Neutron and X-ray reflectivity studies of the gas/solid/liquid interface

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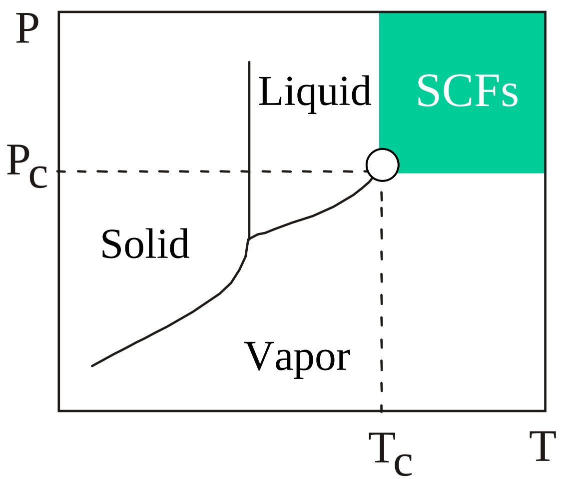
What is SCFs ?



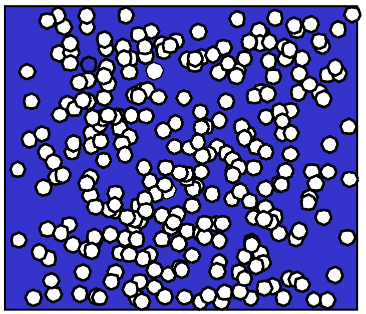
Tc: critical temperature
Pc: critical pressure

Substance	T_c(°C)	P_c(MPa)
CO_2	31.3	7.38
H_20	374.1	22.03
NH_3	132.5	11.39

How do SCFs look like in microscopic scale?

Inhomogeneous media with high and low-density region

<Schematic view of molecular distribution>



Key word "density fluctuations in space and time"

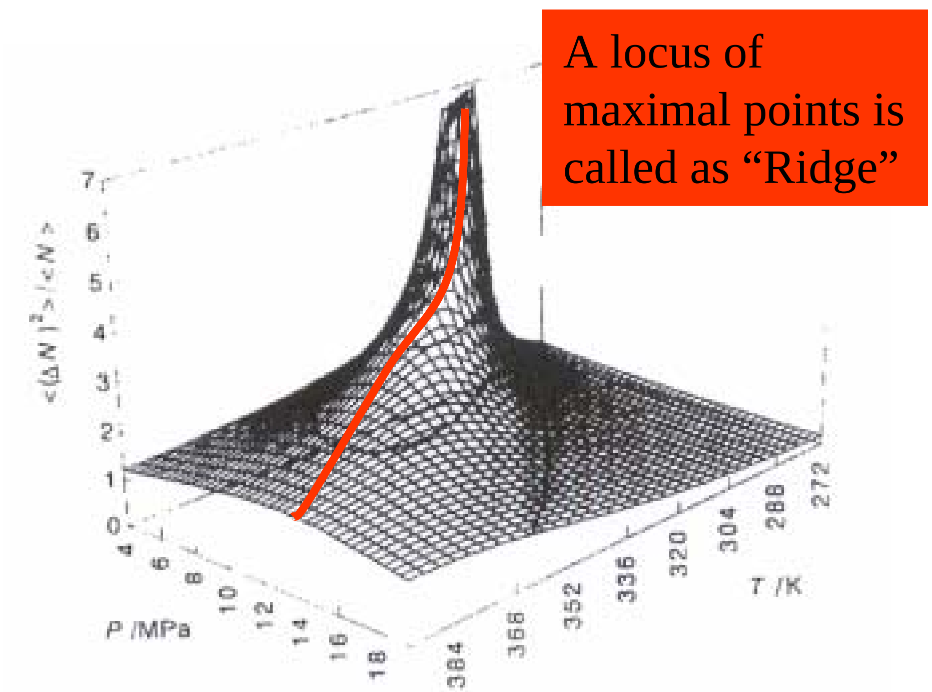
Unique features of both gas and liquid: Gas-like diffusivity and viscosity with liquid-like density

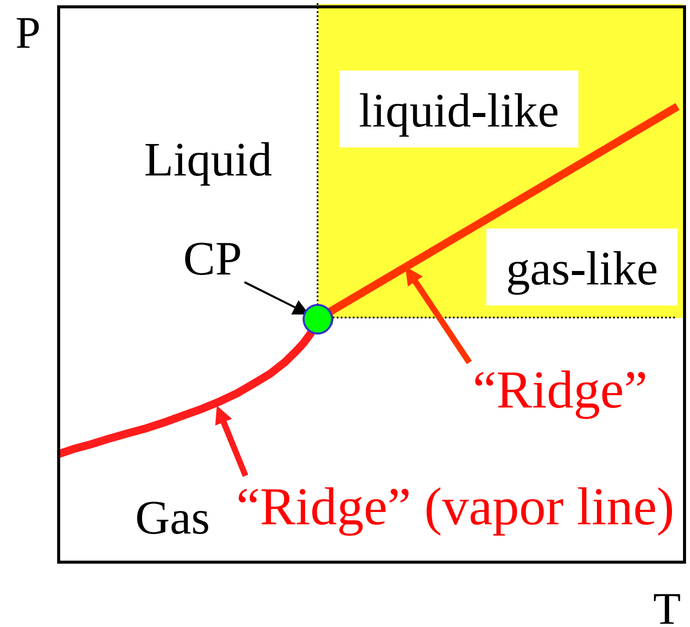
Density Fluctuations

$$<(\Delta N)^2>/<N> = (N/V)\kappa_T k_B T$$

κ_T: Isothermal compressibility k_B: Boltzman constant

N: Number of molecules in the corresponding volume V





Various physical properties of SCFs, such as sound velocity, thermal conductivity, partial molar volume, show maximum or minimum on the ridge.

Density fluctuations of CF_3H vs. T and P, derived from empirical state equation (Nishikawa et al., 1998)

Advantages of Supercritical Fluids

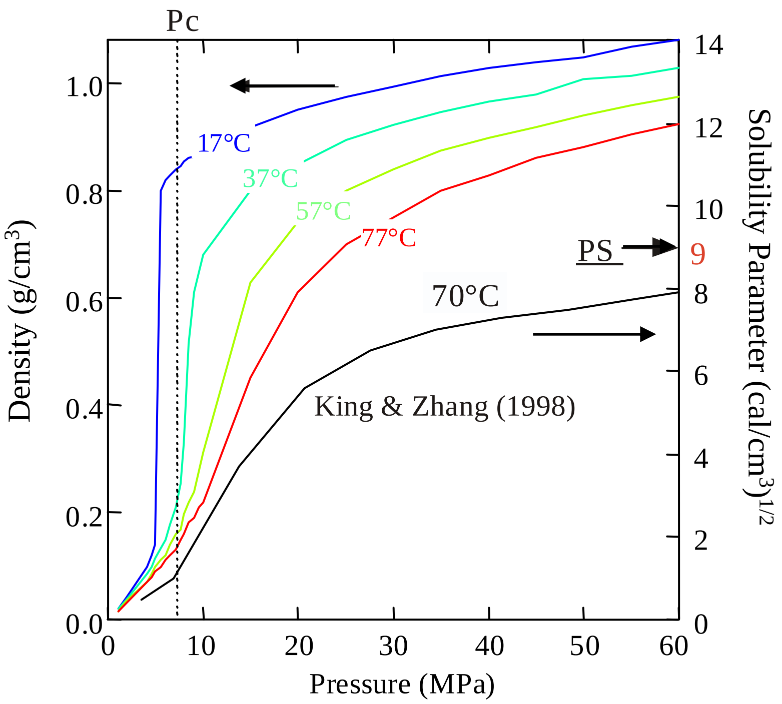
1. Tunability of solvent quality: Classical density dependent properties enhanced

- Low solvent dielectric constant
- Large diffusion coefficient
- Solute solvation

2. Enhancement of diffusion controlled rates (low viscosities)

3. Favorable heat transfer properties

4. Enhanced separations



No enhancement for polymers which are immiscible- unfavorable χ

Why Supercritical Fluids (especially $scCO_2$) important ?

1. Environmental reasons

- > 30 billion pounds of organic and halogenated solvents/year
- Much more water used and contaminated in related processes

→ liquid & $scCO_2$ are developed to reduce the above

2. New Chemistry (synthesis) and Physics (processing & phenomena)

- Cost reduction
- New products
- Fundamental science versus application

→ "Green" alone is ***insufficient***

3. Very few polymers are miscible in CO_2- so procedure is of limited use.

Density-Fluctuation-Induced Swelling

Density Fluctuations

$$<(\Delta N)^2>/<N>=(N/V)\kappa_T k_B T$$

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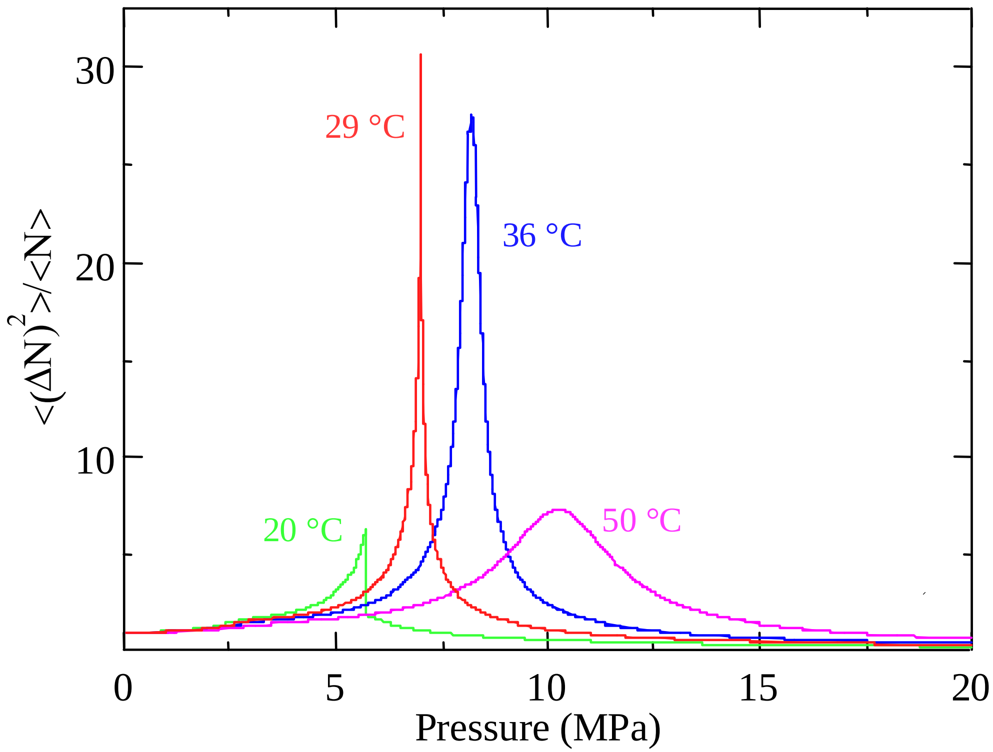
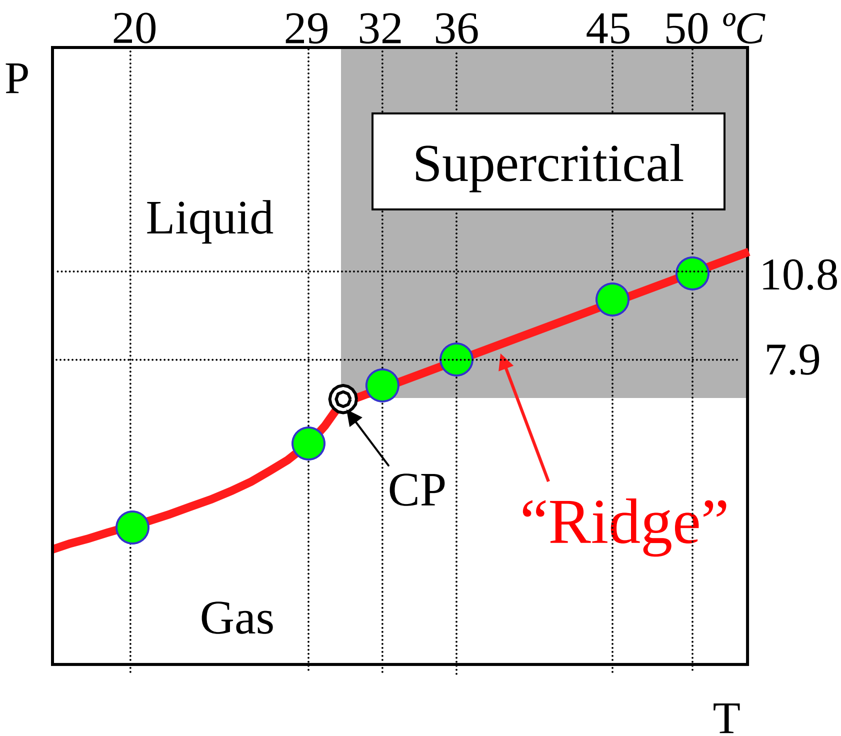
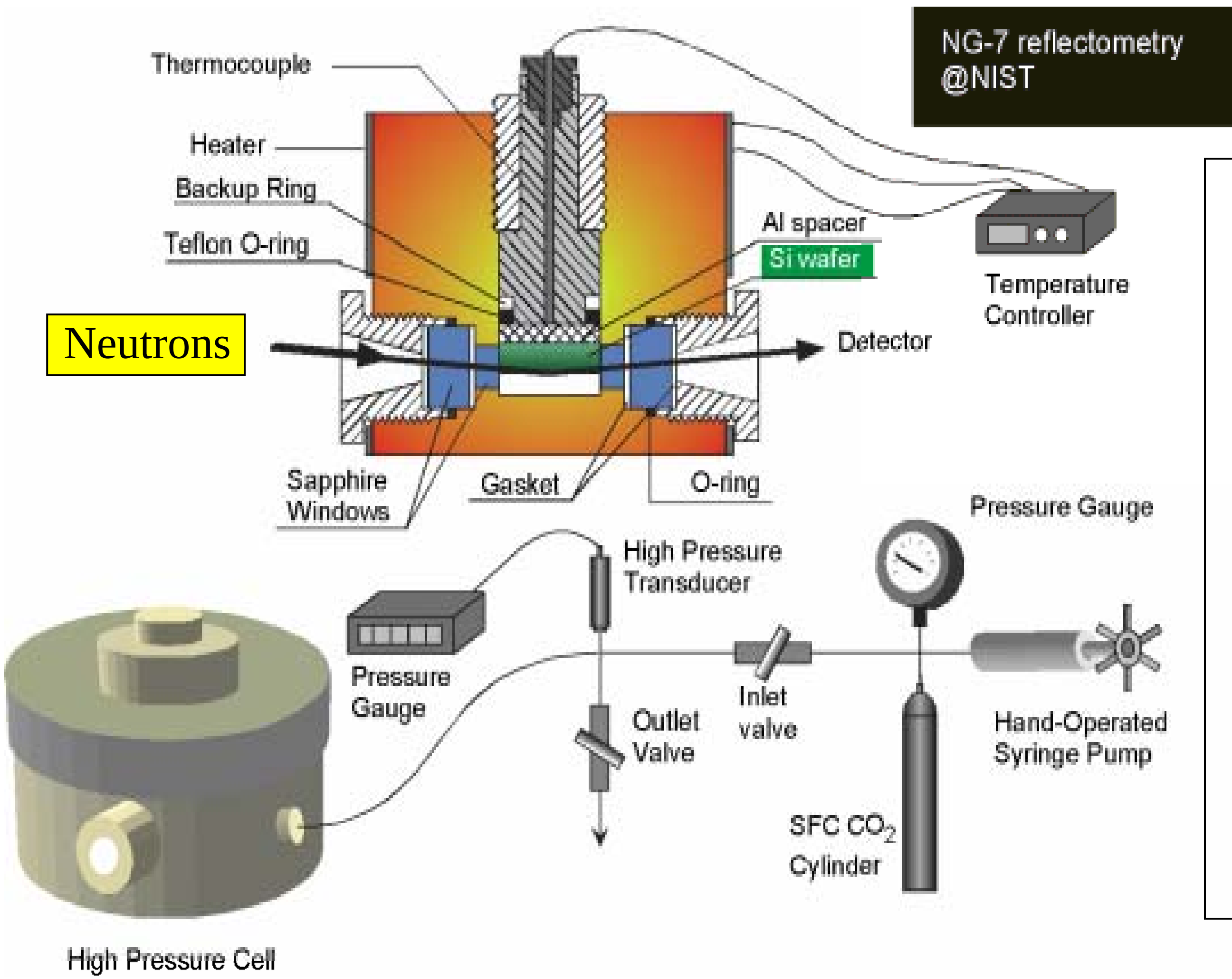


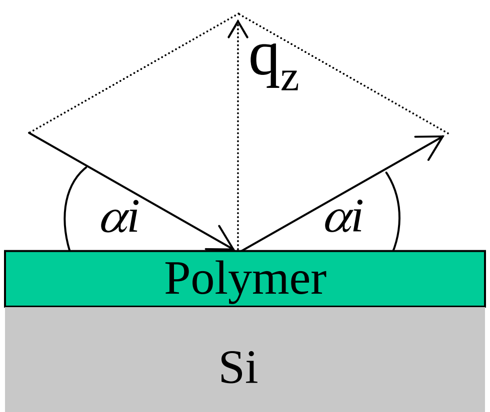


- Polymer matrix damps fluctuation amplitude and drives the supercritical liquid into the polymer.
- The distance is determined by the correlation length of the fluctuations.
- **Focus on thin films**

High Pressure Neutron Reflectivity



<Reflectivity geometry>



(1) Thickness
(2) Roughness
(3) Density
can be obtained

Experimental

(i) Samples

- Deuterated styrene-budadiene copolymer (d-SBR) (Mw = 84K, Mw/Mn=1.08, ϕ_{PS}=0.47).
- 450 Å thickness were spun cast onto clean Si water and then dried under vacuum at 150 ºC for 5 hours).

(ii) NR measurements

- NG-7 reflectometry at NIST
- Wavelength of neutrons: 4.7 Å
- Six different isothermal conditions at T=20, 29, 32, 36, 45, 50 ºC (T<Tc, T~Tc, T>Tc) and two isobaric conditions at P=7.9 MPa and 10.8 MPa (P~Pc, and P>Pc) were investigated.
- Temperature and pressure stability : ± 0.1ºC and ± 0.2%.

Samples

Deuterated polybutadiene (dPB, M_w=96K, Mw/Mn=1.1, Polymer Source) with COOH end-group.

dPB brushes were prepared by spin-coating on cleaned Si wafer.

