Role of Interfacial Interactions on the Anomalous Swelling of Polymer Thin Films in Supercritical Carbon Dioxide

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ABSTRACT: It has recently been shown that thin polymer films in the nanometer thickness range exhibit anomalous swelling maxima in supercritical CO_2 (Sc-Co_2) in the vicinity of the critical point of CO_2. The adsorption isotherm of CO_2 on carbon black, silica surfaces, porous zeolites, and other surfaces, is known to exhibit anomalous maxima under similar CO_2 conditions. It is believed that because CO_2 possesses a low cohesive energy density, there would be an excess amount of CO_2 at the surfaces of these materials and hence the CO_2/polymer interface. This might cause excess CO_2 in the polymer films near the free surface, and hence the swelling anomaly. In addition, an excess of CO_2 would reside at the polymer/substrate and polymer/CO_2 interfaces for entropic reasons. These interfacial effects, as have been suggested, should account for an overall excess of CO_2 in a thin polymer film compared to the bulk, and would be responsible for the anomalous swelling. In this study, we use *in situ* spectroscopic ellipsometry to investigate the role of interfaces on the anomalous swelling of polymer thin films of varying initial thicknesses, h_0, exposed to Sc-CO_2. We examined three homopolymers, poly(1,1′-dihydroperflurooctyl methacrylate) (PFOMA), polystyrene (PS), poly(ethylene oxide) (PEO), that exhibit very different interactions with Sc-CO_2, and the diblock copolymer of PS-*b*-PFOMA. We show that the anomalous swelling cannot be solely explained by the excess adsorption of CO_2 at interfaces. ©2007 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 45: 1313–1324, 2007
Keywords: diblock copolymer; interfaces; supercritical CO_2; swelling; thin films

INTRODUCTION

Extensive attention has been paid to the use of supercritical CO_2 (Sc-CO_2) as an alternative to water or organic solvents in many polymer processes.[1–4] In addition to the environmentally benign character of CO_2, the tunable property of this supercritical fluid, through varying the pressure or temperature, enables control of its properties as a solvent. Recently, several studies of block copolymer thin films used CO_2 to induce the ordering of copolymer templates,[5–8] to control the spatial distribution of metal nanoparticles in copolymer matrices,[9] and to diffuse precursors in copolymers for the synthesis of nanoporous materials.[10] In addition to polymer processing, supercritical CO_2 has been investigated as a

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potential medium in many microelectronic thin film processes.[11–18] For example, it has been shown that CO_2 promotes penetration and removal of aqueous surfactant cleaning solutions in methylsilsesquioxane (MSQ) low dielectric constant (k) films.[15] Moreover, the cleaning and drying steps may be integrated with silylation in CO_2 to convert the hydrophilic surface after etching and ashing to a hydrophobic surface to restore the k-value.[15]

In this article, we are particularly interested in Sc-CO_2 processing of polymer thin films. Polymer thin films exhibit film thickness dependent properties. Properties that include the glass transition temperatures, wetting, and phase equilibrium are of scientific and technological interests for a range of thin film based technologies, from microelectronics to sensors. There have been a few investigations on the effects of Sc-CO_2 on the properties of thin polymer.[5–8,19–25] Pham et al. found a Sc-CO_2 induced devitrification transition in polymethyl methacrylate (PMMA) and polystyrene (PS) thin films.[21,22] Meli et al. showed that the kinetics of the morphological destabilization of PS thin films in Sc-CO_2 are suppressed.[20] Studies have also shown that the order-disorder transition (ODT) temperature of A-*b*-B diblock copolymer films in Sc-CO_2 are increased appreciably compared to the case in vacuum; on the other hand, for bulk copolymers, the effect is opposite.[5,7,8]

With regard to the behavior of CO_2 in the vicinity of its critical point, an anomalous maximum is known to occur, which was first observed in the adsorption isotherm of CO_2 on carbon black[26] and on silica surfaces.[27,28] Similar observations were made for other adsorbents,[29–32] including porous Zeolite,[31] and activated carbon.[29,32] Anomalous adsorption has been rationalized by the fact that long-range density fluctuations of CO_2, affects the Gibbs excess adsorption of CO_2 under critical conditions.[33] The swelling of polymer thin films in CO_2 also exhibits anomalous maximum in the vicinity of the critical point.[25,34–39] Specifically, Sirard et al. first discovered the anomalous maxima in the swelling isotherms of PMMA thin films in CO_2 by *in situ* spectroscopic ellipsometry.[25] Koga et al. used neutron reflectivity to explore the anomalous swelling of polymer thin films with thickness h less than 10 R_g in Sc-CO_2.[34–36,38,39] The effect of CO_2 on the welding kinetics of colloidal crystals of PS was examined by *in situ* measurement of Bragg diffraction and by scanning electron microscopy.[40] An anomalous excess in the welding rate was observed in the region where CO_2 is highly compressible.[40] It has been suggested that interfacial effects are primarily responsible for the anomalous swelling exhibited by thin polymer films. This follows from the fact that there exists an excess of CO_2 in thin polymer films compared to the bulk. This occurs for two reasons: (1) there is an excess of CO_2 at the polymer/substrate interface as well as at the CO_2/polymer interfacial region due to entropic reasons; (2) the low cohesive energy density of CO_2 would account for excess CO_2 in the interfacial region of the polymer at the CO_2/polymer interface. While additional studies have shed further insight into thin film swelling in CO_2,[37] the role of interfaces on the anomalous maximum remains unclear.

