Long Range Concentration Gradients at the Free Surface of Polymer Films Swollen by Carbon Dioxide

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ABSTRACT: The local swelling through the thickness of a polymer film induced by exposure to carbon dioxide is assessed using in situ selective modification of a swollen amphiphilic polymer template. The swollen film is selectively modified by condensation of tetraethylorthosilicate within the hydrophilic domains. Monitoring the size of pores resulting from the unmodified hydrophobic domains provides a measure of the local CO_2 concentration within the film. A maximum in the average pore size is obtained near the density fluctuation ridge with a gradient in pore size extending approximately 150 nm into the film from the free surface and a short (<10 nm) gradient at the buried interface. Far from this maximum, the pore size through the thickness of the film is uniform.

Introduction

The physical properties of polymer thin films are known to be impacted strongly by their interfaces.[1] These interfacial effects are manifested as gradients in material properties such as the glass transition temperature (T_g)[2] or physical aging.[3] The glass transition of polymer thin films has been an active research topic since the reported thickness dependence of T_g in thin films by Keddie et al.[4] The interaction of the polymer with a substrate is known to impact the T_g of thin films,[5,6] but the free surface is also important.[1] More recently, there have been some efforts in determining how the repeat structure impacts the T_g of thin films with some correlations with cooperativity reported.[7−9] A more comprehensive picture has been reported in several review articles.[10,11] de Gennes predicted that the measured changes in the T_g of thin films was actually resulting from a gradient of T_gs from the interfaces;[12] Torkelson and co-workers have since experimentally confirmed this prediction.[2] Other physical properties of polymers are altered when confined in thin films such as local chain dynamics,[13,14] physical aging,[15] thermal expansion,[16] polymer mobility,[17] and modulus[18,19] as examples.

Additionally, the potentials imposed by the interfaces can alter the local solubility of small molecules leading to enhancement in thin film swelling relative to the bulk.[20,21] For polymer film swelling from moisture, this generally results in a relatively short-range interaction leading to observation of thin film deviations only for films thinner than 50 nm. These deviations have been quantitatively attributed to accumulation of water at the buried interface in excess of the bulk water solubility in the polymer.[21] However, relatively thick (<500 nm) polymer films swollen with CO_2 near the density fluctuation ridge exhibit tremendous enhancements in CO_2 solubility in comparison to the bulk,[22,23] resulting in a maximum in isotherm swelling as a function of pressure. It is not clear how density fluctuations within the CO_2 fluid phase would lead to enhancements in the solubility of the CO_2 within the polymer film, but experimentally there is a definite correlation between density fluctuations and the anomalous swelling of polymer films.[24] However, thick coatings of PDMS do not exhibit these deviations in CO_2 solubility from the bulk.[25] Unlike moisture induced swelling,[21] this anomalous maximum in the CO_2 swelling is not strongly dependent upon the substrate chemistry.[26] Neutron reflectivity measurements of the swollen films have not been able to quantify any concentration gradients, but there does appear to be some suppression of the Kiessig fringes, which suggests the presence of a gradient.[22,24] The density fluctuation ridge[27] has been cited as the source of the anomalous swelling.[22] From thermodynamics, the fluctuations in the density of a fluid is proportional to the product of the isothermal compressibility and temperature.[28] The isothermal compressibility approaches infinity as the critical point of a fluid is approached; thus at conditions (T, P) near the critical point, there exists large fluctuations in the fluid phase density. However, why fluctuations in fluid density would result in a maximum in swelling of polymer films, but not in the bulk, has not been adequately explained to date. Sanchez and co-workers used the Sanchez−Lacombe equation of state (SLEOS) along with gradient theory[29] to attempt to elucidate the origins of the enhanced swelling in thin films. These calculations suggested that the source of the swelling maximum is an adsorbed dense CO_2 layer on top of the polymer film with less than 1 nm gradient into the polymer film. The calculated thickness of the adsorbed layer is not consistent with the large swelling determined experimentally[26] as might be expected for the SLEOS. Generally the polymer physics are accurately depicted for SLEOS, but the adsorbed thickness of CO_2 on silica at the anomalous maximum[23] is still not sufficient to account for the anomalous swelling of polymer films reported in the literature. Due to the attractive nature of CO_2 with glass, the adsorption in this case should be more favorable than for polystyrene surfaces which lack specific attractive interactions with CO_2. Therefore, a phenomenon other than solely an adsorbed CO_2 layer is likely responsible for some of the anomalous swelling; it most likely is a heterogeneous distribution of CO_2 through the film thickness.

