Neutron Scattering Study on Miscibility of Statistical Copolymer / Homopolymer Blends

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We have recently found that 4-substituted polystyrene derivatives and polyisoprene (I) are weakly interacted and likely to be miscible with each other. Among the various combinations, poly(4-tert-butylstyrene) (B) and I exhibit a lower critical solution temperature (LCST) type phase diagram, while poly(4-tert-butoxystyrene) (O)/I blend shows an upper critical solution temperature (UCST) type one. Hence, competition between two interactions having opposite temperature dependence is expected when a copolymer consists of B and O is blended with I. The objective of this study is to investigate the phase behavior of statistical copolymers composed of B and O, abbreviated as s-BO, with I by optical microscopic (OM) observation and small-angle neutron scattering (SANS) measurements. Several blends of s-BOs having mol fraction of B, mB, comparable to 0.50, with I showed both UCST and LCST type phase diagram. Furthermore, UCST type phase behavior was observed for blends having small mB, while LCST type one was for that of large mB at all employed temperatures. These results imply that the attractive interaction of B/I leads to miscibility and that the repulsive interaction of O/I induces immiscibility of the blends within the temperature range studied. Hence, the phase behavior of s-BO/I blend can be understood as a result of the competition of two interactions having opposite temperature dependence.

To elucidate the interaction between blend components indirectly from SANS data, the structure factors at q=0, S(0)s, which correspond to the thermodynamic susceptibility were determined by using the Ornstein-Zernike equation. S(0)s were obtained from the fittings of inverse S(q) vs. q^2 data to Ornstein-Zernike equation. Figure 1 gives the relation between inverse S(0) and inverse temperature, for s-BO/d-I blends together with those for O/d-I and B/d-I blends for comparison. The inverse S(0) for O/d-I blend in Figure 1(a) decreased with a decrease in inverse T, whereas that for B/d-I blends increased with inverse T as shown in Figure 1(e). This shows that the interaction of O/d-I becomes less repulsive as temperature becomes higher and vice versa for the interaction of B/d-I. Hence, these results indicate that O/d-I blend shows an UCST and B/d-I blend has a LCST type phase behavior.

Figure 1(b) for s-BO35/d-I blend showed qualitatively the same trend as that O/d-I, however, the temperature dependence of the inverse S(0) for s-BO/d-I blends changed dramatically when mB reaches to 0.49 as shown in Figure 1(c). Namely, the inverse S(0) first increased, but went through a maximum at 170 °C and then turned to decrease. This implies that s-BO49/d-I blend shows both UCST and LCST type phase behavior. Furthermore, as mB goes up more, opposite temperature dependence was observed as shown in Figure 1(d) for s-BO66/d-I blends. The inverse S(0) increased with decreasing inverse T, indicating LCST behavior which is similar to B/d-I blend. These results revealed by SANS experiments for s-BO/d-I blends are in good accordance with OM observation. Thus, we were able to display that the phase behavior of s-BO/d-I blends change from UCST to LCST type one with an increase in mB due to the competition of B/I and O/I opposite interactions and show both UCST and LCST type phase behavior at balanced condition.

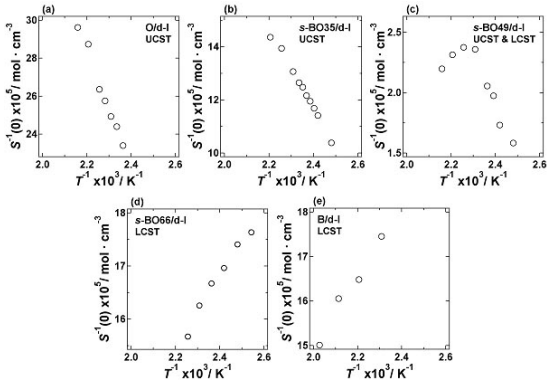

Fig. 1. Temperature dependence of the inverse S(0) of (a) O/d-I, (b) s-BO35/d-I, (c) s-BO49/d-I, (d) s-BO66/d-I and (e) B/d-I blends.