

Phase Behavior of Nearly Symmetric Polystyrene-*block*-polyisoprene Copolymers in the Presence of CO₂ and Ethane

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ABSTRACT: The phase behavior of nearly symmetric styrene–isoprene (SI) diblock copolymers in the presence of compressed CO₂ or ethane was studied using small-angle neutron scattering. Sorption of either fluid depresses the upper order–disorder transition (UODT) by as much as 55 °C at fluid densities of less than 0.35 g/cm³. The solvent-induced transitions are fully reversible upon fluid desorption. The magnitude of the depression can be controlled by manipulating the mass fraction of fluid sorbed through pressure-mediated adjustments in solvent density. Consequently, the location of the UODT can be tuned over broad ranges, and the state of segregation can be controlled via isothermal adjustments in total system pressure. The influence of hydrostatic pressure, inherent to the use of compressed solvents, is small in comparison to the solvent effect over the range of pressures studied.

Introduction

The phase behavior of block copolymers has fascinated theoreticians and experimentalists for many years. Systems comprised of segments that exhibit a region of miscibility will self-assemble into periodic mesophases upon cooling from the disordered melt through the upper order–disorder transition (UODT).^{1–3} Leibler's mean field theory, which is based on the incompressible random phase approximation, can be used to parameterize phase behavior in terms of χN , the product of the Flory interaction parameter and the number of segments, and f_i , the volume fraction of one component.⁴ Refinements of the theory to account for fluctuations proposed by Fredrickson and Helfand reveal that the UODT is a first-order transition at all compositions and increase the limiting values of $(\chi N)_{\text{UODT}}$ that dictate the onset of segregation.⁵ Recently a few systems, including poly(styrene-*block-n*-butyl methacrylate) (SBMA), have been reported to segregate upon heating through a lower disorder–order transition (LDOT), so named by analogy to lower critical solution temperatures (LCSTs) in polymer blends.^{6–8} The requisite increase in χ as lower critical transitions are approached can be ascribed to a weakening of specific favorable intersegment interactions, an enthalpic effect, disparities between the free volumes of the phases as temperature increases, an entropic effect, or a combination of both factors.^{9,10} The LDOT can be predicted by combining the incompressible random phase approximation with an equation-of-state theory to account for compressibility (free volume) in the melt.^{11,12}

Recently, the behavior of concentrated block copolymer/liquid solvent systems has been the subject of considerable interest. The mean field dilution approximation assumes that neutral solvents are distributed in a spatially uniform manner and predicts a shift in the UODT that scales as $\phi\chi N$, where $1 - \phi$ is the volume fraction of the solvent.^{13,14} Lodge and co-workers have shown that this approach markedly underpredicts the magnitude of the depression for lamellar polystyrene-

block-polyisoprene (SI) copolymers in the nominally neutral solvents, toluene and dioctyl phthalate (DOP).¹⁵ By contrast, the addition of a highly selective solvent, one that is a good solvent for one block and a nonsolvent for the other, has been likened to moving horizontally across the temperature–composition plane of χN vs f_i phase map.¹⁶ An extreme example is the addition of a homopolymer that is identical to one of the blocks, which is analogous to increasing f_i and can induce order–order transitions (OOTs). Solvents with selectivities between these limits are expected to exhibit intermediate behavior. In SI copolymers, the slightly selective solvent di-*n*-butyl phthalate (DBP) stabilizes the disordered state as evidenced by a depression of the UODT while the temperature dependence of DBP selectivity affords access to novel sequences of OOTs.¹⁶

We have initiated a program to investigate the influence of compressible fluids on the phase behavior of multicomponent polymer systems. This class of solvents differs from liquid solvents in three important ways: First, pressure-mediated adjustments in density provide access to a continuous range of solvent quality and a means to manipulate the degree of solvent sorption directly. For example, Lemert reported that CO₂ sorption in symmetric SI copolymers at 35 °C ranges between 2.0 and 11.2 wt % upon increasing pressure from 14 to 103 bar.¹⁷ Precise, isothermal control over ϕ and selectivity is ideally suited for studying solvent-induced phase transitions. Second, the use of compressed solvents requires an accounting for hydrostatic pressure effects on phase behavior, although these are expected to be relatively small over the pressure range of interest. Third, while a low-density fluid experiences a large reduction in volume upon sorption, the compressibility of the polymer/fluid mixture can increase substantially relative to that of the undiluted melt.¹⁸ In multicomponent systems this factor, which is unique to compressible solvents, can lead to rapid and disparate increases in compressibilities of the mixture components that exacerbate the entropic penalty of mixing. This conclusion can be drawn directly by a straightforward stability analysis based on dif-