In this article, we examine the role of interfaces and polymer–CO_2 interactions on the swelling of a variety of polymer thin films exposed in Sc-CO_2. We examine a highly CO_2-philic polymer, poly(1,1′-dihydroperflurooctyl methacrylate) (PDHFOMA, also abbreviated as PFOMA) in addition to other polymer systems: PS, poly(ethylene oxide) (PEO), and the diblock copolymer of polystyrene-*b*-poly(1,1′,2,2′-tetrahydroperflurooctyl methacrylate) (PS-*b*-PTHFOMA). We are interested in a larger thickness regime (100–300 nm) than the previously examined thickness range (below 50 nm).[34,35] We show that the thickness of the swollen film exhibits a linear dependence on the initial film thickness, regardless of the polymer. The magnitude of the dependence (slope) increases with increasing CO_2-philicity of the polymer.

EXPERIMENTAL

Materials

Three homopolymers, poly(1,1′-dihydroperflurooctyl methacrylate) (PDHFOMA, or abbreviated as PFOMA), polystyrene (PS) and poly(ethylene oxide) (PEO), and the diblock copolymer of polystyrene-*b*-poly(1,1′,2,2′-tetrahydroperflurooctyl methacrylate) (PS-*b*-PTHFOMA) are studied in this work. Their molecular weights, dissolving solvents and sources are listed in Table 1.[6,41] Thin films were prepared by dissolving each polymer in its corresponding solvent (polymer concentration about 1–2 wt %) and then spin-casting the solution onto silicon wafers with a native oxide layer (Wafer World). Different thicknesses (100–

Table 1. Molecular Weights and Sources of Polymers

Polymer	Molecular Weight (kg/mole)	Casting Solvent	Source
PDHFOMA	100	1,1,2-Trichlorotrifluroethane (Freon-113)	Synthesized by Dr. Lim, see ref. 41
PS-*b*-PTHFOMA	27/127	Co-solvent mixture of Freon-113 (~80 wt %) and toluene (~ 20 wt %)	Synthesized by Dr. Lim, see ref. 6
PS	30	Toluene	Purchased from Pressure Chemical
PEO	8.6	Chloroform	Purchased from Polymer Source

300 nm) were obtained by controlling the spin rate and concentration of polymer solutions. Prior to swelling experiments, PS and PS-*b*-PTHFOMA films were annealed in vacuum ovens at 120 °C for 3 h while PEO and PFOMA films were annealed in vacuum ovens at 70 °C for 3 h to remove any residue solvent.

In Situ Swelling Experiments

Spectroscopic ellipsometry (J. A. Wollam Co.) and a customer-built high pressure cell were used to measure *in situ* swelling of polymer films in supercritical CO_2 (Sc-CO_2). The design of the cell and the experimental setup had been described elsewhere.[23] The ellipsometry angle of incidence of 70° was used for all samples. CO_2 pressure was controlled by a strain gauge pressure transducer (Sensotec). The cell was heated using four cartridge heaters (Omega) that were inserted at the top and a PID temperature controller (Omega) was used to control temperature within an accuracy of ±0.2 °C.

The experimental procedure can be described as the following. Once a sample was loaded into the high pressure cell and subsequently sealed, at least 1 h was allowed for thermal equilibration at the desired experimental temperatures (35 or 50 °C). Then CO_2 (Air Products, >99.999%) was charged into the cell using a manual pressure generator (High-Pressure Equipment Co.). At each pressure point, 5–10 min was allowed for the swollen films to reach equilibrium, and then ellipsometry angles ψ and Δ were measured.

A four-layer model (from top to bottom, a bulk CO_2 ambient layer, a swollen polymer layer, a native silicon oxide layer, and a silicon substrate layer) was used to fit the swelling data. Detailed fitting procedures can be found elsewhere.[23] The swelling percentage was determined by the following equation assuming uniaxial swelling

$$S(\%) = \frac{\Delta V}{V_0}(\%) = \frac{h - h_0}{h_0} \times 100\% \ . \qquad (1)$$

Here V_0 is the initial volume of the film, h is the thickness of the swollen film, and h_0 is the initial thickness of the polymer film determined by spectroscopic ellipsometry at 0 psig.

Ellipsometry Fitting

It is well known that the results of spectroscopic ellipsometry can be model dependent. Therefore a model that closely describes the composition of a film is crucial to assure the accuracy of measured thickness and optical constant.[42] Previous attempts have been made to model an adsorbed CO_2 layer between the swollen polymer layer and the CO_2 environment.[21,25] However, this model of a CO_2 absorbed layer proved to be unreliable, producing correlations in the fitting parameters and destroyed the uniqueness of the fitting results.[21,25] In the case of soft materials interfaces, such a layer is extremely thin compared to the film, and is not measurable with ellipsometry. This effect would be apparent in very thin films where the overall percent swelling is large.[21,25]

Data from all of the swelling measurements and the corresponding mean squared error (MSE) values are presented in tabular form in the section for "Supporting Information."

