Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Synthesis of amorphous low T_g polyesters with multiple COOH side groups and the utilization for elastomeric vitrimers based on post-polymerization cross-linking†

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1. ^{1}H-NMR

^{1}H-NMR measurements were performed to estimate the unit ratio of PD/AdA/ThA in the polyesters synthesized by polycondensation reaction. The spectra for the polyesters synthesized with different feed mole ratios are provided in Figure S2, where Hx with alphabet (x) in the spectra corresponds to the protons with the same alphabet in the chemical structures shown in Figure S1. Integral values on the signals are presented in Table S1.

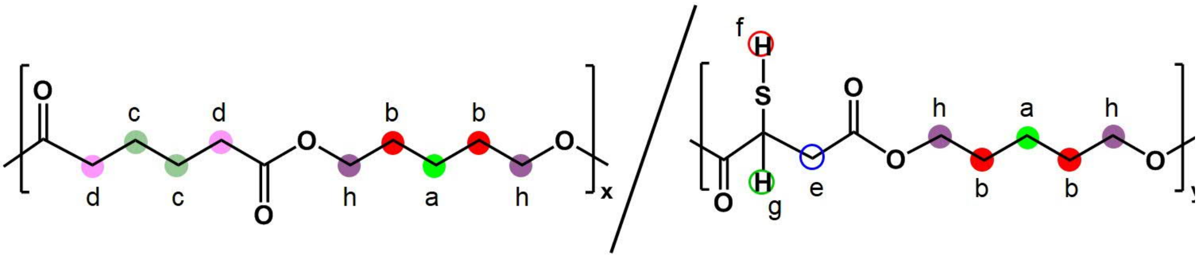


Figure S1. Assignment for proton signals for NMR spectra in Figure S2.

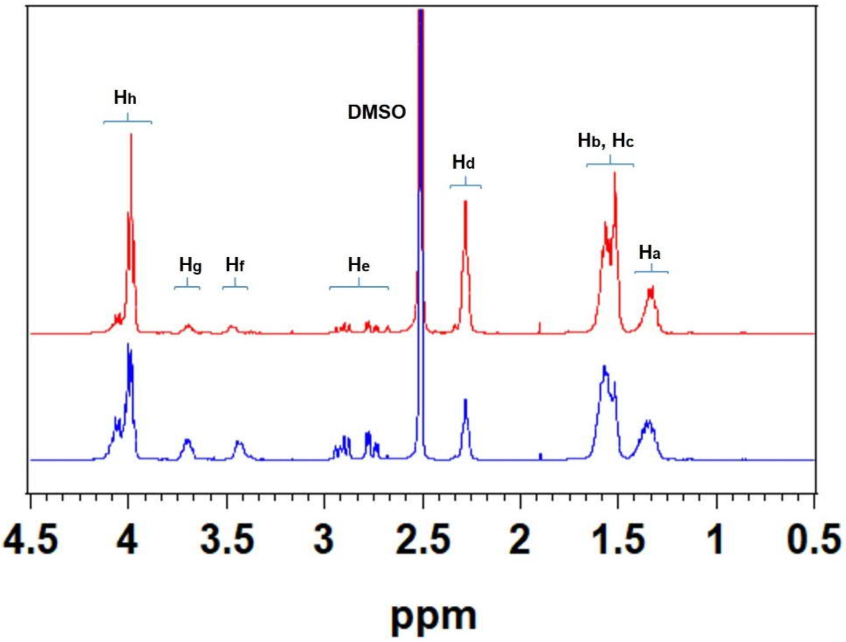


Figure S2. ^{1}H-NMR spectra of the SH-attached polyesters. The spectra were taken from the ones synthesized by the feed mole ratio, PD/AdA/ThA = 1/0.7/0.3 (red) and 1/0.3/0.7 (blue). Integral values for the signals are provided in Table S1.