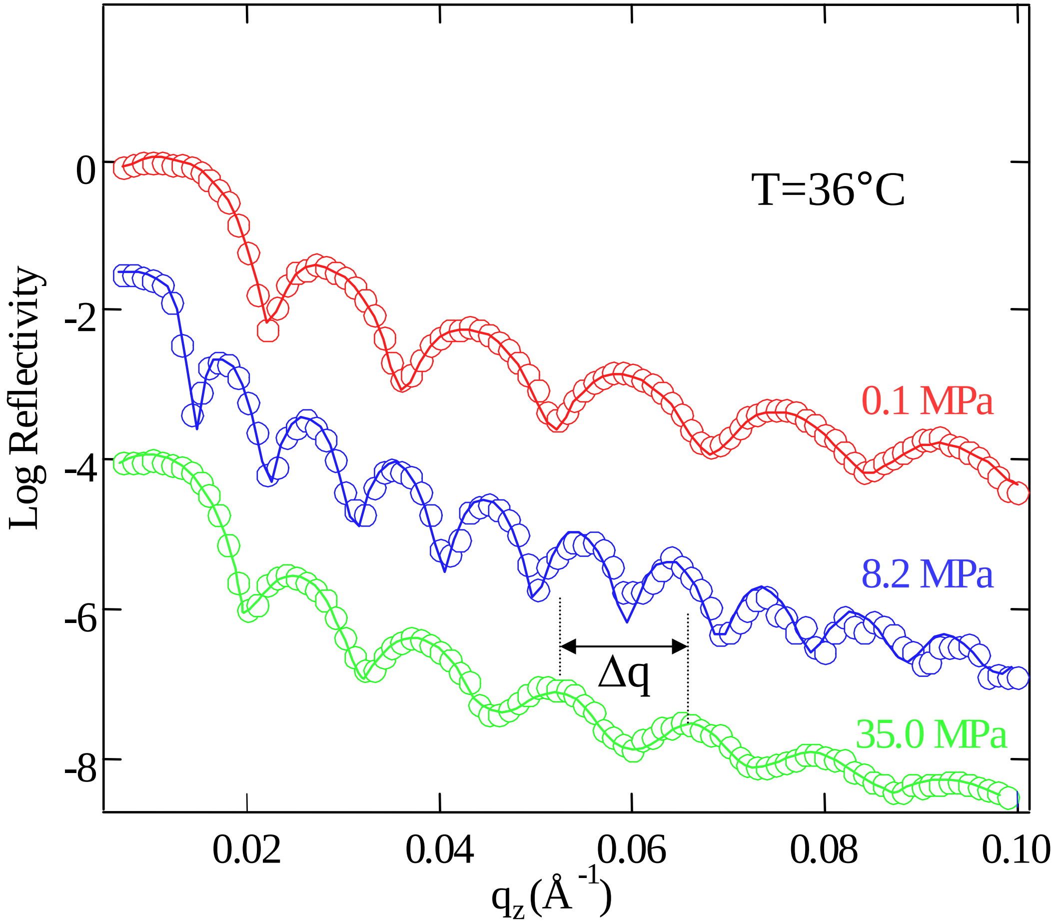
Unreacted polymers for the brushes were washed off the surface when exposed to toluene for 48 hours.

Film thickness (L_0) (Å)	L_0/Rg	Grafting density(σ) (chains/Å^2)
175	1.8	0.0011
207	2.2	0.0013
243	2.6	0.0015
282	3.0	0.0018

Neutron Reflectivity Measurements

Isothermal swelling behavior of dPB brushes in supercritical ethane (scC_2H_6) (T=37.2 ^{o}C) was monitored by in situ NR.

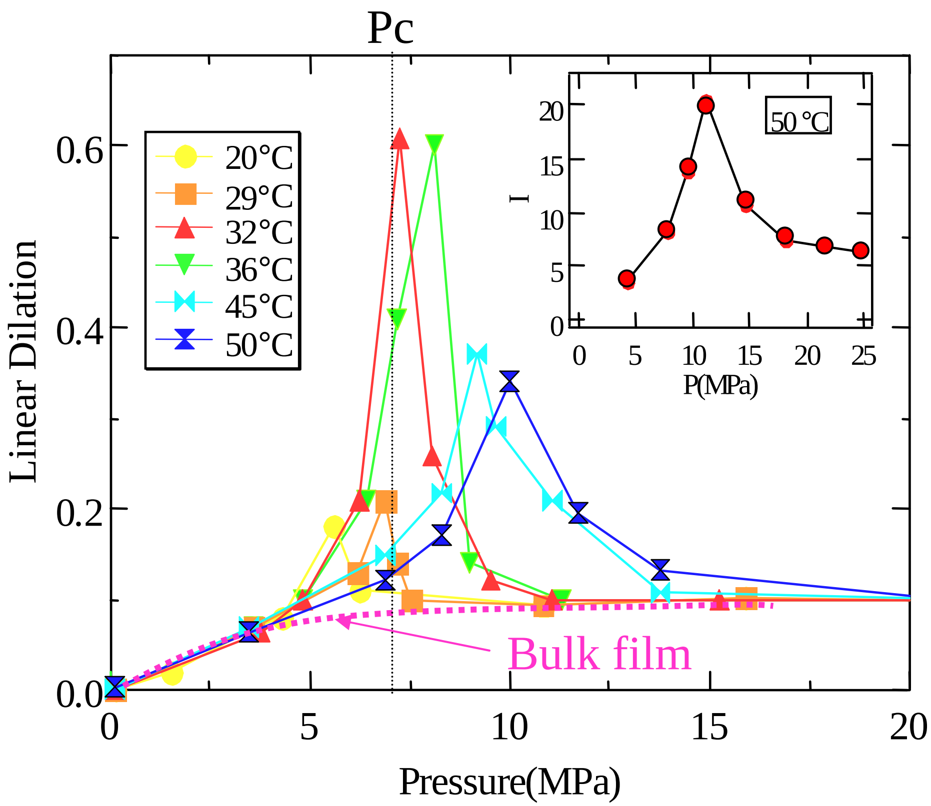
Neutron Reflectivity Profiles



Deuterated styrene-butadiene random copolymer (d-SBR) (M_w=84K, ϕ_{PS}=0.47).

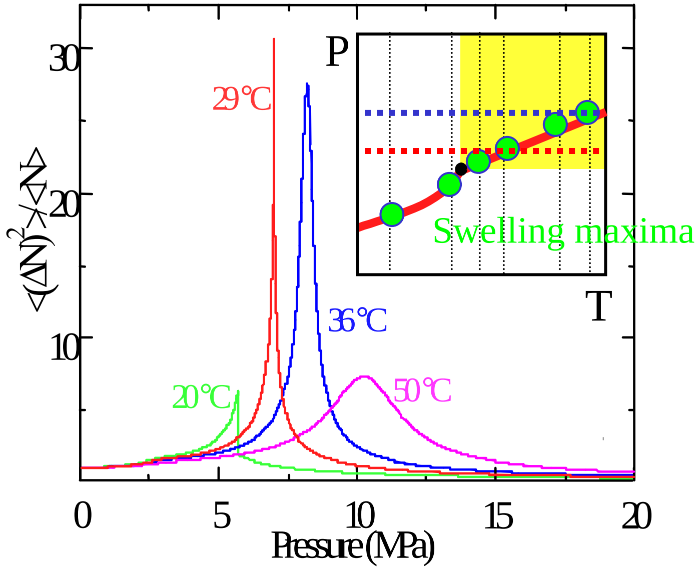
Film thickness: $D=2\pi/\Delta q$

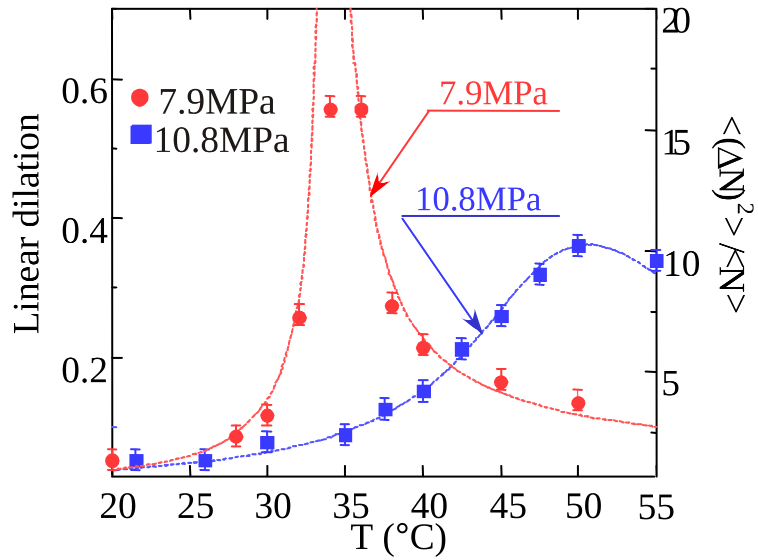
Density-Fluctuation-Induced Swelling



deuterated styrene-butadiene copolymer
(d-SBR, Mw=84k, 450 Å thickness)

Linear dilation=(L-L0)/L0
*L0:*Unswollen film thickness
L: Swollen film thickness





Density-Fluctuation-Induced Swelling

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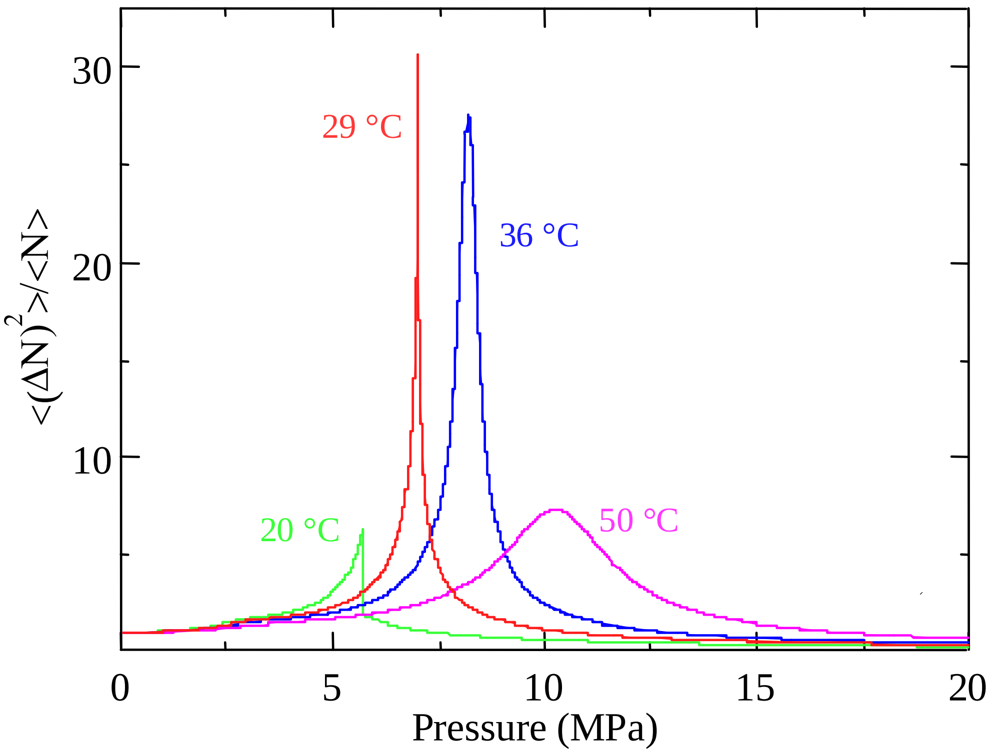
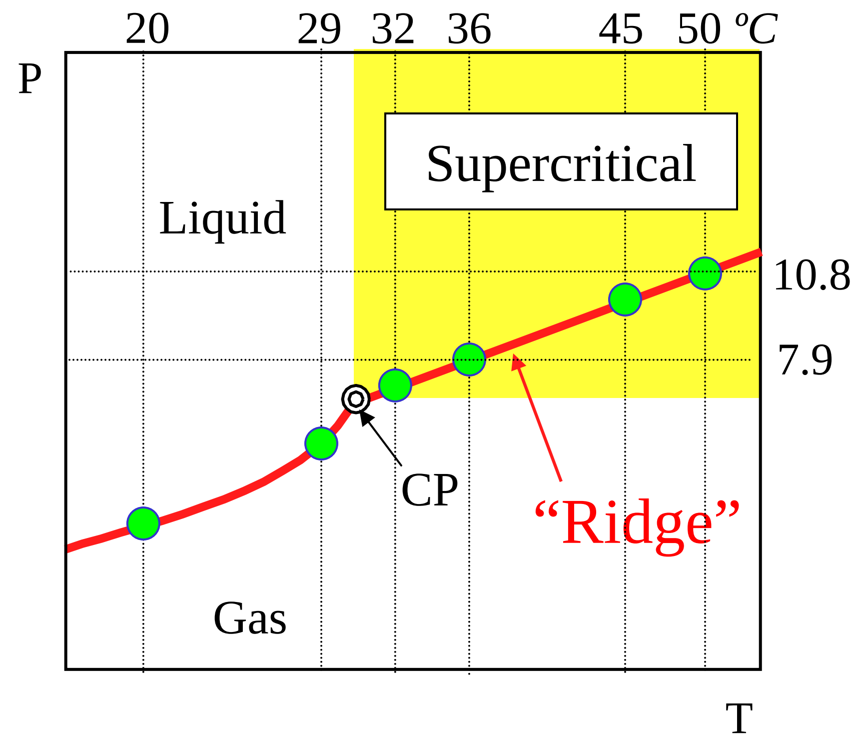
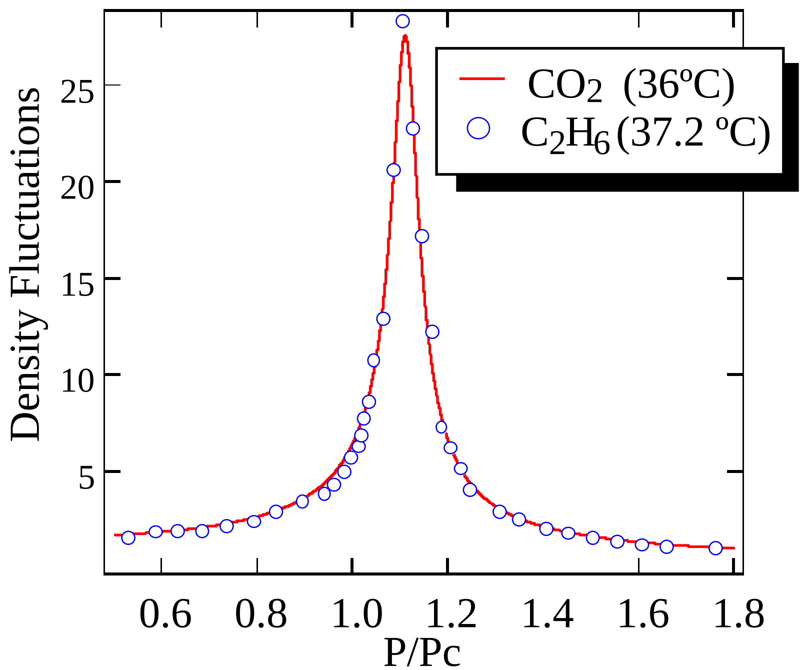
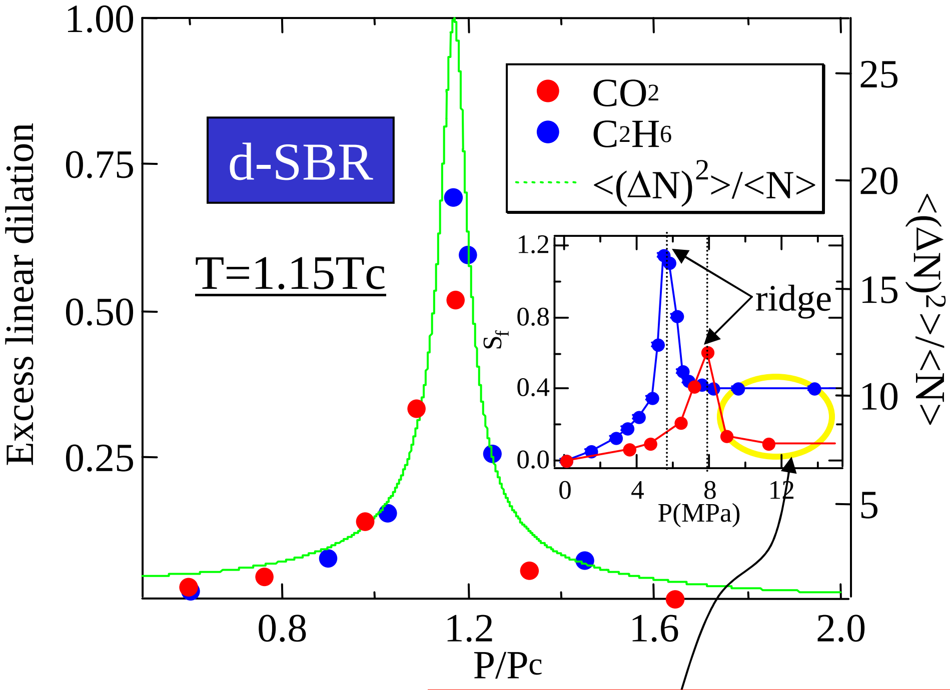




Anomalous swelling of polymer thin films in CO_2 is associated to the density fluctuation ridge. Density fluctuations can significantly enhance the solvent quality in thin films even when the bulk miscibility with CO_2 is very poor.

Universal Behavior in SCFs





Bulk miscibility is different

The magnitude of the density fluctuations in CO_2 and C_2H_6 could be scaled by Tc and Pc.

The excess dilation depends only on the magnitude of the density fluctuation in SCFs.

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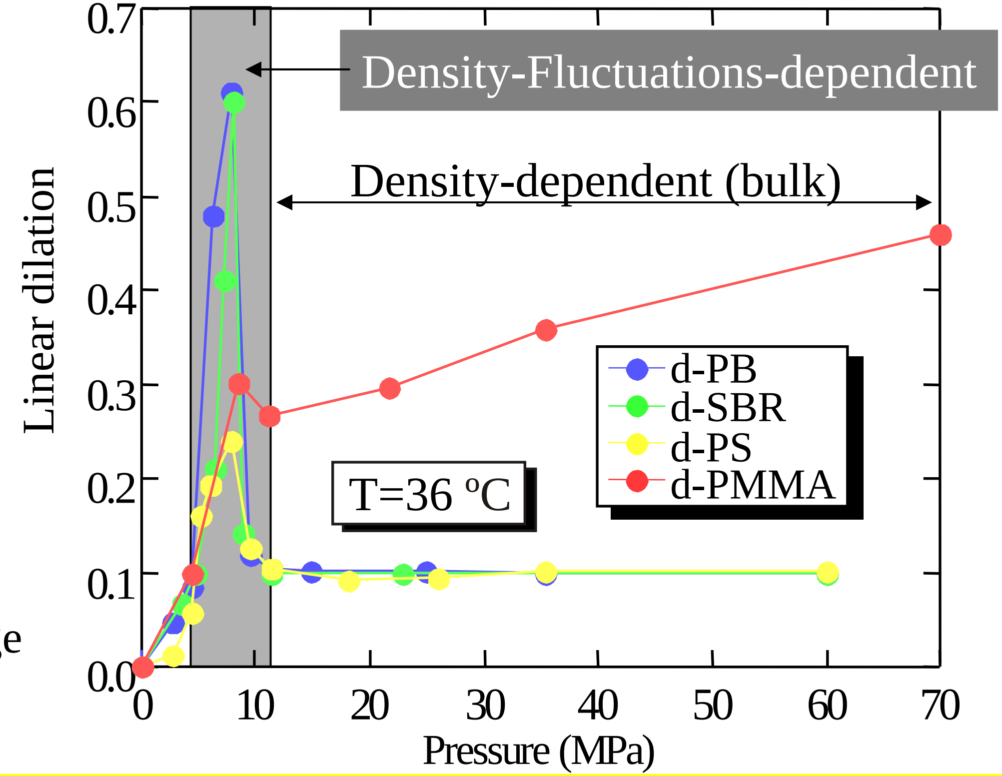
Effect of Elasticity on Anomalous Swelling

Sample Characteristics

Polymers	Mw	$\phi_{1,4}$ (%)	L0(Å)
d-PB	264k	80	615
d-SBR	84k	80	370
d-PS	155k		445
d-PMMA	137k		450

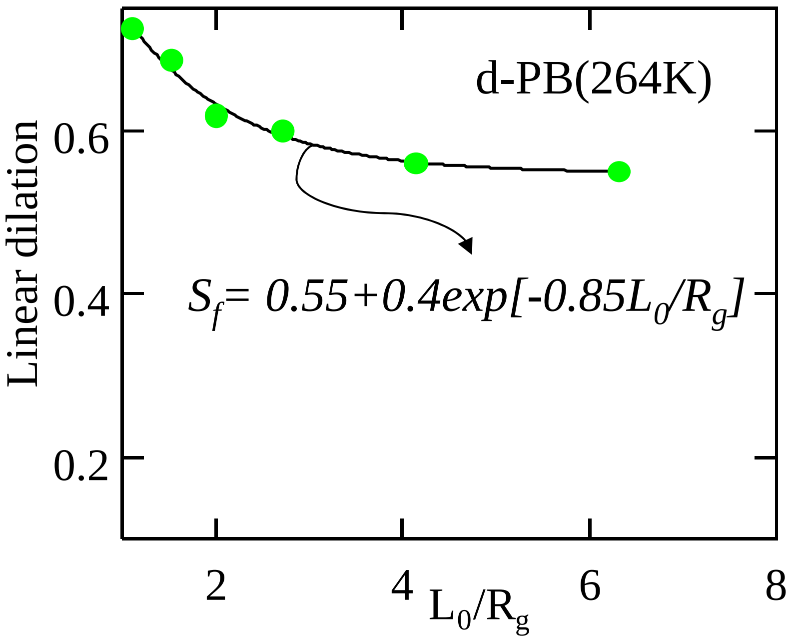
$\phi_{1,4}$ (%):Volume fraction of 1,4-linkage



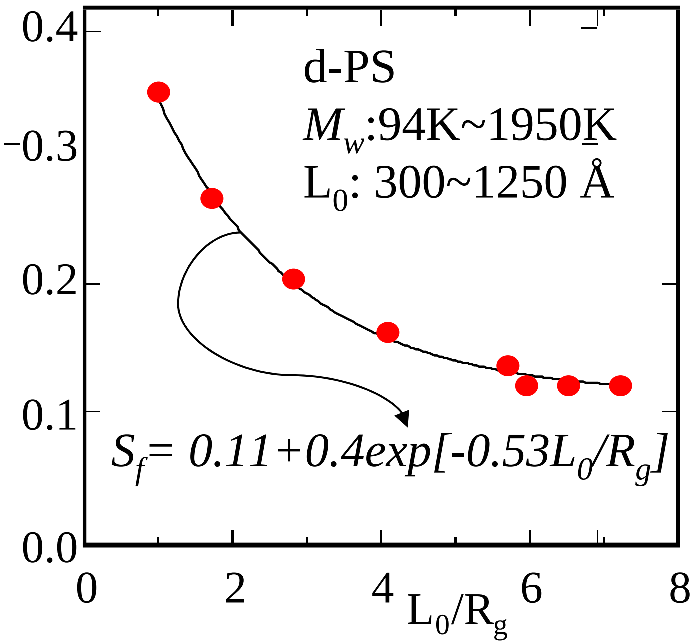
- The Magnitude of the Dilation is mostly a function of elasticity, rather than bulk miscibility.
- Dilation in rubbery polymers (~0.6) is much larger than in glassy polymers (~0.3) despite the bulk miscibility (PMMA is the best).

