Phase Behavior of Polystyrene-*block*-poly(*n*-alkyl methacrylate)s Dilated with Carbon Dioxide

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ABSTRACT: The influence of carbon dioxide (CO_2) sorption on the phase behavior of two polystyrene-*block*-poly(*n*-alkyl methacrylate) copolymers was studied. One, polystyrene-*block*-poly(*n*-hexyl methacrylate), P(S-*b*-nHMA), exhibits an order−disorder transition (ODT), whereas the other, polystyrene-*block*-poly(*n*-butyl methacrylate), P(S-*b*-nBMA), exhibits a lower disorder−order transition (LDOT). CO_2 sorption increases miscibility of the segments in P(S-*b*-nHMA) slightly: the ODT is depressed by less than 7 °C at a CO_2 fluid density of 0.25 g/cm^3, which corresponds to 7 vol % dilation of the copolymer with CO_2 at the conditions studied. In contrast, CO_2 sorption decreased the miscibility of P(S-*b*-nBMA) markedly: the LDOT was depressed by more than 70 °C at densities < 0.06 g/cm^3, which corresponds to less than 3 vol % sorption of CO_2. Unlike P(S-*b*-nHMA), ordering transitions in CO_2-dilated P(S-*b*-nBMA) exhibit a pronounced thermal hysteresis that increases with increasing volume fraction of sorbed diluent. The hysteresis is a consequence of the sensitivity of the LDOT system to differences in CO_2 sorption between the ordered and disordered states, as evidenced by neutron reflectivity measurements. The difference in the effect of CO_2 sorption on the phase behavior of the copolymers is attributed to the different nature of the transitions. The entropically driven LDOT is depressed by differential dilation of the copolymer domains, which increases both the compressibility of the system and disparities in compressibility between the blocks. In contrast, the enthalpically driven ODT is depressed by the screening of segmental interactions by CO_2 and is less sensitive to compressibility.

Introduction

The phase behavior of diblock copolymers has been studied extensively both theoretically and experimentally.[1−3] The majority of the systems studied exhibit order-to-disorder transitions (ODTs), where the copolymer segments are intimately mixed at temperatures above the ODT, but upon cooling below the transition temperature the copolymers phase separate into nanoperiodic structures. A few copolymer systems exhibit phase separation upon heating at lower disorder-to-order transitions (LDOTs), named for their analogy to lower critical solution transitions (LCSTs) in polymer blends.[4,5] The driving force behind transitions in LDOT and ODT systems is fundamentally different. The ODT is enthalpically driven, whereas the LDOT results from the inverse temperature dependence of strong specific interactions between segments and/or from entropic contributions, i.e., “equation-of-state”, (EOS), effects that arise due to an increase in the disparity of component compressibilities upon heating.[4,6−9] Such disparities can result in negative volume changes on mixing that destabilize the system. This contribution dominates the phase behavior of the polystyrene-*block*-poly(*n*-alkyl methacrylate) copolymers that exhibit LDOT behavior.[5]

The presence of solvents can influence block copolymer phase transitions in a number of ways. The vast majority of studies involve ODT systems and liquid solvents, where two effects are dominant. First, the solvent can screen unfavorable interactions between the segments leading to a depression in the ODT.[10,11] Second, depending on its selectivity, the solvent can preferentially swell one phase leading to an apparent change in the composition of the block copolymer. Changes in the apparent composition can give rise to order-to-order transitions (OOTs).[12] In contrast to extensive experimentation with ODT systems, very few studies have dealt with the effect of solvents on LDOT systems. One study suggested that liquid solvents such as bis(2-ethylhexyl) phthalate (DOP) have little effect on the location of the LDOT for polystyrene-*block*-poly(*n*-butyl methacrylate).[13]

Over the past several years, we have examined the influence of compressed fluid sorption on the phase behavior of multicomponent polymer systems including diblock copolymers and blends.[9,13−15] Our studies involve heterogeneous systems in which fluid sorption (CO_2 or a light alkane) is equilibrium limited and can be controlled precisely through pressure-mediated adjustments in fluid density, even at exceedingly low volume fractions. In comparison to good liquid solvents, there are several further distinctions for the systems studied. First, the compressed fluids are generally poor solvents with Flory−Huggins interaction parameters, χ, greater than one.[9,15] Second, sorption of a compressed diluent can lead to an increase in isothermal compressibility relative to the neat melt.[16,17] Fluid sorption can therefore add contributions to phase instability related to increases in component compressibility that are negligible in liquid solvent systems. Finally, the effects of hydrostatic pressure, which are inherent for compressed solvent systems, must be considered. While understanding the influence of compressed fluid sorption can provide insight into the importance of compressibility

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in polymer phase transitions, it is also necessary for the development of emerging applications of supercritical fluids. These include the use of carbon dioxide as a solvent for polymer synthesis,[18] for preparation of nanocomposites,[19] for spin coating and development of photoresists,[20,21] to facilitate ordering of high molecular weight block copolymers,[16] and for in situ reactions within CO_2-swollen polymers.[22]