Table S1. Attribution of signals and integral values for three polyesters 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	3.34	3.40
H_d	~2.4	1.40	1.40
H_e	2.7-3.0	0.32	0.30
H_f	~3.45	0.13	0.15
H_g	~3.7	0.13	0.15
H_h	3.9-4.1	1.92	2.00

*) feed mole ratio, PD/AdA/ThA, = 1/0.7/0.3

	σ (ppm)	integral found	expected
H_a	1.3-1.4	1.00	1.00
H_b, H_c	1.5-1.6	2.50	2.60
H_d	~2.4	0.60	0.60
H_e	2.7-3.0	0.64	0.70
H_f	~3.45	0.30	0.35
H_g	~3.7	0.30	0.35
H_h	3.9-4.1	1.88	2.00

*) feed mole ratio, PD/AdA/ThA, = 1/0.3/0.7

^{1}H-NMR measurements were also performed to check the progress of Michael addition reaction to attach COOH groups to the polyesters. The spectra for PE-*X* samples are provided in Figure S3 (the explanation for the code, PE-*X*, is indicated in the manuscript). Note that the signals from protons of SH, i.e., H_f in Figure S2, disappeared while new peaks, H_A and H_B (see the proton assignment in Figure S3), appeared after the Michael addition reaction.

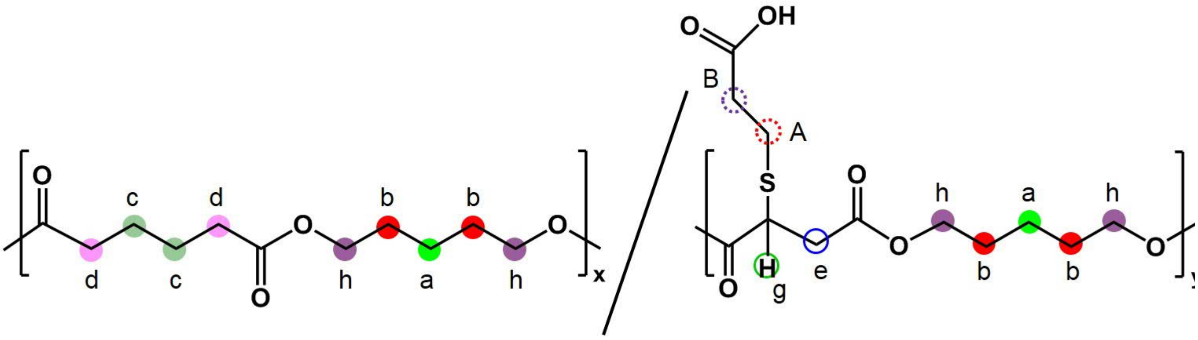


Figure S3. Assignment for proton signals for NMR spectra in Figure S4.

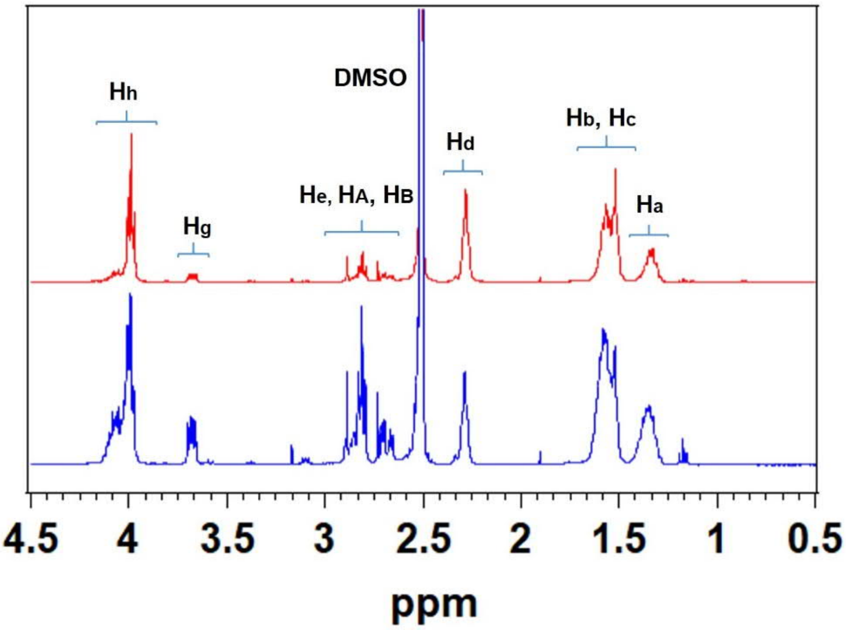


Figure S4. ^{1}H-NMR spectra for the polyesters after Michael addition reaction. The red and blue spectrum corresponds to PE-720 and PE-310, respectively.

