

Supporting Information
for

Closed-loop Recyclable & Biodegradable Thioester Based Covalent Adaptable Networks

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Experimental Section:

Materials: Following chemicals are used during experiments without further purification unless otherwise mentioned, Malonic Acid LR (SD Fine Chemicals, 98.0%), Dichloromethane (DCM, SRL, 99 %), N, N-dimethyl formamide (DMF, Thomas Baker, 99.5%), Butane Thiol (BT, TCI, >97%), Oxalyl Chloride (Spectrochem, 98%), Benzyl Mercaptan (BzT, Aldrich, 99%), Tin(II)2-ethylhexanoate (TCI, 85%), CDCl_3 (Sigma Aldrich, 99.8 atom%D), Pentaerythritol Tetra (3-mercaptopropanoate) (PETMP, TCI, >90%), n-Hexane extra pure (Finar, 95%).

Instrumental Details: At 25 °C, CDCl_3 was used to record proton and carbon NMR data using a JEOL 400 YH instrument. Fourier Transmission Infrared spectroscopic data were recorded by using PerkinElmer spectrometer Spectrum Two series instrument under Attenuated Total Reflection (ATR). The Ultimate Tensile Strength (UTS) was measured with the help of Tinius Olsen (H5KL-UTM) at a strain rate of 5 mm/min. The dimension of the material is 0.76 mm thickness and 5.88 mm width for the recording of tensile data. An average of three experiments were taken for the demonstration of the data. The Young's Modulus value was calculated from the stress-strain curve at the linear zone from the initial point. The DMTA data of the samples were recorded by DMA-Q 800 TA instrument (50 ASTM, D-406501 norm). The stress relaxation property of the PTE-0.5 (width 1.3 mm and thickness 6.5 mm) was observed under compression mode. During the stress relaxation experiment, we followed 0.1% constant strain for 10 min temperature equilibrium. The DMTA experiment was recorded in DMA multi-frequency strain mode. The rectangular strip (thickness \approx 1.5 mm & width \approx 6.2 mm) was used for the analysis. The creep experiment of the samples was done at 35 °C and the constant stress of 70 kPa. The sample dimension for the creep experiment is as follows; thickness \approx 0.4 mm and width \approx 4.0 mm. The DSC (Differential Scanning Calorimetry) of the sample was recorded using a Hitachi, DSC7020

instrument at 5 °C/min under N₂ environment. SEM (Scanning Electron Microscopy) images of the biodegraded sample were recorded by the JSM-7900F instrument equipped with EDAX. For the SEM images, we used 5 kV current, a working distance of 15.0 mm and LED mode to record freeze-dried samples.

Synthesis of Precursor (BPT): Oxalyl Chloride (2.44 g, 19.22 mmol) was added slowly to the mixture of malonic acid (1.00 g, 9.61 mmol) and anhydrous DCM (24.8 ml). This mixture was stirred for 30 minutes under an inert atmosphere at 25 °C. DMF (0.07 g, 0.96 mmol, 5 mol% with respect to the carbonyl group) was injected very slowly to the above reaction mixture by retaining an inert condition. This mixture was stirred for 30 minutes at 25 °C. Butane thiol (6.93 g, 76.84 mmol) was added to the above mixture, when the colour of the solution changed from white to orange. Stirring was further continued for five hours. Subsequently, the excess butane thiol was evaporated by a rotary evaporator under reduced pressure. The ¹H, ¹³C, HRMS and FT-IR analysis was carried out of the product without further purification – ¹H NMR (400 MHz, δ, ppm, CDCl₃): 3.77 (s, 2H, -COCH₂CO-), 2.93 (t, 4H, -SCH₂-), 1.58 (m, 4H, -SCH₂CH₂-), 1.38 (m, 4H, -S(CH₂)₂CH₂-), 0.91 (t, 6H, -CH₃). ¹³C NMR (100 MHz): δ (ppm) 190.84 (-CH₂-CO-), 57.99 (-OCCH₂CO-) 30.98 (-S-CH₂-CH₂-), 29.27 (-S-CH₂-), 21.71 (-S(CH₂)₂CH₂-), 13.94 (-CH₃). FT-IR (cm⁻¹): 1674 (C=O), 2956 (C-H), 639 (S-C). HRMS (ESI- TOF, m/z): [M+H] calc. 249.0983; found, 249.0984; [M+Na] calc. 271.0802, found, 271.0799.

Transthioesterification of BPT with Benzyl Mercaptan (BzT): BzT (7.50 g, 60.39 mmol, 15 equiv. with respect to precursor) was added slowly to BPT (1.00 g, 4.03 mmol). This reaction mixture was stirred at 140 °C in the presence of Sn(Oct)₂ (0.16 g, 0.40 mmol, 5 mol% with respect to each reacting site). The reaction was continued for 3 h under stirring conditions. The final product was characterized by NMR, HRMS and FT-IR Spectroscopy. ¹H NMR (400

MHz, δ , ppm, CDCl₃): 7.31 (m, 8H, ArH), 7.21 (m, 2H, ArH), 4.10 (s, 2H, -CH₂-CO-), 3.57 (s, 4H, -S-CH₂-). ¹³C NMR (100 MHz): δ (ppm) 188.01 (-CH₂-CO-), 141.29 (substituted-CAr), 137.54 (CAr), 136.24 (CAr), 128.29 (CAr), 43.43 (-CO-CH₂-CO-), 33.35 (-CH₂-Ar). FT-IR (cm⁻¹) 3028 (C-H), 1691 (S-C=O), 1601 (Ar), 1250 (C-O). HRMS (ESI- TOF, m/z): [M+H] calc. 317.0670; found, 317.0665.