The effect of CO_2 sorption on phase behavior has been determined for a number of blends and block copolymer systems. Blends of polystyrene and poly(vinyl methyl ether) phase separate at temperatures far below the binary LCST upon sorption of small amounts of CO_2.[9] The substantial decrease in the LCST is attributed to an increase in compressibility of the system arising from sorption of the CO_2, which destabilizes the system. Likewise, sorption of CO_2 or the light alkanes induces phase segregation in poly(styrene-*block*-*n*-butyl methacrylate), P(S-*b*-nBMA), diblock copolymers that exhibit LDOT transitions. In contrast, the sorption of CO_2 has been shown to promote miscibility in low molecular weight polystyrene/polyisoprene blends, which exhibit UCST behavior,[23] and the sorption of CO_2 or the light hydrocarbons promotes miscibility in poly(styrene-*block*-isoprene), P(S-*b*-I), diblock copolymers, which exhibit ODTs.[13,14] Overall, the behaviors of these systems suggest that sorption of CO_2 and the light alkanes in multicomponent polymer systems promotes miscibility in UCST-type systems by screening unfavorable interactions in a manner similar to that of traditional organic solvents, whereas for systems exhibiting lower critical phenomena, sorption of highly compressible fluids promotes phase segregation due to large changes in the compressibility of the dilated polymers.

While the results to date are consistent, a number of factors specific to the polymer systems studied should be considered. First, for all the systems that exhibit an LCST or LDOT studied to date, there is a large difference in CO_2 sorption between the polymer components.[24,25] Moreover, in each case, the component that exhibits the higher compressibility, as calculated from equation-of-state parameters, is selective for CO_2 sorption. By comparison, studies of ODT systems have been limited to those in which the component homopolymers exhibit similar sorption isotherms and thus low solvent selectivity.[26] Differences in gas sorption between the segments may destabilize the homogeneous state by preferentially swelling one phase, which can lead to a large negative change of volume on mixing diblock segments. Direct comparison of LDOT and ODT systems with similar selectivities are required to determine whether these considerations dominate phase behavior in each case. Second, in polystyrene/poly(vinyl methyl ether) blends, there is a specific interaction between the polymer segments that may be affected by interactions with CO_2. Recent models have shown that PS/PVME phase behavior can be captured without accounting for these interactions,[27] and thus their contribution may be secondary to equation-of-state effects. A stability analysis based on the Sanchez−Lacombe EOS supports this view for the ternary PS/PVME/CO_2 system.[9] Although the favorable interactions between PS and PVME are diluted by CO_2, this contribution to instability was found to be small by comparison. Nonetheless, enthalpic contributions should be considered when assessing LCST-type systems. Third, carbon dioxide can interact strongly with polymethacrylates due to quadrupole−dipole interactions, which may affect phase behavior. A number of these issues were addressed in a recent study of the influence of light *n*-alkanes (methane through butane) on the phase behaviors of P(S-*b*-I) and P(S-*b*-nBMA).[15] The use of a series of light alkanes provided the opportunity to vary solvent compressibility significantly, while maintaining nearly equivalent solvent−segment interactions within the ODT or LDOT systems. It was found that for P(S-*b*-I) solvent sorption promoted miscibility, and the ODT scaled with the volume fraction of the sorbed diluent, independent of solvent chain length. By comparison, for the P(S-*b*-nBMA) systems at equivalent solvent volume fractions, the sorption of methane most severely destabilized the system, and the degree of LDOT depression was progressively less pronounced as the solvent chain length increased. While this study highlighted the importance of solvent compressibility on transitions in distinct ODT and LDOT systems, it did not provide the opportunity to examine LDOT and ODT block copolymers with similar chemical compositions and, thus, similar solvent/segment interactions.

Table 1. Characteristics of the Diblock Copolymers Used in This Study

sample	M_n (kg/mol)	f_{PS}	PDI	transition (°C)
P(S-*b*-nHMA)	36.6	0.51		162 (ODT)
68K P(dS-*b*-nBMA)	68	0.57	1.02	
40K P(S-*b*-nBMA)	39.9	0.53	1.10	
65K P(S-*b*-nBMA)	64.5	0.53	1.03	188 (LDOT)

Table 2. Neutron Scattering Length Densities (NSLD) of the Polymers Used in This Study

component	NSLD (10^{-6} Å^{-2})
deuterated polystyrene	6.19
poly(*n*-butyl methacrylate)	0.505

The homologous series of polystyrene-*block*-poly(*n*-alkyl methacrylate) (PS-*b*-nAMA) copolymers exhibits a rich variety of phase behaviors as the length of the alkyl chain is changed. For a short chain ($n \leq 4$) with the exception of the methyl group, the copolymers exhibit LDOT type behavior. In contrast, for larger alkyl chains and for methyl methacrylate, an ODT is observed. Since polystyrene-*block*-poly(*n*-alkyl methacrylate)s exhibit both ODT and LDOT behavior depending on the pendant alkyl chain length and because the segmental interaction of CO_2 with the *n*-alkyl methacrylates considered should be very similar, these materials provide a unique opportunity to examine the influence of CO_2 sorption in LDOT and ODT systems in which solvent−segment interactions, CO_2 sorption, and solvent selectivity are nearly identical.

