Supporting Information

Impact of pre-crosslinks on the self-transformation performance of thermoplastic polyesters into vitrimers via intermolecular transesterification

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1. Feed ratio

The actual feed mole ratio and feed weight ratio are summarized in Table S1.

Table S1. The feed mole ratio and feed weight ratio

		2-SH	2-epoxy	4-epoxy
P-0	mole ratio	100	100	0
	weight ratio	10.0	14.3	0
P-5	mole ratio	100	90	5
	weight ratio	10.0	12.9	0.9
P-10	mole ratio	100	80	10
	weight ratio	10.0	11.4	1.8
P-20	mole ratio	100	60	20
	weight ratio	10.0	8.6	3.5

2. Summary of gel fraction

Table S2. Summary of gel fraction for polymers

Sample	Gel fraction
P-0	0
P-5	0
P-10	0
P-20	63
P-30	76

Table S3. Summary of gel fraction for cross-linked polymer

Sample	Gel fraction
CL-0	96
CL-5	97
CL-10	98
CL-20	100
CL-30	100

*) The values are for the samples after heating at 170 °C for 24h.

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3. SEC data

The number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index ($Đ$) were determined using size exclusion chromatography (SEC). The set-up was composed of an LC20AD pump system and a RID-20A RI detector (SHIMADZU), where Shodex-gel columns, K-803, K-804, and K-805 (Shodex) were attached. The column temperature was 40 °C, and DMF containing LiBr (0.05 wt%) was used as an eluent at an elution rate of 1.0 mL/min. The standard series of poly(methyl methacrylate) was used for the estimation. SEC data for P-0, P-5, and P-10 are summarized in Figure S1. The values of M_n, M_w and $Đ$ are summarized in Table S4.

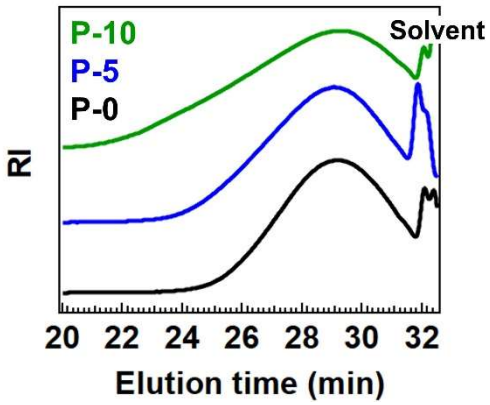

Figure S1. SEC spectra for P-0, P-5, and P-10.

Table S4. Characteristics of polyesters

Sample	M_n	M_w	$Đ$
P-0	6700	11000	1.7
P-5	7900	14000	1.8
P-10	8000	22000	2.7

4. ^{1}H-NMR of polyesters

^{1}H-NMR was measured for the polyesters. The measurement was performed in dimethyl sulfoxide-d_6 with a Bruker Analytik DPX400 spectrometer (400 MHz). Each signal with a different alphabet corresponds to the protons with the same alphabet in the chemical structures shown in the figure.