Synthesis of BPT-PETMP based CANs (PTE-n): PETMP (0.99 g, 2.03 mmol) was added slowly to the BPT (1.00 g, 4.03 mmol) in the PTFE beaker. Subsequently, Sn(Oct)₂ (0.16 g, 0.40 mmol, 5 mol% with respect to the thioester group) was added to the aforementioned reaction mixture and the components were mixed thoroughly. The PTFE beaker along with all the components was kept at 130 °C for 6 h. For the curing purpose, the sample was pressed under a 90 kg load at 120 °C for 6 h. Mechanical data was recorded after curing of the sample. Three different PTE-n CANs were synthesized by changing the molar equivalent of PETMP. Namely, PTE-0.5 (BPT = 4.03 mmol, PETMP = 2.01 mmol, ~0.5 equiv. with respect to BPT), PTE-0.6 (BPT = 4.03 mmol, PETMP = 2.42 mmol, ~0.6 equiv. with respect to BPT), PTE-0.7 (BPT = 4.03 mmol, PETMP = 2.82 mmol, ~0.7 equiv. with respect to BPT).

Closed-loop Recycling: Butanethiol was added in an excess amount to the crushed film of PTE-0.5 in a 15 ml glass vial. This reaction mixture was heated at 90 °C for 9 h. After the said time, most of the pieces got dissolved in butanethiol. This mixture was then added to n-Hexane to separate the liquid layers. The NMR data of the precipitate and the hexane soluble fraction were separately recorded and analyzed.

Remoulding ability of PTE-n: To demonstrate the remoulding ability, two rectangular strips of PTE-0.5 (dimension: length \approx 3.0 cm, thickness \approx 0.9 mm and width \approx 1.0 cm) were overlapped at the end. The overlapping zone was approximately 0.5 cm. The above was wrapped

with an aluminium foil and placed at 120 °C under a 90 kg weight for 6 h. The self-welded sample was subsequently removed and used for further mechanical analysis.

Self-healing ability of PTE-n: For the analysis of the self-healing ability of PTE-0.5; thin cuts were made on the sample surface with a sharp blade. The sample with cut was placed under 120 °C for self-healing. The microscopic images of the cuts were recorded after different time periods using a microscope.

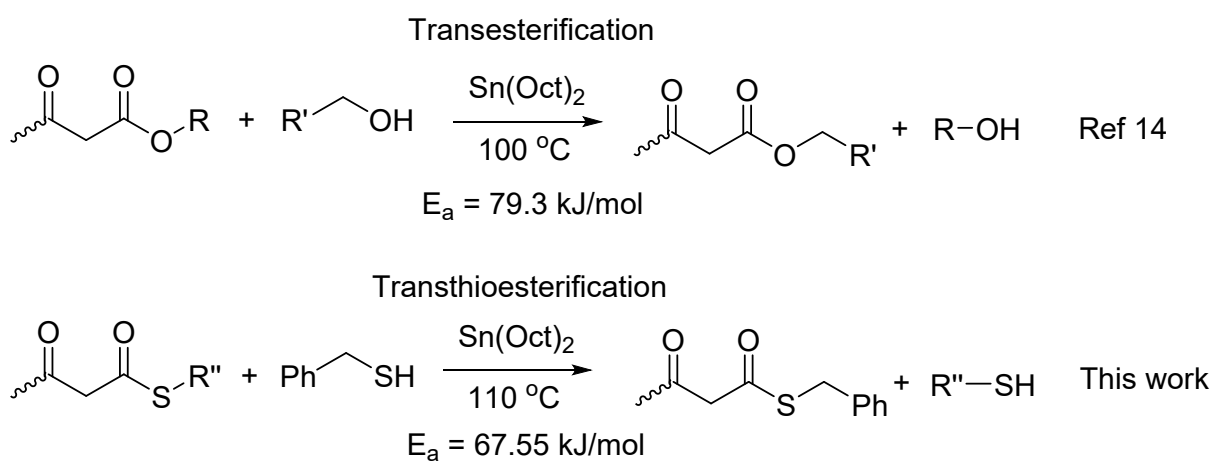
Reprocessing ability of PTE-n: To check the reprocessing ability, a uniform PTE-0.5 film was cut into small pieces using a razor blade. These pieces were collected and wrapped in an aluminium foil. The same was then pressed under a 90 kg load at 120 °C for 6 h. The pieces joined together to form a continuous as well as transparent film. The mechanical analysis of the samples were carried out and the photographs were captured for demonstration purposes.

Biodegradability of PTE-n: To analyze the biodegradation ability of the samples, uniform rectangular strips (initial weight = 217.4 to 230.0 mg) of PTE-0.5 were buried in wet soil. The samples were of the following dimension: thickness \approx 0.3 mm and width \approx 6.2 mm. The samples were removed from wet soil after 23, 29 and 35 days and the weight loss, morphology change along with tensile properties were recorded.