Penetration Depth of Anomalous Swelling

<Rubbery Polymer>



<Glassy Polymer>



•Swelling data collapse onto one exponential curve when they are scaled by R_g.

•The characteristic constant in exponential function for d-PB is larger than that for d-PS.

•S_f values of d-PB are larger than bulk even at large L_0/R_g while that of d-PS is close to the bulk value for 3Rg.

Polymer Brush in SCFs

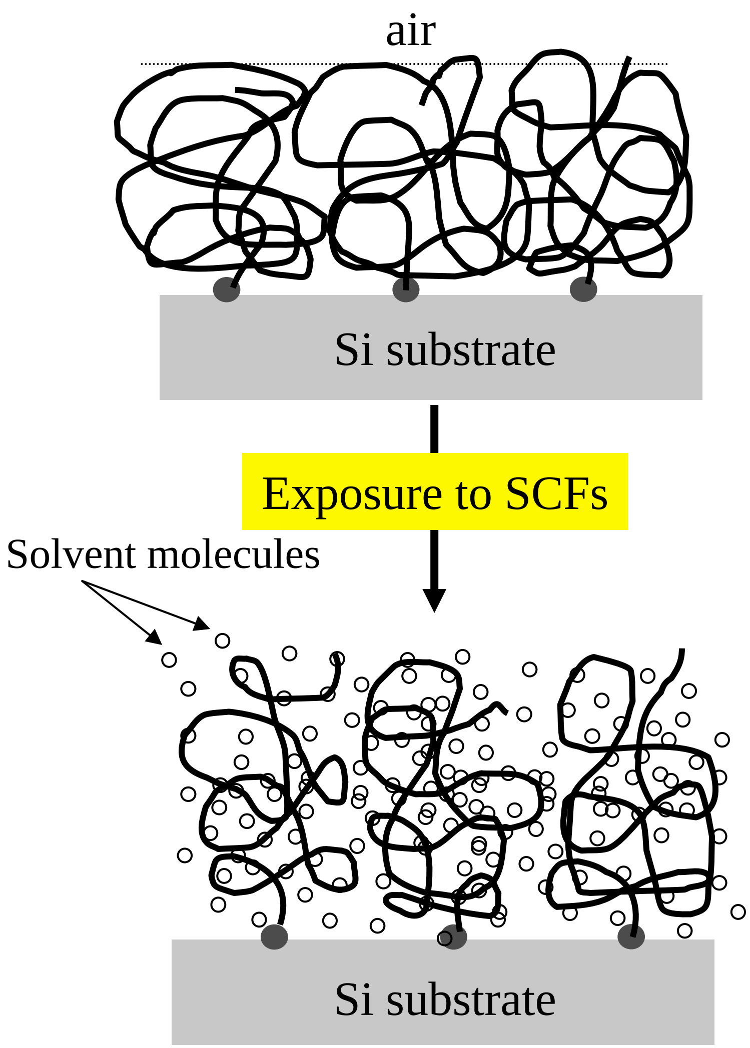
<u>Polymer Brush</u>

• Chain ends are chemically grafted to a solid surface.

• A good model system for study of solvent quality

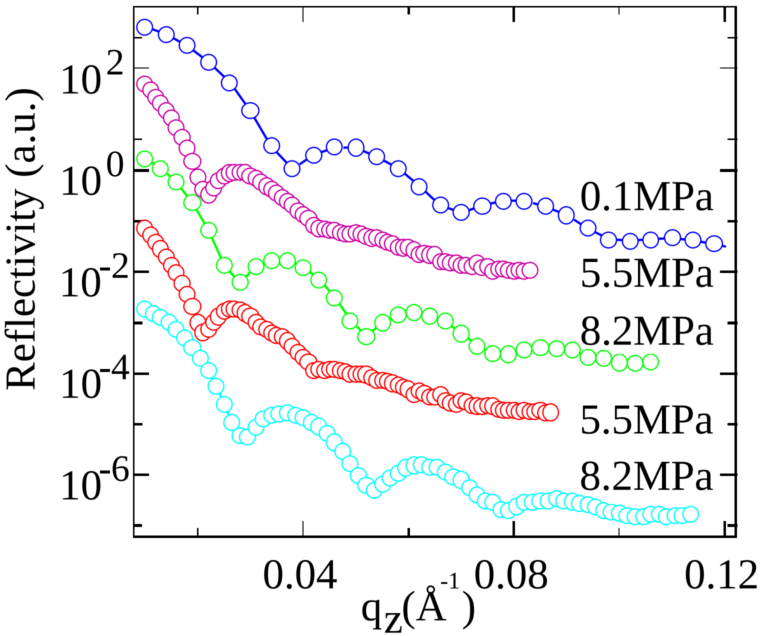
<u>Objective</u>

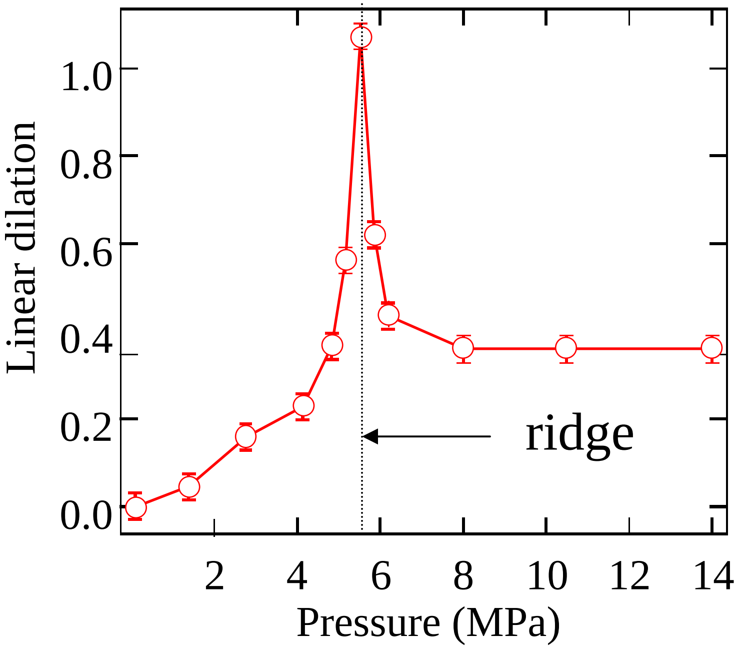
1. What is the solvent quality of the density fluctuating SCFs?
2. Does this confinement of the chain ends lead to a different conformation from the free chain situation in SCFs?



Neutron Reflectivity Results

dPB brush (L_0=2.5Rg) in C_2H_6 @ 37.2ºC



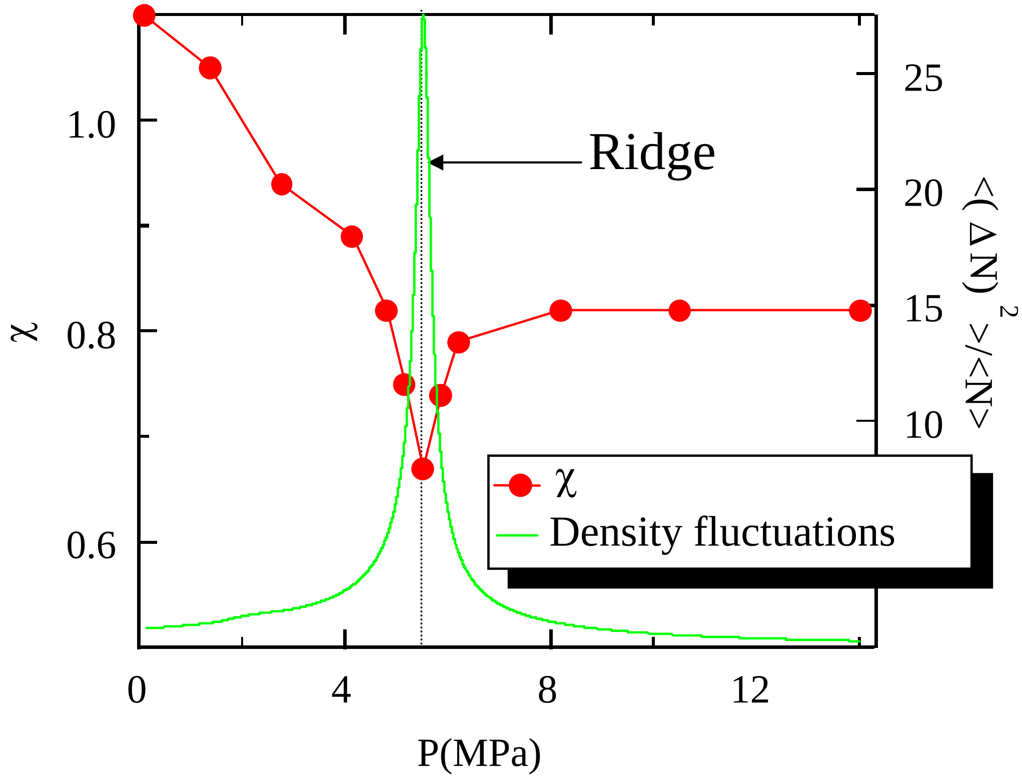


Linear dilation (S_f) $=L_1-L_0/L_0$,
L_1:Swollen thickness, L_0:Unswollen thickness

(1) The swelling of the brush was an equilibrium quantity, which was a function only of the C_2H_6 pressure and temperature.
(2) At the ridge of C_2H_6, an anomalous peak of 1.1 in S_f occurred.

Evaluation of χ-parameter using self-consistent field (SCF) model

Pressure dependence for 2.5Rg thick

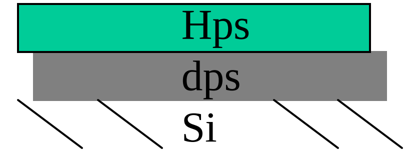


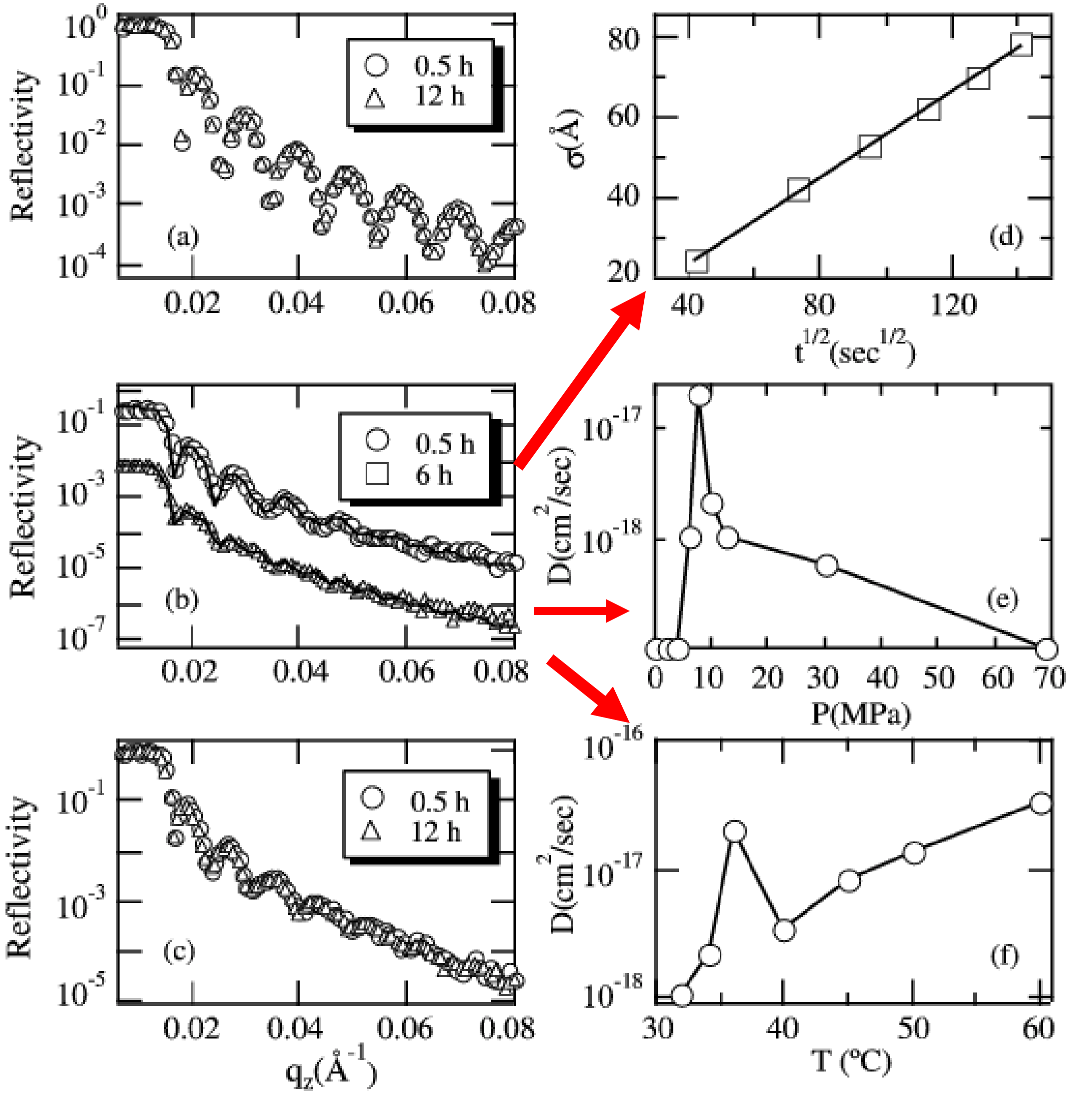
SCF model based on the method developed by Scheutjens and Fleer (1993). **Determination of the χ-parameters with the given N and grafting density.**

The pressure dependence of the χ-parameters showed a minimum at the ridge, indicating that the χ-values depended solely upon the magnitude of the density fluctuations in scC_2H_6.

Enhanced Diffusion on the Ridge

Europhys. Lett., **60** (4), p. 559 (2002)





Finding the Ridge

(a) 2 MPa: No diffusion

(b) 8.2 Mpa, T=36C

(c) 70M Pa, T=36C

HPS 697K 700A/ DPS 400K 500A

At the Ridge

“molten” on ridge (Tg =100C)

σ~t $^{1/2}$ (20–>44–>73 A)

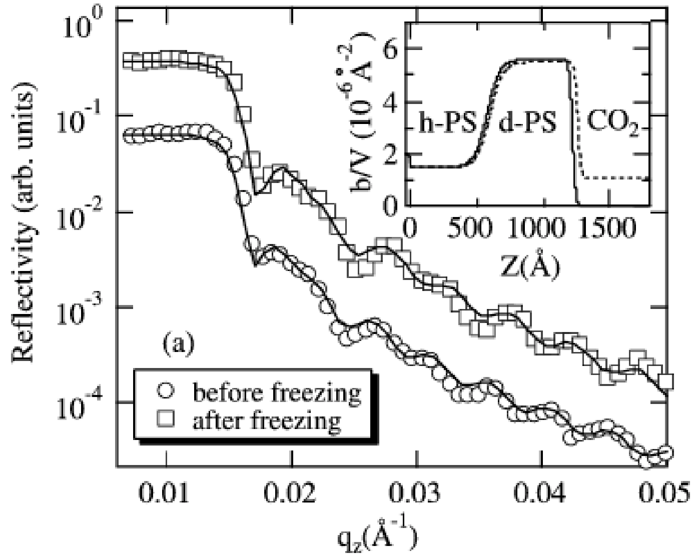
D=σ^2/2t , D=2x10^{-17} cm^2/sec

Equivalent to annealing at T~140C

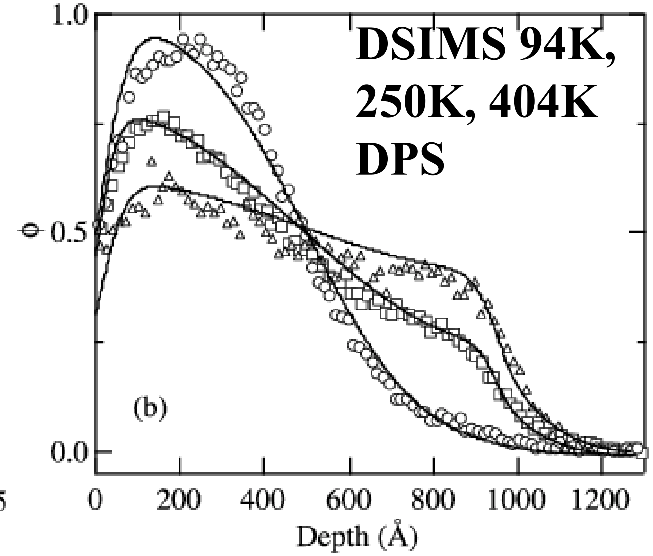
Scaling dependence

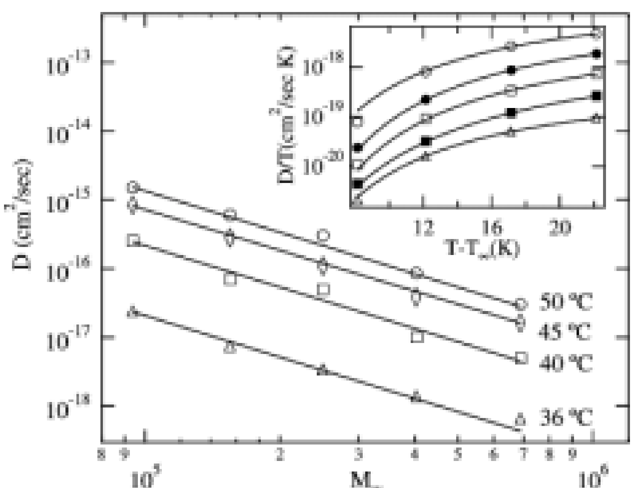
- Lower Mw, D is too fast to measure in situ
- Compare NR and DSIMS evaporated films.
- Flash evaporation maintains the in-situ swollen structure

