Effect of Hydrostatic Pressure on Closed-Loop Phase Behavior of Block Copolymers

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The effect of hydrostatic pressure (P) on closed-loop phase behavior of deuterated polystyrene-*block*-poly(n-pentyl methacrylate) copolymers [dPS-PnPMA] was investigated by using small-angle neutron scattering and birefringence. For $P < 20.7$ bar, dPS-PnPMA exhibited a lower disorder-to-order transition temperature (T_{LDOT}) at 175 °C, and then an upper order-to-disorder transition temperature (T_{UODT}) at 255 °C. With increasing pressure both T_{LDOT} and T_{UODT} were markedly changed, where dT_{LDOT}/dP was 725 °C/kbar and dT_{UODT}/dP was -725 °C/kbar. These are consistent with predictions by the Clausius-Clapeyron equation using measured values of the volume and enthalpy changes of both transitions. The large pressure coefficients imply that the closed-loop phase behavior observed for PS-PnPMA is an entropic-driven phase transition.

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During the past few years the pressure dependence of phase transitions in polymer blends and block copolymers has been a subject of intense research both experimentally [1–11] and theoretically [12–17]. It has been found that the upper critical solution transition (UCST) of polymer mixtures and the order-to-disorder transition (ODT) for block copolymers are only weakly dependent on pressure. However, the lower critical solution transition (LCST) of mixtures and the lower disorder-to-order transition (LDOT) have been found to be strongly dependent on pressure [7,8]. Since the LCST and LDOT are related to differences in thermal expansion coefficients of the components, arguments based on equation-of-state theories [12–17] have been developed to predict the pressure dependence of these transitions. Negative volume changes on mixing (ΔV_{mix}) characterize the LCST and LDOT, and therefore, miscibility is enhanced by increasing hydrostatic pressure (P). For instance it has been determined that $dT_{\mathrm{LDOT}}/dP \sim 150$ °C/kbar for polystyrene-*block*-poly(n-butyl methacrylates) copolymer [PS-PnBMA] [7]. On the other hand, dT_{ODT}/dP can be positive or negative depending on the nature of constituent blocks (or the sign of ΔV_{mix}) . For example, dT_{ODT}/dP is $\sim +20$ °C/kbar for PS- *block*-polyisoprene (SI) [3], whereas it is ~ -20 °C/kbar for poly(ethyl propylene)-*block*-poly(ethyl ethylene) (PEP-PEE) [5]. For PEE-*block*-poly(dimethyl siloxane) (PEE-PDMS) and PEP-*block*-PDMS copolymers, the sign of dT_{ODT}/dP has been found to depend on the pressure range [4,10]: $dT_{\mathrm{ODT}}/dP \sim -20$ °C/kbar at pressures lower than a certain pressure ($500 \sim 700$ bar), but it changes to $+20$ °C/kbar at higher pressures, quite possibly due to the increase in unfavorable contacts between dissimilar segments at these higher pressures. A similar change in sign of dT_{ODT}/dP with pressure was also reported for SI [9].

Recently, a closed-loop phase behavior was observed for PS-*block*-poly(n-pentyl methacrylates) (PS-PnPMA) where the LDOT and upper order-to-disorder transition (UODT) form the lower and upper bounds of a close loop [18–20]. Closed-loop phase behavior was first reported for nicotine/water mixture [21] as well as mixtures of polyethylene oxide/water and poly(vinyl alcohol-*co*-vinyl acetate)/water [22]. These systems, however, have strong specific directional interactions (hydrogen bonding) at lower temperatures and at least one component (water) has a lower molecular weight.