From the integral ratios, we confirmed that the unit ratios of PD/AdA/ThA are approximately the same as the feed mole ratios (see Table S1). Then, we estimated the number of SH groups (N_{SH}), which corresponds to N_{COOH} in PE-COOH, from the unit ratios and M_{n} determined by SEC measurements. The procedure of N_{SH} calculation is described below. In the synthesized polyesters, there are two kinds of unit; one is composed of ThA and PD (Unit-ThA), and the other is composed of AdA and PD (Unit-AdA). By using M_{n} from GPC and each unit mass (218.3 for Unit-ThA and 214.3 for Unit-AdA), we obtain the equation S1,

$M_{\mathrm{n}} = 218.3 \times n_{\mathrm{ThA}} + 214.3 \times n_{\mathrm{AdA}}$ (S1),

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

$n_{\mathrm{ThA}} : n_{\mathrm{AdA}} = x : y$ (S2)

, where x and y is the values of the ratio. Finally, the simultaneous equation of S1 and S2 is solved to provide the values of n_{ThA} and n_{AdA}, leading N_{SH} ($= N_{\mathrm{COOH}} = n_{\mathrm{ThA}}$).

2. FT-IR spectra for PE-COOH

Figure S5 shows FT-IR spectra for two PE-COOHs to check the existence of COOH groups.

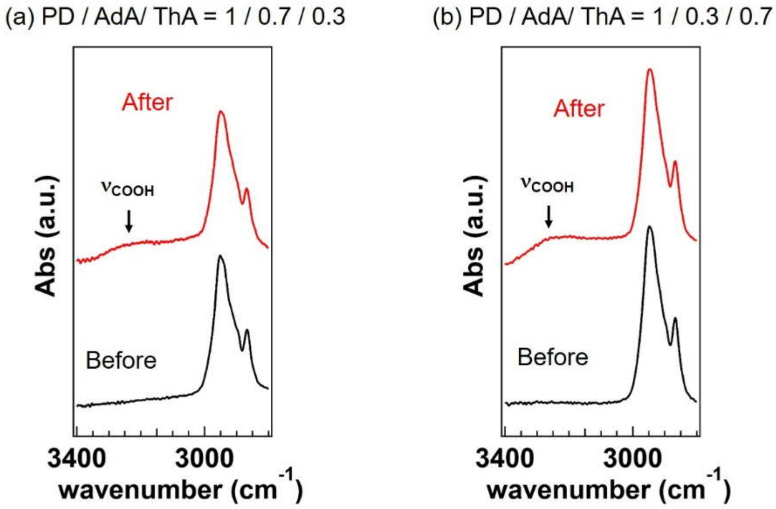


Figure S5. FT-IR spectra for two PE-COOHs at the region for COOH peaks. In the spectra, ν_{COOH} represents the stretching vibration of OH in COOH.

3. TGA thermograms

Figure S6a and S6b represents the TGA thermograms for PE-COOH and cross-linked samples.

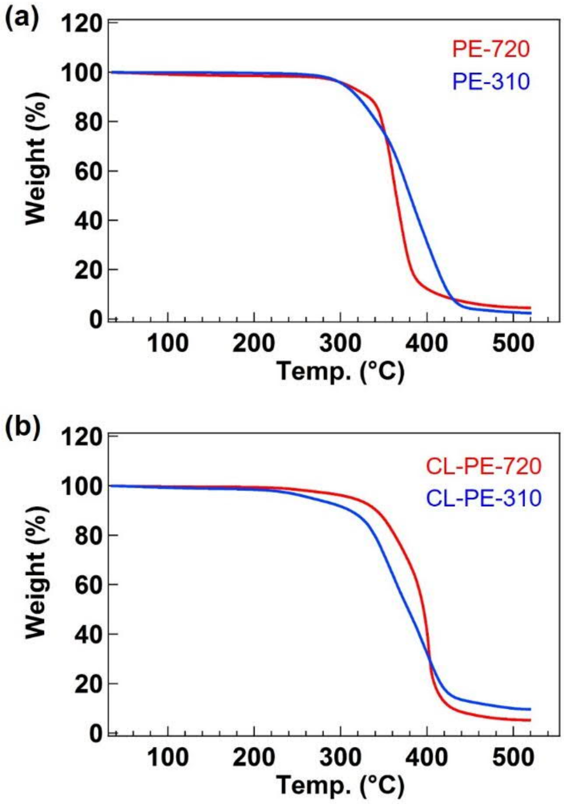


Figure S6. TGA thermograms for (a) PE-*X* (before cross-linking) and (b) CL-PE-*X* (after cross-linking).

