Phase Behavior of Diblock Copolymers Dilated with Light Alkanes: Influence of Solvent Compressibility on Upper and Lower Ordering Transitions

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Received December 10, 2001; Revised Manuscript Received February 20, 2002

ABSTRACT: The phase behaviors of polystyrene-*block*-poly(*n*-butyl methacrylate) (P(S-*b*-nBMA)) and polystyrene-*block*-polyisoprene (P(S-*b*-I)) copolymers were studied in the presence of methane, ethane, propane, butane, and tetradecane. Sorption of the light alkanes induces phase segregation in P(S-*b*-nBMA), depressing the lower disorder-to-order transition (LDOT). The chain length of the solvent dictates the severity of the depression. At equivalent volume fractions, methane induces the most substantial shift of the LDOT, and as the length of the alkane chain is increased, the degree of the depression is diminished. In contrast to the influence of expanded solvents, dilution of the P(S-*b*-nBMA) melt with tetradecane slightly increases the miscibility of the segments. In all P(S-*b*-I)/alkane systems studied, solvent sorption increases the region of miscibility and depresses the upper order-to-disorder transition (UODT). This effect is independent of alkane chain length and depends only on the volume fraction of alkane sorbed into the copolymer. The difference in behaviors between the copolymers is due to the nature of microphase separation. In the P(S-*b*-I) system, the UODT is enthalpically driven and solvent sorption screens unfavorable contacts. In the P(S-*b*-nBMA) system, the LDOT arises due to disparities in compressibility between the segments that are exacerbated by the selective sorption of compressible solvents.

Introduction

The phase behavior of diblock copolymers has been studied quite intensively both theoretically[1−6] and experimentally.[7−9] The majority of the studies have focused on the location of the upper order-to-disorder transition (UODT), common behavior for diblocks, where microphase separation occurs from a homogeneous melt as the temperature is decreased through the transition. Recently, diblock copolymers exhibiting a lower disorder-to-order transition (LDOT), analogous to the lower critical solution temperature (LCST) observed in polymer blends, have been reported.[10−12] In the absense of strong specific interactions between segments, phase separation at the LCST or LDOT is driven by entropic considerations, namely equation-of-state effects that arise due to the disparities in component compressibilities.[5,10,13,14] Such disparities can impose unfavorable volume changes on mixing that destabilize the system. This is the case for polystyrene-*block*-poly(*n*-butyl methacrylate) {P(S-*b*-nBMA)} copolymers for which the LDOT is accompanied by an increase in volume upon demixing of the copolymer segments.[55] In contrast, the UODT is an enthalpically driven transition, resulting from unfavorable interactions between the segments.

The use of solvents is intimately associated with the processing and application of block copolymers. In recent years, the use of compressible solvents has received considerable interest, especially carbon dioxide due to its low environmental impact, its utility in photoresist development,[15] and the use of dilated diblock copolymers as templates for composite materials.[16,17] Little information is available, however, on how compressed fluid sorption influences the phase behavior of multicomponent polymer systems, including block copolymers.

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Several characteristic features of compressed diluents distinguish them from good liquid solvents. First, compressible fluids are generally poor solvents for most polymers. Often a polymer is readily dilated by a compressed fluid but is not soluble in it. For these heterogeneous polymer/solvent systems, temperature and pressure dictate solvent quality and, in turn, the extent of swelling. Second, the use of compressible solvents requires accounting for hydrostatic pressure effects, which are inherent to these systems. Finally, it has been shown that sorption of compressible fluids such as carbon dioxide increases the compressibility of the polymer matrix.[18,19] Fluid sorption may therefore add contributions to phase instability related to increases in component compressibility that are negligible in liquid diluents. The effect of these contributions would be most pronounced for systems exhibiting LDOT- or LCST -type behavior but may be less important for systems exhibiting UODT-type or upper critical solution temperature (UCST)-type behavior.

Recently, we reported experimental results that are in line with the above observations. Sorption of CO_2 or ethane in polystyrene-*block*-polyisoprene (P(S-*b*-I)) copolymers, which exhibit an UCST-type order-to-disorder (ODT) transition, increases segment miscibility.[44] This result is consistent with the influence of liquid diluents and can be attributed to solvent screening of unfavorable contacts. In marked contrast to this behavior, we observe solvent-induced phase segregation in polymer blends and block copolymers exhibiting LCST-type phase behavior upon sorption of compressed carbon dioxide. For example, sorption of low volume fractions of CO_2 into polystyrene/poly(vinyl methyl ether) blends induces phase segregation at temperatures far below the ambient temperature LCST. In another study, it was found that the LDOT of P(S-*b*-nBMA) can be depressed by hundreds of degrees by sorption of small weight

