Supporting Information

Dominant factor of bond-exchange rate for catalyst-free polyester vitrimers with internal tertiary amine moieties

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1. Analytical methods

Characterization of component polyester. The dispersity index, PDI, for the component polyester was determined by size exclusion chromatography (SEC). The measurement was performed using Shodex KD803+804 columns, combined with a Tosoh DP8020 pump system and an RI (Tosoh RI-8020) detector. Dimethylformamide (DMF) with an addition of LiBr (0.05 wt%) was used as the eluent, and the flow rate was set to 0.5 ml/min. The elution volume was calibrated with a standard series of poly(methyl methacrylate)s. The fraction of monomer units in a chain was determined by ^{1}H-NMR in *d*-DMSO using a Bruker Analytik DPX400 spectrometer (400 MHz). The progress of Michael addition reaction was checked by ^{1}H-NMR in *d*-DMSO, where a tiny amount of trifluoroacetic acid (TFA) was added to shift the signal from water.

Spectroscopy. Fourier transform infrared spectroscopy (FT-IR) measurements were performed to confirm the progress of cross-linking reaction. The measurements were carried out at room temperature, using a FT/IR 430 spectrometer with an ATR attachment (JASCO Co.).

Thermal properties. The glass transition temperatures (T_gs) were measured by differential scanning calorimetry (DSC) with using DSC7020 (HITACHI). The data was taken from the second heating from -70 to 200 °C at a constant temperature ramp rate of 10 °C/min. Thermogravimetric analysis (TGA) was performed to investigate the thermal decomposition temperature with using TG/DTA7300 (HITACHI). The temperature ramp rate was set to 10 °C/min. All the above thermal investigations were performed for approximately 10 mg samples under N_2 gas flow (20 ml/min).

Mechanical properties. Tensile tests were performed by using AGS-500NX (SHIMADZU) to evaluate the cross-link density. Dogbone-shaped samples were prepared with a cutting die, where the thickness, gauge length, and gauge width was set to be 0.6 mm, 13 mm, and 4 mm, respectively. The tests were performed at an elongation rate of 100 mm/min (~ 0.1 sec^{-1}) at room temperature. The stress-relaxation dynamics was performed with an application of 3% strain, using shear-type rheometer (MCR302, TA Anton paar) and 8 mm parallel plates. Before measurements, the samples were kept for 20 min at each target temperature for thermal equilibration. The rheological measurements with temperature-sweep

mode were also performed with MCR 302 and the same geometries. The frequency was fixed to be 10 Hz, and the measurements were conducted within the linear regime (strain = 0.1%). The temperature was decreased from 180 °C to glass transition temperature with a rate of 5 °C/min. All the above mechanical measurements, except tensile tests, were operated under a N_2 gas atmosphere.

2. Synthesis of PE-COOH

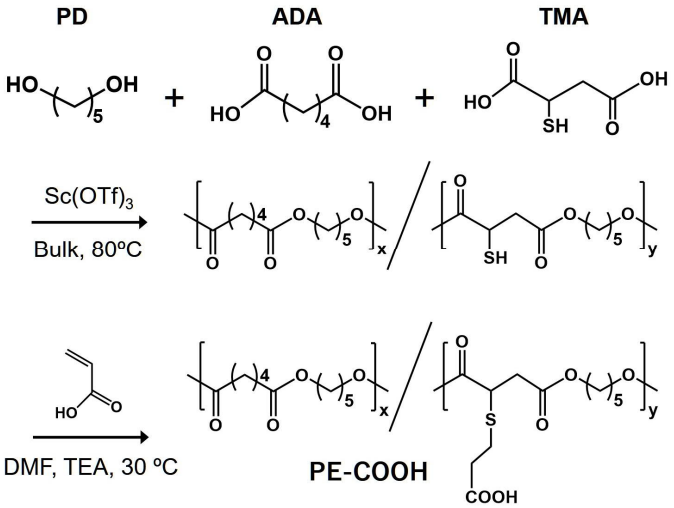
Materirals.

1,5-pentanediol (PD), thiomalic acid (TMA), acrylic acid, the catalyst for polycondensation $Sc(OTf)_3$ were purchased from TCI. 4,4'-Methylenebis(*N*,*N*-diglycidylaniline) (Mb-epoxy) was purchased from Aldrich. Adipic acid (ADA) was purchased from Wako Pure Chemical Industries. These chemicals were all used as received.

