UODT Phase Behavior of Weakly Segregated Block Copolymer Polystyrene-*block*-poly(iso-butyl acrylate)

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Introduction

Phase behavior of polystyrene (PS)-block-poly(alkyl methacrylate) (PAMA) has been investigated by smallangle 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, PSblock-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(npentyl 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(npentyl 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

We investigated an upper critical order-disorder phase transition (UODT) for polystyrene (PS)-b-poly(iso-butyl acrylate) (PiBA) be means of SAXS and POM. Figure 1 shows temperature dependent SAXS profiles PS-block-PiBA with a molecular weight of 24.3k. The square of line width of the first peak was plotted against the observation temperature. As temperature exceeded 184 °C, the width abruptly increased. This phenomenon arises from the order-disorder transition (ODT) of this sample. We obtained the ODT temperature (T_{ODT}) for various samples of PS-b-PiBA. Matsen calculated the phase diagram of block copolymer using self-consistent field theory.³ Using the phase diagram, if the ODT and the total degree of polymerization N (related to the molecular weight) is given, the temperature dependence of the Flory-Huggins interaction parameter χ (=*A*+*B*/*T*) can be found. The ODT obtained from SAXS measurement for our samples was almost the same value obtained using POM. Temperature dependence of χ is obtained as follow:

$\chi = A + B / T = 0.0519 + 1.27 / T$

The value of B in of PS-b-PiBA was relatively small to other block copolymers. When volume fraction was 0.5, the border line of molecular weight whether, or not, the

sample is ordered state was found to be around 30k at room temperature. The various phase behaviors of PS-*b*-PiBA and PS-*b*-PnBA series were obtained in narrow range (20k - 40k) of molecular weight, e.g. fully ordered state without UODT but LDOT-like (lower critical order-disorder transition), having UODT and, fully disordered.



Figure 1. SAXS profiles of PS-*block*-PiBA with a molecular weight M_p of 24.3k (M_p/M_p 1.12), ϕ_{ps} =32%.



Figure 2. Line width vs observation temperature obtained from SAXS profile.

References

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