Experimental Section

Details of the block copolymer samples used for this study are shown in Table 1. The polystyrene-*block*-poly(*n*-hexyl methacrylate) P(S-*b*-nHMA) sample was a blend of two diblocks in order to observe an accessible ODT. Details of the synthesis of the materials are provided elsewhere.[5] The blend compositions was 45% of a 25 000 g/mol diblock and 55% of a 46 000 g/mol diblock. Two samples of polystyrene-*block*-poly(*n*-butyl methacrylate) were purchased from the Polymer Synthesis Facility at the University of Minnesota. For neutron reflectivity experiments, a perdeuterated polystyrene-*block*-poly(*n*-butyl methacrylate), characterized previously, was used (see Table 1).[4] For all phase behavior measurements, samples were melt pressed into 1 mm thick, 8 mm diameter rings. Carbon dioxide (Coleman grade, 99.99%) was purchased from Merriam Graves and used as received.

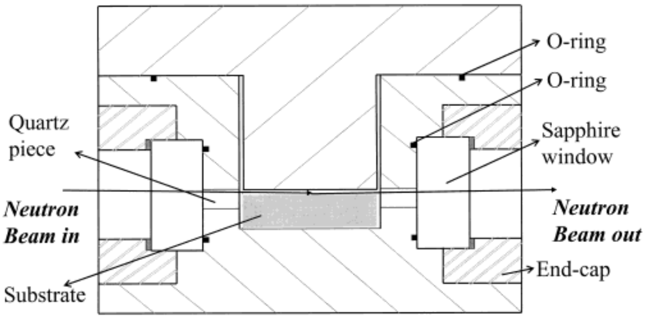

Figure 1. Schematic of the high-pressure neutron reflectivity cell.

The transitions of the diblock copolymers were measured using high pressure in situ small-angle neutron scattering (SANS) and birefringence (measured depolarized transmitted light intensity). A high-pressure cell was used for both SANS and birefringence measurements. Details of the cell design have been previously reported.[13] Prior to both SANS and birefringence measurements, the cell was purged using the fluid of interest. Fluid phase densities were calculated using the NIST Standard Reference Database.[28] The experimental setup for the birefringence measurement was the same as previously described.[15]

Small-angle neutron scattering (SANS) measurements were conducted at the Cold Neutron Research Facility at the National Institute of Standards and Technology (NIST) using the NG7 30 m instrument. A train of four high-pressure cells in tandem were heated using the sample autoloader for liquid cells (provided by NIST) and connected via a series of valves to a manifold containing the fluid of interest. The instrument configuration for the measurements was as follows: $\lambda = 8.0$ Å, $\Delta\lambda/\lambda = 0.10$, sample-to-detector distance = 2.6 m, and beam diameter = 3.27 cm. The 2-D raw data were corrected for background scattering and detector sensitivity, radially averaged, and scaled to absolute cross section using a Si standard. The transitions were detected by discontinuities in both the primary peak width, σ, and maximum scattered intensity, $I(q^*)$.

Quantitative fluid sorption measurements were performed for homopolymers of polystyrene, poly(*n*-butyl methacrylate), and poly(methyl methacrylate) using a pressure decay method similar to that described by Koros and Paul.[29] The molecular weights for the homopolymers were 280 000, 180 000, and 75 000 g/mol for polystyrene (Aldrich), poly(*n*-butyl methacrylate) (Scientific Polymer Products, Inc.), and poly(methyl methacrylate) (Scientific Polymer Products, Inc.), respectively. Measurements were made in 20 °C increments between 40 and 100 °C at pressures ranging from ambient to 130 bar.

Neutron reflectivity (NR) experiments were conducted on the SURF reflectometer at the neutron spallation source at ISIS (Rutherford Appleton Laboratory, U.K.). NR yields measurements of copolymer film dilation and ordering simultaneously. A schematic of a custom-designed and built high-pressure neutron reflectivity cell is shown in Figure 1. Details of the cell construction are provided elsewhere.[30] The NR profiles were obtained at three different angles of incidence: 0.25°, 0.45°, and 0.80° for each condition. The data sets were merged into a composite curve covering a k range from 0.0045 to 0.047 Å^{-1}. The raw data were reduced using a subroutine provided by ISIS. To correct for the attenuation of the neutron beam at higher pressures, transmission data obtained using the same setup as described above less the polymer sample were subtracted from the raw data. The fitting procedure used in this study is very similar to that applied to diblock copolymer systems of polystyrene and poly(methyl methacrylate) exhibiting order-to-disorder transition (ODT) that has been described in detail elsewhere.[31,32] The expression used for the polymer concentration profile is given in eq 1, as proposed by Fredrickson[33]

$$\phi_{\mathrm{PS}} = \max\left[\phi_{\mathrm{A}} \mathrm{e}^{-z/\xi_1} \cos\left(\frac{2\pi z}{L}\right), \phi_{\mathrm{s}} \mathrm{e}^{-(E-z)/\xi_2} \cos\left(\frac{2\pi(E-z)}{L}\right)\right] + \bar{\phi}_{\mathrm{PS}} \quad (1)$$

where ϕ_{A} and ϕ_{S} are excess PS concentration at the polymer−air interface and polymer−substrate interface, respectively; E is the total thickness of the sample; z is the distance from free surface in the film; L is the average period of copolymer (two layers of polymers, A and B each comprising in turn of two similar blocks); ξ_1 and ξ_2 are the decay lengths from the air−polymer and polymer−substrate interfaces and are representative of the distance over which there is order (concentration gradients) in the film; and $\bar{\phi}_{\mathrm{PS}}$ is the average concentration of PS in the diblock copolymer.

