

Miscibility evaluation of blends of poly(4-alkylstyrene) with moderately branched side groups and polyisoprene by small-angle neutron scattering

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Blends of polyisoprene (PI) and poly(4-alkylstyrene) (P(alkylS)), where the latter has various alkyl groups on 4th-position in polystyrene (PS), exhibit miscibility depending on their observation temperature [1,2]. Particularly, poly(4-*tert*-butyl styrene) (PtBS) with highly-branched alkyl groups shows a lower critical solution temperature (LCST) type phase behavior with PI [1], whereas a series of poly(4-*n*-alkyl styrene)s (P(*n*-alkylS)) connected by linear alkyl groups exhibit upper critical solution temperature (UCST) type one [2]. Thus, it is important to understand the P(alkylS) chemical structure effect on their temperature dependent phase behavior with PI, as well as their miscibility mechanism.

In our previous beamtime in FY2022 (Proposal No. 22577), we confirmed from small-angle neutron scattering (SANS) measurements that blends of PI and poly(4-*iso*-butyl styrene) (PiBS) exhibit LCST-type phase behavior with much lower interaction parameter χ than PtBS/PI blends. In this beamtime, the miscibility of poly(4-*iso*-propyl styrene) (PiPS) and PI was evaluated by SANS as further study of P(alkylS).

Hydrogenated (*h*-) PiPS ($M_w = 178$ kg/mol, $M_w/M_n = 1.02$) was anionically synthesized. Deuterated (*d*-) PI ($M_w = 18.0$ kg/mol, $M_w/M_n = 1.03$) was purchased from Polymer Source. Samples for SANS measurements were prepared in the same way as previously. That is, *h*-PiPS and *d*-PI were mixed at a given volume fraction Φ_{d-PI} (= 0.4, 0.5 and 0.6) and dissolved in benzene. After solvent-casting, film samples were filled in an assembly cell at the SANS-U beamline with a homemade Teflon spacer under an argon gas atmosphere.

SANS measurements were performed at the SANS-U beamline at JRR-3 with a beam wavelength of 7 Å, sample-to-detector length of 8 and 1 m, and a sample changer in the temperature T range of 20~80 °C, from lower T at 10 °C intervals. All samples were measured after at least one hour of thermal equilibration at each temperature.

Figure 1 shows SANS profiles of *h*-PiPS/*d*-PI blend with $\Phi_{d-PI} = 0.4$ at different T . A typical UCST-type scattering behavior was observed, where the scattering intensity $I(q)$ at low- q side decreased with increasing T . The χ parameters were estimated through RPA analysis [3] from Zimm plots and whole $I(q)$ spectrum in Figure 1.

Figure 2 shows the $1/T$ -dependence of χ for PtBS/PI [1], *h*-PiBS/*d*-PI and *h*-PiPS/*d*-PI. From Figure 2, *h*-PiPS/*d*-PI in this study exhibits similar χ values to those of PtBS/PI [1], although their T -dependence is opposite. Thus, Thus, it was experimentally confirmed for the first time that small differences in the side-chain branching structure of P(alkylS) have a significant effect on the miscibility with PI.

- [1] K. Yurekli, et al., *J. Polym. Sci.: Part B* **42**, 3204 (2004).
- [2] S. Matsushima, et al., *J. Polym. Sci.: Part B* **55**, 1791 (2017).
- [3] P. G. de Gennes, *Scaling Concept in Polymer Physics*, Cornell Univ. Press (1979).

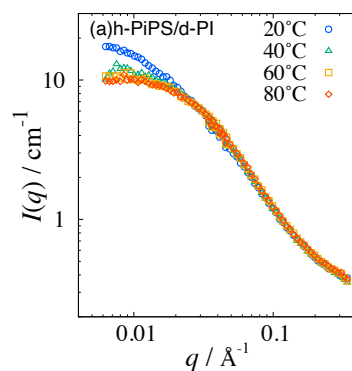


Fig. 1. SANS profiles of *h*-PiPS/*d*-PI at $\Phi_{d-PI} = 0.4$ measured at different T .

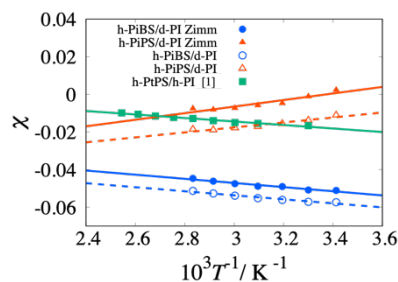


Fig. 2. $1/T$ -dependence of χ for PtBS/PI, *h*-PiBS/*d*-PI and *h*-PiPS/*d*-PI blends.