10.1021/ma012154k CCC: $22.00 © 2002 American Chemical Society
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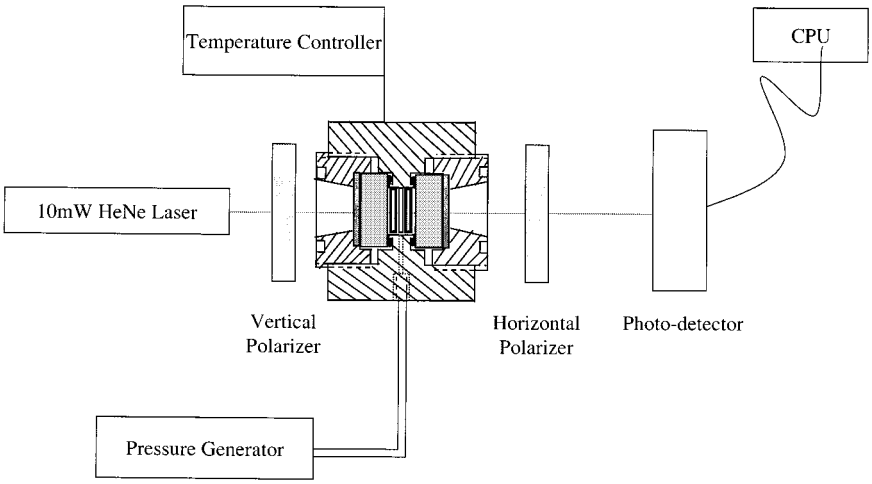

Figure 1. Schematic of the high-pressure birefringence optical train.

fractions of CO_2.[20] Solvent-induced phase segregation in LCST systems is attributed to the entropic consequences of fluid sorption, namely a disparate increase in component compressibility. We note that disparities in compressibility are at the heart of equation-of-state effects that drive LCST-type phase separation in block copolymer melts and blends in systems with weak interactions. In polymer melts dilated with supercritical fluids there are two factors that influence compressibility. Hydrostatic pressure tends to decrease compressibility, but this contribution can be dominated by the consequences of fluid sorption,[18] which can increase compressibility by the incorporation of a high free volume diluent and/or the disruption of polymer chain packing.

While the results of our studies to date provide an indication that the entropic consequences of fluid sorption can dramatically influence the phase behavior of blends and block copolymers dilated by compressible fluids, the explicit decoupling of these effects from enthalpic (screening) interactions in multicomponent polymer/solvent sytems is difficult. In the present study, the effect of solvent compressibility is examined more directly by using a series of *n*-alkanes and block copolymers exhibiting UODTs (P(S-*b*-I)) and LDOTs (P(S-*b*-nBMA)). Previous reports indicate that alkane chain length has little effect on the enthalpic interactions in polymer/liquid solvent systems. This is reflected by Flory−Huggins interaction parameters (χ) that are invariant with alkane chain length.[21] To a first approximation, the change in thermodynamic properties between different *n*-alkanes is due to differences in free volume.[22] The influence of light alkane sorption on copolymer phase behavior will thus contain contributions from solvent screening, hydrostatic pressure, and increases in component compressibility. Each of these factors must be considered.

Experimental Section

Three poly(styrene-*block*-isoprene) (P(S-*b*-I)) copolymers were purchased from Polymer Source (Dorval, PQ). The samples are designated as SI 7/8, SI 11/10, and SI 16/11 with total molecular weights (M_n) of 15 000, 20 200, and 27 300 g/mol, respectively (Table 1). The polystyrene-*block*-poly(*n*-butyl methacrylate) diblock copolymer used in this study was purchased from the Polymer Synthesis Facility at the University of Minnesota. The total molecular weight of the sample is 64 450 g/mol with a polydispersity of 1.04 as determined by size exclusion chromatography. For calculating volume fractions for the copolymers, the densities of the phases were assumed to be 1.05, 0.90, and 1.053 g/cm^3 for polystyrene, polyisoprene, and poly(*n*-butyl methacrylate), respectively.[23] Methane (C.P. grade, 99.0%), ethane (C.P. grade, 99.0%), propane (C.P. grade, 99.0%), and butane (C.P. grade, 99.0%) were obtained from Merriam Graves and used as received. The properties of these gases are summarized in Table 2. Tetrahydrofuran (Aldrich) was used as a cosolvent for samples containing tetradecane (Aldrich). The cosolvent was allowed to evaporate at room temperature, followed by removal under vacuum at room temperature until the sample maintained a constant mass over time. For calculating the composition of the solutions, the density for tetradecane was assumed to be 0.763 g/cm^3.

