

Closed-Loop 상거동을 가지는 블록공중합체의 압력가소성

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Baroplastic Behavior in the Closed-Loop Phase Block Copolymer

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Abstract

The effect of hydrostatic pressure on closed-loop phase behavior of deuterated polystyrene-*block*-poly(*n*-pentyl methacrylates) copolymer [dPS-PnPMA] was investigated by using small angle neutron scattering and birefringence. For hydrostatic pressures (P) up to 20.7 bar, with increasing temperature, dPS-PnPMA exhibited a lower disorder-to-order transition temperature (T_{LDO}) at 175 °C, and then an upper order-to-disorder transition temperature (T_{UOD}) at 255 °C. With increasing pressure both T_{LDO} and T_{UOD} were markedly changed, where dT_{LDO}/dP was 725 °C/kbar and dT_{UOD}/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, determined by dilatometry and differential scanning calorimetry, respectively. The large pressure coefficients for T_{LDO} and T_{UOD} imply that the closed-loop phase behavior observed for PS-PnPMA is an entropic-driven phase transition

Introduction

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 closed-loop [1-3]. With increasing temperature, the copolymer was found to undergo a transition from disordered to ordered state at the T_{LDOT} and then from ordered to disordered state at the T_{UODT} . Closed-loop phase behavior was first reported a century ago for nicotine/water mixture [4]. Mixtures of polyethylene oxide/water and poly(vinyl alcohol-*co*-vinyl acetate)/water also exhibited similar phase behavior [5]. 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 free energy of mixing [1-3,6]. There is no report in the literature on the pressure dependence of upper UCST that corresponds to a closed loop. 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.

Experimental

dPS-*block*-PnPMA copolymer [dPS-PnPMA-BH] having a number-average molecular weight (M_n) of 50,000 and a polydispersity index (M_w/M_n in which M_w is the weight-average molecular weight) of < 1.04 was synthesized by the sequential anionic polymerization of *d*-styrene and *n*-pentylmethacrylate in tetrahydrofuran at -78 °C [1-3]. The M_w and M_n were measured by multi-angle laser light scattering with size exclusion chromatography (SEC). 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. Scattering intensities were collected on a 2D position-sensitive detector and then circularly averaged. 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 ~ 150 bar) and another at high pressures (1 ~ 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.

Result & Discussion

The temperature dependence of $I(q^*)$ and the full width at half maximum (FWHM) of the primary peak are shown in Figure 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 Figure 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. Due to 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 distinctly different from the enthalpic-driven ODT found in SI, PS-*block*-polybutadiene, and PEP-PEE. 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 [7].

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

$$dT_{(\text{LDOT or UODT})} / dP = T_{(\text{LDOT or UODT})} \frac{\Delta V}{\Delta H} \quad (1)$$

where ΔV is the volume change and ΔH is the enthalpy of the transition. Shown in Figure 4 are results from dilatometric and calorimetric experiments, where ΔV 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, 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 specific interaction, increasing pressure enhances the miscibility between PS 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 behavior.

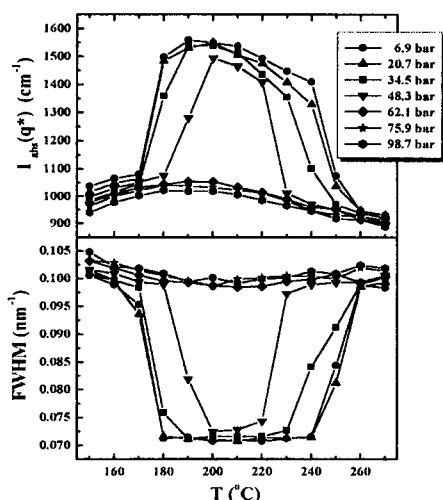


Figure 2. Temperature dependence of $I_{abs}(q^*)$ and FWHM for dPS-PnPMA-BH at various pressures. With increasing pressure, the temperature for LDOT increased but that for UODT decreased

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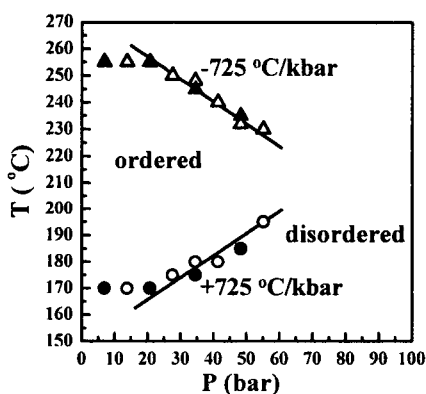


Figure 3. The changes of T_{LDOT} (circle) and T_{UODT} (triangle) for dPS-PnPMA-BH with hydrostatic pressure measured by SANS (closed symbols) and optical birefringence (open symbols).