

## Phase Separation in Polymer Blends and Diblock Copolymers Induced by Compressible Solvents

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**ABSTRACT:** The influence of compressed carbon dioxide sorption on the phase behavior of polymer blends and diblock copolymers exhibiting lower critical solution temperatures (LCSTs) and lower disorder-to-order transitions (LDOTs), respectively, was studied using in situ high-pressure small-angle neutron scattering. Homogeneous blends of poly(deuterated styrene) and poly(vinyl methyl ether) phase separate at temperatures more than 115 °C below the ambient pressure LCST upon sorption of less than 3.3 wt % CO<sub>2</sub>. The LDOTs in symmetric poly(deuterated styrene)-*block*-poly(*n*-butyl methacrylate) copolymers having total molecular weights of 78 000 and 32 000 g/mol are depressed by as much as 250 °C upon exposure to supercritical CO<sub>2</sub> at modest fluid-phase densities.

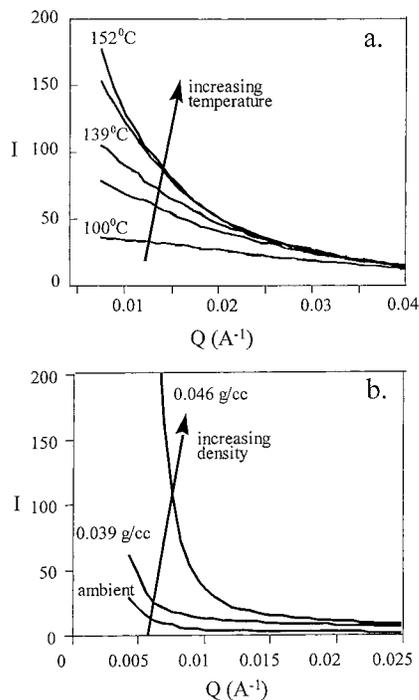
### Introduction

Phase separation upon heating through a lower critical solution transition is common to polymer solutions, blends, and block copolymers.<sup>1–3</sup> In polymer solutions, phase separation typically occurs at temperatures between 0.7 and 0.9  $T_c$ , where  $T_c$  is the critical temperature of the light component, due to a widening disparity between the compressibilities (free volumes) of the polymer and solvent.<sup>1,3</sup> This simple heuristic is remarkably robust and can be applied to mixture critical temperatures of multicomponent solvents, including those that contain a compressible diluent.<sup>4</sup> The nature of lower critical solution temperatures (LCSTs) in polymer blends, and the analogous lower disorder–order transitions (LDOTs) in block copolymers,<sup>2,5–7</sup> is more subtle. Mixing of large polymeric chains provides only a small entropy gain, and thus miscibility is governed by a delicate balance between enthalpic and noncombinatorial entropic contributions to the free energy of mixing.<sup>8,9</sup> For systems that exhibit a region of miscibility, phase separation occurs when the product of the Flory interaction parameter and the degree of polymerization,  $\chi N$ , exceeds a critical value of approximately 10.5 and 2 for symmetric block copolymers and blends, respectively.<sup>10</sup> While a straightforward stability analysis indicates that entropy changes upon segregation must be positive, the requisite increase in  $\chi$  necessary to induce the transition can be attributed to either enthalpic or entropic factors, acting alone or in combination.<sup>3</sup> In systems with strong specific intersegment interactions, the favorable enthalpic contribution to phase miscibility weakens with heating until it can no longer overcome the entropic penalty associated with maintaining contact-mediated preferred orientations of the interacting chain segments. In nonpolar systems that lack specific interactions, phase separation is attributed to negative volume changes upon mixing that arise due to the widening disparities between the free volumes of the phases as temperature increases. This “equation-of-state effect” reflects differences in compressibilities between the mixture components.<sup>9</sup>

To date, LCSTs in blends and block copolymers have been induced thermally and by reductions in hydrostatic pressure at temperatures above the ambient LCST. The latter pathway exploits the well-known pressure dependence of the LCST that can be used to suppress the transition.<sup>11–13</sup> Here we report phase separation by an alternate mechanism: sorption of low mass fractions of compressed carbon dioxide causes a differential dilation of the polymeric components that induces lower critical phase transitions at temperatures hundreds of degrees below those at ambient pressure. Moreover, the transition temperature can be precisely tuned by controlling the degree of CO<sub>2</sub> sorption via pressure-mediated adjustments in CO<sub>2</sub> density over broad ranges.

