Closed-Loop Phase Behavior and Baroplasticity of deuterated Polystyrene-*block*-Poly(n-pentyl methacrylate) Copolymer investigated by SANS and FTIR Spectroscopy

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Summary: The closed-loop phase behavior of deuterated polystyrene-*block*-poly(n-pentyl methacrylate) copolymer (dPS-PnPMA) was investigated by small-angle neutron scattering (SANS) and temperature-dependent Fourier transform infrared (FT-IR) spectroscopy. The effect of hydrostatic pressure on the transition temperatures was studied by using SANS. We found that dPS-PnPMA has large pressure coefficients of transition temperatures ($dT/dP = \pm 725\ ^\circ C/kbar$). Since this block copolymer exhibited excellent baroplastic property, it was easily molded into a desirable shape at a relatively low temperature under medium pressure. On the other hand, commercially available polystyrene-*block*-poly(ethylene-*co*-butylene)-*block*-polystyrene copolymers were not molded at the same processing condition. Finally, we investigated the driving force inducing the closed-loop phase behavior by using temperature-dependent FT-IR.

Keywords: a closed-loop phase behavior; baroplasticity; deuterated polystyrene-*block*-poly(n-pentyl methacrylate); FT-IR; neutron scattering

Introduction

Block copolymer exhibits various microdomains such as lamellae, cylinder and sphere, due to the incompatibility and connectivity of the two chains in the block copolymer. In general, upon heating, enthalpic repulsive interactions between constituent segments are weakened, resulting in a transition from a phase-separated to a phase-mixed state.[1–3] This phase transition has been referred to as the order-to-disorder transition (ODT) for block copolymers. Some block copolymers undergo a transition from the phase-mixed to phase-separated state on heating.[4–7] This is referred to as the lower disorder-to-order transition (LDOT). It is known that the difference in thermal expansion coefficients of two segments, the so-called free volume effect, increases with increasing temperature; when this effect dominates over the reduction in the enthalpic repulsive energy, LDOT occurs. Also, directional entropic loss becomes dominant with increasing temperature. Recently, we found that polystyrene-*block*-poly(n-pentyl methacrylate) copolymers (PS-PnPMA) exhibited closed-loop phase behavior composed of both LDOT and UODT occurring at a lower and a higher temperature, respectively.[8–14]

In this work, the closed-loop phase behavior of deuterated polystyrene-*block*-poly(n-pentyl methacrylate) copolymer (dPS-PnPMA) was investigated by small-angle neutron scattering (SANS) and temperature-dependent Fourier transform infrared (FT-IR) spectroscopy. The effect of hydrostatic pressure on the transition temperatures was studied by using SANS.

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We found that dPS-PnPMA has large pressure coefficients of transition temperatures (dT/dP = ±725 °C/kbar). These large coefficients imply that dPS-PnPMA exhibits excellent baroplastic property, namely, it could be easily processed at a relatively low temperature and pressure. To prove this postulation, we performed compression molding of dPS-PnPMA and commercially available polystyrene-*block*-poly(ethylene-*co*-butylene)-*block*-polystyrene copolymers. Finally, we investigated the driving force inducing the closed-loop phase behavior by using temperature-dependent FT-IR. We found that the conformation of C-C-O stretching band of the PnPMA chain changed with temperature.

Experimental

Deuterated PS-PnAMA (dPS-PnPMA) was synthesized by sequential anionic polymerization of deuterated styrene and n-alkyl methacrylate in tetrahydrofuran (THF) at −78 °C in the presence of LiCl under purified Ar using a sec-BuLi initiator.[9] LiCl (high purity, Aldrich) was dried overnight at 150 °C and then dissolved in dried THF. The THF was purified first by refluxing over CaH_2 and then by stirring over fresh sodium-benzophenone complex until it showed a deep purple color indicating an oxygen- and moisture-free solvent. Before the polymerization, deuterated styrene (99.5%, CDN isotopes) and pentyl methacrylate (high purity, Scientific Polymer Products Inc.) were first vacuum distilled from CaH_2 after degassing to remove moisture and then distilled over of dried dibutyl magnesium and trioctyl aluminum, respectively, until a persistent characteristic color was observed: yellow for dPS and yellowish green color for PnPMA. It took 1 h to synthesize deuterated styrene for full conversion. A small quantity of first polymerized solution was transferred into a tube and then terminated with purified 2-propanol to determine the molecular weight of dPS block. After pentyl methacrylate monomer was introduced very slowly into the reactor and then stirred for 5 h, the polymer solution terminated with purified 2-propanol was precipitated in methanol/water (80/20 wt/wt) mixture.