Table 1. Characteristics of Diblock Copolymers Used in This Study

sample	M_n (kg/mol)	f_{PS}	PDI	transition (°C)
SI 7/8	15.0	0.44	1.03	105 (UODT)
SI 11/10	21.3	0.49	1.05	153 (UODT)
SI 16/11	27.3	0.54	1.05	205 (UODT)
65K SnBMA	64.5	0.53	1.03	188 (LDOT)

Table 2. Light *n*-Alkane Properties

alkane	MW (g/mol)	T_c (K)	P_c (bar)	ω
methane	16.04	109.6	46.0	0.008
ethane	30.07	305.4	48.8	0.098
propane	44.10	369.8	42.5	0.152
n-butane	58.12	425.2	38.0	0.193

Transitions in the diblock copolymers were determined using static birefringence (depolarized transmitted intensity). The samples were placed between two glass spacers within a high-pressure cell, equipped with two oriented [0001] sapphire windows. Details of the cell design are provided elsewhere.[20] The sample cell was heated by an aluminum heating jacket using electric resistance heaters. For all experiments, the cell was purged with the fluid of interest, except in the case of tetradecane where an atmosphere of methane was used (~1 bar). The pressure of the fluid was controlled using a high-pressure syringe pump (High-Pressure Equip. Co.) connected to a manifold containing the fluid.

A schematic of the experimental setup is shown in Figure 1. Light from a 10 mW HeNe laser was polarized vertically and passed through the sample. The transmitted beam was analyzed using a horizontal polarizer and recorded using a photodiode. For ordered systems, the polarization state of the transmitted light is determined by both form birefringence, originating from anisotropy in composition in the ordered state (except for bcc spheres), and intrinsic birefringence from chain stretching at the interface.[24] The disordered state is isotropic in nature and should have no significant effect on the polarization state of the transmitted light. Therefore, little if any light

will emerge from the crossed-polarizers. A transition from an ordered state to disorder is thus observed by a discontinuous change in the transmitted intensity, from a large value to near zero. The measured birefringence in the disordered state in our system was not precisely zero, due to an error in the cut angle of the sapphire (±2°). This led to a finite, but small, transmitted intensity, even through the empty cell. Over the pressure and temperature range studied, the birefringence of the sapphire remains nearly constant.[25,26] The fluid densities were obtained from the NIST Standard Reference Database.[27] The range of pressures required for the experiments was dependent on solvent chain length: methane (ambient to 400 bar), ethane (ambient to 300 bar), propane (ambient to 75 bar), and butane (ambient to 25 bar).

Fluid sorption measurements were conducted to quantify the effect of the light *n*-alkanes, in particular ethane, in comparison to liquid diluents. Sorption was measured in homopolymers of polyisoprene and polystyrene. Ethane sorption in polyisoprene was measured at 40 °C using a pressure decay method similar to that described by Koros and Paul.[28] Instead of measuring the total pressure in both chambers, however, the total pressure was measured in the ballast section (±0.3 bar) and a differential pressure (±0.01 bar) was measured between the sample and ballast chambers to increase precision. Specific volumes of the fluid were determined using the NIST Standard Reference Database.[27] Previously reported data for CO_2 sorption in polystyrene[29] and poly(vinyl methyl ether)[30] were reproduced within 5%.

Results and Discussion

Light Alkane Sorption in Polymers. In a series of *n*-alkanes, chain length has little effect on the enthalpic interactions in polymer/solvent systems. There are however a number of subtle differences that must be considered. One of the most obvious is end effects, which must account for enthalpic differences between methylene ($-CH_2-$) and methyl ($-CH_3$) groups, but this effect has been found to be small.[31] Another effect of chain length, which is magnified in light *n*-alkanes, is the differences in polarizability. Differences can also be seen in the large disparities in the acentric factor, which accounts for nonspherical charge distribution in the molecule (Table 2). There are also variations in the degrees of freedom, both external and internal for the alkanes being studied. The external degrees are a result of connectivity and contribute to the conformational entropy of the system. The role of internal degrees of freedom is evident when comparing methane and ethane, which do not exhibit rotational modes about the carbon atoms, with larger *n*-alkanes in which these modes are present. There are a number of other factors including creation of order by packing that contribute to thermodynamic differences in the series of alkanes, but these are primarily associated with longer chain lengths.[22] Despite these differences, a series of light alkanes provide the opportunity to vary solvent compressibility significantly while maintaining nearly constant enthalpic interactions.

One of the challenges of this study was developing a meaningful comparison of the data obtained for the various alkanes. Typically for block copolymer solutions, the transitions are compared as a function of volume fraction of polymer, ϕ.[32−34] The volume fraction can be directly calculated for liquid diluents when preparing the samples. However, for the alkanes studied here, a direct measurement cannot easily be made as solvent is added through manipulation of the fluid density, and the solution compositions are determined by sorption equilibrium. There has been much work on measuring gas sorption in various polymers for a variety of alkanes.[35−39] However, given the large number of samples and fluids used in this study, it is desirable to avoid a separate measurement to determine the composition for each of the measured transitions. It has been proposed that for a homologous set of solvents, such as alkanes, solvent quality is determined almost exclusively by density. If this were true, then the alkane sorption should be a function of density, temperature, and polymer matrix but independent of choice of alkane. Figure 2a shows the sorption of methane, ethane, and propane in PDMS as a function of density.[40] It can be seen that the sorption is not independent of chain length. This is not unexpected, due to the reasons cited earlier. Moreover, the equivalency of solvent quality at a fixed density has been disproved directly for the case of ethane and pentane.[41] The use of chemical potential, or an analogue of it to describe the thermodynamic state of the solvent, may be more effective in collapsing the sorption isotherms for the alkanes. One of the more attractive options is the use of activity of the fluid in the polymer at equilibrium. Correlation of activity with fluid sorption has previously been applied to polymer/CO_2[42] and polymer/toluene[43] systems.

