Supplementary Information for:

Spatiotemporal Vitrimerization of a Thermosetting Polymer using a Photo-Latent Catalyst for Transesterification

Jinyoung Park[a], Hyeong Yong Song[b], Subi Choi[a], Suk-kyun Ahn[a,c], Kyu Hyun[a], and Chae Bin Kim[a,c]*

[a]*School of Chemical Engineering, Pusan National University, Busan, 46241 Republic of Korea*
[b]*Institute for Environment and Energy, Pusan National University, Busan 46241, Republic of Korea*
[c]*Department of Polymer Science and Engineering, Pusan National University, Busan, 46241 Republic of Korea*

*Corresponding Author. E-mail address: cbkim@pusan.ac.kr

Methods

Materials. Pentaerythritol triacrylate (PETA, technical grade), pentaerythritol tetrakis(3-mercaptopropionate) (PETMP, >95%), and TPS were purchased from Sigma-Aldrich (Korea). Acetone (99.5%) was purchased from Samchun Pure Chemical Co. Ltd. (Korea). Benzoyl peroxide (74%) was purchased from Daejung Chemicals & Metals Co. Ltd. (Korea). Acetonitrile (>99.5%) and methyl red (>98.0%) were purchased from TCI (Korea). All chemicals were used directly without further purification unless otherwise specified.

Instrumentation. ATR-FTIR spectra were recorded on a Nicolet 6700 (Thermo Fisher Scientific, USA) spectrometer equipped with a diamond ATR probe. DSC analyses (DSC25, TA Instruments, USA) were performed under a nitrogen atmosphere at a heating rate of 10 °C/min. TGA (Q50, TA Instruments, USA) was performed under a nitrogen atmosphere or air at a heating rate of 10 °C/min. DMA (DMA 850, TA Instruments, USA) was conducted at a ramp rate of 3 °C/min, a frequency of 1 Hz, and a fixed oscillatory strain of 0.1%. The tensile strengths of the model polymer materials were measured using a UTM (LRX plus, AMETEK) at a crosshead speed of 100 mm/min. UV–Visible spectra were obtained using a Mega-800 (SCINCO, Korea) spectrophotometer. All linear viscoelastic properties were measured using a strain-controlled rotational rheometer (ARES-G2, TA Instruments) with 13 mm parallel plates. The frequency sweep measurements were taken in the temperature range of 30–180 °C (10 °C intervals) at a strain amplitude of 0.5%, which lay in the linear regime. All measurements were taken in a nitrogen environment to prevent oxidative degradation. For each sample, a pseudo-master curve was constructed by applying the time-temperature superposition (TTS) principle at a T_{ref} of 70 °C.

Model polymer synthesis. A solution of BPO and TPS PAG dissolved in acetone was mixed with PETMP and PETA in a 20 mL vial. The molar ratio between the thiol and acrylate was

maintained at 1:1. The amount of BPO with respect to the total monomer weight was 1 wt.%, whereas that of TPS with respect to acrylate (or thiol) was 7 mol%. The mixture was vigorously stirred using an applicator at room temperature, followed by vacuum drying at room temperature for 12 h and finally heating at 60 °C for 3 h to yield the prepolymer. The prepolymer was then simultaneously cured and molded into a film by heat-pressing at 180 °C and 15 MPa for 3 h. Thickness for the samples was kept in 0.3 mm, unless otherwise noted.

Light exposure. Broadband UV irradiation (OmniCure S1500 Spot UV Curing System, Canada) was conducted at room temperature with an output wavelength ranging from 200 to 500 nm. A working distance of 30 mm was used and the light intensity was determined to be 85 mW/cm^2 using a radiometer (PM100D, Thorlabs, USA) equipped with an S405C thermal power sensor head.

