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Supplementary Materials for

On-demand catalyst-regulated distinctive topological isomerization in a dynamic covalent network

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Materials and Methods:

Materials:

ε-Caprolactone (ε-CL), 1,1,2,2-tetrakis (allyloxy) ethane, tin (II) 2-ethylhexanoate, 2,2-dimethoxy-2-phenylacetophenone (photoinitiator), dibutyltin dilaurate (DBTDL), 3,6-dioxa-1,8-octanedithiol, 1,5,7-triazabicyclo [4.4.0] dec-5-ene (TBD), and ketoprofen were purchased from TCI. Allyl isocyanate and pentaerythritol were acquired from Aladdin. Trimethylolpropane diallyl ether was procured from Sigma-Aldrich. Toluene and dimethyl formamide (DMF) were purchased from Sinopharm. All chemicals were used as received.

Synthesis of the tetravinyl-functionalized polycaprolactone:

Tetravinyl-functionalized polycaprolactone was synthesized by ring-opening polymerization. Specifically, ε-CL (50 g), pentaerythritol (0.681 g), and tin (II) 2-

ethylhexanoate (0.254 g) were weighed into a Schlenk flask. The mixture was reacted at 120 °C for 8 hours under nitrogen. Afterward, allyl isocyanate (2.490 g), DBTDL (0.250 g) were added into the flask. The mixture was kept at 80 °C for 6 hours under nitrogen. The obtained polymer was precipitated in cold methanol after dissolved in toluene. The above dissolve-precipitation process was repeated three times. Finally, the solid product was obtained after filtration and vacuum-dried at room temperature overnight. The chemical structure of tetravinyl-functionalized polycaprolactone was characterized by ^{1}H NMR (Figure S1).

Synthesis of the polymer network

The polymer network was synthesized by thiol-allyl radical addition. Tetravinyl-functionalized polycaprolactone (0.532 g), trimethylolpropane diallyl ether (0.300 g), 1,1,2,2-tetrakis(allyloxy)ethane (0.007 g), 3,6-dioxa-1,8-octanedithiol (0.294 g), 2,2-dimethoxy-2-phenylacetophenone (0.010 g), and DMF (0.150 g) were weighed into a glass vessel. The mixture was melted at 80 °C and sandwiched into two glass slides with a 0.6 mm PDMS spacer. Afterwards, it was exposed to UV light (365 nm, 100 mW/cm^2) for 240 s. The film was kept in a 70 °C vacuum oven for 6 hours to remove the residual solvent.

Synthesis of the photo switchable catalyst (PTBD)

TBD (0.200 g,) and ketoprofen (0.384 g,), toluene (2.366 g) were added into a glass bottle. The reaction was conducted at room temperature by stirring for 2 hours. The obtained solution was stored away from light.

Topological isomerization

The PTBD was introduced into the film by soaking in 1.0 wt% solution as obtained above. The solvent was then removed in a 70 °C vacuum oven for 30 min. The release of TBD was through exposure under UV light (365 nm, 100 mW/cm^2) for 1000 s at 80 °C with a distance of 16 cm. Topological isomerization was conducted followed by heating at 100 °C away from light and water.

Topological patterning

The sample with 1 wt% PTBD was exposed to UV light carpeted by a physical mask at 80 °C with a distance of 16 cm, followed by heating at 100 °C for 2 hours to complete the topology isomerization away from light and water.

Network reprocessing and thermal healing

In a reprocessing experiment, the polymer film with 1 wt% PTBD was cut into many small pieces, put into a 0.5-mm-thick iron mold, and pressed under a pressure of 4 MPa at 120 °C for 240 min. In a thermal healing experiment, the sample with 1 wt% PTBD with a rectangular dimension (12×5×0.6 mm) was cut into two halves, pushed together, and then allowed to heal at 120 °C for 240 min at minimum external forces. The thermal healing efficiency was calculated as the strain at break of the original sample divided by the strain at break of the self-healed sample. At least three specimens were tested.

Materials characterization

Mechanical properties of samples in a rectangular shape (12×5×0.6 mm) were determined by using a Zwick/Roell Z005 machine under a tensile speed of 10 mm/min at 25 °C. Melting temperatures and crystallinities were measured by differential scanning calorimetry (DSC) using a TA Q200 instrument at a heating and cooling speed of 5 °C/min. The stress relaxation with the samples in rectangular shapes (10×3×0.6 mm) were conducted using a dynamic mechanical analyzer (TA Q800).

Conflicts of interest

There are no conflicts to declare.

