Scaling of Interdomain Spacing of Diblock Copolymers in a Selective Diluent

Timothy J. Francis,[†,§] **Bryan D. Vogt,**[⊥,‡] **Michael Xiaohui Wang,**[‡,#] **and James J. Watkins***[†]

Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003, and Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

ABSTRACT: Interdomain spacing, d, of microphase-separated poly(styrene-*b*-dimethylsiloxane) in high-pressure carbon dioxide (CO_2) was found to follow a modified power law scaling, $d/\xi \sim \phi_{diblock}^{-\gamma}$, where ξ is a swelling asymmetry factor and $\phi_{diblock}$ is the volume fraction polymer. This interdomain spacing was measured in situ both isothermally and at constant $\phi_{diblock}$ using small-angle neutron scattering. The use of high-pressure CO_2 as the diluent enabled precise control of sorbed solvent volume fraction in highly concentrated systems at elevated temperatures. Data measured at constant $\phi_{diblock}$ are in agreement with theoretical predictions and experimental data for dilution by traditional liquid solvents and follow the scaling law $d \sim \chi_{AB}^{-\beta}$. In the highly concentrated regime, the isothermal dependence on $\phi_{diblock}$ cannot be described by the simple power law scaling previously suggested for liquid diluents, $d \sim \phi_{polymer}^{-\gamma}$. By accounting for solvent selectivity using ξ, however, d-spacing as a function of $\phi_{diblock}$ for a system exhibiting lamellar morphology collapses to a common scaling.

Introduction

Microphase-separated block copolymers are promising nanoscopic templates due to their ability to self-assemble into ordered structures with prescribed morphologies.[1,2] These templates can be used for numerous applications including the preparation of ordered metal−polymer nanocomposite materials,[3] nanowires for integrated magnetoelectronic devices,[4] magnetic storage media,[5,6] and mesoporous silica.[7−9] The utility of these materials is generally strongly dependent upon the size of the nanostructures and thus the interdomain spacing of the phase-separated copolymer. One route to control the characteristic interdomain spacing of the copolymer is synthetic through the size of the macromolecule, N, where the interdomain spacing, d, has been shown to follow the scaling $N^{2/3}$.[10] However, precise control of domain spacing can be difficult, and the synthesis of new polymer is necessary for even slight variation in the domain size.

A more facile approach to control of the interdomain spacing is through dilation of the block copolymer with a small molecule diluent. Variation of d is possible through adjustments in the concentration of the solvent and solvent selectivity.[11−15] The interdomain spacing of a microphase-separated copolymer dilated with liquid solvents at concentrations of less than ∼10% of the diluent generally follows a simple power law

$$d \sim \phi_{diblock}^{-\alpha} \qquad (1)$$

where α is the scaling coefficient describing the change in d with $\phi_{diblock}$. For the case of a nonselective diluent added to a phase-separated copolymer, experimental measurements have shown that α varies from $\alpha = -0.23$ to $\alpha = -0.33$.[11−15] Numerical calculations of α for nonselective solvents predict that in the strong segregation limit $\alpha = -0.50$ and in the weak segregation limit $\alpha = -0.20$.[16,17] Thus, dilution by nonselective solvents appears to be well understood, with agreement between experiment and theory.