Results and Discussion

The transitions of neat block copolymers were determined first to provide a baseline for comparison with copolymer/CO_2 systems (Table 1). The measurements with carbon dioxide were conducted at a constant bulk fluid density, unless otherwise noted. SANS results for the P(S-*b*-nHMA) swollen with 0.20 g/cm^3 of CO_2 are shown in Figure 2. The primary scattering peak exhibits a discontinuity in half-width and intensity as the sample is cooled from 160 to 150 °C, as would be expected for a sample exhibiting ODT behavior. Large temperature steps necessitated by time limitations prohibited the definition of the ODT by SANS to better than ±5 °C. Birefringence measurement can yield accurate determinations of order−disorder transitions.[34] Birefringence measurements employing small step changes in temperature were used to determine transitions within 1 °C as a function of density. Because of the kinetic limitations on ordering, the transition was only determined by heating from the ordered state. The heating rate was less than 1 °C/30 min for all the measured data. Following a temperature change, the sample was allowed to equilibrate until a constant light intensity was measured. The signal is highly dependent on the orientation of the block copolymer grains and can be influenced by heating and cooling rates. Once the grains begin to grow, there is a fixed grain orientation for that portion of the sample.[34] Thus, after disordering and reordering, substantially different intensity values for the ordered state were observed. A summary of the birefringence and the SANS data for the P(S-*b*-nHMA) is shown in Figure 3. As can be seen from the data, CO_2 sorption increases the miscibility of the segments. This is in agreement with the behavior of other ODT systems in the presence of CO_2.[14]

A much different effect of CO_2 sorption was previously reported for polystyrene-*block*-poly(*n*-butyl methacrylate).[13] Carbon dioxide was found to induce phase separation by hundreds of degrees at relatively modest solvent loading. However, there is limited data available on the dependence of the LDOT depression on CO_2 loading. Using the birefringence technique and sorption measurements, the “scaling” of the transition with concentration can be determined. The birefringence data for the 65K P(S-*b*-nBMA) sample both without CO_2 and with 0.05 g/cm^3 CO_2 are shown in parts a and b of Figure 4, respectively. For the neat sample, the LDOT is completely thermoreversible with a transition at 188 °C. However, for the sample swollen with CO_2, there is a hysteresis in the transition. Upon heating at constant fluid density, the sample orders at 141 °C, but on cooling the sample does not disorder until 136 °C. This discrepancy in the phase transition temperature between

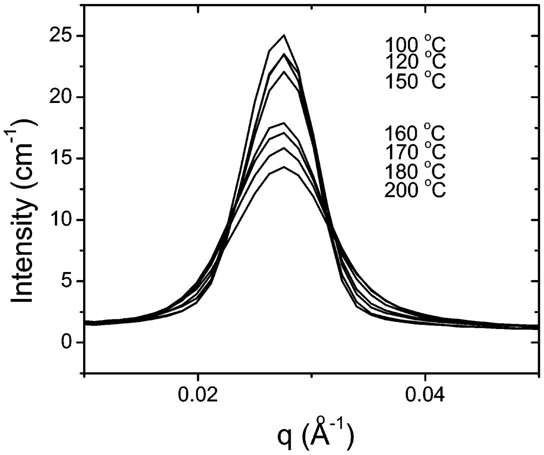

Figure 2. SANS scattering profiles for PS-*b*-nHMA as a function of temperature at a constant CO_2 fluid density of 0.20 g/cm^3.

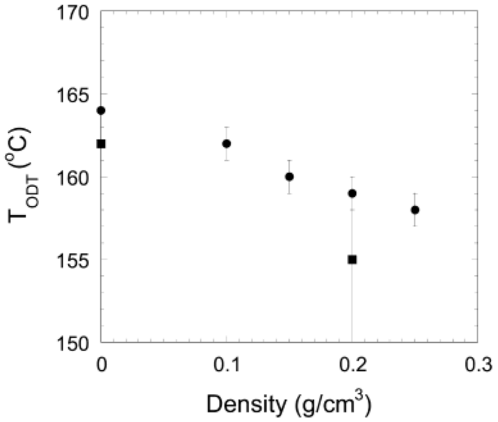

Figure 3. Location of ODT's in PS-*b*-nHMA as a function of CO_2 fluid density by birefringence (●) and SANS (■).

ordering and disordering of the sample cannot be explained by kinetic limitations, as the size of the region of metastability (5 °C) remains constant as a function of heating/cooling rates down to gradients of less than 1 °C/20 min. This is consistent with previous observations for P(S-*b*-nBMA) phase behavior in the presence of *n*-alkanes.[15] As discussed later, the hysteresis is likely a consequence of differences in solvent sorption between the ordered and disordered states. A transition from the ordered to disordered state for the swollen copolymer requires expulsion of solvent, which is entropically unfavorable. These conclusions are supported by the results of neutron reflectivity experiments.