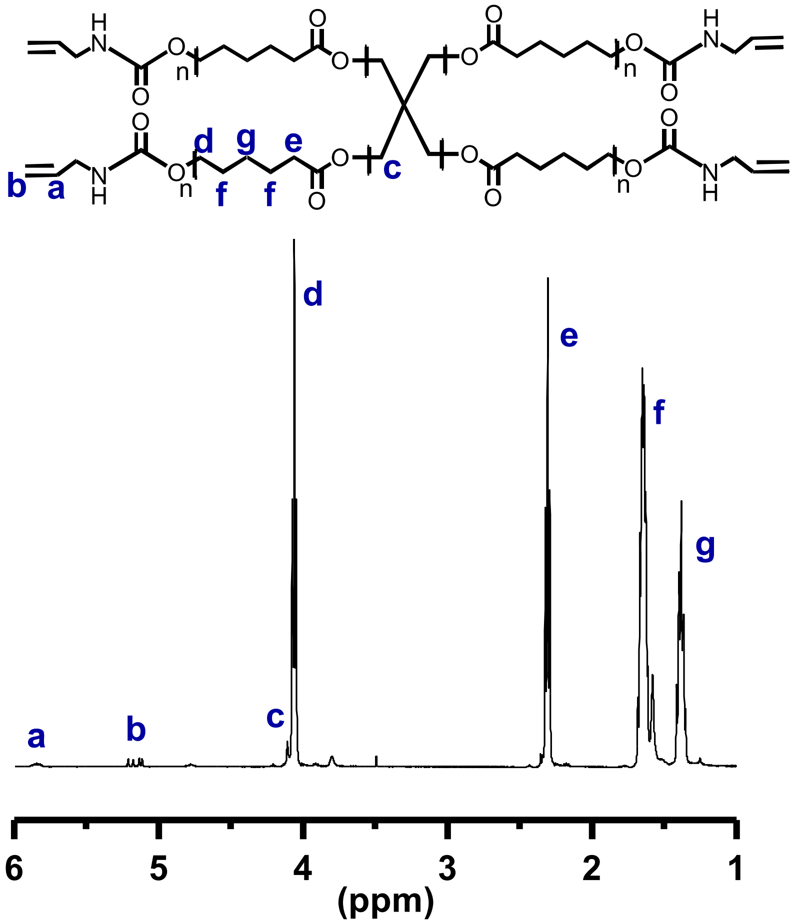

Figure S1. The ^{1}H NMR spectrum of the tetravinyl-functionalized polycaprolactone. The molecular weight was calculated as the equation followed: $M_n = S_d / S_b \times 114 \times 4$ (i.e. $23.245 \times 114 \times 4 = 10600$ Da), where S_d and S_b are the normalized area of the peak d and b, respectively.

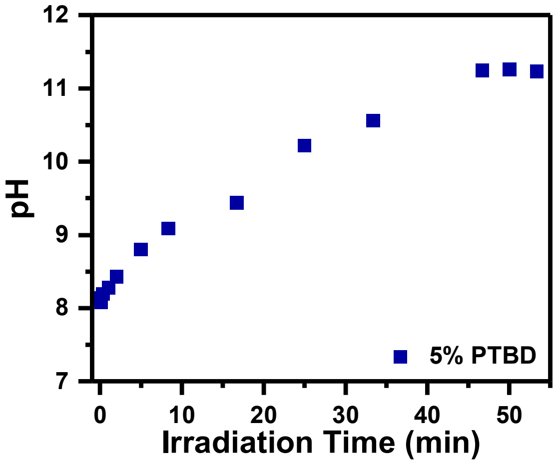

Figure S2. The pH of the photo switchable catalyst after different UV irradiation time. 5 wt% PTBD methanol solution was used for characterization. It has a primary pH of 8. The pH of the solution gradually increases with UV irradiation time, reaching equilibrate pH of 11.4 upon 45 min of UV exposure. All tests were performed with an electronic pH detector at room temperature.