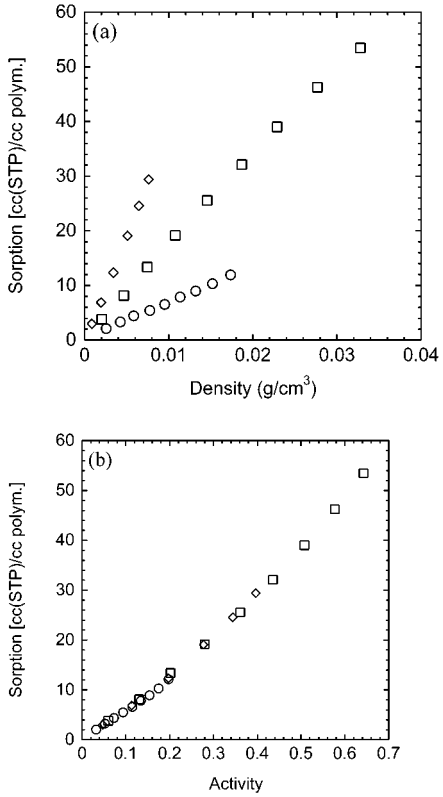

Figure 2. Sorption of (○) methane, (□) ethane, and (◇) propane in PDMS at 35 °C as a function of (a) fluid density and (b) activity. Alkane sorption data from Merkel et al.[40] We find the sorption of light *n*-alkanes collapses to a single curve as a function of activity.

The relationship between solvent activity and solution composition was given by Flory:

$$\ln a = \ln(1 - \phi) + \phi + \chi\phi^2 \qquad (1)$$

where ϕ is volume fraction of polymer, a is the activity of the solvent in the polymer, and χ is the Flory−Huggins interaction parameter. Since the fluid sorption in the cases studied here is equilibrium limited, the activity of the fluid phase is equal to the activity of the fluid sorbed in the homogeneous polymer phase. The

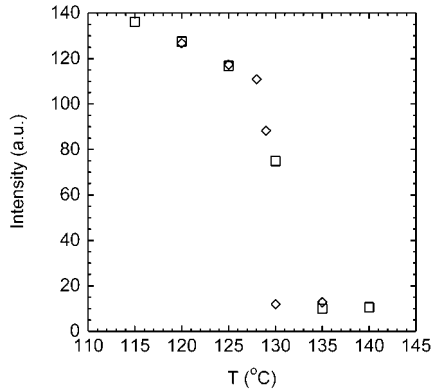

Figure 3. Transmitted intensity from SI 11/10 swollen with butane at a constant density of 0.03 g/cm^3 upon cooling (□) and subsequent heating (◇). The transition is depressed from 153 to 130 °C.

activity can be calculated via

$$a = \frac{P(T,V)\,\Phi(T,V)}{P^{sat}(T,V^{sat})\,\Phi(T,V^{sat})\,\exp\left(\frac{\bar{V}_R}{RT}(P - P^{sat})\right)} \quad (2)$$

where P is the pressure, T is the temperature, V is the fluid phase volume, R is the gas constant, Φ is the fugacity coefficient, and $\bar{V}_R$ is the specific volume of the sorbed alkane. Fugacity coefficients were calculated using the Peng–Robinson equation of state (PR EOS) via an isothermal Gibbs departure function. The superscript "sat" indicates the saturation value. For measurements at $T > T_c$ of the solvent, the vapor pressure is extrapolated using the Antoine equation, and values for the specific volume of the sorbed alkanes are taken from the work of Kamiya and co-workers.[21] The sorption of the alkanes in PDMS at 35 °C as a function of activity is shown in Figure 2b. We find better agreement between the sorption isotherms using activity. This is not unexpected as χ should not vary much between alkanes due to the similarity in their chemical nature. Sorption data for methane and ethane in poly(*n*-butyl methacrylate) can be collapsed using the same approach with equivalent results.