The effect of the addition of selective diluents on α is more complicated. Experimental work[11,12,18] has revealed that α for a selective solvent depends on the degree of solvent selectivity, solvent volume fraction, the relative volume of the two phases, and the morphology of the ordered state. Depending on these factors, α has been shown to vary from $\alpha = -0.51$ to $\alpha = 0.46$ for various polymer−solvent systems. Several numerical estimations[16,18] of α for various model copolymer−diluent systems predict that α can vary from $\alpha = -0.31$ to $\alpha = 1.00$ for selective diluents. The work of Lai, Russel, and Register illustrates the complexity of the behavior of the interdomain spacing when block copolymers are dilated with selective solvents.[12] In their study, the behaviors of several poly(styrene-*b*-isoprene)s dilated by a series of isoprene selective solvents were studied. The scaling exponent of the power law given by eq 1 was found to increase with solvent selectivity and was shown to be dependent upon the copolymer composition and the copolymer morphology. As the fraction of styrene was increased from the symmetric case, α was also found to increase as the morphology of the copolymer progressed from spheres to cylinders to lamellae. One surprising feature noted by the authors is that interdomain spacings for diluted systems exhibiting a lamellar phase in three solvents of varying selectivity do not extrapolate to the same bulk domain spacing, with the discrepancy becoming more severe as the diluent becomes more isoprene selective.[12] This suggests that in the limit of highly concentrated copolymer solutions the scaling relationship given by eq 1 may fail, although for the system studied the analysis is complicated by the presence of an OOT at high $\phi_{diblock}$. (The

* Corresponding author. E-mail: watkins@polysci.umass.edu.
† University of Massachusetts.
‡ National Institute of Standards and Technology.
§ Present address: Department of Polymer Physics, BASF AG, Ludwigshafen, Germany.
⊥ Present address: Department of Chemical Engineering, Arizona State University, Tempe, AZ 85287.
Present address: Intel Technology Development (Shanghai) Ltd., PR China.

neat copolymer used in the study exhibits a cylindrical morphology.)

Although organic liquid solvents have traditionally been used to modify polymer properties, recently compressible fluids, such as CO_2, have been investigated for similar purposes.[19–22] Polymers dilated by CO_2 are useful as media for chemical modification,[23,24] including synthesis of nanostructured materials using block copolymers as templates.[9,25] Additionally, since most polymers are not soluble in CO_2,[26,27] the concentration of carbon dioxide in the polymer is equilibrium controlled and can be varied through changes in pressure and temperature. Accurate equations of state for CO_2 allow for the effects of pressure and temperature to be determined through calculation of the fluid activity, which collapses CO_2 sorption isotherms onto a master curve.[28,29] Because of the tunable solvent quality of CO_2, the polymer volume fraction in a dilated system, $\phi_{polymer}$, can be continuously adjusted using temperature and pressure.[30,31] These attributes of CO_2 sorption allow for probing of highly concentrated polymer solutions at elevated temperatures and precise solvent volume fractions, which is generally difficult to achieve using liquid solvents.

In this work, we explore the interdomain spacing in concentrated block copolymer solutions. We use compressed carbon dioxide as a tunable, partially selective diluent for poly(styrene-*b*-dimethylsiloxane) while measuring the interdomain spacing in situ with small-angle neutron scattering. The interdomain spacing is examined isothermally while varying the CO_2 pressure and therefore $\phi_{diblock}$. The temperature dependence of d for the swollen diblock was measured at constant $\phi_{diblock}$ by holding the fluid phase activity of CO_2 constant.

Experimental Section

Poly(styrene-*b*-dimethylsiloxane) with a number-average molecular weight (M_N) of 12.5 kg/mol, weight fraction of polystyrene (w_{PS}) of 0.44, and a polydispersity index of 1.09 was obtained from the Polymer Synthesis Facility at the University of Minnesota. Samples were prepared by melt pressing the copolymer at 150 °C into a 1.0 mm thick, 8.0 mm diameter aluminum ring. Measurements were performed using a stainless steel high-pressure cell utilizing sapphire windows. The design of this cell has been previously reported in the literature.[32] Prior to measurements, the cell was purged with low pressure (<100 psi) CO_2 to remove residual air.

Small-angle neutron scattering (SANS) measurements were performed on the NG-1 8 m beamline at the Center for Neutron Research at the National Institute of Standards and Technology, Gaithersburg, MD, utilizing a wavelength, λ, of 6 Å with a wavelength spread, $\Delta\lambda/\lambda$, of 0.12. The sample-to-detector distance was 3.84 m. The resultant scattering vector, q, ranged from 0.01 to 0.18 Å^{-1}, where $q = 4\pi/\lambda \sin\theta$ and θ is the scattered angle. The interdomain spacing was determined from the center of the primary scattering peak, q^*, as $d = 2\pi/q^*$.