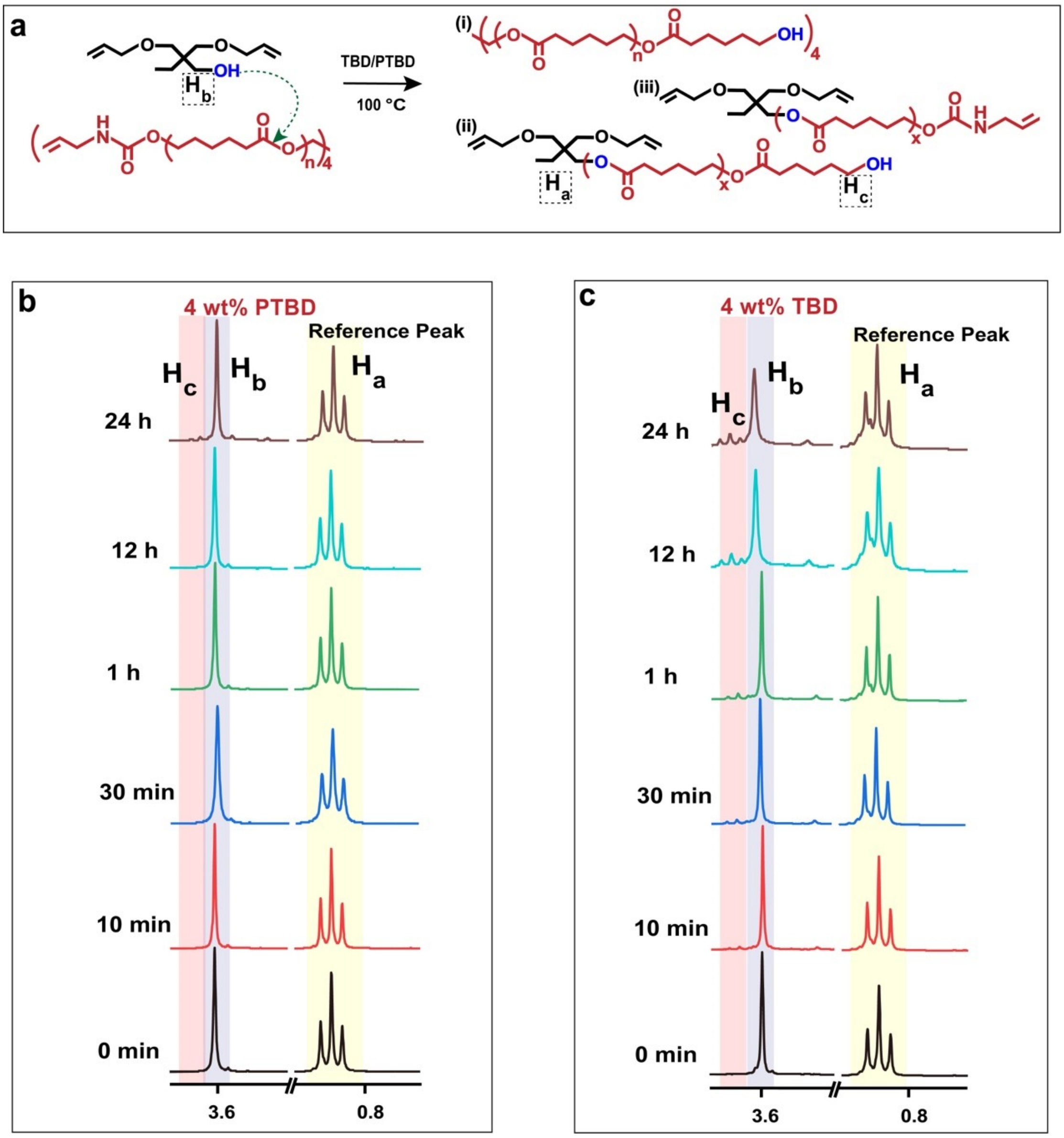

Figure S3. Detailed ^{1}H NMR spectra of the model study at different time corresponding to Figures 2c and 2d. (a) Transesterification between V-PCL chains and hydroxyls in the model study. **(b)** ^{1}H NMR spectra of the system catalyzed by 4 wt% PTBD. **(c)** ^{1}H NMR spectra of the system catalyzed by 4 wt% TBD. All systems were thermal annealed at 100 °C. Hydroxyl conversion under different water contents. Hydroxyl conversion was calculated by the equation as follows: Hydroxyl conversion (%) = (1-SH_{bi}/SH_{ai})×100%. (SH_{bi} and SH_{ai} represent the normalized area of the peak H_a and H_b. i represents the peak area at different annealing time.)

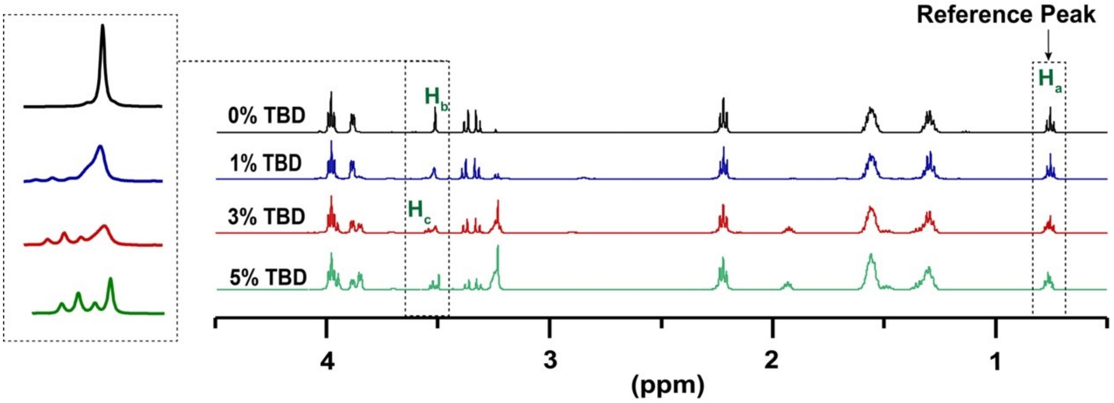

Figure S4. Detailed ^{1}H NMR spectra of the model study with different amount of TBD corresponding to Figure 2e. All systems were thermal annealed at 100 °C for 120 min. Hydroxyl conversion (%) = (1-SH_{bi}/SH_{ai})×100%. (SH_{bi} and SH_{ai} represent the normalized area of the peak H_a and H_b. i represents the peak area at different amounts of TBD.)

