중수소 치환한 폴리스티렌-폴리펜틸메타아크릴레이트 블록공중합체의 닫힌루프형 상거동

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Closed-loop phase behavior of deuterated polystyrene-block-poly(n-pentyl methacrylate) copolymer

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Introduction

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. (Ryu et al, 2002-2004 and Kim et al., 2004)

In this work, the closed-loop phase behavior of deuterated polystyrene-*block*-poly(n-pentyl methacrylate) (dPS-PnPMA) copolymers was investigated by small angle neutron scattering (SANS). Also, the effect of hydrostatic pressure on the transition temperatures of the block copolymer was studied by using SANS. Finally, we investigated the driving force inducing the closed-loop phase behavior for PS-PnPMA by using temperature-dependence of Fourier transform infrared (FT-IR) spectroscopy. (Kim et al, 2006) We found that the conformation of C-C-O stretching band of the PnPMA chain (and thus the directional enthalpic gain) was different in the two disordered states outside the closed-loop; therefore, the driving force to induce the disordered state at lower temperatures was different from that at higher

temperatures.

Experimentals

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. The weight and number average molecular weights (Mw and Mn) were measured by size exclusion chromatography (SEC) equipped with a multi-angle laser light scattering device. The polydispersity index (Mw/Mn) was determined by SEC. The Mw and Mw/Mn 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 λ = 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 °C < T < 255 °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

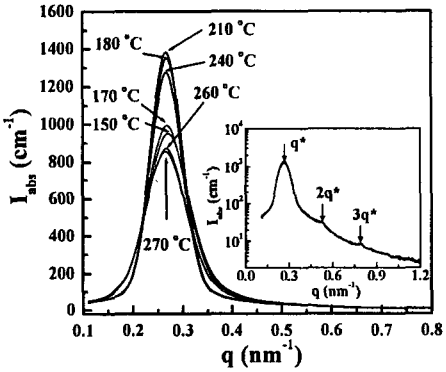

Figure 1. Absolute SANS intensity ($I_{abs}(q)$) versus scattering vector (q) of dPS-PnPMA at various temperatures at 6.9 bar. This block copolymer has a closed-loop phase behavior with LDOT at ~175 °C and UODT at ~255 °C. The inset gives SANS profiles at 180, 210 and 240 °C in the ordered state where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

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