The closed loop found in PS-PnPMA arises from a delicate balance between enthalpic and entropic contributions to the free energy of mixing [18–20,23]. There might exist a weak interaction between PS and PnPMA segments even if strong directional interactions such as hydrogen bonding are absent. For weakly interacting polymer systems, the origin of the LCST (or LDOT) might be twofold [24]. The first is a free volume effect arising from the difference in compressibilities of the two components (or the equation-of state variables). The volume change results in the negative entropic contribution to the free energy of mixing, thus, decreases miscibility. When the absolute value of the negative entropy is larger than the translational (or combinatorial) entropy, an LCST (or LDOT) occurs at intermediate temperatures. The second is related to the directional entropy. At lower temperatures, a weak interaction, though small, can surpass the directional entropic loss resulting from pairing two monomers. But, the directional entropic loss becomes huge with increasing temperature. Then, the pair interactions turn into van der Waals-type repulsive interaction, which results in a LCST (or LDOT). At present, we cannot determine the relative significance of the two possible contributions. Yet, in either case (or the combination of these two), the LDOT is entropically driven [24]. Therefore, the LDOT observed in PS-PnPMA should be very sensitive to external hydrostatic pressure, as observed.

At higher temperatures, translational (or combinatorial) entropic contribution can in principle prevail over the combination of the repulsive interaction and the negative entropic contribution due to the free volume. Therefore, an upper UCST (UODT) should appear, and the system becomes disordered.

With increasing temperature, the effective Flory-Huggins interaction parameter ($\chi_{\rm eff}$) of deuterated PS and PnPMA (obtained by SANS from 110 to 270 °C) increases initially, goes through a maximum, and then decreases at higher temperatures [19,20], which is a typical behavior for closed-loop type of phase behavior [22,25]. Furthermore, $\chi_{\rm eff}$ for $T > T_{\rm UODT}$ is found to be similar to that for $T < T_{\rm LDOT}$ [20]. By temperature jumping, one can go from one disordered state to another, without ordering. Also, with pressure the closed-loop phase transitions can be completely eliminated, and one can proceed over the entire temperature range without ordering. Consequently, the disordered states at higher and lower temperature regimes should be essentially the same, except the volume (or density) change due to thermal expansion.

A closed-loop behavior for block copolymers was first predicted by Dudowicz and Freed [15] using lattice cluster theory (LCT), for PS-*block*-poly(vinyl methyl ether) (PS-PVME). According to the LCT for PS-PVME, the predicted value of dT/dP for the LDOT is $+400\ ^\circ{\rm C/kbar}$, while that for the UODT is $-400\ ^\circ{\rm C/kbar}$. For PEO/water, on the other hand, $dT_{\rm LCST}/dP$ is only $-5\ ^\circ{\rm C/kbar}$ [26]. There is no report in the literature on the pressure dependence of upper UCST that corresponds to a closed loop.

To elucidate the difference in the origin of the closed-loop phase behavior between a weakly interacting polymer/polymer blend (or a block copolymer) and a strongly interacting mixture having at least one low molecular weight component, the pressure dependence on transition temperature should be investigated. If the closed-loop phase behavior is related to strong intermolecular interactions, the pressure dependence on transition temperature should be quite small. If the lower and upper transition temperatures of a closed-loop result from free volume effects and/or negative directional entropic loss, and translational (combinatorial) entropy, respectively, then these two transitions should depend strongly on pressure.

Here, small-angle neutron scattering (SANS) was used to study the effect of pressure on the LDOT and UODT of a deuterated PS-*block*-PnPMA that exhibits a closed-loop phase behavior. In conjunction with optical birefringence, it is shown that the UODT has a very strong pressure dependence, similar in magnitude to that of the LDOT. The pressure coefficients of the LDOT and UODT are $725\ ^\circ{\rm C/kbar}$ and $-725\ ^\circ{\rm C/kbar}$, respectively. The large coefficients of both transitions imply that the closed-loop phase behavior is an entropically driven phase transition.

dPS-*block*-PnPMA copolymer (dPS-PnPMA-BH) having a number-average molecular weight (M_n) of 50 000, a polydispersity index (M_w/M_n in which M_w is the weight-average molecular weight) of <1.04, and a volume fraction of the *d*-PS block of 0.5 was synthesized by the sequential anionic polymerization [20]. Samples for SANS were prepared by compression molding plaques at 115 °C, followed by annealing at 125 °C under vacuum for 24 h.