Synthesis

Polyesters with multiple COOH side groups (PE-COOH) were synthesized based on our previous report (see Scheme S1). Melt polycondensation was first performed using 1,5-pentanediol (PD), thiomalic acid (TMA), adipic acid (ADA) in the presence of a small amount of $Sc(OTf)_3$ catalyst. In the synthesis, the stoichiometric ratio between COOH and OH was kept to be unity, and the mole ratio of TMA to ADA was set to PD/ADA/TMA = 1/0.7/0.3. The polycondensation was kept at 80 °C for approximately 20 hours with vacuum stripping. The polymer was purified by precipitating its THF solution into methanol repeatedly. To attach COOH groups into the chain, the thiol (SH) groups in the obtained polyester was reacted with vinyl group of acrylic acid via Michael addition reaction. For the reaction, the polyesters with SH groups were dissolved in DMF, and then acrylic acid (3 eq. to SH groups in the polyester) and triethylamine (1/3 eq. to SH groups in the polyester) were added. The reaction was kept at room temperature overnight. Unreacted acrylic acid monomers were removed by re-precipitation of the THF solution into methanol repeatedly.

Scheme S1. Synthesis of PE-COOH



^{1}H-NMR measurement was performed to determine the unit ratio of PD/ADA/TMA in the polyesters. The spectrum of the polyester with SH side groups is provided in Figure S2 (black). Integral values on the signals are presented in Table S1. The polyester with COOH side groups (PE-COOH) after Michael addition is provided in Figure S2 (red). Hx with alphabet (x) in the spectra corresponds to the protons with the same alphabet in the chemical structures shown in Figure S1.

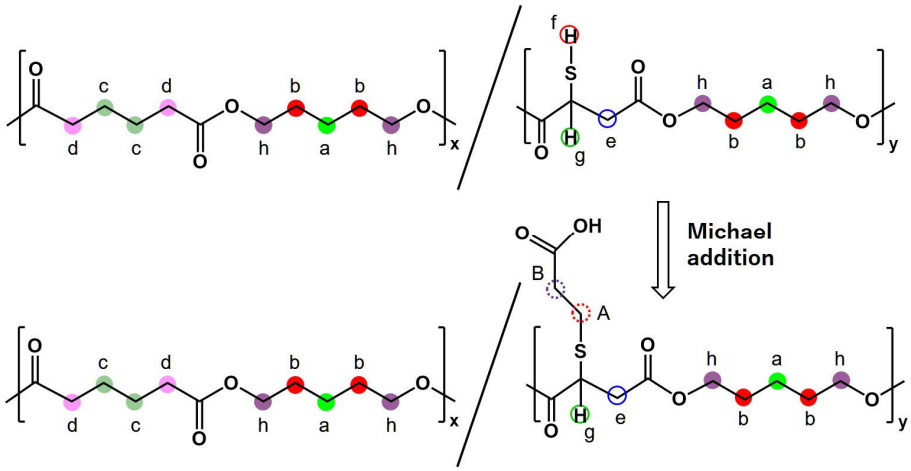


Figure S1. Assignment for proton signals for ^{1}H-NMR spectra in Figure S2.