4. FT-IR spectra for samples after cross-linking reaction

Figure S7 represents FT-IR spectra for samples before and after cross-linking reaction. The explanation and assignment for the signals is provided in the manuscript.

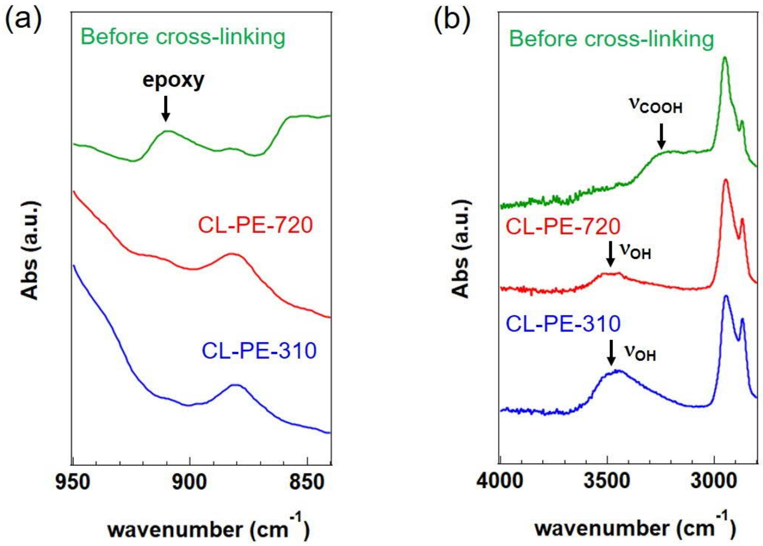


Figure S7. Changes of FT-IR spectra after cross-linking reaction at (a) epoxy group region, and (b) COOH and OH group region. In the spectrum (a) , an arrow indicates the signal from expoxy while ν_{COOH} and ν_{OH} represents the stretching vibration of COOH and OH, respectively, in the sepctrum (b).

5. Changes of FT-IR spectra after long time cross-linking reaction

Figure S8 show the changes of FT-IR spectra for long cross-linking reaction time. The sample measured was the mixture of PE-720, diepoxy cross-linker, $Zn(OAc)_2$. The wavenumber region between 1000 and 1300 cm^{-1} is mainly composed of the vibrarion signal from O-H bending of alcohol and C-O streching of ester C-C(=O)-O, which are expected to increase with the progress of epoxy-COOH cross-linking reaction. Ths intensity of this region increased from the spectra of 1 h reaction time to 2 h reaction time, but the intensity did not change from 2 h reaction time to 5 h reaction. The result indicates 4 h cross-linking reaction time is sufficient.

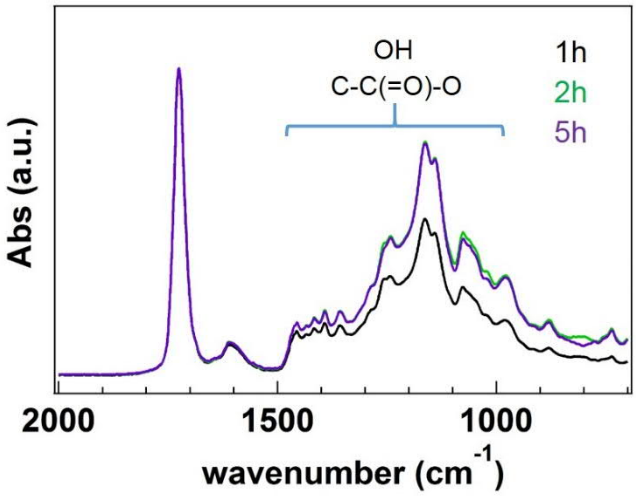


Figure S8. Changes of FT-IR spectra for long cross-linking reaction time at 120 °C**.** The sample measured was the mixture of PE-720, di-epoxy cross-linker (1,4-butanediol diglycidyl ether), $Zn(OAc)_2$.