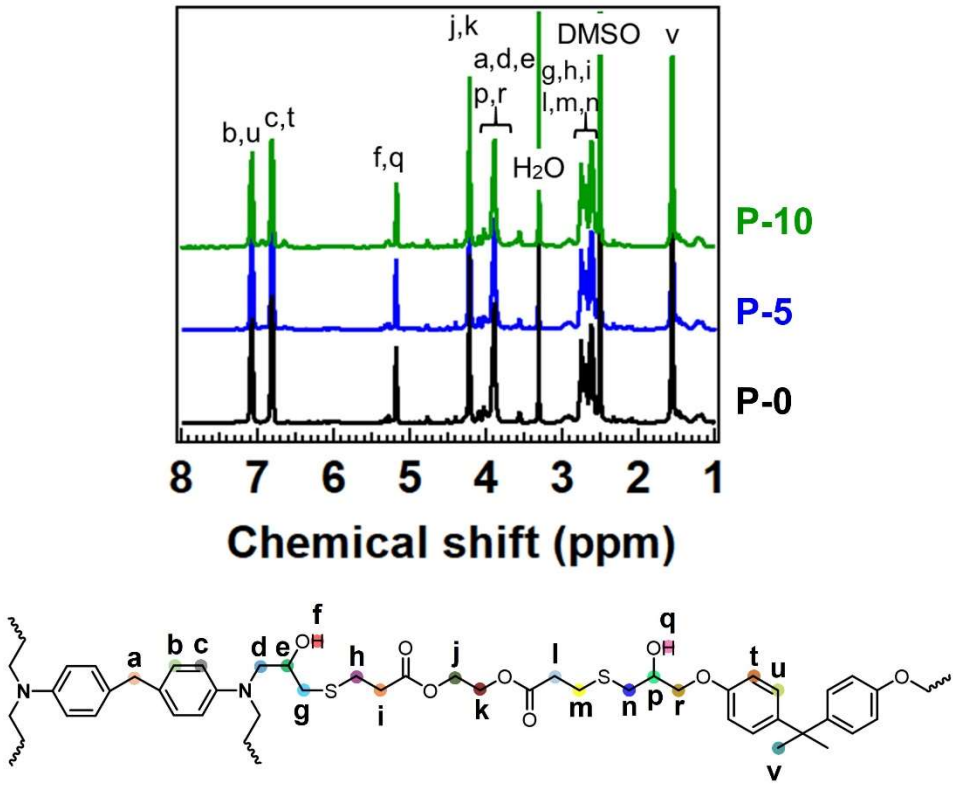

Figure S2. ^{1}H-NMR for polyesters, P-0, P-5, and P-10. The signals in the spectra correspond to the protons with the same alphabet in the chemical structures.

Table S5. Integral ratio of characteristic signals in the ^{1}H-NMR spectra

	a+d+e+p+r	b+u	c+t	f+q	g+h+i+l+m+n	j+k	v
P-0	5.7	4.5	4.5	1.8	11.5	4.0	7.4
P-5	5.4	4.1	4.0	1.6	11.1	4.0	6.9
P-10	5.3	3.8	3.9	1.5	11.4	4.0	6.7

5. Temperature-sweep rheology

Individual data of temperature-sweep rheology for polyesters are provided in Figure S3.