The weight and number average molecular weights (M_w and M_n) were measured by size exclusion chromatography (SEC) equipped with a multi-angle laser light scattering device. The polydispersity index (M_w/M_n) was determined by SEC. The M_w and M_w/M_n are 50,000 and 1.03, respectively. The volume fraction of the dPS block (f) in the block copolymer was 0.5, which was determined by nuclear magnetic resonance and mass densities measured at room temperature of the two components.

Samples for small angle neutron scatterings were prepared by compression molding in the homogeneous state followed by annealing under vacuum for 24 h. SANS experiments were performed at the Hanaro Reactor (Korea) with a $\lambda = 0.431$ nm and $\Delta\lambda/\lambda = 0.12$ at a sample-to-detector distance of 3 m. Scattering intensities were collected on a 2-D area detector and then circularly averaged. The sample thickness was 1 mm and the exposure time was 1 h. SANS profiles at temperatures higher than 120 °C were obtained every 10 °C during heating. Before SANS profiles were measured, the samples were equilibrated for 1 h at each temperature.

FT-IR spectra were measured at a spectral resolution of 4 cm^{-1} with a Bomem DA8 FT-IR spectrometer equipped with a liquid-nitrogen-cooled MCT detector. The Seagull attachment (Harrick Scientific Corporation), which includes a heating block attachment, was used in this study. A powder consisting of dPS-PnPMA and KBr was prepared by using a freezer mill. Before making the power, we annealed dPS-PnPMA in the disordered state for 2 days to obtain the fully disordered state. All diffuse reflectance FT-IR spectra were measured by co-adding 256 scans from 100–250 °C at an interval of 5 °C after the sample was equilibrated for 30 min at the measurement temperature.

Results and Discussion

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 at different temperatures with P = 6.9 bar.

The first order peak is sharp at temperatures between 175 °C and 255 °C and broad at all other temperatures. At the same temperature region ($175\,^\circ C < T < 255\,^\circ C$) a second and a weak third order diffraction peaks ($2q^*$ and $3q^*$) are observed as shown in the inset of Figure 1, indicating that this block copolymer exhibited the closed-loop phase behavior [10].

We previously reported that dPS-PnPMA has a very large pressure coefficient [10] ($dT_{LDOT}/dP = 725\,^\circ C/kbar$ and $dT_{UODT}/dP = -725\,^\circ C/kbar$). Therefore, even if a relatively small P (~60 bar) was applied, the lamellar microdomain was easily destroyed into disordered state, as shown in Figure 2. We further found that this transition is reversible with respect to pressure, as shown in Figures 2 and 3.

Large pressure coefficients allow one to use dPS-PnPMA as a "baroplastic" material, which can be processed at a low tem perature under medium pressure.[10,15–17] To demonstrate the processability of dPS-PnPMA at a lower temperature and pressure, we performed compression molding of this block copolymer at 90 °C and 50 bar, from which this block copolymer was indeed well-shaped into the desired form, as shown in Figure 4(a). On the other hand, even when much larger pressure of 1000 bar and higher temperature of 120 °C was employed for the compression molding of PS-*block*-poly(ethylene-*co*-butylene)-*block*-PS (Kraton G 1652: Shell Chem. Co.), the powders were clearly seen; thus we could not shape SEBS into the desired form at this processing condition(Figure 4(b)).

It is noticed that the molecular weight of Kraton G 1652 was 54,000, very close to that of dPS-PnPMA, but the glass transition of PEB block in Kraton G 1652 was −40 °C which is ~70 °C lower than that of PnPMA block.

To find the driving force for LDOT and UODT consisting of the closed-loop, we performed temperature-dependent FT-IR

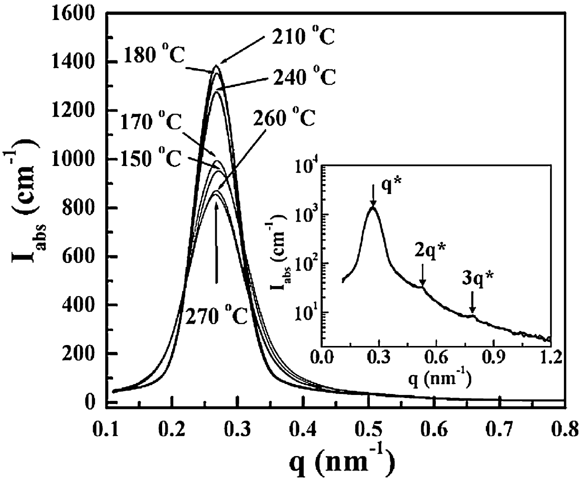

Figure 1.