NR
Mw=94KDPS



DSIMS 94K, 250K, 404K DPS





- **D ~ M^{-2} reptative motion (slope: 2.0)**
- **WLF like scaling with temp at $P=P_{ridge}$**

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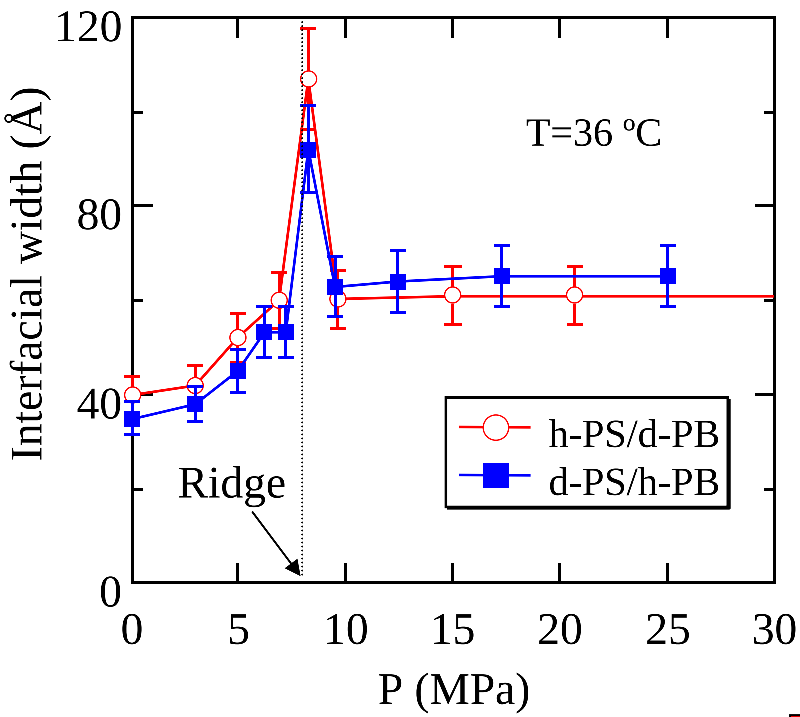
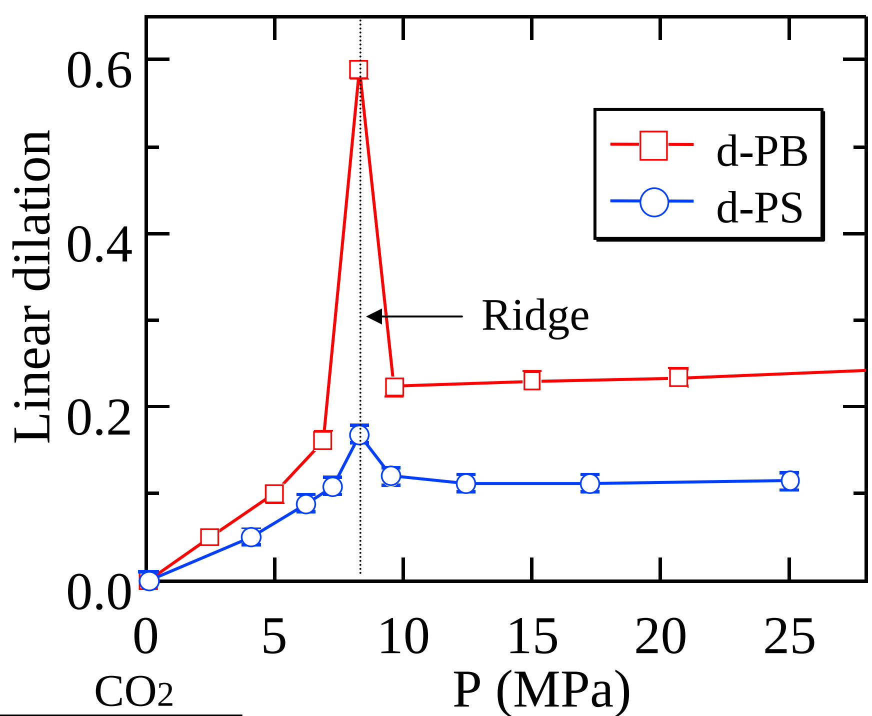
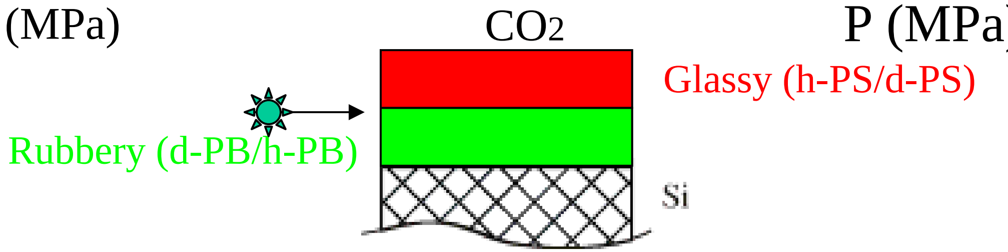
Polymers at Engineered Interfaces

Co-Solvent Effect for Immiscible Polymer Interfaces

In situ NR results @36 ºC in CO_2







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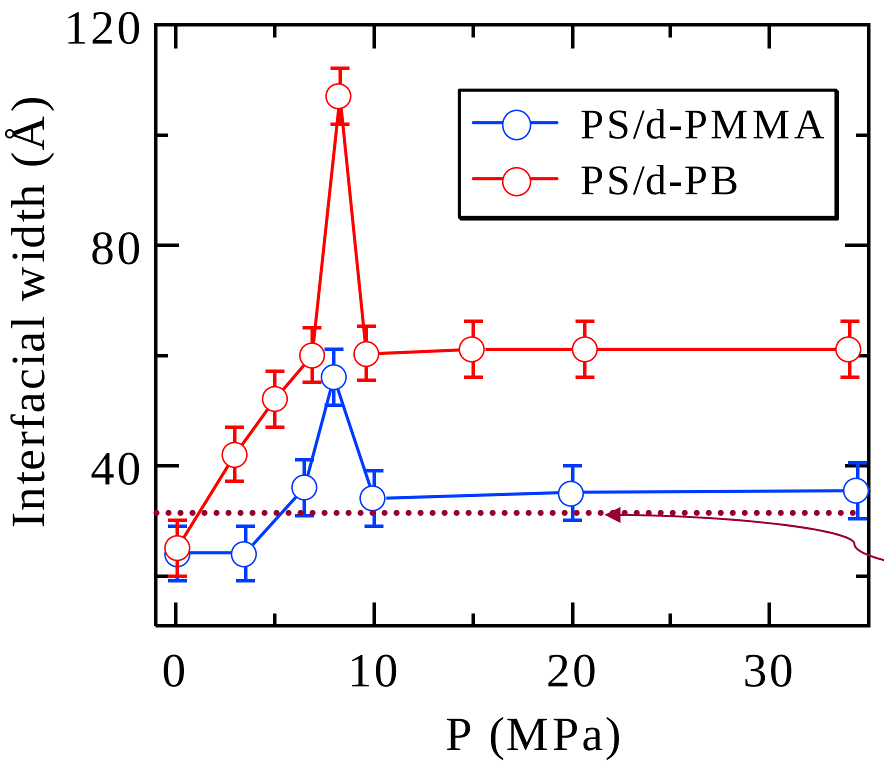
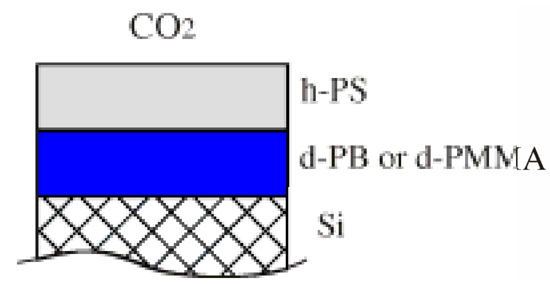
Effect of Elasticity on Miscibility



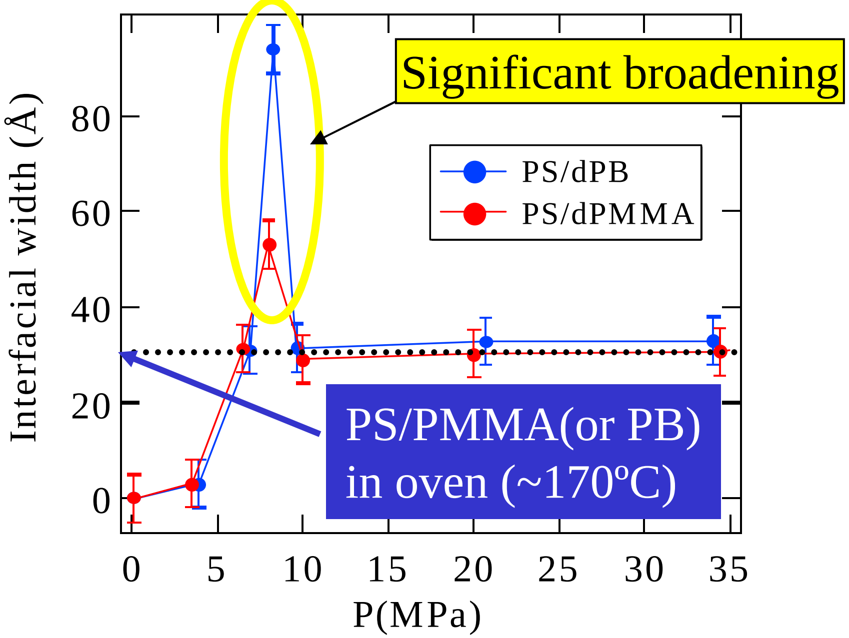


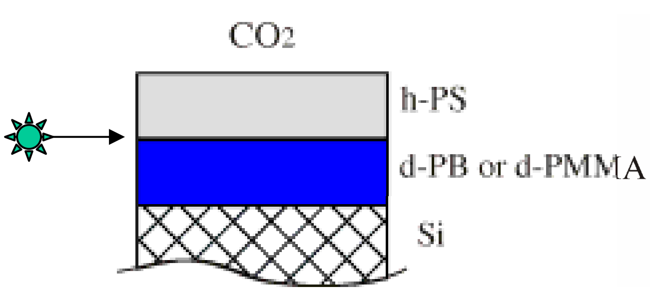
PS/PMMA(or PB) in oven (~170ºC)

The interfacial width for PS/PB bilayer was 2 times larger than that of PS/PMMA bilayer, while the compatibility of pure PS/PMMA is much better relative to pure PS/PB system. Even at the pressures far away from the ridge, the significant broadening was observed in the PS/PB bilayer.

Improved Compatibility for Immiscible Polymers

In situ NR results @36 ºC



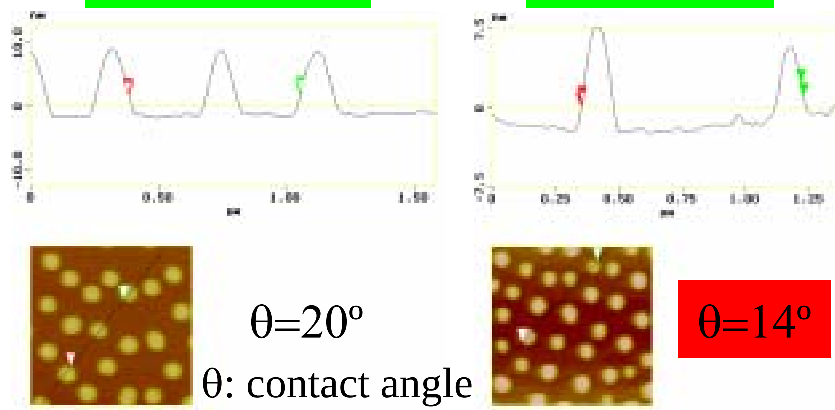


AFM result for freezing samples

<surface micelle of PS-b-PMMA>

CO2 untreated

CO2 treated



θ=20º

θ: contact angle

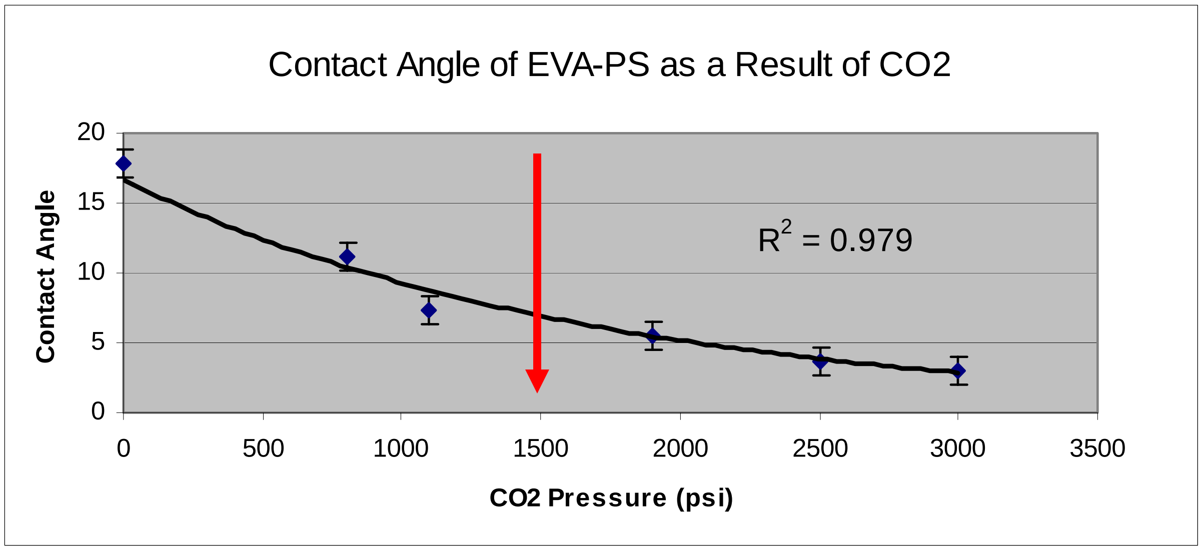
θ=14º

CO_2 plays a role as "co-solvent" for two immiscible polymers. The effect is further enhanced in PS/PB system, which is less compatible than PS/PMMA without CO_2 solvent.

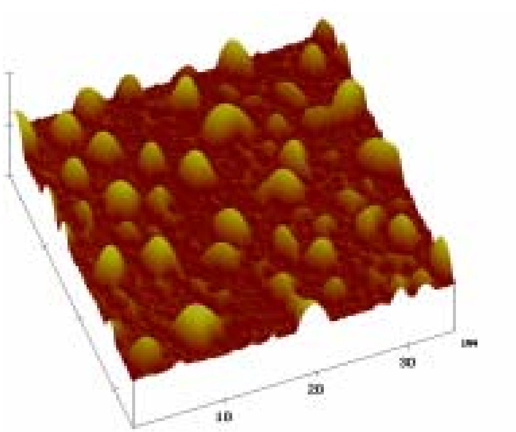
Polymers Blends: PS/EVA and PS/PMMA

Polymer	**Company**	**M_w**	**Tg (°C)**
EVA	DuPont	100k	-20
PS	Aldrich	45K	100
PMMA	Aldrich	120K	100

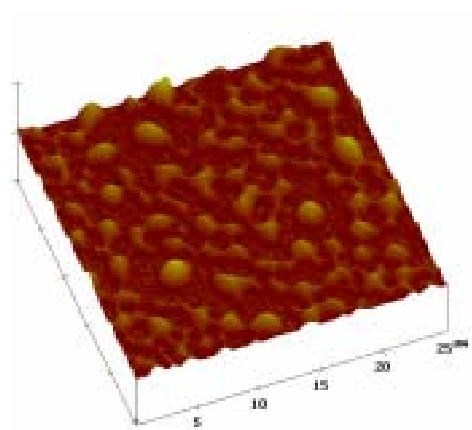
Atomic Force Microscopy



a)



b)



- Sharp decrease in contact angle at the ridge consistent with increased interfacial width.

Young's Modulus

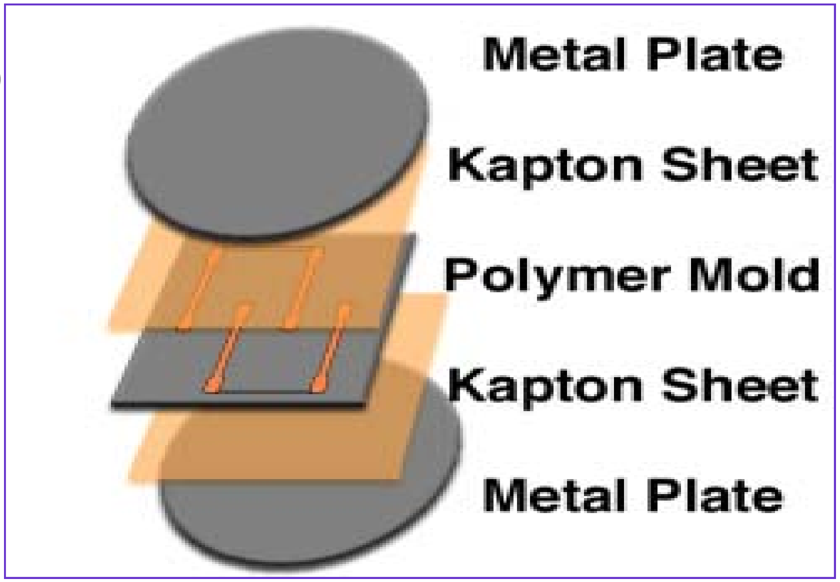
$$\gamma_{EVA} = \gamma_{PS} \cdot \cos\theta + \gamma_{EVA/PS}$$

- By using contact angle measurements, the value of γ EVA/PS can be determined
- Assume unchanged values of the vacuum surface energies in ScCo2

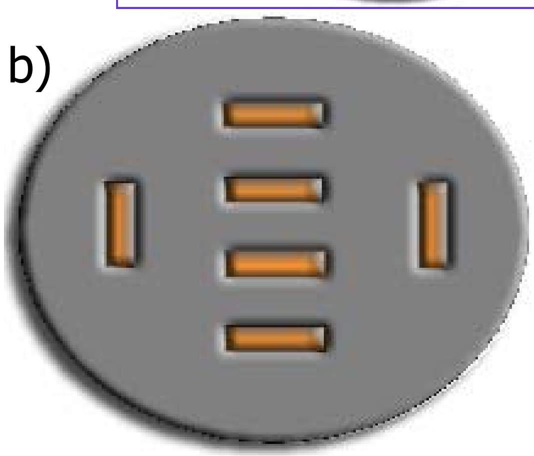
Pressure of SC CO_2 (psi)	Interfacial Tension ($\gamma_{EVA/PS}$)	
	Mean (dyne/cm)	Standard Deviation
Control (0)	2.905	0.102
Liquid (800)	1.746	0.077
1100	1.323	0.076
1900	1.186	0.055
2500	1.084	0.067
3000	1.057	0.051

