

Influence of Carbon Dioxide Swelling on the Closed-Loop Phase Behavior of Block Copolymers

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ABSTRACT: The influence of carbon dioxide sorption on the closed-loop phase diagram of polystyrene-*block*-poly(*n*-pentyl methacrylate) copolymers, PS-*b*-PnPMA, was investigated. Differential dilation of the constituent blocks was used to induce microphase separation of the PS-*b*-PnPMA. With increasing carbon dioxide loading an appreciable expansion in the size of the closed loop was found. At a carbon dioxide activity of 0.1 the upper order-to-disorder transition temperature (UODT) was elevated by more than 20 °C, whereas the lower disorder-to-order transition temperature (LDOT) was depressed by the same magnitude. This arises from the entropic nature of the closed-loop miscibility gap in this weakly interacting system, where microphase separation is driven by disparity in free volumes between dissimilar segments of the chain.

Introduction

Polymer phase behavior, and specifically that of block copolymers, continues to be an area of vigorous theoretical^{1,2} and experimental³ investigation. Many block copolymers (BCPs) exhibit an order-to-disorder transition (ODT), where nonfavorable segmental interactions are reduced with increasing temperature and mixing is favored. Russell and co-workers discovered the lower disorder-to-order transition (LDOT) where, upon heating BCPs of polystyrene (PS) and poly(*n*-butyl methacrylate) (PnBMA), the opposite behavior is observed and the BCPs microphase separate.⁴ In a series of publications this LDOT-type behavior has been found in BCPs of PS with poly(*n*-propyl methacrylate) and mixtures of PS-*b*-poly(*n*-alkyl methacrylates).^{3,5,6} Of particular note in these BCPs is that there are no strong specific interactions between the segments, as for example hydrogen bonding, and the transition appears to be entropic in origin. LDOT behavior has also been described theoretically by several groups using lattice cluster theory,⁷ equation of state,⁸ regular solution,⁹ and compressible mean-field approaches.¹⁰ Common to each of these approaches is the entropic origin of the phase transition.

Recently, this picture of BCP phase behavior was expanded by Ryu et al.¹¹ to include the existence of a closed-loop-type phase diagram. Closed-loop phase behavior has been observed in small molecule systems, such as in nicotine and water,¹² or more recently in polymer–solvent systems, such as poly(ethylene oxide) and water.¹³ These systems, however, have strong specific interactions, like hydrogen bonding, that are mediated with increasing temperature. The experimental observations of Ryu et al., however, showed a closed-loop phase

diagram in the polystyrene-*block*-poly(*n*-pentyl methacrylate) (PS-*b*-PnPMA) where there are no such specific interactions. Technically, any polymer that exhibits an LDOT should, also, undergo mixing at even higher temperatures where the combinatorial entropy would drive the system back into the phase-mixed state. However, for most polymers this temperature is usually inaccessible due to degradation. Dudowicz and Freed predicted a closed-loop behavior for the polystyrene-*block*-poly(vinyl methyl ether) system using lattice cluster theory;¹⁴ however, only a lower critical solution temperature behavior was observed experimentally.¹⁵ Lattice cluster theory also predicted a closed-loop phase diagram for poly(hh-propylene)/poly(ethylene-*co*-butene) blends,¹⁶ although this behavior has not been reported experimentally in the literature. PS-*b*-PnPMA was the first known example of a weakly interacting system exhibiting closed-loop phase behavior, and this phase behavior has since been observed in weakly interacting blends of poly(ethylene-*co*-styrene) and poly(ethylene-*co*-butene).¹⁷

Most polymers are insoluble in supercritical carbon dioxide, SC CO₂. The exceptions to this rule are fluoropolymers, such as amorphous Teflon AF,¹⁸ polysiloxanes, such as PDMS, and poly(ether-*block*-carbonate) copolymers.¹⁹ While other classes of polymers fail to dissolve in SC CO₂, they can be swollen.²⁰ Carbon dioxide sorption has a substantial effect on the properties of the polymer, the most notable of these being the depression of T_g ²¹ and the increase of small molecule²² and polymer chain diffusivity within dilated substrates.^{23,24} In addition to influencing transport properties, carbon dioxide sorption increases the free volume of the swollen polymer. As was mentioned above, polymer free volume can influence the compatibility of polymer systems. The influence of SC CO₂ on the ODT was explored by Vogt et al. using polystyrene-*b*-polyisoprene (PS-*b*-PI)²⁵ and polystyrene-*block*-poly(*n*-hexyl methacrylate) (PS-*b*-PnHMA)²⁶

