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Supplementary Information

One-shot transformation of ordinary polyesters into vitrimers: Decomposition-triggered cross-linking and assistance of dynamic covalent bonds

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1. Experiment

Materials.

PE was kindly supplied by TOYOBO CO., LTD. The epoxy cross-linker, 4-epoxy, was purchased from Sigma-Aldrich. DBU was purchased from TCI. Before preparation, PE was dried in vacuum at 100 °C for 12 h. Other chemicals and organic solvents were used as received.

Blend preparation and cross-linking.

PE, 4-epoxy, and DBU were dissolved by THF, individually. Each THF solution was mixed in a Teflon-made mold. THF was evaporated on a hot stage at 25 °C for 24 h and vacuum oven dried at 25 °C for 10 h, and then the bulk mixture was cured at 200 °C under vacuum.

Polymer characterization.

A number average molecular weight (M_n) was determined via size-exclusion chromatography (SEC), using Shodex-gel columns K-803, K-804, and K-805 (Shodex), equipped with a LC-20AD pump system and a RID-20A RI detector (SHIMADZU). The column temperature was 40 °C, and tetrahydrofuran (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 of M_n.

Estimation of gel fraction.

Swelling tests were conducted to assess the variation of gel fraction depending on the reaction time. The samples were immersed in THF (good solvent for the polyester used), and the solvent was replaced with new one at the interval of 10 h for three times. The remaining solid (remaining gel component) was dried to weight the mass. The mass of remaining gel component (m_g) was compared with the initial mass (m_i) to obtain the gel fraction, according to, $\text{gel fraction (\%)} = \frac{m_g}{m_i} \times 100$.

Spectroscopy.

The generation of functional groups by the hydrolysis and the progress of epoxy-opening reaction were investigated via FT-IR spectroscopy. The measurements were conducted at 25 °C using an FT/IR 430 spectrometer with an attenuated total reflectance (ATR) attachment (JASCO Co.).

TGA and DMA measurements.

TGA was performed to check the thermal decomposition temperature using a TG/DTA7300 (Hitachi High-Tech). The sample was heated from 30 °C to 550 °C at a rate of 10 °C/min, using a ceramic crucible. The investigation was conducted for 10 mg sample under N_2 gas flow (20 mL/min).

The plateau modulus and the flow properties were investigated with DMA using a uniaxial rheometer (DMS6100; Hitachi High-Tech) in a temperature sweep mode. For the measurements, strip-shaped samples with approximately 1 mm thickness, 4 mm width, and 20 mm length were prepared using a razor blade. The frequency, f, was fixed to 1 Hz, and a constant strain of 0.1% was applied. The temperature was raised from −50 °C to 200 °C at a ramp rate of 3 °C/min. All the measurements were performed under N_2 gas flow.

Rheology.

Frequency sweep rheology was performed for the original PE to estimate the entanglement molecular weight by using a shear-type rheometer (MCR302; Anton Paar) and 8 mm parallel plates. The temperature was ranged from 20 to 110 °C with an interval of 10 °C, and the frequency range was $0.1 \leq \omega \leq 100$ (ω represents the angular frequency) All the measurements were performed in the linear regime. The gap between the plates was set to be approximately 1 mm. The master curve was constructed with a reference temperature of 30 °C. The measurements were all conducted under N_2 gas.

The gelation mechanism was also assessed using frequency sweep rheological measurements. The samples after various t_r values were measured using a shear-type rheometer (MCR302; Anton Paar) and 8 mm parallel plates. The gap between the plates was set to be approximately 1 mm. The frequency sweep measurements were conducted at 80 °C (>> T_g) within the range of $0.1 \leq \omega \leq 100$. The measurements were all conducted under N_2 gas.

The bond exchange properties of the cross-linked samples were assessed with stress relaxation tests using a shear-type rheometer (MCR302; Anton Paar) and 8 mm parallel plates. Disc-shaped samples with 8 mm diameter and approximately 1 mm thickness were prepared using a cutting die. The tests were performed at several temperatures, 170 to 210 °C (with an interval of 10 °C) under application of 5% strain (linear regime) and 5 N normal force. All the measurements were made under N_2 gas flow.