Experimental Methods

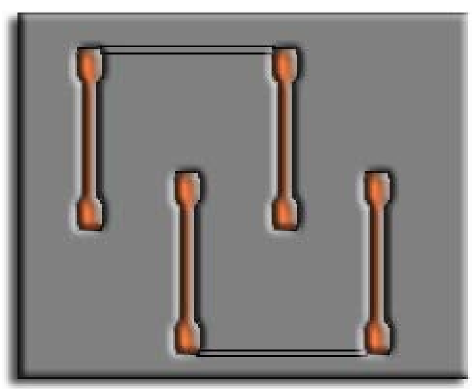
a)



b)

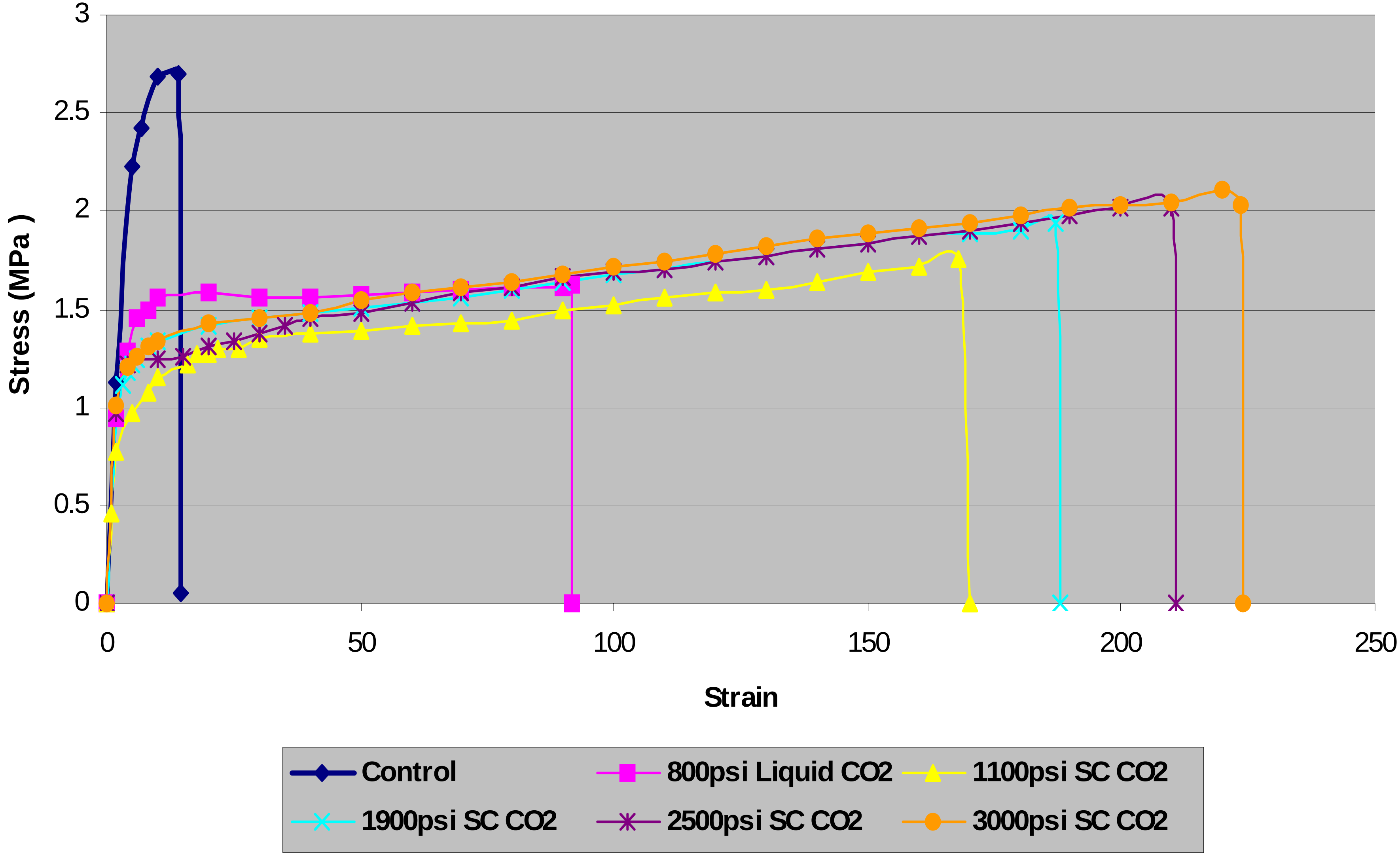


c)

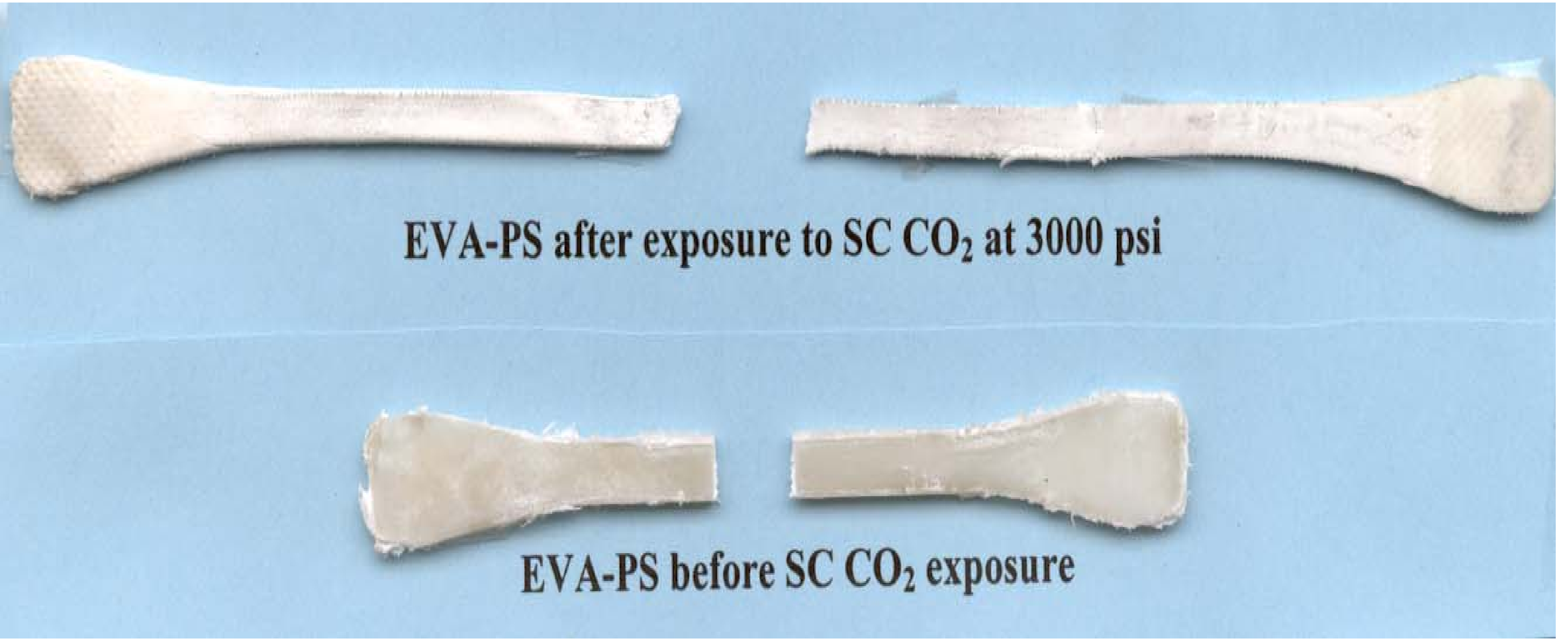


- Component polymers were obtained to total 50g. Polymers were combined using a CW Brabender at 170º C
- The resulting raw material was molded (a) using a heat press at 305º F and 4 tons of pressure into rectangle (b) or dogbone (c) molds.
- Molds were then exposed to SC CO2 at 115º F and 1200 psi for one hour.
- The chamber was vented after exposure at a constant rate as not to mar results.

Tensile Testing

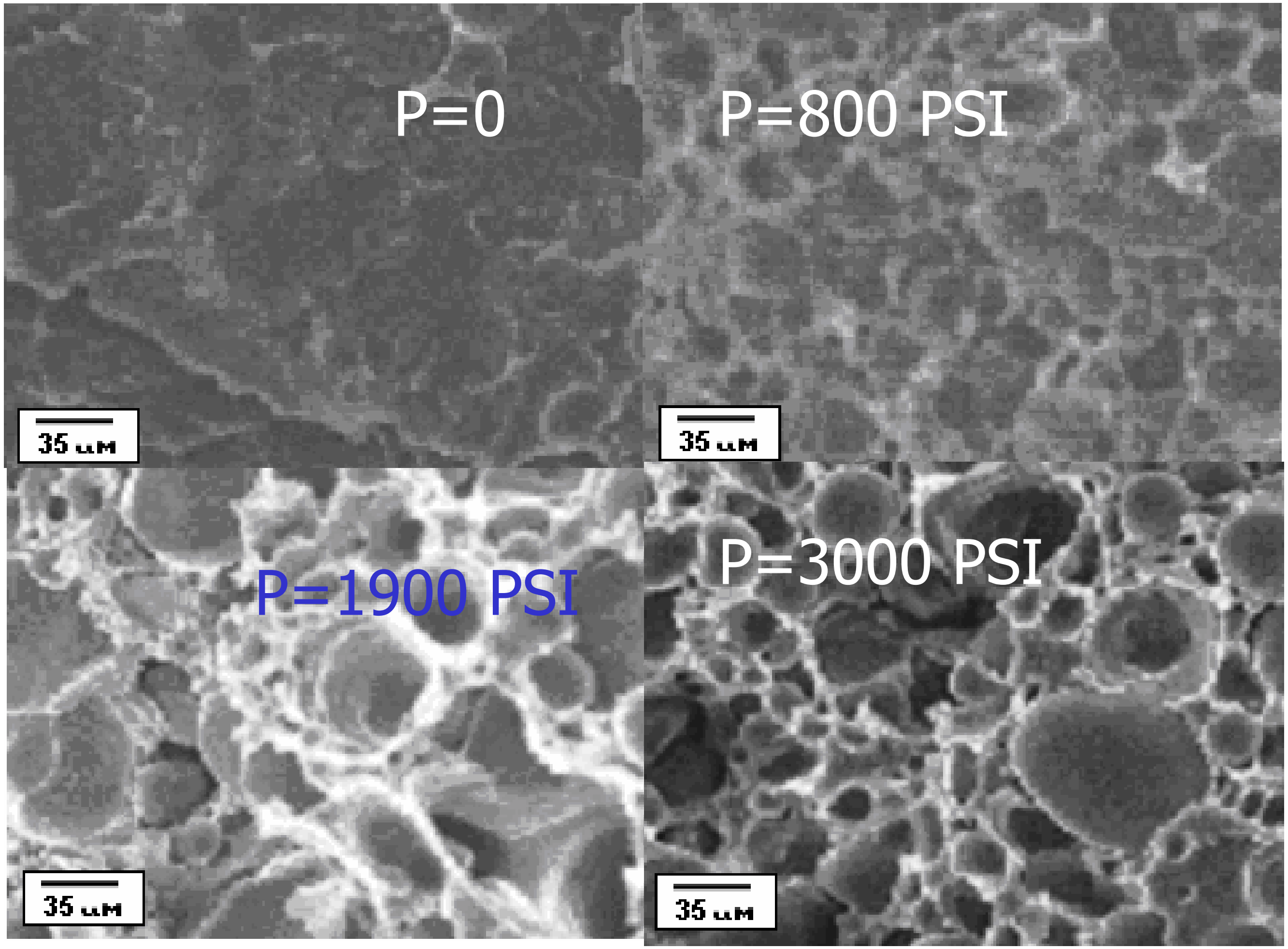


Mechanical properties



- Foaming increases surface to volume ratio.
- Compatibilization occurs inside the splines where penetration depth becomes significant relative to the diameter.

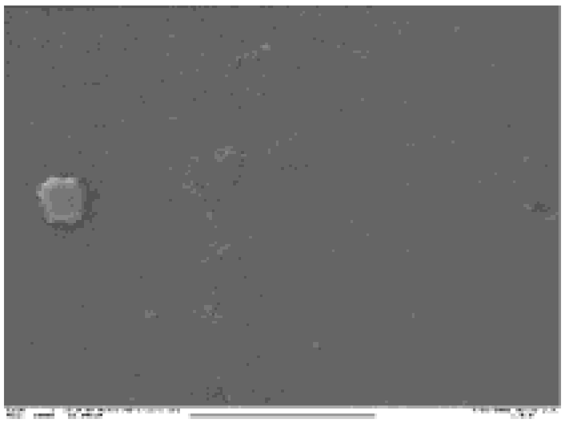
PS:EVA (1:1)

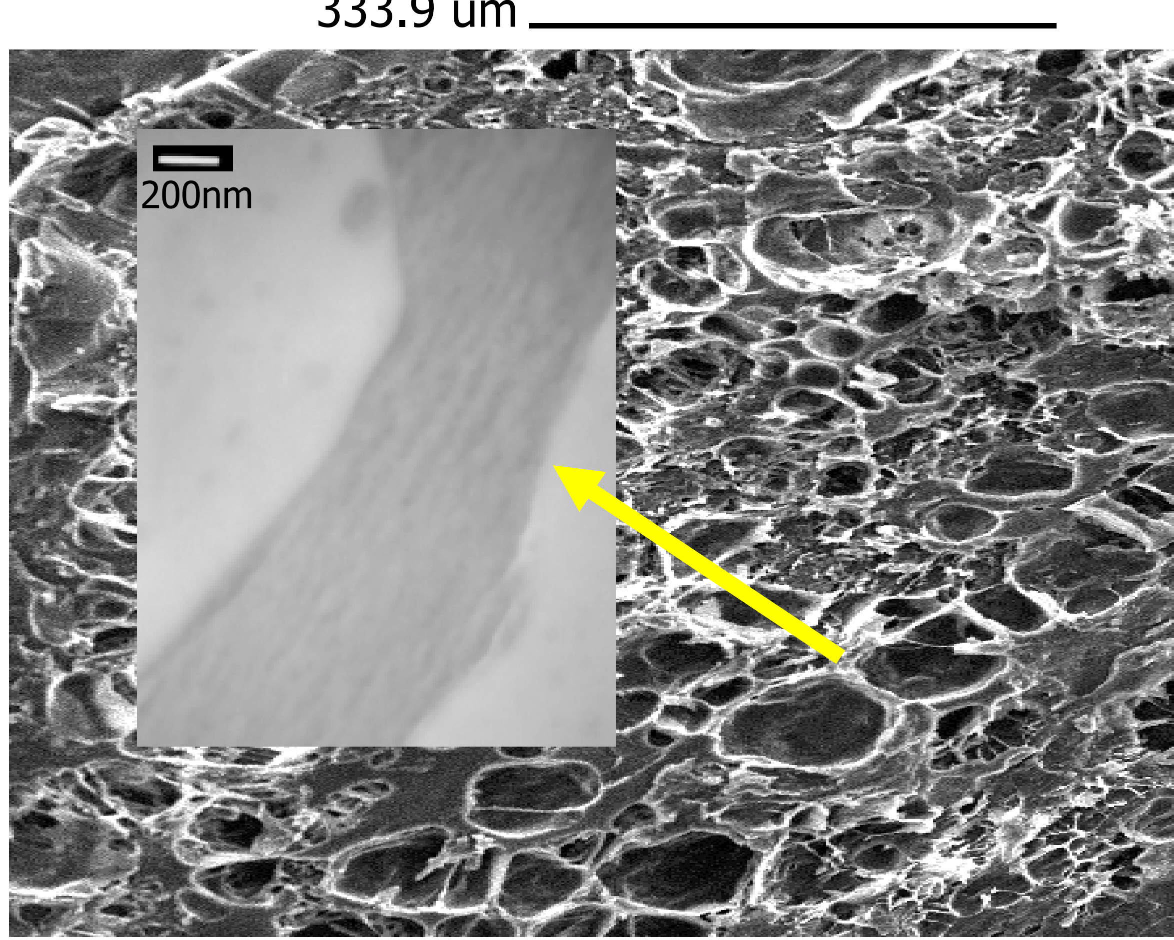


- Polymer blend foams.
- Diameter of cells increases with exposure pressure.

PS-PMMA

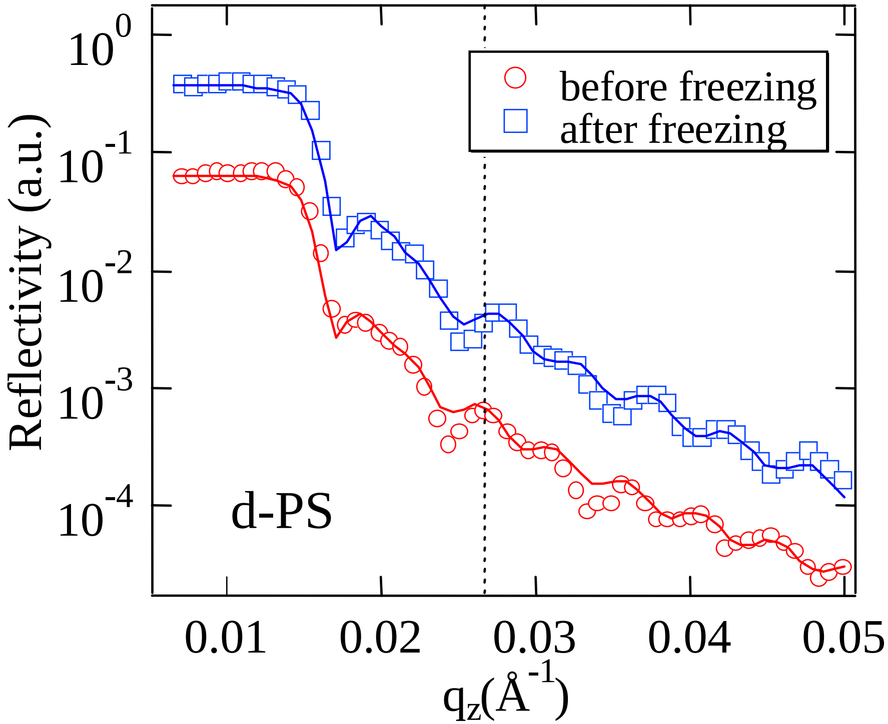
a)



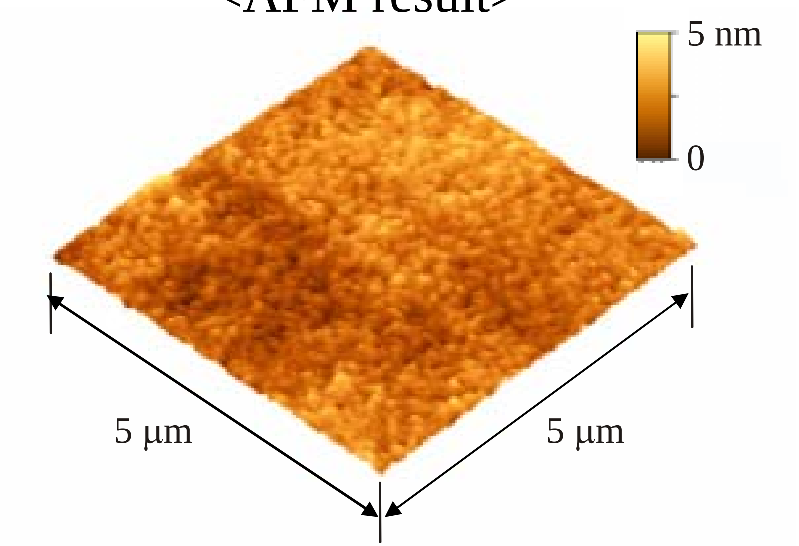


a) SEM image of 1:1 PS-PMMA after supercritical exposure. Note the drastic surface change, with a surface covered in air holes replacing the flat surface.