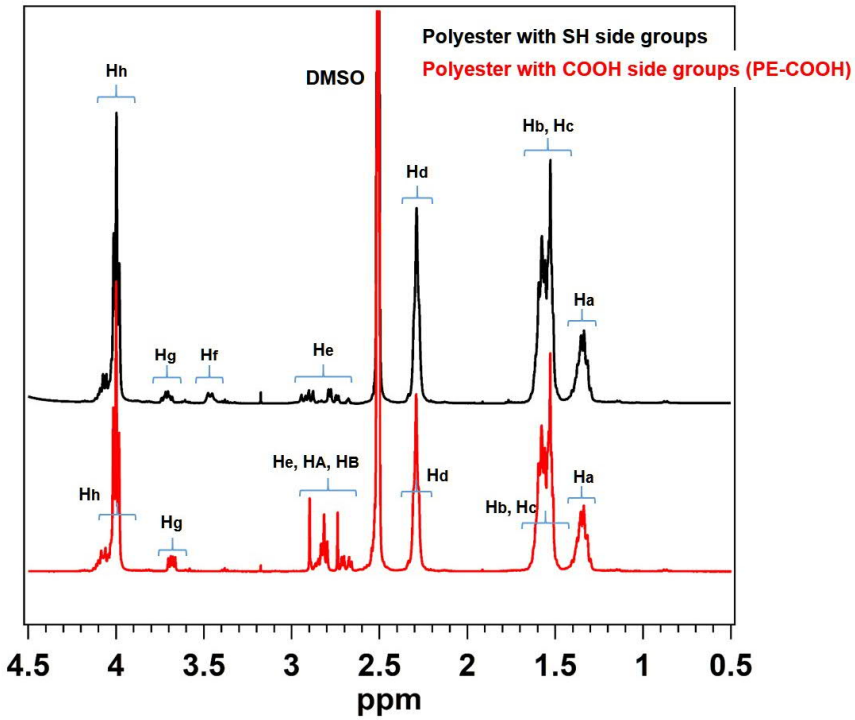


Figure S2. ^{1}H-NMR spectra for polyester with SH side groups (black) and COOH side groups (red).

Table S1. Attribution of signals and integral values for polyester with SH groups.

	σ (ppm)	integral found	expected
H_a	1.3-1.4	1.00	1.00
H_b, H_c	1.5-1.6	3.13	3.40
H_d	~2.4	1.34	1.40
H_e	2.7-3.0	0.27	0.30
H_f	~3.45	0.11	0.15
H_g	~3.7	0.12	0.15
H_h	3.9-4.1	1.86	2.00

From the integral ratios, it was confirmed that the unit ratio of PD/ADA/TMA (= 1/0.71/0.29) was nearly the same as the feed mole ratio (PD/ADA/TMA = 1/0.7/0.3). We estimated the number of SH groups (N_{SH}), which corresponds to N_{COOH} in PE-COOH, from the unit ratios and M_n (~ 18500 g/mol) determined by SEC measurements. In the polyester, there are two kinds of repeating unit; one is composed of TMA and PD (Unit-TMA), and the other is composed of ADA and PD (Unit-ADA). By using M_n from SEC and each unit mass (218.3 g/mol for Unit-TMA and 214.3 g/mol for Unit-ADA), we obtain the equation S1,

$M_n = 218.3 \times n_{TMA} + 214.3 \times n_{ADA}$ (S1),

where n_{TMA} and n_{AdA} represents the number of unit per chain for Unit-TMA and Unit-ADA, respectively. The ratio between n_{TMA} and n_{ADA} can be estimated from the ^{1}H-NMR. This leads to

$n_{TMA} : n_{ADA} = x : y$ (S2)

, where x and y is the values of the integral ratio for the characteristic signals from TMA and ADA. The simultaneous equation of S1 and S2 is solved to provide the values of n_{TMA} and n_{ADA}, leading $n_{TMA} = N_{SH} = 25$ and $n_{ADA} = 60$.

After Michael addition, the unit mass of Unit-TMA was changed to 290.3. Since the number of COOH groups per chain (N_{COOH}) corresponds to n_{TMA}, the molecular weight of PE-COOH was calculated by,

$M_n = 290.3 \times n_{TMA} + 214.3 \times n_{ADA}$ (S3)

, leading to M_n for PE-COOH ~ 20100 g/mol.

Figure S3 represents FT-IR data for PE-COOH. In Figure S3a, two kinds of signals were observed; one corresponds to the ester C=O peak and the right shoulder does to the C=O of COOH side groups. In Figure Sb, the OH stretching vibration of COOH was observed.

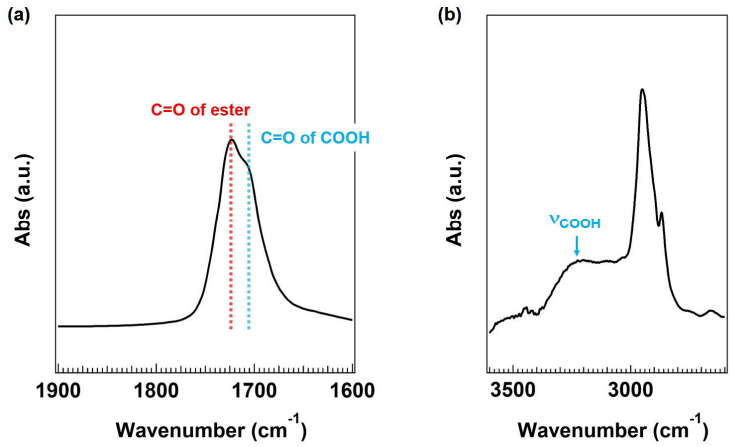


Figure S3. FT-IR spectra for PE-COOH at (a) carbonyl stretching and (b) OH stretching regions.