Curve Fitting of Stress Relaxation Experiment: The stress relaxation curve was fitted by the utilization of the Maxwell viscoelastic model. The formula used for fitting of the graph is given below-

$$\sigma(t) = \sigma_0 e^{-\frac{E}{\eta}t}, \quad (\text{Equation 1})$$

E denotes Young's modulus, η denotes the Viscosity coefficient, σ_0 represents the initial stress, t denotes the time, and $\sigma(t)$ denotes the stress at the time t . R^2 and constant parameter values were calculated with the help of a mathematical tool (MATLAB software version - 7.5).



Scheme S1: The transesterification studies on β -CO ester systems reported earlier and the current transthoesterification study on β -CO thioester in presence of $\text{Sn}(\text{Oct})_2$

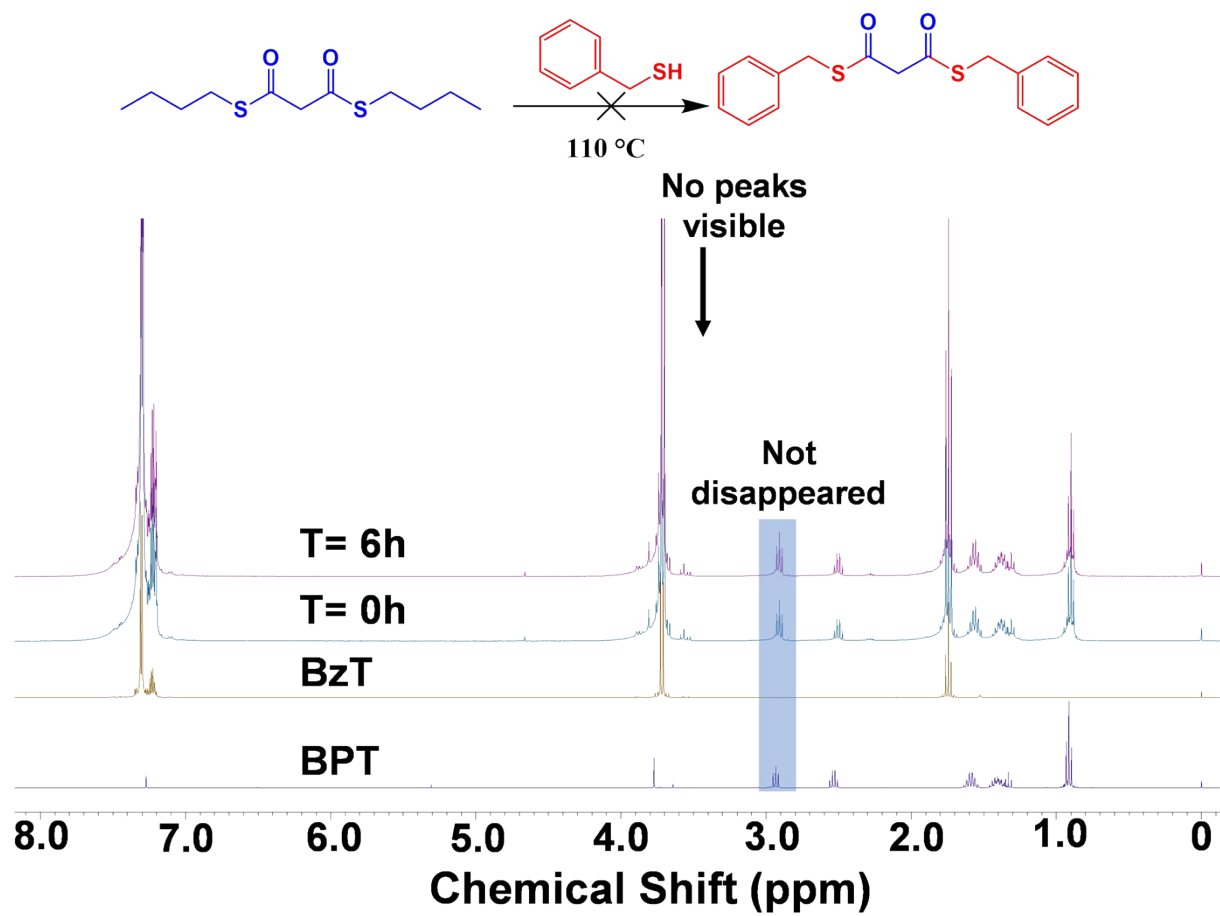


Figure S1: ^1H NMR spectra of the BPT, BzT and the reaction mixture under catalyst free condition at 110°C for 6 h.

