# Fluctuation-Induced Swelling of Polymer Thin Films-CO<sub>2</sub> Systems at Gas-Supercritical Transition

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The swelling behavior of deuterated polystyrene (d-PS) thin films in contact with carbon dioxide (CO<sub>2</sub>) was monitored by means of *in-situ* neutron reflectivity at P < 700 bar. The results clearly showed an anomalous swelling maximum at the gas-supercritical CO<sub>2</sub> cross-over line while the swelling was uniform throughout the films and did not produce large voids.

KEYWORDS: supercritical carbon dioxide, polymer thin films, swelling, neutron reflectivity, critical phenomena

## §1. Introduction

With increasing temperature and pressure beyond its critical point, a one-component fluid can have its density approaching that of a corresponding liquid and acquire solvent properties much like those of liquids. Such fluids are known as *supercritical fluids* (SCFs). The unique features of SCFs are that the solvent quality of SCFs is pressure or/and temperature dependent while the diffusion coefficient is closer to that of a gas.<sup>1)</sup> By varying the external parameters of temperature and pressure, one can control the interactions between the polymer and the fluid environment. In particular, much attention has been focused on supercritical carbon dioxide,  $scCO_2$ , since CO<sub>2</sub> has a moderate critical point with  $T_c = 31.3$ °C,  $P_c = 73.8$  bar and scCO<sub>2</sub> is also an environmentally clean solvent. Supercritical  $CO_2$  has also been shown to be effective plasticizers as well as solvents for numerous polymers. Numerous studies exist on the  $CO_2$  induced swelling, plasticization and viscoelastic behavior of bulk polymers, however, very little is known about the interaction of  $CO_2$  with polymer thin films. The behavior of  $CO_2$  with thin films may differ from those in the bulk since one must also consider the effect of surface interactions and confinement.<sup>2</sup>) The introduction of a third component, such as a solvent which can compete with the polymer for adsorption to the surface introduces yet another variable in determining the properties of thin films.

Neutron reflectivity (NR) is the method of choice for quantitative determination of both the thickness, composition, and interfacial structure of polymer thin films on a nanometer scale. To achieve this we have developed a temperature and pressure controlled chamber for neutron reflectivity. In this paper we report on the *in situ* swelling behavior of thin deuterated PS films in scCO<sub>2</sub> as a function of temperature and pressure. Three different isothermal conditions at T = 20, 36, and 50 °C and one isobaric, P = 79 bar were investigated. We found anomalous swelling induced at the cross-over line from gas to scCO<sub>2</sub>.

#### §2. Experimental

Deuterated polystyrene (d-PS,  $M_w = 9.5 \times 10^5$ ,  $M_w/M_n = 1.17$ , Polymer Source, Inc.) thin films were spun cast on HF etched Si substrates with a thickness of 440 Å. The films were pre-annealed for 5 hours in vacuum at 150 °C to relax strains induced in the spinning process.

The specular reflectivity measurements were performed on the NG7 neutron reflection spectrometer. A high pressure cell was designed and built by HIP specifically for these experiments. Details on the design will be published elsewhere.<sup>3)</sup> The NR data corrected for the background scattering was analyzed by the comparing the observed reflectivities with calculated ones based on model density profiles.<sup>4)</sup>

## §3. Results and Discussion

Figure 1 shows representative NR data of d-PS for a pressurized cycle at 50 °C. The reflectivity is plotted as a function of the momentum transfer normal to the surface,  $q_z=4\pi \sin\theta/\lambda$ , where  $\theta$  is the glancing angle of incidence and  $\lambda$  is the neutron wavelength, respectively. The solid lines are fits to the single layer profiles shown in the inset. From the figure we can see that the frequency of the Kiessig oscillations, or the film thickness, first increases with increasing pressure and then decreases again when  $P > P_c$ . From the inset we can see that good fits can be obtained with uniform concentrations of CO<sub>2</sub> into the polymer layer and no preferential adsorption of either CO<sub>2</sub> or polymer occurs at the Si substrate. The persis-