3. Blend information

Table S2. Summary of blend ratio and gel fraction of cross-linked samples

Sample code	$w_{PE\text{-}COOH}$	$w_{Mb\text{-}Epoxy}$	Gel fraction[1]
CL-PE-1	900 mg	118 mg	100%
CL-PE-0.5	900 mg	59 mg	100%
CL-PE-0.25	900 mg	29.5 mg	93%
CL-PE-0.125	900 mg	14.75 mg	85%

[1)] Gel fraction was measured by swelling tests. The samples were immersed in THF (good solvent for PE-COOH), and the solvent was replaced with new one at the interval of 1 day for three times. Each solution taken out was dried to weight the mass of remaining components. The mass of remaining component was compared with the initial mass of sample.

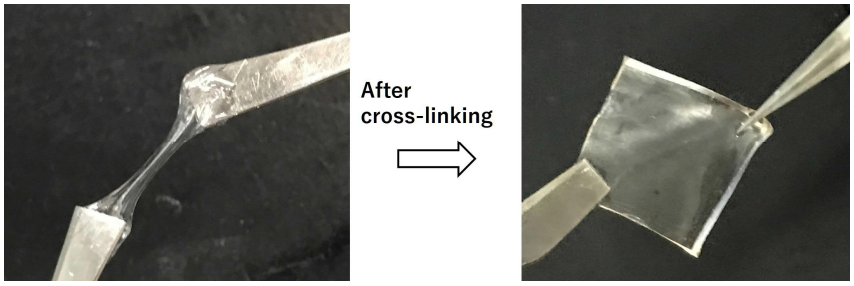


Figure S4. Macroscopic appearance of neat PE-COOH and cross-linked sample (CL-PE-0.125)