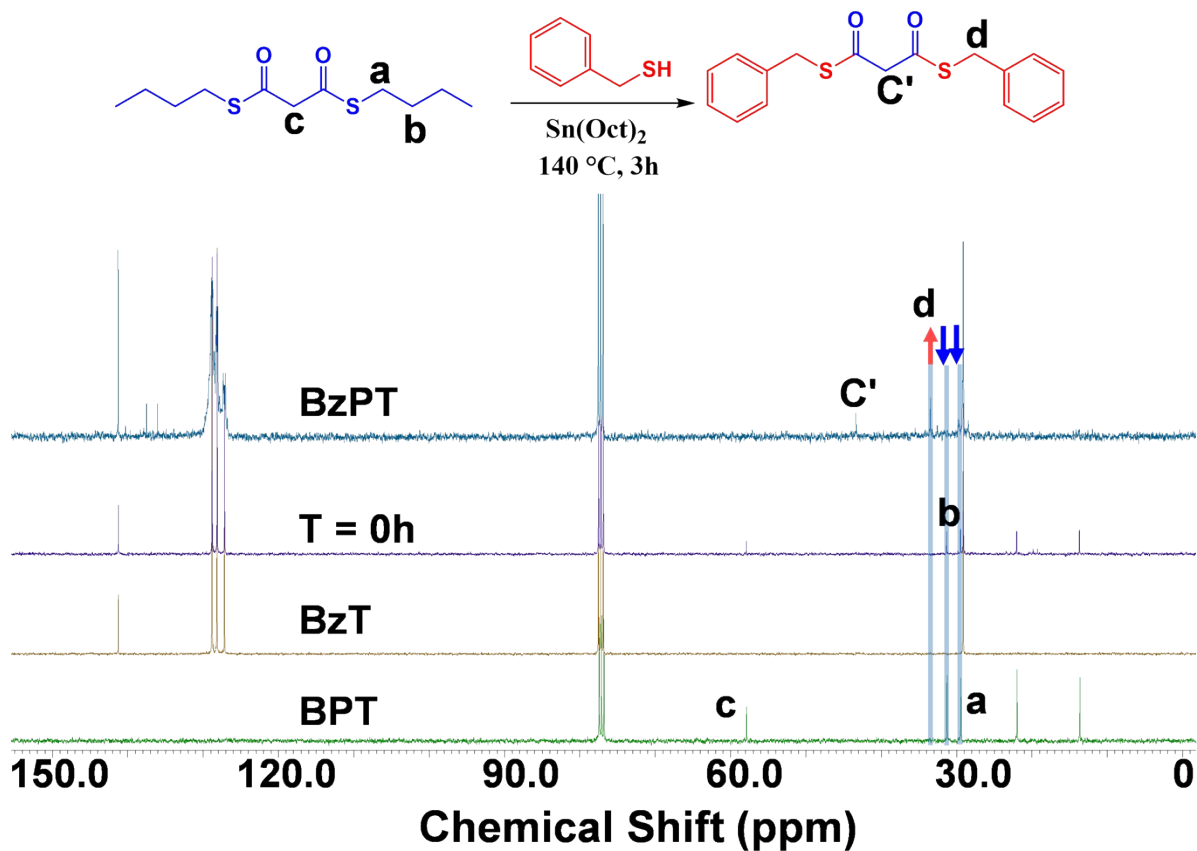


Figure S2: ^{13}C NMR spectra of the BPT and BzT exchange reaction, $[\text{BPT}] = 1\text{ mol}$, $[\text{BzT}] = 15\text{ mol}$, $[\text{Sn}(\text{Oct})_2] = 5\text{ mol}\%$ with respect to thioester group and Temperature = $140\text{ }^\circ\text{C}$.