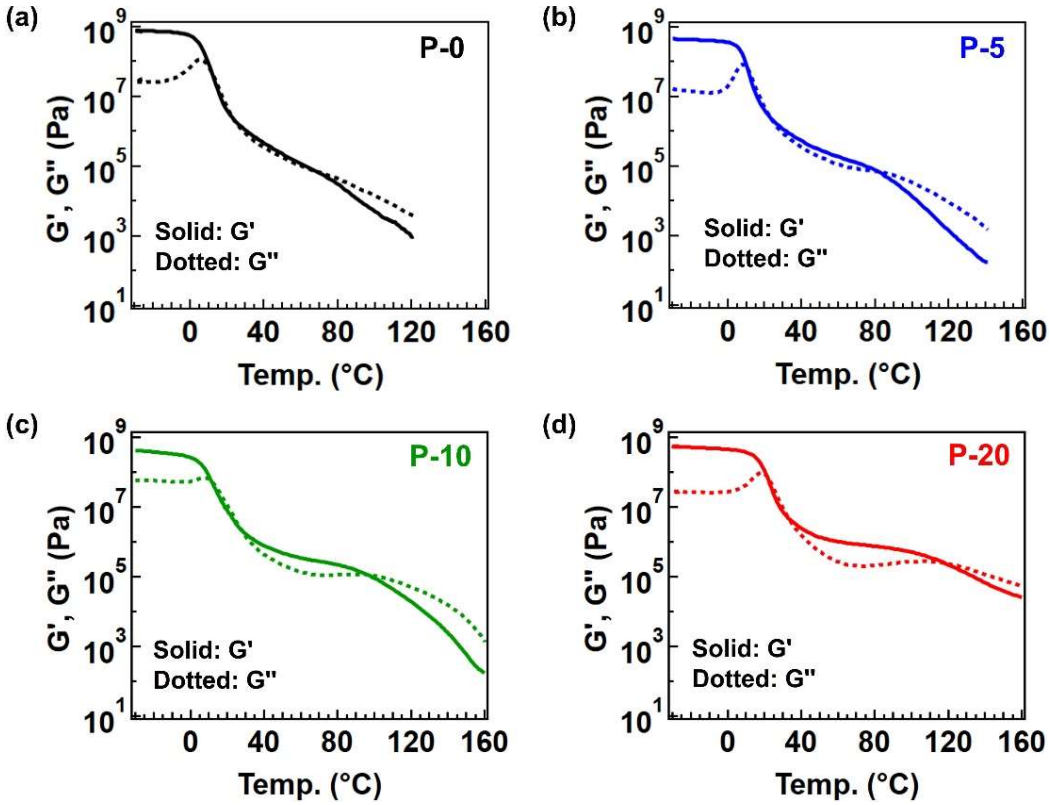

Figure S3. Temperature-sweep rheology data for the polyesters with different fractions of 4-epoxy, i.e., (a) P-0, (b) P-5, (c) P-10, (d) P-20.

Table S6. Summary of flow temperature

	P-0	P-5	P-10	P-20
T_{flow} (°C)	68	82	97	119

6. Rheology data for P-30

Figure S4 provides a temperature-ramp rheology data for P-30. Unlike other samples with lower fractions of 4-epoxy, P-30 did not exhibit distinct flow region with loss modulus $G'' >$ storage modulus G'. Instead, G' and G'' were always close at high temperature region, which is a characteristic of the polymer near the percolation threshold. Figure S5 represents frequency sweep for P-30 obtained at 80 °C and 90 °C. It has been known that the sample should represent $G' \sim G'' \sim \omega^n$ at the percolation threshold.[S1,S2] Thus, these data indicate that P-30 was very close to the percolated network.

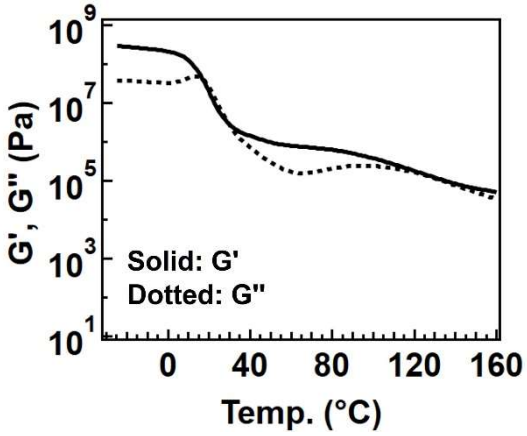

Figure S4. Temperature-sweep rheology data for P-30.

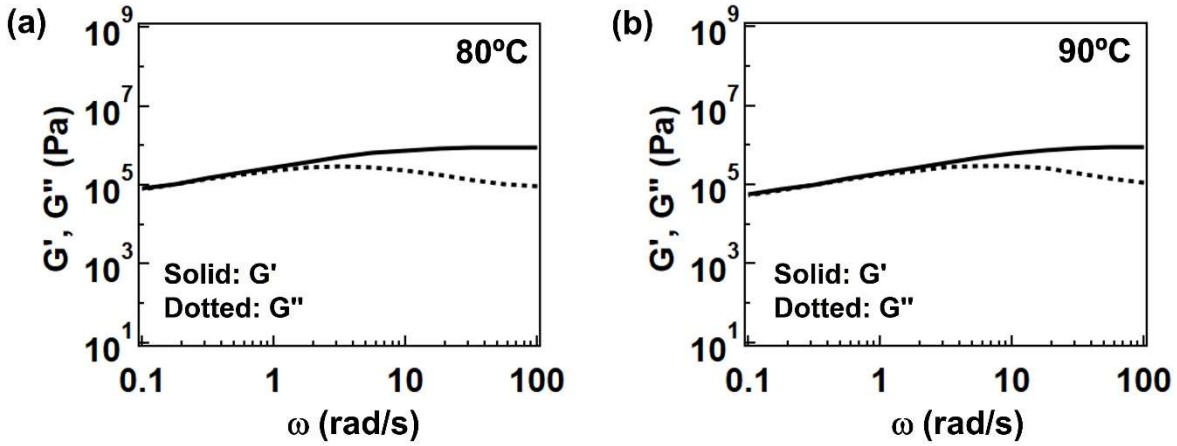

Figure S5. Frequency-sweep rheology data for P-30 at (a) 80 °C and (b) 90 °C.

