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Supporting Information

Design and Basic Properties of Polyester Vitrimers Combined with an Ionomer Network

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1. ^{1}H-NMR

^{1}H-NMR measurement was performed to confirm the synthesis of PE-SH. The spectrum of PE-SH 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 reaction 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.

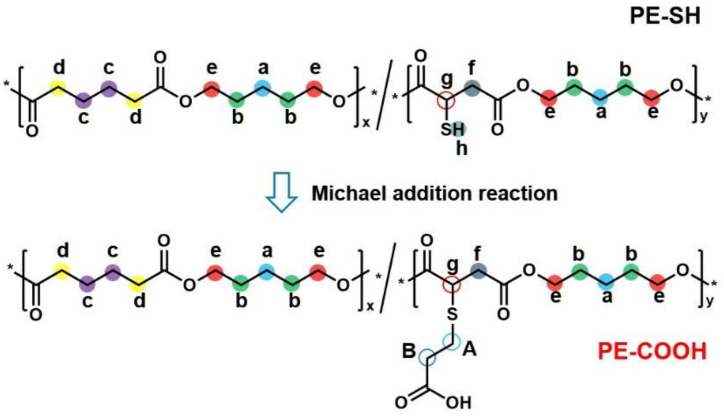

Figure S1. Assignment for proton signals for ^{1}H-NMR spectra in Figure S2.

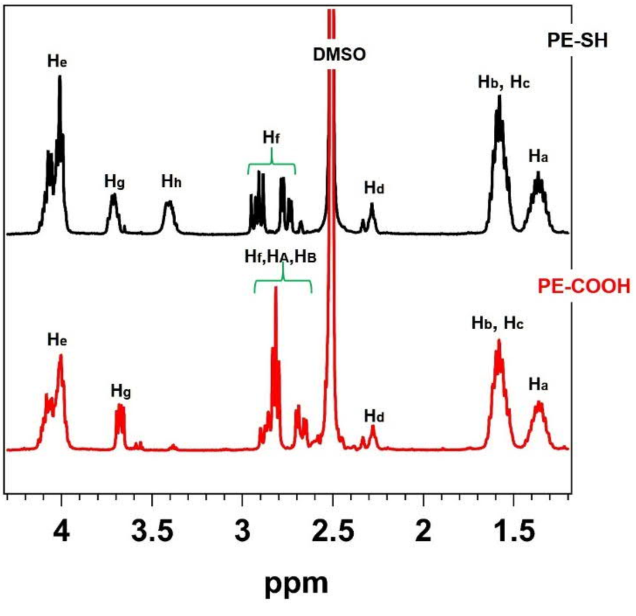

Figure S2. ^{1}H-NMR spectra for PE-SH (black) and PE-COOH (red).

Table S1. Attribution of signals and integral values for PE-SH

	σ (ppm)	integral found	expected
H_a	1.3-1.4	1.00	1.00
H_b, H_c	1.5-1.6	1.95	2.20
H_d	~2.4	0.20	0.20
H_f	2.7-3.0	0.80	0.90
H_h	~3.45	0.46	0.45
H_g	~3.7	0.40	0.45
H_e	3.9-4.1	1.76	2.00

From the integral ratios, it was confirmed that the unit ratio of PD/ADA/TMA (= 1/0.10/0.9) was the same as the feed mole ratio (PD/ADA/TMA = 1/0.1/0.9). We estimated the number of SH groups (N_{SH}), which corresponds to N_{COOH} in PE-COOH, from the unit ratios and M_{n} (~ 11000 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,

$M_{\mathrm{n}} = 218.3 \times n_{\mathrm{TMA}} + 214.3 \times n_{\mathrm{ADA}}$ (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

$n_{\mathrm{TMA}} : n_{\mathrm{ADA}} = 9 : 1$ (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 $n_{\mathrm{TMA}} = N_{\mathrm{SH}} = 45$ and $n_{\mathrm{ADA}} = 9$.

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,

$M_{\mathrm{n}} = 290.3 \times n_{\mathrm{TMA}} + 214.3 \times n_{\mathrm{ADA}}$ (S3)

, leading to M_{n} for PE-COOH ~ 15000 g/mol.

2. Additional FT-IR data

The whole FT-IR spectra for PE-COOH and PE-IV are shown in Figure S3a. In Figure S3b, ν_{COOH} and ν_{OH} represents the stretching vibration of COOH and OH group, respectively. The disappearance of COOH signal and appearance of OH signal were noticeable by comparing the spectra of PE-COOH and PE-IV. In Figure S3c, the red spectrum corresponds to the blend sample of PE-COOH and the diepoxy cross-linker, where the signal from epoxy was clearly observed. For PE-IV, the epoxy signal disappeared,[S1,S2] meaning the epoxy was consumed for the cross-linking reaction. These FT-IR data support the progress of epoxy-COOH reaction.