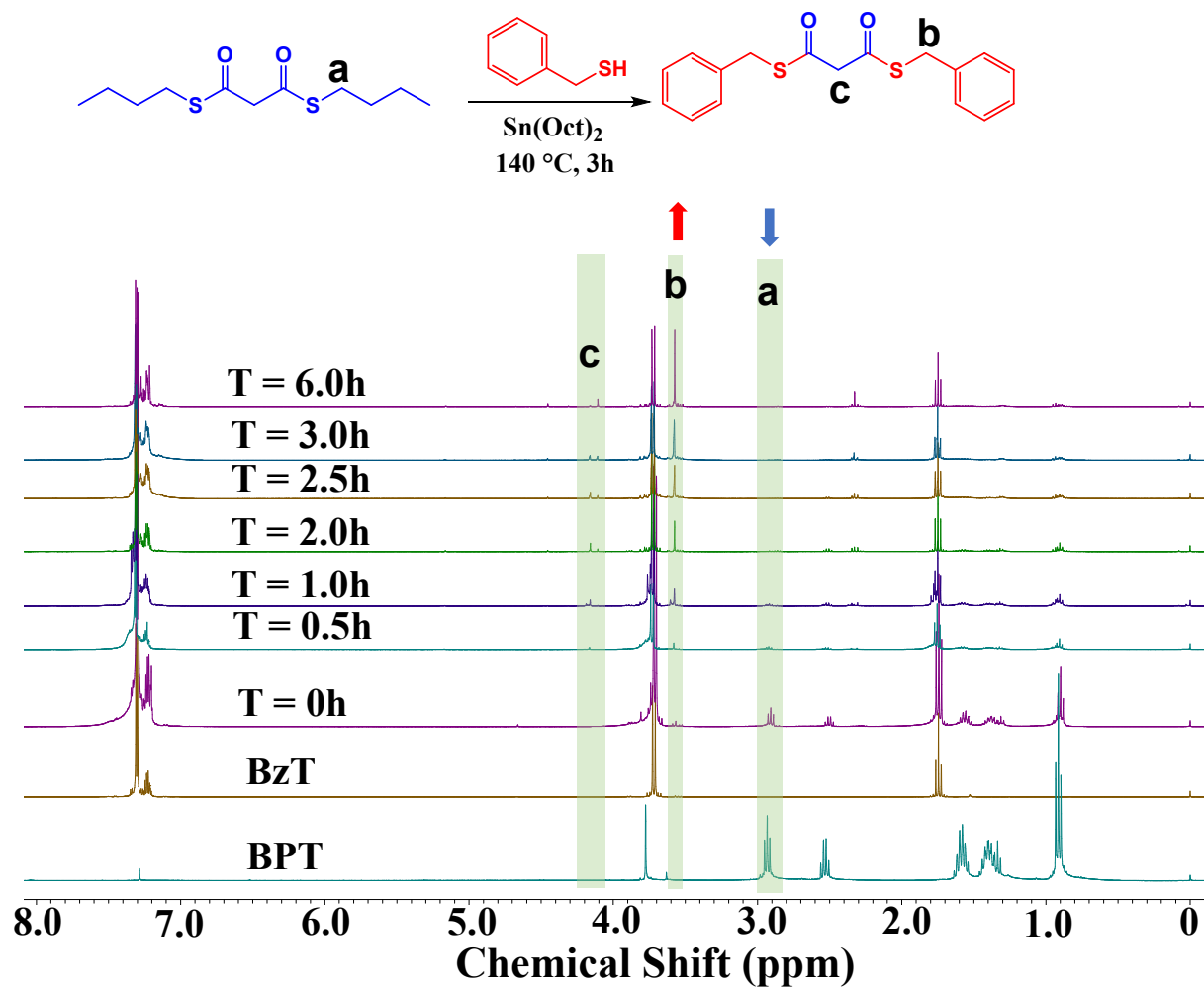


Figure S3: ^1H NMR spectra of the BPT and BzT exchange reaction recorded at different time periods, $[\text{BPT}] = 1\text{ mol}$, $[\text{BzT}] = 15\text{ mol}$, $[\text{Sn}(\text{Oct})_2] = 5\text{ mol}\%$ with respect to thioester group and temperature = $140\text{ }^\circ\text{C}$.