The CO_2 distribution within polymer films has implications in energy efficient separations using thin film asymmetric polymeric membranes or mixed matrix membranes.[30] Given the large length scales over which the anomalous swelling occurs (films greater than 500 nm thick have shown a maximum in swelling), neutron reflectivity is likely limited by the length scale of a gradient that is several orders of magnitude larger than the probing wavelength. Additionally, spectroscopic ellipsometry studies using longer wavelengths have not been able to quantify the extent of swelling as a function of depth through the thickness of the film even at the anomalous maximum.[23] To address the visualization of the CO_2 concentration profile, an alternative strategy has been implored here based upon in situ modification of a swollen amphiphilic polymer template following the work of Watkins and co-workers.[31,32] Briefly, the films were swollen with CO_2 containing dilute concentrations

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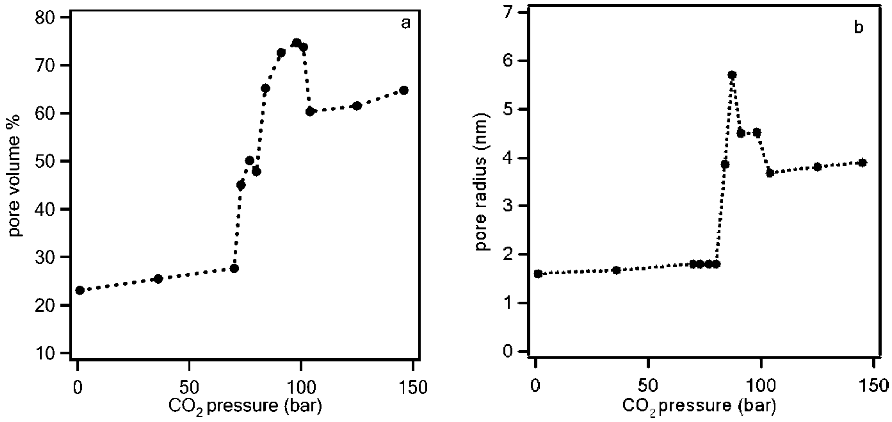

Figure 1. Synthesis pressure dependence on (a) film porosity and (b) average (mode) pore size after depressurization of the resultant porous silica film. The pore size is calculated from ellipsometric porosimetry using the Kelvin equation.

of water and tetraethylorthosilicate (TEOS) to form a rigid silica network within the hydrophilic domains. The low concentration of the reactive species decreases the reaction rate and allows swollen hydrophobic domains to be templated. The silica domains are assumed to stay rigid during depressurization, thus the pores templated by the swollen hydrophobic domains can be interrogated at ambient pressure. How the templated pore size is spatially impacted through the depth of the film provides a picture of the swelling of the hydrophobic domains as a function of depth while the system was still under pressure. These efforts demonstrate for the first time that gradients in the CO_2 concentration are present in polymer films swollen near the density fluctuation ridge; these gradients extend from both the free and buried interfaces.