To determine the influence of CO_2 on the interdomain spacing, two distinct experiments were performed: isothermal measurements with increasing pressure (hence CO_2 concentration) and constant composition through fixed CO_2 activity,[28,29,33] varying the temperature to elucidate thermal effects. The activity of fluid phase was calculated using the Peng–Robinson equation of state.[29,34]

The copolymer swelling was calculated as the volume fraction weighted average of the swelling of the constituent homopolymers

$$\Delta V = f_{PS}\Delta V_{PS} + f_{PDMS}\Delta V_{PDMS} \tag{2}$$

where ΔV is the fractional volume change of the phase-separated diblock copolymer, ΔV_i is the fractional volume change of the constituent homopolymers, and f_i is the volume fraction of the i domain. For microphase-separated diblock copolymers, this has been shown to be an accurate method[35] for determining copolymer
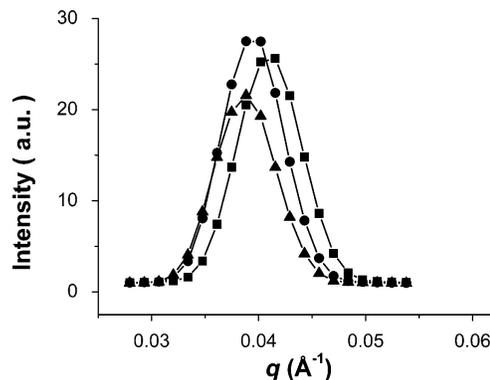

Figure 1. SANS data for poly(styrene-*b*-dimethylsiloxane) dilated with carbon dioxide. The overlay shows the primary scattering peak measured at 40 °C and three pressures, corresponding to (■) $\phi_{diblock} = 1.0$, (●) $\phi_{diblock} = 0.923$, and (▲) $\phi_{diblock} = 0.782$. Lines are drawn as a guide to the eye.

volume fraction, $\phi_{diblock}$. We used data for CO_2 swelling of polystyrene[30,36] and un-cross-linked poly(dimethylsiloxane)[31,37] from the literature in combination with the Flory equation to calculate ΔV at each condition, where the Flory equation simplified for a polymer–diluent system is

$$\ln a = \phi_{polymer} + \ln(1 - \phi_{polymer}) + \chi_{AS}\phi_{polymer}^2 \tag{3}$$

where χ_{AS} is the polymer–diluent interaction parameter, a is the activity of the diluent in the polymer, and $\phi_{polymer}$ is the volume fraction of polymer in the dilated polymer phase. Since the CO_2 concentration in the polymer is equilibrium controlled and the diblock is insoluble in CO_2 at the conditions examined, the CO_2 activity in the polymer phase is equal to its activity in the fluid phase. For polystyrene dilated by CO_2 $\chi_{AS} = 1.72$, while for poly-(dimethylsiloxane) $\chi_{AS} = 0.855$. The A–B interaction parameter for P(S-*b*-DMS) has been reported[38] as

$$\chi_{AB} = \frac{68}{T} + 0.037 \tag{4}$$

where the temperature, T, is in kelvin. This χ_{AB} is used for the constant $\phi_{diblock}$ data to elucidate the thermal effects for this system.