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Table 1. Characteristics of the Copolymers Used in This Study

copolymer	M_n (PS)	M_n (PI)	ϕ_1	PDI	UODT
SI 7/8	7200	7800	0.56	1.05	105
SI 11/10	11100	10100	0.51	1.03	145

ferentiation of Gibbs free energy for the ternary system.¹⁰

Our broad objective is to evaluate the interplay of enthalpic contributions and equation-of-state effects for determining the state of segregation in block copolymer/compressible solvent systems across the phase diagram. Our recent work focused on systems near the LDOT, where entropic consequences of fluid sorption are important. We reported that sorption of low weight fractions of CO₂ in SBMA copolymers can induce phase segregation at temperatures more than 250 °C below the ambient pressure LDOT.¹⁹ The lack of exothermic intersegment interactions in the SBMA system⁷ suggests that these solvent-induced transitions are due predominantly to a free-volume mismatch between the components upon fluid sorption. The present paper is the first to examine the effect of fluid sorption near the UODT. Specifically we report the phase behavior of two nearly symmetric styrene–isoprene diblock copolymers in the presence of CO₂ or ethane. If the sorbed diluent influences phase behavior predominately through intersegment screening, as may be expected near the UODT, controlling the degree of dilation should permit the location of the transition to be tuned directly.

We choose to initiate our study of the effects of compressed fluid sorption on the location of the UODT using polystyrene-*block*-polyisoprene copolymers predominantly because the phase behavior of the SI system has been characterized extensively.^{20–24} The SI melt exhibits a minimum of five distinct morphologies across the composition range.²¹ The nature of the ordered state is primarily dictated by the volume fraction of the minor component although recently thermoreversible^{20–22} and solvent-induced OOTs²⁵ have been identified. The influence of liquid solvents,^{26–28} pressure,^{29,30} and homopolymer diluents³¹ on the UODT in SI copolymers has also been investigated. Hajduk et al.²⁹ reported a small, positive pressure coefficient, $\Delta T_{\text{UODT}}/\Delta P$, of 19 K/kbar at elevated pressures that was later confirmed by Stühn and co-workers.³⁰ At lower pressures, Stühn found that a minimum in the UODT occurs at approximately 8 bar, a total depression of almost 5 °C. The negative coefficient at low pressure presumably arises due to a negative volume change on mixing. Finally, Hammouda studied the effect of pressure on SI copolymers in dioctyl phthalate (DOP).³² The change in the UODT is approximately 22 °C/kbar, which is in rough agreement with values obtained for hydrostatic pressure alone.

Experimental Section

Two nearly symmetric polystyrene-*block*-polyisoprene copolymers were purchased from Polymer Source (Dorval, PQ Canada). The sample designated SI 7/8 had a total number-average molecular weight (M_n) of 15 000 g/mol, a polydispersity of 1.05, and a polystyrene volume fraction (f_2) of 0.56. The copolymer designated SI 11/10 had a M_n of 21 200 g/mol, a polydispersity of 1.03, and a f_2 of 0.51 (Table 1). The PS volume fraction for each copolymer was estimated using densities of 1.05 and 0.90 g/cm³ for the styrene and isoprene segments, respectively. Carbon dioxide (Coleman grade, 99.99%) and ethane (C.P. grade, 99.0%) were purchased from Merriam-Graves and used as received.

