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Unexpected Scaling Behavior of the Order–Disorder Transition of Nearly Symmetric Polystyrene-*block*-polyisoprene Diblock Copolymers Dilated with a Nominally Neutral Solvent at Very Low Dilution

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ABSTRACT: The scaling behavior of the order–disorder transition (ODT) temperature for several nearly symmetric P(S-*b*-I) copolymers has been studied over a polymer volume fraction range of $0.9 \leq \phi_{\mathrm{diblock}} \leq 1$. To enable precise control of the concentration at high ϕ and at elevated temperatures as the concentration approaches the neat melt, compressed CO_2 is used as the diluent in place of more traditional liquid solvents. Swelling of polymer films by CO_2 over the concentration range of interest was determined using high-pressure ellipsometry, while high-pressure static birefringence measurements were used to determine the location of the ODT in dilated bulk samples. Log–log plots of χ_{ODT} vs ϕ_{diblock} allowed the determination of the scaling parameter, α, for comparison with the dilution approximation. At polymer volume fractions between 0.88 and 0.98, α varied between −1.2 and −1.3, which is consistent with scaling for neutral liquid diluents. At very low dilution, however, the scaling changes abruptly, and unusually high scaling parameters are observed for all copolymers at nearly identical polymer concentrations. This behavior suggests that solvent is initially segregating at the interface before beginning to distribute throughout the polymer. These data further illustrate the inadequacies of the dilution approximation (mean field) to correctly predict the ODT temperature, especially at very high polymer concentrations.

Introduction

Block copolymers are well-known for their ability to self-assemble into a wide variety of morphologies, which have proven exceptionally useful in creating materials and templates with ordered, nanometer-scale features.[1−4] Their phase behavior in the melt has also been the subject of extensive research in the past few decades with many theoretical and experimental advancements.[5−8] In cases where the unfavorable interactions between the dissimilar chains segments are relatively weak, these systems can undergo an order–disorder transition (ODT) in which the copolymer transitions from a disordered melt or solution upon cooling into domains having a periodically spaced domain structure. Because the transition is reversible, heating the copolymer back through the transition returns the system to a phase-mixed state. According to mean field theory, diblock copolymer phase behavior in the undiluted melt can be broken down into two relevant terms, χN and f, which are the product of the Flory–Huggins interaction parameter and the degree of polymerization, χN, and the volume fraction of a specific copolymer block, f, respectively.[9] For a symmetric diblock copolymer, theory predicts phase separation will occur at $(\chi N)_{\mathrm{ODT}} = 10.5$. Fredrickson and Helfand introduced modifications to Leibler's theory to include fluctuations in composition near the ODT.[10] The modified theory predicts that these fluctuations will result in lower ODTs in comparison to predictions by simple mean field theory, that the transition is first-order for all compositions, and that a direct disorder to lamellae transition is accessible. Khandpur et al.[11] confirmed these predictions experimentally using a series of styrene-*block*-isoprene copolymers.

Although neat block copolymer systems are quite well-understood, it is often important or advantageous to use a solvent–copolymer mixture in order to achieve a desired structure or specific physical properties. In the simplest case, the solvent is neutral toward the different segments and predominately acts to screen unfavorable intersegmental enthalpic interactions. The addition of good, neutral solvent to a diblock copolymer has become a common[12−15] and practical method of studying block copolymer behavior and is especially useful when extending to those systems which have ODTs that are difficult or even impossible to observe experimentally due to thermal stability limits. Such is the case for polymer chains with blocks possessing high molecular weights or strong unfavorable interactions (large χN). The solvent-mediated screening of these enthalpic interactions causes a shift in the phase diagram to lower temperatures and facilitates equilibration by enhancing chain mobility.[16] The results of these solution experiments have often been interpreted by scaling the T_{ODT} with the polymer volume fraction, ϕ:

$$\phi^{\alpha}(\chi N)_{\mathrm{ODT}} = \frac{F(f)}{2} \qquad (1)$$

This scaling concept, first proposed by Helfand and Tagami,[17] replaces χ in the melt with an "effective" interaction parameter, $\phi^{\alpha}\chi$, where α is the scaling parameter describing the effect of ϕ on χ and enables prediction of the phase diagram of the copolymer–neutral solvent system from the original melt-phase diagram by replacing changes in temperature with changes in neutral solvent concentration so that $\chi = \chi_{\mathrm{eff}} \equiv \phi^{\alpha}\chi$. Helfand and Tagami obtained a universal scaling exponent of $\alpha = -1$ from mean field theory, termed the dilution approximation.[17] The applicability of the dilution approximation, however, rests on the assumptions that the solvent is uniformly distributed with respect to the

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segregation, that it is nonselective for both blocks ($\chi_{AS} = \chi_{BS}$, where A and B denote copolymer blocks and S denotes solvent), and that it is a good solvent if using a liquid diluent.[16] This approach has been quite successful in predicting changes in *d*-spacings and order−order transitions (OOTs) with addition of solvent. This latter success is due in part to the strength of the mean field theory in calculating the free energies of the two strongly segregated phases.[14,15,18,19] However, extension of the dilution approximation to changes in T_{ODT} reveals weaknesses of the current fluctuation-corrected mean field theory. Whereas theory has suggested[16] that agreement may exist for concentrated solutions, no valid region for the dilution approximation has been observed experimentally. Furthermore, it has been established that the dilution approximation can significantly underestimate the ODT depression by a neutral solvent.