Tensile properties.

The tensile properties were measured using an AGS-500NX (Shimadzu). Dumbbell-shaped samples were prepared using a cutting die, and the thickness, gage length, and gage width were set to approximately 1, 13, and 4 mm, respectively. The tests were performed at an elongation rate of 10 mm/min at 25 °C.

2. Master curve of the original PE

We performed the frequency sweep rheology for the original PE to construct the master curve (Figure S1). From the master curve, we estimated the entanglement molecular weight (M_e) based on the G' value at the minimum tanδ (G'_{min}) in the plateau region, according to the simple equation,

$$M_e = \frac{\rho RT}{G'_{min}} \quad \text{(S1)}$$

where ρ, R, and T represent the density, gas constant (8.314 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$), and absolute temperature, respectively. The estimated M_e was 3.1k.

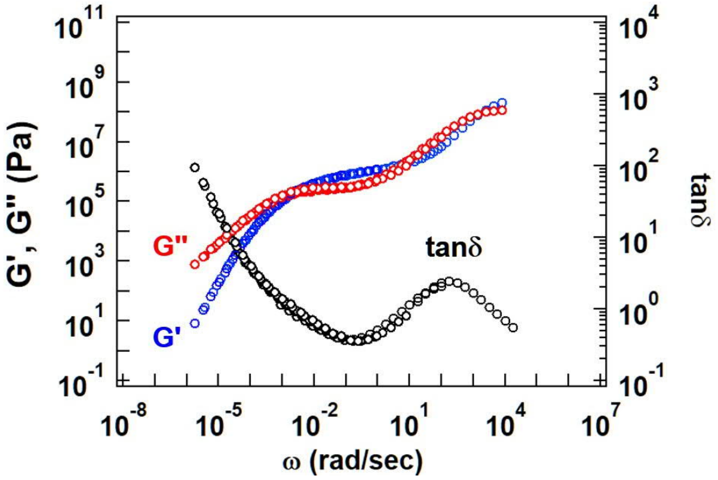

Figure S1. Master curve of the original PE constructed by the time-temperature superposition with a reference temperature of 30 °C.

3. TGA thermogram for cross-linked PE

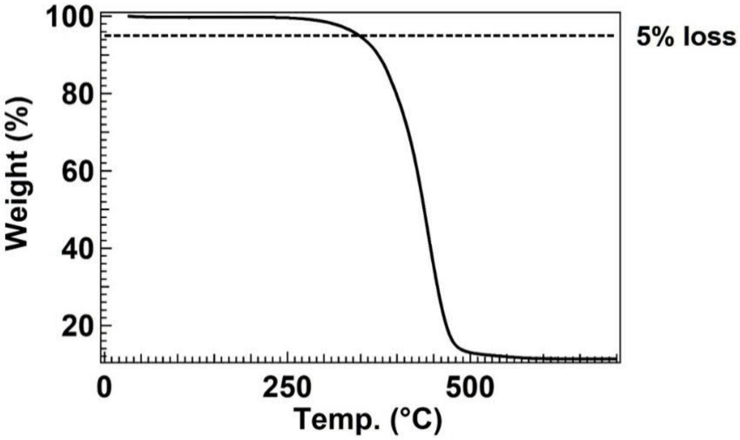

Figure S2. TGA thermogram for the cross-linked PE.

4. Tensile test

Tensile properties were compared between the original PE and the cross-linked PE in Figure S3.