Self-healing experiments. Scratches were made using a razor blade on the sample frozen using liquid nitrogen. Upon heating at 180 °C in an oven, uniform pressure was applied to the scratched sample by placing it between two glass slides, which were clamped using four binder clips at the middle of each side.
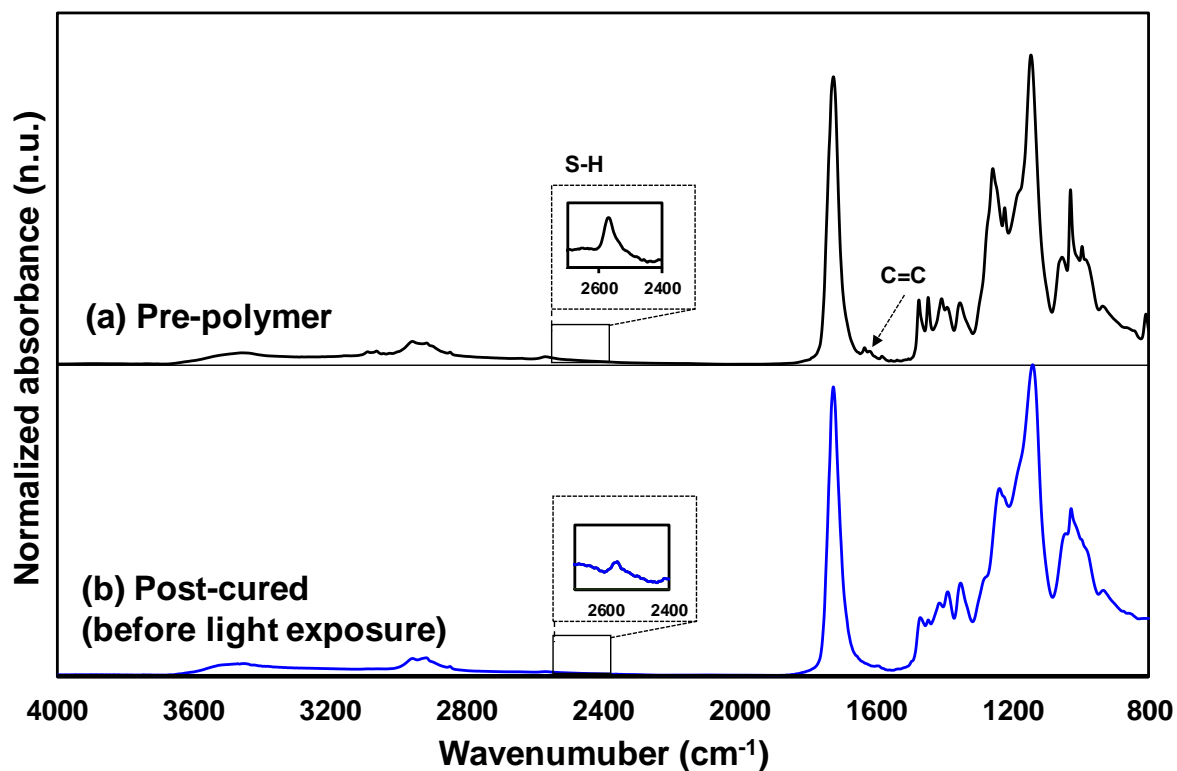
Fig. S1. Attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR) spectra of the prepolymer (black) and fully cured (blue) sample with 7 mol% TPS with respect to thiol (or acrylate). The peaks were normalized using the area