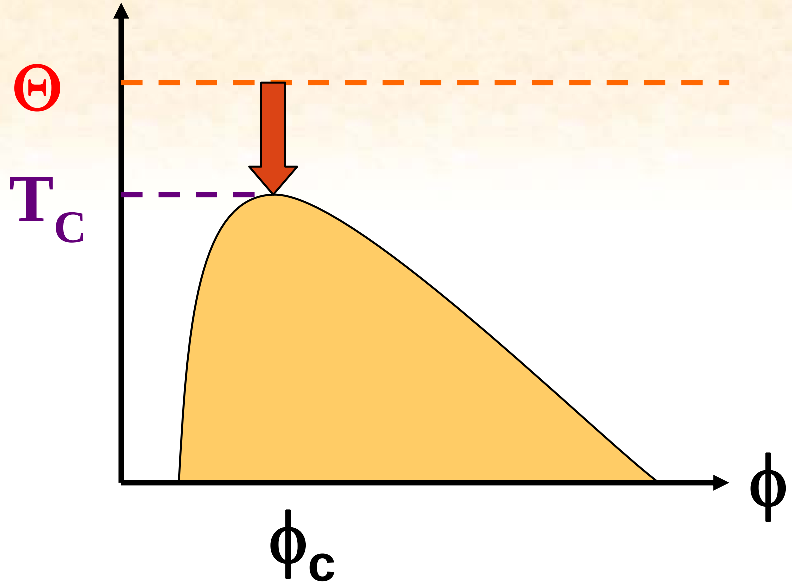
$$d\sigma/d\Omega(Q,x) \cong \{(b_H - b_D)^2 x(1-x) F_D(Q) + [b_H x - (1-x) b_D - b'_S] S_t(Q)\}$$

$F_D(Q)$ GIVES THE DIMENSION OF POLYMER CHAINS (R_g) BY FITTING TO DEBYE FUNCTION:

$$F_D = (2/y^2)(y - 1 + e^{-y}) \quad , \quad y = Q^2 R_g^2$$

$S_t(Q)$ GIVES THE CORRELATION LENGTH (ξ) OF THE CONCENTRATION FLUCTUATIONS BY FITTING TO A STRUCTURE FACTOR, E.G. O-Z FORMULA

$$S(Q)_t = \frac{S(0)}{1 + \xi^2 Q^2}$$



THEORETICAL PREDICTIONS FOR R_g IN SEMIDILUTE POLYMER SOLUTIONS NEAR CRITICAL POINT ($T=T_C$, $\phi=\phi_C$)

UNPERTURBED COILS

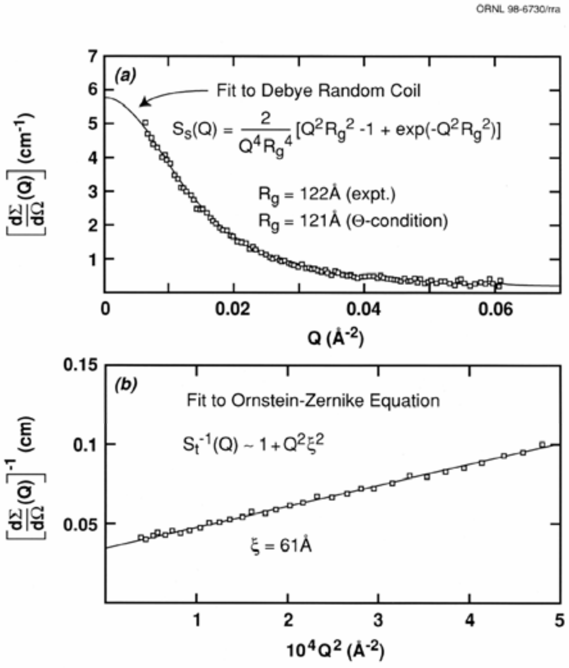
$R_g(T_C)$ ~$M_W^{0.5}$ (Raos, Allegra, 1996)
~$M_W^{0.5}$ (Muthukumar, 1986)

COLLAPSED COILS

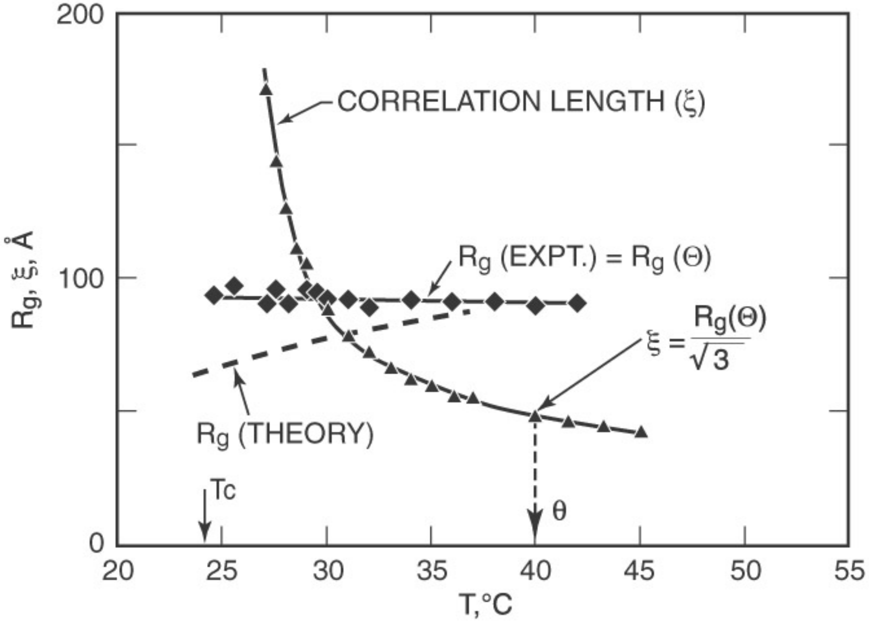
~ $M_W^{0.46}$ (Izumi, Miake 1984)
~$M_W^{0.47}$ (Lhiuillier, 1992)
~$M_W^{0.46}$ (Cherail, 1994)