Experimental Section

The template films, a blend of 14 wt% polyhydroxystyrene (DuPont Electronic Materials; $M_n = 8$ kg/mol), 81 wt% poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) (BASF; Pluronic F108), and 5 wt% *p*-toluenesulfonic acid (Sigma Aldrich), were spun coat onto clean silicon wafers from an ethanol:water (9:3.6) mixture. This blend enables long-range order and improvements in the uniformity of the size of the self-assembled domains.[33,34] All template films were nominally 500 nm thick. The films were then exposed to humidified (saturated, < 0.06% water) CO_2 containing approximately 0.03% by volume tetraethylorthosilicate (Sigma Aldrich; TEOS) at 60 °C. This temperature was chosen to avoid any ambiguities resulting from the crystallization of the PEO phase of the template. The CO_2 swells the film, which is then slowly converted to a nanostructured silica-polymer hybrid via condensation of the TEOS. All the reactions were allowed to proceed for 30 min. Following the reaction, the vessel was slowly depressurized to prevent foaming or other deformations in the film morphology. A postsynthesis aging in a sealed vessel with saturated water vapor at 90 °C for 2 h was used to enhance silica network formation. The template was removed via calcination at 450 °C for 5 h at a heating rate of 1 °C/min in air to yield a mesoporous silica film. For all conditions examined, there is no change in the film morphology (body centered cubic spheres).

Film Characterization. Ellipsometry was used to characterize the evolution of the film thickness and refractive index in processing with a UV−visible-NIR (240−1700 nm) variable angle spectroscopic ellipsometer (VASE M-2000, J.A. Woollam Co.). To fit the data, a Cauchy model was found to effectively approximate the optical properties of the polymeric template, the silica−polymer nanocomposite after reaction, and the mesoporous film. The Bruggemann effective medium approximation (BEMA) model was used to calculate the film porosity (*P*) from the refractive index of the film. This model assumes that the mesoporous film consists of silica framework and voids and a fixed refractive index for glass silica skeleton.[35] The pore size distribution (PSD) of the film was determined using ellipsometric porosimetry (EP) by utilizing toluene (Aldrich) as the probe solvent. The partial pressure of toluene was controlled using two mass flow controllers (MKS) for saturated toluene and air streams. Both adsorption and desorption isotherms were measured. To calculate the PSD, the EP data were analyzed on the basis of the change in refractive index as a function of relative pressure.[36] TEM cross sections were prepared by manual polishing of a cut section of the film/substrate and subsequent imaging with a JEOL 2010F operating at 200 keV.

Results and Discussion

To provide a baseline for the CO_2 induced swelling of the template, a mesoporous silica film was synthesized utilizing only the vapor pressure of the reactants with the identical template; all changes in pore size from CO_2 swelling are referenced with this sample. The swelling of the polymeric template by CO_2 increases the porosity of the synthesized films as would expected due to dilation of the hydrophobic domains. Figure 1a illustrates the changes in the porosity of the films as determined from the refractive index of the film using the BEMA model. This calculation assumes that the mesoporous film consists of silica framework and voids with an assumed fixed refractive index for glass silica skeleton.[35] A maximum in the porosity is observed for films synthesized between 80 and 100 bar. This maximum is consistent with the anomalous swelling reported previously for polymer films.[22,23,26,37] It is important to note that the pressure where this maximum occurs in this work is shifted to lower pressures than the reported anomalous swelling maximum for polymer films using pure CO_2. The addition of dilute water and TEOS concentrations to the CO_2 results in a shift in the critical pressure of the mixture in comparison to pure CO_2. These results are consistent with the hypothesis that the anomalous maximum in swelling of polymer thin films is correlated with the density fluctuations in the fluid.[22] Additionally in Figure 1a, there appears to be a break in the porosity above and below the anomalous maximum. This increase in porosity at pressures in excess of the anomalous maximum is consistent with an enhanced solubility of CO_2 in polymer films in comparison to the bulk at these pressures.[37] The increase in porosity of these templated silica films should be accompanied by an increase in the pore size as the hydrophobic domains of the polymer will be swollen by CO_2 during synthesis. The average (mode) pore size of the films shows a maximum near the pressure where the maximum in film porosity occurs as shown in Figure 1b. Since the porosity is dependent upon the extent of the condensation reaction, there are some differences between the pressure dependence of porosity and pore size. CO_2 pressure impacts the partitioning of the TEOS between the