While the overwhelming majority of work published on the impact of copolymer dilution on their phase behavior involves neutral organic solvents such as dioctyl phthalate (DOP) or toluene in poly(styrene-*b*-isoprene),[15,19,20] this work focuses on the phase behavior of diblock copolymers diluted by compressed CO_2. A compressible fluid, in contrast to a traditional liquid solvent, enables adjustments in solvent strength by pressure-mediated changes in the fluid density. This attribute allows for continuous, reversible control over the solvent uptake in a polymer, especially at high polymer volume fractions. Previous work by Vogt and Watkins has shown that sorption of small volume fractions of CO_2 can increase the miscibility of styrene-*b*-isoprene copolymers, resulting in a depression of the ODT.[21] The high ODT temperatures of many diblock copolymers necessitates solvents with higher molecular weights (and lower vapor pressures) to prevent vaporization. As a consequence of their size, the solvent diffusion rates through the polymer can be low, leading to inhomogeneities in the solvent distribution at high ϕ. As $\phi \rightarrow 1$, CO_2 offers several advantages over these liquid solvents: the high diffusivity of CO_2 in polymers and the tunability of ϕ through changes in temperature and pressure.

Here, we will take advantage of these properties to examine the scaling of the ODT for a series of nearly symmetric poly(styrene-*b*-isoprene)s at high ϕ. We measure the location of the ordering transition by cooling from the disordered melt. Thus, in practice we are measuring a disorder-to-order transition (DOT). The literature referenced throughout the discussions describes both ODTs and DOTs, often using the term ODT generically to describe either. We use the term ODT throughout the text. The phase behavior of P(S-*b*-I) is well-established in the melt[11,18,22,23] and in solution near the ODT[12−15,20,24,25] and enables easy comparison between a compressible fluid (CO_2) and liquid solvents. To estimate $\phi_{polymer}$ when swollen with CO_2, careful swelling measurements of both individual homopolymers as a function of temperature and pressure are utilized. Previously, Lemert and co-workers[26] have demonstrated that CO_2 sorption in ordered block copolymers is equivalent to the weighted average of the respective homopolymers. Homopolymer swelling data are then utilized to elucidate how the ODT scales when $\phi > 0.9$, which can be extremely difficult or impossible with liquid solvents. The effect of hydrostatic pressure on the ODT has to be considered when working with high pressures, but this is nearly negligible (~19 K/kbar) for P(S-*b*-I) systems[27,28] for the pressures examined in this work.

Experimental Section

Sample Preparation: Birefringence. Three poly(styrene-*block*-isoprene) (P(S-*b*-I)) copolymers (SI 7/8, SI 11/10, SI 16/11) were obtained from Polymer Source (Dorval, PQ), and the fourth (SI 14/14) was obtained from the Polymer Synthesis Facility at the University of Minnesota. Volume fractions were calculated by assuming the densities of the phases to be 1.05 and 0.90 g/cm^3 for polystyrene and polyisoprene, respectively. Carbon dioxide (Coleman grade, 99.99%) was purchased from Merriam-Graves and used as received. The polymer properties are listed in Table 1. The copolymers were codissolved in toluene with Irganox 1076 (Ciba, 0.002 g/g polymer) to inhibit degradation of the isoprene block at high temperatures, and solutions were vacuum-dried at 115 °C until their weights remained constant. The polymers were melt-pressed at 110 °C into 1 mm thick aluminum sample-retaining rings, placed between two amorphous borosilicate (BK7) windows (ESCO Products), and the circumference wrapped in perforated Teflon tape. The sample was placed into the pressure cell and purged with CO_2.

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

sample	M_n (kg/mol)	f_{PS}	PDI	ODT (°C)
SI 7/8	15.0	0.44	1.03	109
SI 11/10	21.2	0.49	1.05	161
SI 16/11	27.3	0.54	1.05	222
SI 14/14	28.0	0.48	1.10	237