SEMIDILUTE SOLUTIONS OF POLYSTYRENE IN CYCLOHEXANE

PRL, 78, 686 (1997)



DEBYE AND ORNSTEIN-ZERNIKE FITS FOR 7 VOL% POLYSTYRENE IN CYCLOHEXANE (T ≃ 40°C) WITH LABELING CHOSEN TO ISOLATE *(a)* POLYMER R_g AND *(b)* CORRELATION LENGTH (ξ)



DIVERGING CONCENTRATION FLUCTUATIONS NEAR THE PHASE BOUNDARY PREVENT THE PREDICTED (DEGENNES) CHAIN COLLAPSE
THE CONDITION $\xi = R_g(\Theta)/\sqrt{3}$ DEFINES THE Θ-TEMPERATURE

$\sim M_w^{0.5}$	**Raos, Allegra, 1996**	**Unperturbed Coils (no collapse)**
$\sim M_w^{0.5}$	**Muthukumar, 1986**	

POLYMER BLENDS: RANDOM PHASE APPROXIMATION (de Gennes, 1974)

$$\frac{1}{S_t} = \frac{1}{\phi_A N_A \upsilon_A F_D(Q^2 R_{g,A}^2)} + \frac{1}{\phi_B N_B \upsilon_B F_D(Q^2 R_{g,B}^2)} - 2\chi$$

STRUCTURE

TOTAL SCATTERING (OZ FUNCTION)

$$S_t(Q,T) = S(0,T)/(1+Q^2\xi^2)$$

SINGLE CHAIN SCATTERING (DEBYE FUNCTION)

$$F_{D,i} = (2/y^2)(y-1+e^{-y}) \quad , \quad y = Q^2 R_{g,i}^2$$

THERMODYNAMICS

INTERACTION PARAMETER χ

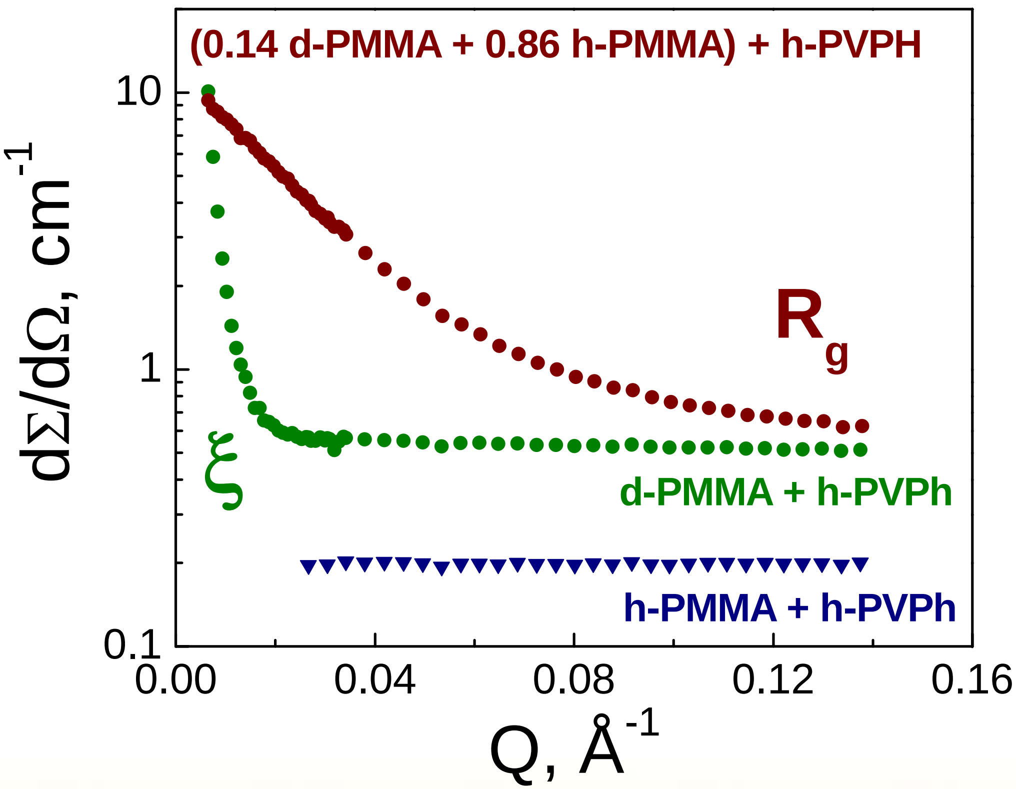
RPA IS BASED ON THE ASSUMPTION THAT THE DIMENTIONS OF POLYMER CHAINS REMAIN UNPERTURBED AFTER MIXING $R_{g,A}(\Theta)$, $R_{g,B}(\Theta)$ SAME AS IN POLYMER SOLUTION AT Θ TEMPERATURE)

WHO	HOW	WHAT	RESULT
RUSSELL 1987	SANS	PEO-PMMA CONCENTRATED	UNPERTURBED COILS
Wignall 1987	SANS	PEO-PMMA DILUTE	~20% SWELLING
Briber 1994, 1997	SANS	PS-PVME DILUTE	~10% SWELLING
Peterson 1990	FLUORESC. SPECTR.	PVNcoMMA-PVAc DILUTE	~15% COLLAPSE
Theobald 1997	LIGHT SCATTER.	PDMS-PEMS CONCENTRATED	~100% COLLAPSE

ZERO AVERAGE CONTRAST (Williams et al., Ackcasu, 1980)