Results and Discussion

The interdomain spacing of poly(styrene-*b*-dimethylsiloxane) was measured in high-pressure carbon dioxide using small-angle neutron scattering, both isothermally and at constant $\phi_{diblock}$. The isothermal scattering profiles for the copolymer at three pressures at 40 °C are shown in Figure 1. There is a slight shift in the peak position to lower q with increasing pressure, indicating CO_2 sorption increases the interdomain spacing, d. This illustrates the selective nature of CO_2 for the PDMS over PS, as d generally decreases as the system becomes more concentrated for weakly selective solvents.[12,18] In addition to the primary scattering peak, a second-order reflection at $q = q_2^*$ is clearly visible in the scattering (not shown in Figure 1). From ratio of the secondary scattering peak to the primary scattering peak, it was determined that a lamellar phase is present in the copolymer at all conditions examined in these experiments as $q_2^*/q_1^* \approx 2$. Irrespective of the temperature (40 °C < T < 140 °C) or pressure (<250 bar), the copolymer remained in the lamellar phase. This indicates that although other copolymer systems have shown that dilution of a copolymer by highly selective solvents can induce order-to-order transitions (OOTs), a sufficient change in f_A from selective dilatation to cause an OOT was not realized in our experiments. From the raw scattering data, it appears as though CO_2 behaves similarly to a partially
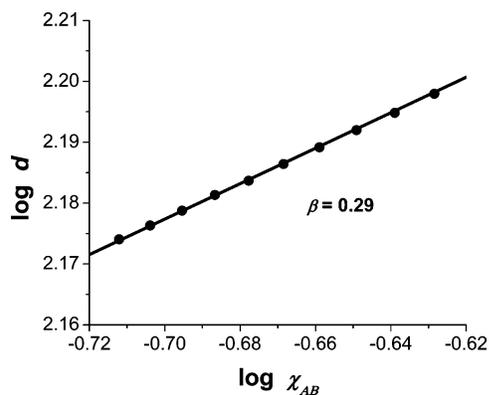
Figure 2. Interdomain spacing of P(S-*b*-DMS) as a function of the segregation parameter, χ_{AB}, in CO_2 at a constant activity of $a = 0.92$. The scaling exponent, β, is determined to be 0.29 from a fit to the data using eq 5.

selective liquid solvent, except that probing high ϕ is facilitated by using sorption equilibrium to control concentration.

Hydrostatic pressure that is inherent to CO_2 processing can also influence the phase behavior and hence the interdomain spacing. Work by Schwahn and co-workers utilizing poly-(ethylene propylene-*b*-dimethylsiloxane) has shown the effect of hydrostatic pressure on d to be small.[39] A decrease in d of less than 1 Å was observed when the hydrostatic pressure is increased from $P \approx 0$ bar to $P \approx 1764$ bar. The highest pressure examined in this study was less than 250 bar; thus, we can assume that the effect of hydrostatic pressure on the measured interdomain spacing is negligible. We can test this assumption by measuring the domain spacing at constant CO_2 concentration, by holding the fluid phase activity constant,[28] while varying the temperature (and thus the pressure to maintain constant activity).

The temperature effect on the domain spacing in dilated as well as neat systems has been well characterized.[18,40−42] The effect of temperature on d is usually adequately described by the power law

$$d \sim \chi_{AB}^{\beta} \qquad (5)$$

where the effect of temperature is described by use of the A−B interaction parameter, χ_{AB}, which varies inversely with temperature, and β is the scaling coefficient describing the effect of χ_{AB} on d. Experimental work[11,12] has shown that β varies from $\beta = 0.23$ to $\beta = 0.33$ depending on the copolymer characteristics and solution conditions. Numerical prediction[17] of the scaling of d with χ_{AB} has shown that β varies from $\beta = 0.2$ in the strong segregation limit to $\beta = 0.33$ in the weak segregation limit, in agreement with experimental observations.

