

SANS Study of Ring Topology Effects on the Miscibility of Polymer Blends

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S1. Preparation of ring *h*-R-PT and *d*-R-PI samples.

Ring *h*-R-PT and *d*-R-PI samples utilized in this study were prepared in the same manner as reported previously.¹⁻² Here, the results of preparation of *h*-R-PT-42 ($M_w = 41.7$ kg/mol, $M_w/M_n = 1.07$, purity $\sim 99\%$) are shown while displaying the SEC and IC profiles in the process of preparation.

Figure S1a shows a SEC profile of telechelic *h*-L-PT-42 ($M_w = 42.0$ kg/mol, $M_w/M_n = 1.06$). This L-PT was cyclized in dilute THF solution (ca. 0.1%), and the cyclization product was obtained as shown in Figure S1b. This product includes ca. 40% of ring R-PT eluted at 20-22 min, which eluted slower than L-RT, together with various kinds of polycondensation products at 14-20 min. To isolate the R-PT, the preparative SEC and IC fractionations were successively conducted. Figure S1c shows the SEC profile of the final product obtained after fractionations. A unimodal main peak eluted at 19.5-22.5 min as well as a small peak shoulder at 18-19.5 min is observed in SEC. Here, the peak shoulder corresponds to the dimeric ring R-PT.

To confirm that the linear chains were successfully excluded from the final product, R-PT, IC measurements were conducted, and the result is shown in Figure S2. For R-PT in Figure S2b, the main peak was eluted at 9.5-15 min, and any other signals were not detected at the time range of 7.5-10.5 min where L-PT eluted in Figure S2a. Thus, we confirmed that no linear contaminations remain in the R-PT. This purified ring sample was utilized for SANS and OM measurements.

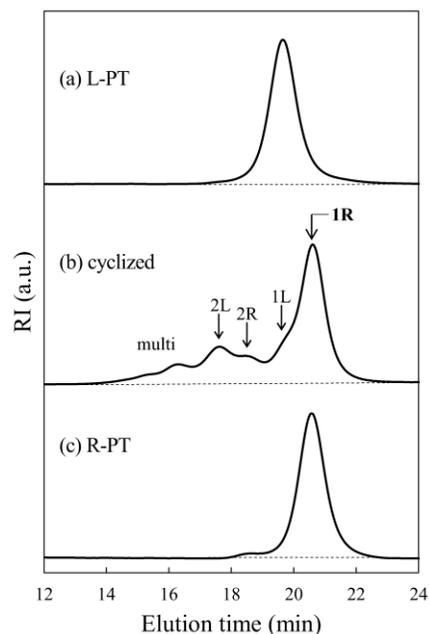


Figure S1. SEC profiles of (a) *h*-L-PT-42, (b) cyclization product of *h*-L-PT-42 and (c) *h*-R-PT-42 (i.e., the product after SEC and IC fractionations).

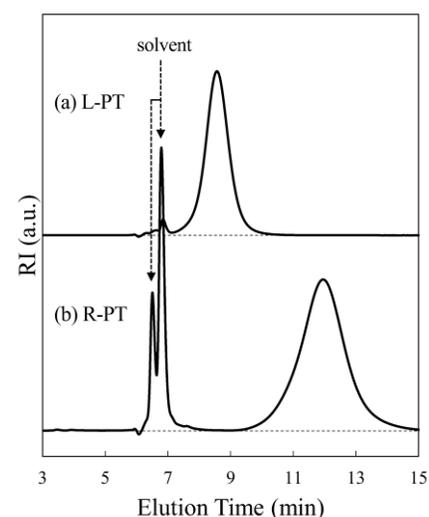


Figure S2. IC profiles of (a) *h*-L-PT-42 and (b) *h*-R-PT-42. The peaks eluted at 6-7.5 min indicate the solvent.

Following the same procedure, *d*-R-PI-28 ($M_w = 27.8$ kg/mol, $M_w/M_n = 1.07$, purity ~99%) was also successfully prepared (see Table 1 in the main text), and was utilized for SANS measurements.

S2. Determination of incoherent scattering intensity.