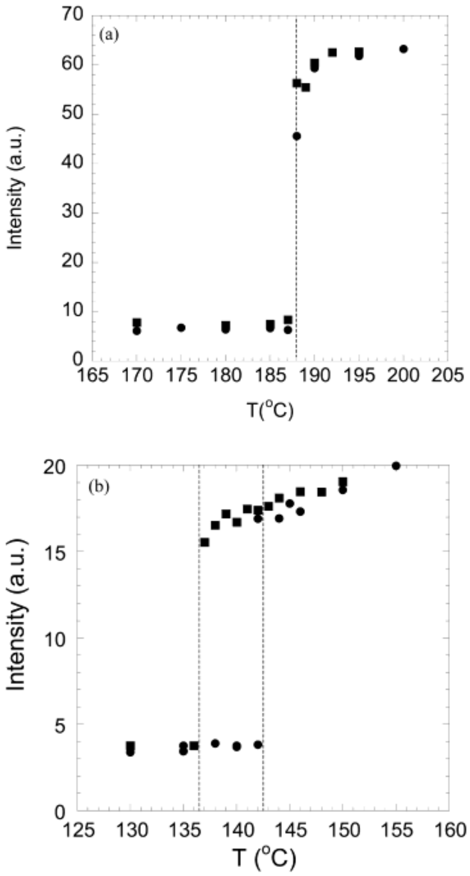

Figure 4. Measured depolarized transmitted light intensity for 65K P(S-*b*-nBMA) (a) without CO_2 and (b) swollen with 0.05 g/cm^3 CO_2 as a function of temperature for (●) heating and (■) cooling curves.

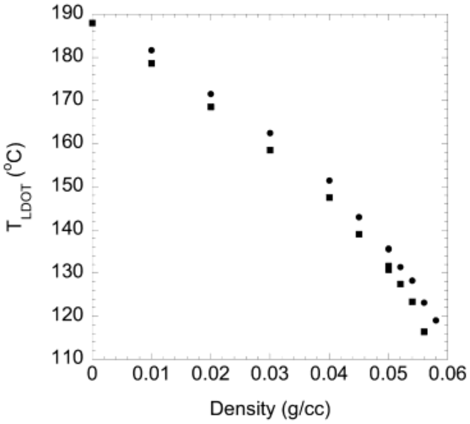

Figure 5. LDOT of 65K P(S-*b*-nBMA) as a function of CO_2 fluid phase density for (■) order-to-disorder and (●) disorder-to-order transitions.

A summary of the LDOT transitions as a function of CO_2 fluid density is presented in Figure 5. As the density of CO_2 is increased, the depression of the LDOT becomes more severe and is nearly linear with density throughout the range studied. At densities of 0.06 g/cm^3 and greater, the transition becomes difficult to measure due to kinetic limitations as the LDOT transition is depressed to temperatures that approach the glass transition of the polystyrene phase. Consequently, no transitions are reported at higher densities. However, in the narrow window of CO_2 density where the LDOT of the P(S-*b*-nBMA) is readily accessible, a number of important observations can be made. First, the depression of the LDOT is striking; more than 60 °C decrease in the transition temperature is measured at a fluid density of 0.058 g/cm^3. In comparison, the ODT of P(S-*b*-HMA) was depressed by only 7 °C at a density of 0.25 g/cm^3. It is important to note that as the density of the CO_2 is increased, the difference in sorption between the homopolymers of polystyrene and poly(*n*-butyl methacrylate) increases (Figure 6). The difference in sorption, and thus segment compressibility, is unfavorable for mixing. Consequently, as the density of CO_2 is increased, the driving force for the microphase separation of the copolymer (differential dilation) increases. Second, the width of the metastable regime of the LDOT for the swollen diblock copolymer increases as the density increases, which is consistent with the argument

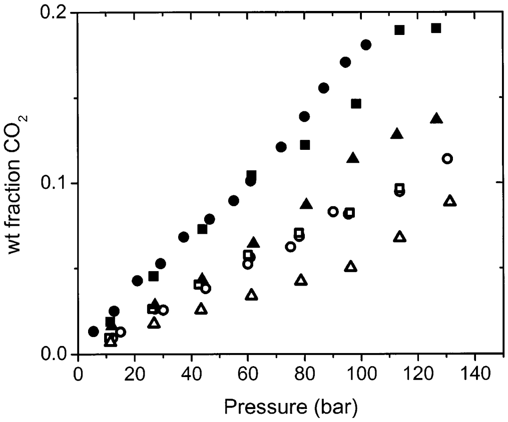

Figure 6. Sorption of CO_2 into (▲) polystyrene, (■) poly(*n*-butyl methacrylate), and (●)[36,40] poly(methyl methacrylate) at 60 °C (closed symbols) and 100 °C (open symbols).

that the hysteresis is a consequence of differences in sorption between the ordered and disordered states.