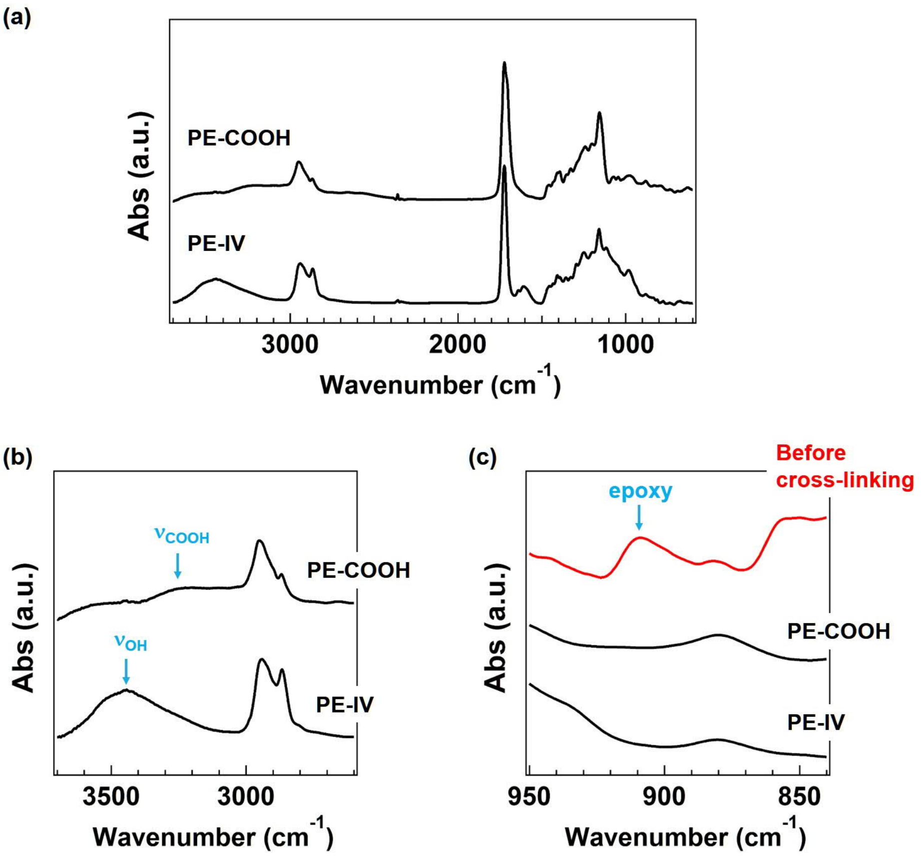

Figure S3. FT-IR data (a) at the whole region, (b) at the OH and COOH peak region, and (c) at the epoxy region.

S1) Hayashi, M.; Yano, R.; Takasu, A. *Polym. Chem.* **2019,** 10 (16), 2047-2056.

S2) Hayashi, M.; Yano, R. *Macromolecules* 2020, 53 (1), 182-189.

3. Macroscopic appearance of the cross-linked samples

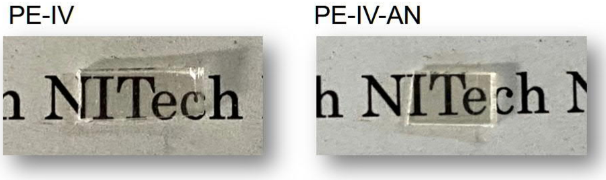

Figure S4. Macroscopic appearance of the cross-linked samples

4. Effect of annealing time on the ion aggregation

Figure S5 displays the variation of SAXS spectra for PE-IV depending on the annealing time at 180 °C.

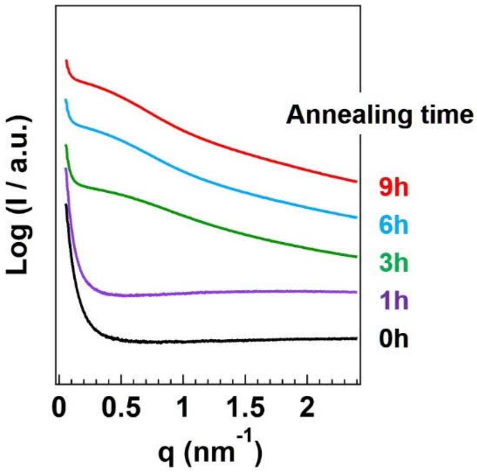

Figure S5. Variation of SAXS spectra for PE-IV depending on the annealing time at 180 °C.