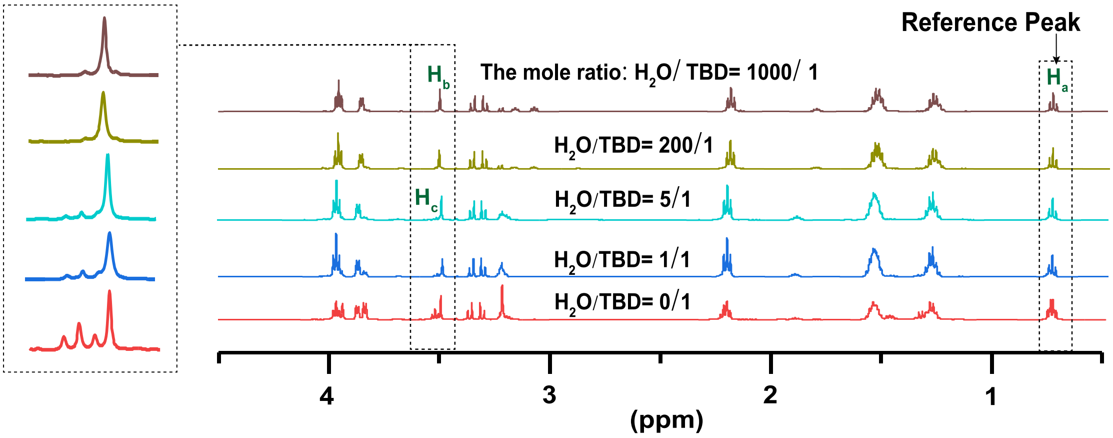

Figure S5. ^{1}H NMR spectra of the model study with different amounts of water. All systems were thermal annealed at 100 °C for 120 min with 8 wt% TBD.

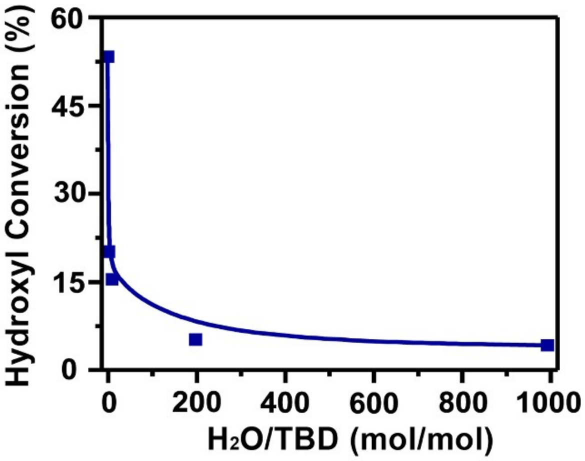

Figure S6. Hydroxyl conversion under different water contents. Hydroxyl conversion was calculated by the equation as follows: Hydroxyl conversion (%) = (1-SH_{bi}/SH_{ai})×100%. (SH_{bi} and SH_{ai} represent the normalized area of the peak H_a and H_b. i represents the peak area at different amounts of water shown in Figure S5.) The results show that the hydroxyl conversion decreases drastically with water content and reaches an equilibrium at a sufficiently high water/TBD ratio.