Effect of Light Alkane Sorption on the UODT of P(S-*b*-I). The UODT's of the P(S-*b*-I) copolymers were measured as a function of fluid density for each alkane: methane, ethane, propane, and butane. The transitions were found to be thermoreversible and reproducible within 1 °C. The transitions for the neat copolymers have been previously reported for SI 7/8 and SI 11/10 using SANS; subsequent measurements using birefringence agree within experimental error. One complication with previous work was the limited time for SANS measurements.[44,45] It is important to note that all the studies involving the light alkanes were heterogeneous: fluid is dissolved in the polymer phase, but the polymer is insoluble in the fluid. The solvent quality for these alkanes can be tuned by varying the fluid density. Figure 3 shows a heating and cooling profile for SI 11/10 swollen with butane at a fluid density of 0.03 g/cm^3. A discontinuity in the intensity is observed at 130 °C, indicating a transition. For this case, the transition is depressed by more than 20 °C. The depression of the UODT upon sorption of compressible diluents is consistent with the behavior of weakly selective liquid diluents such as di-*n*-butyl phthalate (DBP).[46] As discussed earlier, the effect of hydrostatic pressure on the transition of P(S-*b*-I) in the presence of compressed diluents must be accounted for. In the neat melt, the hydrostatic pressure coefficient is 0.019 °C/bar.[47,48] This coefficient is valid in solution as well.[49] UODTs, corrected for hydrostatic pressure contributions, are shown as a function of activity in Figure 4. The transitions collapse to a single curve for SI 7/8. For the other copolymers there are some minor differences among the solvents. These trends, however, are not systematic with respect to alkane chain length and may reflect the subtle differences among the alkanes noted earlier. In all cases, differences in compressibility of the alkanes do not appear to have a profound effect on the location of UODTs for P(S-*b*-I), since the degree of depression scales with the volume fraction of sorbed diluent. Consequently, the effect of screening interactions between the copolymer segments appears to be dominant, as would be expected for the enthalpically driven UODT.

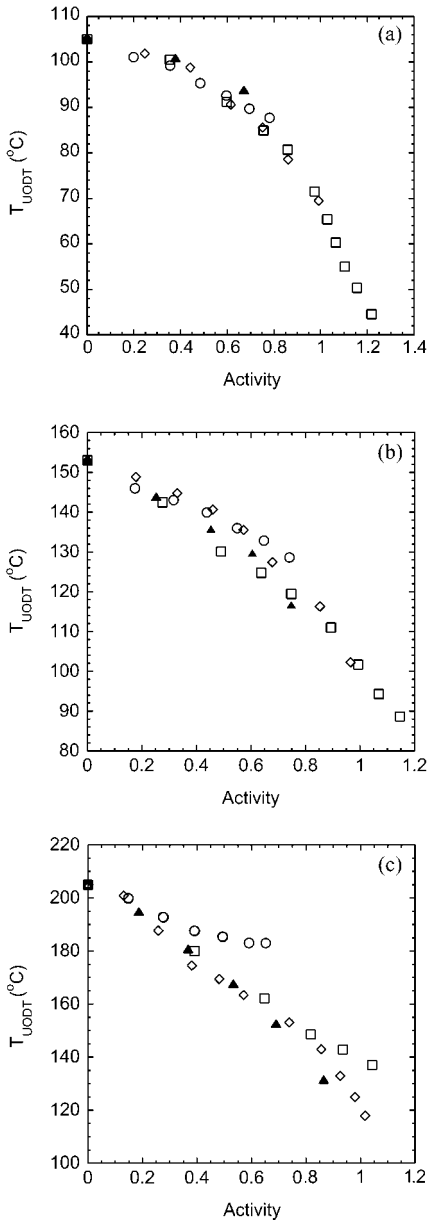

Figure 4. Effect of light *n*-alkanes on the ODT of (a) SI 7/8, (b) SI 11/10, and (c) SI 16/11 for (○) methane, (□) ethane, (◇)-propane, and (▲) butane as a function of fluid activity. The depression is found to be a function of the activity of the fluid, but nearly independent of the chain length.

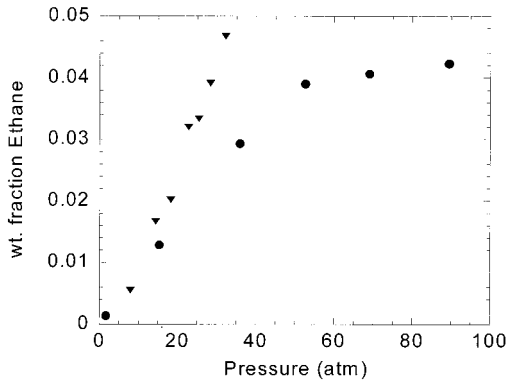

Figure 5. Sorption of ethane in (▼) polyisoprene and (●) polystyrene at 40 and 35 °C, respectively. Polystyrene sorption data from RamachandraRao and Watkins.[52]

Table 3. Comparison of χ Values for Various *n*-Alkanes in Polystyrene[54] and Polyisoprene[53]

solvent	χ PS	χ PI
ethane	2.1	1.7
n-pentane		0.580
n-hexane		0.534
n-heptane		0.504
n-octane		0.478
n-decane	1.869	
n-dodecane	1.870	
n-tetradecane	1.972	
n-hexadecane	2.143	

