

# Miscibility evaluation of poly(alkyl styrene)s and polyisoprene and investigation of their miscibility mechanism

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Blends of polyisoprene (PI) and poly(4-alkylstyrene) (P(alkylS)), where the latter has various alkyl groups on 4<sup>th</sup>-position in polystyrene (PS), exhibit miscibility depending on their observation temperature [1,2]. In particular, 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)) linked 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 this study, the miscibility between poly(4-*iso*-butyl styrene) (PiBS), which possesses a moderately branched alkyl groups at 4<sup>th</sup>-position in PS, and PI was evaluated by small-angle neutron scattering (SANS) measurements.

Hydrogenated (*h*-) PiBS ( $M_w = 133$  kg/mol,  $M_w/M_n = 1.01$ ) was anionically synthesized. Deuterated (*d*-) PI ( $M_w = 18.0$  kg/mol,  $M_w/M_n = 1.03$ ) was purchased from Polymer Source. *h*-PiBS and *d*-PI were mixed at a given volume fraction  $\Phi_{d-PI}$  ( $= 0.4, 0.5$  and  $0.6$ ) and dissolved in benzene. After solvent casting, the film samples were filled in an assembly cell at the SANS-U beamline with a homemade Teflon spacer (which served to reduce the required sample volume) under an argon gas atmosphere. Preliminary experiments using an optical microscope in the lab confirmed that PiBS/PI blends exhibit an apparent LCST phase behavior.

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*-PiBS/*d*-PI blend with  $\Phi_{d-PI} = 0.5$  at different  $T$ . An increase in  $I(q)$  at low  $q$  is seen with increasing  $T$ , indicating LCST-type phase behavior.

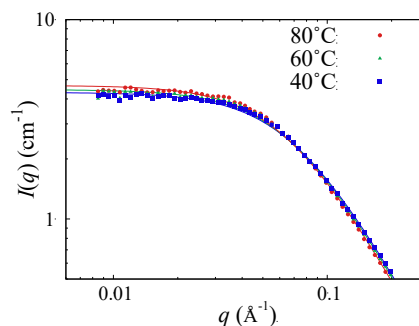
Figure 2 shows a Zimm plot (i.e.,  $1/I(q)$  vs  $q^2$  at low  $q$ ) of *h*-PiBS/*d*-PI blend at  $\Phi_{d-PI} = 0.5$ . From this plot,  $I(0)$  is estimated, and analyzed by random phase approximation (RPA) to determine the Flory-Huggins interaction parameter  $\chi$  is negative on the order of  $10^{-2}$  within the range of observations, which is comparable to that of PtBS/PI blends [1].

Using the  $\chi$  values obtained for each  $T$  and each  $\Phi_{d-PI}$ , we performed RPA analyses of the  $I(q)$  data for the entire  $q$  range, where the results are shown as curves in Figure 1. The RPA analysis results were in good agreement with the experimental data, confirming the reliability of the experimental data and the analysis.

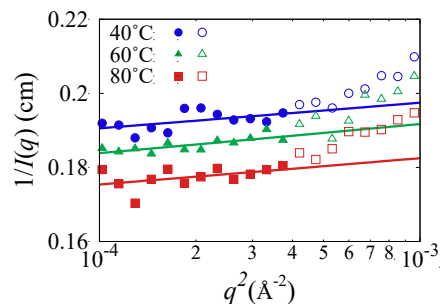
[1] K. Yurekli, et al., *J. Polym. Sci.: Part B* **42**, 3204 (2004).

[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*-PiBS/*d*-PI blend with  $\Phi_{d-PI} = 0.5$  measured at different temperatures. Symbols represent the experimental data, while the curves indicate the RPA prediction.



**Fig. 2.** Zimm plot of *h*-PiBS/*d*-PI blend with  $\Phi_{d-PI} = 0.5$  measured at different temperatures.