The interdomain spacing at a constant CO_2 activity of 0.92, which corresponds to $\phi_{diblock} = 0.78$, was investigated over the temperature range from 60 to 160 °C (Figure 2). From these data the scaling parameter, β, as given by $d \sim \chi_{AB}^{\beta}$, was determined to be $\beta = 0.29$, where χ_{AB} was calculated according to eq 4. The fact that the data are well described by eq 5 supports the assumption that hydrostatic pressure does not significantly affect d. A value of $\beta = 0.29$ agrees well with the previously reported values of β for liquid diluents.[13] The linear scaling of β with χ_{AB} also suggests that hydrostatic pressure does not contribute significantly to the interdomain spacing because the nonlinear dependence of pressure corresponding to a given value of χ_{AB} for a constant activity of $a = 0.92$ would otherwise introduce curvature in Figure 2.
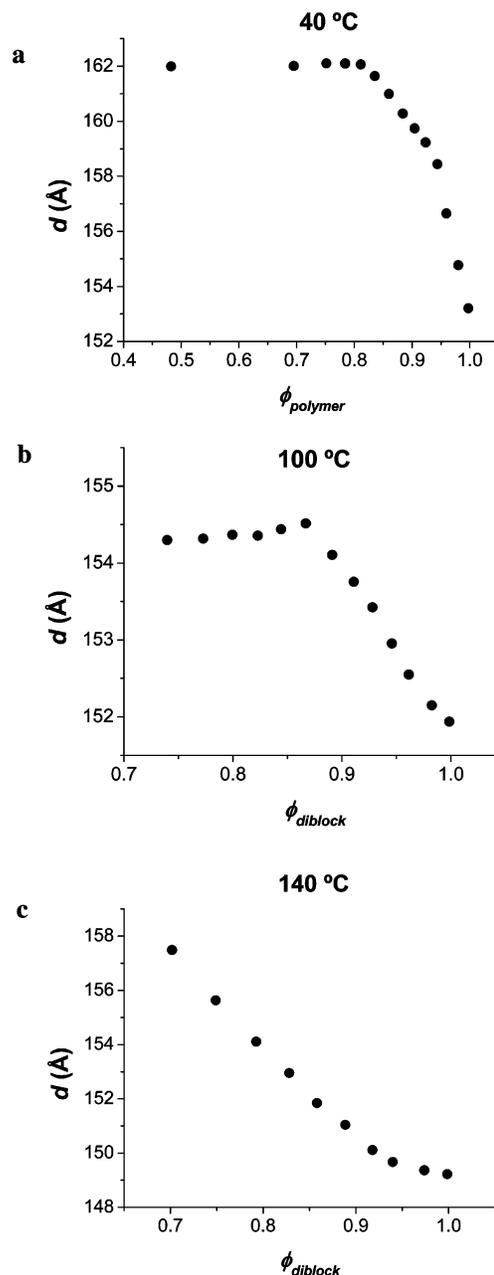

Figure 3. The d-spacing of P(S-*b*-DMS) dilated with CO_2 as a function of $\phi_{diblock}$ at 40 (a), 100 (b), and 140 °C (c).

The interdomain spacing of P(S-*b*-DMS) was also examined as a function of $\phi_{diblock}$, isothermally at 40, 100, and 140 °C. For liquid diluents, the scaling of d with $\phi_{diblock}$ is strongly dependent upon the solvent selectivity but generally conforms to a power law (eq 1) at $\phi_{diblock}$ below 0.9.[11,12,18] Examination of d at high $\phi_{diblock}$ is generally hindered by difficulty in preparing homogeneous samples at high polymer volume fraction and maintaining constant solvent concentration at elevated temperatures; however, for compressed CO_2, whose concentration is equilibrium controlled, measurements in the concentrated regime at elevated temperatures are easily realized, allowing for the interdomain scaling to be probed as $\phi_{diblock} \rightarrow 1$.