RESULTS

The results of experiments performed at 35 °C are first discussed. The swelling experiments were conducted by performing alternating pres-

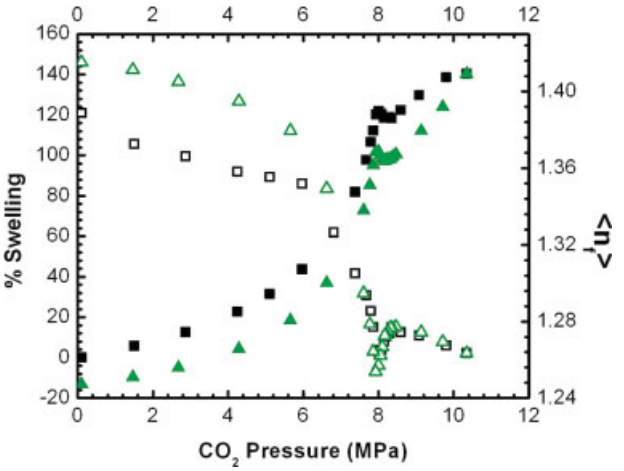

Figure 1. Representative swelling isotherm and the change in average refractive indices at 35 °C for an $h_0 = 109$ nm PFOMA film. Filled symbols (■, ▲) represent % swelling and open symbols (□, △) represent the change in average refractive indices. Squares (■, □) represent data obtained during the pressurization run and triangles (▲, △) represent data obtained during the depressurization run. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

surization/depressurization runs, where both film thickness and average reflective index of the CO_2-swollen film were recorded.[23,25] Figure 1 shows a representative isotherm as well as the changes in average refractive indices at 35 °C for an $h_0 = 109$ nm PFOMA film. Several observations may be made. First, the swelling isotherm exhibits an anomalous maximum, which also corresponds to a sharp minimum in the refractive index curves. The pressure at which this anomalous swelling shows, 8.0 MPa, is in excellent agreement with the location of the maximum in the compressibility of CO_2, that is, density fluctuation, $(\partial\rho/\partial P)_r$, at 35 °C.[25,34,35] Secondly, the swelling isotherms for PFOMA at low pressures possess positive curvature (concaved up), suggesting that PFOMA films reside in a rubbery state.[23,25] Because the glass transition temperature of bulk PFOMA is 50 °C at ambient conditions,[6] and can be highly depressed in Sc-CO_2, it is not surprising that PFOMA films are rubbery at 35 °C in CO_2. Thirdly, hysteresis between sorption and desorption runs was observed in both the swelling isotherm and the change in average reflective index. Hysteresis is often due to the nonequilibrium state of the initial sorption run for glassy polymers.[25] However, since PFOMA is believed to be in rubbery state, this discrepancy between sorption and desorption is more likely to be the result of PFOMA dissolution in CO_2. Dissolution rates of fluorinated polymer films in CO_2 are found to decrease significantly with decreasing films thicknesses.[43] This might be due to the more dominant role of the polymer/substrate interaction.[43] Although some dissolution is expected and evident in PFOMA films with thickness below 300 nm, its effect on the sorption isotherms is not obvious. Multiple swelling experiments of PFOMA films shows consistent results at 35 and 50 °C. (These results will be shown next). The influence of dissolution will not be discussed in this article.

Figure 2(a) shows the swelling isotherms for four PFOMA films with various thicknesses at 35 °C. The four isotherms for these films of different thicknesses are consistent. At low pressures, the percent swelling increases slightly with decreasing film thickness. This small swelling enhancement for thinner films in Sc-CO_2 is reasonable because strong enhancement in swelling of polymer thin films was only found when the thickness of film is below 10 R_g ($h_0 < 10\ R_g$).[35] On the other hand, the influence of film thickness on the anomalous swelling maximum is distinct. From Figure 2(a), it is evident that the two thinner films have smaller swelling maxima (S_{max}) than the two thicker ones. The biggest S_{max} was observed for the $h_0 = 179$ nm film.

To place the results for the anomalous swelling maxima in perspective, a baseline can be constructed by interpolating the data on either side of the anomalous maxima as shown by the solid lines in Figure 2(b,c).[25] An effective excess swelling thickness (h_{exc}) at the maxima can be defined by

$$h_{exc} = h_0 \times (S_{max} - S_{base}). \quad (2)$$

Here S_{base} is the interpolated swelling percentage from the baseline at the pressure where S_{max} is observed. Table 2 lists the values of S_{max}, h_{exc} and the proportional excess swelling, Δ_{exc} for each sample. It is clear that h_{exc} increases as increasing film thickness, consistent with the results of Sirard et al. on the swelling PMMA films in Sc-CO_2.[25]

It is noteworthy that Koga et al. used the absolute values of S_{max} to examine the effect of film thickness on anomalous swelling.[34,35] They found that S_{max} decreases as increasing film