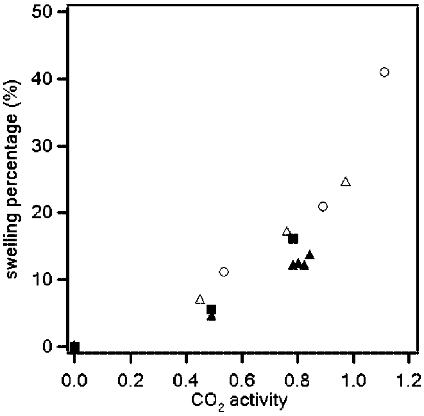

Figure 2. Comparison of swelling data between poly(propylene oxide) domains of a swollen and modified amphiphilic polymer template in CO_2 at 60 °C determined from (■) TEM and (▲) porosimetry to swelling at identical CO_2 fluid activity of bulk poly(propylene glycol) at (○) 25 °C and (△) 35 °C from Guadagno and Kazarian. The pore swelling is determined from TEM micrograph cross sections. Bulk data are from ref 39.

polymer and fluid phase and thus the overall reaction extent (from the reactant concentration within the film impacting the overall reaction rate). This reaction extent dependence will alter the porosity of the sample, thus the pore size is a more accurate measure of CO_2 swelling within the polymer film. The pore size is determined from the desorption isotherm of toluene vapor at ambient temperature and application of the Kelvin equation with a correction for the adsorbed layer, which has been shown to agree well with TEM micrographs for mesoporous silica films.[38] Below the maximum in pore size, the change in the pore radii is comparable to the reported swelling at identical CO_2 fluid activity of bulk poly(propylene glycol),[39] which comprises the hydrophobic domains of the Pluronic surfactant. The linear dilation of the poly(propylene oxide) domains in the film is determined from the change in the pore size using TEM micrographs or the PSD from EP assuming the swelling in CO_2 is one dimension due to overall restriction from the rigid substrate. These data agrees well with the bulk volumetric expansion of poly(propylene glycol) reported in the literature[39] as illustrated in Figure 2. For example, the pore radius (in the plane of the film measured from TEM micrographs) increases from 1.694 nm without CO_2 to 1.790 nm when swollen at 36 bar at 60 °C, an expansion of 5.7%. Extrapolation of the reported swelling of poly(propylene glycol)[39] at the same activity results in a predicted volumetric expansion of 7.2% at these conditions. Swelling at 70 bar at 60 °C results in a pore size expansion of 16.1% to 1.968 nm compared to a bulk swelling of PPG of 17.5%. Better agreement is found from direct measurement of the pore size using TEM then using the average pore size obtained from porosimetry. The reason for this discrepancy is the one-dimensional contraction of the pores that occurs during calcination. This leads to a decrease in the average pore dimension and therefore an underestimation of the swelling. Despite this limitation, the changes in the pore size appear to be an indirect, but accurate, measure of the CO_2 induced swelling of the hydrophobic domains within the polymer film.

However, these measurements of porosity and average pore size do not provide evidence for any swelling gradients within the film. The full pore size distribution (PSD) of the films does provide evidence that the CO_2 distribution is nonuniform through the film at the anomalous swelling maximum. Figure 3 shows the PSD of films synthesized at 70, 87, and 104 bar. In Figure 1b, these correspond to the third point in the grouping at 1.7 nm pores (70 bar), the maximum in pore size (87 bar) and the third highest pressure (104 bar). For films synthesized far from the maximum in pore size, the PSD shows a sharp well-defined peak, which is consistent with a templated mesoporous material.[40] However, the PSD broadens significantly for films near the maximum pore size. A gradient in the CO_2 concentration through the film is responsible for the broad PSD as will be illustrated later. At 87 bar (maximum pore size), the PSD is much broader than would be expected for a templated material. As the pressure is decreased or increased from this maximum, the PSD narrows; 104 bar is on the edge of the pore size maximum and thus the PSD of the film obtained at these conditions is broader than that at 70 bar.

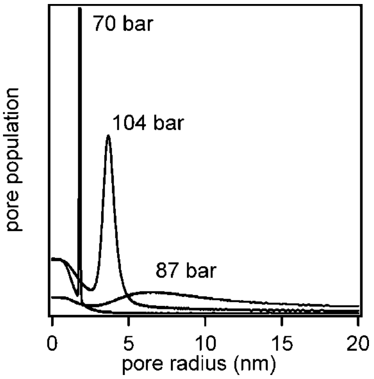

Figure 3. Pore size distribution of films synthesized at 70, 87, and 104 bar. The pore size distribution is calculated from ellipsometric porosimetry using the Kelvin equation.