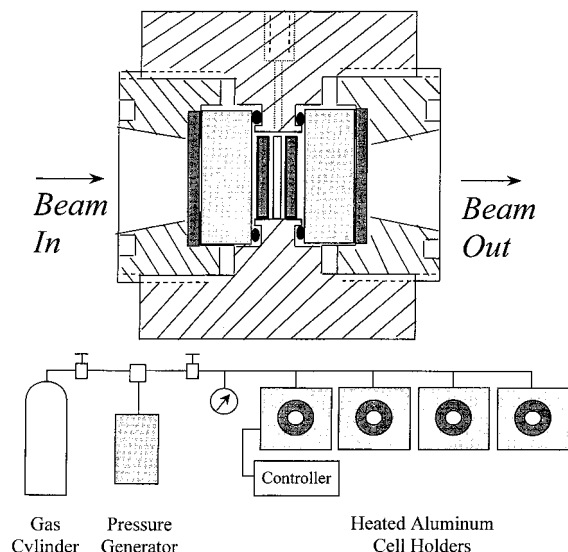


Figure 1. Schematic of the high-pressure SANS cells and gas manifold.

Samples of the copolymers were cast from toluene solution containing Irganox 1076 (Ciba Geigy, 0.002 g/g polymer) to prevent the degradation of the isoprene block during the experiments. The samples were dried under vacuum at 90 °C for at least 24 h, subsequently pressed into 1 mm thick aluminum rings at 60 °C, and finally annealed at 100 °C for 24 h under vacuum. Small-angle neutron scattering (SANS) measurements were conducted at the Cold Neutron Research Facility (National Institute for Standards and Technology (NIST), Gaithersburg, MD) using the NG7 30 m instrument. Four small high-pressure stainless steel cells equipped with sapphire windows were inserted directly into the standard, heated sample autoloader for liquid cells (provided by NIST) and attached to a high-pressure manifold through a series of valves (Figure 1). Each cell has a clear aperture of 8.6 mm and a path length of 7.8 mm. Prior to data collection, the cells were purged thoroughly with the fluid of interest. For experiments at elevated pressures, solvent was charged using a manual syringe pump and a high-pressure manifold.³³ Analysis by size exclusion chromatography conducted after the SANS data collection confirmed that the molecular weight distribution of the copolymers was unaffected by the experimental conditions. All SANS data were collected using the following configuration: $\lambda = 8.0$ Å, $\Delta\lambda/\lambda = 0.10$, beam diameter = 3.27 mm, and 2.6 m sample-to-detector distance. 2-D raw data were corrected for background scattering and detector sensitivity and radially averaged. UODTs in these nearly symmetric copolymers are expected to be first order and can be detected by discontinuities in either the square of the primary peak width, σ , or the maximum scattered intensity, $I(q^*)$. The methods have been shown to yield consistent results.³⁴ Peak intensities and widths were determined quantitatively from Lorentzian fits of the primary scattering peak. At ambient pressure, the location of the UODT was confirmed by optical birefringence. The sample was placed between crossed polarizers, and the intensity of transmitted light was measured as a function of temperature. A slow cooling heat (0.5 °C/min) was used to avoid kinetic limitations when ordering the sample. The location of the UODT was determined by a discontinuous increase in the intensity. Densities of the fluid phases were calculated using the NIST Standard Reference Database.³⁵

Results and Discussion

Scattering profiles of the nearly symmetric copolymers as a function of the scattering vector, $q = (4\pi/\lambda) \sin(\theta/2)$ where θ is the scattering angle, for a series of temperatures were collected at ambient pressure. The results for the SI 7/8 copolymer are shown in Figure