COMPONENT 1: **MIXTURE OF (d+h) POLYMERS**
COMPONENT 2: **h-POLYMER**

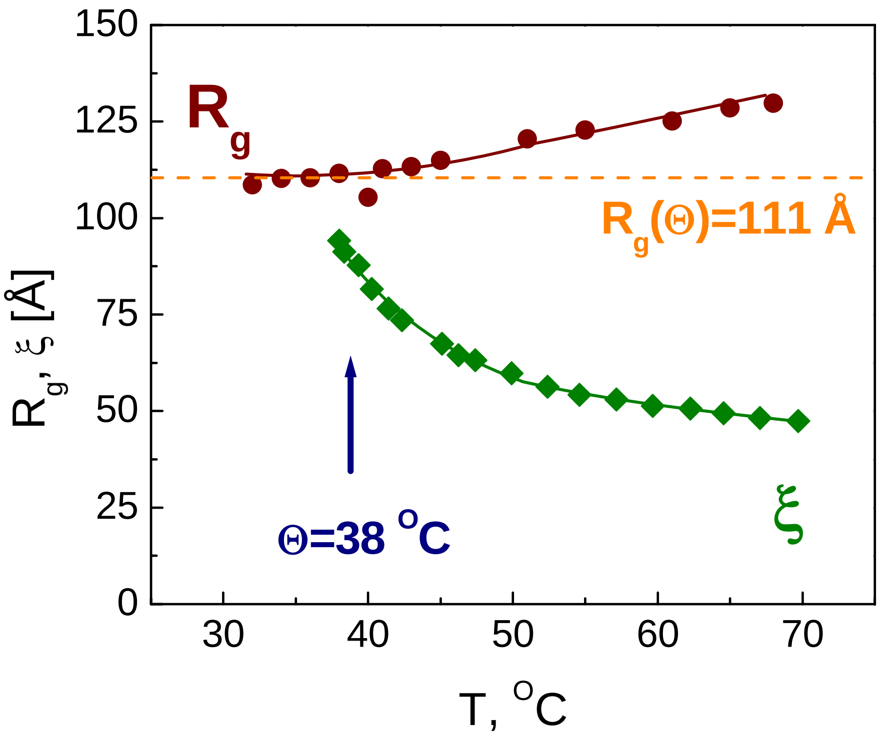
$$I(Q)=(b_h-b_d)^2x(1-x)F_D(Q)\ +\ [xb_d+(1-x)b_h-b_s]^2S_t(Q)$$

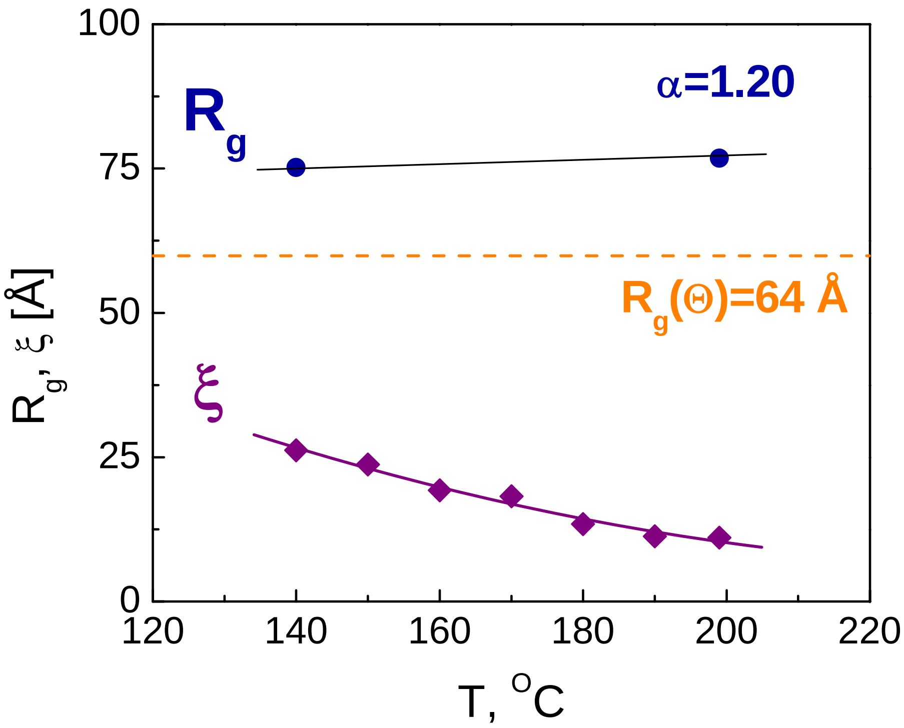


FOR BLEND PMMA - PVPh THE PREFACTOR IS ZERO AT x=0.14 AND $d\Sigma/d\Omega$ GIVES $F_D(Q)$