Effect of Tetradecane Sorption on the Phase Behavior of P(S-*b*-I). The effect of selective solvents on the phase behavior of P(S-*b*-I) was studied previously by Lodge and co-workers.[46,50] Most applicable to this work was the effect of tetradecane on the phase behavior; however, unlike the lamellar morphology of the nearly symmetric copolymer studied here, the sample was asymmetric, displaying both gyroid and cylindrical phases in the melt with a minority component of polystyrene. More recently, Register and co-workers have studied the effect of more strongly selective solvents with the least selective solvent being tetradecane.[51] Again, tetradecane was found to depress the UODT. To facilitate further comparison between the behavior of compressible solvents and liquid diluents in UODT systems, we examined the influence of tetradecane on the phase behavior of the nearly symmetric copolymers. Since tetradecane sorption is not equilibrium limited at the conditions of interest, a comparison on the basis of solvent activity is not useful: a direct comparison on the basis of volume fraction polymer is used. Isotherms for ethane sorption in polyisoprene and polystyrene[52] at 40 and 35 °C, respectively, are presented in Figure 5. As expected, ethane is selective toward the isoprene phase, but to a lesser degree than tetradecane. Returning again to the Flory activity equation, the interaction parameter for PS/ethane and PI/ethane can be calculated assuming a molar volume of 61 cm^3/g for ethane sorbed in either polymer to determine the volume fraction for each composition.[35] The calculation yields χ values of 1.7 for PI/ethane and 2.1 for PS/ethane. Interaction parameters have been previously determined for various liquid *n*-alkanes in polystyrene or polyisoprene and are listed in Table 3.[53,54] Comparison of these interaction parameters with those determined for ethane is informative. First, the liquid diluents are much better solvents for both polystyrene and polyisoprene than ethane. In addition, the selectivity for the polyisoprene over polystyrene phase is much greater for the case of the liquids than ethane, which should impact phase behavior. Figure 6 shows the order−disorder transitions in SI 7/8 as a function of volume fraction for ethane and tetradecane. The reported ODTs with ethane as solvent were corrected for hydrostatic pressure. There is a rather distinct difference between the ethane and the liquid alkane that is due to the selectivity of tetradecane toward polyisoprene. This selectivity leads to an accumulation of solvent in the polyisoprene phase and reduces the ability of the alkane to screen interactions between the microphases.

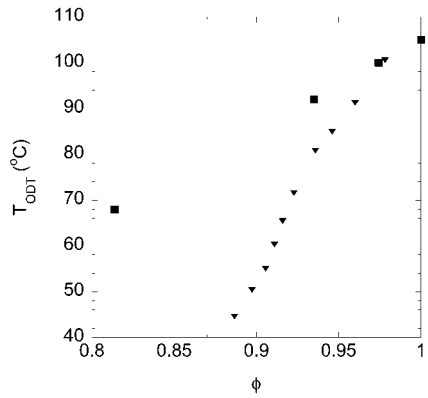

Figure 6. Comparison of effect of liquid *n*-alkanes with ethane on the phase behavior of SI 7/8. Transition temperature is shown as a function of volume fraction polymer for (▼) ethane and (■) tetradecane.

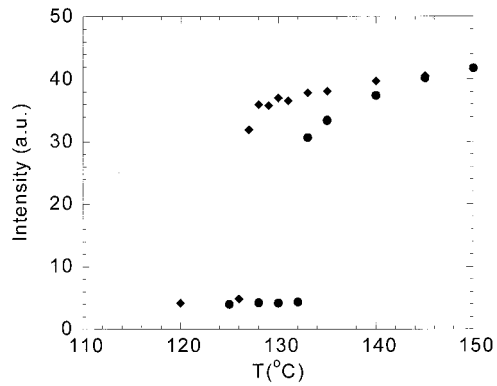

Figure 7. Measured birefringence in P(S-*b*-nBMA) swollen with 0.04 g/cm^3 ethane (●) on heating from disorder to order and (◆) on cooling from order to disorder.

Effect of Light Alkane Sorption on the LDOT of P(S-*b*-nBMA). The neat P(S-*b*-nBMA) copolymer has a LDOT at 188 °C as determined by birefringence and is found to be thermoreversible within 1 °C. The sorption of small fractions of light alkanes leads to a severe depression in the LDOT. Figure 7 shows a representative curve of the birefringence data for pressurized systems containing P(S-*b*-nBMA). In this case, P(S-*b*-nBMA) is swollen with 0.04 g/cm^3 ethane. The sample orders upon heating from 132 to 133 °C, a depression of 55 °C from the neat copolymer. However, upon cooling, the sample does not disorder until 126 °C. This discrepancy in the phase transition temperature between ordering and disordering of the sample cannot be explained by kinetic limitations, as the size of the region of metastability (6 °C) is independent of the rate of heating/cooling for rates less than 1 °C/20 min. It is interesting to note that the magnitude of the metasta-