The d-spacing of P(S-*b*-DMS) as a function of $\phi_{diblock}$ at 40, 100, and 140 °C is shown in Figure 3 using a linear scale and compared on a log−log scale in Figure 4a. Interestingly, unlike the single power law obtained for liquid diluents at greater dilutions, α varies with $\phi_{diblock}$ even when the CO_2 concentration
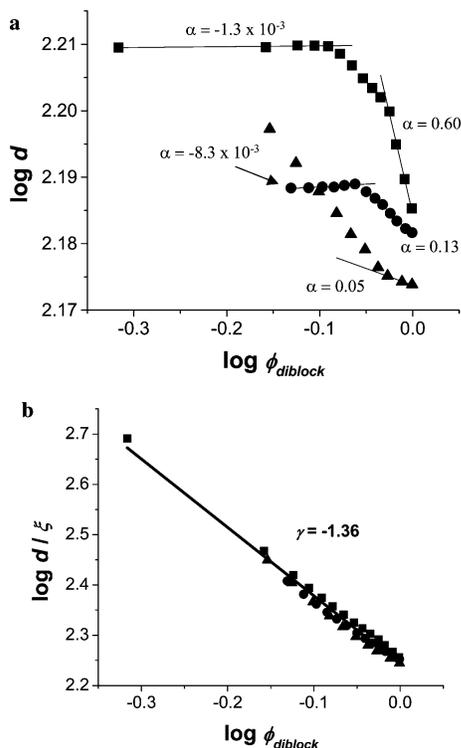
Figure 4. (a) A log−log plot of the *d*-spacing of P(S-*b*-DMS) dilated with CO_2 as a function of $\phi_{diblock}$. The lines are power law fits using eq 1 over the regions indicated and are labeled with the corresponding exponent. (b) A log−log plot of d/ξ as a function of $\phi_{diblock}$. Data points in both plots indicate temperatures of (■) 40, (●) 100, and (▲) 140 °C. The data shown in (b) have been fit with a line that has a slope of $\gamma = -1.36$.

is less than 20%. In the limit of a concentrated copolymer at 40 °C, fits to eq 1 provide a power law exponent, $\alpha = 0.60$, but as the CO_2 concentration increases, α decreases until it plateaus to $\alpha \approx 0$ at $\phi_{diblock} < 0.82$ (Figure 4a). Changes in the scaling can be associated with a change in the block copolymer morphology through an OOT.[11,12,18] However, as previously discussed, the SANS data show $q_2^*/q_1^* \approx 2$ at all conditions measured, indicating the lamellar phase is present. In addition, the variation of α with $\phi_{diblock}$ shown here is consistent with published data[12] for poly(styrene-*b*-isoprene) in squalane, which shows that α determined at moderate $\phi_{diblock}$ for a selective diluent does not always accurately describe *d* in the limit of a concentrated system. In this study, the parameter α decreases as $\phi_{diblock}$ decreases, despite maintaining a lamellar morphology.

From the measurements at constant ϕ, the interdomain spacing was well behaved as a function of temperature (Figure 2). Thus, it was suspected that the scaling with $\phi_{diblock}$ would be independent of temperature. Data collected for P(S-*b*-DMS) at 100 °C, dilated with carbon dioxide, are shown in Figures 3b and 4. As with the data collected at 40 °C, α at a low degree of dilation is different from α at a high degree of dilation. At 100 °C and high $\phi_{diblock}$ $\alpha = 0.13$, which is significantly less than $\alpha = 0.60$ at 40 °C and high $\phi_{diblock}$. As with the data collected at 40 °C, the scaling at 100 °C transitions to $\alpha \approx 0$ at low $\phi_{diblock}$. Further increasing the temperature to 140 °C results in a substantial change in the concentration dependence of the interdomain spacing with $\phi_{diblock}$ (Figure 3C). The data are no longer described well by the power law given by eq 1 over any substantial range of $\phi_{diblock}$. In the limit of $\phi_{diblock} \rightarrow 1$, $\alpha = 0.05$, indicating further decrease in α with increasing temperature at high $\phi_{diblock}$.

Again, sharp changes in α observed between 40 and 100 °C as a function of $\phi_{diblock}$ cannot be explained by an OOT, as q_2^*/q_1^* has a constant value of ≈ 2, which indicate that lamellae are present at all conditions measured. Further, hydrostatic pressure appears to have a negligible effect on the interdomain spacing at the conditions examined (Figure 2). Thus, the failure of eq 1 to describe the interdomain spacing over the entire range of $\phi_{diblock}$ appears to have a fundamental origin, especially considering similar observations for liquid diluents.[12]