Investigations of the effect of liquid solvents on polymer/polymer compatibility have a long history, with most recent emphasis on the upper order–disorder temperature (UODT) in block copolymers.<sup>14–18</sup> Unlike lower critical transitions, upper critical solution transitions, including UODTs, are enthalpically driven: phase separation occurs upon reducing temperature when insufficient thermal energy is available to overcome unfavorable interactions between dissimilar segments. The addition of liquid organic solvents that screen interactions between dissimilar chains can produce substantial shifts in the location of the UODT. Provided that the liquid diluent is far from its critical point, equation-of-state contributions are relatively unimportant, and incompressible mean field models can be used to describe the effect.

Compressible fluids such as CO<sub>2</sub> differ from liquid solvents in a number of important ways. First, 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.<sup>19</sup> Thus, unlike liquid diluents, preferential sorption of compressible fluids can lead to rapid and disparate increases in the free volume of the mixture components that exacerbate the entropic penalty for mixing and promote phase segregation. This effect should be particularly pronounced near lower



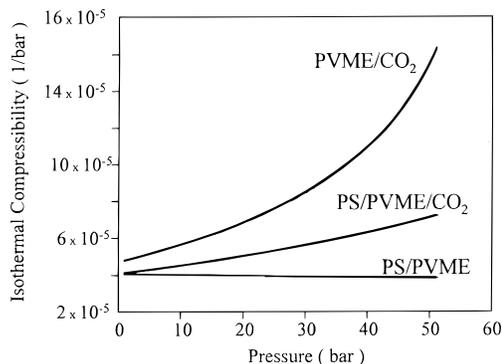
**Figure 1.** (a) Scattering profile of a d-PS/PVME blend as a function of the scattering vector  $Q$  as temperature is increased. The LCST occurs at 155 °C. (b) Scattering profile of a d-PS/PVME blend at 40 °C in the presence of CO<sub>2</sub> as density of the CO<sub>2</sub> phase is increased. The system is phase-separated at densities above 0.05 g/cm<sup>3</sup>.

critical solution transitions: our results validate this prediction. Second, pressure-mediated adjustments in fluid density provide a means to control the degree of solvent sorption directly.<sup>20–23</sup> For example, increasing pressure from 20 to 45 bar at 65 °C raises the solubility of CO<sub>2</sub> in poly(*n*-butyl methacrylate) from approximately 3.5 to 10 wt %.<sup>22</sup> Finally, 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.

In this paper, we demonstrate the influence of CO<sub>2</sub> sorption on lower critical solution transitions in two systems. First, we consider blends of perdeuterated polystyrene (d-PS) and PVME, a system that exhibits a weakly attractive charge-transfer interaction between the segments. Next, we consider diblock copolymers of d-PS and poly(*n*-butyl methacrylate), a system in which favorable specific interactions are absent. A detailed analysis of the phase behavior of both systems will be presented in future publications.

## Experimental Section

The phase behavior of symmetric diblock copolymers of d-PS and poly(*n*-butyl methacrylate), denoted P(d-S-*b*-nBMA) and d-PS/PVME blends, in the presence of compressed carbon dioxide was studied in situ using small-angle neutron scattering (SANS). The block copolymers were synthesized by living anionic polymerization. Copolymers having total molecular weights of 32 000 and 78 000 g/mol, denoted 32K and 78K, and volume fractions of PS of 0.60 and 0.48, respectively, were melt-pressed at 120 °C into 1.3 cm (o.d.) by 2.5 mm thick disks that were inserted into stainless steel sample rings. Blends of d-PS and PVME having molecular weights 90 000 and 104 000 g/mol, respectively, were cast from toluene, dried under vacuum, and melt-pressed directly into the sample rings at 60 °C. Scattering profiles were collected as a function of CO<sub>2</sub> density at temperatures between ambient and 200 °C and