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Fig. 1. Representative reflectivity data for the first pressurization process at 50 °C. Consecutive reflectivities have been offset from each other for clarity. Solid lines are reflectivity calculated from corresponding density profiles shown in the inset: solid line: P = 1 bar, dotted lines: P = 95 bar, solid-dotted lines: P = 350 bar.

tence of the Kiessig fringes to large  $q_z$  values is consistent with the small interfacial roughness ( $\sigma = 35 \text{ Å}$ ) between the swollen films and the CO<sub>2</sub> layer obtained from the fits. The roughness after complete depressurization at P= 1 bar decreases slightly to  $\sigma < 25 \text{ Å}$ , indicating that large voids such as those reported in thicker films<sup>5)</sup> do not occur. This is further confirmed by an AFM scan of the surface topography from a typical sample exposed to several cycles of in beam pressurizing and depressurizing (Figure 2), where the surface appears flat with an RMS roughness of only about 10 Å.

In Figure 3 (a) we plot the measured thickness of the films for two alternating pressurizing and depressurizing cycles at 50 °C. In order to compare to bulk measurements we also plot the change in volume.<sup>6)</sup> From the figure we can see that in the first pressurizing cycle the film thickness increases monotonically with pressure as the gas-scCO<sub>2</sub> cross-over line,  $P_{T=50\circ C}$  ( $\approx 100$  bar at 50  $^{\circ}C)^{7)}$  is approached. When the pressure was further increased above  $P_T$ , 130 < P < 700 bar, the film thickness decreased to a constant value, approximately 9 % higher than the initial value. In the depressurization cycle this thickness remained constant in the range 110 < P < 700bar and then began to increase again with decreasing pressure. The maximum thickness, which again occurred at  $P_T$ , was approximately 25 % higher than the initial film thickness,  $D_0$ . Depressurizing further resulted in a collapse of the film to a minimum thickness, at P = 1bar approximately 13 % higher than  $D_0$ . Hence the first cycle is not reversible. In order to check reproducibility of further cycles, we repeated the same pressurized and depressurized processes. As shown in Figure 3 (a), the swelling behavior of the second cycle was almost identical to the first. Further cycling also yielded identical results. Hence, except for the initial pressurization the swelling behavior in d-PS-CO<sub>2</sub> mixture is reversible. Similarly, except for the first depressurization process, the swelling behavior at 20, 36 °C was also reversible as a function of pressure. Therefore, we conclude that the film thickness



Fig.2. Three-dimensional AFM image of d-PS thin films after high-pressure reflectivity measurements.

appears to be an equilibrium quantity which is solely a function of the  $CO_2$  pressure and temperature.

In Figure 3(b) we compare the swelling as a function of pressure at 20, 36 and 50 °C for the second cycle. From the figure we can see that the shape of the swelling curve is the same for 36 and 50 °C, except that the position of the maximum is shifted to slightly toward lower pressure ( $\approx 83$  bar), which corresponds to the gas-scCO<sub>2</sub> cross-over line at 36 °C. Only minimal swelling occurs with increasing pressure at 20 °C. From the phase diagram shown in the inset of Figure 4 we can see that at 20 °C CO<sub>2</sub> undergoes a simple gas to liquid transition without becoming supercritical. Therefore, we can say that a pronounced swelling maximum only occurs only at the cross-over line between gas and scCO<sub>2</sub> rather than gas and liquid CO<sub>2</sub>.

These results can be compared to those of Zhang et al<sup>8)</sup> and Chang et al.<sup>9)</sup> who studied the swelling behavior of bulk PS at 35 °C as a function of pressure in the range up to P < 270 bar using a cathetometer. Their results showed that the swelling of PS increased linearly with pressure and then leveled off at  $\approx 10$  % for pressures in the range, 100 < P < 270 bar. No swelling maximum was seen, hence we propose that the anomalous swelling occurs only at the surface area.