Absolute SANS intensity ($I_{abs}(q)$) versus scattering vector (q) of dPS-PnPMA 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.[10]

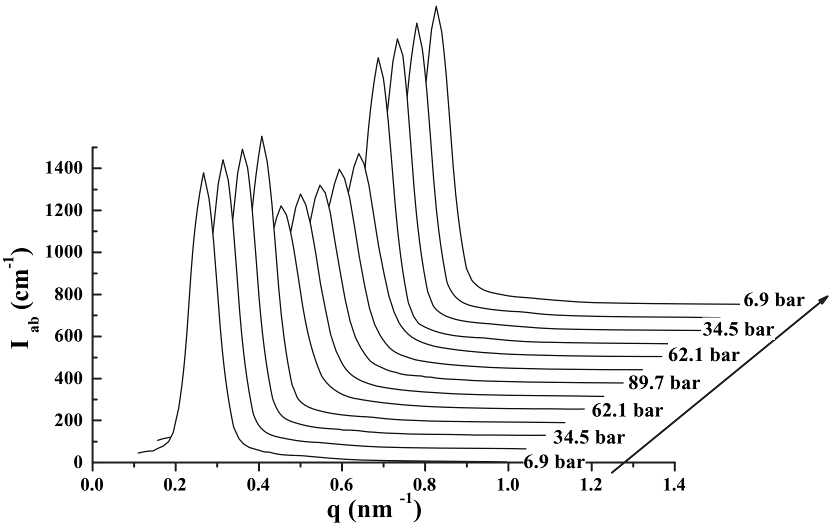

Figure 2.
SANS profiles of dPS-PnPMA at various pressures at 190 °C.

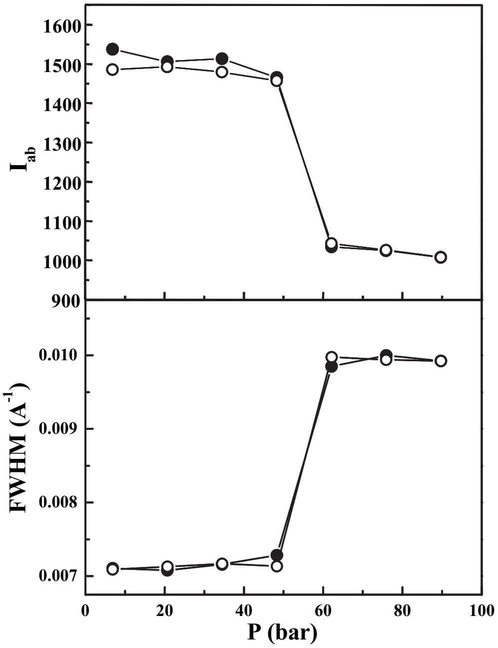

Figure 3.
Changes of (a) $I_{abs}(q^*)$ (a) and (b) full width at half-maximum at various P at 190 °C. Closed and open symbols are obtained during increasing and decreasing pressure, respectively.

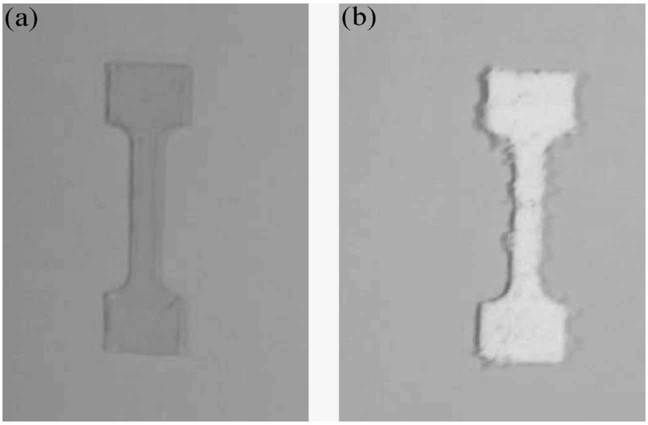

Figure 4.
Compression-molded articles prepared by (a) dPS-PnPMA at 90 °C and 50 bar, and (b) Kraton G 1652 at 120 °C and 1000 bar.

spectroscopy. Figure 5 shows the FT-IR absorption spectra of dPS-PnPMA measured during heating from 100 to 300 °C. Interestingly, the absorption (*A*) at 1238 cm^{-1} was greater than that at 1265 cm^{-1} at lower temperatures, while the former was smaller than the latter at higher temperatures, as shown in the inset. This indicates that the conformation of C-C-O group would be different in both temperature regions. Consequently, the driving forces for disordering transitions might be different in the two temperature regimes.