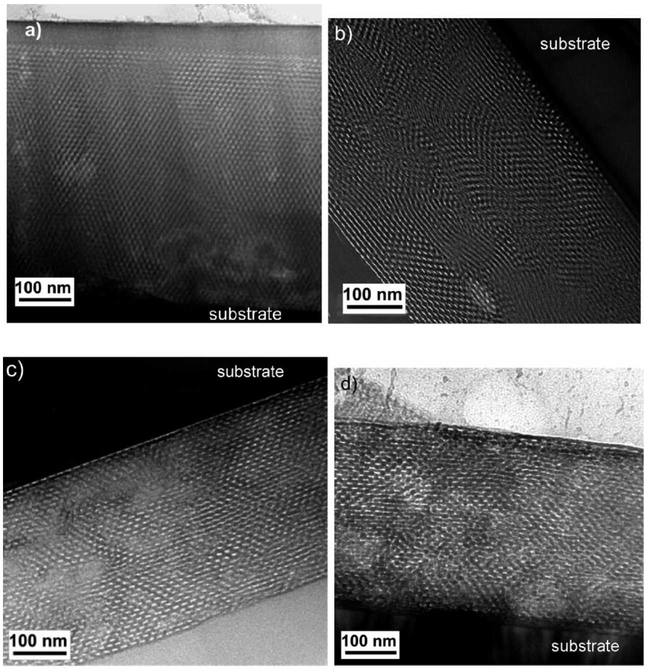

Figure 4. Cross section TEM micrographs of the films fabricated at (a) the vapor pressure of TEOS, (b) 70 bar, (c) 87 bar, and (d) 104 bar.

To visualize any pore size gradients induced by a heterogeneous distribution of CO_2 in the swollen film, TEM cross sections of the silica films formed by the CO_2 swollen polymer template after depressurization are used. Representative micrographs for the silica films prepared with vapor phase condensation, reacted at a CO_2 pressure of 70, 87, and 104 bar, are shown in Figure 4. The porous silica film prepared with vapor phase condensation ($P_{CO2} = 0$) shows a quite uniform pore size throughout the film and a surface layer on top of the mesoporous films formed by this vapor exposure which was observed in previous study.[38] The film synthesized at 70 bar exhibits a very

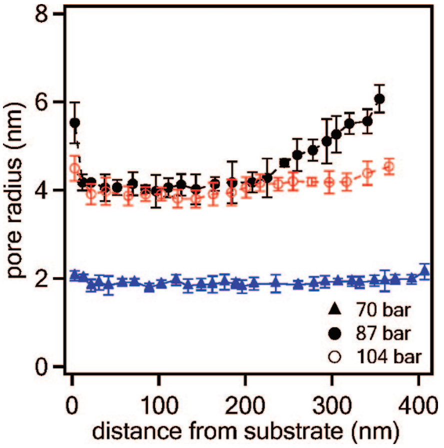

Figure 5. Dependence of pore size on location within film for (▲) 70 bar, (●) 87 bar, and (○) 104 bar for the synthesis pressure. The pore size is determined from TEM micrograph cross sections.