This effect was further investigated by observing the swelling of the d-PS film as a function of temperature under isobaric condition at P = 79 bar. The phase diagram of  $CO_2$  is shown in the inset. The vertical dashed lines correspond to the isothermal scans shown in Figure 3 and the horizontal dashed line corresponds to the isobaric scan shown in the Figure 4. As can be seen in the inset the advantage of the isobaric experiment is that one enters into the  $scCO_2$  state from liquid state. In Figure 4 we plot the volume change of the d-PS film as a function of temperature. The liquid-scCO<sub>2</sub> and scCO<sub>2</sub>-gas cross-over lines are marked by vertical dashed lines. From the figure we can see that no swelling occurs in the deep in liquid phase  $(T \ll T_c)$ . As  $T_c$  is approached, the volume change tends to increase slightly with increasing temperature to a value estimated to be only 5 % at  $T_c$ . After passing over the scCO<sub>2</sub>-gas crossover temperarure  $(T_s)$ , the volume change drastically in-



Fig.3. (a) Pressure dependence of film thickness at 50 °C. (b) Comparison of swelling of d-PS in scCO<sub>2</sub> at three isothermal conditions.

creased to 25 % which is the same value observed previously as pressure approached to  $P_{T=50^{\circ}C}$  and  $P_{T=36^{\circ}C}$  in the isothermal scans.

In contrast to the isothermal scans shown in Figure 3 where the films collapse as the pressure is increased beyond the critical value, increasing the temperature beyond the gas-scCO<sub>2</sub> cross-over line does not collapse the films. This may be due to the fact that CO<sub>2</sub> is an effective plasticizer only at the gas-scCO<sub>2</sub> cross-over line where the initial swelling occurs. At higher temperatures  $(T_s < T << T_g)$ , the polymer becomes glassy again and high pressures are required to collapse the films.

The overall swelling results are summarized in the inset. The filled points represent conditions where a volume change exceeding 25 % is observed, while the open points represent volume changes less than 10 %. It is clear from the figure that the large anomalous swelling is observed in the thin films only at the supercritical/gas cross-over line. This effect does not seem to be related to a reduction of  $T_g$ . Thin films of rubbery polymers where  $T_g << T_s$ , such as deuterated styrene-butadiene copolymer ( $T_g = -10$  °C) and deuterated polybudadiene ( $T_g = -30$  °C) were studied and their behavior was completely identical to that of d-PS thin films, except for much higher swelling values at the gas-scCO<sub>2</sub> cross-over line ( $\Delta V/V_0 \approx 1$ ).<sup>3</sup>

At this point we can only speculate that the anomalous swelling behavior may be related to the second order nature of the supercritical/gas cross-over line which induces larger density fluctuations in the  $CO_2$  than the first order transition at the liquid/gas transition.

Experimentally these fluctuations are clearly seen in Figure 4 (unfilled points) by the sharp increase in background scattering from the  $CO_2$  at the supercritical/gas cross-over line. Adsorption of the  $CO_2$  into the viscous



Fig.4. Temperature dependence of swelling of d-PS thin film at P = 79 bar (filled circles). Open circles show the integrated scattered intensity of CO<sub>2</sub> as a function of temperature. The scCO<sub>2</sub>-gas cross-over temperature was estimated to be about 34 °C. In the inset, a schematic phase diagram of CO<sub>2</sub> near the critical point is shown.

polymer film may suppress these fluctuations thereby lowering the energy of the system.

In conclusion, we report on in situ neutron reflectivity swelling measurements of d-PS thin films in CO<sub>2</sub> at P <700 bar. The results show an anomalous large swelling maximum ( $\Delta V/V_0 \approx 25$  %) which occurs only at the supercritical/gas cross-over line. The swelling is uniform throughout the films and does not produce large voids.

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