Freezing by Flush Evaporation



<AFM result>



NR results showed that film thicknesses were identical before and after the quench. In addition, AFM show that the surface still flat without voids.

Enable to study using other techniques (SIMS, x-ray reflectivity, ellipsometry, AFM) and to yield a stable new material with different properties.

Freezing:

1) Annealing at the ridge
2) Quick depressurization
3) Then evaluation by NR

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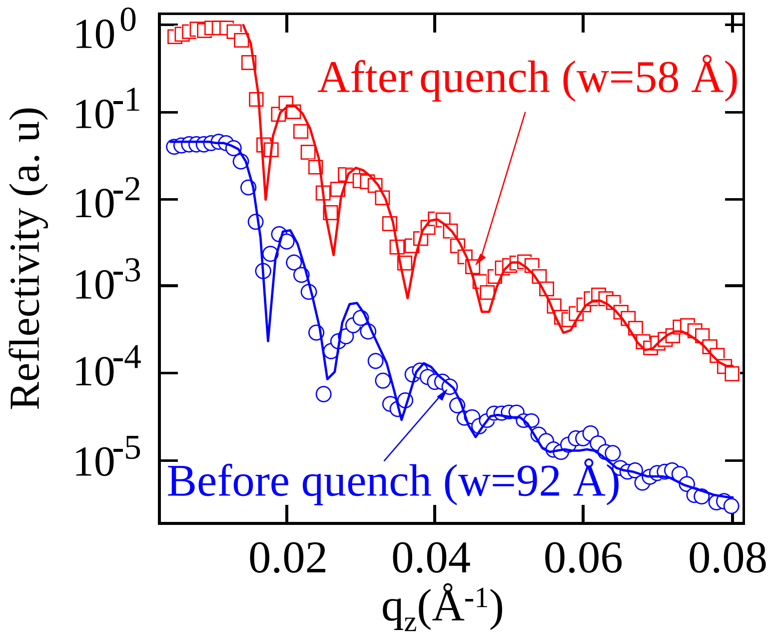
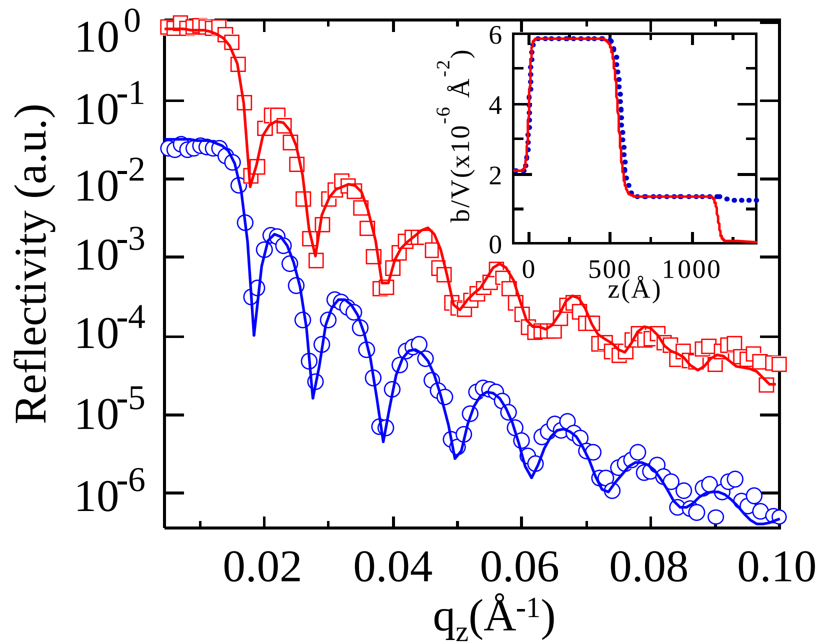
Freezing of Bilayers

< PB / d-PS >



< d-PMMA / PS >

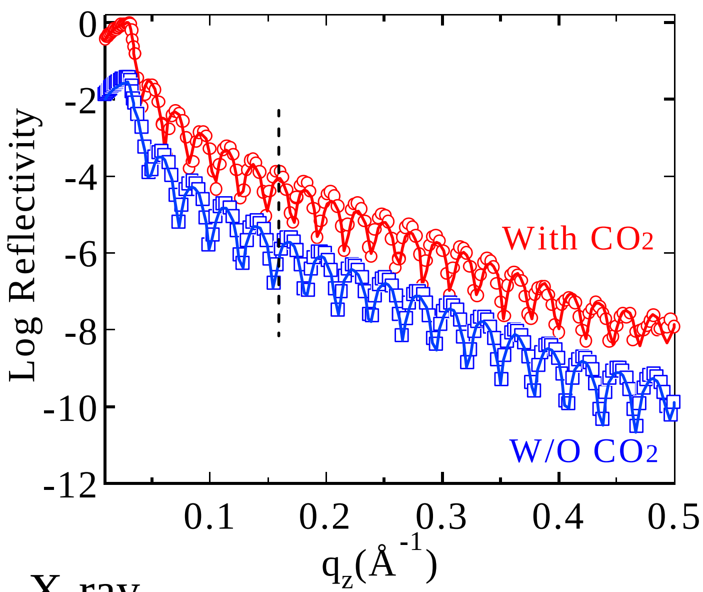


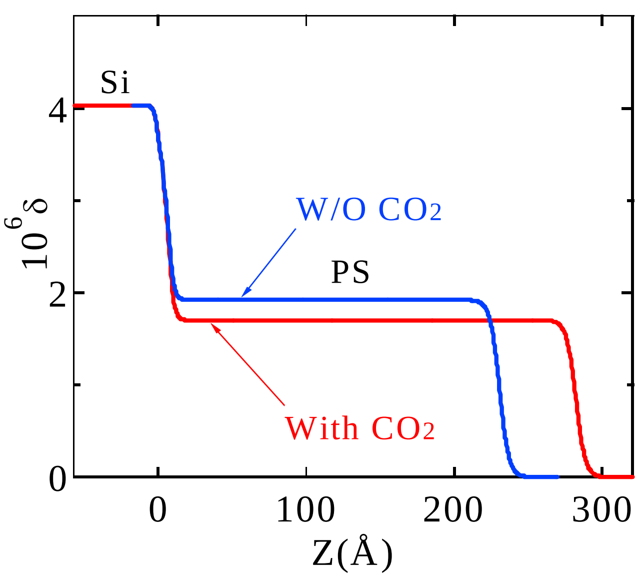
The interfacial width after the quench was much smaller than that before the quench, while film thickness of d-PS layer could be frozen.

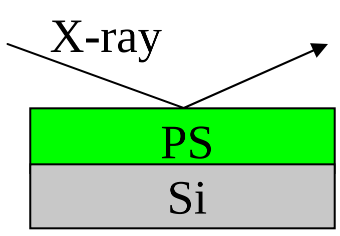
In situ film quality, i.e., density, roughness and film thickness, could be frozen by flash evaporation of CO_2.

Low-Density Polymer Films

X-ray reflectivity @X10B (NSLS) PS 200K (223 Å, Rg=120 Å) frozen film



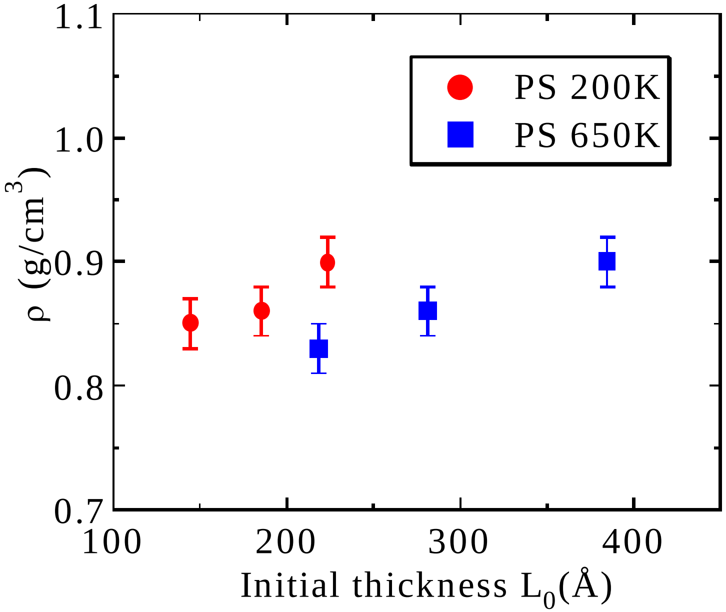


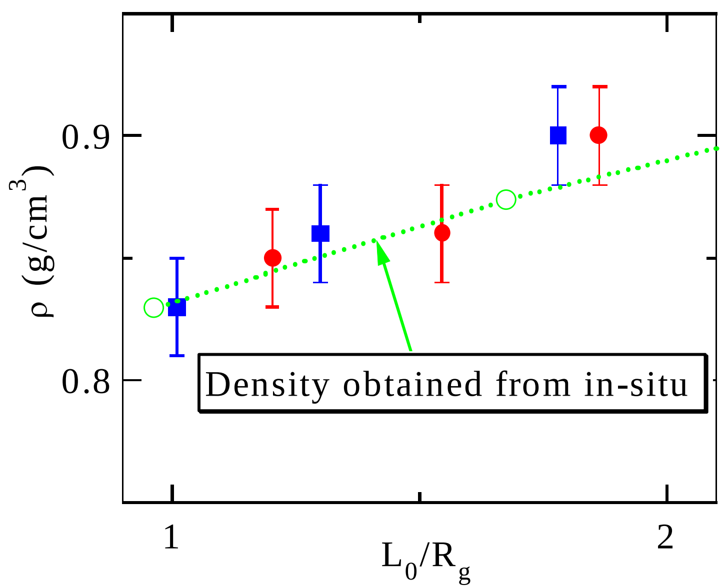


1) Polymer layer has thickened after exposed to $scCO_2$.
2) Dispersion in x-ray refractive index, which is proportional to density of film, decreased by 14%.

Exposed to CO_2 in the density fluctuating regime can be used to produce uniform, low-density polymer films.

R_g Dependence of Polymer Low-Density





(1) The data can be collapsed on a universal curve when L_0 is scaled by R_g. Hence, when confined as a thin film on a surface, thickness as well as molecular structure influence the density.

(2) The fact that the density obtained from the differing experiments (in situ neutron reflectivity and XR) are in good agreement, indicating that in the case of PS, rapid sublimation of the gas preserves the in-situ dilation of the films.

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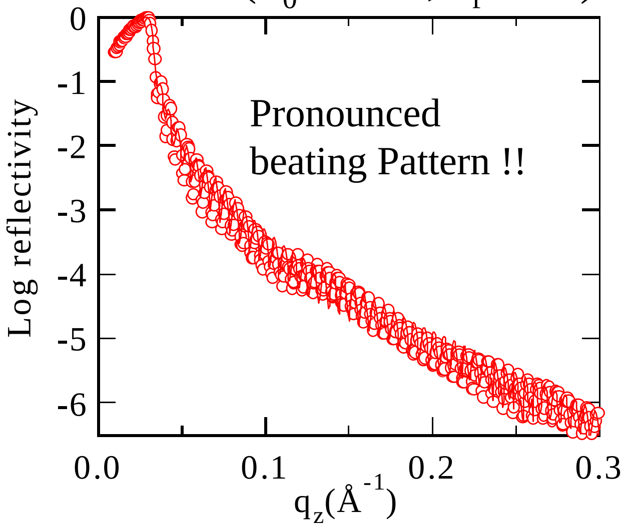
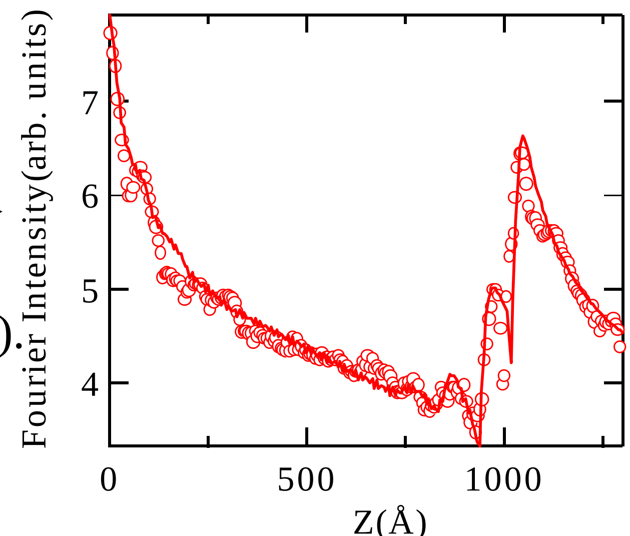
Density Gradient in Thicker Films

PS200K (L_0=930 Å, S_f=0.10)

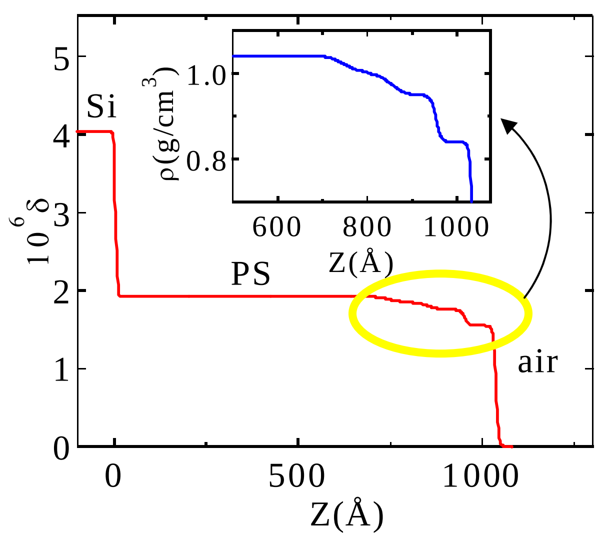


Fourier Transform

Seeck et al. APL (2000).

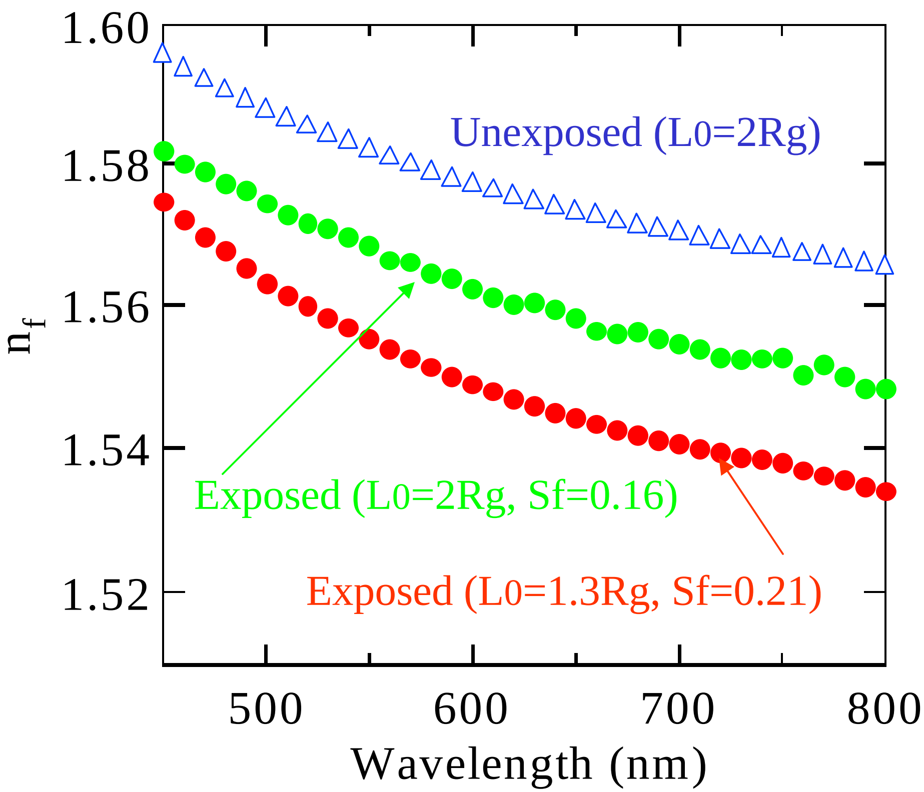


Four different PS layers were formed, based upon the number of the FT peaks.



- A layer about 100 Å in thick is formed at the polymer/vacuum surface with a reduced density of $r=0.83 g/cm^3$.
- The subsequent layers also have reduced density, but these layers are more diffuse and decay over a region of approximately 200 Å towards a uniform layer with the bulk density.
- This behavior, which was independent of M_W, was observed in all films larger than 4-5R_g.

Refractive Index



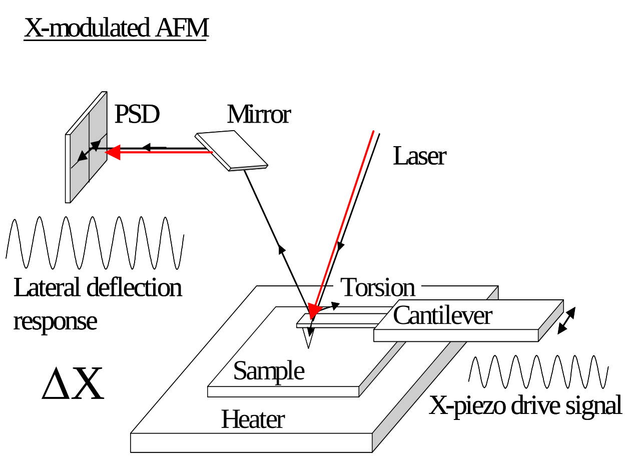
Method: A H-VASE spectroscopic ellipsometry (J.A. Woollam Co., Inc.) was used with a wide spectral range of 300-800 nm with 10 nm increments.

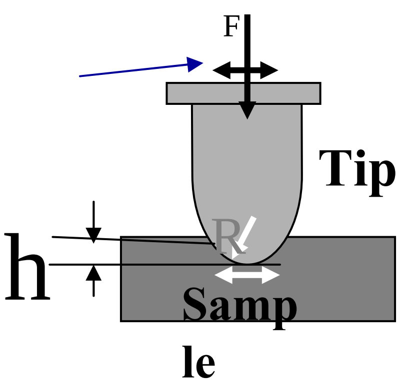
In order to fit the spectroscopic data, the same three-layer model mentioned in the text was used with the literature refractive indices for the native oxide and silicon substrate. The film thickness for each layer determined by XR was used for the fit.

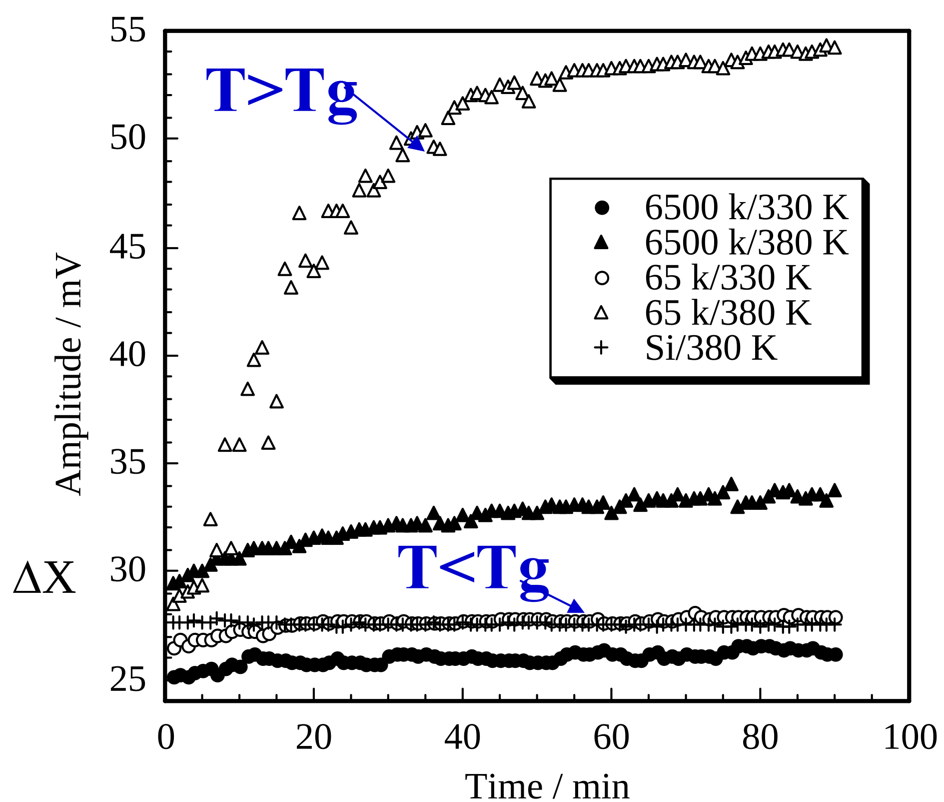
The n_f values for the exposed films decreased with increasing the S_f values over the wide wavelength range of 450-800 nm. Since dielectric constant of materials can be derived from a square of refractive index, we can therefore vary the dielectric constant for PS film from 2 to 4% in the same L_0, R_g parameter space.