**Figure 2.** Compressibility of PVME/CO<sub>2</sub>, a 50/50 homogeneous blend of PS/PVME and CO<sub>2</sub> and a 50/50 blend of PS/PVME, as a function of pressure at 20 °C calculated with the Sanchez–Lacombe–Balasz equation of state. Interaction parameters were determined using published sorption data.<sup>21</sup>

pressures between atmospheric and 350 bar in a stainless steel scattering cell equipped with sapphire windows. At ambient pressure, the location of the LCST was determined from plots of reciprocal intensity at  $q = 0$  vs reciprocal temperature. For the block copolymer samples, thermal history was first erased by disordering the sample at ambient pressure prior to the experiments. Temperature control was provided via cartridge heaters inserted into an aluminum heating jacket and controlled using a PID controller. CO<sub>2</sub> was charged to the cell using a high-pressure manifold and manual syringe pump. The experiments were conducted at the National Institute of Standards and Technology (NIST) Cold Neutron Research Facility on the 30 m spectrometer. Instrument configuration was as follows:  $\lambda = 8$  Å,  $\Delta\lambda/\lambda = 15\%$ , sample diameter = 0.63 cm, sample-to-detector distance was 5 m for the 32K copolymer sample and 6 m for all others. 2-D raw data were normalized, corrected for background scattering and detector sensitivity, scaled to absolute differential scattering cross sections (cm<sup>-1</sup>) using SiO<sub>2</sub> standards, and radially averaged to one dimension.

## Results and Discussion

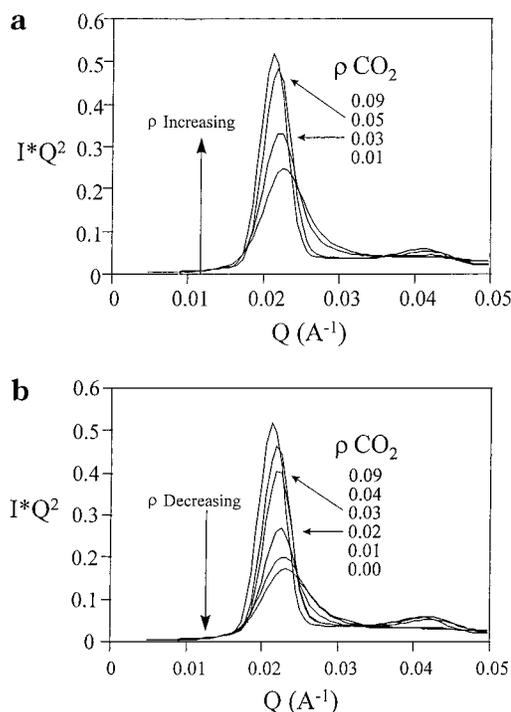
PS/PVME is one of the most thoroughly studied polymer blends. SANS profiles of a 50/50 d-PS/PVME blend at ambient pressure as a function of the scattering vector  $q$  ( $q = (4\pi/\lambda) \sin(\theta/2)$  where  $\theta$  is the scattering angle) show an increase in scattered intensity with increasing temperature that diverges at the LCST of 155 °C (Figure 1a). Figure 1b shows the scattered intensity as a function of the density of CO<sub>2</sub> in contact with the blend at 40 °C. The blend is phase-mixed at ambient pressure, but sorption of CO<sub>2</sub> at a slightly elevated pressure (2.4 MPa) induces phase separation as indicated by divergence of the scattered intensity at low  $q$ . Note that at this pressure CO<sub>2</sub> is a gas with a density of  $\sim 0.05$  g/cm<sup>3</sup>. Using published sorption data<sup>21</sup> and the Sanchez–Lacombe equation of state (S–L EOS),<sup>24</sup> we estimate a CO<sub>2</sub> uptake of less than 3.3 wt % in the 50/50 blend at the onset of phase separation at 40 °C. The magnitude of the LCST depression, 115 °C, is striking given the modest sorption of CO<sub>2</sub> at these conditions.