uniform pore size throughout the film. The film synthesized at 87 bar, which exhibits the maximum in average pore size and also has a broad PSD, has a gradient in the pore size that extends from the free surface into the film that can be determined from the micrograph. Additionally, the pores at the silicon substrate appear to be larger than the bulk of the film. Thus, both interfaces are responsible for the anomalous swelling of polymer films. For the film prepared at 104 bar, there are also larger pores closer to the free surface and buried interface, but to a lesser degree. To quantify the effect, the pore sizes from a series of TEM micrographs at different CO_2 pressures are measured as a function of distance from the substrate interface. During template removal, the film shrinks due to additional condensation of silanol species; this shrinkage results in a decrease in the pore dimensions normal to the film surface, but those parallel are not significantly influenced. Therefore, the reported pore radii are those parallel to the film surface. Figure 5 illustrates the dependence of pore radii on the distance from the interfaces for the three films whose PSDs are shown in Figure 3. The film with the very narrow PSD synthesized at 70 bar has a statistically invariant pore size throughout its thickness. However the films with the broader PSDs show statistically significant gradients in pore size at both interfaces; this is especially apparent for the film synthesized at 87 bar, which corresponds to pressure for the maximum in the average pore size. One interesting observation is that the average pore size (Figure 1b) calculated using the Kelvin equation from toluene sorption isotherms does not agree with the pore size from TEM when a gradient in pore size is present, but the Kelvin equation does provide an accurate estimate of the pore size when no gradients in pore size are present. This suggests that the pore gradients impact the sorption behavior of these films, which is consistent with reports on the sorption in multilayered films with different pore sizes.[41]

At the free surface of this film, the pores are enlarged more than 3-fold from the average pores of the film synthesized without CO_2. Changes in the pore size appear to be accurate measures of the concentration in the hydrophobic domains of the template based upon pore expansion at pressure below the anomalous maximum in comparison to published CO_2 swelling in the bulk of PPG.[39] If we assume that this also provides an accurate measure of the local CO_2 concentration, we can estimate the concentration of CO_2 within the film at any depth from the free surface at the temperature and pressure of the synthesis by assuming swelling is confined to one dimension due to the large area to volume ratio of the film. One dimensional swelling is typically utilized to calculate solubility within polymer films.[42] To calculate the local volume fraction of CO_2 within the polymer film, we use the CO_2-free synthesized pore radius (in the plane of the film) as the PPG volume and the pore radius (in the plane of the film at the location of interest) of the mesoporous silica film synthesized at the temperature and pressure of interest as the PPG + CO_2 volume. This is the same calculation as used in calculating the swelling in Figure 2. For the film synthesized at 87 bar (anomalous maximum), the near surface of the polymer film is calculated to be approximately 70 vol % CO_2 based upon the average pore size of the topmost layer of pores. On the basis of bulk swelling of the polypropylene glycol,[39] the expected pore expansion is less than 25%; therefore the CO_2 solubility at the polymer film surface appears to be enhanced by an order of magnitude at the anomalous maximum. It is important to note that swelling of this magnitude is generally only observed for polymers that are soluble in CO_2.[43]

In addition to this anomalous solubility at the free surface, the gradient in pore size extends nearly 150 nm into the film interior. This length scale is significantly larger than typically reported for interfacial effects in polymer films with the noted exception of the physical aging of PMMA films.[3] The large concentration of CO_2 and corresponding long length scale of the gradient provides an explanation of the enhanced welding of PS colloidal crystals in CO_2.[44] The authors suggested that enhanced welding kinetics at the anomalous swelling maximum was likely due to excess CO_2 at the interfaces as is shown here. At the buried interface where the polymer template is in contact with the native oxide of the silicon wafer, a similar enhanced CO_2 concentration is present based upon the expansion in the pore size. However, the pore size drops rapidly from the buried interface. Increasing the pressure from 87 to 104 bar reduces the heterogeneity in the pore size through the thickness of the film. A gradient at both interfaces remains, but the extent of the pore size variation is significantly reduced. The length of the gradient at the free interface is difficult to assess for the film synthesized at 104 bar as the pores at the surface are only marginally statistically different from the interior of the film. The limited gradient through this film is consistent with the pore size distribution determined from SE (Figure 3) which is intermediate in breadth of the three films examined. Additionally, the average pore size of the film synthesized at 104 bar is near the edge of the maximum and therefore a small gradient might be expected in this film. Thus, it appears that the enhanced solubility of CO_2 in polymer films is a result of concentration gradients that extend from both interfaces.