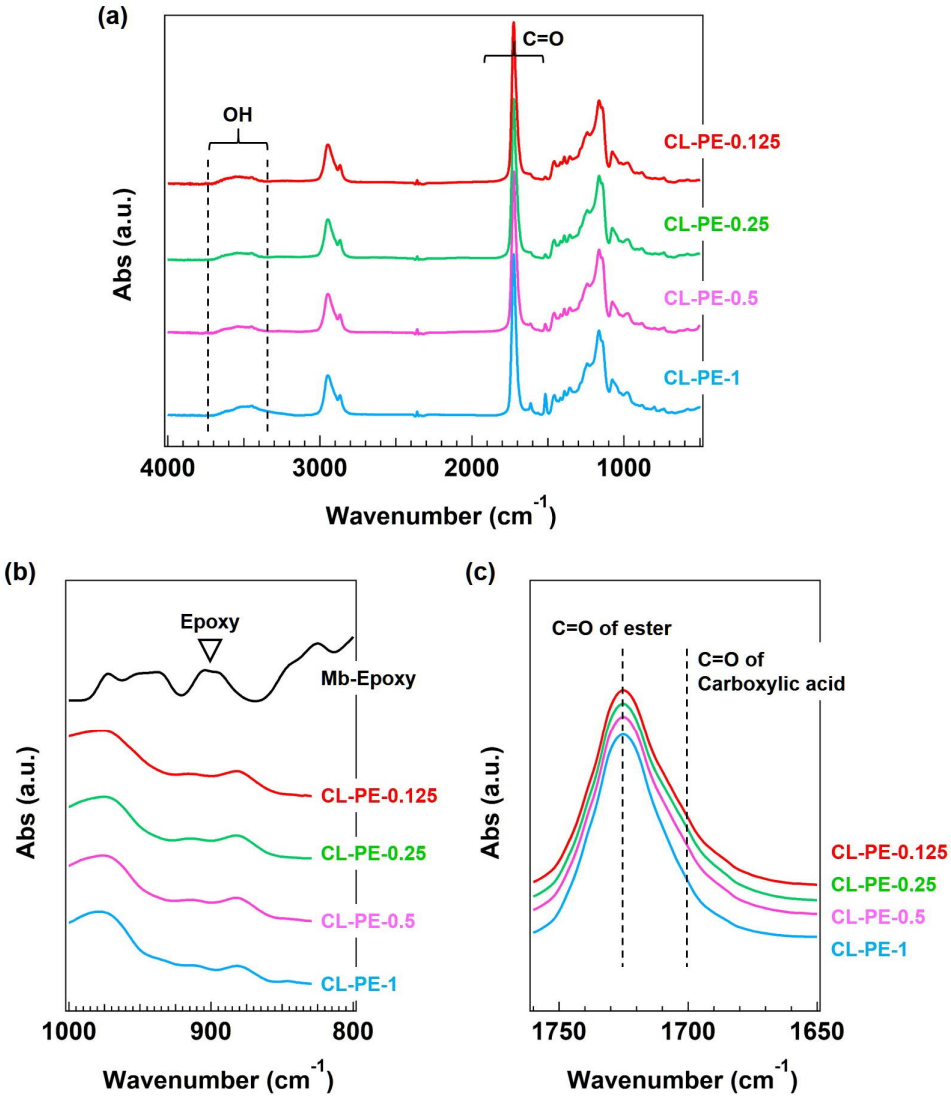


Figure S5. FT-IR data (a) at the whole wavenumber region, (b) at the epoxy peak region, and (c) at the carbonyl peak region. In (b) and (c), the peak (or shoulder) from epoxy and C=O of carboxylic acid disappeared (or decreased) for the samples after cross-linking.

4. DSC data

Figure S6 represents the 2nd heaing DSC thermograms for CL-PE-*X*.

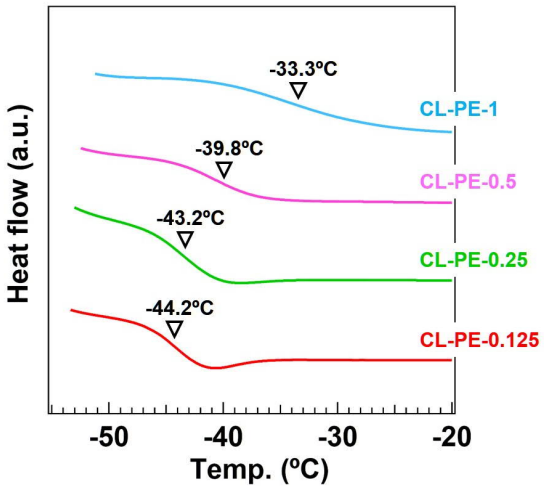


Figure S6. 2nd heating DSC thermograms for CL-PE-*X*. The inverse triangles and values represent T_g.

5. TGA thermograms

Figure S8 represents the TGA thermograms for CL-PE-*X*.

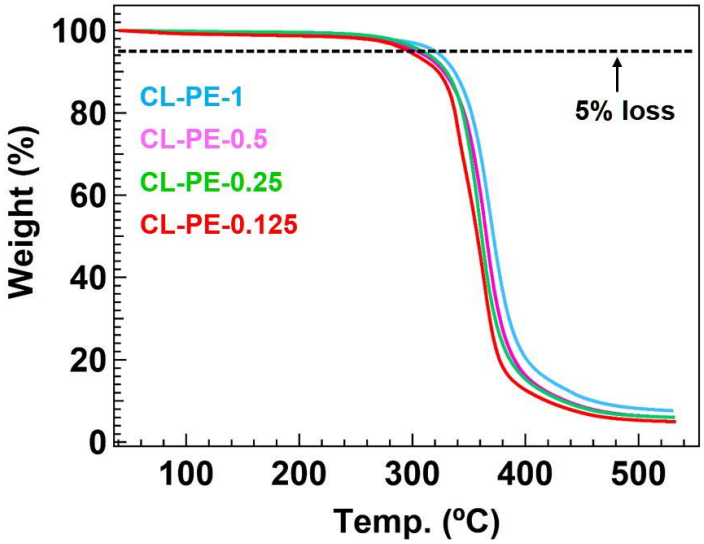


Figure S7. TGA thermograms for CL-PE-*X*.

6. Temperature ramp FT-IR

Figure S7 represents the change of FT-IR spectra with an increase in temperatures. The instrument used was a FT/IR-6300 spectrometer (JASCO) combined with a microscopic positioning tool. Because the cross-linked samples were too thick to obtain accurate spectra under the condition of relfection mode with the temperature stage, only the sample PE-COOH was measured. The thin film sample was prepared by drop casting method using THF. The temperature dependence of FT-IR spectra was obtained using a Linkam hot stage, where the measuremnt temperature range was from 30 °C to 180 °C with an interval of 30 °C. The equribration time for each target temperature was set to 3 min. The measurements were conducted under N_2 gas atomosphere.

The signal at 3245 cm^{-1} at 30 °C was attributed to the OH streching of COOH in the hydrogen bonded state.[S1,S2] The signal was shifted to higher wavenumers with an increasing in temperatures, showing the weakining and dissociation of the hydrogen bonds.