The sensitivity of the transition to small uptakes of a gaseous diluent suggests that the driving force for phase separation is primarily entropic rather than enthalpic in nature. CO<sub>2</sub> is a nonsolvent for both components at all conditions, but at modest pressure dilates PVME preferentially relative to PS.<sup>21</sup> Figure 2 shows isothermal compressibility,  $\kappa$ , for PVME/CO<sub>2</sub>, a homogeneous 50/50 PS/PVME blend in the presence of CO<sub>2</sub> and a neat 50/50 PS/PVME blend as a function of

system pressure calculated using the S-L EOS.<sup>24,25</sup> Interaction parameters for the diluted systems were determined using the CO<sub>2</sub> sorption data of Monnerie and co-workers for PVME and PS/PVME blends over the range of conditions shown.<sup>21</sup> Compressibility of the phase-mixed system increases rapidly with CO<sub>2</sub> sorption, and differential dilation of the components leads to a disparate increase in compressibility of the segregated components: this free-volume disparity promotes phase separation.  $\kappa$  for the binary PS/CO<sub>2</sub> system was not calculated as PS remains a glass at these conditions,<sup>26</sup> though it is expected to be very small.

Our analysis does not exclude screening of favorable PS-PVME contacts by the presence of CO<sub>2</sub> as the primary driving force behind phase separation, but two factors, low concentration of the diluent and weak selectivity, argue against it. The compatibility of PS/PVME/liquid solvent systems has been studied extensively.<sup>27-29</sup> Solvents such as benzene, toluene, and cyclohexane *do not* induce phase separation; however, highly selective solvents that exhibit specific interactions with PVME, such as chloroform, trichloroethylene (TCE), and dichloromethane, can lead to immiscibility at high dilution. For example, addition of approximately 40 wt % TCE to a PS/PVME blend can induce immiscibility at temperatures 60 °C below the neat LCST. In such systems, charge-transfer interactions between the halogenated hydrocarbon and the ether oxygen of PVME disrupt the favorable PS-PVME contacts.<sup>28</sup> No such specific interactions exist in the CO<sub>2</sub>/PS/PVME system. Moreover, the low concentration of CO<sub>2</sub> upon blend segregation (~3.3 wt %) produces a reduction in the LCST (115 °C) that is incommensurate with solvent screening. We are presently conducting an extensive PS/PVME/CO<sub>2</sub> phase behavior study and stability analysis to assess the relative magnitude of the entropic and enthalpic contributions to mixture instability.

Dilation of block copolymers with CO<sub>2</sub> yields a similar phenomenon. P(d-S-*b*-nBMA) exhibits a transition from the homogeneous to microphase-separated state upon heating.<sup>2,30</sup> The existence of a UODT at low temperatures in this system precludes the possibility of exothermic intersegment interactions, which suggest the LDOT is predominantly the result of a free-volume mismatch between the components.<sup>30</sup> At ambient pressure, the LDOT of the 78K sample is 180 °C, in agreement with previous studies.<sup>2</sup> CO<sub>2</sub> sorption is known to be preferential for polyacrylates, including PnBMA, relative to polystyrene.<sup>22,23</sup> Figure 3a shows the SANS profiles of this sample in the presence of CO<sub>2</sub> as a function of density of the fluid phase at 145 °C. The copolymer is disordered at ambient pressure as evidenced by the weak, diffuse correlation hole maximum. A marked increase in the peak intensity and the appearance of higher order reflections indicate that the system has ordered upon CO<sub>2</sub> sorption at fluid densities greater than 0.05 g/cm<sup>3</sup>. The copolymer disorders upon depressurization (Figure 3b), indicating that SCF-induced LDOTs are fully reversible. At a constant CO<sub>2</sub> density of 0.1 g/cm<sup>3</sup>, the copolymer remains ordered as the system is cooled to 40 °C, which is below the CO<sub>2</sub>-depressed glass transition temperature of the styrene phase.<sup>26</sup> The elimination of the segment miscibility gap suggests the UODT and LDOT have merged. In a companion experiment, the addition of a nominally nonselective liquid solvent, dioctyl phthalate, did not depress the LDOT. The magnitude of CO<sub>2</sub>-induced