Static Birefringence. Static birefringence, shown by both Lodge and Balsara to be a reliable method of determining block copolymer ODTs for anisotropic phases,[19,24,29] was used to determine the ordering transitions for the SI samples. Schematics of both the experimental setup and the stainless steel pressure cell have been reported previously.[30] Modifications to the setup include a custom written LabView routine interfaced with an electronic pressure gauge (calibrated with a dead-weight tester), PID temperature controller, photodiode (Melles-Griot), and computer-controlled syringe pump (Teledyne Isco).[31] The LabView routine was designed to adjust temperature (0.2 °C intervals) and pressure to maintain constant CO_2 activity. Recent cell modifications include custom stainless steel window holders designed to allow for free-floating, circumferentially sealed windows in order to significantly reduce artifacts in the measurements resulting from stress-induced birefringence.[32] The direct O-ring-to-window sealing force at the face seal in the previous design led to significant temperature-dependent fluctuations in birefringence. Two oriented [0001] sapphire windows (Crystal Systems) were used as the pressure-retaining windows and sealed with Kalrez O-rings and Teflon backup rings. The cell was heated using an aluminum heating jacket with cartridge heaters. The measurement involves monitoring of the intensity of a HeNe laser as it passes through orthogonally oriented polarizers that are placed on opposite sides of the sample. A small amount of light was transmitted in the absence of sample due to error in the cut angle of the sapphire windows (±2°). This intensity, however, remained small and nearly constant over the experimental conditions. Before beginning the acquisition, the block copolymer was heated in the cell above its ODT until the transmitted intensity reached a minimum, which was approximately identical to the empty cell. The sample was equilibrated for 6 min between set points, which was found to be sufficient for reproducible data as no change was observed in the T_{ODT} for longer periods. Upon ordering into a lamellar morphology, the copolymer becomes birefringent and the transmitted intensity increases abruptly. The ODT was calculated as the inflection point of the sigmoidal transmitted depolarized intensity curve obtained by cooling through the transition.

Sample Preparation: Ellipsometry. For measuring polymer swelling by CO_2, films of both polystyrene (91 000 g/mol) and polyisoprene (84 200 g/mol) (Polymer Source) were used as received. The polymers were dissolved in toluene in concentration ranges of 1−8 wt % and spin-coated at 2000 rpm onto 2 in. prime grade silicon wafers (University Wafer). While the polyisoprene was spun on as-received wafers, the polystyrene was spun on wafers that had first been pretreated in a 4:1 H_2SO_4 (conc):H_2O_2 (30%) (by volume) piranha solution. [*Caution*: Handle with extreme care. Piranha solution reacts violently with organics.] Monohydroxy-terminated polystyrene (100 000 g/mol; Sci. Poly. Products) was immediately

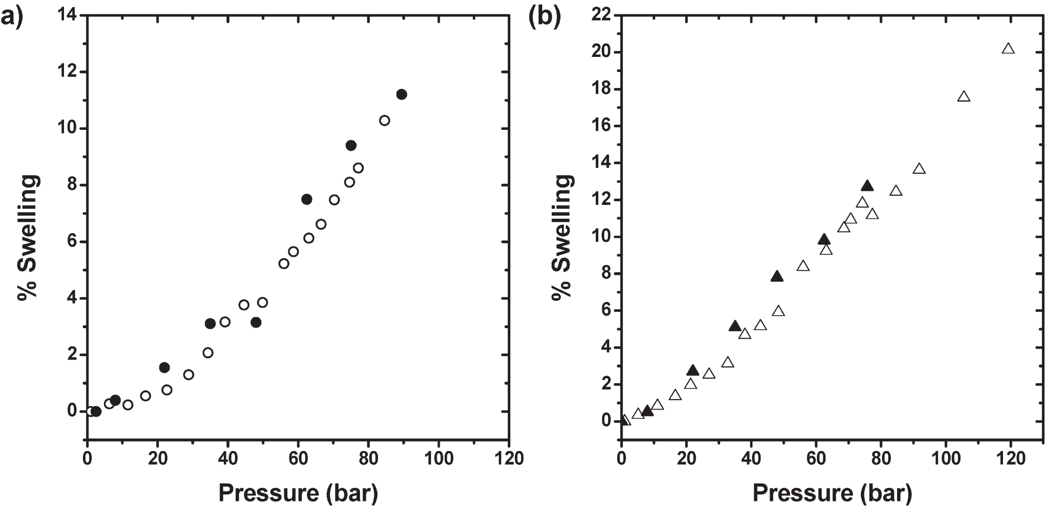

Figure 1. Swelling of 200 nm (a) PS (○, ●) and (b) PMMA (△, ▲) and films at 65 °C obtained using spectroscopic ellipsometry (△, ○) and neutron reflectivity (▲, ●) in compressed CO_2. There is good agreement between the different measurements.

spin-coated after piranha treatment and baked for 48 h at 150 °C to form a covalently attached brush. Unreacted polymer was removed by both sonicating and rinsing in toluene, and the final polystyrene films were spun to thicknesses of 160, 195, and 545 nm. The use of a brush layer was found to reduce the dewetting of PS films upon exposure to CO_2 at elevated temperatures during the ellipsometry measurements. The polyisoprene films used in this study were spun to 60 nm. All films were subsequently vacuum-annealed above their T_g's to remove any residual solvent. For the neutron reflectivity comparisons, PS (96 000 g/mol) and PMMA (77 000 g/mol) films were prepared as described above, but without piranha or brush treatment.