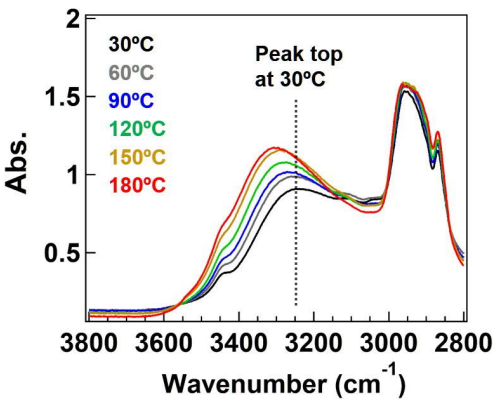


Figure S8. Temperature ramp FT-IR spectra for PE-COOH.

S1) Lee, J. Y.; Painter, P. C.; Coleman, M. M. *Macromolecules* 1988, 21, 346−354.

S2) Cazares-Cortes, E.; Baker, B. C.; Nishimori, K.; Ouchi, M. *Macromolecules* 2019, 52, 5995−6004.

7. Summary of mechanical properties

Table S3. Summary of mechanical properties

Sample code	G_P (MPa)[1]	ν (mmol/cm^3)[2]	E_Y (MPa)[3]	ε_b (%)[4]
CL-PE-1	2.14	0.69	7.83	23.6
CL-PE-0.5	0.87	0.28	2.68	33.3
CL-PE-0.25	0.40	0.13	1.23	108.3
CL-PE-0.125	0.15	0.048	0.35	617.1

[1)] Plateau modulus taken at 100 °C. [2)] Cross-link density estimated by G_P. [3)] Young's modulus measured by tensile tests in the region of 5% elongation. [4)] Elongation at break.

8. Stress-relaxation data at different temperatures for CL-PE-0.125

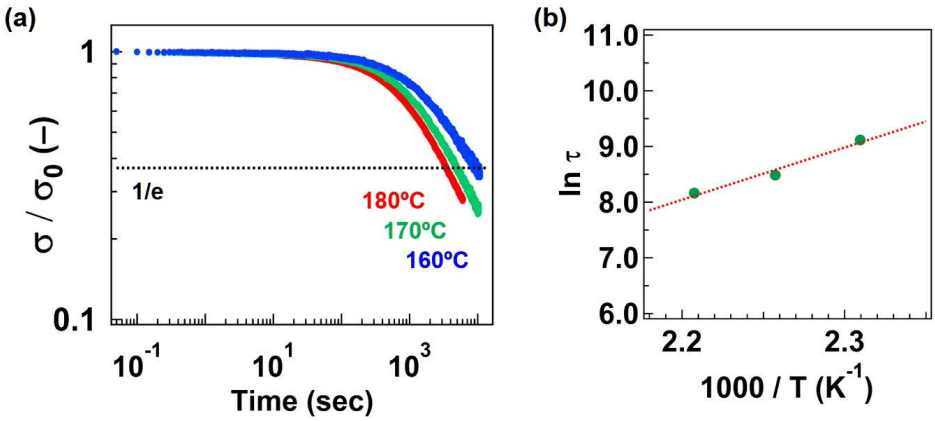


Figure S9. (a) Stress-relaxation curves for CL-PE-0.125 at various temperatures. The dotted line represents 1/e of initial modulus. (b) Arrhenius plot of τ for CL-PE-0.125, where the values of τ was defined as the time at which the modulus reaches 1/e.