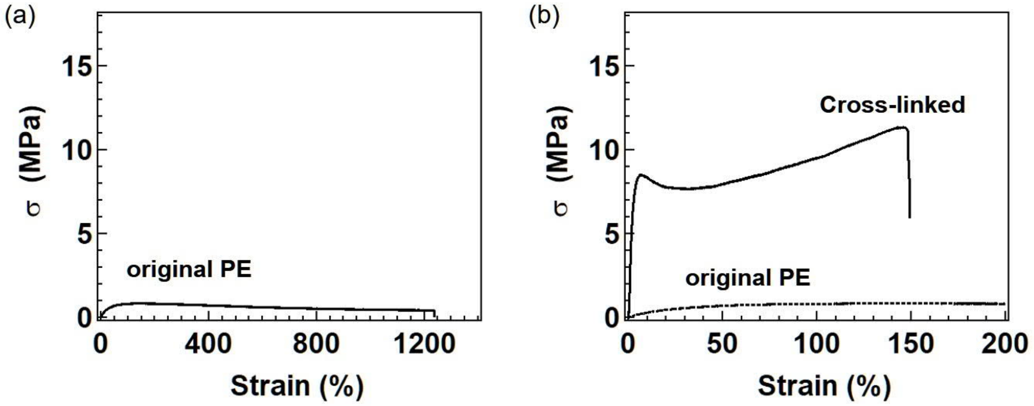

Figure S3. (a) Stress-strain curves for the original PE and (b) the comparison with cross-linked PE samples in the low strain region.

5. Reproducibility check of the cross-linking reaction

Three different trials of the cross-linking reaction were made to check the reproducibility. The samples were measured for DMA, and the data are shown in Figure S4.

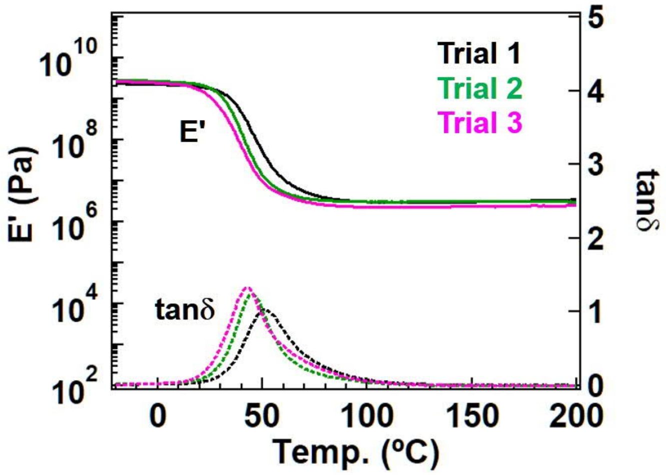

Figure S4. Storage modulus (*E′*) and loss tangent (tanδ) as a function of temperatures for three different trials with the same cross-linking process.

6. SEC of PE after solvent casting and heating

We assessed the possibility of hydrolysis of PE in the presence of base catalyst, DBU, in solution state. PE and DBU were homogeneously blended in THF, and casted at 25 °C for 24 h under air. SEC curves after the solvent casting is provided in Figure S5 and compared with the curve of original PE. The peak was shifted to a longer elution time, and the M_n value was lowered to 17 k from the original 37 k. The peak was further shifted to a longer elution time after keeping the bulk mixture at 200 °C for 2 h, where the M_n was still lowered to 12k.

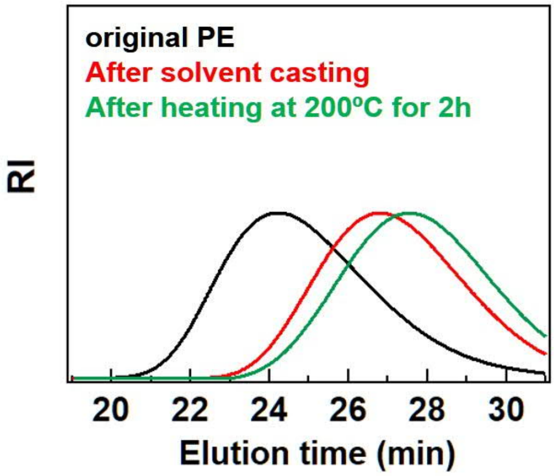

Figure S5. SEC curves for original PE, and the samples after solvnet casting and after heating in bulk at 200 °C for 2 h.