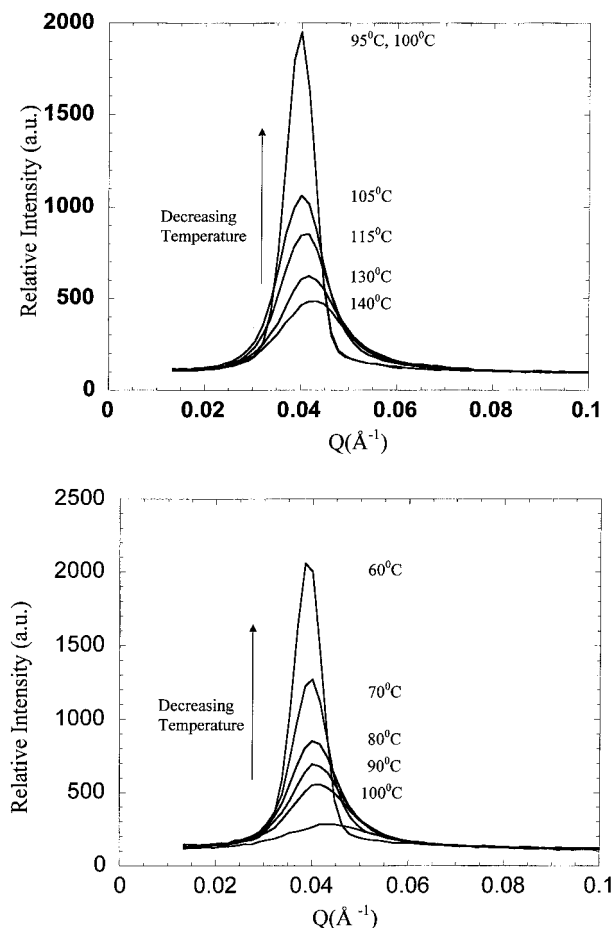


Figure 2. (a, top) SANS scattering profiles for the symmetric SI diblock copolymer SI 7/8 as a function of temperature at ambient pressure. (b, bottom) SANS profiles for SI 7/8 in the presence of supercritical CO₂ as a function of temperature at a constant fluid density of 0.4 g/cm³.

2a. At 140 °C the broad and weak correlation peak indicates that the system is disordered. As temperature is decreased through 100 °C, there is a rapid increase in peak intensity and a distinctive narrowing of the primary peak, indicating a transition to the ordered state. Analysis of the data yields a UODT of 105 °C as indicated by an abrupt change in the slope of plot of the square of the full width at half-maximum intensity (σ^2) vs reciprocal temperature (Figure 3). The location of the transition was confirmed by an independent measurement of optical birefringence. The ambient pressure UODT of the SI 11/10 copolymer was found to be 145 °C. These results are in agreement with the literature.

The location of the UODT in the presence of the compressed solvents was determined using temperature profiles at constant fluid density. The critical points of both ethane ($T_c = 32.3$ °C, $P_c = 48.8$ bar) and CO₂ ($T_c = 31$ °C, $P_c = 73.8$ bar) are conveniently located, providing access to a broad range of densities with slight to moderate changes in pressure at the conditions studied.³⁵ The copolymers are not soluble in either fluid at the conditions of interest but are swollen by them. Figure 2b shows SANS profiles for the SI 7/8 copolymer as a function of temperature at a constant CO₂ density of 0.4 g/cm³. The system orders as it is cooled through 60 °C: sorption of CO₂ at these conditions depresses the UODT by 45 °C. Further experimentation indicates that the location of the UODT is a function of solvent density

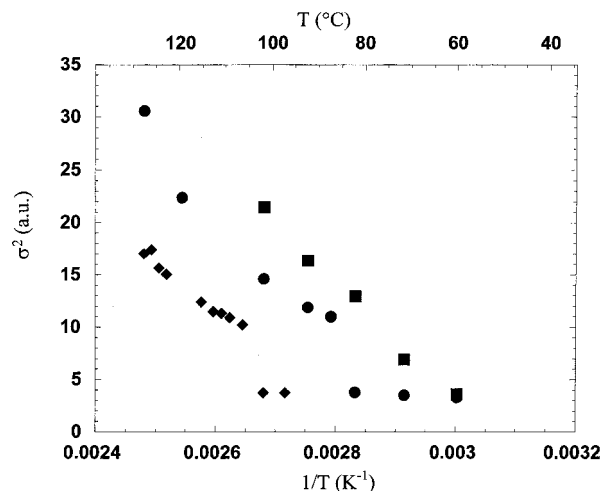


Figure 3. Square of the full width of the primary peak vs reciprocal temperature for the symmetric SI diblock copolymer, SI 7/8, at ambient pressure (\blacklozenge) and in the presence of supercritical CO₂ at fluid densities of 0.2 (\bullet) and 0.4 g/cm³ (\blacksquare).

