Materials Science

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Analysis of Peculiar Electron Density Profile of Weakly Segregated Block Copolymer Polystyrene-*block*-poly(n-butyl acrylate)

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Introduction

Phase behavior of polystyrene (PS)-*block*-poly(alkyl methacrylate) (PAMA) has been investigated by small-angle X-ray scattering (SAXS) and small angle neutron scattering (SANS). Molecular weight and pressure dependence of the phase behavior revealed unique feature of PS-*block*-PAMA block copolymers. Among them, PS-*block*-poly(*n*-butyl methacrylate) (PnBMA) as a weakly segregated pair was reported to show an interesting phase behavior that a lower critical disorder-order transition and an upper critical order-disorder transition appear.[1] Recently, Kim et al. discovered that PS-*block*-poly(n-pentyl methacrylate) showed a closed-loop phase behavior.[2] Solubility parameter of poly(alkyl acrylate) (PAA) exhibits similar tendency of PAMA depending on the length alkyl side-chain. According to the solubility parameter, poly(*n*-butyl acrylate) (PnBA) or poly(*n*-pentyl acrylate) is expected to be weakly segregated with PS. An external field such as pressure and temperature is expected to cause a drastic change in phase-behavior of PS-*block*-PAA because the glass transition temperature of PAA is considerably lower than PAMA.

Result and Discussion

Figure 1 shows temperature dependent SAXS and SANS profiles PS-*block*-dPnBA with a molecular weight of 30k. Around at room temperature, the primary scattering peak disappeared but the second peak was still observed, suggesting an ordered state. Two different glass transition temperatures was detected by a temperature modulated DSC measurement of this specimen. On the other hand, a low molecular weight (11k) of PS-*blcok*-PnBA was in disordered state at room temperature, which was revealed by SAXS and DSC. SANS measurement also revealed the ordered state of PS-*block*-dPnBA (30k). In the SAXS measurement, it was hard to detect the scattering from this block copolymer without using synchrotron radiation. In fact, the electron density difference between PS and PnBA was quite small. In contrast, the neutron scattering length density between two phases was sufficient to observe the neutron scattering from the phase separated structure. The SAXS profiles around at 30 °C in Figure 1 indicated the intensity of the first order reflection from the microphase separated structure was considerably small. The peculiar SAXS profile can be explained as assuming “three-layer model” that the electron density of center layer is largest/smallest, that is, the electron deinsty of the interface is the largest/smallest, which may be ridiculous for diblock copolymers. The mass density of the disordered PS-*block*-PnBA was larger than each homopolymer where a volume contraction occurred by mixing. The electron density difference between PS and PnBA is originally so small that the change in electron density by the volume contraction becomes relatively prominent. In this condition, the SAXS intensities were reproducible by calculation as shown in Figure 2.

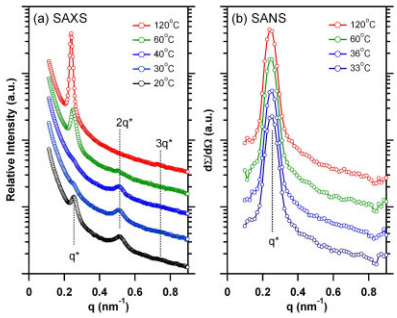

Figure 1. SAXS and SANS profiles of PS-*block*-dPnBA with a molecular weight of 30k.

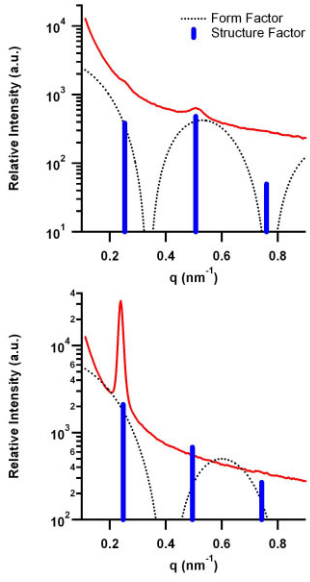

Figure 2. Calculated SAXS intensity, blue sticks and dotted lines represent intensity of structure factor and form factor.

References

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