

Supporting Information

Microstructure separation/crosslinking competition-based ternary microstructures evolution of poly(ether-*b*-amide)

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Table S1 Thermal properties of the P35D films quenched from different T_{iso} by liquid nitrogen after the 2 hours isothermal treatments.

T_{iso} (°C)	$T_{\text{m,HS}}^a$ (°C)	$\Delta H_{\text{m,HS}}^a$ (J g ⁻¹)	X_c^b
Untreated	141.4	5.91	0.08
180	145.1	5.74	0.08
230	145.1	4.48	0.06
270	145.2	4.35	0.06

a. The melting temperature and the corresponding enthalpy for PA12 hard segments ($T_{\text{m,HS}}$ and $\Delta H_{\text{m,HS}}$) were determined by DSC heating traces from 35 to 200 °C with a rate of 10 °C min⁻¹.

b. The crystallinity of PA12 segment (X_c) was calculated by the normalized ΔH_m with the fraction of PA12 dividing by the fusion enthalpy of perfect PA12 crystals (246 J g⁻¹).

Table S2 Intrinsic viscosity ($[\eta]$) obtained from the dilute m-Cresol solutions of the P35D samples after the 2 hours isothermal treatments at various T_{iso} .

T_{iso} (°C)	$[\eta]^a$ (dL g ⁻¹)
Untreated	2.60
180	2.70
230	2.96
270	3.34

a. $[\eta]$ was determined by the specific viscosity measured by using a Ubbelohde viscometer at 30 °C divided by the solution concentration of 2 mg mL⁻¹.

From Table S2, the obtained $[\eta]$ increases with the T_{iso} , indicating that the viscosity-average molecular weight of P35D becomes higher due to the branched chains.