5. Tensile properties

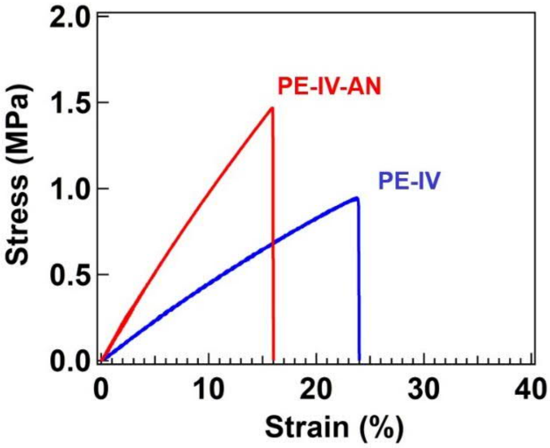

Figure S6. Stress-strain curves for PE-IV and PE-IV-AN.

6. DSC thermograms

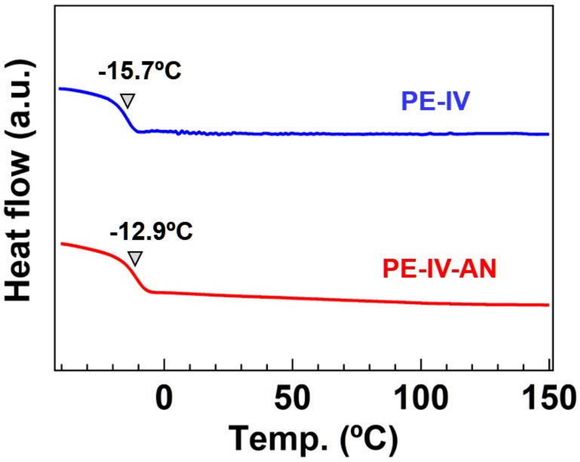

Figure S7. 2nd heating DSC thermograms for PE-IV and PE-IV-AN.

7. Summary of fitting parameters for stress-relaxation

Table S2. Summary of τ^* and β for the fitting and $< \tau^* >$

	τ^* (sec) [1] 180 °C / 170 °C / 160 °C	β (-) [2] 180 °C / 170 °C / 160 °C	$< \tau^* >$ (sec) [3] 180 °C / 170 °C / 160 °C
PE-IV	409 / 897 / 2105	0.76 / 0.72 / 0.71	481 / 1109 / 2629
PE-IV-AN	3789 / 18116 / 62500	0.59 / 0.53 0.51	5828 / 32987 / 122746

1) Characteristic relaxation time. 2) Relaxation time distribution based on the KWW equation. 3) Calculated by equation (2) in the main test.

8. Effect of annealing time on the stress-relaxation

In Figure S8, the stress relaxation data measured at 180 °C is shown for samples after thermal annealing of 0 h, 2 h, and 6 h, in which the samples after 0h and 6h annealing corresponds to PE-IV and PE-IV-AN, respectively. Due to the limitation of sample amounts, only one measurement at 180 °C was conducted for the sample after 2h annealing. The data clearly indicated that the annealing time is correlated with the relaxation rate.

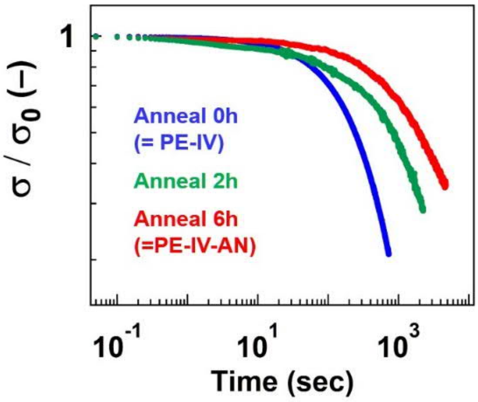

Figure S8. Stress relaxation curves for samples after thermal annealing of 0h, 2h, and 6h, in which the samples after 0h and 6h annealing corresponds to PE-IV and PE-IV-AN, respectively.

9. SAXS profile of PE-I after annealing

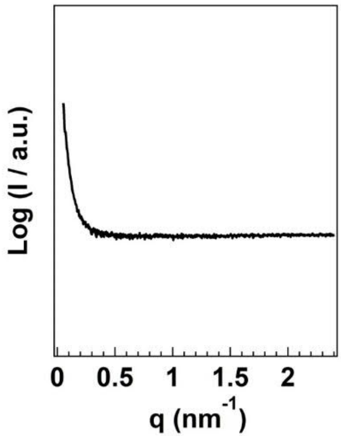

Figure S9. SAXS profile of PE-I after annealing at 180 °C for 6 hours.