under the peak corresponding to the ester group at wavenumber from 1850 to 1650 cm^{-1}.
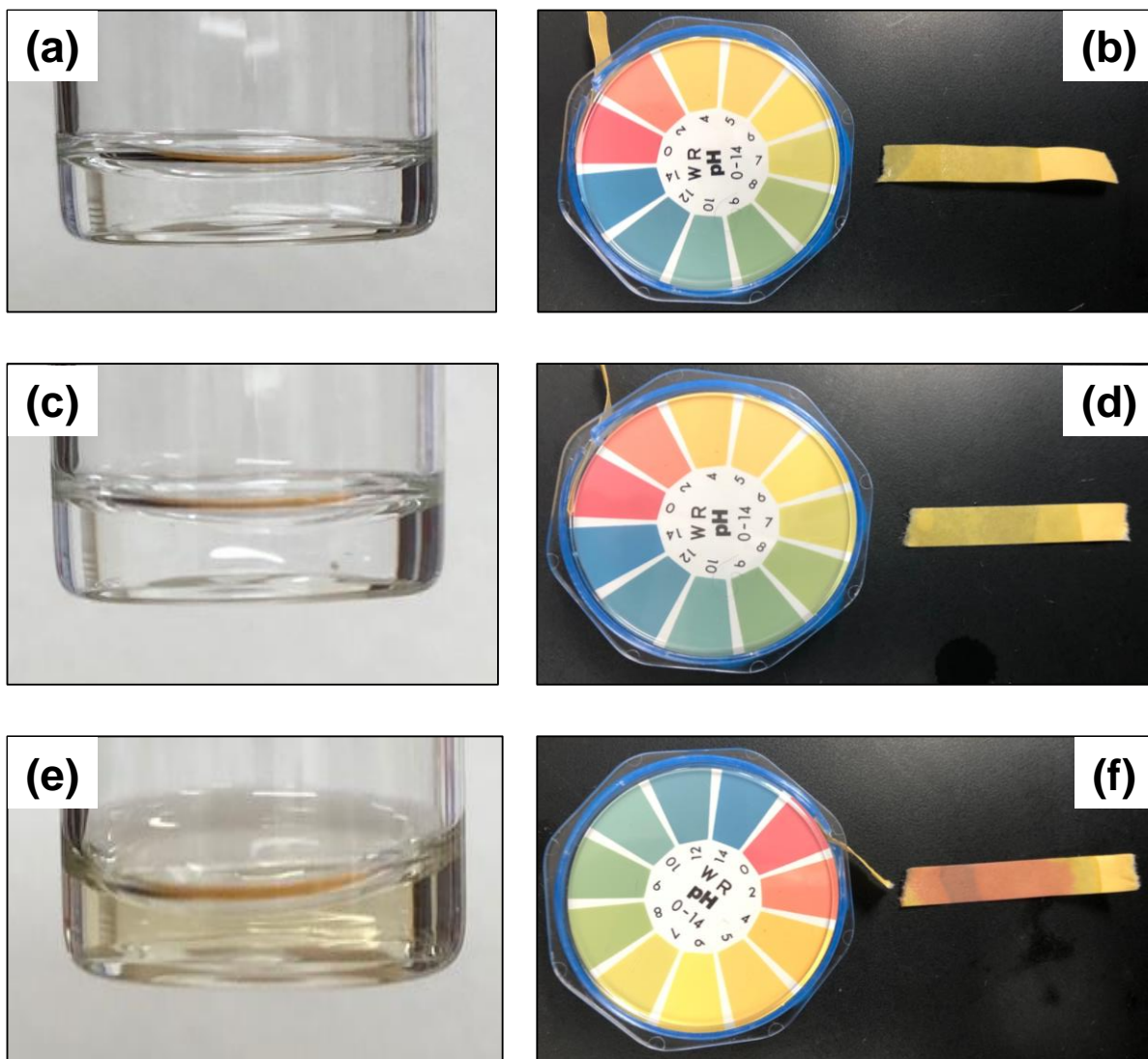
Fig. S2. Photographs showing triphenylsulfonium triflate (TPS) solution in acetonitrile (a) as prepared, (c) after annealing at 180 °C for 4 h, and (e) after light exposure. Photographs for pH paper immersed in the corresponding solutions are shown in (b), (d), and (f), respectively. Light exposure dosage using broadband light was 10.2 J/cm^2. This dosage corresponds to 2 min exposure with a power density of 85 mW/cm^2.
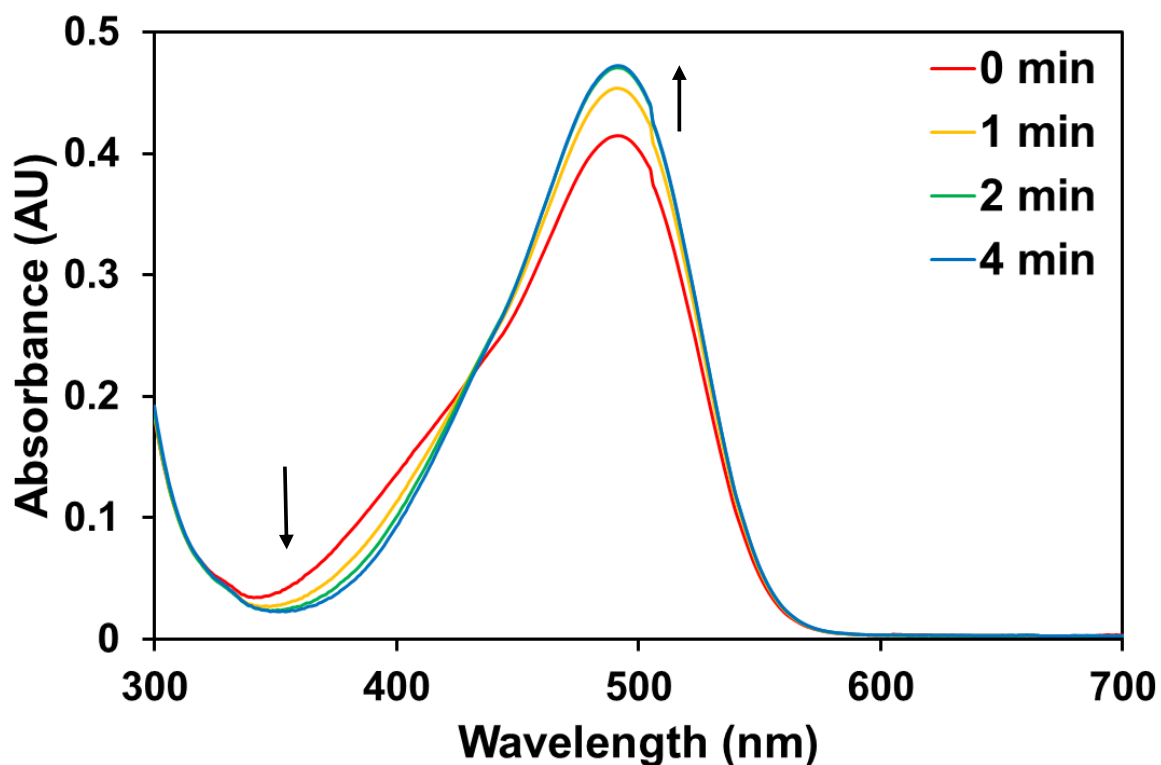