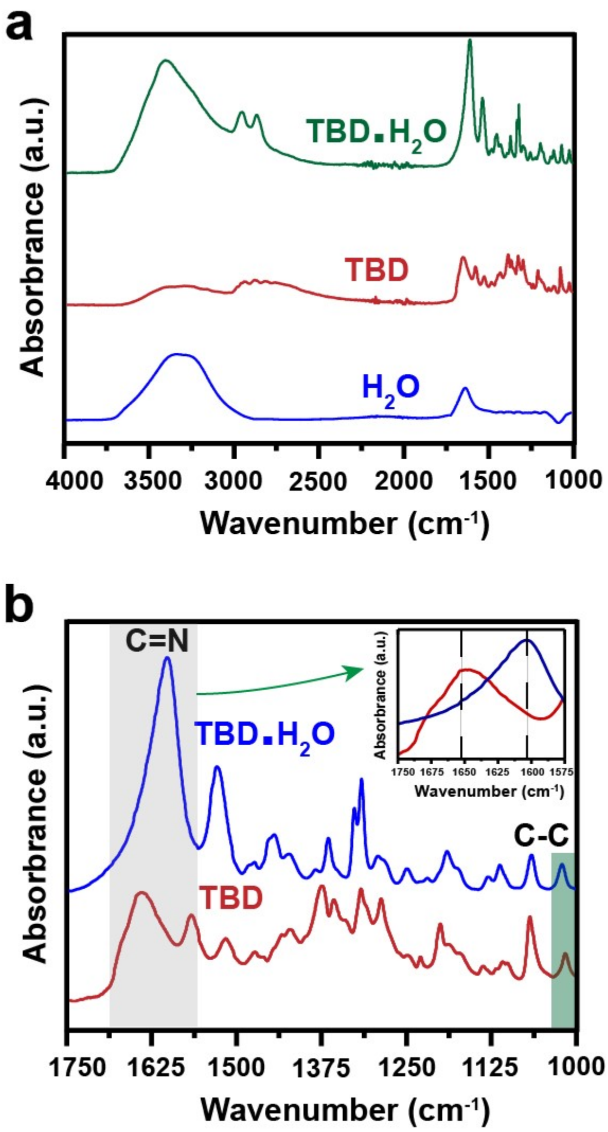

Figure S7. The infrared spectra of TBD, TBD•H_2O, and H_2O. (a) Comparison of the infrared spectra about TBD, TBD•H_2O, H_2O. (b) Infrared spectra of the TBD before and after water treatment. C-C is the reference peak. As demonstrated in Figure S7b, A distinct peak shift in C=N, means a formation of intermolecular hydrogen bonding between water and TBD. Which leads to a decrease in the activity of the catalyst. As shown in Figure S5, it can be seen that the infrared peaks are obviously shifted after adding water to TBD.

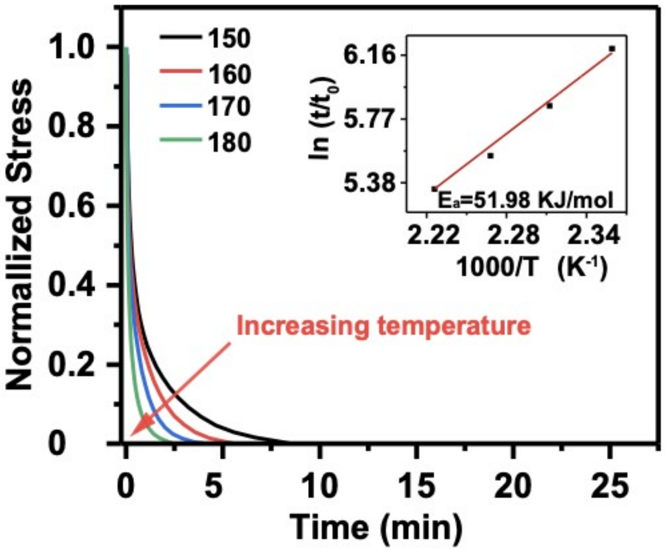

Figure S8. Iso-strain stress-relaxation curves of the sample catalyzed by UV released TBD at different relaxation temperatures (150 °C-180 °C) (strain: 20%).

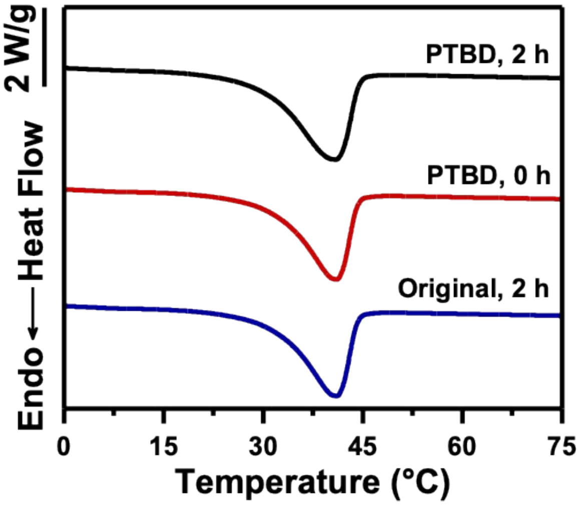

Figure S9. DSC curves of the sample with 5 wt% PTBD at different annealing time at 100 °C.

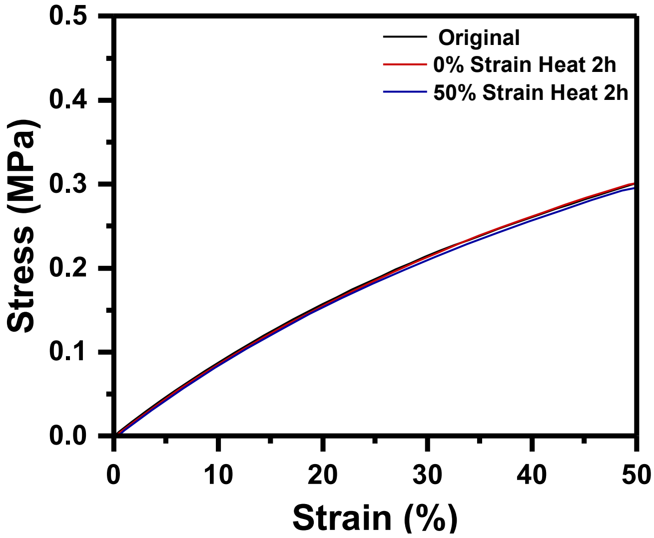

Figure S10. The stress-strain curves of the original sample and the samples after transesterification with and without external force. The transesterification was carried out at 100 °C for 2h with 1% PTBD catalyst. The test temperature is 100 °C which is higher than the melting temperatures of the samples. All samples possess the same crosslinking density 0.1×10^{-3} g mol^{-1}, which is calculated by the following equations. where the modulus is calculated from the 0-5% strain in stress-strain curves.

$$d = \frac{E_r}{3kT}$$

where d represents the crosslinking density per unit volume (mol cm^{-3}), Er is rubbery modulus (MPa), k and T are the gas constant and the absolute temperature, respectively.