Determination of transition temperatures as a function of solvent volume fraction in the copolymer rather than fluid density requires knowledge of sorption data and a suitable correlation. In the ordered state, sorption in the diblock copolymer should be nearly equivalent to the weighted sorption in each of the respective homopolymers;[26] thus, sorption data for polystyrene and poly(*n*-butyl methacrylate) can be used as a surrogate for sorption in the P(S-*b*-nBMA) copolymer. Sorption isotherms for polystyrene, poly(methyl methacrylate) (PMMA), and poly(*n*-butyl methacrylate) (PnBMA) at two temperatures are shown in Figure 6. Carbon dioxide is selective toward the methacrylates due to the favorable interaction of CO_2 with the acrylate moiety. An interesting result is that the sorptions in PMMA and PnBMA are nearly equal when both polymers are in a rubbery state (note that the sorption of CO_2 severely depresses the glass transition of PMMA at modest pressures[35]). To calculate the concentration of CO_2 in the block copolymers at the transitions, the homopolymer sorption data were fit using Flory's activity equation. The activity of CO_2 was calculated using the Peng–Robinson equation of state as previously described.[15] A temperature-independent value of $\chi = 1.45$ is obtained for the poly(*n*-alkyl methacrylate)/CO_2 system using our sorption data as well as data from the literature.[24,36] For polystyrene/CO_2, the fit value for χ is 1.61 using a large collection of isotherms at temperatures ranging from 35 to 200 °C.[37–40] This value is consistent with previously reported interaction parameters for polystyrene/CO_2. However, we note that the determination of χ is very sensitive to small discrepancies between sorption data sets. For example, our data and data from Sato and co-workers for CO_2 sorption in PS at 100 °C are essentially equivalent within experimental error, yet the fits of the individual isotherms yield values for χ of 1.75 and 1.62, respectively.[37] Using value for χ calculated from all available sorption isotherms, the volume fraction of CO_2 in each block of the ordered copolymers is estimated at each of the transitions.

Figure 7a,b shows the effect of CO_2 sorption on the LDOT of polystyrene-*block*-poly(*n*-butyl methacrylate) upon ordering. The transition temperature is corrected for the effect of hydrostatic pressure (147 °C/kbar) to show only the effect of carbon dioxide sorption on the phase behavior.[41] For the 65K sample, the transition depends linearly on the volume fraction of copolymer. A significant depression (>65 °C) of the LDOT is measured at solvent volume fractions of less than 3% CO_2. The 40K P(S-*b*-nBMA) sample does not have an experimentally observable LDOT at ambient pressure as the transition is well in excess of 220 °C. The experiments to measure the LDOT for this copolymer swollen with CO_2 were carried out isothermally, with increasing pressure until the sample ordered. Neither heating studies nor depressurization studies were feasible in this case due to the high concentration of CO_2 required to induce microphase separation. Slowly heating or depressurizing the sample led to foaming, which made optical measurements impossible. In these cases, only the transition upon ordering was determined. The LDOT is depressed by over 200 °C by sorption of less than 20% CO_2. The pressure required to induce the transition is in excess of 300 bar. The curvature in the LDOT data with respect to volume fraction may be simply an artifact of the volume fraction calculation. Simultaneous swelling and sorption measurements at elevated temperatures (383 K) have revealed an overprediction of the swelling (volume fraction of CO_2) at high pressures (>300 bar) using the Sanchez–Lacombe equation of state.[39] Similar results are found for using the activity equation.[39] Using the same values for the interaction parameter of PMMA and PnBMA for PHMA, an estimate of the amount of CO_2 in the system at each of the conditions studied can be made (Figure 7c).

The differences between the sorption in the ordered state and disordered state can be determined directly by in-situ swelling experiments using neutron reflectivity (NR). Moreover, sorption-induced ordering of the film can be observed simultaneously. The ambient pressure LDOT of the 68K copolymer used in this study is greater than 220 °C as measured by small-angle neutron scattering (SANS) on bulk samples.[4] Figure 8 shows neutron reflectivity profiles of a 1563 Å film of 68K P(d-S-*b*-nBMA) at 90 °C before the addition of CO_2 and at various CO_2 pressures between 1 and 76 bar. At a pressure of 45 bar, the onset of ordering is indicated by the emergence of two distinct interference peaks arising from a multilayered structure where in the d-PS and PnBMA lamellar microdomains are oriented parallel to the surface. As the density of the CO_2 is further increased, the degree of ordering increases as evidenced by the emergence of a third Bragg reflection.