S1) H. H. Winter, F. Chambon, *J. Rheol.*, 1986, **30**, 367-382.

S2) H. H. Winter, M. Mours, *Adv. Polym. Sci.*, 1997, **134**, 167.

7. ^{1}H-NMR of starting monomers

^{1}H-NMR was measured for the starting monomers, 2-epoxy, 4-epoxy, and 2-SH, to investigate the presence of impurities. The measurement was performed in dimethyl sulfoxide-d_6 with a Bruker Analytik DPX400 spectrometer (400 MHz). Each signal with a different alphabet corresponds to the protons with the same alphabet in the chemical structures shown in the figure.

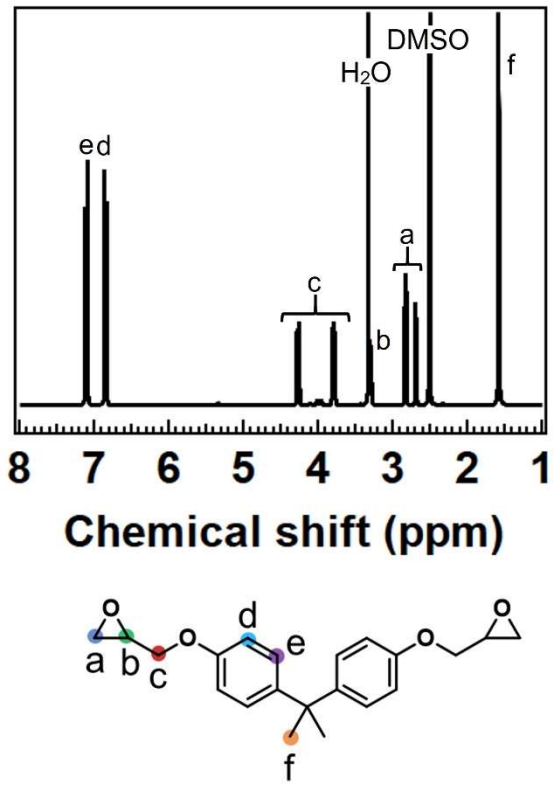

Figure S6. ^{1}H-NMR spectrum for 2-epoxy. The signals in the spectra correspond to the protons with the same alphabet in the chemical structures.

Table S7. Integral ratio of characteristic signals of 2-epoxy

Signal	a	b	c	d	e	f
Integral ratio	3.9	1.9	3.9	4.3	4.3	6.4

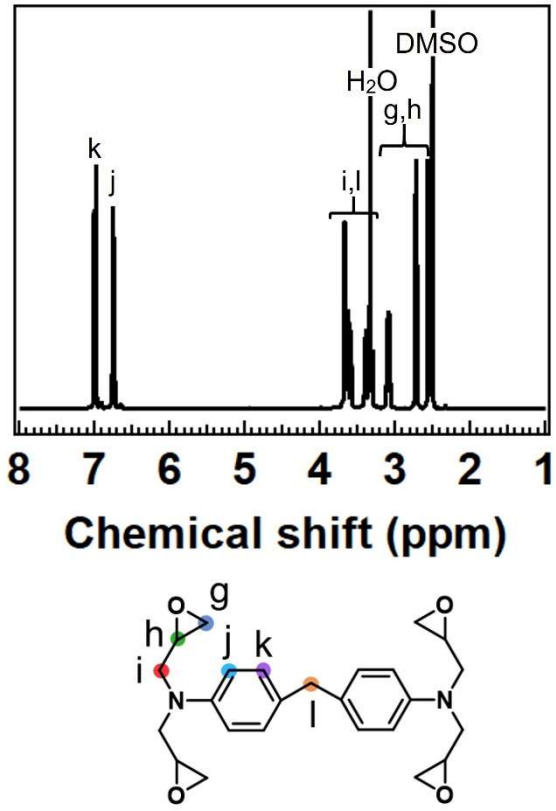

Figure S7. ^{1}H-NMR spectrum for 4-epoxy. The signals in the spectra correspond to the protons with the same alphabet in the chemical structures.