9. Fitting analysis of stress-relaxation curves

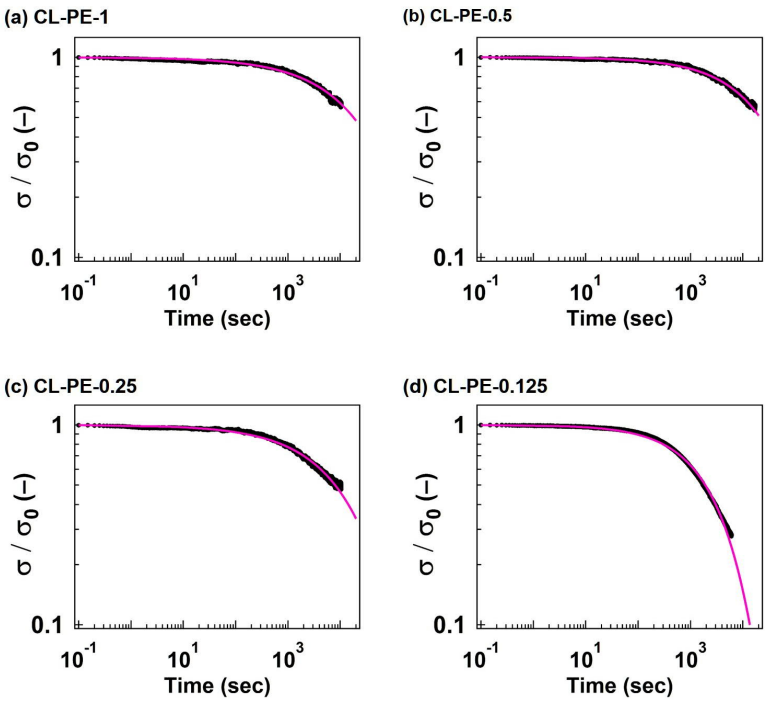


Figure S10. Individual fitting data for stress-relaxation curves.

Table S4. Summary of τ^* and β for the fitting

Sample code	τ^* (sec)[1]	β (-)[1]
CL-PE-1	39500	0.465
CL-PE-0.5	49000	0.50
CL-PE-0.25	17100	0.48
CL-PE-0.125	3480	0.48

[1)] Characteristic relaxation time (τ^*) and relaxation time distribution (β) based on the KWW equation.

10. Stress-relaxation data at 160 °C

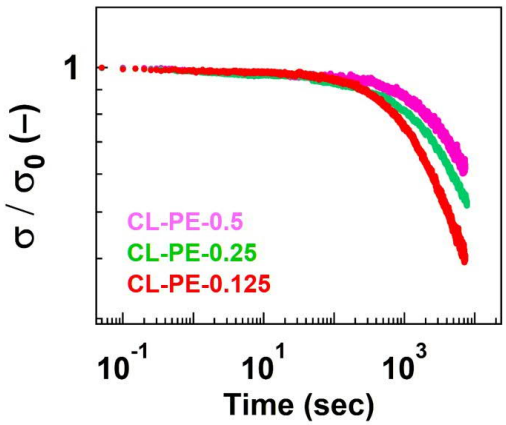


Figure S11. Stress-relaxation curves taken at 160 °C.

11. Stress-relaxation data for cross-linked samples using PE-COOH with larger fraction of COOH side groups

To confirm the universality of the stress-relaxation efficiency for CL-PE-*X* samples in the main manuscript, different cross-linked samples were prepared using another PE-COOH with larger fraction of COOH side groups (coded as PE-COOH-L). PE-COOH-L was synthesized based on the different feed ratio of ADA and TMA (see scheme S1), and PE-COOH-L has M_n = 24200 g/mol, and the number of COOH groups (M_n/N_{COOH}) = 68. The equivalent COOH molecular weight (M_{COOH}), which was estimated by M_n/N_{COOH}, was 356 g/mol. PE-COOH in the main manuscript has M_{COOH} = 805 g/mol, and thus PE-COOH-L possesses larger fraction of COOH groups per chain. The cross-linked samples were prepared by blending PE-COOH-L and Mb-epoxy, where the blend weight ratio was adjusted to be the same as that for CL-PE-0.125, CL-PE-0.25, CL-PE-0.5, and CL-PE-1 in the main manuscript (see also Table S2). Thus, the mass of Mb-epoxy used in each cross-linked sample was varied as 118 mg, 59 mg, 29.5 mg, and 14. 75mg, where the mass of PE-COOH-L was all 900 mg.

First, tensile tests were performed to confirm the difference of cross-link density (Figure S12a). The obtained Young's modulus and cross-link density for the new cross-linked samples are summarized in Table S5, showing the increase in cross-link density with an increase in Mb-epoxy. The stress-relaxation tests were then performed to see the difference of bond-exchange rate (Figure S12b). The normalized stress remaining after 2h measurement, $(\sigma/\sigma_0)_{r,2h}$, is summarized in Table S5. Based on the values of $(\sigma/\sigma_0)_{r,2h}$, in this new cross-linked sample series using PE-COOH-L, the sample with a lowest fraction of Mb-epoxy showed the shortest relaxation rate. By increasing the amount of Mb-epoxy from 14.75mg to 59 mg, the relaxation rate became slower, while the relaxation rate became shorter for the sample with 118 mg Mb-epoxy than the sample with 59 mg Mb-epoxy. This is indeed the same result as observed for CL-PE-*X* in the main manuscript.