Ellipsometry. Spectroscopic ellipsometry (GES-5 spectroscopic ellipsometer (SOPRA), $\lambda = 400-800$ nm) was performed to obtain the swelling of several polystyrene and polyisoprene homopolymers by compressed CO_2 at elevated temperatures. A custom-built, stainless steel high-pressure cell, whose schematic has been reported elsewhere,[31] uses the same circumferentially sealed window design as the birefringence cell, with angles of incidence and reflection of 75°, approximately the Brewster angle of silicon. The window design eliminated nearly all artifacts in the acquired data from stress-induced birefringence caused by heating the confined window in the cell. Cartridge heaters and a PID controller (Omega) were used to heat and maintain the cell temperature. After heating, the spectra were not collected until the internal fluid temperature remained constant. Samples were equilibrated for 15 min after each increase in pressure, which was controlled by a needle valve connected to the syringe pump. Analysis of the elevated pressure data was performed using a custom written routine based on simulated annealing[33] whose source code has been previously reported.[31] This routine included a correction to compensate for inherent window birefringence as described in a patent by J.A. Woollam Co., Inc.[34] The routine also modeled the refractive index of the polymer film using a Cauchy dispersion relationship,[35] and the refractive index of the CO_2 atmosphere was determined by the Lorentz–Lorenz equation using data previously reported for CO_2 at various pressures and wavelengths.[31,36]

Results and Discussion

Homopolymer Swelling. In order to obtain a quantitative description of the ODT scaling behavior, a reliable method of determining the ϕ_{diblock} is required as this is thermodynamically controlled through equilibrium sorption of CO_2 in the copolymer. The use of individual homopolymer swelling has been demonstrated to be a satisfactory method of estimating ϕ_{diblock} in a phase-separated solvent–polymer mixture. This is accomplished as shown in eq 2

$$\phi_{\mathrm{P}(S-b-\mathrm{I})} = f_{\mathrm{PS}}\phi_{\mathrm{PS}} + f_{\mathrm{PI}}\phi_{\mathrm{PI}} \tag{2}$$

where the swelling of each diblock constituent is weighted by its composition in the copolymer.

Accurate swelling measurements in the presence of CO_2 are key to calculating the scaling relationships, and swelling measurements by several techniques, such as direct visual observation of bulk polymers,[26,37,38] neutron reflectivity[39−41] of thin films and polymer brushes, and waveguide spectroscopy,[42] have been reported in the literature. High-pressure spectroscopic ellipsometry (HPSE) has also received notable attention in the past several years. Sirard and co-workers[43] have used ellipsometry to measure the chain extension of end-grafted PDMS monolayers altered through CO_2 sorption. Additionally, the group demonstrated successful swelling and refractive index measurements of PMMA[44] and PDMS[45] of varying thicknesses and on different substrates. We have followed a similar methodology and have performed preliminary swelling measurements to verify the ellipsometric technique used in this study. The ellipsometry measurements were compared to neutron reflectivity (NR) values for similar films as shown in Figure 1. The NR swelling data obtained previously[46] and the ellipsometry data for 200 nm PS and PMMA films swollen in the presence of CO_2 at 65 °C are in good agreement. One item to note is that these PS films were not prepared on wafers containing PS brushes. These swelling measurements are also in reasonable agreement with bulk swelling data reported by Wissinger and Paulaitis at lower pressures.[37] At higher pressures, Wissinger's data begins to deviate from the film measurements as the bulk sample undergoes a glass transition. Any minor discrepancies between the NR and HPSE data may be a result of differences in film uniformity and possibly equilibration times between scans due to the polymers being below their glass transitions.

Figure 2 shows the homopolymer swelling data that are used to calculate ϕ_{diblock} for the P(S-*b*-I) copolymers in this study as a function of CO_2 activity. Scaling the swelling with the activity of the CO_2 fluid phase allows the pressure and temperature dependence of the swelling to be collapsed into a single parameter, greatly simplifying comparisons between