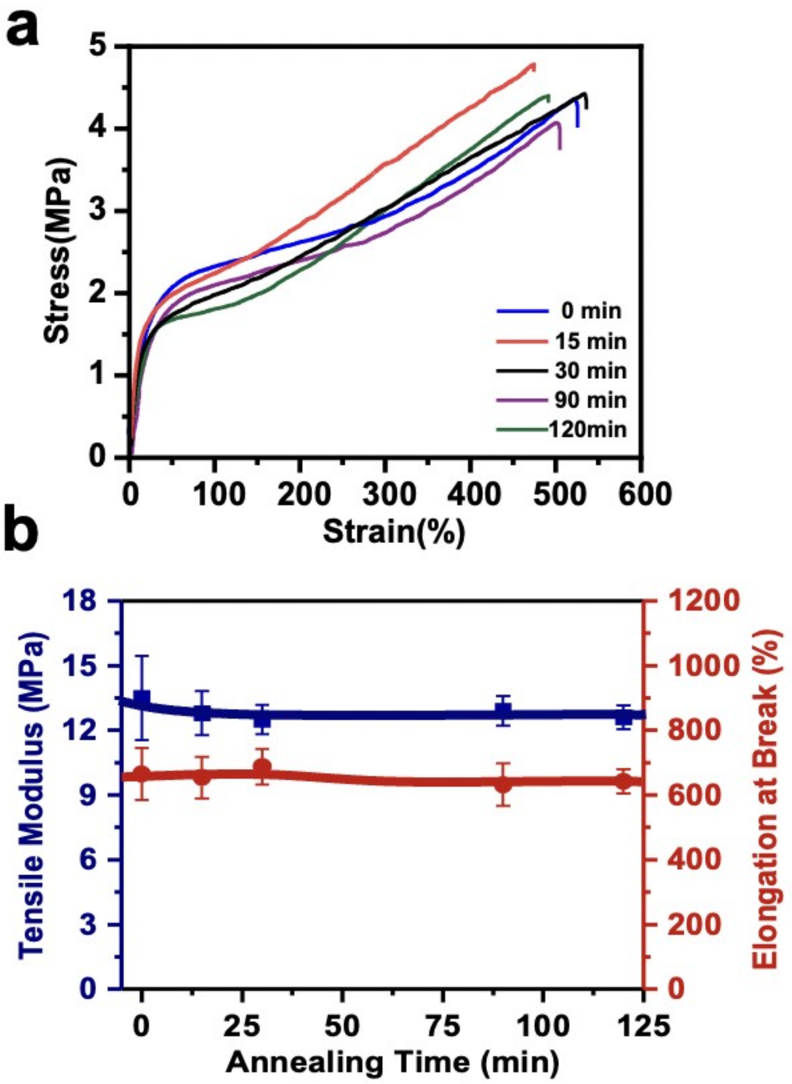

Figure S11. Mechanical properties of the samples catalyzed by 5 wt% PTBD with different annealing time at 100 °C. a) The strain-stress curves. b) Tensile moduli and elongations at break.

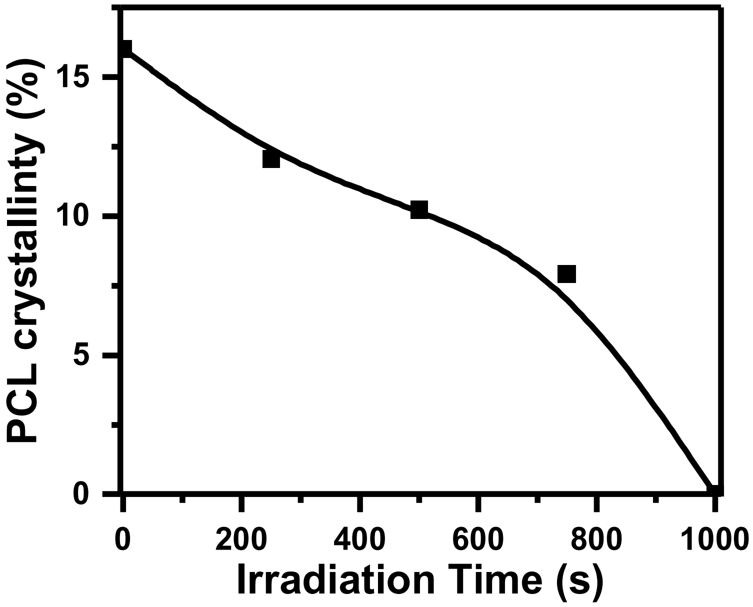

Figure S12. The relationship between PCL crystallinities in the network and UV irradiation time. The crystallinity X_c was calculated by the following Equation:

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_{m^0}}$$

where ΔH_m represents the melting enthalpy, ΔH_{cc} represents cold crystallization enthalpy, and ΔH_{m^0} is the melting enthalpy for 100% crystalline PCL.