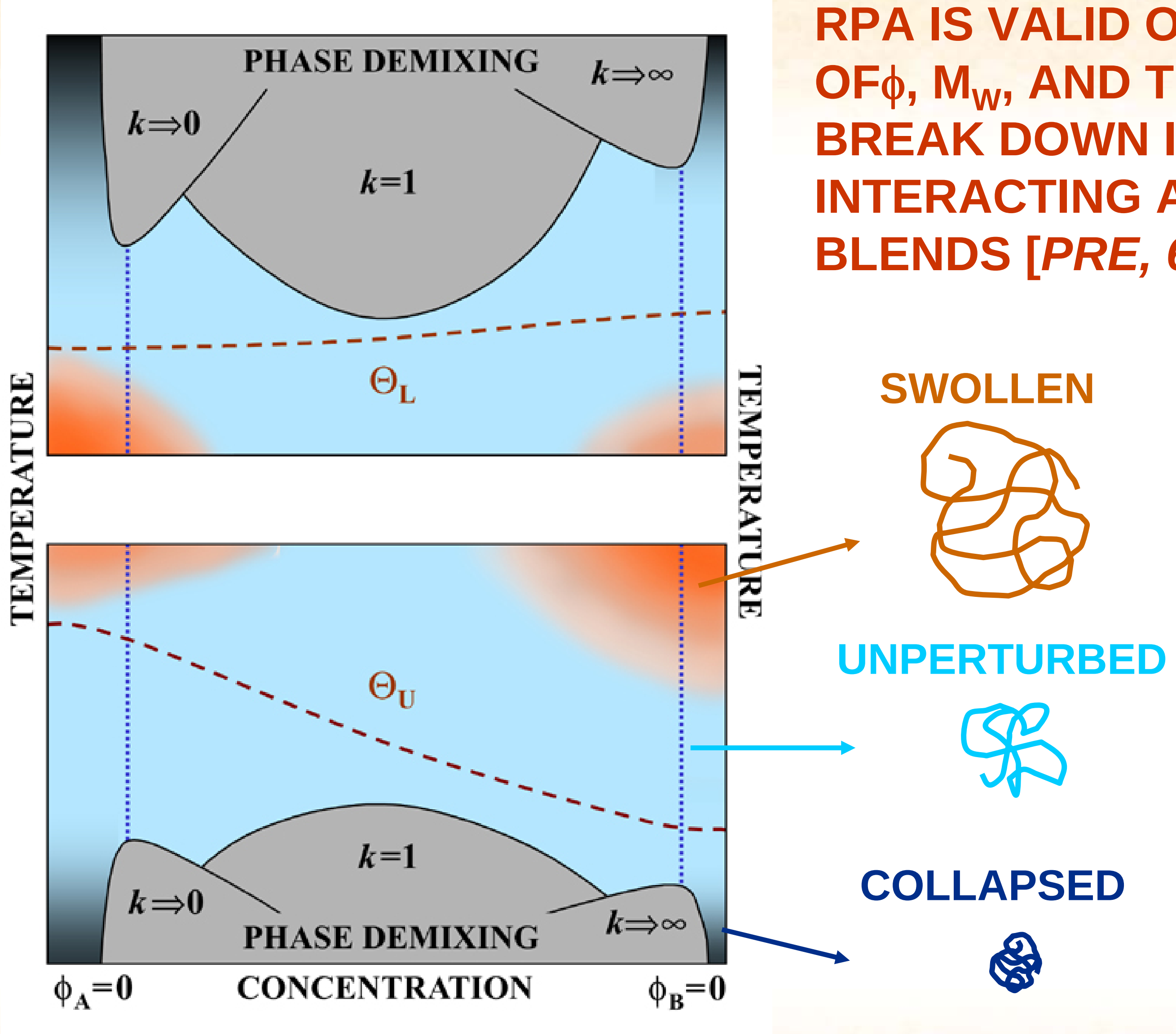
PS (M_W=172000) IN A GOOD SOLVENT CYCLOHEXANE *(Cotton et al., 1976)*

PMMA (M_W=60000) IN A GOOD POLYMERIC SOLVENT PVPh (M_W=8000) *PRE, 65, 061802, 2002)*





RPA IS VALID OVER A WIDE RANGE OFϕ, M_W, AND T, HOWEVWR IT MAY BREAK DOWN IN STRONGLY INTERACTING AND ASYMMETRIC BLENDS [*PRE, 65, 061802, 2002)*]