7. FT-IR data of PE after solvent casting and heating

The changes of FT-IR spectra after solvent casting and heating are investigated (Figure S6). The sample and thermal treatment condition was the same as described in the previous page (6. SEC of PE after solvent casting and heating). After solvent casting, a new signal appeared at ca. 1650 cm^{-1} and the intensity was increased after heating in bulk at 200 °C for 2 h. According to the literature, this signal is derived from OH and COOH groups.$^{S1-S4}$ The data indicated the occurrence of hydrolysis of PE, which generated the reactive functional groups.

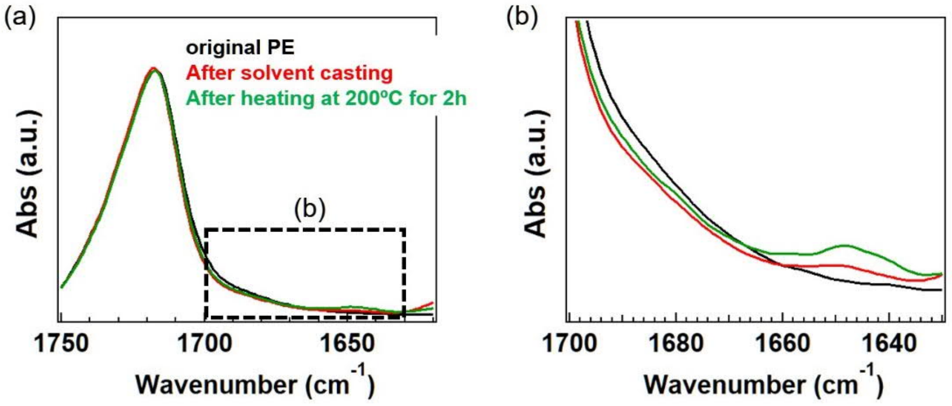

Figure S6. Variation of FT-IR spectra after solvent casting and heating. The spectra are normalized using the signal from ester bonds (1720 cm^{-1}).

S1) Tang, Z. H., Liu, Y. J., Guo, B. C. & Zhang, L. Q. Malleable, Mechanically Strong, and Adaptive Elastomers Enabled by Interfacial Exchangeable Bonds. *Macromolecules* **50**, 7584-7592 (2017).

S2) Sinh, L. H. *et al.* Curing behavior, thermal, and mechanical properties of epoxy resins cured with a novel liquid crystalline dicarboxylic acid curing agent. *Polym. Eng. Sci.* **54**, 695-703 (2014).

S3) Lyu, Z. Y., Sun, S. Q. & Wu, T. F. Highly stretchable covalent adaptive networks enabled by dynamic boronic diester linkages with nitrogen → boron coordination. *J. Polym. Sci.* **60**, 72-80 (2022).

S4) Nikolic, G. *et al.* Fast Fourier Transform IR Characterization of Epoxy GY Systems Crosslinked with Aliphatic and Cycloaliphatic EH Polyamine Adducts. *Sensors* **10**, 684-696 (2010).