Fig. S3. UV−vis absorption spectra for acetonitrile solution with TPS and a pH indicator, methyl red, in an equimolar ratio after various light exposure dosages. Upon light irradiation, absorbance peak ~ 370 nm diminished while peaks at ~ 500 nm intensified. Longer exposure times than 2 mins did not alter the absorbance further, indicating the photochemical reaction of TPS was complete after only 2 min of UV exposure. A broadband microscope illuminator (Omnicure S1500) with output wavelength ranges from 200 to 800 nm was used. A 30 mm working distance was used with a light intensity of 85 mW/cm^2. Since TPS absorbs only a fraction of the broadband output, significantly lower doses limited to effective wavelengths (*i.e.* ≤ 300 nm) could give an equivalent result.
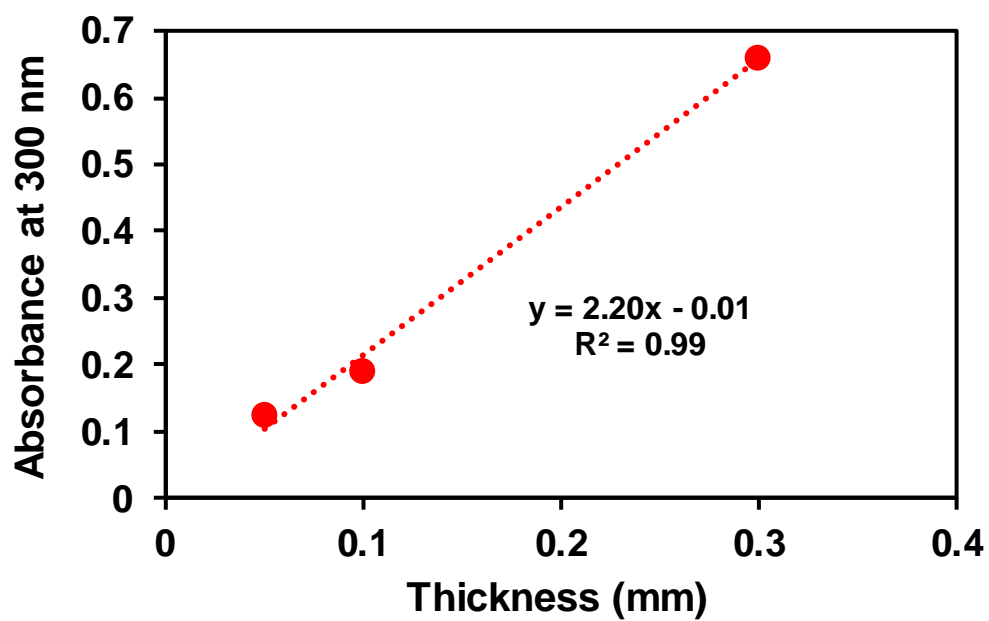
Fig. S4. UV−vis absorption at 300 nm for the polymer sample with TPS (7 mol% with respect to acrylate or thiol) at various thicknesses. Red dotted line corresponds to a Beer-Lambert law fit.
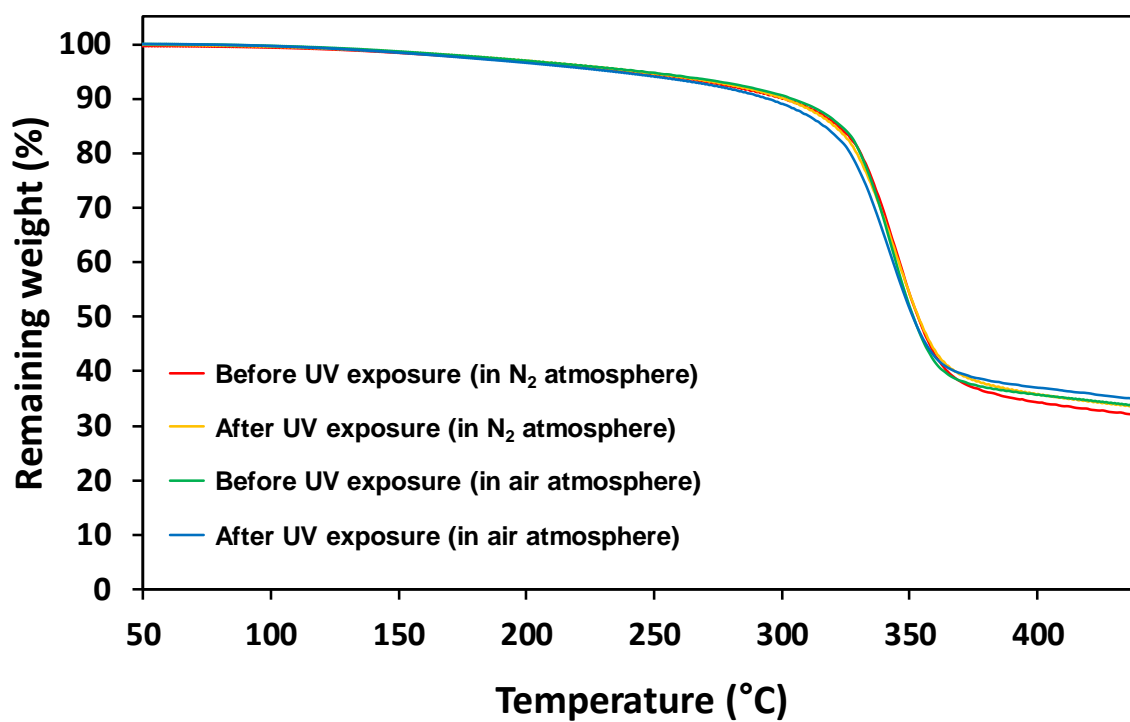