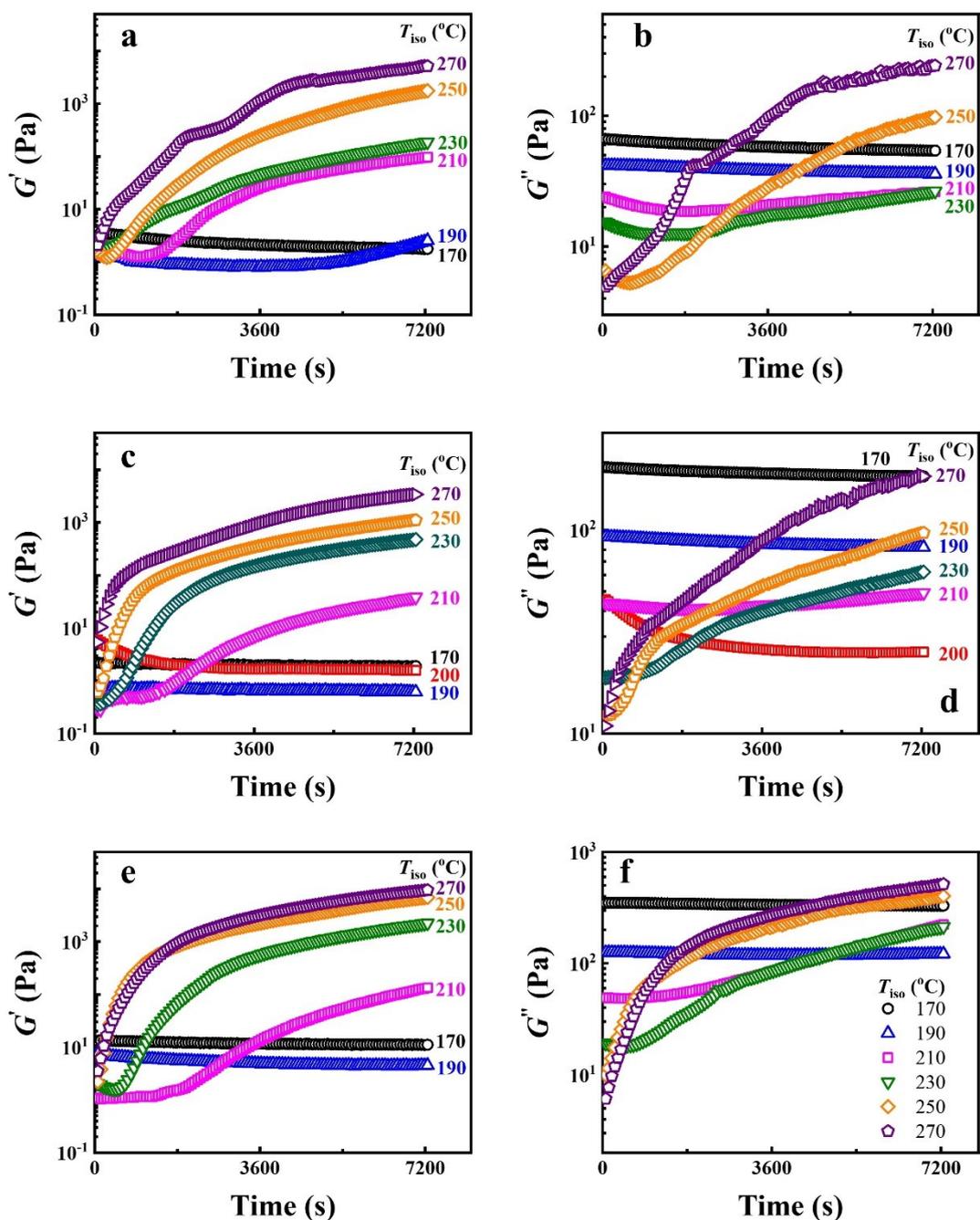


Fig. S1 Time dependence of G' and G'' obtained from (a)(b) P25D, (c)(d) P35D, and (e)(f) P40D melts at different T_{iso} with the applied ω of 0.1 rad s^{-1} . Each sample was only heated once.

Based on Fig. S1, only the P25D melt, which contains the lowest fraction of PA ($W_{PA}=0.27$), shows a G' upturn behavior at $190 \text{ }^\circ\text{C}$, whereas that didn't be seen in P35D and P40D. In other words, the crosslinking network is easier to be formed in P25D.

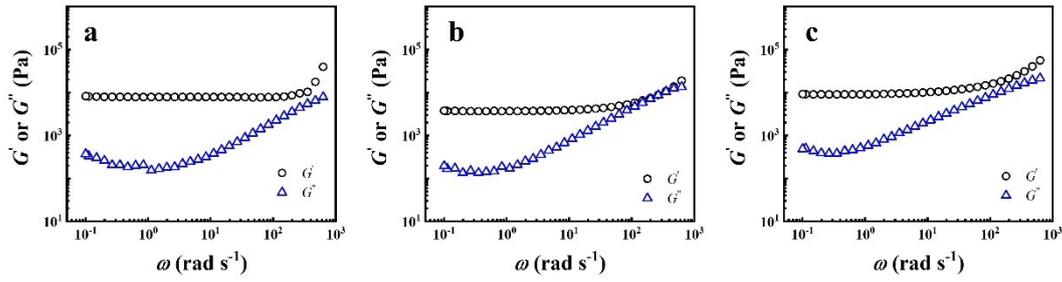


Fig. S2 Dynamic moduli of G' and G'' as a function of ω obtained from (a) P25D, (b) P35D, and (c) P40D melts after the 2 hours isothermal process at 270 °C.