8. Summary of rheology spectra during the thermal treatment

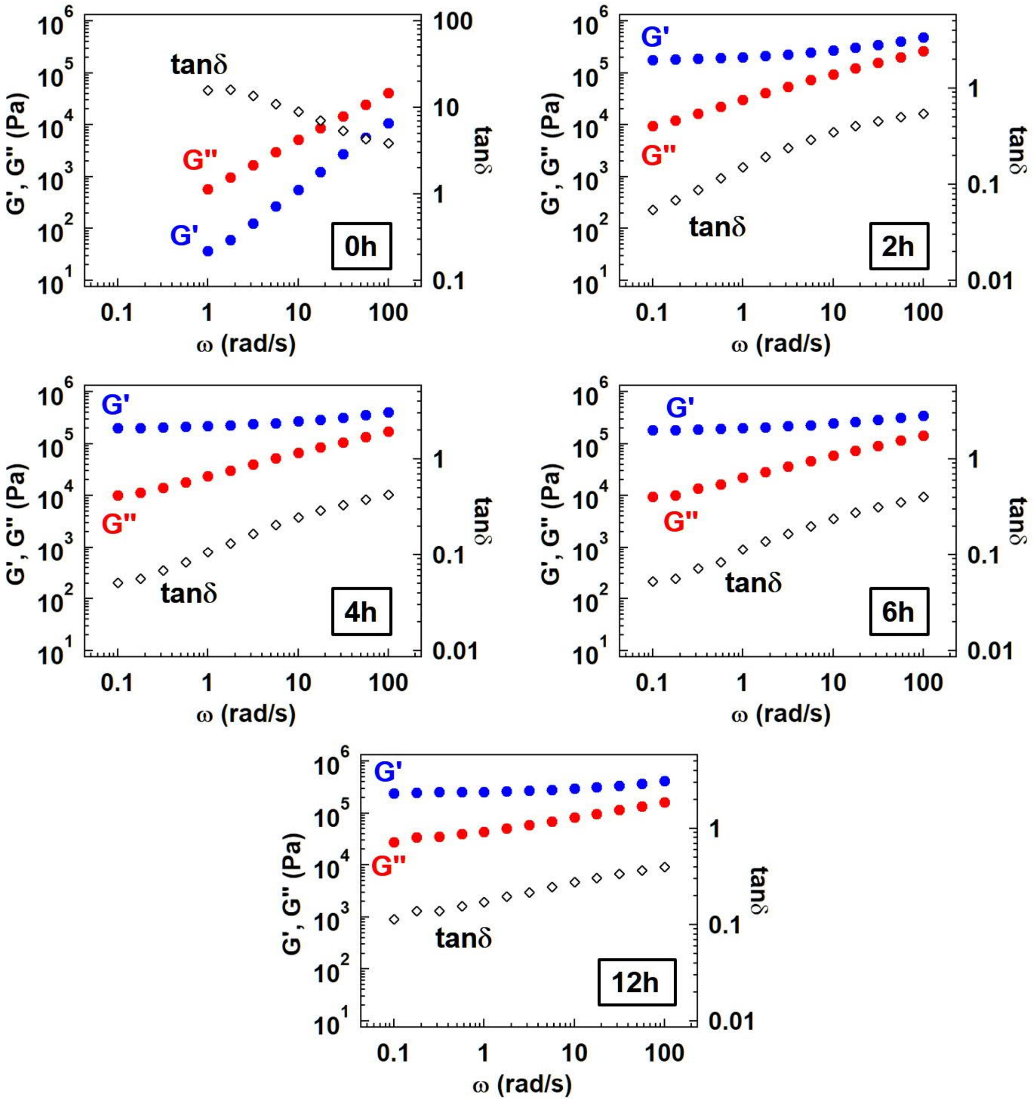

Figure S7. Summary of rheology spectra at different t_r. The time (0 h, 2 h, 4 h, 6 h, and 12 h) in each graph represents t_r.

9. Comparison of rheology spectra between the original PE and the sample at $t_r = 0$ h

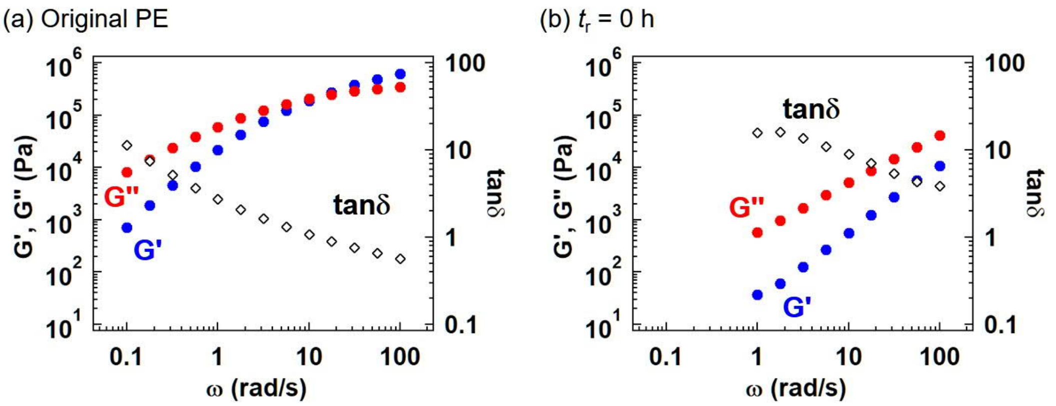

Figure S8. Comparisn of rheology spectra between the original PE and the sample at $t_r = 0$ h. Note that the sample at $t_r = 0$ corresponds to the sample right after the solvent casting.