6. Swelling tests

We conducted the swelling tests to determine the gel fraction (f_{gel}) depending on the cross-liking reaction time. The data was taken for both PE-COOHs. The reaction was carried out at 120 ºC with various reaction time. After the reaction, the samples were immerced in the solvent ($CHCl_3$) for 3 days, where the solvents were replaced with new one every one day. The remaining sample after 3 days was dried, and the dried mass (m_{dry}) was compared with the initial mass (m_{i}). The f_{gel} was estimated by the relationship (S1).

$$f_{gel} = \frac{m_{dry}}{m_i} \times 100 \qquad \text{(S1)}$$

The values of f_{gel} (%) are plotted as a function of reaction time in Figure S9, where the amount of catalysts were considered for calculation of f_{gel}.

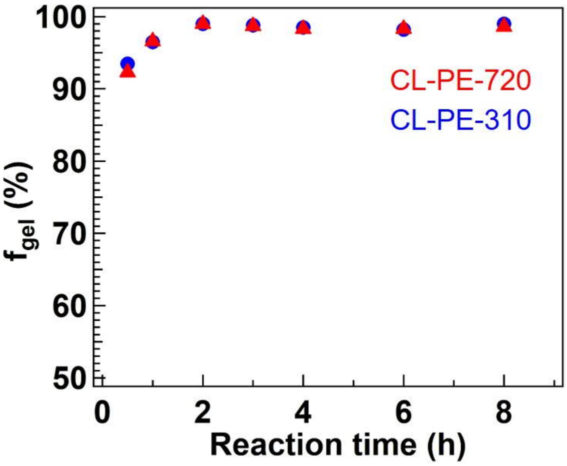


Figure S9. Plots of f_{gel} as a function of cross-linking reaction time.

7. DSC curves

The glass transition temperature (T_g) was evaluated by DSC. The second heating thermograms are shown in Figure S10. The T_g value is -39 °C and -18 °C for CL-PE-720 and CL-PE-310, respectively.

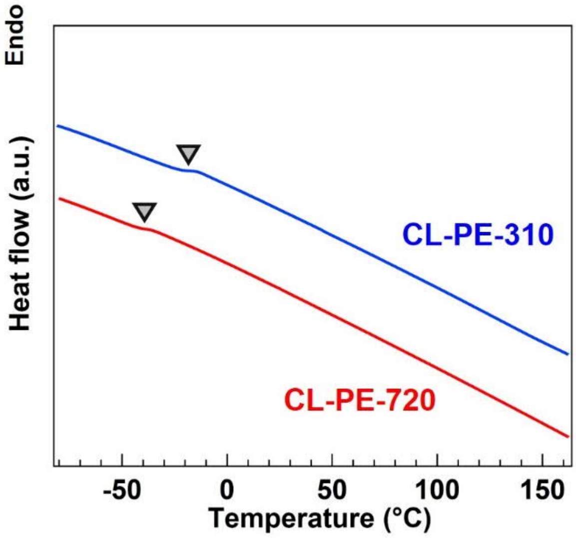


Figure S10. DSC thermograms on 2nd heating for CL-PE-310 (blue) and CL-PE-720 (red). The arrows represent the T_g position.

8. Dynamic temperature ramp rheology

We conducted the rheology test with a dynamic temperature ramp mode by using a uniaxial-type rheometer (RSA-G2, TA instruments). The measurements were performed with a frequency of 1 Hz, from -50 ºC to 150 ºC for CL-PE-310 and from -70 ºC to 150 ºC for CL-PE-720 at a temperature ramp rate of 5 ºC/min, under N_2 gas atmosphere, in the linear regime. The strage modulus (*E'*) and loss modulus (*E"*) are shown in Figure S11.

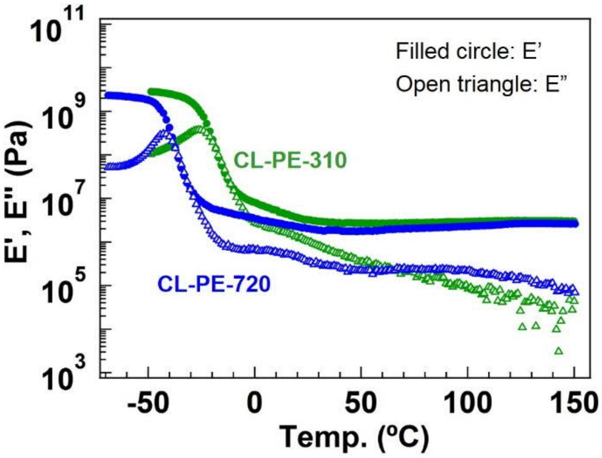


Figure S11. The *E'* and *E"* spectra for CL-PE-310 and CL-PE-720 as a function of temperatures.