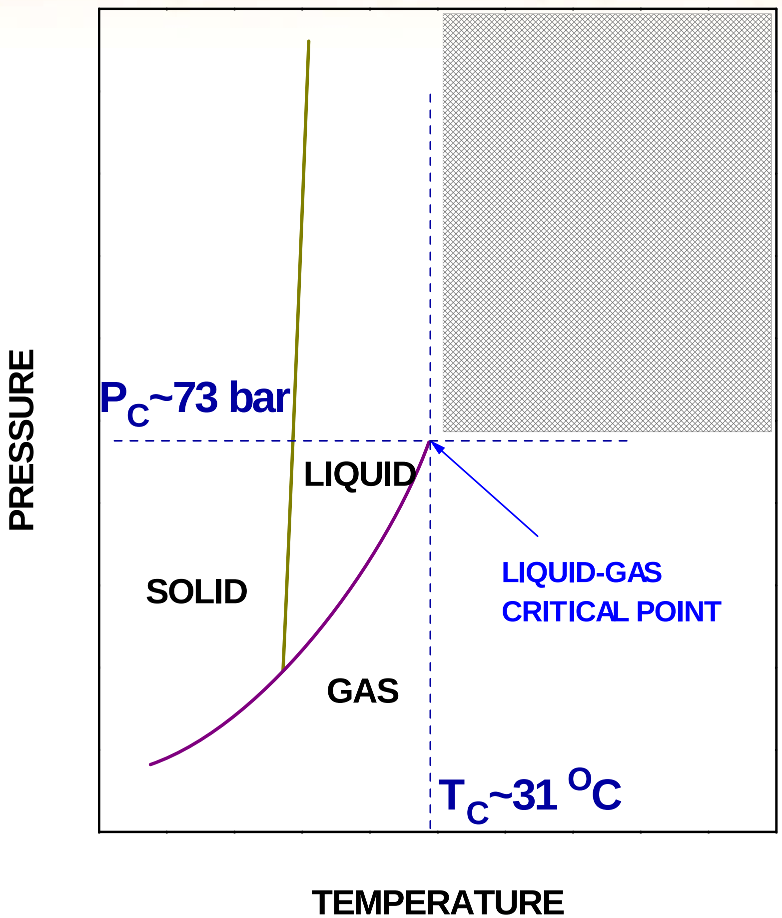


POLYMERS IN SUPERCRITICAL FLUIDS

SUPERCRITICAL CO_2: ENVIRONMENTALLY RESPONSIBLE REPLACEMENT FOR TOXIC ORGANIC SOLVENTS

ONLY AMORPHOUS FLUOROPOLYMERS AND SILICONS EXHIBIT SIGNIFICANT SOLUBILITY IN SC CO_2

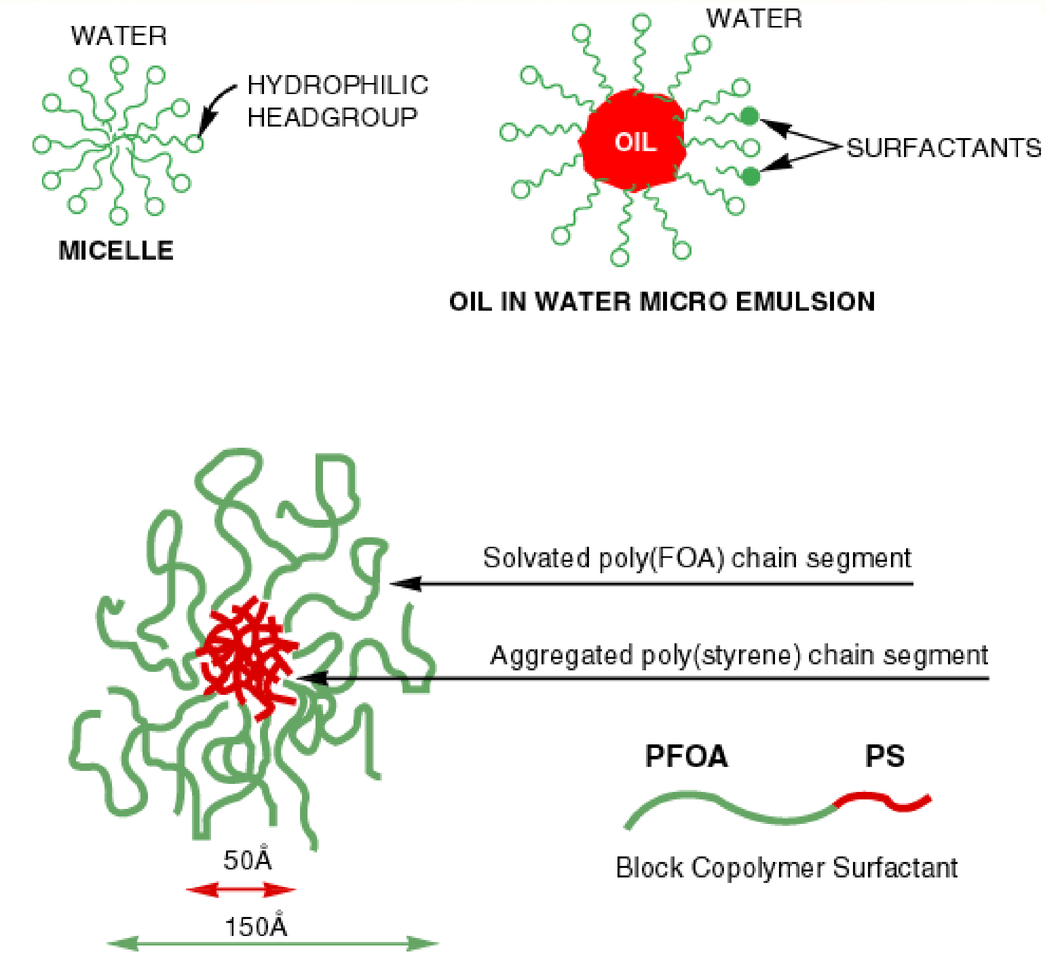
HOW TO MAKE INSOLUBLE SUBSTANCES SOLUBLE IN SUPERCRITICAL CO_2



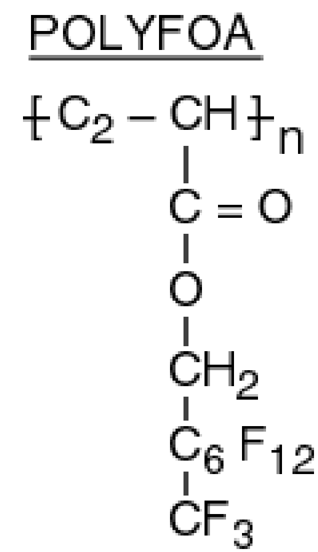
GENERIC PHASE DIAGRAM OF CARBON DIOXIDE

ORNL-DWG 96M-4052

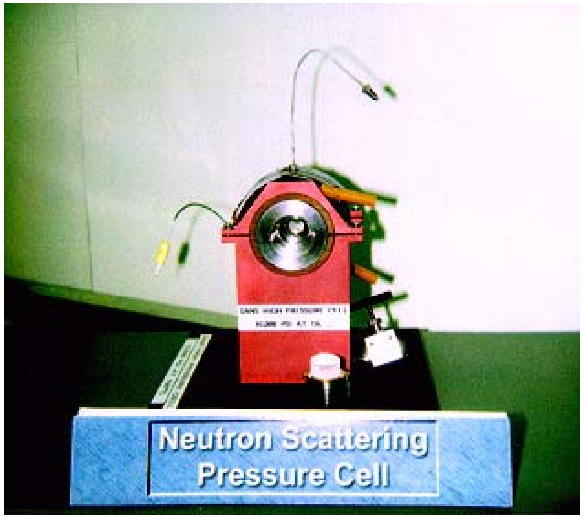
Schematic Representation of Colloidal Aggregates in Water and Supercritical Carbon Dioxide