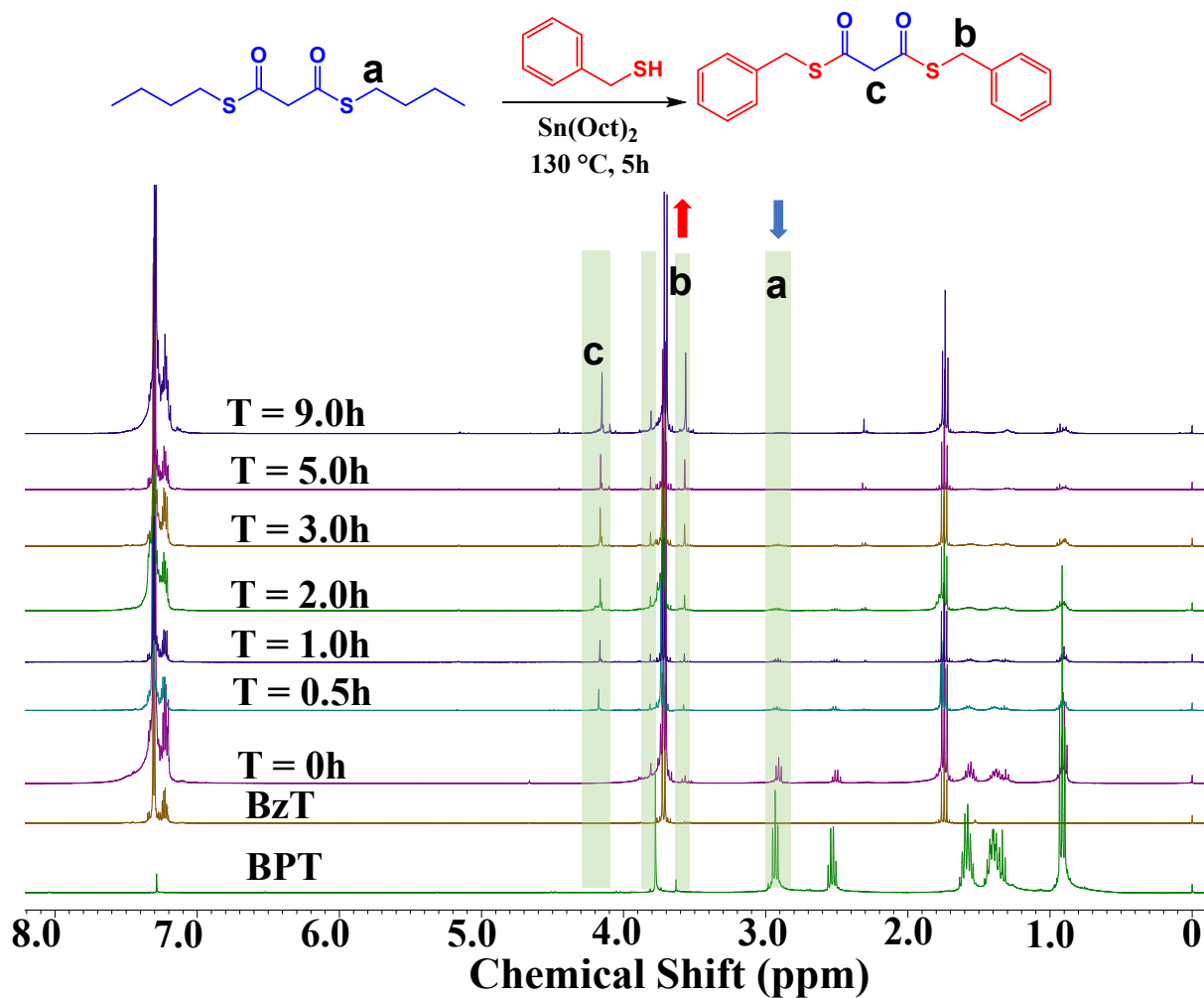


Figure S4: ^1H NMR spectra of the BPT and BzT exchange reaction recorded at different time periods, $[\text{BPT}] = 1\text{ mol}$, $[\text{BzT}] = 15\text{ mol}$, $[\text{Sn}(\text{Oct})_2] = 5\text{ mol}\%$ with respect to thioester group and temperature = $130\text{ }^\circ\text{C}$.

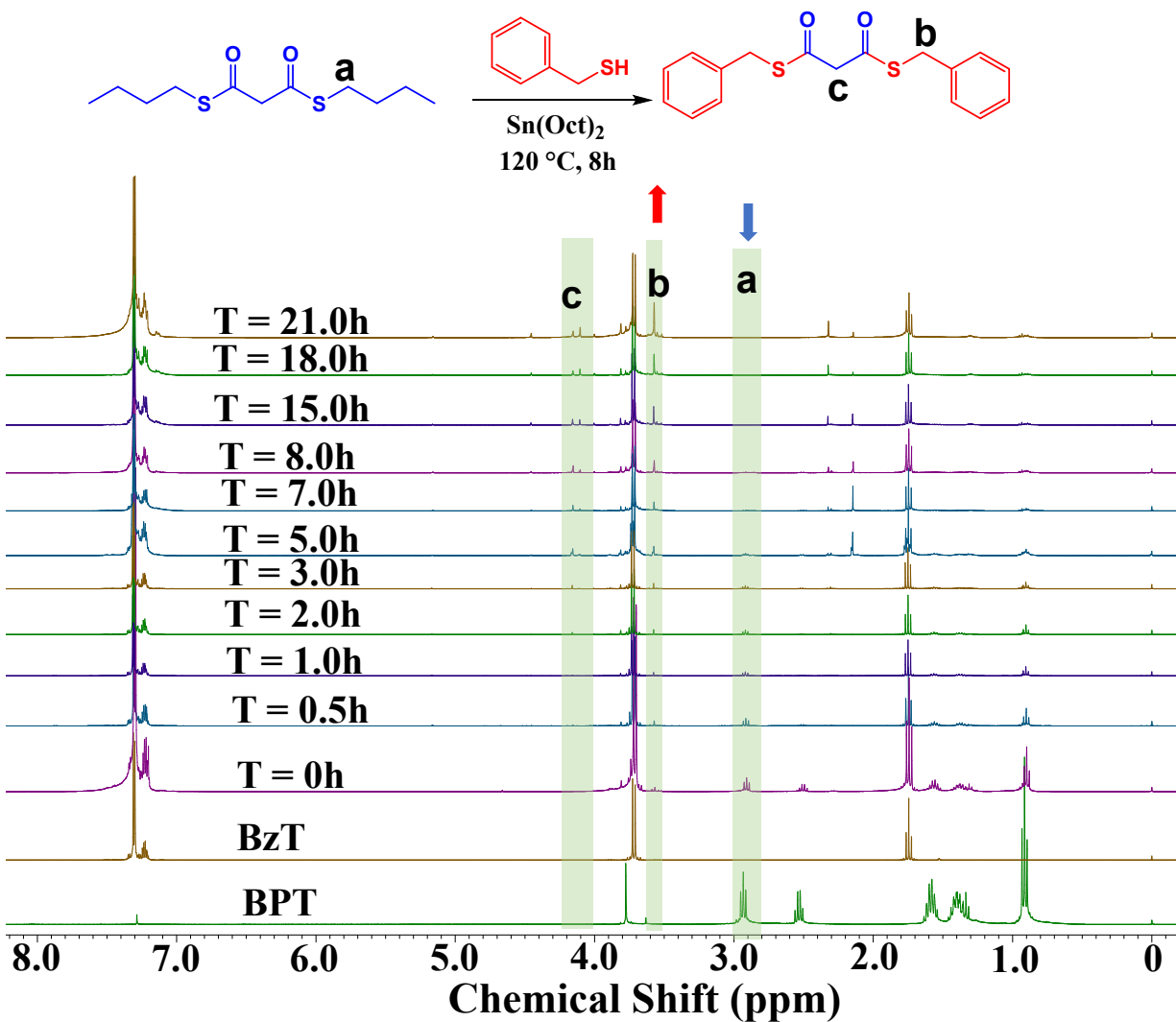


Figure S5: ^1H NMR spectra of the BPT and BzT exchange reaction recorded at different time periods, $[\text{BPT}] = 1\text{ mol}$, $[\text{BzT}] = 15\text{ mol}$, $[\text{Sn}(\text{Oct})_2] = 5\text{ mol}\%$ with respect to thioester group and temperature = $120\text{ }^\circ\text{C}$.