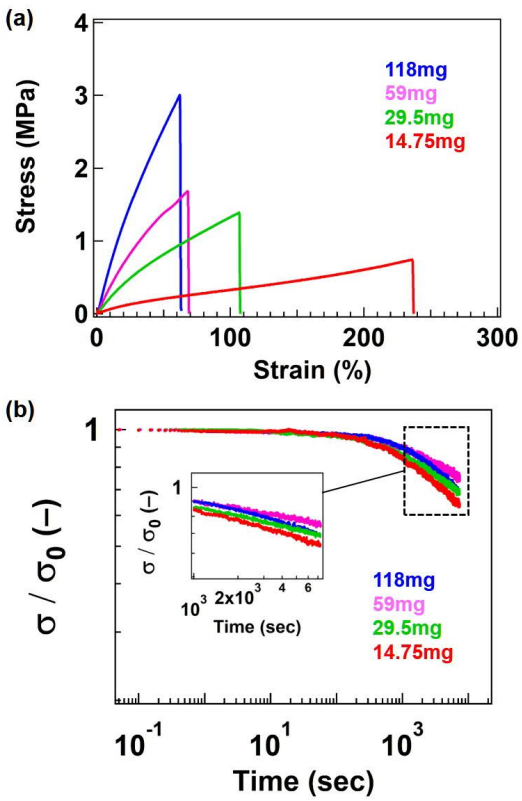


Figure S12. (a) Stress-strain curves and (b) stress-relaxation data for the cross-linked samples using PE-COOH-L. The codes, "118mg, 59mg, 29.5mg, 14.75mg", represents the mass of Mb-epoxy blended in each cross-linked sample. The inset in (b) indicates the magnification of the area surrounded with dotted line to see the difference of remaining stress.

Table S5. Summary of blend ratio and gel fraction of cross-linked samples

Mass of Mb-epoxy	E_Y (MPa)[1]	ν (mmol/cm^3)[2]	$(\sigma/\sigma_0)_{r,2h}$[3]
118 mg	6.53	0.89	0.687
59 mg	3.76	0.51	0.746
29.5 mg	2.14	0.29	0.681
14.75 mg	0.62	0.084	0.639

[1)] Young's modulus measured by tensile tests in the region of 5% elongation. [2)] Cross-link density estimated by E_Y. [3)] The normalized stress remaining after 2h stress-relaxation measurement.

12. Stress-relaxation data for the control sample without amino moieties

As another control sample to see the catalytic effect of COOH side groups, PE-COOH was simply cross-linked with di-epoxy cross-linker (1,4-butanediol diglycidyl ether) in the absence of any trans-esterification catalysts, where only 12.5 mol% of COOH side groups was adjusted to be consumed (see the explanation in the main text). Rheology data with temperature-sweep mode showed the stable rubber plateau up to 180 °C (Figure S13a), meaning the stable network formation. Stress-relaxation was then performed at 180 °C for the control sample, showing very weak stress relaxation (Figure S13b), unlike the data for PE-CL-0.125. The result revealed that the abundant COOH side group did not play a critical role as internal catalysts in the present system.

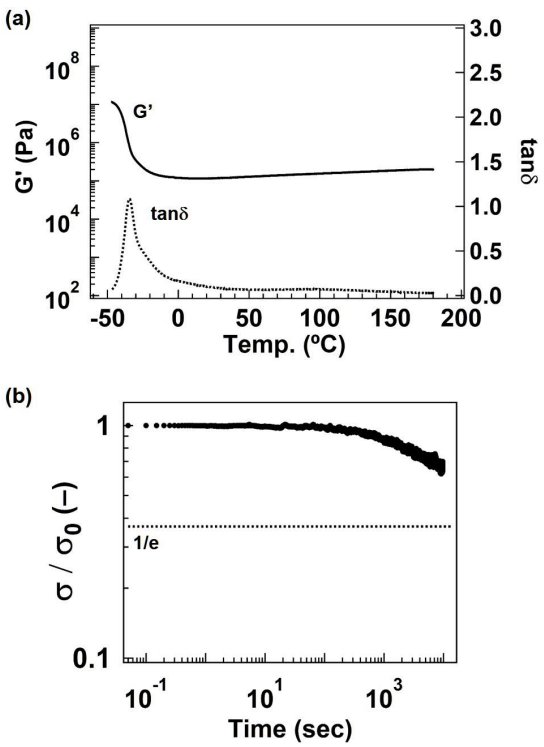


Figure S13. (a) Temperature-dependent rheology data and (b) stress-relaxation curve at 180 °C measured for the control cross-linked sample without amine moieties.