9. SAXS profiles

Figure S12 represents the SAXS profiles at room temperature for CL-PE-720 (red) and CL-PE-310 (blue).

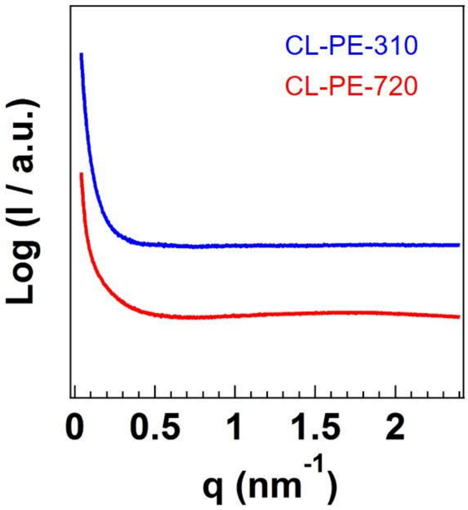


Figure S12. SAXS profiles at room temperature for CL-PE-720 (red) and CL-PE-310 (blue).

10. Model analysis of network quality based on the Young's modulus

We discuss the quality of cross-linked network based on the model analyses for the experimental modulus. Firstly, the modulus in the affine network model (E_{aff}) is expressed as equation (S2) with using molecular weight between cross-links (M_{X}),[1] where the Poisson ratio $\nu = 0.5$ is used in the relationship of $E = 2G\,(1 + \nu)$.

$$\boldsymbol{E_{aff}} = \frac{\boldsymbol{\rho}}{\boldsymbol{M_x}}(\boldsymbol{3RT}) \qquad \text{(S2)}$$

In equation (S2), R, T and ρ represents the gas constant, the measurement temperature, and the density, respectively. There is also another modified model, known as the phantom network model, with considering the fluctuation of cross-link points during the elongation. In the phantom network model, the modulus (E_{ph}) is expressed as equation (S3),[1]

$$\boldsymbol{E_{ph}} = \frac{\boldsymbol{\rho}}{\boldsymbol{M_x}}(\boldsymbol{3RT})\left(\boldsymbol{1} - \frac{\boldsymbol{2}}{\boldsymbol{f}}\right) \qquad \text{(S3)}$$

, where f is the number of branch at a cross-link point (f = 3 in the present design). In this molecular design, M_{X} can correspond to M_{COOH}, if the ideal network is formed where all COOH groups in PE-COOH are intermolecularly reacted with the diepoxy cross-linkers. Therefore, we estimated the ideal elastic modulus based on the affine network model ($E_{\mathrm{ideal,aff}}$) and on the phantom network model ($E_{\mathrm{ideal,ph}}$) by substituting $M_{\mathrm{X}} = M_{\mathrm{COOH}}$ for equation (S2) and (S3), where the contribution from the inorganic catalyst was not taken into account due to the very low weight concentration. Fig. S13 compared the experimental E_{Y} (red plots) with $E_{\mathrm{ideal,aff}}$ (purple) and $E_{\mathrm{ideal,ph}}$ (green) as a function of M_{COOH}.

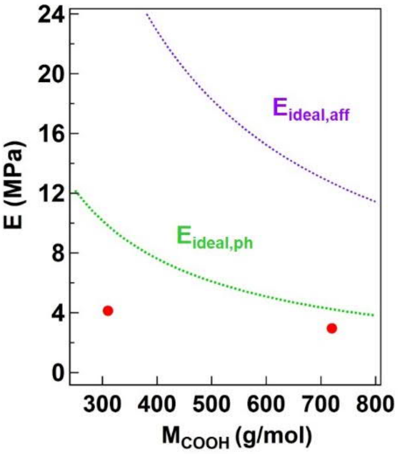


Figure S13. Comparison of moduli (red) of the present materials with ideal values based on the affine network model ($E_{\mathrm{ideal,aff}}$, purple) and phantom network model ($E_{\mathrm{ideal,ph}}$, green) as a function of M_{COOH} in the precursor PE-COOH.