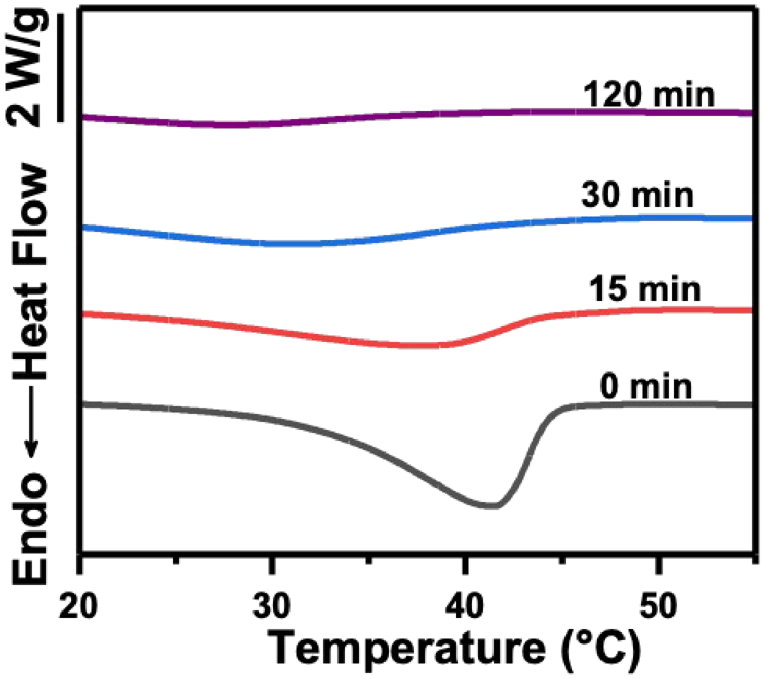

Figure S13. DSC curves of the sample with TBD with different annealing time at 100 °C after UV radiation for 1000 s.

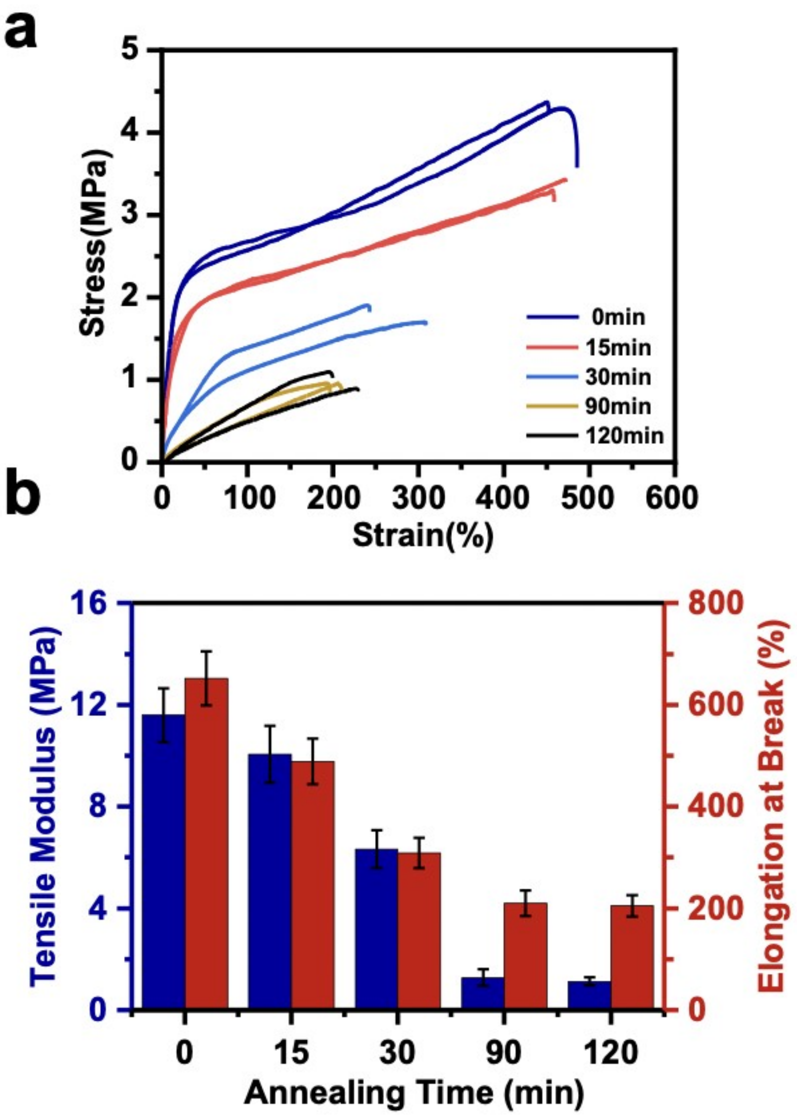

Figure S14. Mechanical properties of the samples catalyzed by TBD with different annealing time at 100 °C after UV irradiation for 1000 s. a) The strain-stress curves. b) Tensile moduli and elongations at break.