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copolymers, where it was shown that carbon dioxide mediates segmental interactions and promotes miscibility, similar to the influence of liquid solvents. Consequently, the ODT was depressed by as much as 10 °C at high carbon dioxide densities. Lodge and co-workers^{27,28} showed a depression in the ODT in PS-*b*-PI upon swelling with the neutral solvent dioctyl phthalate (DOP). They found that the dilution approximation, which assumes the solvent is evenly distributed throughout the block copolymer, did not hold as predicted by an ODT scaling $\sim \phi^{-1}$. Rather, they found that the lamellar copolymer ODT $\sim \phi^{-1.6}$ and the cylindrical phase ODT $\sim \phi^{-1.4}$. The underestimation of the solvent-induced ODT depression was attributed to a preferential segregation of the solvent to the microdomain interface. This served to further mediate interactions, favoring homogenization at lower temperatures. Similarly, the lamellar PS-*b*-PI used by Vogt displayed a scaling of $\phi^{-1.3}$ for similar molecular weights at large polymer volume fraction.²⁵

A lower disorder-to-order transition in block copolymers is driven by volumetric (or free volume) disparities between the blocks. As such, the differential dilation of the components by CO₂ has a pronounced influence on the miscibility of the components. The first LDOT system studied under compressible fluids was PS-*b*-PnBMA by Watkins, Russell, and co-workers.²⁹ It was found that CO₂ significantly depressed the LDOT temperature, promoting microphase separation. Another study involved the sorption of a series of light alkane solvents in PS-*b*-PnBMA. At equivalent volume fractions, sorption of methane resulted in severe depressions of the LDOT. Similar behavior was found with ethane, propane, and butane, in decreasing order of the magnitude of the depression. These results reiterate the importance of compressibility for the compatibility of systems exhibiting LCST-type behavior.³⁰ Moreover, while the ODT-type system PS-*b*-PnHMA exhibited an ODT depression of 7 °C at 7% volume dilation with CO₂, PS-*b*-PnBMA displayed an LDOT depression of 70 °C at a dilation of only 3% CO₂.²⁶ It should be noted that a hysteresis on heating and cooling was found, likely due to the difference in CO₂ sorption in the ordered and disordered states. Carbon dioxide had to be expelled from the polymer in passing from the ordered to the disordered state, thus depressing the transition temperatures upon cooling. Since the closed-loop phase behavior of PS-*b*-PnPMA is expected to be driven by entropy, differential dilation using CO₂ swelling is expected to have a profound impact on the observed phase behavior.

Experimental Section

PS-*b*-PnPMA was prepared by anionic polymerization with a sequential addition of the monomers in tetrahydrofuran (THF) at -78 °C in the presence of lithium chloride salt under an inert argon atmosphere.^{11,31} *sec*-Butyllithium was used as an initiator. Lithium chloride (high purity, Aldrich) was dried overnight at 150 °C and dissolved in THF. The THF was dried by refluxing over calcium hydride and then stirring over a sodium/benzophenone complex until there was a persistent deep purple color indicative of an oxygen-free, moisture-free environment. The monomers were degassed from a calcium hydride solution, and the styrene was distilled from dried dibutylmagnesium. The *n*-pentyl methacrylate monomers were distilled from triethylaluminum. The polymerization of the styrene block took ~1 h to reach full conversion, at which time an aliquot was extracted and the polymerization in the aliquot was terminated using purified 2-propanol for molecular weight analysis. The *n*-pentyl methacrylate component was then slowly added to the reaction vessel and stirred for ~5 h. After completion the polymerization was terminated using purified 2-propanol and precipitated in a 4:1 methanol:water mixture to remove lithium chloride impurities. The total molecular weights were determined

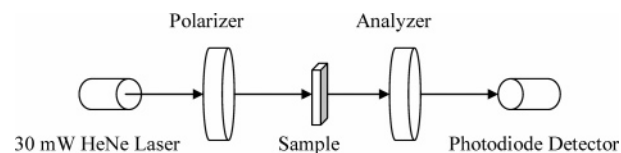


Figure 1. Optical birefringence experimental setup for the identification of transition temperatures in block copolymers used in this study.