Surface modulated force microscopy

$$\Delta x \propto h = \left(\frac{3}{4} \frac{1-\nu^2}{E} \frac{F}{R^{1/2}} \right)^{2/3}$$

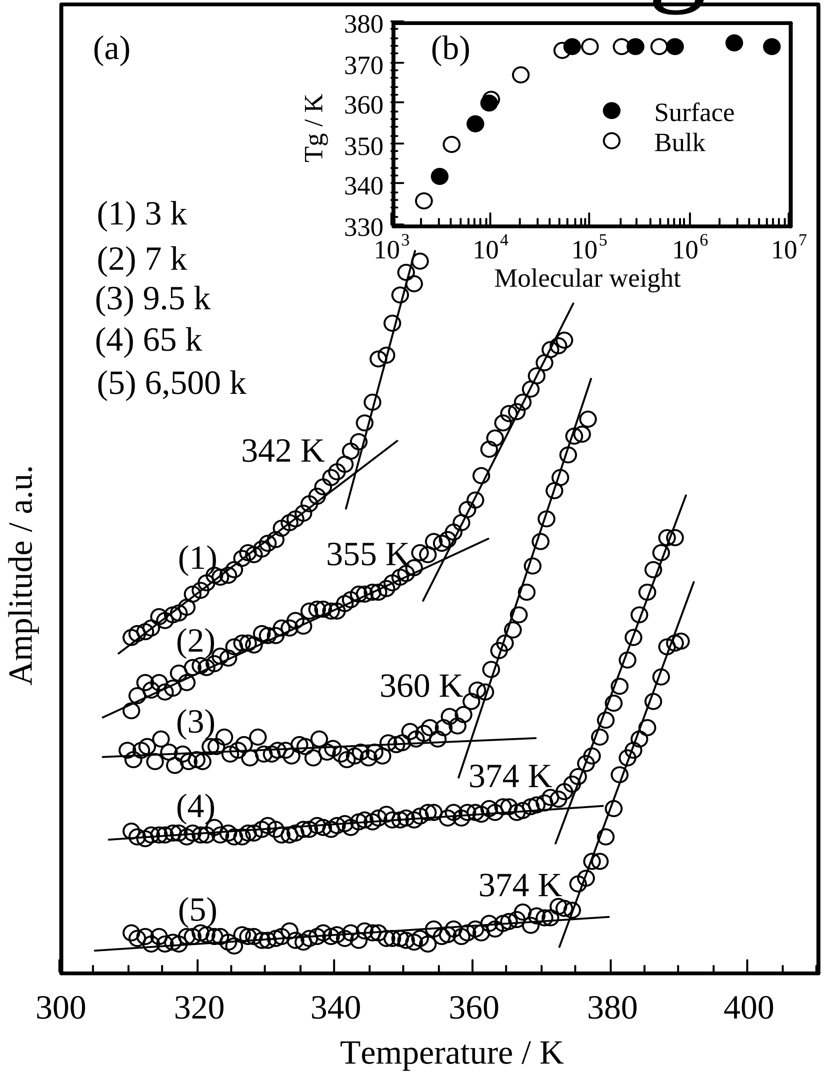






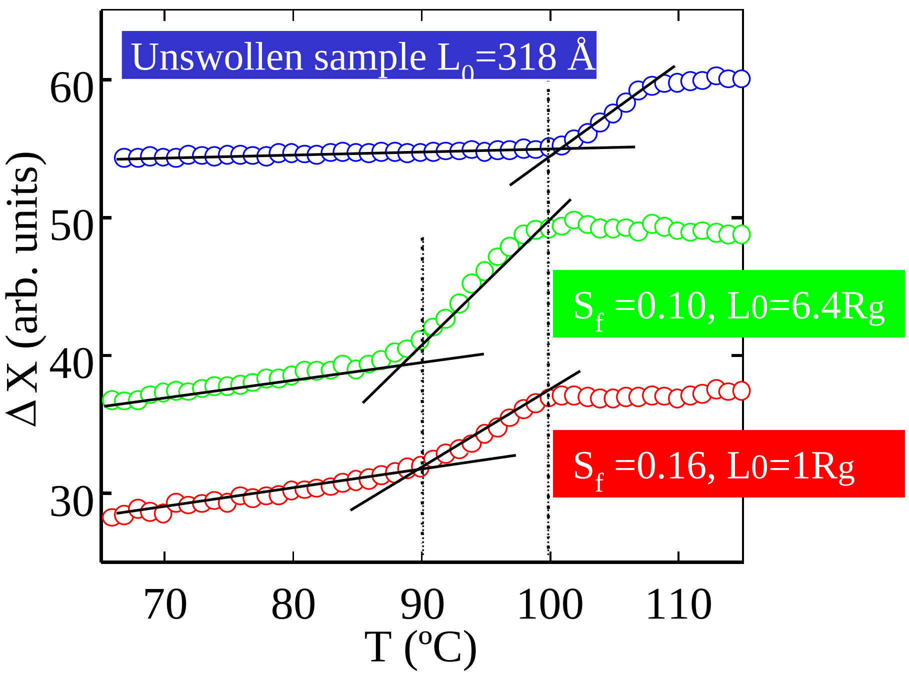
E decreases by three orders of magnitude when T>Tg

The glass transition



- Surface Tg ~ bulk Tg.
- Tg values scale with Mw.
- Technique measures relative creep, or zero shear viscosity and modulus.
- Both quantities change by orders of magnitude at Tm and Tg.
- Technique sensitive to SEGMENTAL chain motion and not to center of mass motion.

Low Surface Tg



The intersection of the two straight lines fit to the data is identified as T_g.

Method: AFM mode, shear modulation force microscopy (SMFM), which is sensitive to the large change in viscoelastic behavior at air/polymer interface (Ge *et al*. *Phys*. *Rev*. *Lett*. 2000).

T_g value for the frozen film (S_f =0.16) decreased about 10 ºC compared with that of the unswollen PS films (T_g=100 ºC). Similarly, for the film 6.4R_g thick a T_g value of 90 ºC. This result is consistent with the x-ray data taht show a region of effective dilation of ~0.2 near the surface.

Useful for an improvement of the adhesion for two immiscible polymers and inorganic/organic interface.

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Polymer Metallization

Advantage

Improvement of polymer surface properties, including wear, conductivity and appearance.

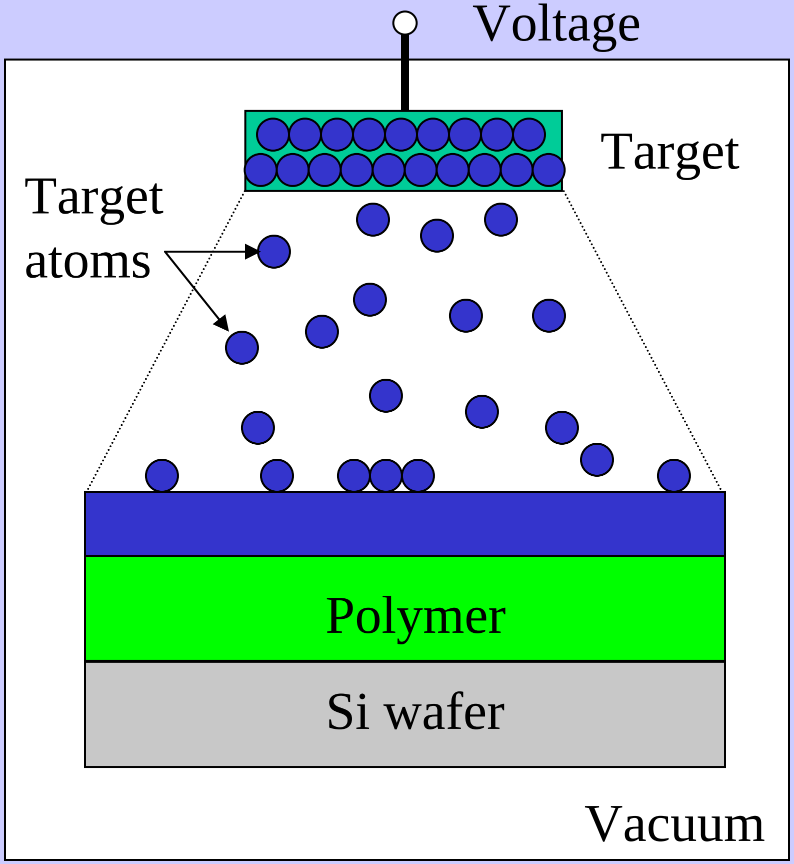
Problem

Sharp metal/polymer interface forms due to the very different surface properties between polymer/metal.

↓

Dewetting will occur and the film properties will severely deteriorate.

Metal deposition



PS/Cr Metallization

(A) Unexposed $scCO_2$

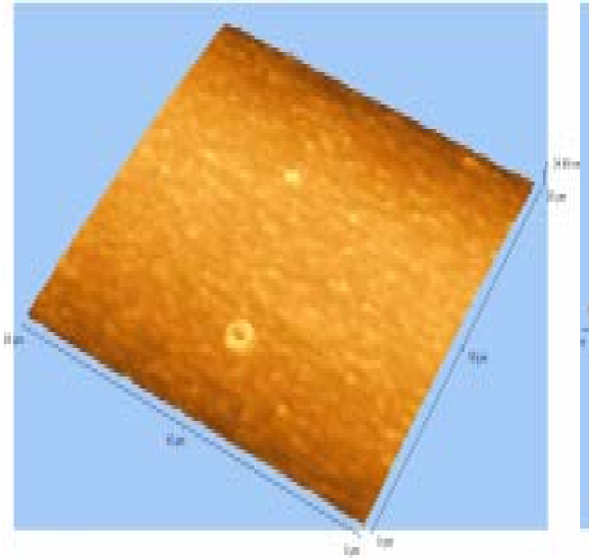


Image size (20 μm×20 μm), height scale (0-40 nm)

Smooth Cr Surface

(RMS roughness~3nm)

(B) Exposed $scCO_2$ before depositing Cr

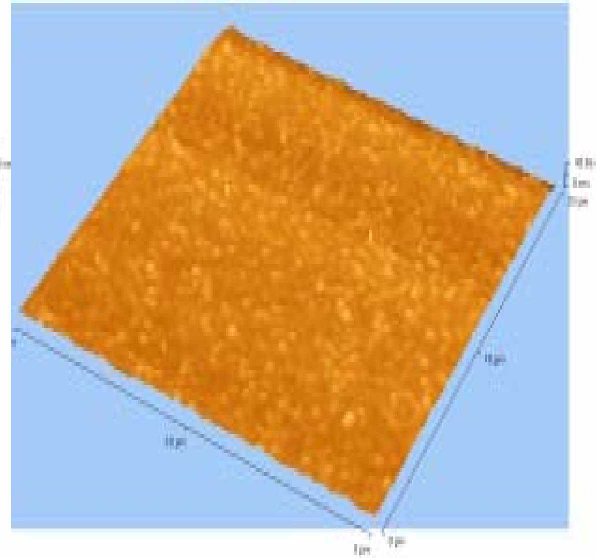


Image size (20 μm×20 μm), height scale (0-50 nm)

No dewetting was induced by exposure to $scCO_2$.

(C) Exposed $scCO_2$ after depositing Cr

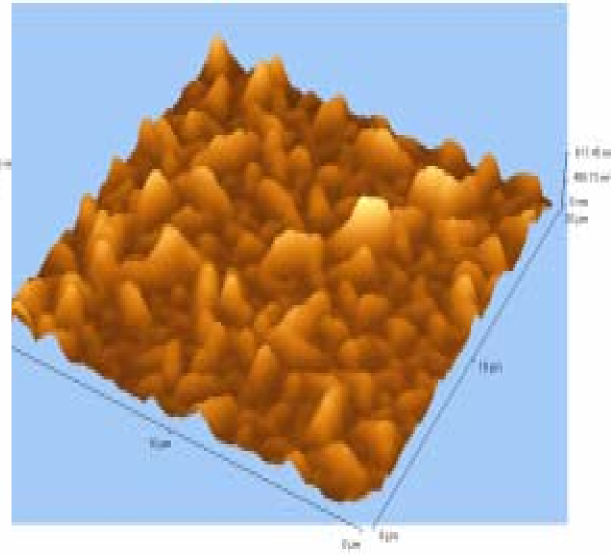


Image size (20 μm×20 μm), height scale (0-800 nm)

Dewetting occurred!!

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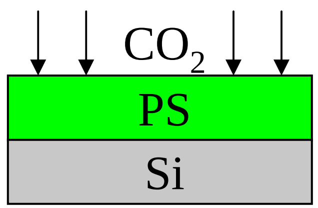
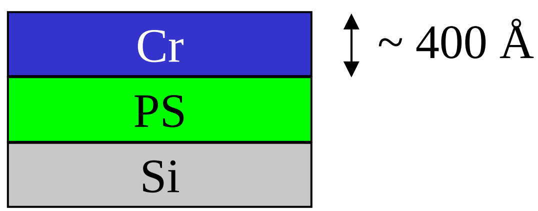
Cr/PS system

Sample preparation

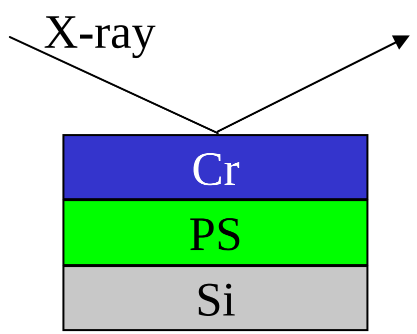
(1) Exposed to CO_2

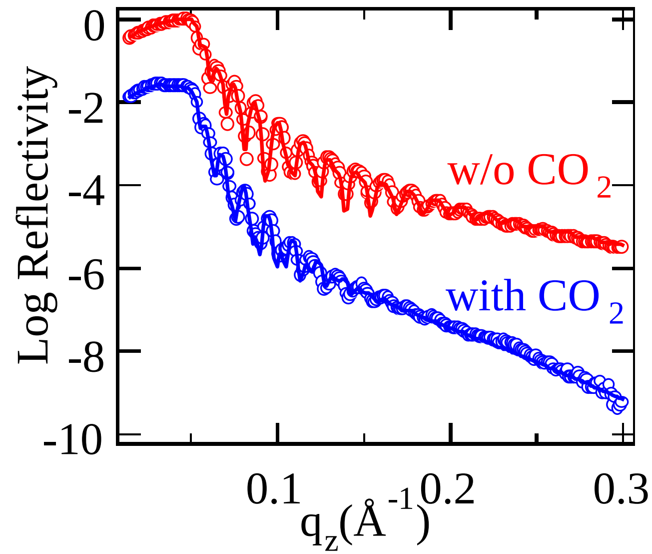


(2) Chromium deposition

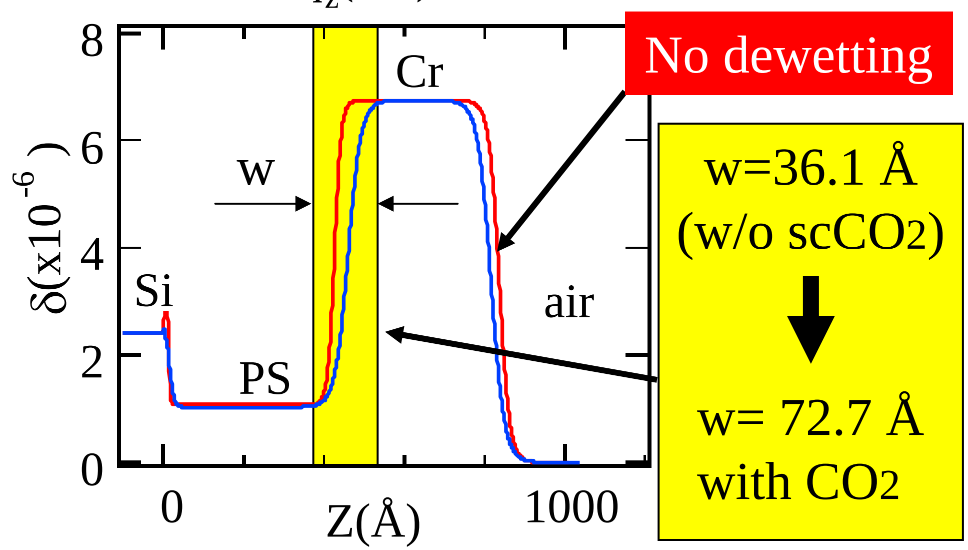


(3) Characterization by XR





PS: 400Å
36 ºC, 8.2 MPa



Fiber Diameter versus Particle Size

New York Times
April 27, 2003

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Membrane for Gas Separation

Motivation: ***Gas Filtration at a Molecular Level***

- *Benefits to society, e.g., SARS; other viruses*
- *Homeland security – bio- & chemical terrorism*

Gas permeation selectivity

$$F = PA\, \Delta p/\sigma$$

F = volumetric flow rate (or the gaseous flux),
σ= membrane thickness,
A=surface area,
P = intrinsic permeability coefficient that characterizes the specific membrane-permeant combination, and
Δp = applied pressure difference.

F is linearly proportional to P, **A,** *and* Δp; but is *inversely proportional to* σ**.**

Membrane should be as thin as possible

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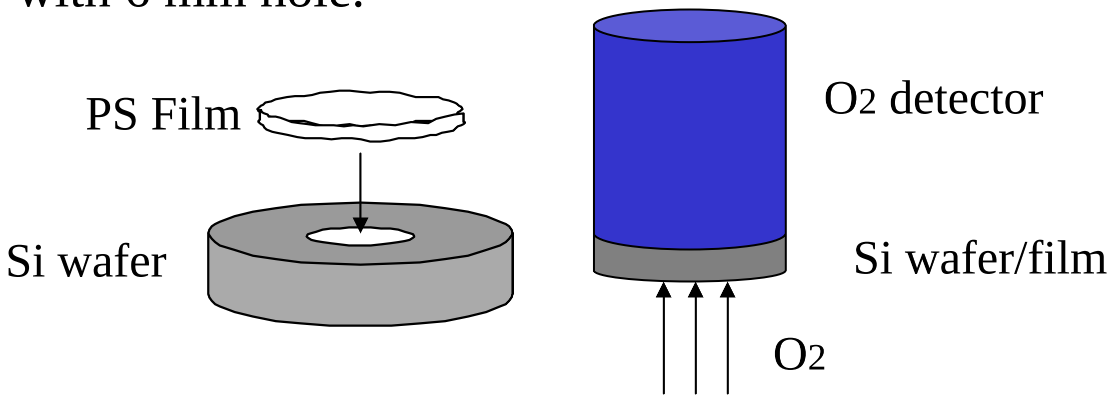
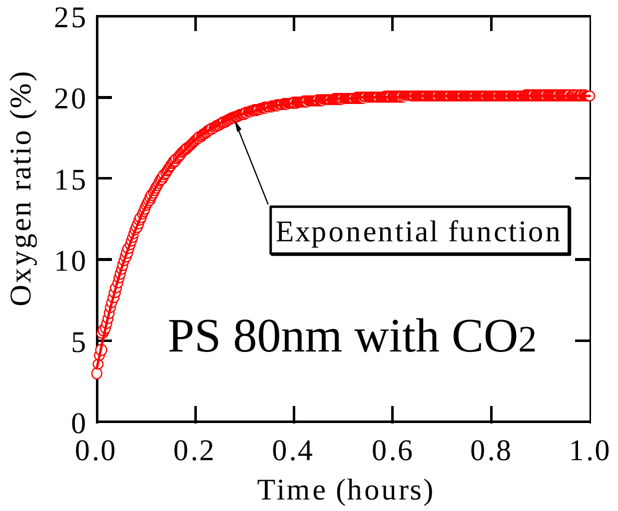
Advantage of $scCO_2$

The size of free volume could be possibly tunable as a function of the magnitude of the swelling ratio, which depends upon initial film thickness, molecular weight of polymers and CO_2 temperature and pressure conditions.