Fig. S5. Thermogravimetric analysis (TGA) using samples possessing 7 mol% TPS under either air or nitrogen atmosphere. Each sample before and after light irradiation was measured. Light exposure dosage using broadband light was 10.2 J/cm^2. This dosage corresponds to 2 min exposure with power density of 85 mW/cm^2 measured by radiometer.
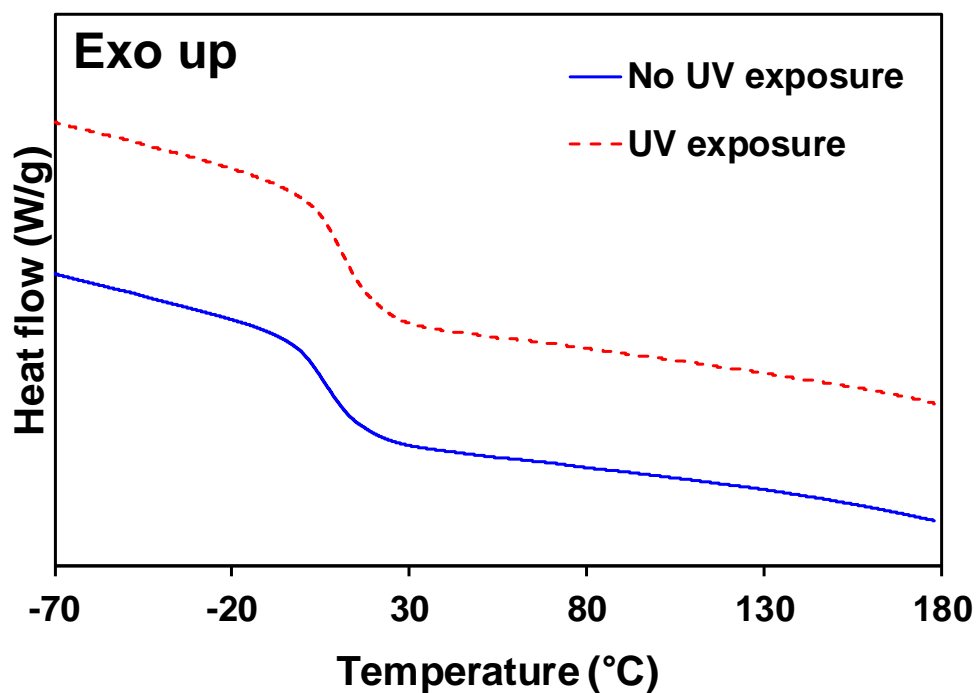
Fig. S6. Differential scanning calorimetry (DSC) thermograms for the light-exposed (dashed red line) and unexposed samples (blue solid line) upon second heating at a rate of 10 °C/min. Mid-T_g was determined to be 10 °C for both samples.
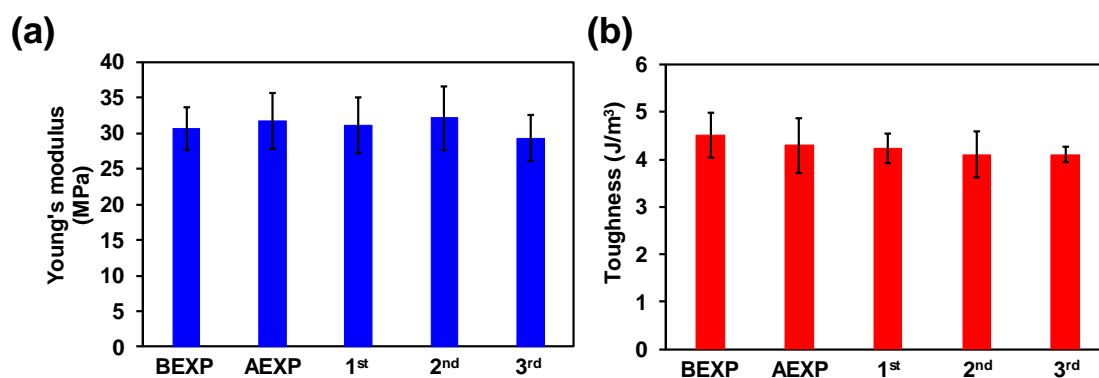