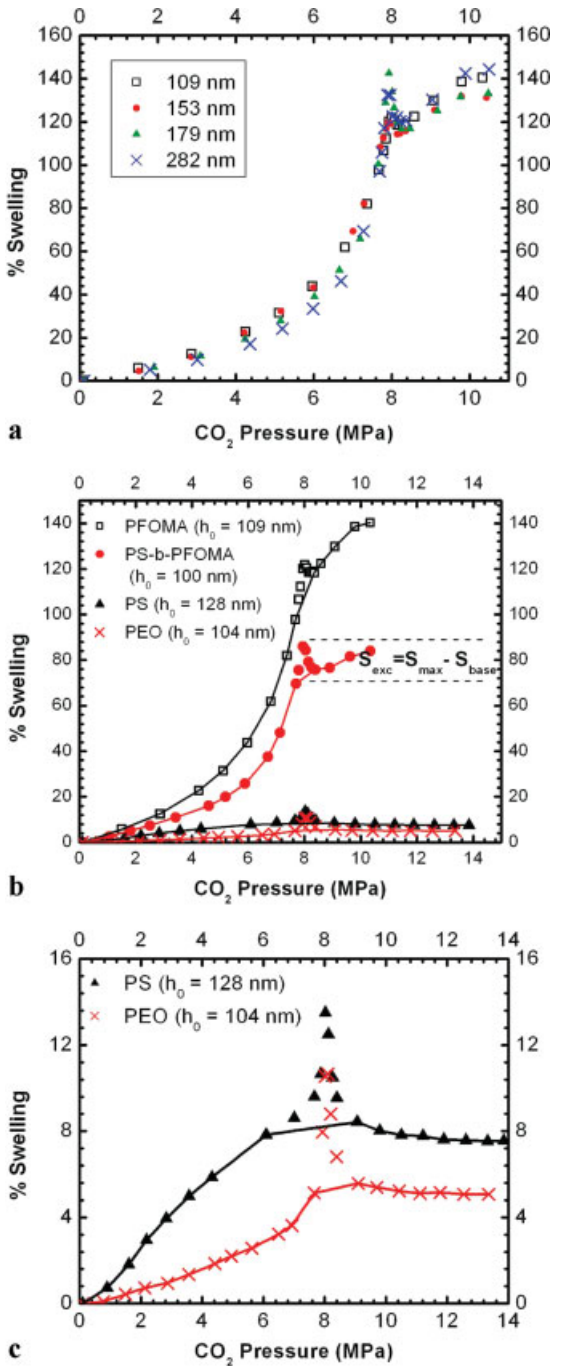

Figure 2. (a) Swelling isotherms for PFOMA films with various thicknesses at 35 °C. (b) Swelling isotherms at 35 °C for various polymer films with thickness around 100 nm. The solid line in each isotherm represents the interpolated baseline, which is used to estimate the excess % swelling at the anomalous peak. (c) Swelling isotherms of PS and PEO films with magnified normal axis. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

thickness and levels off when h_0 approaches 8 R_g.[34,35] Here, we focus on a much thicker regime, and we examine both S_{max} and h_{exc} with different film thicknesses. Because h_{exc} is strongly depended on the initial film thickness ($h_{exc} = h_0 \times (S_{max} - S_{base})$), as film thickness increases (h_0 increases), even if S_{max} decreases (as shown by Koga et al.[34,35]), h_{exc} would still increase (as Table 2 shows).

To examine the effect of polymer–substrate and polymer–CO_2 interactions on anomalous swelling maxima, we studied two other homopolymers, PS and PEO as well as the diblock copolymer of PS-*b*-PTHFOMA. Figure 2(b) compares the swelling isotherm for all four polymers at 35 °C, from which h_{exc} and Δ_{exc} are estimated and listed in Table 2. All four isotherms show the characteristic sigmoidal shape as seen in other polymer–CO_2 systems.[44] As expected, the isotherm for the diblock PS-*b*-PTHFOMA lies in between those of PS and PFOMA. The curvatures of the swelling isotherms for PFOMA and PS-*b*-PTHFOMA at low pressure values are positive (concaved up), indicating that both films reside in the rubbery state. On the other hand, the swelling isotherm for PS [Fig. 2(c)] at low pressure values are slightly negative (concaved down), which is consistent with the fact that the plasticization pressure (P_g) at 35 °C for h_0 = 90 nm PS was found to be 5.2 MPa.[20,21] However, with regard to PEO, another dimension of complexity needs to be considered and will be discussed next.

It is well known that PEO is a crystalline polymer and the crystallization of PEO or copolymers with PEO as a constituent has been widely studied.[45–48] Sc-CO_2 can depress the glass transition temperature of glassy polymers significantly; similarly, it has been found that both the crystallization temperature (T_{cr}) and the melting temperature (T_m) of crystalline polymers decrease with increasing CO_2 pressure.[48–50] Recently, Madsen employed NMR spectroscopy to study bulk PEO exposed to Sc-CO_2 and found T_m (PEO) is depressed from 63 °C at atmospheric pressure to 43 °C at Sc-CO_2, 8.1 MPa.[48] The coupling between crystallization and sorption had also been explored, and it was found that the extent of crystallization can affect Sc-CO_2 sorption by reducing both the equilibrium solubility and the diffusivity of Sc-CO_2 in the polymer.[49]

In our study, the PEO films remain in a partially crystalline state throughout the entire pressure range, leading to an extremely small

Table 2. Analysis of Anomalous Swelling Maximum for Various Polymer Films at 35 °C

Polymer	Initial Film Thickness h (nm)	Pressure at Max. Swelling (MPa)	Max. % Swelling S_{max}	Max. Excess % Swelling S_{exc}[a]	Max. Excess Thickness h_{exc}[b] (nm)	Proportional Max. Swelling Δ_{exc}[c]
PDHFOMA	109	8.0	122	14	15	0.11
	153	7.9	120	18	28	0.15
	179	7.9	143	37	65	0.26
	282	7.9	133	28	80	0.21
PS-*b*-PTHFOMA	100	8.0	86.0	14	14	0.17
PS	128	7.9	13.5	5.0	6.4	0.37
PEO	104	8.1	10.7	5.4	5.6	0.51
PMMA[25]	88	8.0	23	3	2.5	0.13
	321	8.0	25	5	16	0.2

[a] $S_{exc} = S_{max} - S_{base}$
[b] $h_{exc} = h_0 \times S_{exc}$
[c] $\Delta_{exc} = S_{exc}/S_{max}$

degree of sorption. For example, as shown in Figure 2(c), at the highest pressure, 13.8 MPa, PEO film swells 5% at 35 °C. Interestingly, Weidner et al. reported that the solubility of CO_2 in amorphous PEO (4 kg/mol) is as high as 22 wt % at 55 °C and 15 MPa.[51] Because the degree of CO_2 swelling in most polymers increases with decreasing temperature,[52] the small degree of swelling reported in our study is the result of crystalline PEO films. Further evidence showing T_m (PEO) is above 35 °C at 13.8 MPa is that the swelling isotherm levels off at high pressures ($P > 10$ MPa) in the absence of a distinct change in slope; this indicates the absence of a phase transformation at high pressures. Despite of the crystalline state of our PEO films and the associated unusually small degree of swelling, our key finding is, nevertheless, that anomalous swelling maximum is evident in crystalline polymer films.