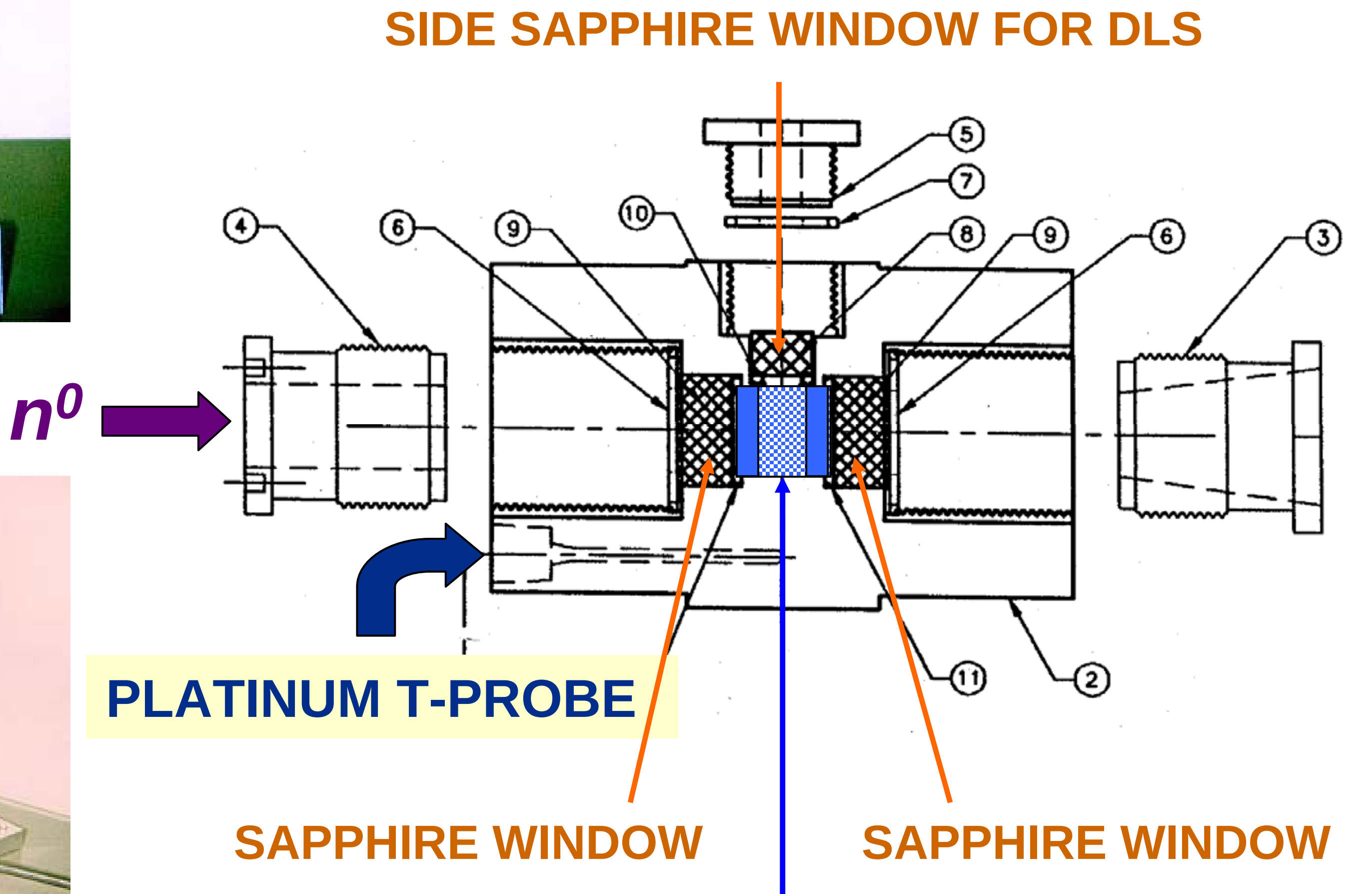
MODEL OF POLY(FOA-b-STYRENE) MICELLE IN SUPERCRITICAL CO_2

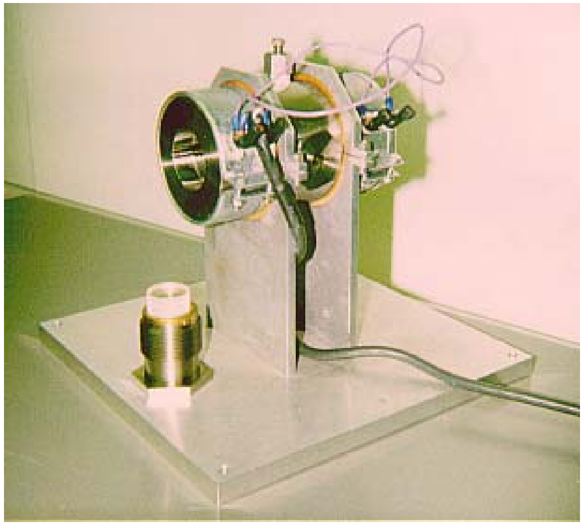


ORNL HIGH PRESSURE CELLS



P_{max}=500 bar
T_{max}=80 ^{O}C

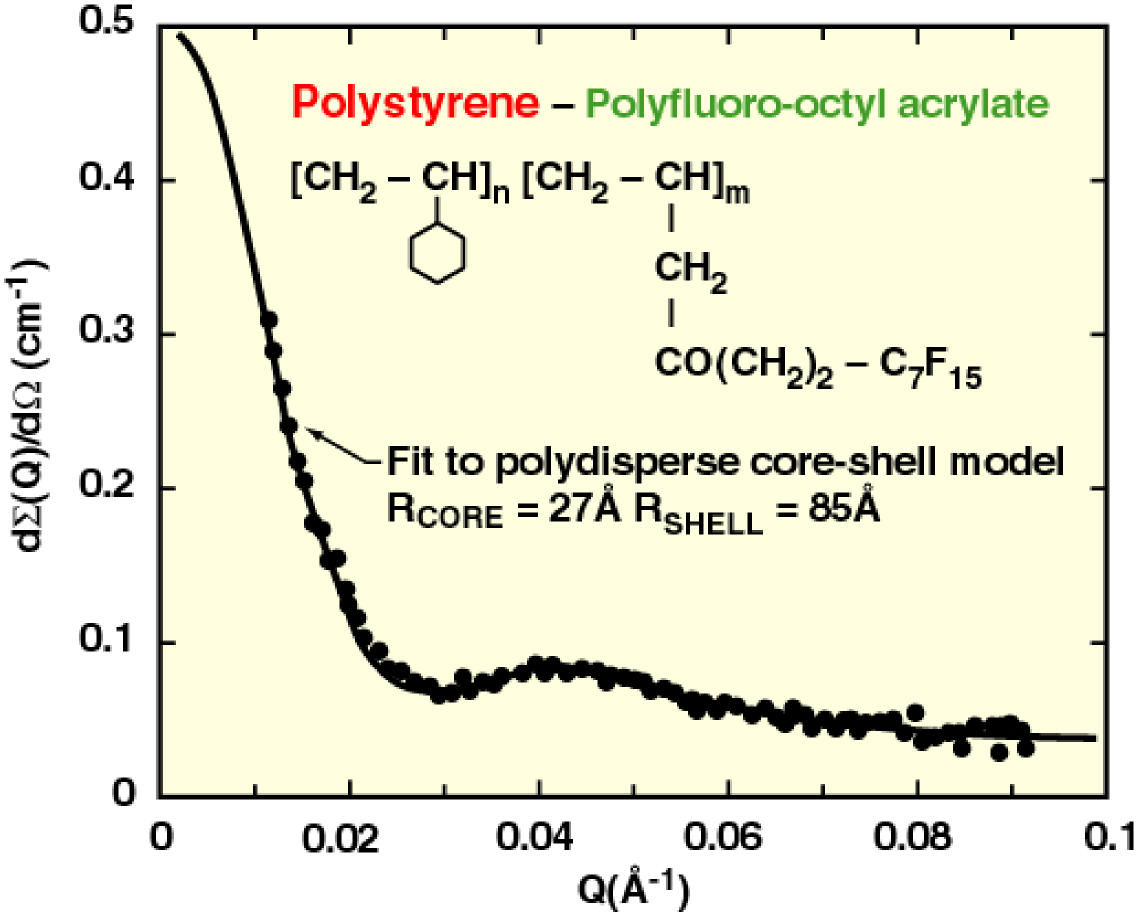




P_{max}=750 bar
T_{max}=250 ^{O}C