10. Preparation and stress-relaxation property for PE-I-photo

The precursor polymer for PE-I-photo was synthesized similarly to the synthesis of PE-COOH (see the whole synthesis scheme in Figure S10). Acrylic acid and 2-hydroxyethyl acrylate were first reacted with the polyester bearing thiol side groups via Michael addition reaction, resulting in the polyester with COOH and OH side groups. The obtained polymer had the mole ratio of acrylic acid (X) and 2-hydroxyethyl acrylate (Y) as X : Y ~ 2 : 8. Cinnamoyl chloride was then reacted with OH groups via esterification reaction. In addition, the remaining COOH groups were all neutralized with Zn^{2+} in the same way as the synthesis of PE- I. The obtained polymer possesses neutralized COOH groups and photo cross-linkable cinnamate groups. Note that the unit ratio of neutralized COOH groups : cross-linkable groups was the same as that in PE-I used for the preparation of PE-IV. For the cross-linking, UV light (365 nm, 40 mW/cm^2) was irradiated at room temperature for 30 min. The progress of photo cross-linking was confirmed by FT-IR and swelling test. The cross-linked sample, abbreviated as PE-I-photo, was then measured for SAXS after annealing at 180 °C for 6 h (Figure 5). The stress-relaxation data for PE-I-photo measured at 180 °C was provided in Figure S11. In comparison with PE-IV, the data for PE-I-photo indicates the significantly slow relaxation, where the relaxation must be mainly caused by the dynamic nature of ionic cross-links.

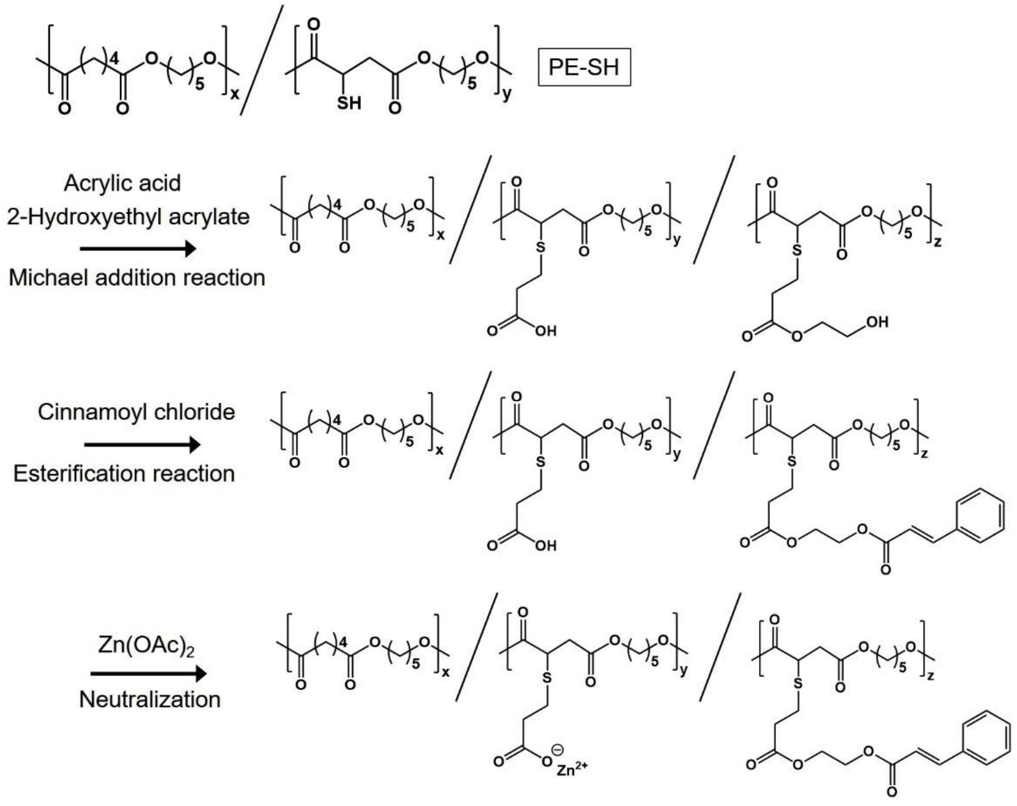

Figure S10. Synthesis scheme of the precursor polymer for PE-I-photo.

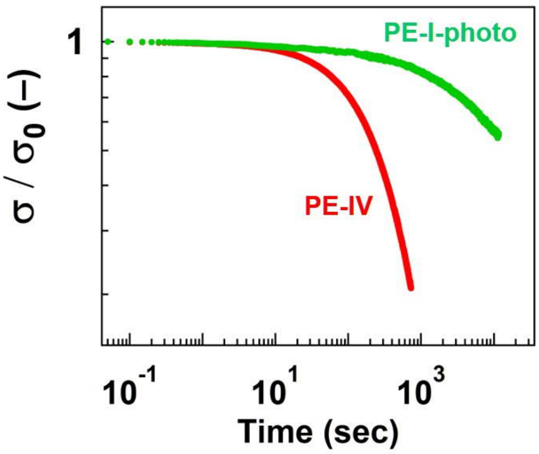

Figure S11. Stress-relaxation curves for PE-IV and PE-I-photo.