Table 2 summarizes the results of the anomalous swelling maximum experiments for all polymer films; for comparison, the results by Sirard et al. on PMMA[25] are included as well. It is clear that the pressure at which anomalous swelling maxima are observed for all films resides in the pressure regime of 7.9–8.1 MPa. Among the polymer films with $h_0 \sim 100 \pm 10$ nm (for PS film, $h_0 = 128$ nm) examined in this article, the trend for both the absolute degree of swelling (S_{max}) and for the effective excess swelling thickness (h_{exc}) in CO_2 is PFOMA > PS-*b*-PTHFOMA > PS ~ PEO. However, if we consider Sirard's data on PMMA,[25] then PMMA swelling percentage is between those for PS and PS-*b*-PTHFOMA, while it possesses the smallest h_{exc} of all polymers. Consistently, Koga et al. also found that PMMA has an enormously smaller anomalous swelling maximum than PS and PB, while PMMA swells the most among the three at other pressures.[34,35] It is also instructive to compare the proportional excess swelling at the anomalous maximum, Δ_{exc}, for different polymers in Table 2. It is evident that the trend for Δ_{exc} is PFOMA < PS-*b*-PTHFOMA < PS < PEO, just opposite to that of S_{max} and h_{exc}. All these results will be discussed in detail later.

The results obtained at 50 °C are now discussed. Figure 3 shows the swelling isotherm for three PFOMA films, of different thicknesses, at 50 °C. The shapes of the isotherms are relatively independent of film thickness. The anomalous maxima are suppressed at this temperature, compared to those at 35 °C, but they do exist. They occur at a higher pressure than at 35 °C and extends over a broader range of pressure; this was identified in an earlier publication.[25] The swelling isotherms of PFOMA films at 35 and 50 °C are plotted versus CO_2 activity in Figure 4(a). The swelling versus activity curves of all seven isotherms representing the PFOMA films superpose into a single curve. These data further indicate that the PFOMA films reside in the rubbery state at both temperatures. Additional swelling versus CO_2 activity plots for PS-*b*-PTHFOMA and PS films are shown in Figure 4(b,c), respectively. In the case of PS [Fig. 4(c)], at lower activities, a small discrepancy between the two isotherms is apparent.

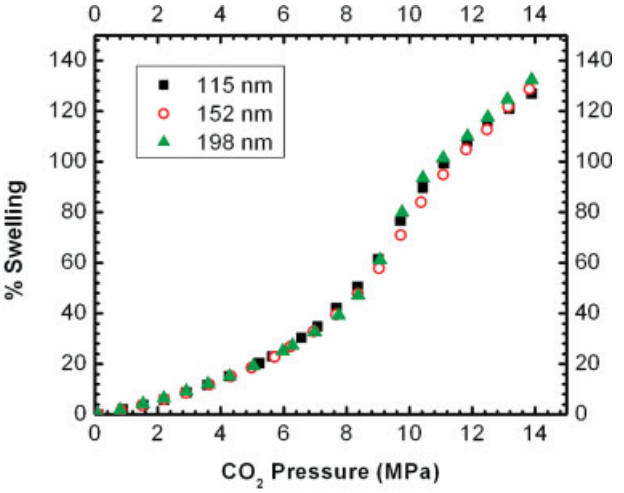

Figure 3. Swelling isotherms for PFOMA films with various thicknesses at 50 °C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

This is because PS undergoes a glassy state to a rubbery state transition. The anomalous swelling maxima are clear for PS films at both temperatures.

The swelling isotherms of PS thin film are compared with those of bulk PS from other groups in Figure 5(a,b).[44,53] It is evident that below the anomalous maximum, PS films with thickness $h_0 \sim 130$ nm swell $\sim 1\%$ more than the bulk analogues. While this slight swelling enhancement in PS films compared with bulk is consistent with the data from Koga et al.[35] and Sirard et al.[23] at lower pressures, the difference between bulk and thin films is significant in the vicinity of the critical point.

DISCUSSION

The role of interfaces on the anomalous swelling of polymer thin films remains an open question, and there is not much agreement among different groups.[25,37,54–56] Some attribute the anomalous swelling to the surface excess adsorption of CO_2,

$$\Gamma_{ex} = \int_0^\infty (\rho(z) - \rho_{bulk})\, dz. \qquad (3)$$

We briefly alluded to this in the experimental section. In this equation, z is the distance from the substrate ($z = 0$ represents the substrate