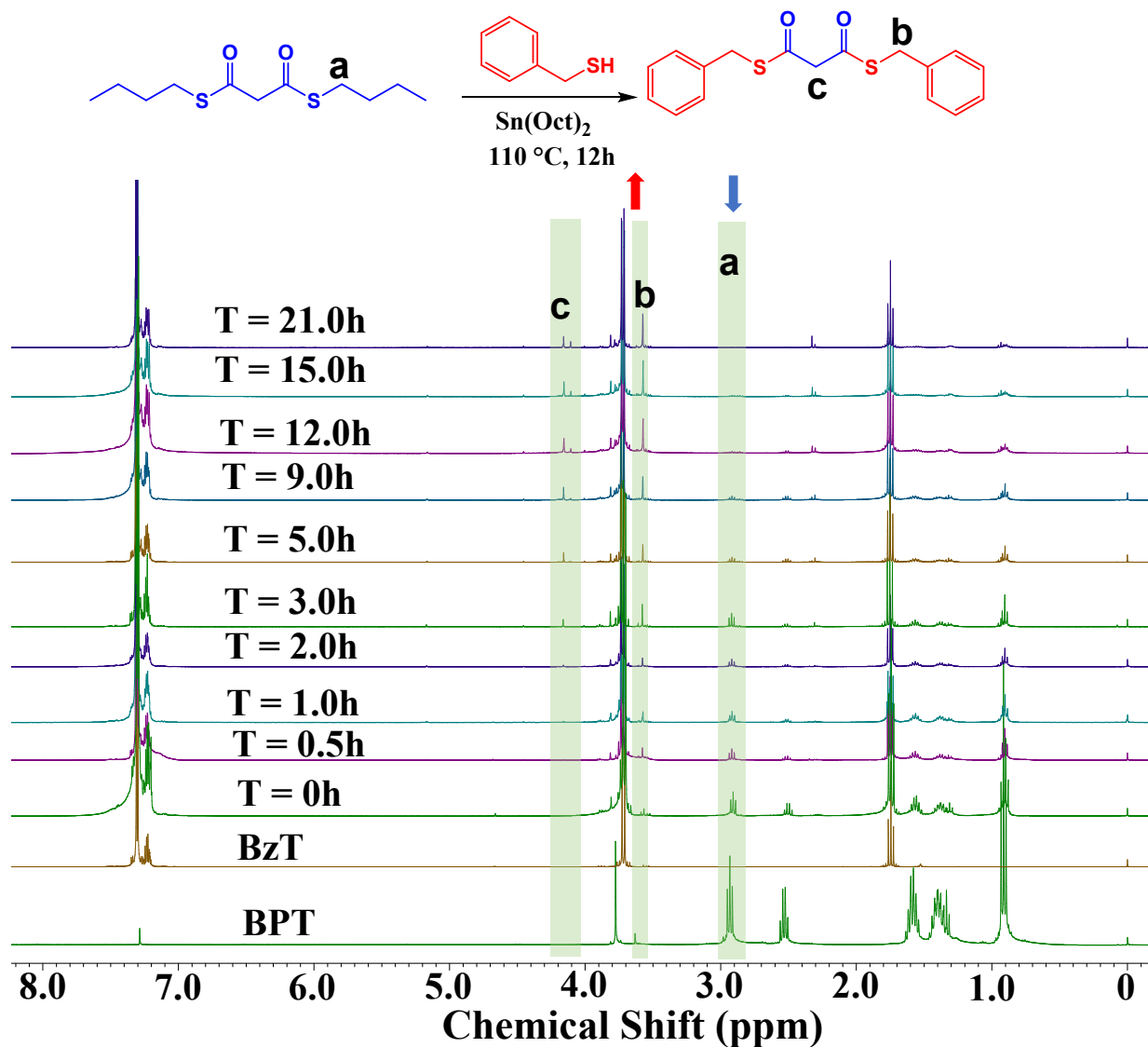


Figure S6: ^1H NMR spectra of the BPT and BzT exchange reaction recorded at different time periods, $[\text{BPT}] = 1\text{ mol}$, $[\text{BzT}] = 15\text{ mol}$, $[\text{Sn}(\text{Oct})_2] = 5\text{ mol}\%$ with respect to thioester group and temperature = $110\text{ }^\circ\text{C}$.

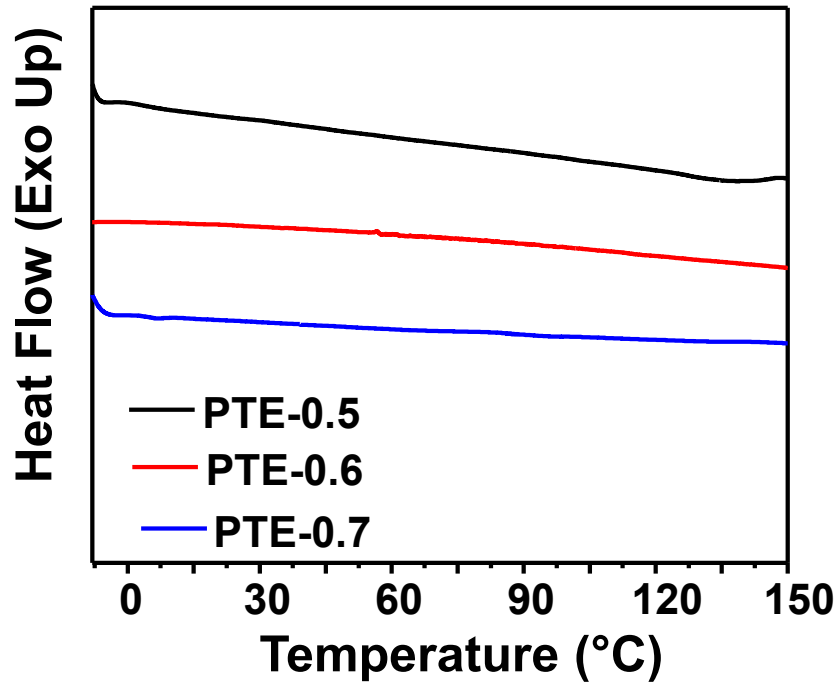


Figure S7: Typical DSC second heating traces of PTE-n at the heating rate of 5 °C/min under N₂ atmospheric conditions.