Table 2. Location of UODTs in SI Copolymers in the Presence of CO₂ and Ethane: Temperature (Pressure)

copolymer	ethane UODT			CO ₂ UODT	
	0.2 g/cm ³	0.3 g/cm ³	0.35 g/cm ³	0.2 g/cm ³	0.4 g/cm ³
SI 7/8	80 °C (98 bar)	60 °C (110 bar)	50 °C (132 bar)	80 °C (94 bar)	60 °C (117 bar)
SI 11/10	120 °C (139 bar)	100 °C (194 bar)	90 °C (251 bar)		

and thus the degree of solvent sorption in the copolymer. Table 2 provides the temperature and system pressure for the UODT at various fluid densities. Plots of σ^2 vs reciprocal temperature for the SI 7/8 copolymer at ambient pressure and in the presence of CO₂ at 0.2 and 0.4 g/cm³ are presented in Figure 3. A comparison of the data reveals a consistency in σ^2 at the ordering transition. The solvent-induced transitions are fully reversible: disordered, CO₂-diluted copolymers reorder upon reductions in fluid phase density at temperatures below the ambient pressure UODT. Thus, the location of the UODT can be tuned over broad ranges by adjusting fluid density, and segregation in the copolymer can be induced or suppressed through minor adjustments in system pressure. This study, which indicates CO₂ sorption promotes miscibility in SI copolymers, is consistent with the results of Wignall et al., who have observed CO₂-enhanced miscibility in mixtures of polystyrene and polyisoprene oligomers.³⁶

Quantitative scaling of the UODT depression with solvent uptake requires the determination of CO₂ sorption in both the SI copolymer and the segment homopolymers over the range of experimental conditions. Although these data are not yet available, a preliminary estimate of CO₂ sorption in the segregated blocks at the UODT can be obtained using the Sanchez-Lacombe equation of state (SL-EOS)³⁷ and the sorption data of Lemert (PI at 35 °C)¹⁷ and Paulaitis (PS at 35 °C).³⁸ The Sanchez-Lacombe equation is

$$\tilde{P}^2 + \tilde{T} + \tilde{T} \left\{ \ln(1 - \tilde{\rho}) + \left(1 - \frac{1}{r}\right) \tilde{\rho} \right\} = 0 \quad (1)$$

where \tilde{P} , \tilde{T} , and $\tilde{\rho}$ are the reduced pressure, temperature, and density, respectively, and r is a size parameter that represents the number of lattice sites occupied by

molecule. The reduced parameters are defined in terms of their characteristic parameters as

$$\tilde{T} = T/T^* \quad T^* = \epsilon^*/R \quad (2)$$

$$\tilde{P} = P/P^* \quad P^* = \epsilon^*/\nu^* \quad (3)$$

$$\tilde{\rho} = \rho/\rho^* \quad \rho^* = M/r\nu^* \quad (4)$$

where ϵ^* is the interaction energy per mer, R is the universal gas constant, and ν^* is the close-packed volume of a mer. For a pure component the size parameter, r , is related to molecular weight by

$$r = \frac{P^* V^*}{RT^*} \quad (5)$$

where V^* is the close-packed volume of the N r -mers. Three characteristic parameters, available from regression of PVT data, are sufficient to completely characterize a pure component. The equation can be formally extended to mixtures using one temperature-dependent adjustable interaction parameter, δ_{ij} , in either P^* or ϵ^* . In this study we use pairwise additivity of the characteristic pressure: the cross term is defined as

$$P_{ij}^* = \{P_i^* P_j^*\}^{1/2} (1 - \delta_{ij}) \quad (6)$$

The close-packed volume fraction of component i , ϕ_i , is given by

$$\phi_i = \frac{m_i/\rho_i^*}{m_i/\rho_i^* + m_j/\rho_j^*} \quad (7)$$

where m_i is the weight fraction.

The mixing rule for ν^* (the average close-packed mer volume) is

$$\nu^* = \phi_i^\circ \nu_i^* + \phi_j^\circ \nu_j^* \quad (8)$$

where the concentrations ϕ° are given by

$$\phi_i^\circ = \frac{m_i/\rho_i^* \nu_i^*}{\sum m_i/\rho_i^* \nu_i^*} \quad (9)$$