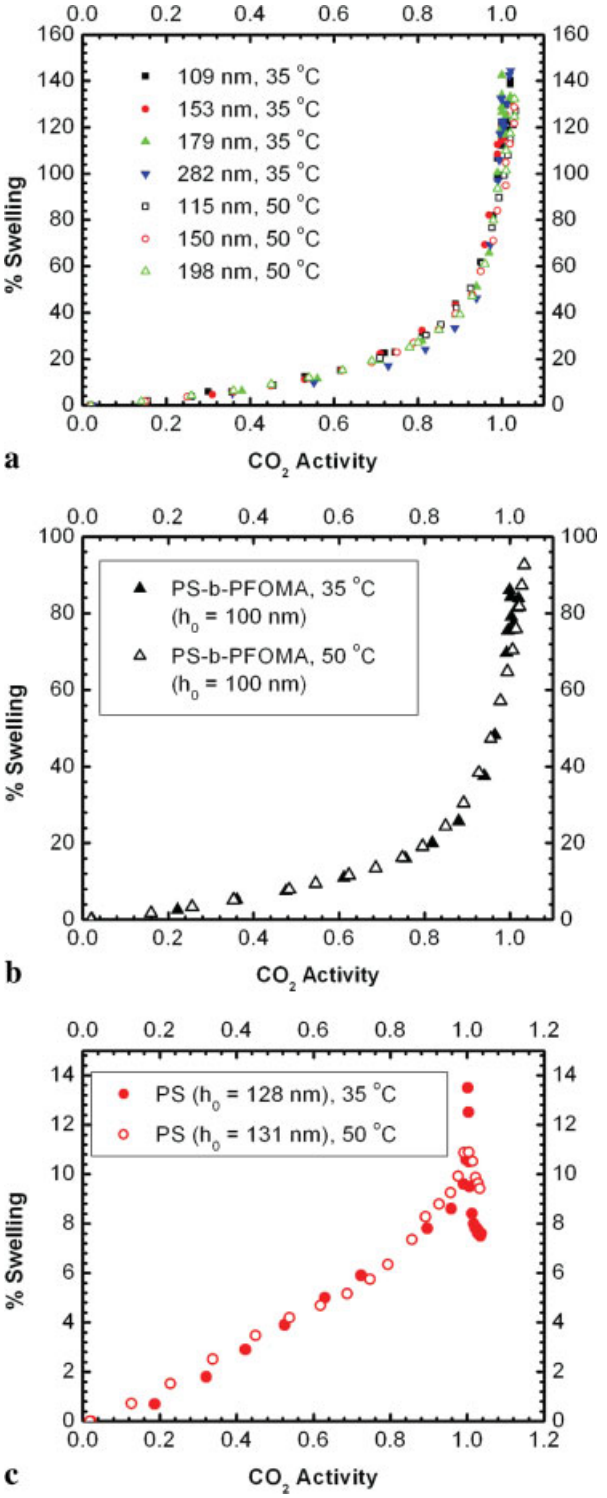

Figure 4. (a) Swelling of PFOMA films with various thicknesses at both 35 °C and 50 °C plotted against CO_2 activity. (b) Swelling of PS-*b*-PFOMA films plotted against CO_2 activity. (c) Swelling of PS films plotted against CO_2 activity. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

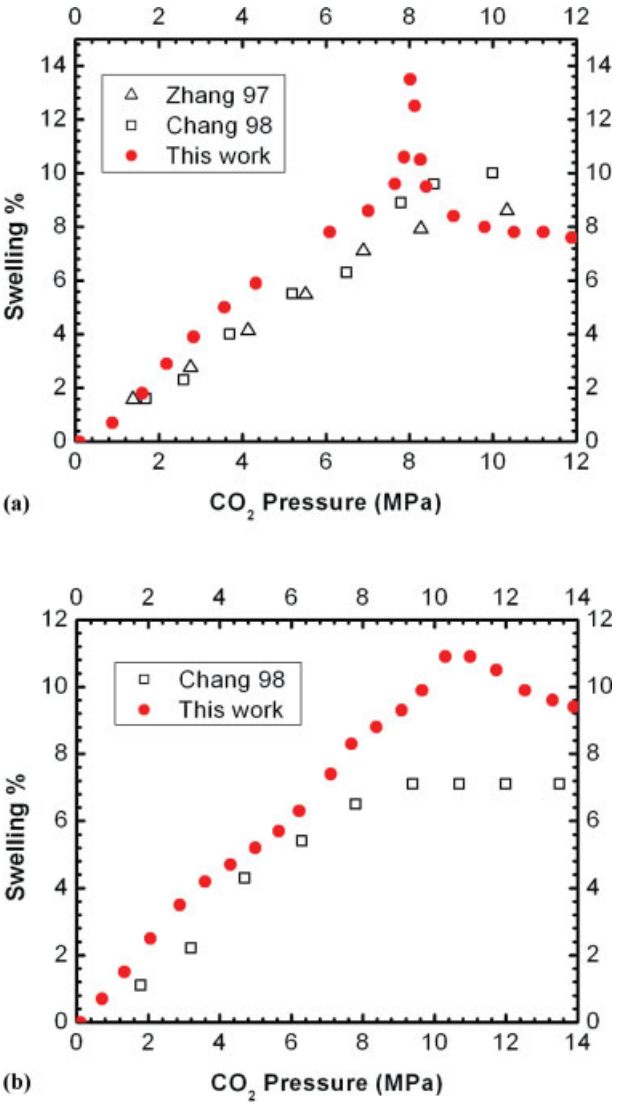

Figure 5. Comparison between our PS swelling isotherms at 35 °C (a) and 50 °C (b) with two reference works. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