Fig. S7. (a) Young's modulus, and (b) toughness for samples before light exposure (BEXP), after light exposure (AEXP), and reprocessed samples after light exposure up to 3rd generation. Error bars indicate standard errors from four measurements for each sample.

Table S1. Equation parameters used for fitting temperature dependence of the horizontal shift factor a_T

Sample	Parameter values		
Before light exposure	WLF equation	C_1 (-)	10.99
		C_2 (°C)	121.31
After light exposure	WLF equation ($T \leq 80$ °C)	C_1 (-)	16.01
		C_2 (°C)	119.38
	Arrhenius equation ($T = 120 - 180$ °C)	K (-)	3.31×10^{-23}
		E_a (kJ/mol)	142.7

[a] WLF equation form: $\log a_T = [-C_1(T - T_{ref})]/[C_2 + (T - T_{ref})]$, where T_{ref} was set to 70 °C in this study.

[b] Arrhenius equation form: $a_T = K\exp(E_a/RT)$, where R is the gas constant (= 8.314 J/mol·K).
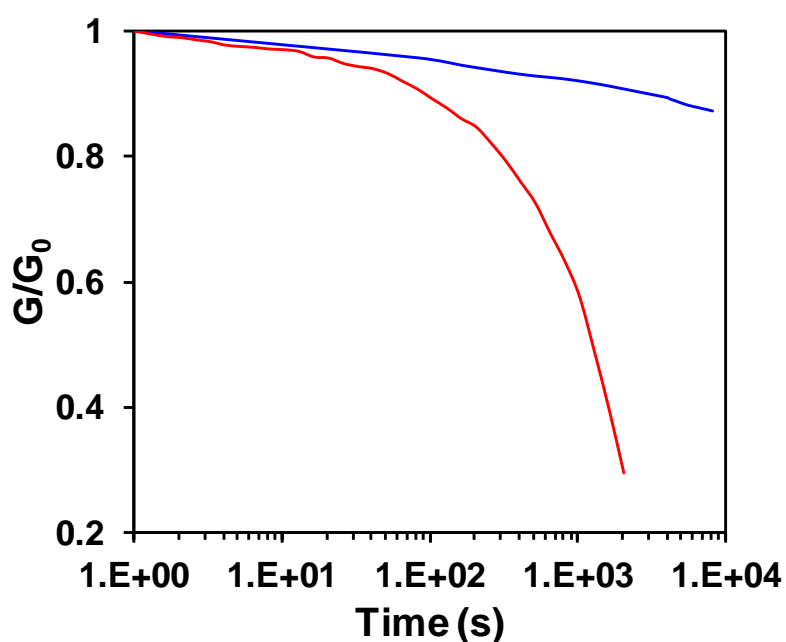