[1] M. Rubinstein and R. Colby, *Polymer Physics*, Oxford University Press, New York, 2003.

11. Dilatometry test for control sample with no catalyst

Figure S14 represent the changing behavior of sample length during the temperature increase for the control cross-linked sample from PE-310 that contains no trasn-esterification catalysts, where the y-axis indicates the sample length on measurements normalized by the length at 100 °C.

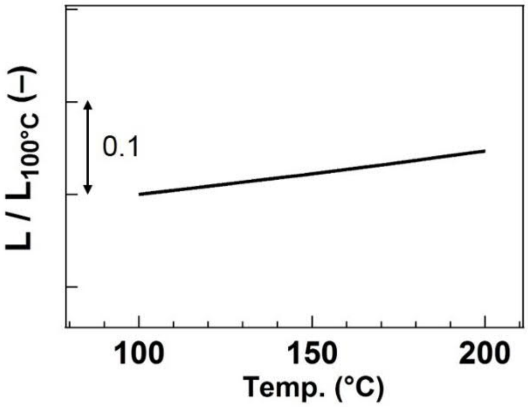


Figure S14. Changing behavior of sample length during the temperature increase for the control cross-linked sample that contains no trasn-esterification catalysts. The y-axis indicates the sample length on measurements normalized by the length at 100 °C.

12. Model analysis of stress-relaxation curves based on KWW equation

The experimental stress-relaxation spectra were fitted with Kohlrausch-Williams-Watts (KWW) equation (S4)[2] as shown in Figure S15,

$$\sigma(t) = (\sigma_0)\exp\left(-\frac{t}{\tau^*}\right)^{\beta} \qquad \text{(S4)},$$

, where t is the experimental time while σ_0 is the stress at t = 0. The parameter β in equation (S4) represents the degree of distribution narrowness, and τ^* is the characteristic relaxation time. These parameters used for the fitting are summarized in Table S2 and S3.

2) G. Williams, D. C. Watts, S. B. Dev, A. M. North, *Trans. Faraday Soc.* 1971, **67**, 1323-1335.

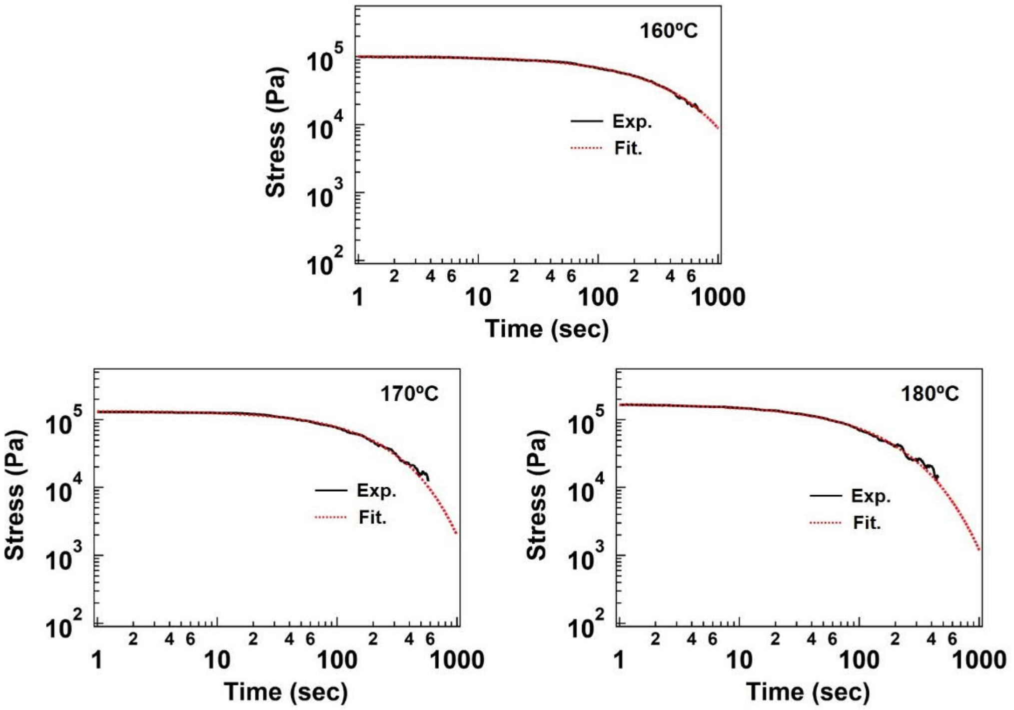
Table S2. The parameters used for KWW model fitting for CL-PE-710.