Table 1. Polymer Samples Used in This Work

sample description	M_n (g/mol)	volume fraction PS	PDI
50 kDa symmetric PS- <i>b</i> -PnPMA	48 000	0.50	1.02
50 kDa cylindrical PS- <i>b</i> -PnPMA	49 900	0.42	1.03
40 kDa symmetric PS- <i>b</i> -PnPMA	39 900	0.50	1.02
43 kDa symmetric PS- <i>b</i> -PnPMA	43 000	0.50	1.02
PS homopolymer	45 500	1.00	1.04
PnPMA homopolymer	20 000	0.00	1.03

using size exclusion chromatography (SEC) equipped with multi-angle laser light scattering (MALLS). Molecular weight distributions were determined from SEC. The polystyrene (or deuterated polystyrene)/ poly(*n*-pentyl methacrylate) block ratios were determined using nuclear magnetic resonance (NMR). The characteristics of the polymers used in this study are given in Table 1.

Equilibrium sorption measurements were performed using a pressure decay method with ~1 g of homopolymer. These measurements were performed as discussed by Koros and Paul.³² The swelling studies were performed from 40 to 100 °C at pressures from atmospheric to 130 bar.

The form birefringence, characteristic of cylinder and lamellae-forming block copolymers, was used to determine the location of the order-to-disorder transition.³³ Figure 1 illustrates the experimental geometry. Light, with a wavelength of 632.8 nm, is directed through an optical polarizer, the sample, an analyzer oriented normal to the polarizer, and into a photodiode detector to measure the transmitted intensity. In the disordered state, no light is transmitted, whereas in the ordered state a form birefringence, arising from the microdomains of the copolymer, depolarizes the incident light and light is transmitted. Block copolymer samples were pressed into an aluminum ring approximately 1.5 mm thick and 8 mm in diameter. High-pressure birefringence measurements were undertaken as a means of determining the locations of the UODT and LDOT temperatures as a function of carbon dioxide activity. A stainless steel pressure cell equipped with sapphire windows was used in the experiments over a pressure range from atmospheric to 310 bar. The cell is described in detail elsewhere.²³ All measurements were performed at constant CO₂ activity, increasing temperature at 0.1 °C/min intervals near the transition temperatures. The sharp increase in detected light intensity indicated the location of the microphase separation transition.

Results and Discussion

CO₂ absorption of the component materials was determined using the equilibrium pressure decay sorption. The data are shown in Figure 2 for 45 kDa PS and 20 kDa PnPMA where the volume fraction of polymer after sorption is plotted as a function of solvent strength or activity of carbon dioxide. With increasing carbon dioxide activity the amount of absorbed CO₂ increases in both PS and PnPMA. The degree of swelling in PnPMA, however, is slightly larger, and this disparity increases with increasing activity such that, at an activity of 1.0, there is almost 40% more CO₂ in PnPMA than in PS. These data were used to describe the swelling of the diblock copolymer in the microphase-separated state, where the total extent of swelling was taken as the arithmetic mean of swelling from each component weighted by the component volume fractions. These calculated activities, then, were used in quantifying the effect of carbon dioxide sorption on the closed-loop phase behavior of PS-*b*-PnPMA block copolymers.

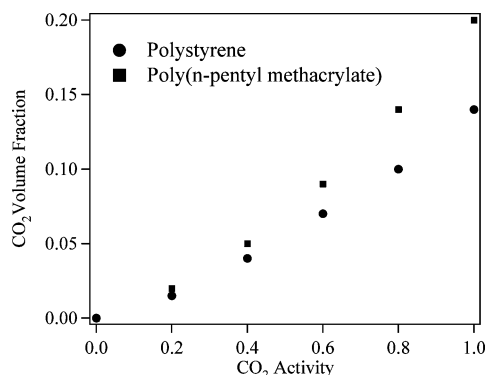


Figure 2. Sorption measurements on 20 kDa PnPMA and 45 kDa PS as a function of carbon dioxide activity.