SANS experiments were performed at the Hanaro Reactor (Korea) with a wavelength (λ) of 0.431 nm and $\Delta\lambda/\lambda = 0.12$ at a sample to detector distance of 3 m [20]. Some SANS data were measured at the time-of-flight small-angle neutron diffractometer (SAND) at the Intense Pulsed Neutron Source at Argonne National Laboratory. Two pressure controllers, one at low pressures ($1 \sim 150$ bar) and another at high pressures ($1 \sim 1.5$ kbar), were used. SANS was performed at several temperatures from 140 to 270 °C, and at each temperature measurements were done for a series of pressures. SANS profiles obtained with increasing and decreasing pressure were identical ensuring pressure reversibility.

Calorimetric measurements were made using a Perkin-Elmer DSC 7 differential scanning calorimeter. The DSC thermograms were obtained during the first heating run at a rate of 10 °C/ min. In order to enhance the signal-to-noise ratio, a large-size DSC pan was used that held ~50 mg of sample. Volumetric data at ambient pressure was measured using a dilatometer (DIL402, Netzsch Co.) at a heating rate of 0.5 °C/ min in a He atmosphere. The aluminum oxide cell contained ~0.4 g of the block copolymer.

Figure 1 shows the SANS intensity, $I(q)$, as a function of the scattering vector, q [$q = (4\pi/\lambda)\sin\theta$, where 2θ is the scattering angle and λ is the neutron wavelength] for dPS-PnPMA-BH at different temperatures with $P = 6.9$ bar. In the disordered state, a single broad peak is seen due to the correlation hole effect [27]. The peak sharpens and intensifies upon odering. In Fig. 1 it is clear that the first order peak is sharp at temperatures between 175 and 255 °C and broad at all other temperatures. In the

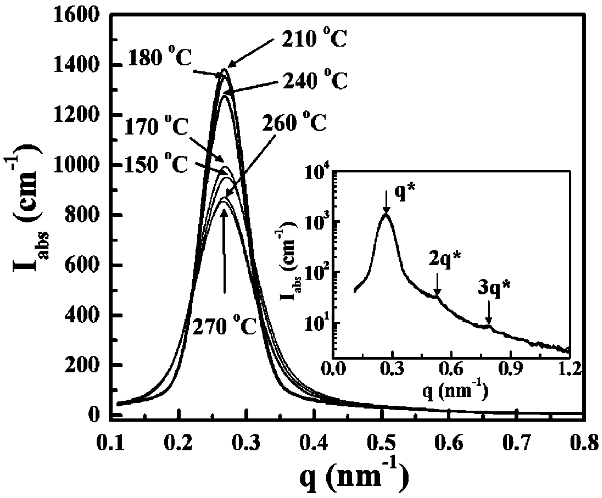

FIG. 1. Absolute SANS intensity [$I_{\mathrm{abs}}(q)$] versus scattering vector (q) of dPS-PnPMA-BH at various temperatures at 6.9 bar. This block copolymer has a closed-loop phase behavior with LDOT at ~175 °C and UODT at ~255 °C. The inset gives SANS profiles at 180, 210, and 240 °C in the ordered state where the second and third order peaks ($2q^*$ and $3q^*$) are clearly seen.

same temperature region ($175\,^\circ\mathrm{C} < T < 255\,^\circ\mathrm{C}$) a second and a weak third order diffraction peaks ($2q^*$ and $3q^*$) are observed as shown in the inset of Fig. 1. Here, $q^*(\sim 0.26\ \mathrm{nm}^{-1})$ is the scattering vector corresponding to the first order peak. Thus both the LDOT and UODT can easily be identified from the SANS data in Fig. 1. The higher order reflection is characteristic of a lamellar microdomain morphology. The closed-loop phase behavior evident in the SANS data is also seen in rheological and small-angle x-ray scattering measurements [20].