We found that a swelling asymmetry factor, ξ, can be used to correct for the dissimilar swelling of the polystyrene and poly-(dimethylsiloxane). The swelling asymmetry factor, ξ, is given by

$$\xi = \frac{f_{PS/CO_2}}{f_{PDMS/CO_2}} \qquad (6)$$

where f_{PS/CO_2} is the volume fraction of the system that is carbon dioxide swollen polystyrene and f_{PDMS/CO_2} is the volume fraction that is carbon dioxide swollen poly(dimethylsiloxane). The swelling asymmetry factor was determined by calculating the swelling of PS and PDMS at the conditions of interest using eq 3 and the polymer−diluent interaction parameters cited earlier.

This swelling asymmetry factor is similar but not identical to the asymmetry factor used by Vavasour and Whitmore,[16] who report calculations elucidating the effect of conformational asymmetry on the order-to-disorder transition. Figure 4 compares a plot of *d* as a function of $\phi_{diblock}$ to a plot of d/ξ as a function of $\phi_{diblock}$. As shown previously, the interdomain spacing does not scale directly with $\phi_{diblock}$; however, when the data are plotted as d/ξ, the *d*-spacings of P(S-*b*-DMS) collected at all temperatures collapse to a line.

This suggests that the failure of the power law given by eq 1 is due to diluent selectivity effects. The effect of diluent selectivity on *d* can be accounted for by considering the ratio d/ξ as a power law in $\phi_{diblock}$ as given by

$$\frac{d}{\xi} \sim \phi_{diblock}^{\gamma} \qquad (7)$$

In this equation, the parameter γ describes the scaling of d/ξ with $\phi_{diblock}$, and for poly(styrene-*b*-dimethylsiloxane) the scaling factor is $\gamma = -1.36$. The sensitivity of γ to variations in the polymer−solvent interaction parameter, χ_{AS}, has been investigated. It was found that with a 10% deviation in χ_{AS} for either polystyrene or poly(dimethylsiloxane) the collapse of the data to a line is not significantly changed. Further, a 10% deviation in χ_{AS} for either polystyrene or poly(dimethylsiloxane) results in a maximum change in γ of 7.1%.

Conclusions

The interdomain spacing of P(S-*b*-DMS) dilated with carbon dioxide was measured isothermally by in-situ small-angle neutron scattering at 40, 100, and 140 °C as well as at constant volume fraction of copolymer, $\phi_{diblock}$. At constant $\phi_{diblock}$ and a range of temperatures, the temperature dependence of *d* is well described by $d \sim \chi_{AB}^{\beta}$, and the scaling coefficient, β, determined for the P(S-*b*-DMS) in CO_2 is in good agreement with previously published experimental results and theoretical predictions. Isothermal measurements show that *d* increases as $\phi_{diblock}$ is decreased, indicating that CO_2 behaves similarly to a selective liquid diluent. The isothermally measured *d* is not adequately described by the traditional scaling, $d \sim \phi_{diblock}^{-\alpha}$. Failure of this scaling is shown to result from the partial

selectivity of CO_2 to the PDMS phase. However, the interdomain spacing of P(S-*b*-DMS) swollen by high-pressure CO_2 is well described by a modification of the power law scaling that accounts for solvent selectivity, which is given by

$$\frac{d}{\xi} \sim \phi_{\text{diblock}}^{\gamma} \qquad (8)$$

where ξ is a swelling asymmetry factor and γ is the scaling coefficient describing the change in the ratio d/ξ as a function of ϕ_{diblock}. This new scaling has been shown to collapse measured values of d/ξ at various temperatures to common exponent, indicating the validity of this scaling approach for lamellar morphologies. The utility of this approach for other morphologies remains to be investigated.

Supporting Information Available: Figures showing swelling data for poly(dimethylsiloxane) and polystyrene as a function of CO_2 activity and tables of SANS data for poly(styrene-*b*-dimethylsiloxane) in CO_2 are provided as supplemental information. This material is available free of charge via the Internet at http://pubs.acs.org.

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