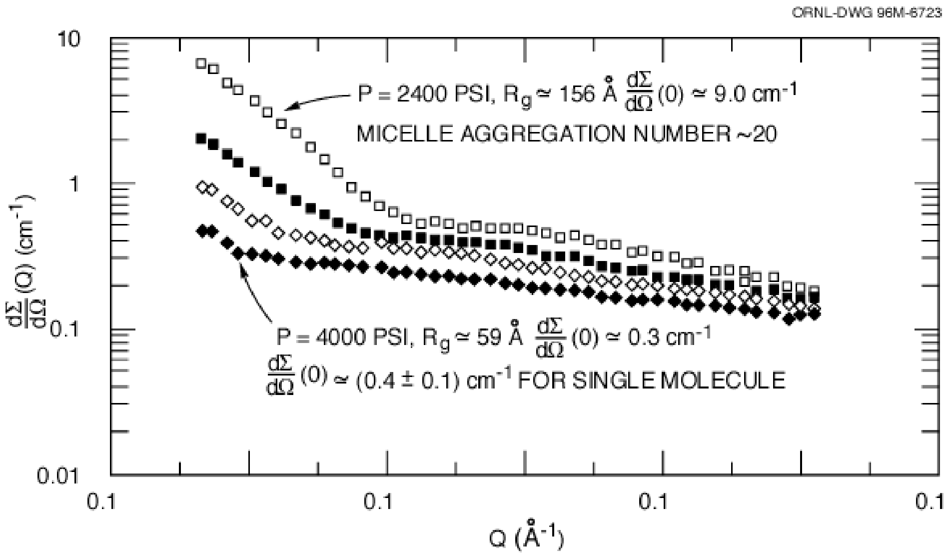
22 mm MAX FLIGHT PASS WITH VARIABLE LENGTH
(ADDITIONAL SAPPHIRE INSERTS, 2 mm STEP)

SANS Characterization of Block Copolymer Micelle in Supercritical CO_2

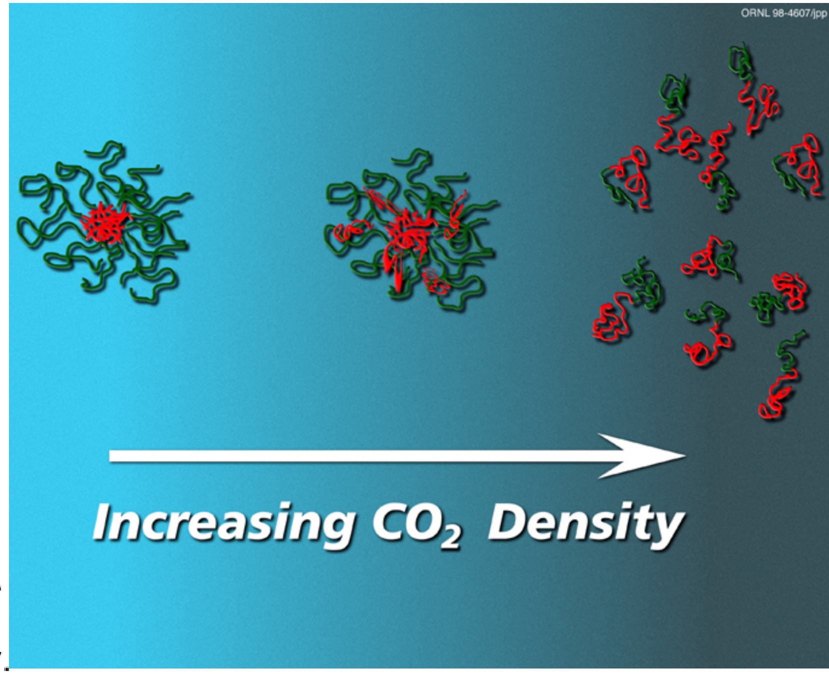


McClain et al., Science, 274, 2049 (1996)