To understand the enhanced concentration at the buried interface, we hypothesize that this is driven by the attractive interaction between CO_2 and silica. Water is well-known to accumulate at polymer−silica interfaces,[21] but CO_2 is one of the few molecules that can effectively remove water from a silica surface.[45] It is thus argued that the favorable CO_2−silica interaction will result in significant enhancements in the local solubility of CO_2 in polymers near a silica interface. This result could have significant implications in high pressure CO_2 separations using mixed matrix membranes. The short length scale (<10 nm) of the enhanced CO_2 solubility near the buried interface is consistent with those observed for moisture at a similar interface.[21] However, the influence of this perturbation in CO_2 concentration at the buried interface is minor in comparison to the gradient at the free surface when the integrated effect on the film swelling is considered. The predominance of the free surface has been confirmed previously for polymer films swollen by CO_2 at the anomalous maximum by using different substrate surfaces; the difference in the swelling between the surfaces is negligible.[26] One issue that does arise from this indirect measurement of the CO_2 concentration from the reactive modification of a swollen polymeric template is that a silica−polymer interface is formed during the reaction. This could lead to some additional increase in the pore size in the interior of the film due to CO_2 accumulation at the in situ formed interface. On the basis of the pore size distribution through the thickness of the films synthesized near the swelling maximum, this effect does not appear to be dominate as the pore size at the native oxide interface is significantly greater than in the interior of the film.

To provide physical insight into the enhancements in the solubility imposed by the free surface, changes in the physical properties of polymer surfaces and the criteria for CO_2 solubility of polymers are considered. First, the solubility of CO_2 within a polymer increases as the density of the fluid phase increases; thus, large positive density fluctuations would tend to increase the CO_2 concentration within the polymer phase. Additionally, two critical parameters for CO_2 soluble polymers have been identified as (1) high flexibility and high free volume segments to enhance the entropy of mixing[46] and (2) strong specific interactions with CO_2 such as Lewis base groups.[47] Although the dissolution of a polymer in CO_2 is different from the swelling of a polymer phase, physical properties that improve solubility in CO_2 phase also tend to increase the polymer swelling. Thus if the surface of the thin films could exhibit a change in one of these criterion in comparison to the bulk, this might provide a physical explanation for the observed gradients. One measure of criterion 1 that was successful in designing CO_2 soluble polymers is T_g of the polymer; a lower T_g can lead to enhanced solubility in CO_2.[46] Multiple studies have shown that the T_g of polymer surfaces is depressed in comparison to the bulk.[1,2] Therefore, it is hypothesized that the free volume and chain flexibility near the surface of a polymer film is greater than that in the bulk and would also lead to enhancements in the solubility of CO_2 at the free surface. However, the length scale of this decreased T_g is generally only on the order of 30 nm significantly less than the length of the gradient observed here. However, the rate of physical aging of a polymer film observed near a free surface is suppressed over approximately 250 nm.[3] This aging effect has been attributed to the decreased driving force ($T - T_g$) resulting from the decreased T_g at the polymer surface. The longer length scale for aging is consistent with the length scale for the surface concentration gradient of CO_2. Conversely, an adsorbed liquid-like layer on the surface as predicted by Sanchez and co-workers might act to swell the polymer at the surface. To prevent concentration discontinuities within the polymer phase, a gradient in CO_2 concentration penetrating into the film might be expected. To test these and other possible explanations, additional experiments and simulations are necessary to determine the exact physical origins of the concentration gradients formed at the surface of thin films.

Conclusions

The swelling of amphiphilic films by CO_2 was indirectly determined using a selective reactive modification methodology to generate a porous film. Changes in the pore size were attributed to swelling by CO_2 and normalized to a film synthesized without CO_2. At low pressures (<80 bar), the reported bulk swelling of poly(propylene glycol) is nearly identical to average pore (templated by an analogous polymeric segment) size expansion at identical conditions, suggesting that this route provides a quantitative measure of the CO_2 concentration within the films. A maximum in the average pore size is obtained near the density fluctuation ridge of CO_2. TEM cross section micrographs identified a gradient in pore size extending approximately 150 nm into the film from the free surface and a short (<10 nm) gradient at the buried interface at this maximum. A uniform pore size through the film thickness is observed at pressures far from the density fluctuation ridge.

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