Fig. S8. Stress relaxation results for unexposed (blue) and light exposed (red) samples at 130 °C (> T_v = 80 °C) measured by rheometer using 13 mm parallel plate at a 1% strain and at a 10 N axial force.
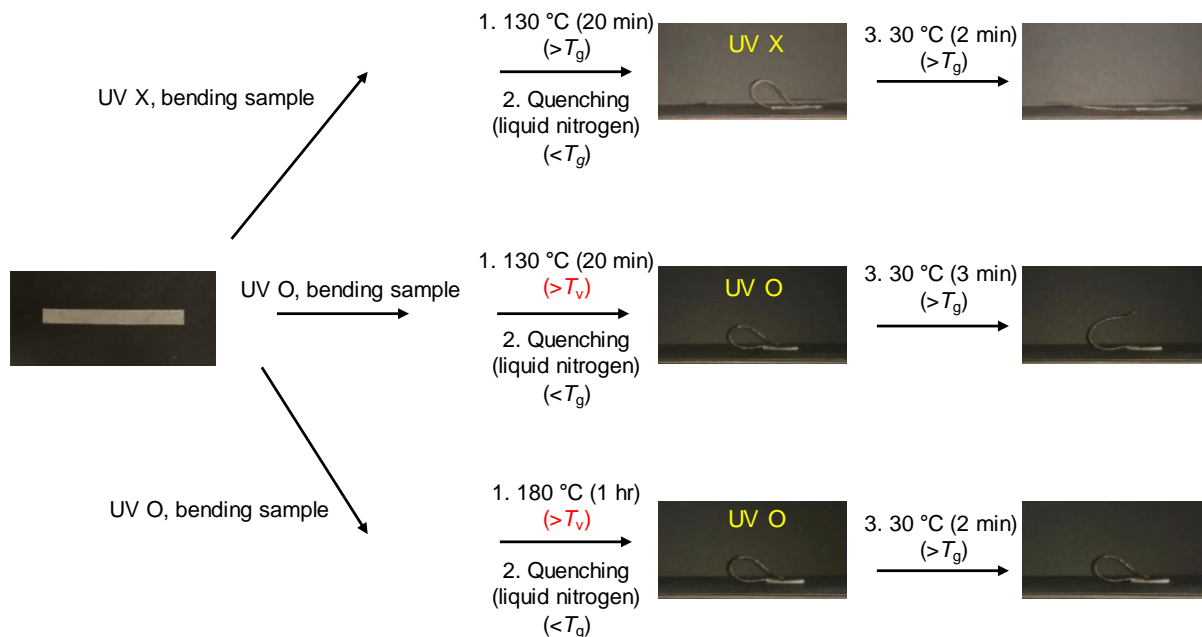
Fig. S9. Controlled straightening behavior comparison between unexposed and light exposed samples. Unexposed sample was bent and then annealed at 130 °C (top row). The sample straightened upon subsequent annealing at 30 °C (or above T_g). Light exposed samples were bent and then annealed at 130 °C (middle row) and 180 °C (bottom row), respectively. The light exposed samples remained bent even upon subsequent heating at 30 °C (or above T_g) owing to the network rearrangement via transesterification. Sufficient post-light exposure annealing at higher temperature resulted in better shape fixity due to the higher degree of network rearrangement.
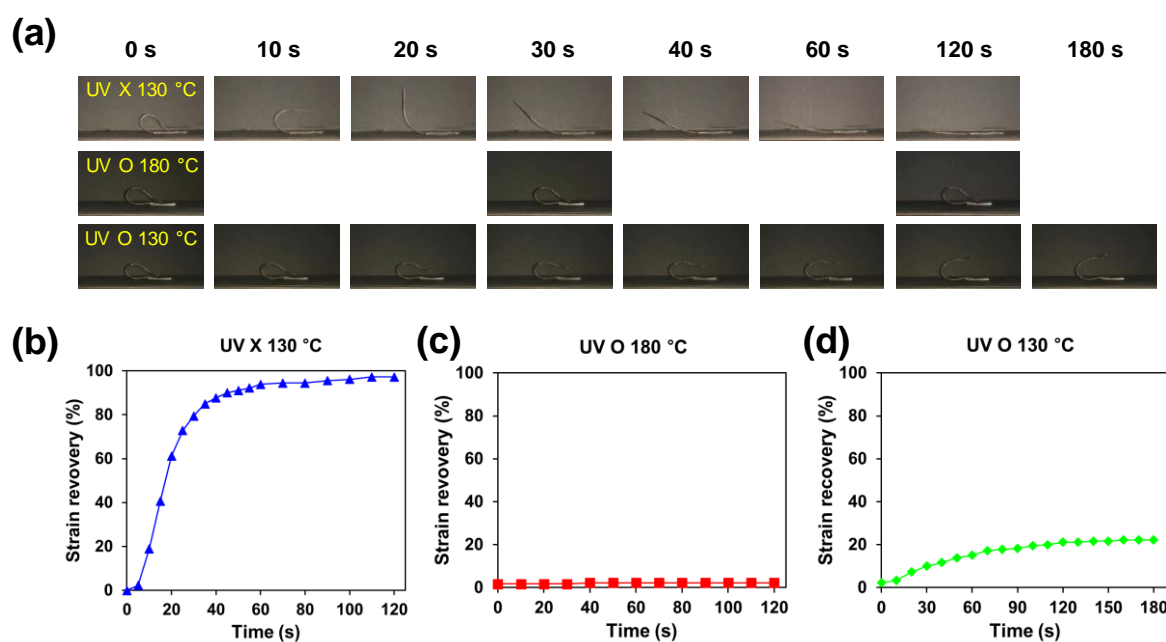
Fig. S10. (a) Photographs demonstrating the shape recovery test. The unexposed sample was bent and then annealed at 130 °C (top row), while the light exposed samples were bent followed by annealing at 180 °C (middle row), and 130 °C (bottom row), respectively. Upon final annealing at 30 °C, the strain recovery (%) rate was calculated from the angle recovered over time.[1] (b) Shape recovery rate for the unexposed sample (pre-annealed at 130 °C) as a function of annealing time at 30 °C. (c) Shape recovery rate for the light exposed sample (annealed at 180 °C after light exposure) as a function of annealing time at 30 °C. (d) Shape recovery rate for the light exposed sample (annealed at 130 °C after light exposure) as a function of annealing time at 30 °C. Sufficient post-light exposure annealing at higher temperature resulted in better shape fixity (or lower strain recovery) owing to the higher degree of network rearrangement *via* transesterification.

Reference

[1] J. Seo, J-W. Choi, Y-H. Koh, J-H. Seo, *ACS Macro Lett.*, 2020, **9**, 389–395.