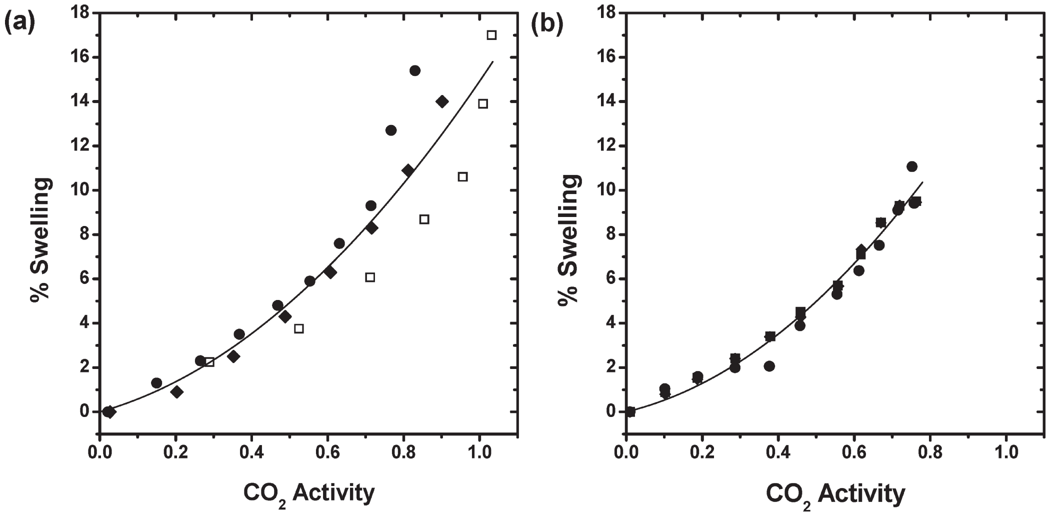

Figure 2. (a) Swelling of 60 nm polyisoprene films at 24 °C (◆) and 49 °C (●) and bulk data from Zhang et al. at 35 °C (□).[26] (b) Swelling of polystyrene films with initial thicknesses of 162 nm (◆), 307 nm (■), and 561 nm (●) dilated with compressed CO$_2$ at 115 °C as measured by spectroscopic ellipsometry. The solid lines are polynomial fits to the data.

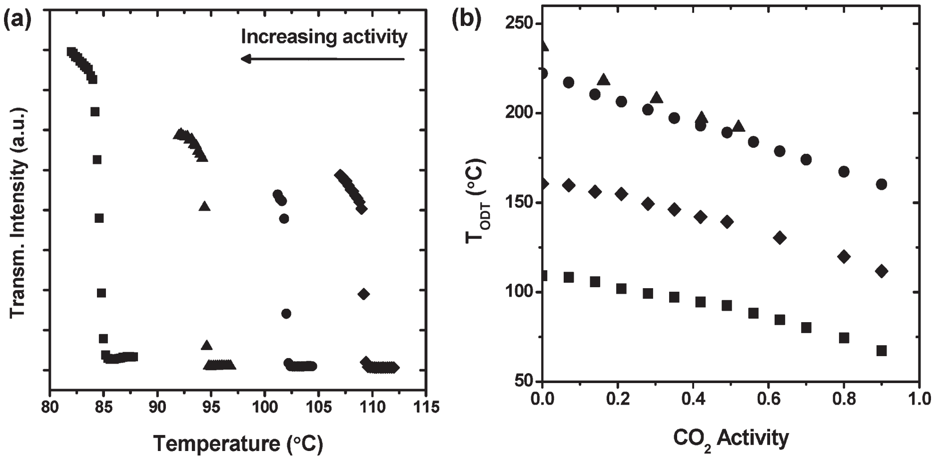

Figure 3. (a) Raw birefringence data of SI 7/8 showing the sharp increase in the transmitted (depolarized) intensity at the ODT for activities of 0.00 (◆), 0.21 (●), 0.42 (▲), and 0.63 (■). (b) ODT temperatures of SI 7/8 (■), SI 11/10 (◆), SI 16/11 (●), and SI 14/14 (▲) as a function of CO$_2$ activity.

swelling isotherms as shown in the literature.[30,47] For measurements above the critical temperature of CO$_2$, the vapor pressure of the fluid was estimated by extrapolation of the Antoine equation. Polyisoprene swelling isotherms at 24 and 49 °C are nearly identical and compare well to reported bulk cathetometer data,[26] which has also been converted to activity. The bulk data begins to deviate at higher pressures from our thin film samples and may be a result of the extrapolation of the styrene−isoprene block copolymer swelling used by Zhang to estimate the polyisoprene swelling. For thin films, anomalous swelling[44] near the critical pressure of CO$_2$ or altered glass transition temperatures[48,49] may lead to differences from bulk behavior due to effects of the polymer−substrate and polymer-free surface interfaces. However, anomalous swelling should have less influence with increasing temperature from the critical point as the compressibility of CO$_2$ decreases.

The polystyrene data in Figure 2 were collected using films of various thicknesses at 115 °C to verify that bulk swelling behavior was observed (since the birefringence samples are 1 mm thick). These data show no thickness dependence and are consistent with bulk measurements reported in the literature. All isotherms also exhibit upward curvature, which is typically observed for polymers above their glass transition temperatures.[37] Comparison of the polystyrene and polyisoprene swelling emphasizes the nominally neutral behavior of CO$_2$. As an example, at a solvent activity of 0.5 the measured swelling was ~5% for both polymers as determined by the fits to the data.