Table S8. Integral ratio of characteristic signals of 4-epoxy

Signal	g+h	i+l	j	k
Integral ratio	11.9	9.9	4.0	4.0

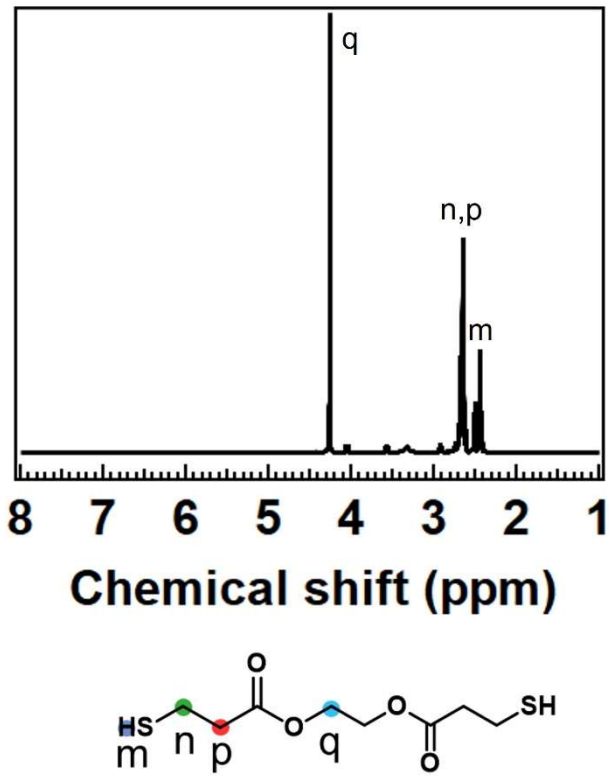

Figure S8. ^{1}H-NMR spectrum for 2-SH. The signals in the spectra correspond to the protons with the same alphabet in the chemical structures.

Table S9. Integral ratio of characteristic signals of 2-SH

Signal	m	n+p	q
Integral ratio	1.7	8.2	4.0

8. Isothermal time-resolved rheology data at other temperatures

Figure S9 represents the isothermal time-resolved rheology data at 150 °C and 130 °C. Figure S10 then summarizes the variation of t_{gel} as function of X in P-X (i.e., the fraction of 4-epoxy) obtained from results at different temperatures.