The solubility of the polymer in the fluid phase is negligible. Thus, CO_2 sorption in homopolymers is modeled by equating the fugacities of pure CO_2 in the fluid phase (μ_1^0) and CO_2 sorbed in the polymer (μ_1^p) via³⁹

$$\begin{aligned} \frac{\mu_1^p}{RT} = & \left\{ \ln \phi_1 + \left(1 - \frac{r_1}{r_2}\right) + r_1^\circ \tilde{\rho} X_1 \phi_2^2 \right\} + \\ & r_1^\circ \left\{ -\frac{\tilde{\rho}}{T_1} + \frac{\tilde{P}_1 \tilde{\nu}_1}{T_1} + \tilde{\nu} \left[(1 - \tilde{\rho}) \ln(1 - \tilde{\rho}) + \frac{\tilde{\rho}}{r_1^\circ} \ln \tilde{\rho} \right] \right\} = \\ & \frac{\mu_1^0}{RT} = r_1^\circ \left\{ \frac{\tilde{P}_1 \tilde{\nu}_1}{T_1} - \frac{\tilde{\rho}_1}{T_1} + \tilde{\nu}_1 \left[(1 - \tilde{\rho}_1) \ln(1 - \tilde{\rho}_1) + \right. \right. \\ & \left. \left. \frac{\tilde{\rho}_1}{r_1} \ln \tilde{\rho}_1 \right] \right\} \quad (10) \end{aligned}$$

where

$$X_1 = \frac{P_1^* + P_2^* - 2(P_1^* P_2^*)^{1/2} (1 - \delta_{ij})}{RT} \quad (11)$$

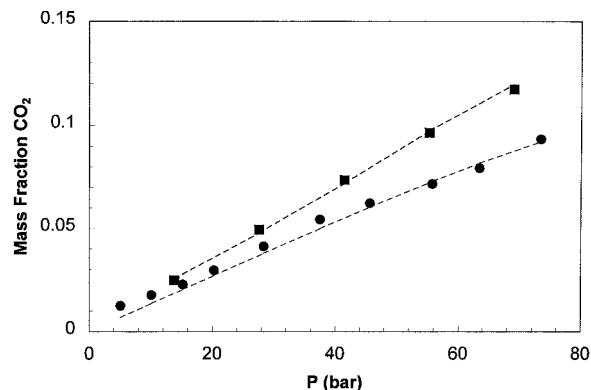


Figure 4. Comparison of calculated (---) and experimental sorption isotherms for CO_2 in polystyrene (●)³⁸ and polyisoprene (■)¹⁷ at 35 °C using the binary interaction parameters specified in the text.

Characteristic parameters for CO_2 , PS, and PI determined near the conditions of interest are taken from the literature.⁴¹ Our fits of Lemert's data yield a binary interaction parameter of 0.049 for polyisoprene/ CO_2 (Figure 4).⁴² The PS sorption data of Paulaitis span pressures at which PS is both above and below the depressed glass transition temperature. Consistent with the inherent constraints of the SL-EOS, we fit only the data in the liquid regime to obtain a PS/ CO_2 interaction parameter of 0.051. Extension of the SL-EOS and other lattice fluid models to the glassy state formally requires the introduction of order parameters, but we find, as did Johnston,⁴⁰ that in this case the sorption data at all pressures is well represented using only the binary interaction parameter (Figure 4).

Both the PS and PI blocks are rubbers at the sorption-induced UODTs. The T_g of the low molecular weight PS segment at ambient pressure is estimated to be on the order of 60 °C.²⁹ Sorption of CO_2 will further depress the transition. Therefore, the degree of CO_2 sorption in each component of the segregated copolymer at the depressed UODT is estimated using the equilibrium fluid model. The analysis, which is approximate for the reasons stated below, yields CO_2 mass fractions of 0.061 and 0.099 in the PS and PI domains, respectively, at the sorption-induced UODT in SI 7/8 at 80 °C and 0.086 and 0.143 mass fractions in the PS and PI domains at the UODT at 60 °C. Note the location of the UODT is shifted to lower temperatures as the fraction of sorbed fluid increases. It is also evident that CO_2 is slightly selective for the isoprene block, but the small, positive values of the interaction parameters suggest that strong, favorable interactions do not occur between sorbed CO_2 and either block. The precision of the sorption estimates is limited by two factors. First, a rather narrow range of data is correlated to determine the interaction parameters. Second, the parameters determined at 35 °C are used for calculations at 60 and 80 °C. The temperature differences are modest, but the assumption of temperature-independent parameters introduces additional uncertainty. A more rigorous analysis based on detailed sorption measurements at the conditions of interest will be the subject of a future publication.