The temperature dependence of $I(q^*)$ and the full width at half maximum (FWHM) of the primary peak are shown in Fig. 2 at various pressures. $I(q^*)$ does not change significantly with pressure up to 20.7 bar, but with further increasing pressure, the T_{LDOT} was shifted toward higher temperatures, whereas the T_{UODT} moved toward lower temperatures. These results are consistent with those obtained from FWHM data. This indicates that the miscibility of dPS-PnPMA is enhanced with increasing pressure. For $P > 62.1$ bar, the block copolymer is disordered at all temperatures and the closed loop disappears. This pressure dependence is also seen in optical birefringence experiments.

The changes in the T_{LDOT} and T_{UODT} with pressure measured by SANS (filled symbols) and birefringence measurements (open symbols) are summarized in Fig. 3. Interestingly dT/dP were very large: for LDOT it is 725 °C/kbar and for UODT it is −725 °C/kbar at pressures above 20.7 bar. The experimental values are comparable with prediction by LCT for PS-PVME [15], where dT/dP for the LDOT is +400 °C/kbar, while that for the UODT is −400 °C/kbar.

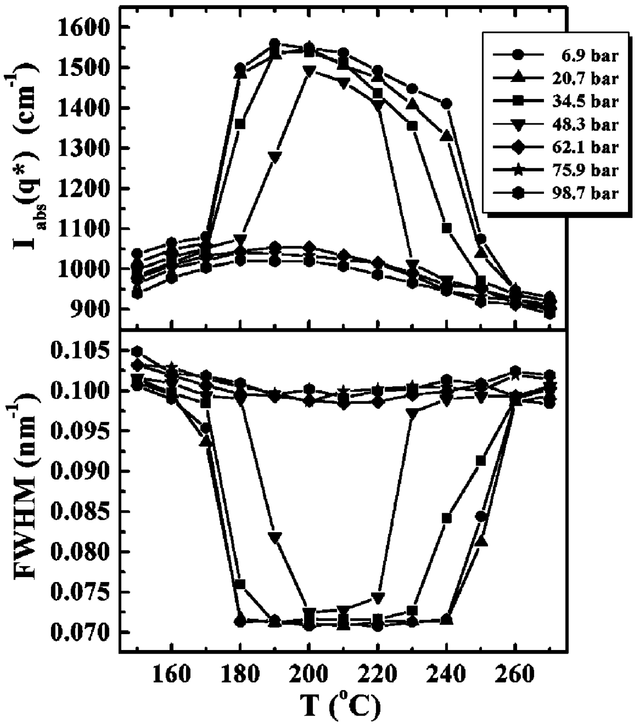

FIG. 2. Temperature dependence of $I_{\mathrm{abs}}(q^*)$ and FWHM for dPS-PnPMA-BH at various pressures. With increasing pressure, the temperature for LDOT increased but that for UODT decreased. The closed-loop phase behavior disappeared at pressures larger than 62.1 bar.

Because of the large value of dT/dP for the UODT as well as LDOT, it can be concluded that the closed-loop phase transition is entropically driven, which is conceptually different from the enthalpic-driven ODT found in SI, PS-*block*-polybutadiene, and PEP-PEE.

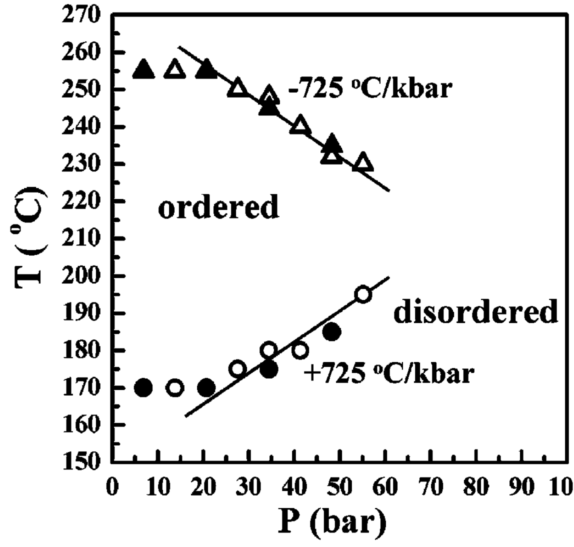

FIG. 3. The changes of T_{LDOT} (circle) and T_{UODT} (triangle) for dPS-PnPMA-BH with hydrostatic pressure measured by SANS (solid symbols) and optical birefringence (open symbols).