Films of polystyrene and poly(*n*-alkyl methacrylates) diblock copolymer on silicon substrates exhibit surface-induced ordering, with the methacrylate block preferentially segregating to the polymer–silicon interface.[42] For P(S-*b*-nBMA) case, *n*-butyl methacrylate has a lower surface tension than styrene, leading to its preferential segregation to the air–polymer interface (symmetric wetting). With this knowledge, as well as the knowledge of the initial film thickness, fits for neutron scattering length density profiles (Figure 9) were obtained for each reflectivity curve (Figure 8). The analysis of reflectivity profiles at various pressures of CO_2 reduces primarily to fitting ξ and L, which accounts for changes in the thickness and ordering of the film. There are also small changes in the interfacial widths, scattering length densities of the diblock microdomain segments, and the roughness at the polymer–air interface.

At 90 °C and ambient pressure, the neutron reflectivity profile of the 68K sample shows oscillations

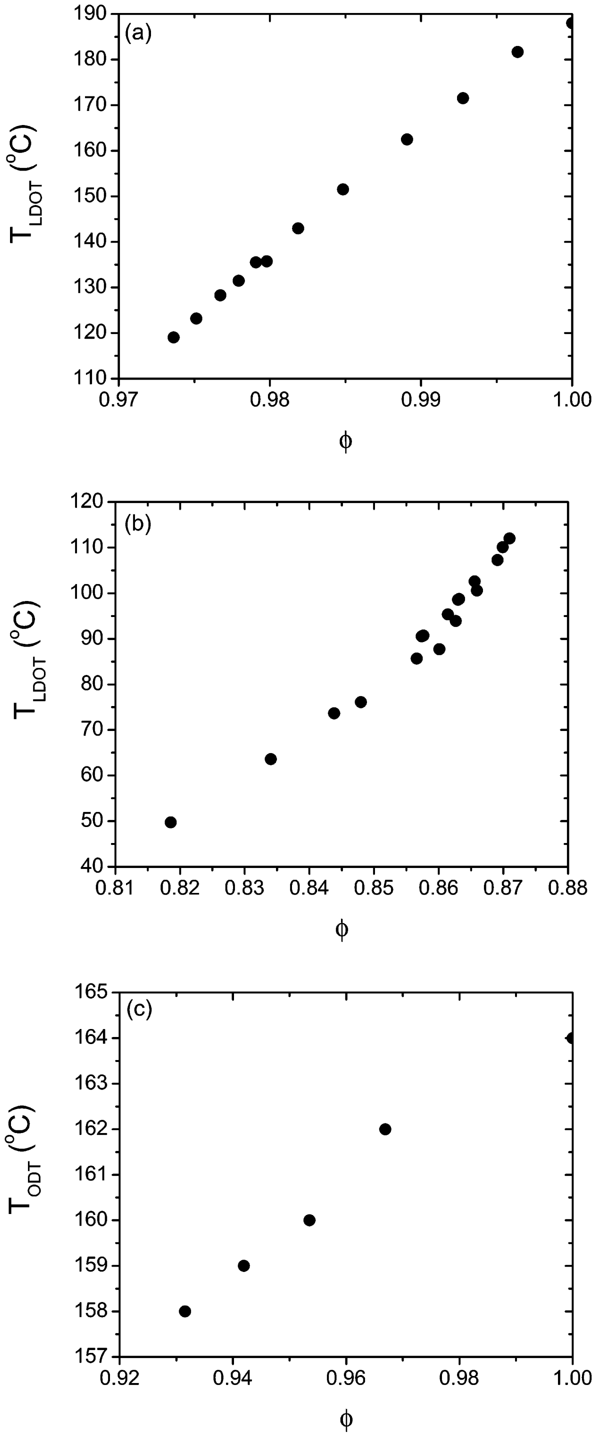

Figure 7. Transitions in (a) 65K P(S-*b*-nBMA), (b) 40K P(S-*b*-nBMA), and (c) P(S-*b*-HMA) as a function of CO_2 volume fraction.

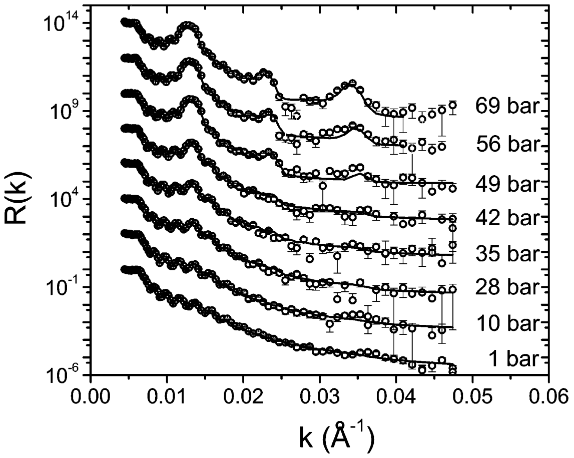

Figure 8. In-situ neutron reflectivity (NR) profiles of 68K P(dS-*b*-nBMA) dilated with carbon dioxide.