Scaling of the ODT. Birefringence data for each SI copolymer were collected as a series of constant activity (constant CO$_2$ volume fraction) experiments. The raw data curves for several CO$_2$ activities for SI 7/8 are shown in Figure 3a. There is a sharp increase in the transmitted intensity upon cooling, consistent with a first-order transition to the ordered lamellae morphology. The ODTs for the copolymers are expected to be transitions to the lamellar phase for all instances, as SANS data has previously confirmed for SI 7/8 and SI 11/10.[21] From the raw data curves, the ODTs for each activity are determined as the temperature at which the slope is maximum, which is associated with the inflection point of the intensity profile. Figure 3b shows the ODT temperatures as determined for all SI samples as a function of activity. It is obvious from the data that CO$_2$ is effective at screening the unfavorable A−B interactions and promoting mixing at lower temperatures than at ambient pressure. In the case of SI 16/11, the ODT temperature is depressed by over 60 °C for the activity range studied. These transitions induced by CO$_2$ sorption are completely reversible by simply reducing the fluid phase activity and are repeatable to within 1−2 °C.

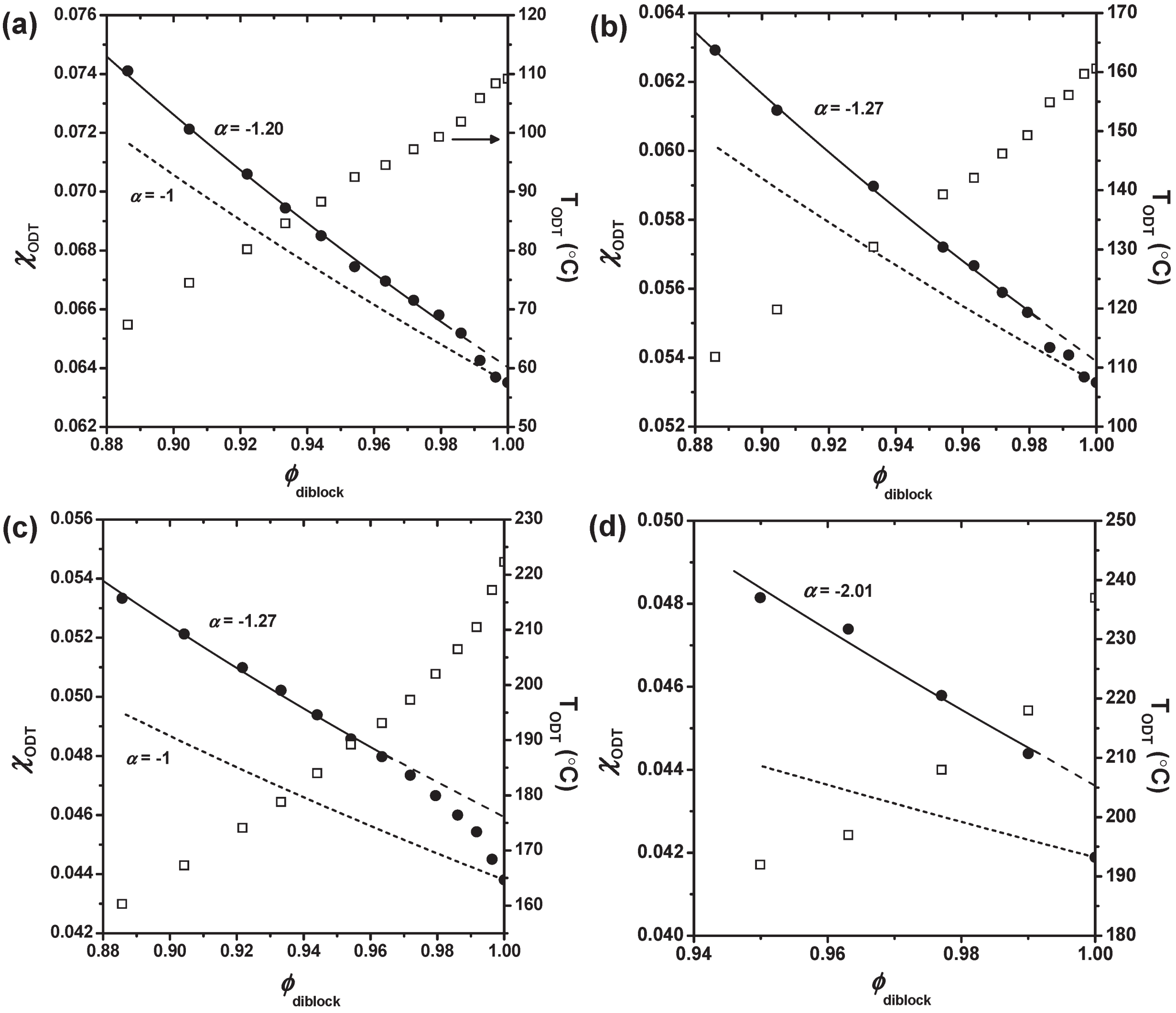

Figure 4. Scaling behavior of χ_{ODT} (●) and T_{ODT} (□) as a function of $\phi_{diblock}$ for (a) SI 7/8, (b) SI 11/10, (c) SI 16/11, and (d) SI 14/14 along with α calculated from the log–log slope (approximated by the solid lines) at higher dilutions. The dashed line that is longer represents the dilution approximation (α = −1), whereas the shorter dashed line is the extrapolation of higher dilution data to the neat melt.