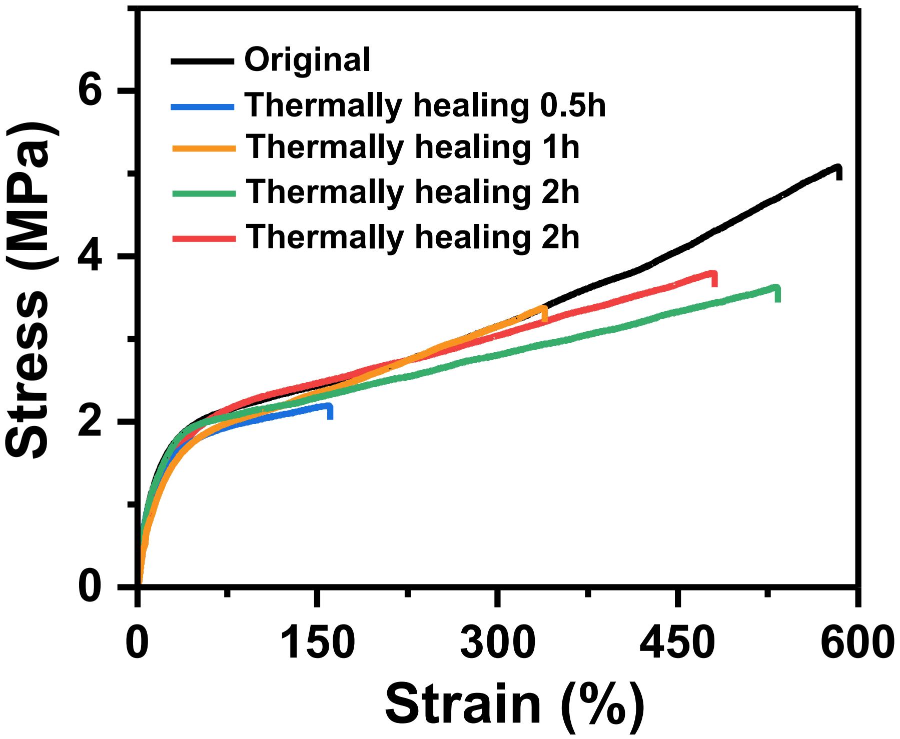

Figure S15. The strain-stress curves of the sample before and after thermal healing catalyzed by PTBD at different time.

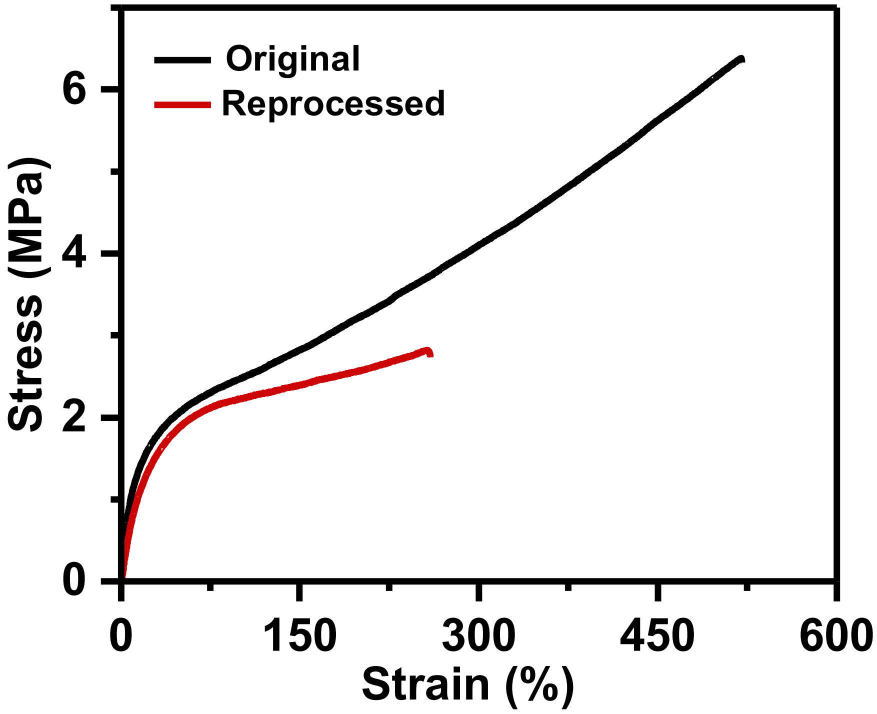

Figure S16. The mechanical properties before and after reprocessing catalyzed by PTBD. The modulus and elongation at break of the reprocessed samples are 13.2 ± 0.6 MPa and 264 ± 13%, respectively. The modulus is similar to the initial state, and the elongation at break decreases significantly, which may be caused by side reactions such as shear stress, hydrolysis, and oxidation.