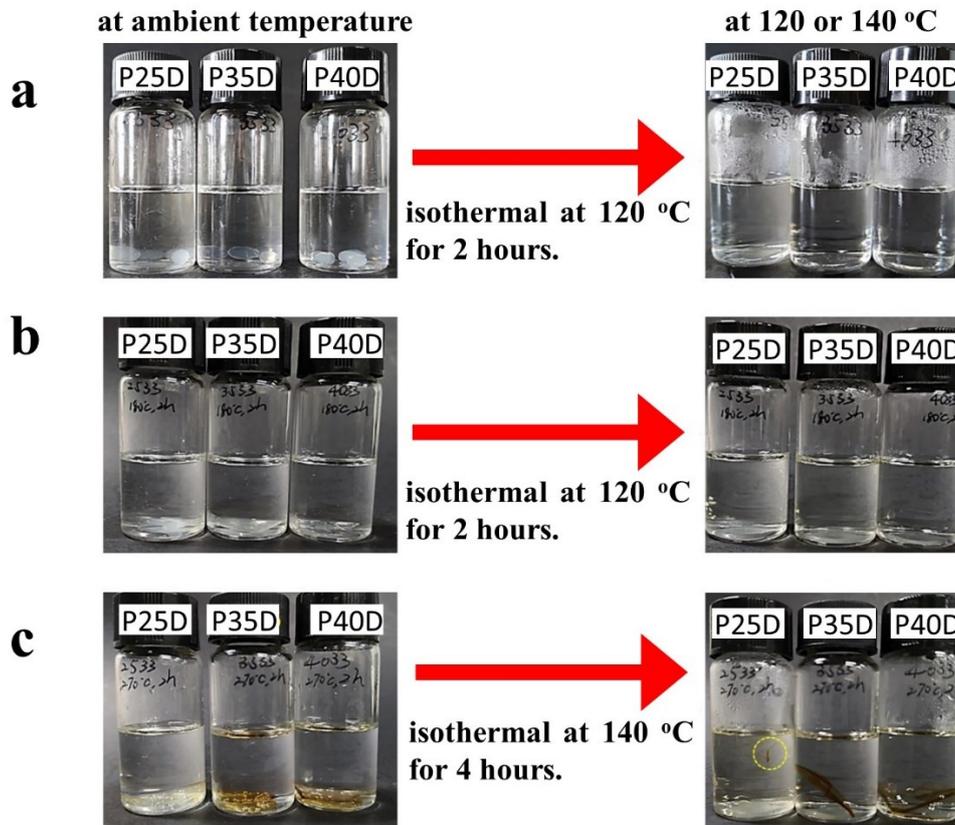


Fig. S3 Appearance photographs of 2 wt% DMF solutions of (a) the raw pellets without any thermal treatment, and that of the films obtained from (b) 180 °C, (c) 270 °C after the 2 hours isothermal at each temperature. For the films treated at 270 °C (see (c)), some swollen and insoluble-matters were observed in the solutions after heating to 140 °C and kept for 4 hours, while the others are apparently dissolved. The films were prepared by melt-pressed under 180 °C and 50 MPa for 3 min, then quickly cooled to room temperature by cold compression for 3 min.

From Fig. S3(a), all the P25D, P35D and P40D raw pellets dissolve in DMF at 120 °C, implying there is apparently physical, not chemical network exist. The same results can be seen in the films quenched from 180 °C (Fig. S3(b)), it is consistent with the rheological results that no G' upturn is observed within the 2 hours isothermal at 180 °C. For instance, P35D is confirmed to be homogenous state at 180 °C from the rheological results, no chemical crosslinking network is detected. It is supposed that the rate of polyamide crosslinking reaction is so slow that the crosslinking reaction can be ignored during the isothermal process of the melt-pressed films at temperatures below 180 °C for the three studied elastomers. However, the content of chemical crosslinking network is high enough that it cannot be ignored after the 2 hours isothermal at 270 °C according to the rheological results (Fig. S2), thus the apparent swollen and insoluble-matters can be seen by the naked eyes. Although the isothermal processes were performed in a vacuum chamber, the oxygen degradation may have slightly occurred for the samples used to the swelling test because their appearance is light yellow. But the measured $[\eta]$ increased with T_{iso} (Table S2), implying the apparent molecular weight getting larger at higher T_{iso} , the thermal degradation may be not severe.