To obtain χ at the ODT for SI diblocks (χ_{SI}), the ODT temperatures were converted using the established temperature dependence of χ for SI melts:[20]

$$\chi_{SI} = \frac{33}{T} - 0.0228 \qquad (3)$$

Combining the calculated $\chi_{SI\text{-}ODT}$ and $\phi_{diblock}$ (calculated from the film swelling data), the scaling parameter, α (recalling that α = −1 for the dilution approximation), from eq 1 can be determined from the slope of their log–log plot. Figure 4 shows the ϕ dependence of χ_{ODT} for all SI copolymers studied and is plotted on a linear scale to simplify viewing due to the limited ϕ range. The dashed lines represent the ODTs predicted by the dilution approximation. For all data sets, the experimental data deviate from the dilution approximation (Figure 4) to larger χ_{ODT}. Thus, the mean field theory[9] underestimates the screening of intersegmental interactions by CO_2 (or any neutral solvent), which acts to stabilize the disordered state. In other words, it does not accurately predict the free energy of the ordered state for a polymer–solvent system near the ODT. The mean field theory does not account for segmental fluctuations in composition (which also act to stabilize the disordered state) and therefore will be inaccurate near the ODT. As the copolymer molecular weight increases, these fluctuation effects are reduced, and the Fredrickson–Helfand fluctuation theory reduces to Leibler's mean field theory in the limit of infinite molecular weight.[16] For short chain lengths such as those examined in this study, fluctuations are an important factor in the free energy term. Also noteworthy is that mean field theory neglects entropic effects of chain stretching. Therefore, the possibility exists that addition of a small fraction of solvent could act to relieve this penalty.[20]

For all copolymers but the highest molecular weight, the scaling parameter appears to reach limiting values of approximately −1.2 to −1.3, as shown explicitly in Figure 5 for $\phi < 0.98$, and persist through the dilution range studied. These values are similar to the scaling exponents reported for lamellar SI diblocks in neutral DOP over a concentration range of approximately 0.55 to 1 (α = −1.31 and −1.38).[19] However, the scaling of the ODT at concentrations near the neat melt ($\phi > 0.9$) has not previously been reported. Fredrickson and Leibler's[16] fluctuation-corrected predictions suggested years ago that the dilution approximation would apply only to concentrated systems ($\phi > 0.1$). However, no apparent range of validity for the dilution approximation has been observed experimentally in the literature where $\phi \leq 0.9$. The ϕ range for SI 14/14 is limited in comparison to the other three, but it appears that α is in a

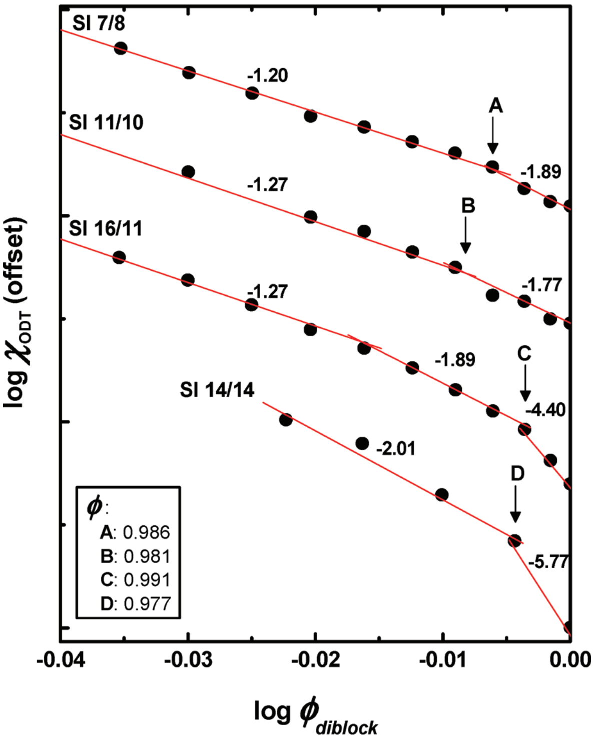

Figure 5. Log−log plot of χ_{ODT} as a function of $\phi_{diblock}$ for each copolymer showing the breaks in the scaling behavior and corresponding values of α. The data are offset for clarity, and ϕ at each initial break is given in the legend.

transient region (similar to $0.97 < \phi < 1$ for SI 16/11). If greater dilutions had been measured, it is possible that a similar limiting exponent for α (approximately −1.3) could have been obtained. Yet, none of the samples appear to approach the dilution approximation at any concentration. As mentioned previously, polymer solutions with traditional solvents at the concentrations reported here ($\phi > 0.9$) may create solvent inhomogeneities due to poor diffusion rates within the polymers. Using compressed CO_2 as a solvent, the scaling behavior has been examined at very low dilutions to complete the concentrated scaling window with no evidence for validity of the dilution approximation for the ODT in any concentration range.