interface), $\rho(z)$ is the local density of CO_2 at distance z, and ρ_{bulk} is the density of the bulk CO_2. Because CO_2 has low cohesive energy density, the interaction between CO_2 and the surface may be expected to exceed the intermolecular attraction between pure CO_2 molecules. Consistently, there is a difference between $\rho(z)$ and ρ_{bulk} ($\rho(z) > \rho_{bulk}$), which leads to excesses of CO_2 at the surface. However, if the anomalous swelling maximum is solely caused by this surface excess CO_2 wetting layer, then h_{exc} should be relatively independent on the initial film thickness. On the contrary, Table 2 indicates that the excess swelling thickness increases with increasing film thickness; clearly the observed excess swelling cannot be explained by the surface excess CO_2 adsorption alone. A theoretical study by Wang and Sanchez[56] determined the thickness of the surface excess CO_2 adsorption layer to be around 2 nm, which is much less than the observed h_{exc}. It turns out that this 2 nm thick surface excess CO_2 layer is too thin to be accurately determined by ellipsometry, particularly with the small contrast. Attempts to add CO_2 adsorption layer into the ellipsometry-fitting model only produce larger uncertainty and compromise the uniqueness of the fitting results.

Another factor that may contribute to anomalous swelling maximum is the excess CO_2 adsorption on the substrate interface. Recent studies[54,55] on moisture adsorption in photoresist films have pointed out that the attractive interaction between water and hydrophilic surfaces causes an accumulation of water on the polymer/silicon interface. As a result, the swelling of photoresist films by moisture increases as decreasing film thickness.[54,55] However, similar to the approach replying on surface CO_2 wetting layer, attempts to explain the anomalous swelling maximum solely by CO_2 adsorption on polymer/substrate interface cannot count the observed thickness dependence of h_{exc}.

The information discussed in the preceding paragraph (the thickness dependence) indicates that the anomalous swelling observed in polymer thin films cannot be solely due to interfaces. However, it is true that there would be excess CO_2 in thin films compared to the bulk, because the entropy would lead to excess molecules at the interfaces. The comparison between PS films and bulk PS, Figure 5, reveals a slight swelling enhancement in thin films compared to the bulk. Moreover, the proportional maximum excess swelling, Δ_{exc}, exhibits the following trend with the polymers from Table 2: PFOMA < PS-*b*-PTHFOMA < PS < PEO. This trend is opposite to that of S_{max}, which be understood by considering the fact that enhanced swelling at interfaces can be more dominant for polymer films that do not have a strong affinity with CO_2.

For a more quantitative assessment of interfacial effects on the anomalous swelling maximum, a simple model is now proposed. Let's simply assume that a polymer film with thickness h_0 is composed, from top to bottom, of a CO_2/polymer interfacial layer h_0^{free}, a middle layer h_0^{m}, and a polymer/substrate interfacial layer h_0^{sub}. By defin-

Table 3. Summary of the Initial and Swollen Film Thicknesses at the Anomalous Maximum for Various Polymer Films in CO_2, 35 °C

Polymer	Data Source	Initial Film Thickness, h_0 (nm)	Swollen Film Thickness, h (nm)
PFOMA	This study	109	242
		153	327
		179	435
		282	657
PMMA	Koga et al.[35]	9.8	14.2
	Sirard et al.[25]	88	108
		321	402
PS	This study	128	145
	Koga et al.[34]	14	19
		17	22
		29	34
		60	66
		80	87
		107	117
		120	130
		44.5	51
PB	Koga et al.[35]	18	30
		32	51
		62	96
		99	153
		17	28
		31	49

ing a swelling coefficient (α) for each layer, the initial thickness (h_0) and the thickness after swelling (h) can be expressed by

$$h_0 = h_0^{\text{free}} + h_0^{\text{m}} + h_0^{\text{sub}}, \tag{4}$$

and

$$\begin{aligned} h &= h^{\text{free}} + h^{\text{m}} + h^{\text{sub}} \\ &= (1+\alpha_{\text{free}})h_0^{\text{free}} + (1+\alpha_{\text{m}})h_0^{\text{m}} + (1+\alpha_{\text{sub}})h_0^{\text{sub}}, \end{aligned} \tag{5}$$

Combining eqs 4 and 5 leads to

$$h = Ah_0 + B, \tag{6}$$

where $A = 1 + \alpha_{\text{m}}$ and $B = (\alpha_{\text{free}} - \alpha_{\text{m}})h_0^{\text{free}} + (\alpha_{\text{sub}} - \alpha_{\text{m}})h_0^{\text{sub}}$.

Equation 6 indicates that at a certain pressure, a linear relationship exists between the swollen film thickness, h, and the initial film thickness, h_0. The slope of this linear relationship is related to the swelling coefficient of the middle layer (α_{m}), while the intercept is dependent on the interfacial interactions (α_{free} and α_{sub}). Using the data in Table 3, a plot of h and h_0 is made in Figure 6, which confirms that regardless of the polymer, the swollen film thickness at the anomalous maxima increases line-