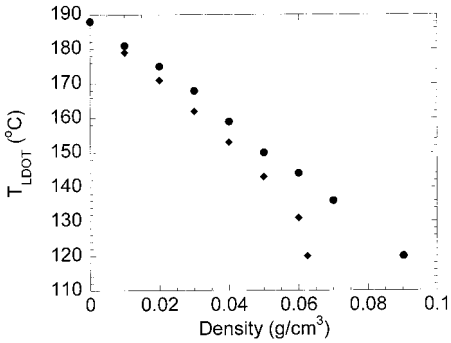

Figure 8. Depression in LDOT by sorption of methane upon (●) ordering and (◆) disordering as a function of the fluid phase density.

bility increases as the density of the fluid is increased. One explanation for this behavior is a difference in fluid sorption between the ordered and disordered states that increases with total pressure. It has been shown for miscible LCST polymer blends of PS/PVME that the sorption of CO_2 is less than that for the weighed average of the sorption for the respective homopolymers.[30] A difference in the equilibrium alkane sorption between the ordered and disordered states in P(S-*b*-nBMA) would require the copolymer to expel fluid upon disordering, which is very unfavorable entropically. It is also important to note that for the P(S-*b*-nBMA)/light alkane systems the region of metastability increases with decreasing chain length of the fluid. We return to this point later. By comparison, the UODT of poly(styrene-*block*-isoprene) swollen with the light alkanes is fully reversible within 1 °C, regardless of fluid density, which suggests the presence of diluent does not present an additional entropic barrier to segmental mixing.

The location of the LDOT as a function of methane density is shown in Figure 8. The transitions were measured as a function of temperature at a constant fluid density except for one case of isothermal pressurization at 120 °C. The depression in the transition upon ordering is linear with density throughout the entire range studied for all alkanes. A depression of over 65 °C is observed at a density of 0.09 g/cm^3 of methane. This is a tremendous depression for two reasons: first, methane is an extremely poor solvent; typically less than 5% solvent uptake is reported for methane sorption in polymers. Second, to achieve this density in methane, a large pressure (185 bar) is required. The effect of hydrostatic pressure alone in this case would be to *increase* the LDOT by over 25 °C, as the pressure coefficient for the LDOT transition has been reported to be +0.147 °C/bar.[55] We note the hydrostatic pressure coefficient is an order of magnitude larger than those reported for many UODT systems.[47,48,56−58] The sensitivity of the LDOT to hydrostatic pressure was predicted by Hino and Prausnitz and arises due the increase in volume upon demixing of the copolymer blocks at the LDOT.[13,55]

The disordering transition in ethane provides for an even more interesting case. As was the case for the ordering in methane, the transition is linear with density up to a density of approximately 0.06 g/cm^3. After this, the LDOT falls rapidly with increasing density. Note that there is an 11 °C decrease with a change of less than 0.002 g/cm^3 in the fluid density. (The difference in pressure is 2 bar, which is within experimental error.) This drop-off is observed for all of the

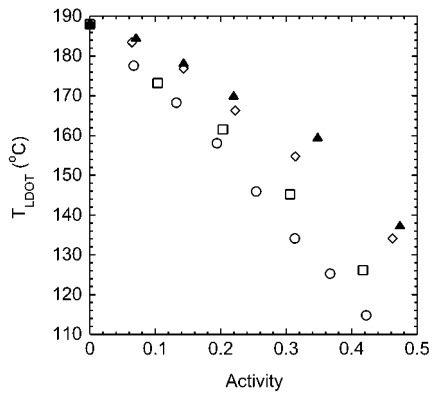

Figure 9. Effect of *n*-alkanes on the LDOT as a function of activity for (○) methane, (□) ethane, (◇) propane, and (▲) butane. The transitions shown here are for disorder-to-order (heating) only. Unlike the UODT system, the locations of the transitions depend systematically on alkane chain length.

light *n*-alkanes studied, and the location is dependent on the fluid. Transitions in the presence of longer alkanes fall off at a lower density; for example, propane exhibits a drop at ~0.03 g/cm^3. A comprehensive study of this behavior is the subject of future work.