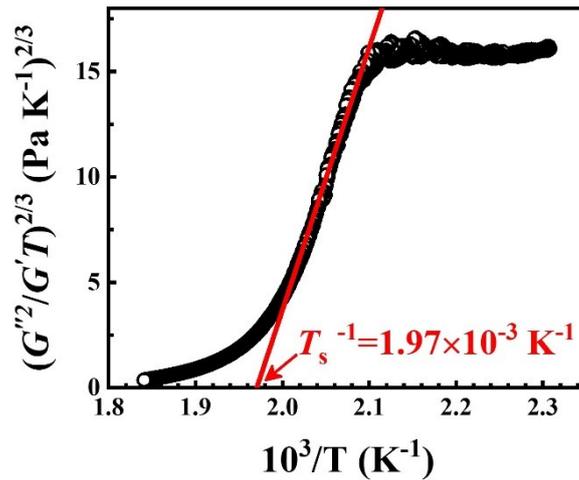


Fig. S4 Plot of $(G''/G'T)^{2/3}$ versus the reciprocal of temperature ($1/T$) at a given heating-rate of 0.5 °C min obtained from P35D melt, the T_s is determined from the extrapolation of the linear regression on the x-axis to be ca. 234.5 °C. The applied ω is 0.5 rad s⁻¹.

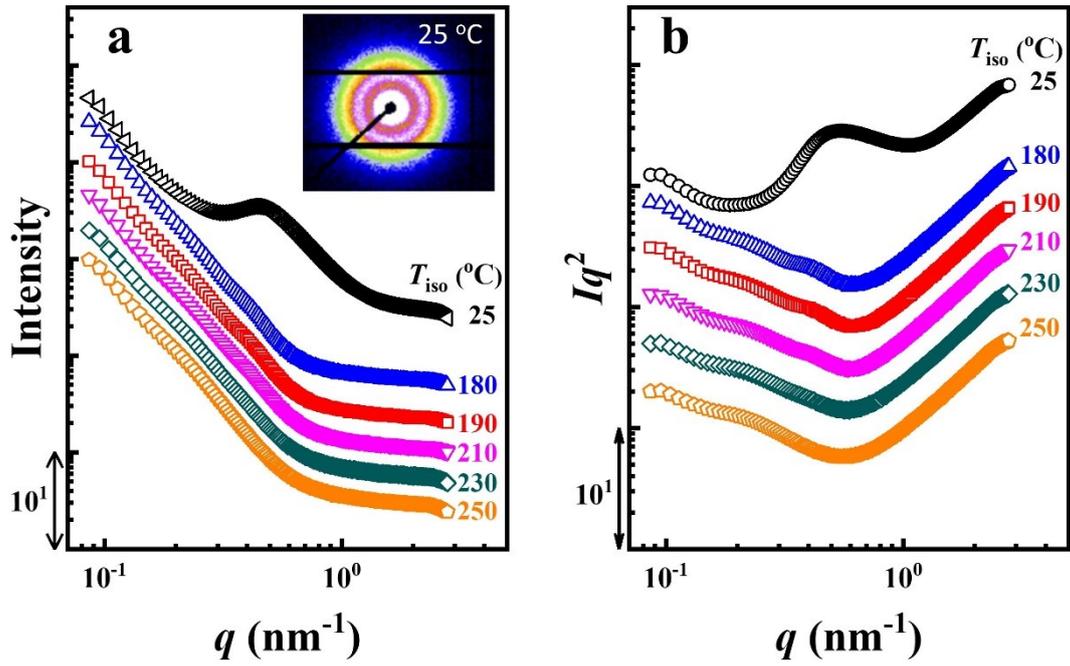


Fig. S5 (a) 1-D integrated and (b) Lorentz-corrected SAXS curves of the melt-pressed P35D film at different T_{iso} . The insert pattern was obtained at 25 °C. Each scattering plot is vertically shifted to avoid overlapping of them. The SAXS experiment was carried out at the BL16B1 beamline of SSRF with the wavelength of the radiation source of 1.24 Å, operated in transmission mode. By using a Linkam TST350 hot stage, the P35D film was step-wised heated from 25 to 250 °C at a rate of 20 °C min⁻¹. After isothermal at 180, 190, 210, 230 and 250 °C for 3 min to reach thermal equilibrium, respectively, the SAXS patterns were collected by accumulating 15 s. All the SAXS patterns were corrected for detector noise, air scattering, and sample absorption.