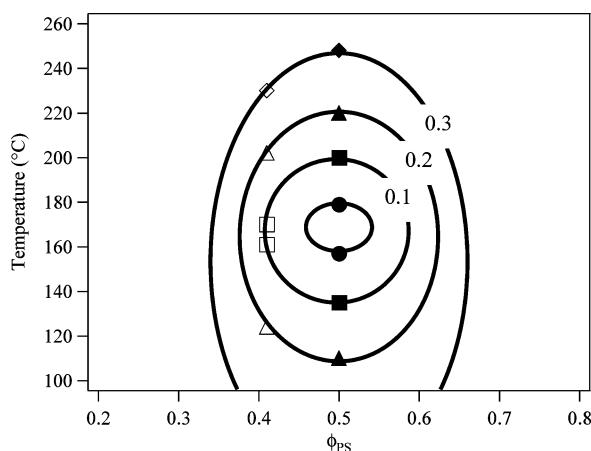


Figure 3. UODT and LDOT temperatures in 50 kDa PS-*b*-PnMA at CO₂ activities of 0.0 (circles), 0.1 (squares), 0.2 (triangles), and 0.3 (diamonds) for volume fraction ratios of 50:50 (closed symbols) and 42:58 (open symbols).

Birefringence measurements were performed using both lamellar (50/50 vol) and cylindrical (42/58 vol) block copolymers having a 50 kDa molecular weight as a function of temperature and CO₂ activity. Figure 3 shows the location of the LDOT and UODT as a function of carbon dioxide activity for these two block copolymers. As seen, the size of the closed loop is appreciably increased at higher carbon dioxide activities. For the symmetric PS-*b*-PnMA, the closed loop was accessible at atmospheric pressure with an LDOT at 157 °C and a UODT at 179 °C. In the presence of carbon dioxide with an activity of 0.1, an appreciable UODT elevation and LDOT depression were seen. This increase in the size of the immiscibility window was due to the differential dilation of the system when swollen with carbon dioxide. As a slightly selective solvent for PnMA, CO₂ swelling magnified the volumetric disparity between the components, driving the block copolymer into the microphase-separated state. Transition temperatures higher than 250 °C were not experimentally accessible. At temperatures below 100 °C, proximity to T_g prohibited the observation of the transitions. Within the experimentally accessible temperature range the closed-loop expansion was symmetric, with the UODT increasing at 23.0 °C/0.1 activity unit and the LDOT decreasing at 23.5 °C/0.1 activity unit.

The asymmetric PS-*b*-PnMA with 50 kDa was fully disordered over the entire temperature range at atmospheric pressure. However, at a carbon dioxide activity of 0.1 the copolymer was driven into the microphase-separated state, showing an LDOT at 162 °C and a UODT at 170 °C. At higher CO₂ activities the closed loop expanded. The change in the

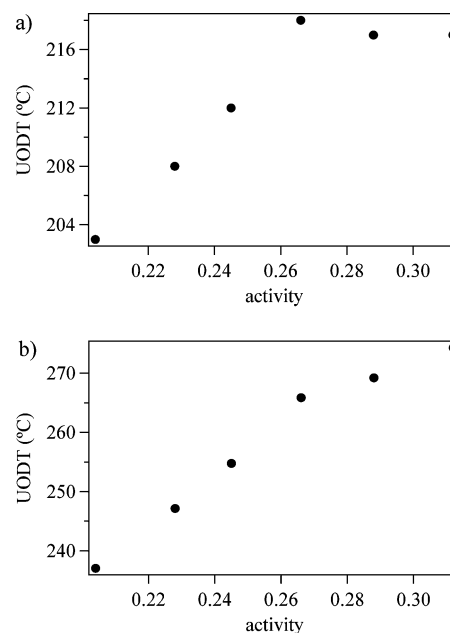


Figure 4. UODT temperature as a function of carbon dioxide activity (a) before and (b) after correction for hydrostatic pressure in 43 kDa (50:50) PS-*b*-PnMA. The pressure coefficient used was -725 °C/kbar.