Figure 9 shows the effect of sorption of alkanes on the phase behavior of P(S-*b*-nBMA) as a function of activity after corrections for hydrostatic pressure. The transitions shown are only for ordering of the sample; the disordering conditions are slightly different due to the metastability induced by the differences in sorption between the ordered and disordered states. However, the trends in both cases are the same: there is a clear dependence on chain length for the transition temperature as a function of activity, unlike the previously described case of P(S-*b*-I). This difference in behavior can be likely attributed to the difference in mechanism of phase separation for the neat block copolymers. The UODT in P(S-*b*-I) is enthalpically driven by the unfavorable interactions between segments. In the P(S-*b*-I) system, sorption of alkanes leads to a screening of these interactions. The LDOT in P(S-*b*-nBMA) is entropically driven by disparities in compressibility between the segments. Sorption of alkanes has two consequences that further destabilize the system. First, fluid sorption increases the total compressibility of the system. Second and more importantly, alkane sorption is selective for PnBMA over PS. This selective dilation of PnBMA exacerbates the compressibility differences between segments and thus drives microphase separation. Recall that disparities in component compressibility are at the heart of equation-of-state-effects that drive phase separations in LCST-type blends and block copolymers that do not exhibit strong specific interactions between the components. We also note recent theoretical work by Cho that highlights the importance of a heterogeneous distribution of free volume in phase separating LCST systems.[5] The differences in the behavior between alkanes for the P(S-*b*-nBMA) also lend credence to this explanation. Butane has the smallest effect on the LDOT, while methane has the largest effect as a function of activity (volume fraction diluent). The concept of a differential dilation of the segments is further supported by the appearance of a region of metastability in the LDOT. A transition from the phase separated to the phase mixed states requires a negative volume change on mixing that is particularly severe for the preferentially dilated block. The region of metastability

Table 4. Effect of Tetradecane on the LDOT of P(S-*b*-nBMA)

ϕ	LDOT (°C)
1.0	188
0.97	197
0.96	202

may arise because the transition to the phase mixed state requires an expulsion of solvent, which carries a penalty due to the loss of combinatorial entropy. This penalty grows as the chain length of the solvent decreases and as fluid sorption increases with increasing pressure. Both trends are evident in the data. Again, we note that a region of metastability does not appear for the UODT transition in P(S-*b*-PI)/alkane systems. We also note, however, that Hong et al. observed anomalous sorption of toluene near the UODT for P(S-*b*-I) and suggest this behavior may be attributed to accumulation of solvent at the interface of the phase-separated copolymer followed by expulsion upon copolymer disordering.[59]

Effect of Tetradecane Sorption on the LDOT of P(S-*b*-nBMA). The final study involved the use of tetradecane ($C_{14}H_{30}$), whose compressibility is negligible in comparison with the light alkanes studied. Tetradecane was chosen for its high boiling point to avoid any complications relating to large loss of solvent through evaporation. Previously for P(d8-S-*b*-nBMA), dioctyl phthalate (DOP) was shown to have no effect on the location of the LDOT.[20] Here it was expected the tetradecane would have no effect on the LDOT as well. However, addition of small amounts of tetradecane is found to increase the observed LDOT slightly. This effect may be due to the selectivity of the solvent, which changes the apparent composition of the diblocks. The effect of tetradecane on the LDOT as a function of composition is shown in Table 4. We also note that the magnitude of the shift in the transition upon the addition of tetradecane is much smaller than for any of the compressible solvents studied. It is expected that for methane the total sorption in any of the reported cases will be less than 2 wt % from sorption data in polystyrene and poly(*n*-butyl methacrylate).[37] The difference in the behavior between the light (C 1−4) alkanes and tetradecane is due to the large difference in compressibility.

Conclusions

The sorption of light *n*-alkanes in poly(styrene-*block*-isoprene) suppresses the microphase separation. At equivalent fluid phase activity, which is shown to correlate with ϕ, methane, ethane, propane, or butane sorption depresses the UODT in a nearly identical manner. This suggests the influence of the sorbed diluent on phase behavior is derived from screening interactions between the chains, an enthalpic effect.

The influence of one of the light alkanes, ethane, was contrasted with the behavior of several liquid hydrocarbons. It was found that there is a large difference in the phase behavior between the gaseous/supercritical ethane and tetradecane, even in the case for a UODT. Ethane is a poor solvent for both polyisoprene and polystyrene while liquid alkanes are good to marginal solvents for the former but poor solvents for the latter. This difference in selectivity imparts a difference in the ϕ dependence of the UODT.

In contrast to behavior observed in the UODT of P(S-*b*-I), sorption of the light alkanes in P(S-*b*-nBMA) induces phase segregation. Moreover, a strong dependence of the LDOT in P(S-*b*-nBMA) on light alkane chain length is observed. At equivalent fluid phase activity (and ϕ), methane induces the most severe depression and the effect diminishes with increasing chain length. Since the LDOT is entropically driven, contributions to compressibility from the sorbed diluent, which induces a selective dilatation of the blocks, are important considerations in determining the effect on phase behavior. In contrast to the behavior noted for the light alkanes, sorption of the liquid alkane, tetradecane, promotes miscibility in the P(S-*b*-nBMA) system, which suggests that contributions to compressibility are less important for liquid diluents as would be expected.

Acknowledgment. The authors acknowledge support from the NSF Materials Research Science and Engineering Center at the University of Massachusetts and the David and Lucile Packard Foundation. B.D.V. acknowledges support from the NSF Graduate Research Fellowship program.

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MA012154K