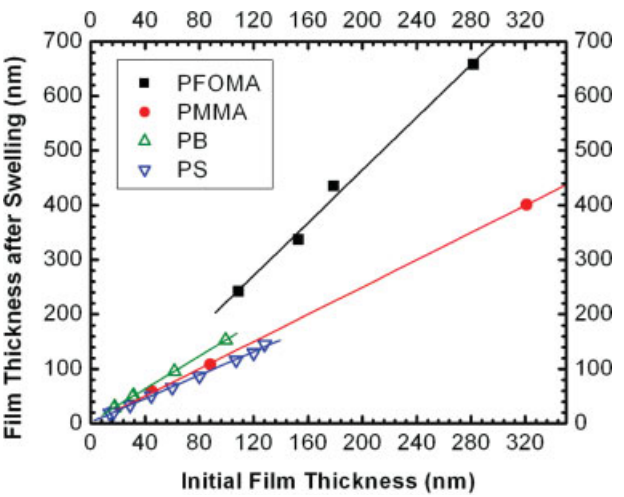

Figure 6. Film thicknesses for the swollen films at the anomalous maximum (7.9–8.0 MPa) versus the initial film thicknesses for a variety of polymer films at 35 °C. Linear lines are the fit from the experimental data. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table 4. Summary of the Fitting Results Obtained from Figure 6

Polymer	Slope $(1 + \alpha_m)$	α_m	Intercept	Linearity R^2
PFOMA	2.42	1.42	−18.9	0.993
PMMA	1.25	0.25	0.602	0.999
PS	1.08	0.08	2.80	0.998
PB	1.51	0.51	3.35	0.999

arly with the initial film thickness. The slopes and intercepts are summarized in Table 4, where the values of α_m are also listed. PFOMA has higher α_m than all other polymers, while PS processes the lowest α_m, which are expected to be based on the polymer/CO_2 interactions.

For internal consistency, the same analysis is applied to PFOMA films with various thicknesses at pressures different from the anomalous swelling maximum. Figure 7 shows fitted curves at 11 pressures distinct from the anomalous maximum. Figure 8 summarizes the results of α_m from fitting the data in Figure 7. It is clear that α_m increases with increasing CO_2 pressure and exhibits a maximum at a pressure $\sim$ 8.0 MPa. This observed maximum in α_m further confirms that the swelling of the middle layer also exhibits an anomalous behavior, which can be understood as follows. Because the phase stability of a binary mixture decreases with its compressibility,[25,57] the solubility of CO_2 in the polymer film decreases abruptly near the region where the compressibility of CO_2 is at maximum. As a result, CO_2-rich phase and polymer-rich phase may coexist in the film, leading to the observed anomalous maximum in α_m. Clearly, the anomalous maximum in α_m further confirms that anomalous swelling is not solely due to the excess adsorption of CO_2 at interfaces.

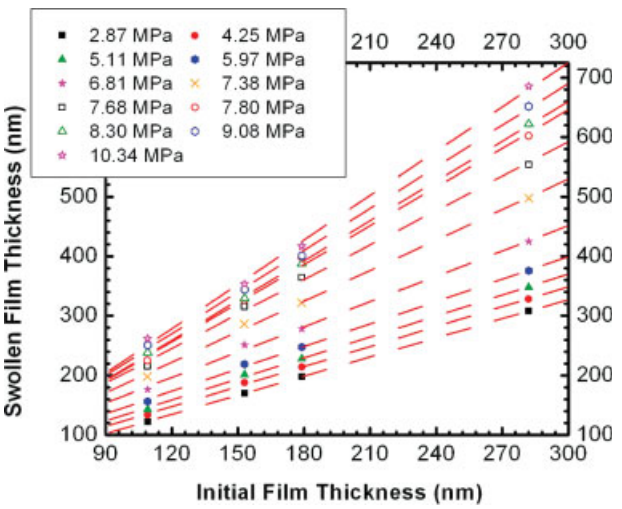

Figure 7. Film thicknesses for the swollen films versus the initial film thicknesses at pressure points other than the anomalous maximum for PFOMA films at 35 °C. Linear lines are the fit from the experimental data.

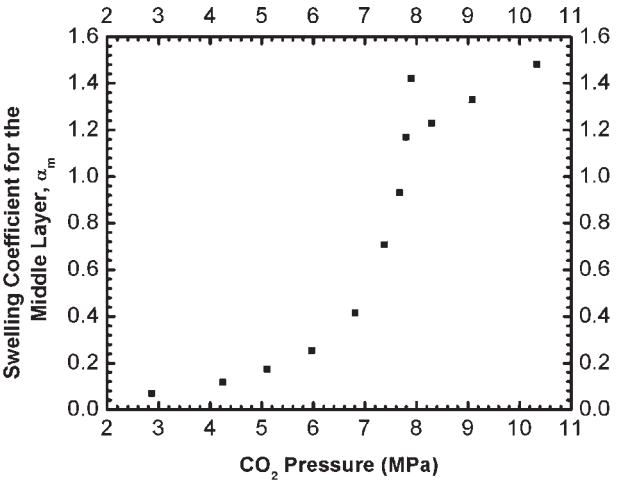

Figure 8. The swelling coefficients for the middle layer, α_m, versus CO_2 pressure for PFOMA films at 35 °C.

CONCLUSIONS

In situ spectroscopic ellipsometry was employed to examine the swelling of PFOMA, PS, PEO, and PS-*b*-PFOMA thin films in Sc-CO_2 with the goal to further understand the role of interfaces on anomalous swelling maximum. The experimental data of the dependence of anomalous maximum on polymers and film thicknesses from this study and several references[25,34,35] can be rationalized by considering a three-layer model, which indicates that the anomalous swelling maximum cannot be solely explained by the excess adsorption of CO_2 at interfaces (α_{free}, α_{sub}). Instead, the swelling coefficient of the interior of the film (α_m) plays an important role; it exhibits an anomalous swelling maximum, consistent with the behavior of the film. Clearly, this study further clarifies the role of interfacial interactions on the anomalous swelling maxima exhibited by polymer thin films exposed to compressible fluids.

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