Figure 6 gives the 2D map[14,18,19] of d*A*/dT as a function of wavenumber and temperature (T) for dPS-PnPMA. It is seen in Figure 6 that the highest value of d*A*/dT was observed at 165 °C for all bands. Another maximum was observed at ~260 °C, though this was much smaller than that

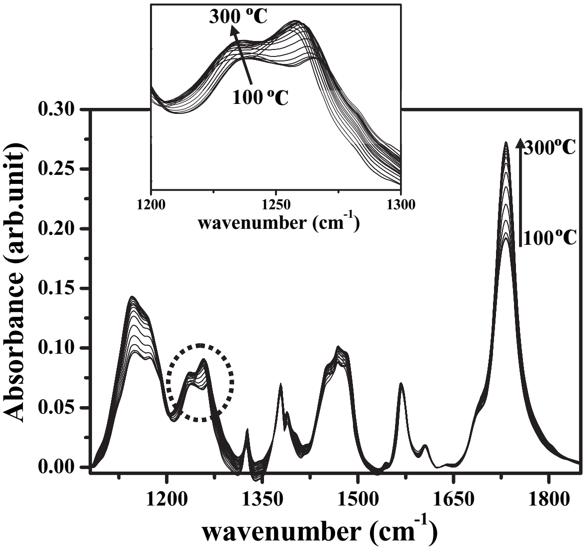

Figure 5.
FT-IR spectra of dPS-PnPMA obtained during heating. Inset is the enlarged spectra of 1200~1300 cm^{-1}.

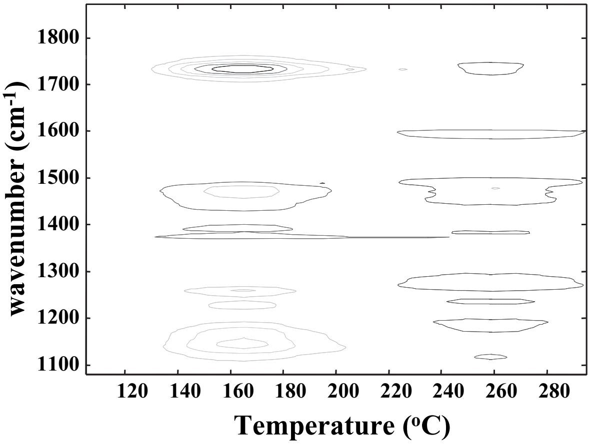

Figure 6.
The 2D map of d*A*/dT as a function of wavenumber and temperature for dPS-PnPMA.

observed at lower temperature. The small change at higher temperature is attributed to thermal fluctuations (or increased combinatorial entropy) of the whole chain. Since the infrared absorption by a bond is proportional to the square of the vibrational transition moment, increased absorption indicates an alignment of the bonds in all chains toward a specific direction. Thus, the chain conformations changed both at 165 °C and 260 °C. These two temperatures are close to those (175 and 255 °C) measured by SANS (see Figure 1), if we consider two different experimental methods as well as the fact that FTIR spectra were measured at every 5 °C. These results indicate that the transition temperatures of the block copolymers can be measured by temperature-dependent FT-IR spectroscopy.

Conclusion

We have shown that dPS-PnPMA exhibitng the closed-loop phase behavior has large pressure coefficients of transition temperatures (dT/dP = ±725 °C/kbar). dPS-PnPMA was easily processed at 90 °C and 50 bar. On the other hand, Kraton G 1652 showing poor baroplasticity could not be molded even at 120 °C and 1000 bar. This excellent baroplastic property of dPS-PnPMA resulted from entropic origin of the close-loop phase behavior. We have also found that the conformation of C-C-O stretching band of the PnPMA chain changed with temperature, suggesting that the driving forces for ordering (or disordering) transitions are different in the two temperature regimes outside the closed-loop.

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