As described in Experimental of the main text, the treatment of a background signal (i.e., incoherent scattering) is a delicate issue for SANS data reduction. Here, we assumed that the incoherent scattering intensity I_{incoh} is a q -independent constant, and determined by using raw data of the *h*-L-PT/*d*-L-PI (L/L) blend sample as follows. In bulk, linear polymer chains are known to follow the Gaussian statistics conformation due to the screening of the excluded-volume effect, and their SANS intensity obeys the q^{-2} power law dependence at high q regime.³ Figure S3 shows the SANS profiles of the L-L blend at 170 °C before and after subtracting an assumed I_{incoh} in (a) a double-logarithmic $I(q)$ vs q and (b) Kratky plot ($I(q) \cdot q^2$ vs q). In Figure S3b, we found that the intensity before subtracting I_{incoh} (i.e., $I(q)_{\text{all}}$) at high- q (≥ 0.05 Å⁻¹) keeps increasing. We carefully determined the I_{incoh} value as 0.20 cm⁻¹, and the intensity after subtracting I_{incoh} , i.e., $I(q)$ ($= I(q)_{\text{all}} - I_{\text{incoh}}$), is also shown in Figure S3. As shown in Figure S3b, $I(q)$ data clearly exhibit a plateau of the Kratky plot at high- q (≥ 0.05 Å⁻¹). This result corresponds to the q^{-2} dependence of $I(q)$. We confirmed that $I(q)$ curves at all temperatures of SANS measurements (130-180 °C) show $I(q) \sim q^{-2}$ at high- q regime by setting $I_{\text{incoh}} = 0.20$ cm⁻¹ (cf. Figure 1a in the main text).

To confirm the validity of this I_{incoh} assumption, we also estimated I_{incoh} by the other method reported by Shibayama et al.⁴ Although we do not describe the details of the estimation, by using the sample thickness (= 1.5 mm) and the volume fraction of hydrogenous polymer (= 0.5), we estimated I_{incoh} as 0.21 cm⁻¹. This value

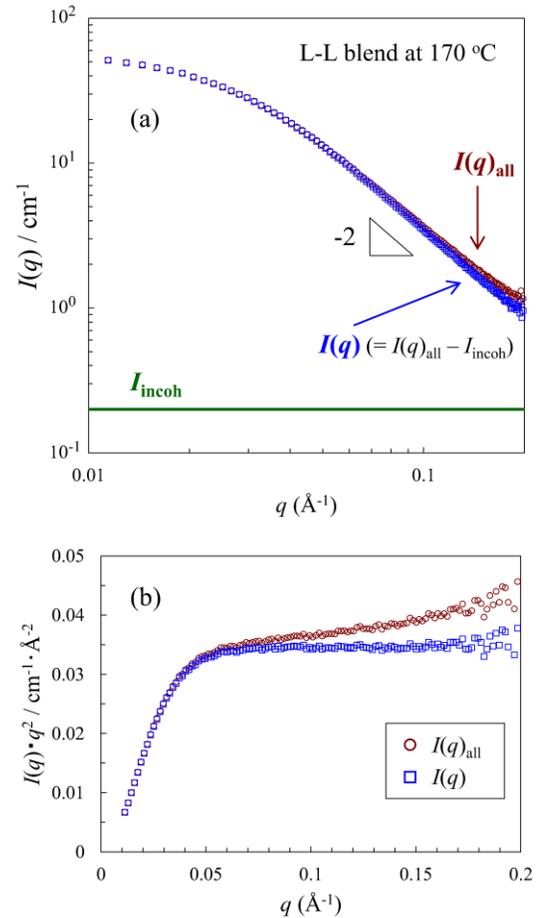


Figure S3. (a) Double-logarithmic plots of the SANS profiles ($I(q)$ vs q) for L-L blend at 170 °C before and after subtracting the incoherent scattering intensity I_{incoh} ($= 0.20$ cm⁻¹). (b) Kratky plots ($I(q) \cdot q^2$ vs q) before and after subtracting I_{incoh} .

is in good agreement with that determined by using the raw scattering data of L-L at high q ($= 0.20 \text{ cm}^{-1}$) within an error of 5%. Thus, we can safely say that our treatment of the incoherent scattering intensities is adequate.