10. Variation of *G′* at different t_r

Figure S9 represents the variation of *G′* at different t_r. *G′* was drastically changed in the initial 2 h, whereas there was slight increase at longer t_r.

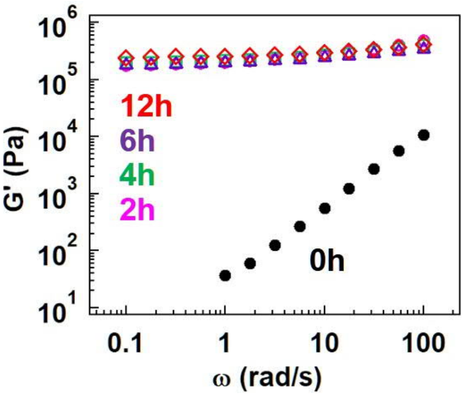

Figure S9. Variation of *G′* at different t_r, where the values, 0 h, 2 h, 4 h, 6 h, and 12 h, represents t_r.

11. Confirmation of the linear regime in stress relaxation tests

Figure S10 represents the strain sweep curves measured at various temperatures.

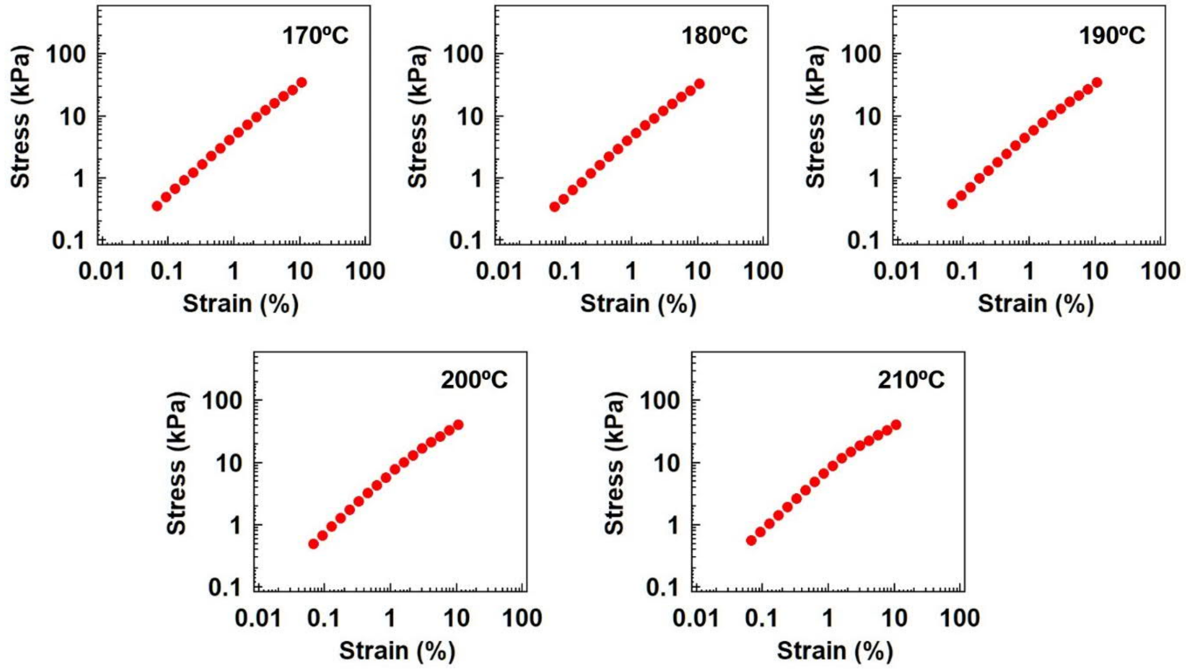

Figure S10. Strain sweep curves at various temperatures for the sample after thermal cross-linking.