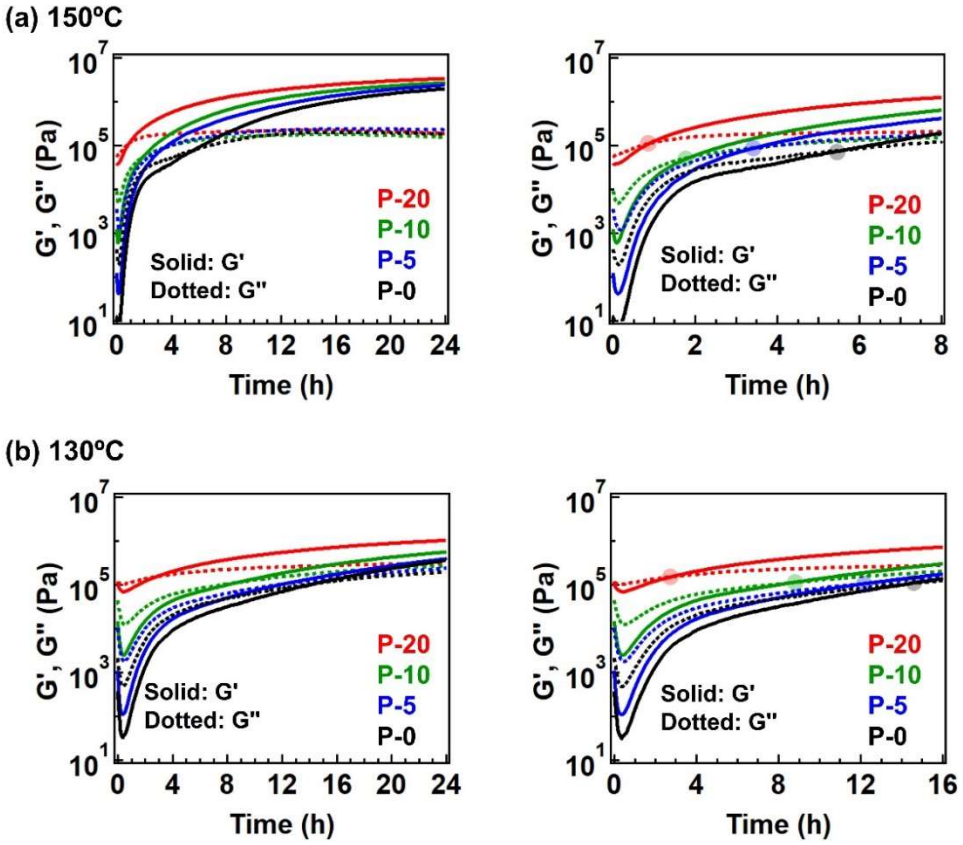

Figure S9. Isothermal time-resolved rheology data measured at (a) 150 °C and (b) 130 °C for 24 h. In the right side, the expanded data are provided for clearer comparison of the cross-point of G' and G''. The translucent circle represents the cross-point of G' and G''.

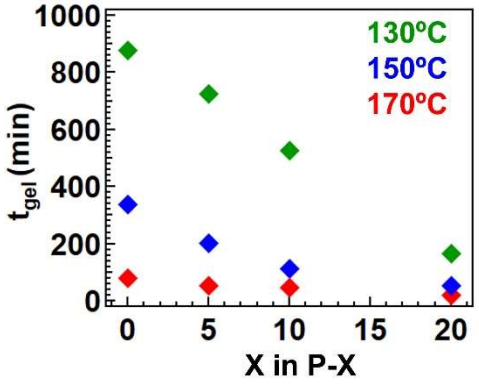

Figure S10. Variation of t_{gel} as function of X in P-X (i.e., the fraction of 4-epoxy) obtained from results at different temperatures.

Table S10. Summary of t_{gel} in heating at 130 °C

	P-0	P-5	P-10	P-20
t_{gel} (min)	876	725	526	167

Table S11. Summary of t_{gel} in heating at 150 °C

	P-0	P-5	P-10	P-20
t_{gel} (min)	337	202	114	53

Table S12. Summary of t_{gel} in heating at 170 °C

	P-0	P-5	P-10	P-20
t_{gel} (min)	79	53	45	20

9. Plot of T_g

Figure S11 summarized the change of T_g as a function of heating time (t_{heat}) at 170 °C. The DSC thermograms of 2nd heating are provided in Figure S12. The Tg values are summarized in Table S13.

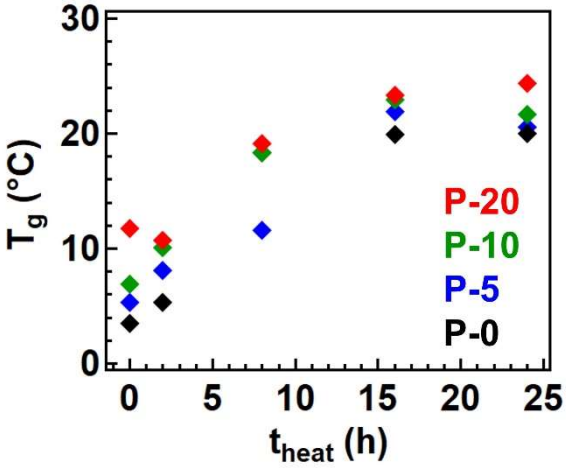

Figure S11. Variation of glass transition temperature (T_g) as a function of heating time (t_{heat}) at 170 °C.