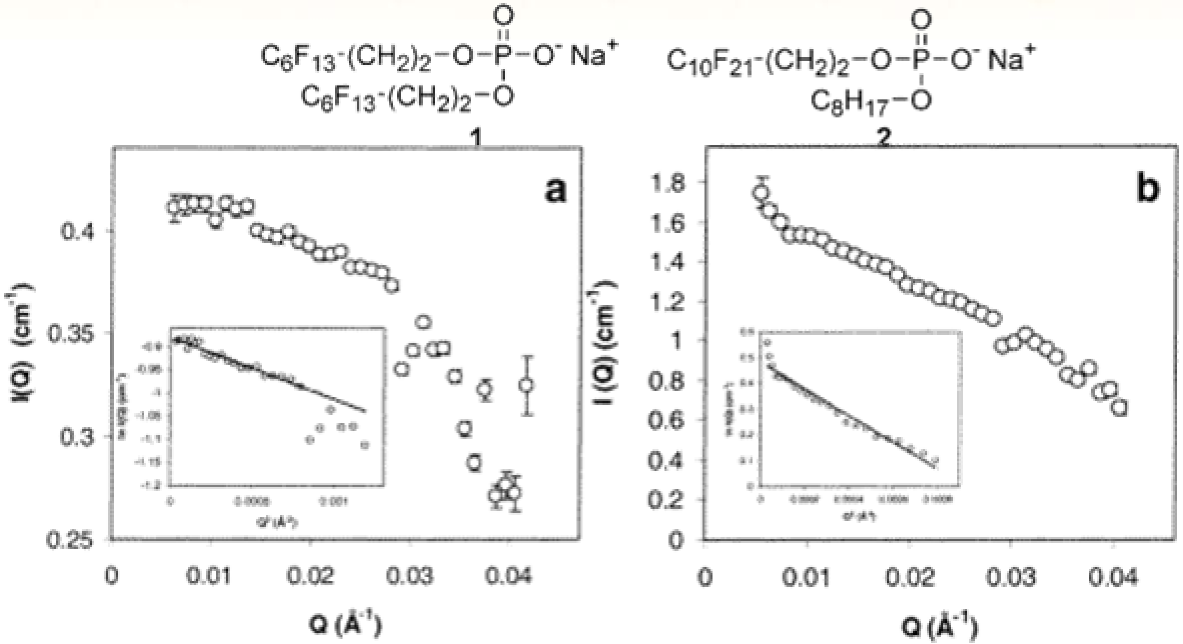
SANS PROVIDES THE FIRST EVIDENCE OF THE CRIRICAL MICELLIZATION PRESSURE IN SUPERCRITICAL CO2 [F. Triolo et al., Langmuir, 16(2), 416 (2000)]



$\frac{d\Sigma}{d\Omega}$(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.

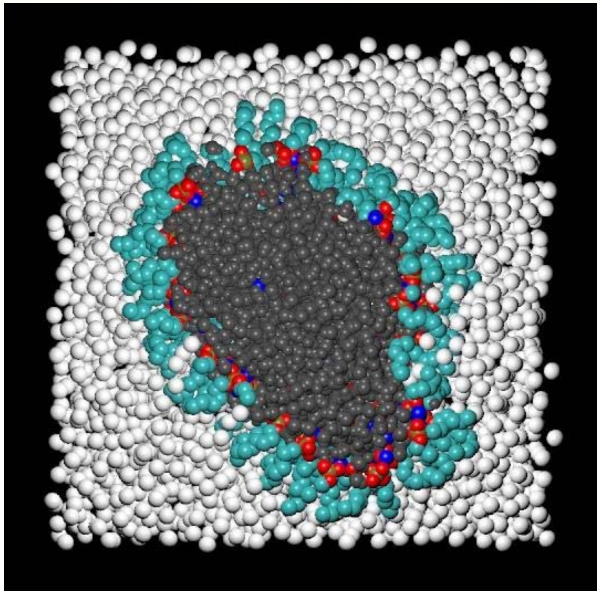


“UNIVERSAL SOLVENT”: DISPERSION OF WATER IN CO_2 [JACS 124, 1834, 2002]



SANS PROFILE OF (a) SURFACTANT 1: (2.7 % wt.% surfactant, W_O=12, P=379 3 BAR, 24 ^{O}C, AND (b) SURFACTANT 2 (6.3 wt.% SURFACTANT, W_O=12, P=317 BAR, 60 ^{O}C).

GUINIER PLOTS (INSETS) GIVE R_G ~ 27 and 35 Å, RESPECTIVELY



MD SIMULATION: 4 NS SNAPSHOT OF THE MICELLE CROSSECTION.

WHITE	CO_2
GREEN	SURFACTANT TAILS
RED	PHOSPHATE OXIGEN
BLUE	Na^+
BLACK	WATER

CONCLUSIONS

KEY ADVANTAGES OF SANS:

- NON-DISTRACTIVE RADIATION
- HIGH PENETRATION POWER
- CONTRAST VARIATION AND ZAC

References

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