12. Strain-sweep curves for the samples before and after stress relaxation tests

Representative data of strain-sweep curves for the samples before and after stress relaxation tests at 200 ºC are shown in Figure S11.

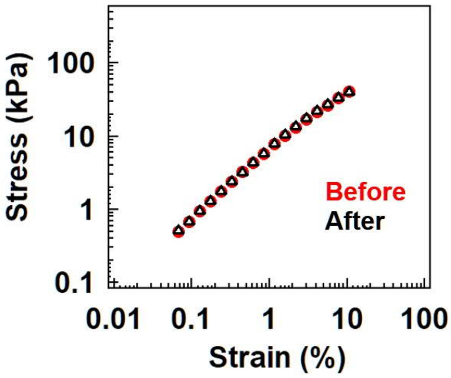

Figure S11. Strain-sweep curves for the samples before and after stress relaxation tests at 200 ºC.

13. Fitting parameters for stress relaxation

Table S1. The fitting parameters for stress-relaxation curves of the cross-linked PE

	τ* (s)[a]	β(-)[b]	<τ*> (s)[c]
170 °C	17754	0.77	20656
180 °C	11073	0.71	13830
190 °C	6212	0.73	7576
200 °C	3690	0.59	5697
210 °C	1964	0.69	4406

[a]Characteristic relaxation time. [b]Degree of distribution narrowness of τ*. [c]Average relaxation time (<τ*>) estimated according to equation (3) in the main text.

14. Temperature-ramp rheology for the sample before and after recycling

Figure S12 compared the data of temperature-ramp rheology for the pristine and recycled sample.

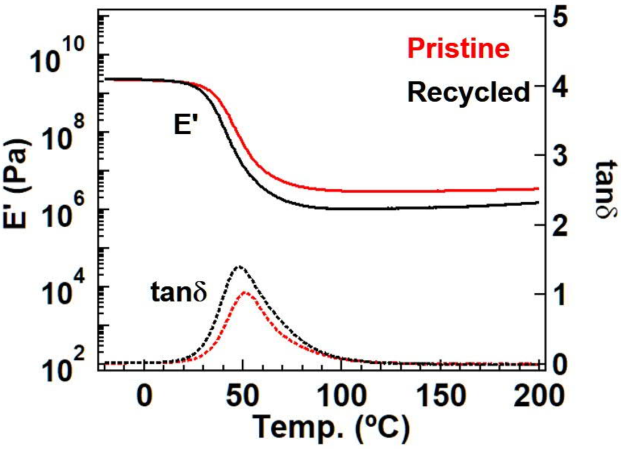

Figure S12. Comparison of E' and tanδ for the pristine sample and recycled sample.

15. SEC curve for the unhydrolyzed PE

Figure S13 show the comparison of SEC curves between the original PE and the PE after quick blending for the control experiment (see the procedure in the main text). The data revealed that the change of peak top position was very small, and the M_n (~ 36 k) after the quick blending was very similar to that of the original PE (~ 37 k).

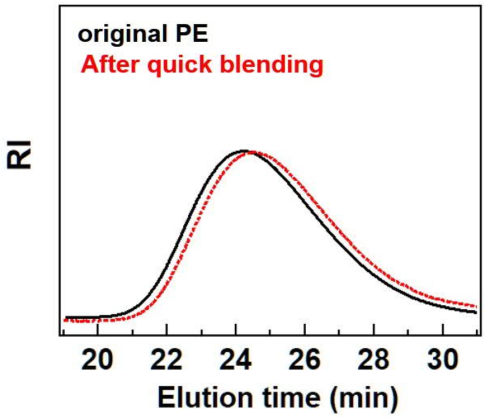

Figure S13. Comparison of SEC curves between the original PE and the PE after quick blending for the control experiment.