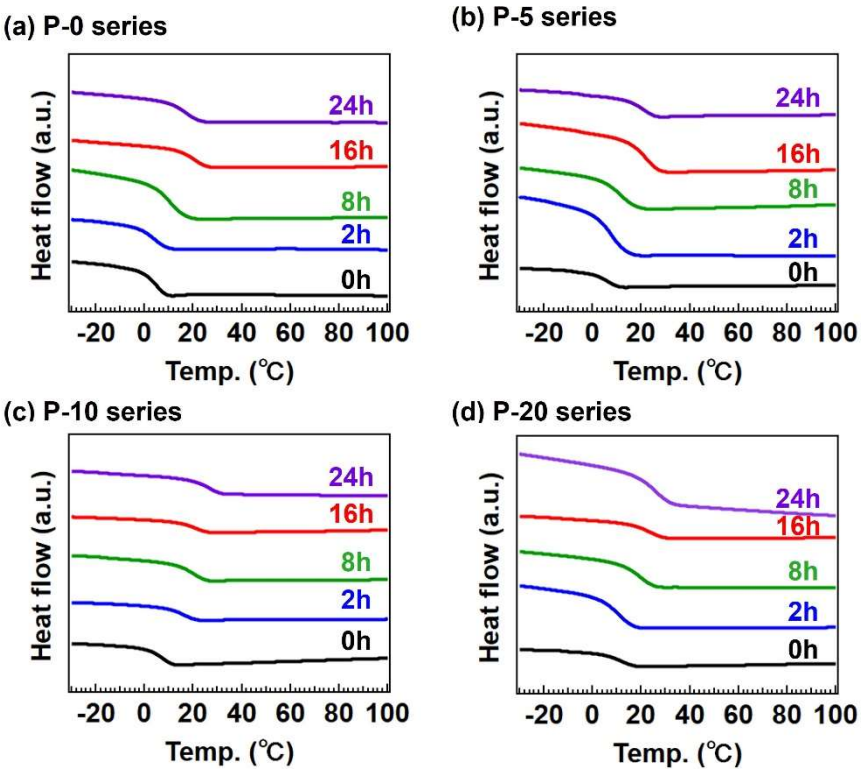

Figure S12. Summary of 2nd heating DSC thermograms for (a) P-0, (b) P-5, (c) P-10, and (d) P-20 series with various t_{heat}.

Table S13. Summary of T_g for the sample after heating at 170 °C for various t_{heat}

t_{heat} (h)	T_g (°C)			
	P-0 series	P-5 series	P-10 series	P-20 series
0	3.5	5.3	6.9	11.7
2	5.3	8.1	10.1	10.7
8	11.2	11.6	18.4	19.1
16	19.9	21.9	22.9	23.3
24	20.0	20.6	21.7	24.4

10. TGA thermograms

Figure S13 represents TGA thermograms for the cross-linked samples, where the cross-linking was performed by heating at 170 °C for 24 h.

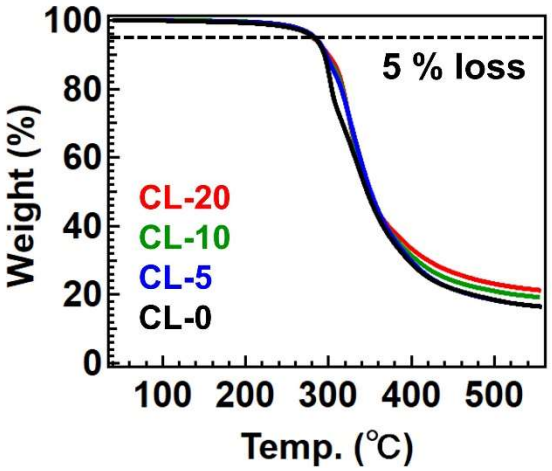

Figure S13. TGA thermograms measured for the sample cross-linked at 170 °C for 24h.