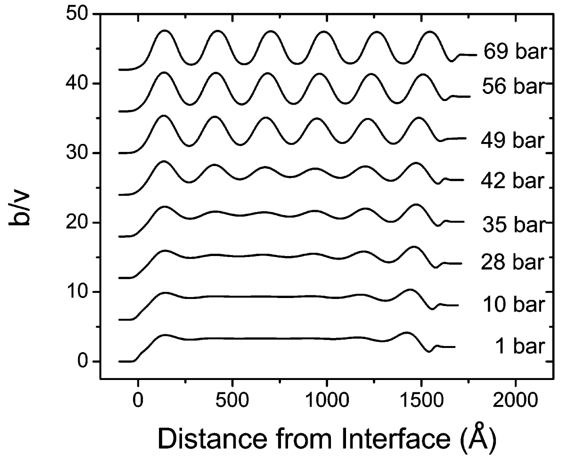

Figure 9. Calculated NSLD profiles of CO_2-dilated films.

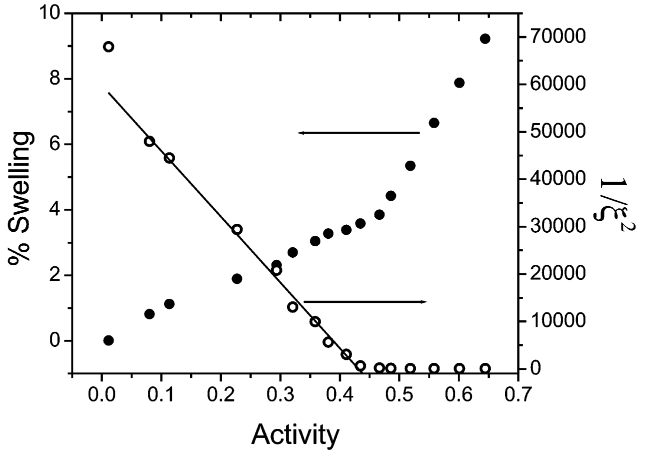

Figure 10. Film swelling and the changes in order parameter induced by sorption of CO_2 as determined by NR.

indicative of the film thickness and exhibits evidence of very weak surface-induced ordering at intermediate scattering vectors (Figure 8). As CO_2 density increases, polymer film thickness increases due to solvent sorption, as does the degree of order in the system. The scattering length density profiles (Figure 9) are characterized by oscillations in concentration that propagate from the interfaces to the center of the film. Increasing order is also evident in the decay length, ξ, which increases with CO_2 pressure as shown in Figure 10. At low CO_2 pressures, the concentration oscillations dampen rapidly with distance from the surface, indicating that the diblock copolymer is disordered in the bulk. With increasing CO_2 pressure, the film thickness increases due to swelling of the copolymer and order propagates through the film. It is important to note that the concentration of CO_2 in the diblock copolymer is only 3−5% under these conditions and, as such, does not change the scattering length densities of the microdomains significantly. The film thickness and the square of the reciprocal of the order parameter as a function of CO_2 activity are plotted in Figure 10.

There is a discontinuity in the film swelling at nearly the same pressure where the copolymer orders as evidenced by the discontinuity in ξ. This change in slope of the swelling is primarily a consequence of differences in CO_2 sorption between the ordered and disordered states although chain extension due to ordering may contribute to some degree. However, since the ξ value plateaus at approximately 60 bar whereas the swelling continues to increase linearly, the change in slope of the film swelling (Figure 10) cannot be attributed simply to a volume expansion of the diblock upon ordering.[43] Thus, there must be differences in the CO_2 sorption between the ordered and disordered states.

Conclusions

The large difference in the effect of CO_2 on the phase behavior of P(S-*b*-nHMA) and P(S-*b*-nBMA) indicates two distinct contributions of CO_2 sorption to the stability of the systems beyond the effects of hydrostatic pressure. The enhancement in miscibility for the P(S-*b*-nHMA) case, as evidenced by a depression in the ODT, reveals an enthalpic contribution that arises from screening of unfavorable segmental contacts. For P(S-*b*-nBMA), the dominant effect of CO_2 sorption is an increase in segment compressibility, an entropic contribution that is unfavorable for mixing. This is evident in the large depression on the LDOT at low solvent loadings, the emergence of a thermal hysteresis between ordered and disordered states, and the sorption data for the ordered and disordered states that indicate expulsion of solvent and/or negative volume changes on mixing are required for order-to-disorder transitions. Clearly, for P(S-*b*-nBMA), the increases in segment compressibility that drive phase separation far outweigh both solvent screening of polymer contacts by sorbed CO_2 and the influence of hydrostatic pressure, which promote miscibility. It is important to note that even though the CO_2 sorption markedly destabilizes P(S-*b*-nBMA), there is no evidence for the inversion of the ODT to an LDOT in the P(S-*b*-nHMA) system.

These results of this study are in agreement with our previous work in which the effect of diluent compressibility on the phase behavior of P(S-*b*-nBMA) was studied directly using a homologous series of light *n*-alkanes. For these systems, the severity of depression of the LDOT and its thermal hysteresis increased dramatically as the chain length of the solvent decreased from butane through methane at equivalent solvent loadings.[15] By comparison, enhanced miscibility in P(S-*b*-I), an ODT system, depended only on the volume fraction of the sorbed light alkane and was independent of solvent chain length.

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