In this study, the same I_{incoh} value ($= 0.20 \text{ cm}^{-1}$) is adopted for the other blends, i.e., R-L and R-R, since all three blends utilized for SANS measurements in this study possess the same hydrated/deuterated compound ratio (i.e., the amount of hydrogen is equivalent in three blends). The scattering behavior of the blends at high- q range, which mainly reflects the local chain conformation of the component chains, is discussed in the main text. Although I_{incoh} does not much influence the scattering behavior at low- q where the intermolecular interactions affect more dominantly, it is still important to estimate the accurate I_{incoh} value of the blends in order to discuss more correctly.

S3. SANS profiles

Figure S4 shows the SANS profiles of three blends, L-L, R-L and R-R, as normal plots of $I(q)$ vs q .

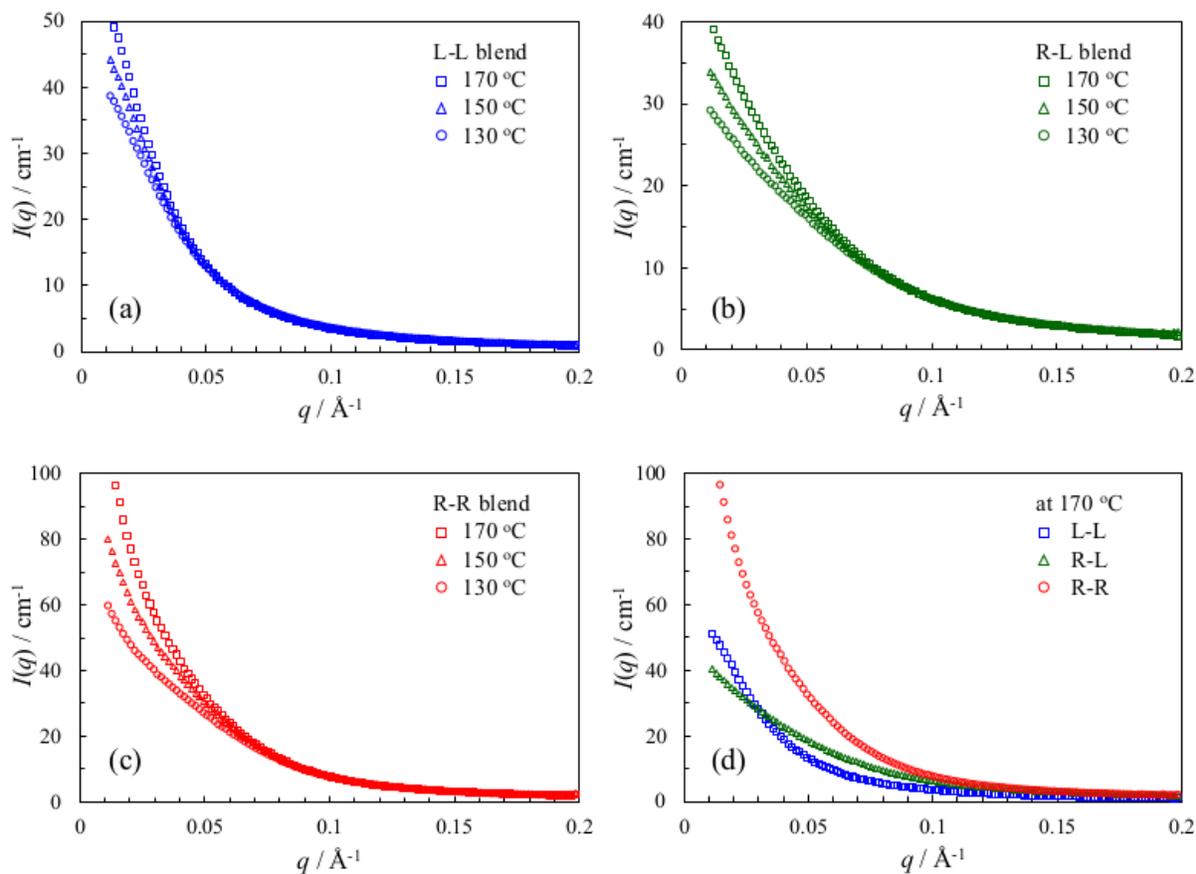


Figure S4. SANS profiles $I(q)$ vs q for (a) L-L, (b) R-L and (c) R-R blends at various temperatures. (d) Comparison of the SANS profiles for L-L, R-L and R-R blends at 170 °C.

References:

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