**Figure 3.** Reversible phase separation in a block copolymer induced by sorption of CO<sub>2</sub>. (a) Scattering profile of 78K P(d-S-*b*-nBMA) as a function of increasing CO<sub>2</sub> density at 145 °C. The LDOT is induced between 0.03 and 0.05 g/cm<sup>3</sup>. (b) Scattering profile of 78K P(d-S-*b*-nBMA) as a function of decreasing CO<sub>2</sub> density at 145 °C, indicating the transition is fully reversible.

depressions in the LDOT is evident in the behavior of 32K P(d-S-*b*-nBMA). The molecular weight dependence of the transition reported by Russell reveals that the LDOT for this copolymer at ambient pressure is inaccessible prior to thermal decomposition.<sup>2</sup> Upon CO<sub>2</sub> sorption, however, the copolymer orders at 100 °C at fluid densities in excess of 0.3 g/cm<sup>3</sup>, more than 250 °C below the projected transition.

In this system the influence of CO<sub>2</sub> sorption, which is slightly selective for the PnBMA block, contrasts the influence of liquid solvents. Previous theoretical and experimental studies consistently conclude that the addition of neutral and slightly selective liquid solvents to diblock copolymers depresses the UODT and stabilizes the disordered state by screening unfavorable interactions between dissimilar segments.<sup>14-18</sup> An increase in the UODT could be possible using a strongly selective solvent that partitions exclusively into one phase and drives the solvated melt through an order-order transition to a morphology of higher intrinsic thermal stability. The addition of such solvents can be compared loosely to increasing the volume fraction of the solvated block.<sup>15</sup> This possibility in the P(d-S-*b*-nBMA)/CO<sub>2</sub> system is precluded by the presence of a second-order reflection at a scattering vector twice that of the primary peak in the solvated systems, which is indicative of a lamellar morphology. Our results do not exclude the possibility that for some systems CO<sub>2</sub> sorption at elevated densities could promote miscibility near the UODT or UCST. If CO<sub>2</sub> sorption 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. In fact, we have shown this is the case for diblock copolymers of poly-

styrene and polyisoprene.<sup>31</sup>

We now consider hydrostatic pressure, which affects the UCST and LCST via different mechanisms. For UCST phenomena, the predominant effect is a reduction of the average distance between dissimilar chains that increases segmental interaction energies and reduces phase miscibility. Recent studies report relatively small positive pressure coefficients at elevated pressures, including  $\Delta T_{\text{UODT}}/\Delta P$  of  $\sim 0.2$  and  $0.15$  °C/MPa for polystyrene/polyisoprene<sup>32,33</sup> and poly(ethylene propylene)/poly(dimethylsiloxane) diblock copolymers,<sup>34</sup> respectively. Negative pressure coefficients for the UODT can occur at low pressures when the copolymer exhibits negative volume changes on mixing.<sup>33</sup> The central role of compressibility in lower critical phenomena suggests that these transitions will be pressure dependent.<sup>1</sup> A pressure coefficient of  $1.45$  °C/MPa for the LDOT has been reported for P(d-S-*b*-nBMA).<sup>11</sup> Pressure coefficients for blend LCSTs are less sensitive, ranging between  $0.12$  and  $0.25$  °C/MPa for polystyrene/PVME depending on composition.<sup>12,13</sup> In each case, hydrostatic pressure suppresses free volume differences between the components and expands the region of miscibility. We find a pressure coefficient of  $-45$  °C/MPa for PS/PVME/CO<sub>2</sub> at  $40$  °C. Dilation with a compressed solvent overwhelms any influence of hydrostatic pressure.

The ability to tune phase transitions over broad ranges by controlled sorption of compressible solvents has consequences for practical applications and new materials. Recently, polymer synthesis and processing in CO<sub>2</sub> have received much attention.<sup>35–38</sup> This work indicates that thermodynamics can play an important and unanticipated role in processing and structure. It also raises new questions regarding stability and transport properties within miscible blends for membrane applications. Finally, the self-assembly of block copolymers into spatially ordered domains provides novel routes to precise nanoscopic materials. Here, sorption of CO<sub>2</sub> drives the system to stronger states of phase separation while simultaneously enhancing diffusion and reducing viscosity relative to the segregated melt. This unique combination provides new opportunities for processing, orienting, and chemically modifying block copolymers to yield advanced, structured materials and composites.

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