	τ^* (sec)	β (–)
160 °C	328	0.80
170 °C	198	0.89
180 °C	127	0.77

Table S3. The parameters used for KWW model fitting for CL-PE-320.

	τ^* (sec)	β (–)
160 °C	173	0.72
170 °C	109	0.71
180 °C	66.6	0.82

(a) CL-PE-720



(b) CL-PE-310

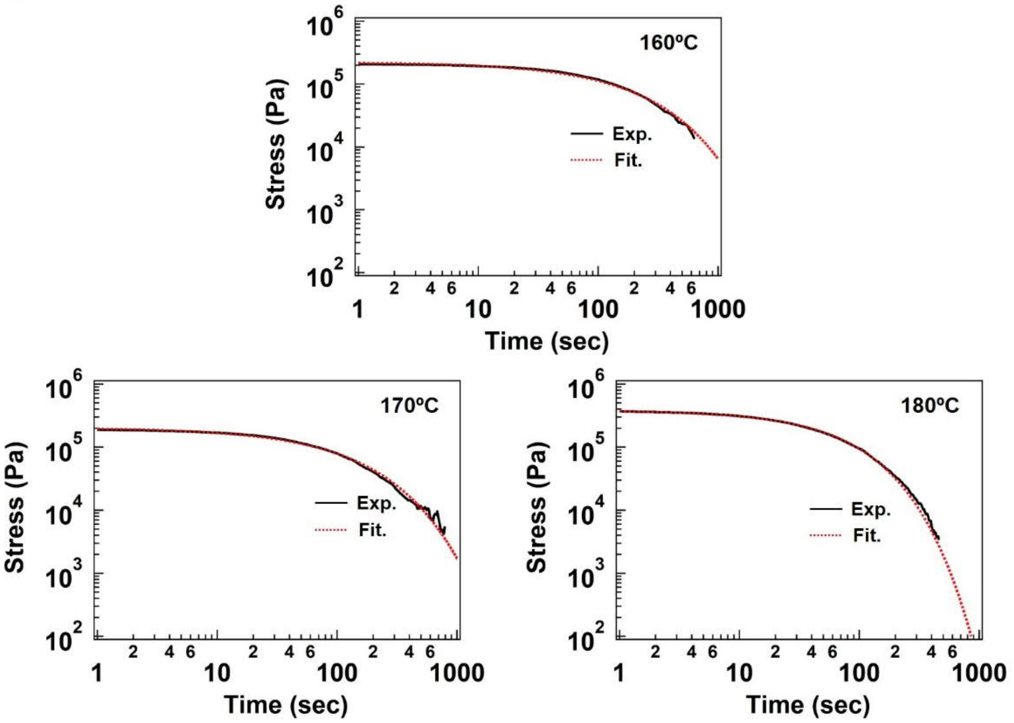


Figure S15. KWW model fitting for the stress-relaxation spectra of (a) CL-PE-720 and (b) CL-PE-310. The black solid curve and red dotted curve respectively corresponds to the experimental curve and fitting curve.

13. FT-IR spectra for recycled samples

Figure S16 represents the FT-IR spectra for recycled samples. The recycle procedure is provided in the manuscript.

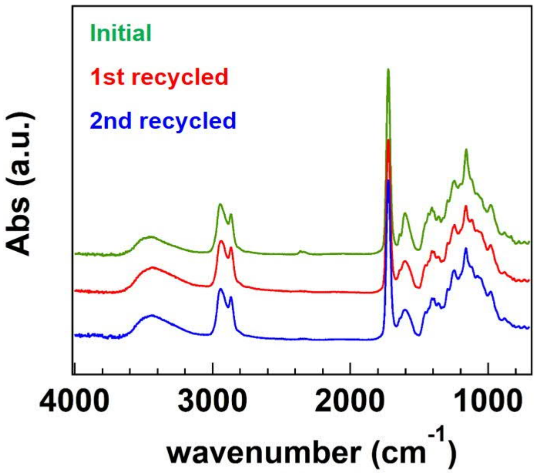


Figure S16. ATR FT-IR spectra for the initial, 1st recycled, and 2nd recycled samples (CL-PE-310).