The UODT in symmetric SI copolymers is also depressed upon ethane sorption (Table 2). Figure 5 shows σ^2 vs reciprocal temperature for SANS profiles of the SI 7/8-ethane system at ambient pressure and ethane densities of 0.2 and 0.3 g/cm³. The UODT decreases

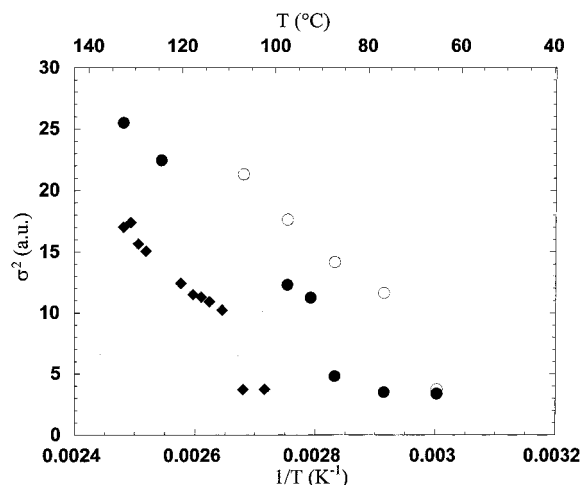


Figure 5. Square of the full width of the primary peak vs reciprocal temperature for the symmetric SI diblock copolymer, SI 7/8, at ambient pressure (\blacklozenge) and in the presence of supercritical ethane at fluid densities of 0.2 (\bullet) and 0.3 g/cm^3 (\circ).

systematically as fluid sorption increases with increasing ethane density. At a density of 0.35 g/cm^3 the UODT is depressed by 55 $^{\circ}\text{C}$. Similar UODT depressions are observed upon sorption into SI 11/10: the UODT for this copolymer decreases from 145 to 90 $^{\circ}\text{C}$ as ethane density is increased from ambient to 0.35 g/cm^3 . Quantitative measurements of ethane sorption in the SI copolymer and the segment homopolymers over the range of conditions of interest are not yet available. On the basis of solubility parameters and results with higher *n*-alkane systems,²⁵ we expect that ethane is selective for the isoprene block.

In each case studied, the effect of fluid sorption on the UODT clearly dominates the effect of hydrostatic pressure. All experiments in the presence of the compressed fluids were conducted at pressures greater than 25 bar, but less than 250 bar. Over this interval, the hydrostatic pressure coefficient for both the melt and systems solvated with a neutral solvent is expected to remain positive and thus opposes the solvent-induced depressions in the UODT to a small degree. The data of Hajduk and Hammouda suggest the hydrostatic pressure contribution will be no more than +5 $^{\circ}\text{C}$ over the range of our experiments.

Conclusions

The location of the UODT for SI copolymers in the presence of compressed ethane or carbon dioxide can be tuned through pressure-mediated adjustments in the degree of solvent sorption. Combined with precise determinations of fluid sorption at the conditions of interest, compressible solvents can provide a convenient avenue to assess the influence of solvent uptake on copolymer segregation and structure. The behavior of the SI copolymers near the UODT contrasts that of SBMA copolymers, which exhibit phase segregation upon sorption of CO_2 . In SI copolymers, enhanced miscibility upon sorption of either fluid suggests that at the conditions studied the screening of unfavorable interactions between the dissimilar segments dominates unfavorable equation-of-state contributions of fluid sorption to the energy of mixing. In SBMA copolymers, the latter contribution induces segregation via lower disorder–order transitions at modest levels of solvent

sorption. Together, these systems suggest that sorption of compressed fluids exerts an enthalpic contribution to miscibility that is consistent with the behavior of slightly selective organic solvents and an unfavorable entropic component that can oppose mixing of dissimilar chains. We are now addressing the relative importance of these contributions across the phase diagram. Such studies are motivated in part by the potential advantages compressible fluids, especially supercritical CO_2 , offer for the processing and synthesis of polymeric materials. Most applications involve heterogeneous systems that exploit improved transport within CO_2 -swollen polymers such as dispersion polymerizations,⁴³ the direct preparation of composites by reactions within swollen polymers,⁴⁴ and melt mixing of polymer blends. An understanding of the phase behavior of multicomponent polymer systems is clearly required for processing in these environments.

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