LDOT and UODT with activity was greater in magnitude for the asymmetric material (30.0 °C/0.1 activity unit for both the UODT and LDOT) than for the symmetric copolymer. This may be due to the increased CO₂ loading since PnMA was the major component. Taking the effect of copolymer composition into account, the initial component volume fraction ratio without CO₂ was near the morphological phase boundary between the lamellar and cylindrical phases, as predicted by the mean-field approximation. With increasing the CO₂ activity, however, the swollen volume fraction of pentyl methacrylate increases, driving the system into the cylindrical phase region.

It should be noted that all measured transitions were corrected for hydrostatic pressure. As shown previously, hydrostatic pressure has an appreciable impact on the phase behavior of PS-*b*-PnMA block copolymers³⁴ and blends.³⁵ When measuring the effect of carbon dioxide dilation on closed-loop expansion, the tendency of hydrostatic pressure to promote mixing must be taken into account. The pressure coefficients of 725 and -725 °C/kbar for the LDOT and UODT were used at each data point in Figure 3 such that the only effect shown is that from preferential swelling. To demonstrate the effect of this correction, parts a and b of Figure 4 show the location of the UODT for symmetric 43 kDa PS-*b*-PnMA before and after the correction for hydrostatic pressure, respectively. At atmospheric pressure the copolymer is disordered over the entire temperature range. However, at activities above 0.20 a closed loop is observed. After the correction for hydrostatic pressure was made the UODT was found to increase in direct proportion to the CO₂ activity, with one outlying data point at an activity of ~ 0.265 . This corresponds to the critical pressure of carbon dioxide. But, since the temperature was far above the critical temperature of CO₂, this deviation could not be due to critical phenomena, such as critical wetting.

Representative heating and cooling curves are shown in Figure 5 for the birefringence of symmetric 40 kDa PS-*b*-PnMA. A hysteresis is seen in these traces, with the cooling curve shifted by ~ 5 °C to lower temperatures than the heating curve. This hysteresis is likely due to differences in CO₂ sorption

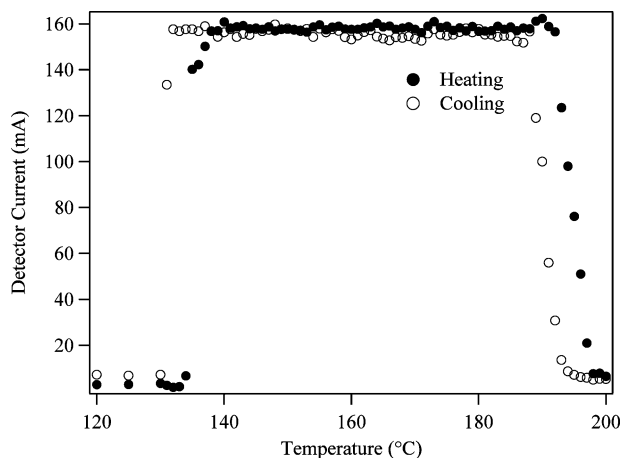


Figure 5. Hysteresis on heating and cooling in 40 kDa (50/50) PS-*b*-PnMA as detected by birefringence.

in the ordered and disordered states. Work by Vogt et al.²⁶ suggested that PS-*b*-PnBMA was able to take up more carbon dioxide in the ordered state than in the disordered state, as determined by film thickness measurements using neutron reflectivity. It is thermodynamically unfavorable to expel carbon dioxide from the polymer, and as a result, there is a lag in the measured transition temperature as one passes from the ordered state into the disordered state. The transition temperature can only be determined accurately when approaching an ordering transition from the disordered state. The phase diagram in Figure 3 was constructed in this way, with UODTs determined on an approach from high temperatures and LDOTs determined on an approach from lower temperatures.

Conclusions

Compressed carbon dioxide was used to investigate the closed-loop phase behavior of PS-*b*-PnMA block copolymers. CO₂ sorption served to differentially dilate the components, thus enhancing the free volume disparity between them. As a result, the closed-loop expanded appreciably with modest fluid sorption. Additionally, PS-*b*-PnMA samples which are fully disordered over the complete temperature range were driven into the ordered state with the application of carbon dioxide. These results reflect the entropic origin of the closed-loop phase behavior of these materials, which is dominated by differences in the free volume of the blocks. The effect of carbon dioxide sorption is distinctly different from the behavior of liquid diluents, where one would expect only a small decrease in the size of the immiscibility window.

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