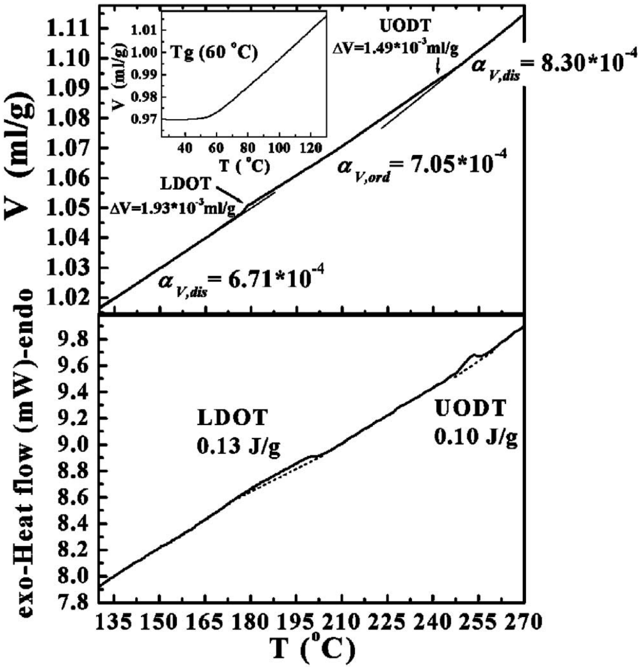

FIG. 4. (a) Volumetric change of dPS-PnPMA-BH during heating at a rate of 0.5 °C/ min. The inset gives T_g (60 °C) for dPS-PnPMA-BH in the homogenous state. (b) DSC thermogram of dPS-PnPMA-BH obtained during the first heating at a rate of 10 °C/ min.

Furthermore, the closed-loop behavior of dPS-PnPMA copolymer is distinctly different from that seen in poly(ethylene oxide)/water, for example, where there are strong intermolecular interactions and dT_{LCST}/dP is only -5 °C/kbar [26].

The value of dT/dP can be estimated from the Clausius-Clapeyron equation where

$$dT_{(\mathrm{LDOT\ or\ UODT})}/dP = T_{(\mathrm{LDOT\ or\ UODT})}\frac{\Delta V}{\Delta H}, \qquad (1)$$

where ΔV is the volume change and ΔH is the enthalpy of the transition. Shown in Fig. 4 are results from dilatometric and calorimetric experiments, whereΔV and ΔH per gram of the block copolymer are 1.93×10^{-3} ml/g and 0.13 J/g for the LDOT, and -1.49×10^{-3} ml/g and 0.10 J/g for the UODT, respectively. Substituting these values into Eq. (1) gives dT/dP of 660 °C/kbar for the LDOT and -780 °C/kbar for the UODT. Thus, the predictions are in very good agreement with the experimental results.

In summary, an entropically driven closed-loop phase behavior was observed for dPS-PnPMA diblock copolymers. The pressure dependence of the T_{LDOT} and T_{UODT} were found to be similar in magnitude, though opposite in sign. The magnitude of the pressure coefficients is consistent with theoretical arguments and with that predicted by the Clausius-Clapeyron equation. For the closed-loop phase behavior in systems with no strong interaction, increasing pressure enhances greatly the miscibility between dPS and PnPMA blocks. For pressures higher than 62.1 bar, the dPS-PnPMA copolymer was phase mixed at all temperatures, completely eliminating the closed loop. Large pressure coefficients allow one to use dPS-PnPMA as a "baroplastic" material, which can be processed at a low temperature under high pressure.

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