Oxygen Permeability Measurements

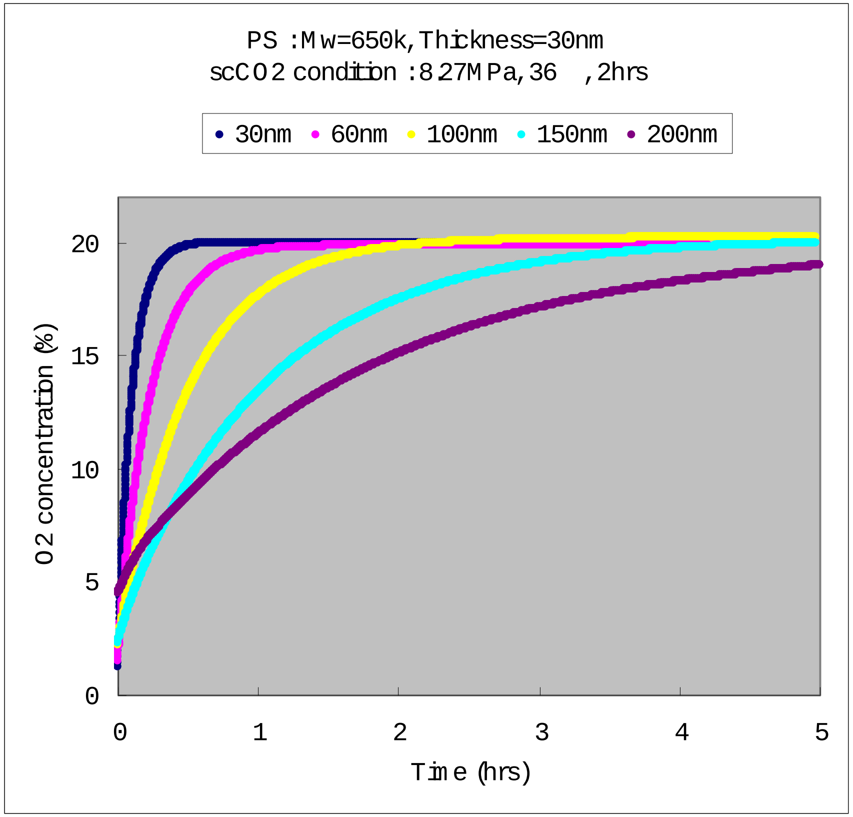
- O_2 detector and interface were purchased from Vernier co. (LabPro).
- Polymer: PS(Mw=280K)
- Polymer films were floated on Si wafer with 6 mm hole.

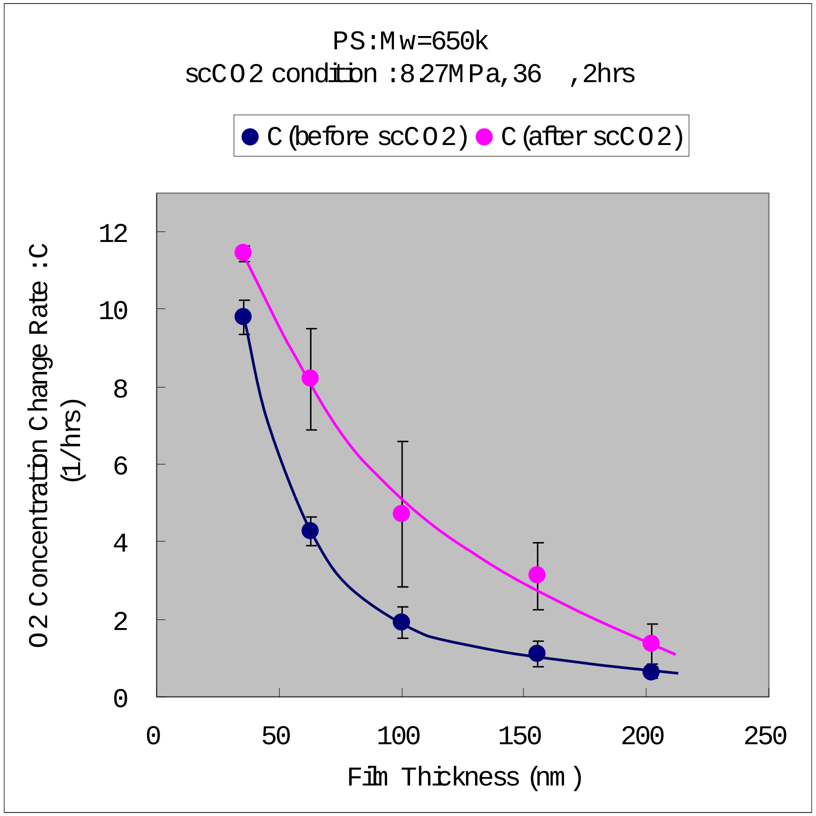




Dependence of O_2 gas permeability on PS film thickness after $scCO_2$ treatment

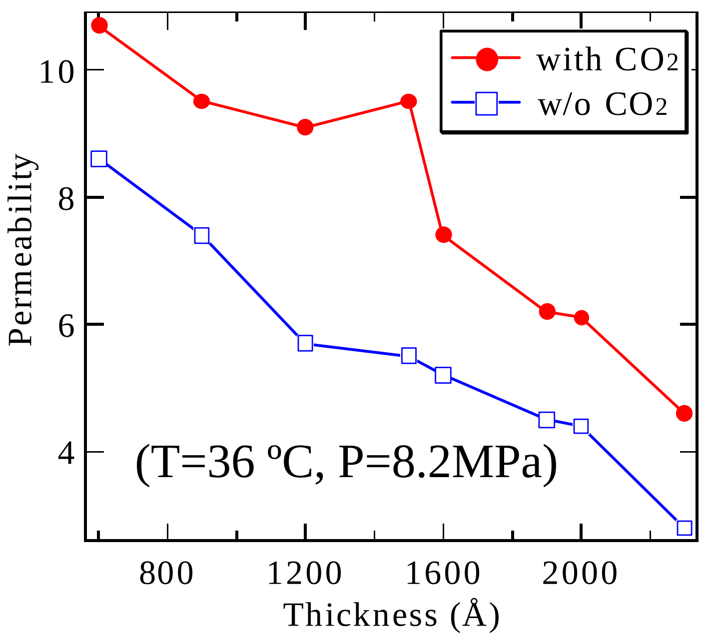
- The $scCO_2$ treatment has a remarkable increasing effect of O_2 gas permeability and the effect decreases with film thickness. The effect is almost same as one of ca. 60nm thinning.



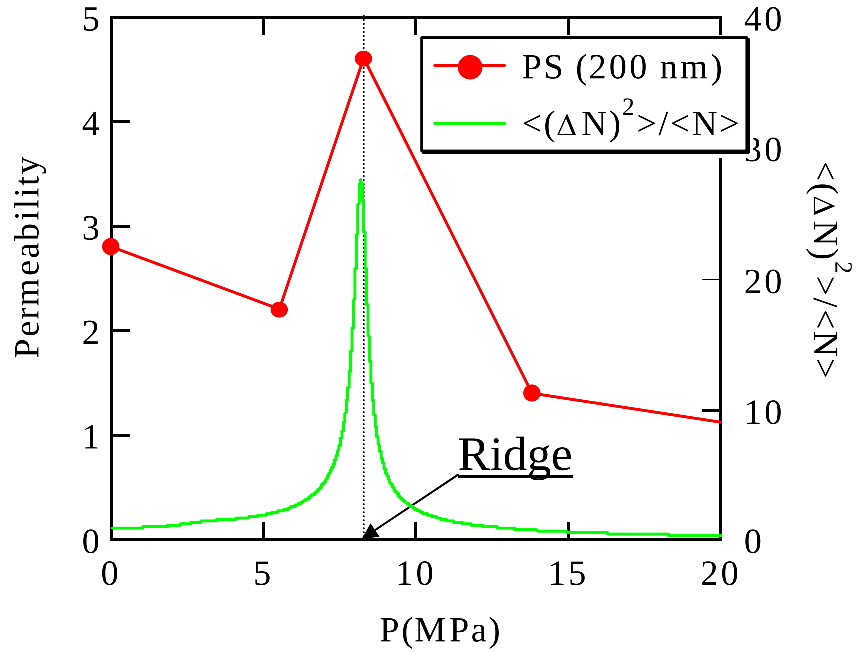


Permeability Results

<Thickness Dependence >



<Pressure Dependence at T=36 ºC>

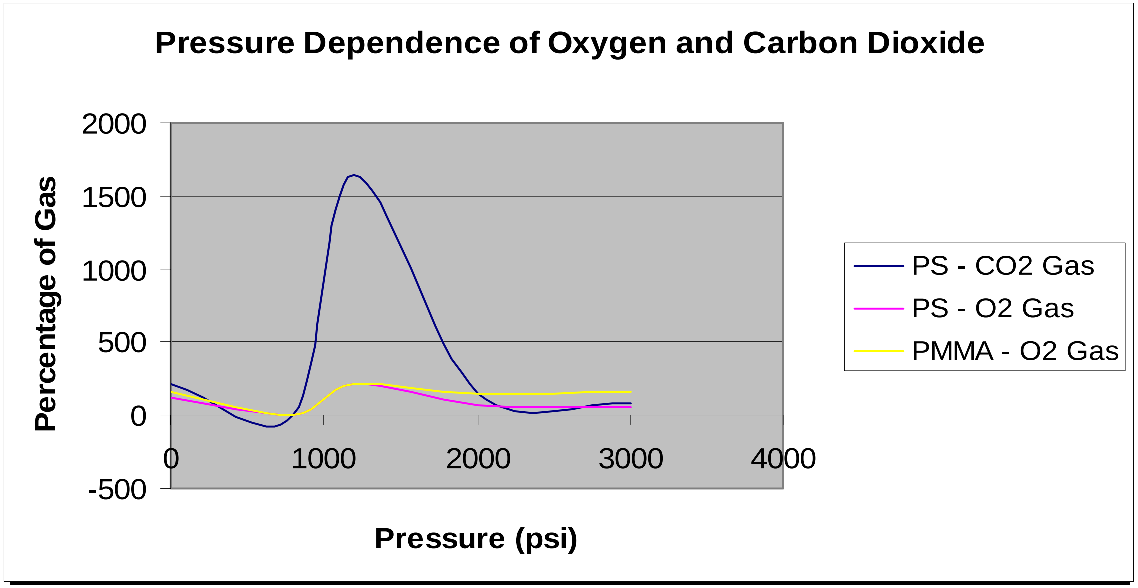


Excess permeability appeared in the wide thickness range measured.

Excess permeability was also seen at the ridge in the PS films.

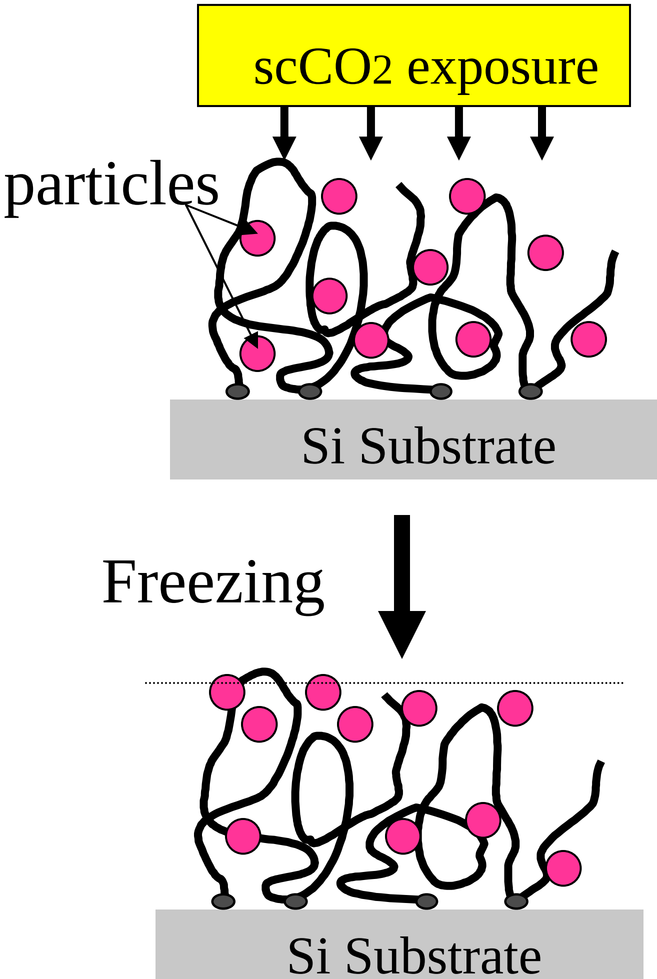
These behaviors are consistent with the swelling behavior, indicating that exposure to $scCO_2$ at the ridge increases the size of the free volumes. A great possibility to select gas permeation by tuning the size of the free volumes as a function of T, P, M_w, L_0.

Results – Pressure Dependence



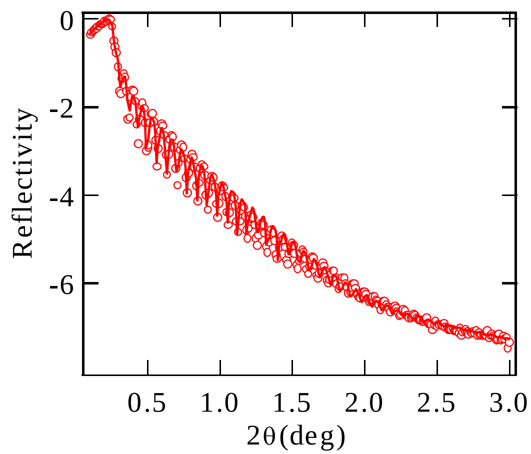
- O_2 had a distinct peak of permeability at 1200 psi for both PS and PMMA
  - Consistent with data of Koga et al, who reported an increase in penetration depth of the $scCO_2$ at this pressure

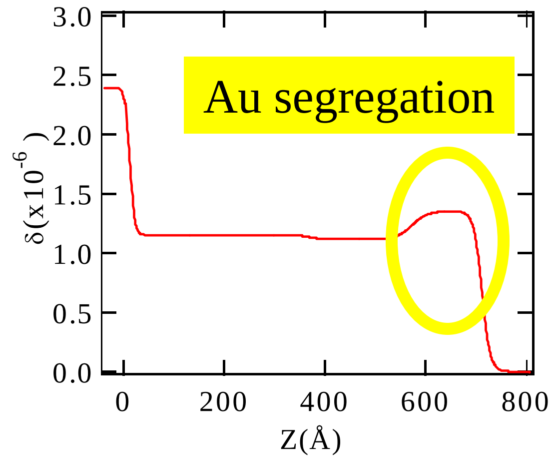
Effect of Nanoparticles on Swelling



Sample: PS (280K, 64nm)/Au (dia. 3 nm, 2% wt)
Exposed to $scCO_2$ at the ridge and then frozen.

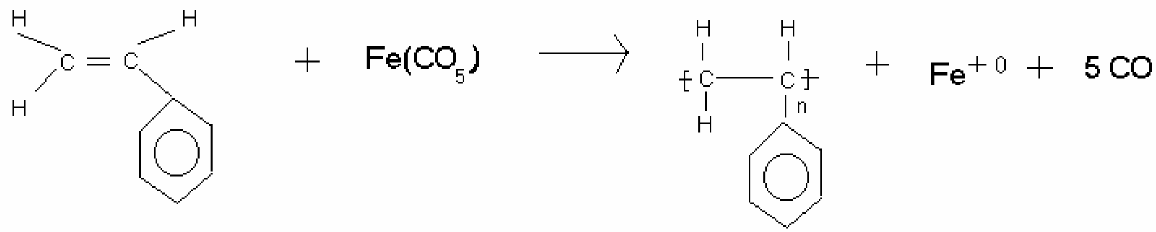
X-ray reflectivity at X10B (NSLS)
Linear dilation=0.16 with Au
=0.15 w/o Au

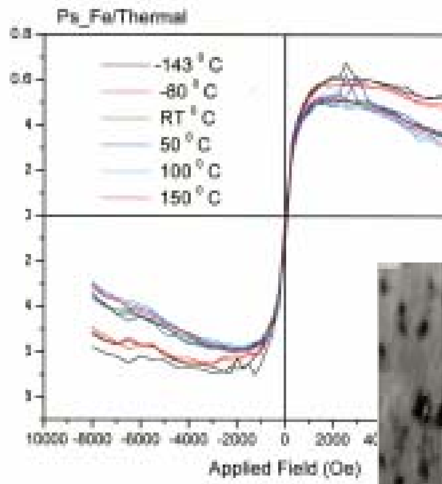


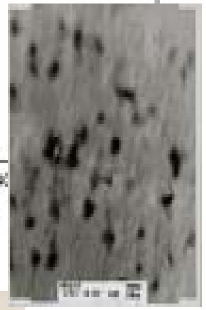


The effect of Au particles on the swelling was not significant, while Au particles aggregated to the air/polymer interface after exposed to $scCO_2$.

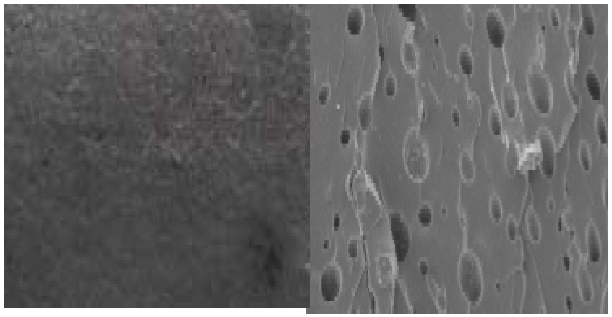
Polymer/ nanoparticles for catalysis:







- Synthesize PS in presence of Fe carbonyl results in the production of nanoparticles which further aid in catalyzing the synthesis procedure.
- Fe particles ~44 nm well dispersed in PS matrix of Mw=56K. Fe burns on exposure to air indication mostly Fe^0
- PS matrix is glassy and impermeable to most gases.
- Iron nanoparticles are used to catalyze Fischer-Tropsch (F-T) synthesis[1]



- Introduce porosity without oxidiazing the Fe particles.

- Solution: Foam with ScCO2-provides access to gas flow without compormising the catalytic activity.

Summary

Long-range density fluctuations drastically increase solubility of scCO2 in arbitrary polymers (universal solvent) .

Polymer Tg~36C is lowered on ridge as determined from D measurements.

Exposure followed by flash evaporation can be used to produce uniform low-density films. The reduction in density increases free volume resulting in:

- Low-refractive index
- Low-dielectric constant
- Lower surface Tg-improved adhesion
- Increased gas permeability.
- Easy metalization
- Improved compatibility between blends