In Fig. S5, the peak signal is only seen clearly at 25 °C, which is contributed by the long period of PA12 crystal. When temperature above $T_{\text{m,HS}}$, such like 180 °C, there is no evident peak signal, which may be caused by two possible reasons. The first one is the poor contrast of electron cloud density (ρ_c) between the PA12 HS and PTMO SS, the ρ_c of PA12 HS and PTMO SS are estimated by $\rho_c = Z\rho N_A/M_0$ to be $3.17 \times 10^{23} \text{ cm}^{-3}$ and

$3.15 \times 10^{23} \text{ cm}^{-3}$, respectively, where Z is the number of electrons of the repeating unit, ρ is the polymer density, N_A is the Avogadro constant, and M_o is the molecular weight of the repeating unit. The two estimated ρ_c are very close to each other, it is possible that no peak signal is observed even the long-range ordered structure exists. The other possible reason is that the long-range ordered structure is inhibited by the chemical crosslinking structure, i.e., the segment/chain motion is restricted by the chemical crosslinking network. In our TEM observations of P35D film quenched from different temperatures after the 2 hours isothermal treatment (Fig. S6), the apparent homogenous morphology is observed at 170 and 190 °C, which is in good agreement with our rheological results that P35D melt is the homogenous state when temperature is below T_b^o . However, no evident long-range ordered structure was observed even when T_{iso} higher than T_b^o . Although somewhat structure with an obscure circle boundary seems to be seen in Fig. S6e and S6f, it is still unable to detect the typical microphase-separated morphologies, i.e., the cylinder, lamellar, gyroid, hexagonal and cubic structures obtained from di- or tri-block copolymer systems,³⁻⁵ *via* SAXS or TEM at this moment. As discussed in the main text, there are two possible reasons: the first one is that the obtained ultra-thin section may contain tens of layers of the microphase separation structures at $T_{iso} \geq T_b^o$, resulting in the homogenous-like morphology. The second one is that the crosslinking network inhibits the formation of the long-range order structures at $T > T_{cross}$ because the chain mobility of P35D melt is probably restricted by the crosslinking structures.

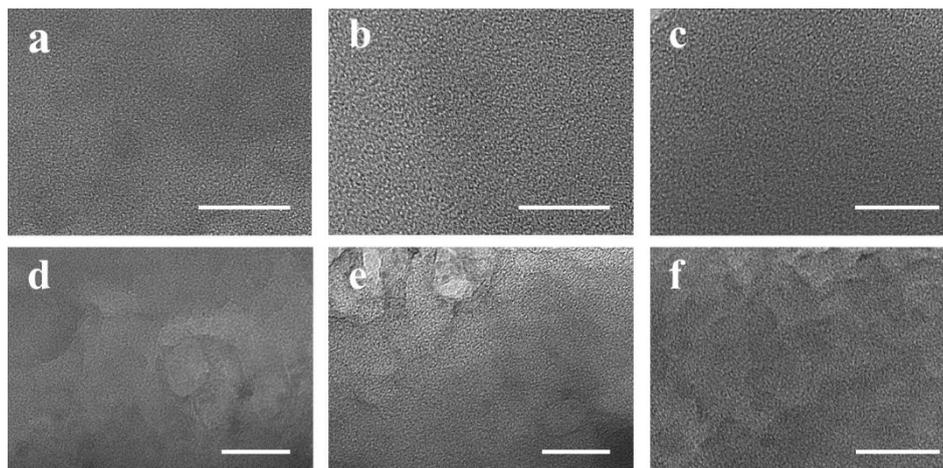


Fig. S6 TEM images of the quenched P35D thin-films bear the 2 hours isothermal treatment in vacuum at various T_{iso} of (a)170, (b)190, (c)210, (d)230, (e)250, and (f)270 °C, respectively. The length of the insert bar is 20 nm. The HT7700 TEM (Hitachi) was operated under 100 kV. The specimens were cut into ultrathin sections of approximately 90 nm in thickness at -60 °C by the ultramicrotome (Lecia EM UC6). The sliced sections were stained with OsO₄ vapor at room temperature to enhance the domain contrast.

Reference:

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