The use of CO_2 has revealed interesting ODT scaling behavior not seen previously with liquid diluents. The behavior is observed in the highest concentrations in Figure 4 in which χ_{ODT} does not extrapolate to the value of the ODT for the pure copolymer as the scaling deviates more severely from the dilution approximation. A similar phenomenon has been shown by Lai et al., where the *d*-spacing in solution does not scale to the value of the neat melt as the concentration of various solvents is extrapolated to the pure diblock copolymer.[50] A recent study[51] describing the effects of CO_2 sorption on the *d*-spacing of P(S-*b*-DMS) suggests that asymmetric swelling of the respective blocks can lead to abrupt deviations from scaling at low dilutions. However, the selectivity of CO_2 in the present study is shown to be negligible. Nonetheless, in the systems considered here we find abrupt deviations in the scaling exponent are observed at moderate dilutions as the system approaches the pure block copolymer melt. This behavior is shown in more detail in Figure 5. Closer inspection reveals that these abrupt changes occur at similar dilutions. The neutral good solvent toluene has been shown by SANS analysis[52] to collect at the interface of segregated styrene-*b*-isoprene systems, which agrees with predictions by Fredrickson and Leibler's mean field analysis.[16] Other work by Naughton and Matsen[53] has suggested that both decreasing the quality of a solvent and increasing its size may drive the solvent to collect at the A−B interface. CO_2 is a poor solvent for both blocks, and it may therefore be possible that solvent collects predominantly at the interface in the initial dilution regions of highest α in Figure 5. Additional solvent uptake may then partition more evenly between each of the copolymer blocks and the interface as the interfacial sites become occupied.

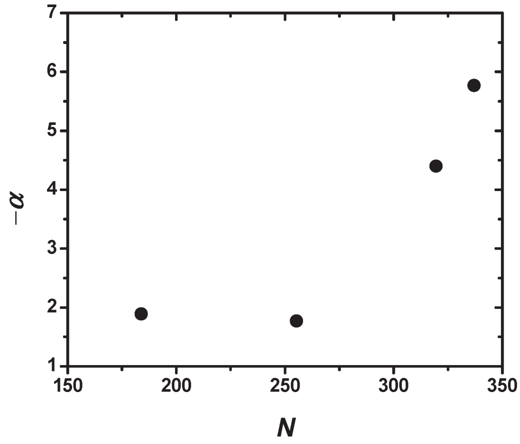

Figure 6. Scaling exponent (α) versus the copolymer total degree of polymerization *N*, represented as the initial slopes in Figure 5 from $\phi \approx 0.97$ up to the undiluted melt.

It is also important to determine whether there may be any effects of *N* on the scaling parameter, α. As previously mentioned, the three lower molecular weight copolymers have apparent limiting values of α = −1.2 to −1.3 as dilution increases, while SI 14/14 appears to be approaching that value. When plotting the scaling parameters obtained from the initial slope region from approximately $\phi \approx 0.98$ to the undiluted melt (shown in Figure 6), an increasing dependence on *N* is evident. Lodge et al.[19] observed a similar dependence for SI copolymers in DOP at higher dilution. This cannot be explained by a greater mean field-type behavior expected with increasing *N* as this would act to decrease α. As mentioned above, the entropic effects of chain stretching at the interface are also neglected in the theory. A minimal amount of solvent may help to reduce these penalties and may be partially responsible for the rapid decreases in α.

Conclusions

The phase behavior of several nearly symmetric P(S-*b*-I) diblock copolymers swollen by compressed CO_2 (as a near-neutral solvent) was determined by static birefringence measurements at constant CO_2 activity (constant $\phi_{diblock}$). We have used high-pressure ellipsometry measurements of thin homopolymer films to estimate the total volume fraction of the diblock in the CO_2/diblock system. This has allowed us to determine the scaling exponent from eq 1 in the concentration region of $0.9 \le \phi_{diblock} \le 1$ by the log−log slope of χ_{ODT} as a function of $\phi_{diblock}$. The use of compressed CO_2 has made this range possible through simple, continuous adjustments in the solvent density (solvent quality). Data obtained at lower concentrations show that α reaches a limiting value of −1.2 to −1.3 for smaller chain polymers but also appears to be approaching this value for the highest molecular weight SI 14/14 sample. These values are close to that previously reported for experiments at lower polymer concentrations, and they reiterate the inability of the dilution approximation to accurately describe the disordered state free energy.

The scaling behavior at very high polymer concentrations also revealed interesting and abrupt changes in α at nearly identical concentrations for all samples. It has been shown that even for a neutral, good solvent there will be some partitioning of the diluent at the interface (which can increase with decreasing solvent quality). This slope change may be attributed to the solvent collecting predominantly at the interface in the higher slope region and then distributing throughout the blocks as contact sites are occupied. Finally, our data suggest that a dependence of α on N exists for this higher ϕ data, which is contrary to mean field theory predictions of decreasing α with increasing molecular weight. However, a similar dependence on N also observed in this work has been reported for SI copolymers in DOP at lower concentrations.

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