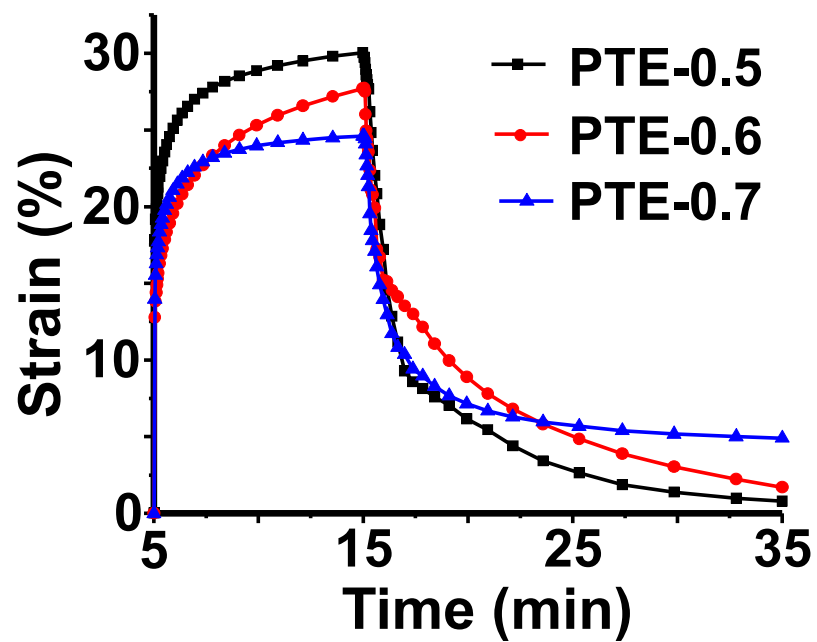


Figure S8: The creep recovery profile of PTE-n recorded at 35 °C under fixed stress mode (70 kPa).

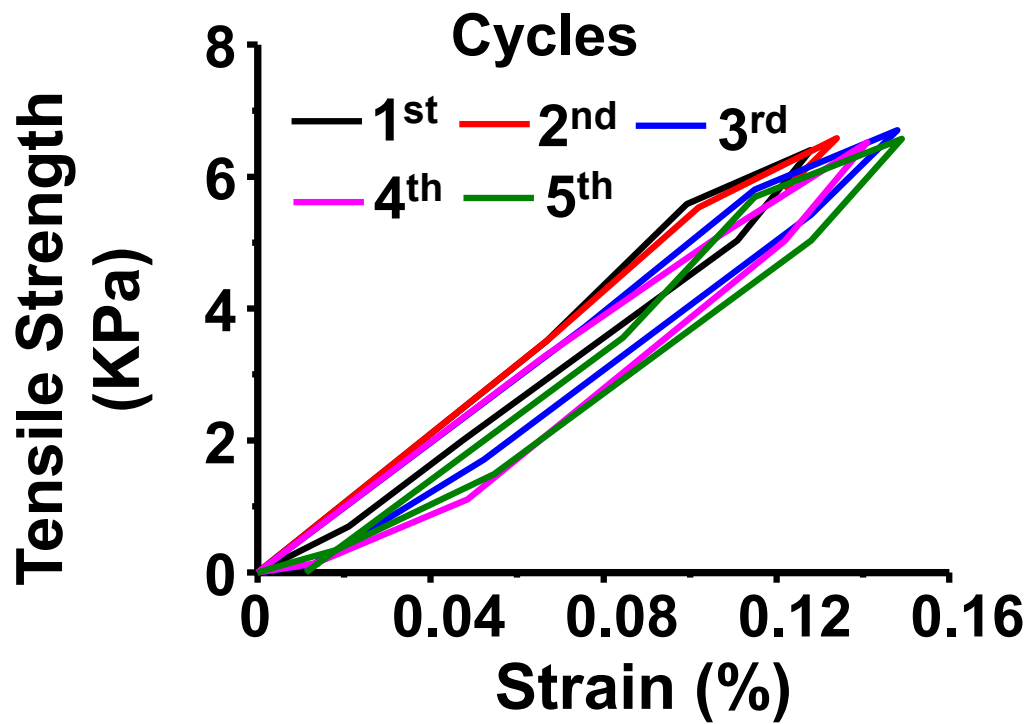


Figure S9: The hysteresis cycles of PTE-0.5 recorded under tensile mode.



Figure S10: Demonstration of self-welding ability of PTE-0.5, (A1) two separated strips, (A2) A1 after completion of welding, (A3) A2 strip under stretched conditions.

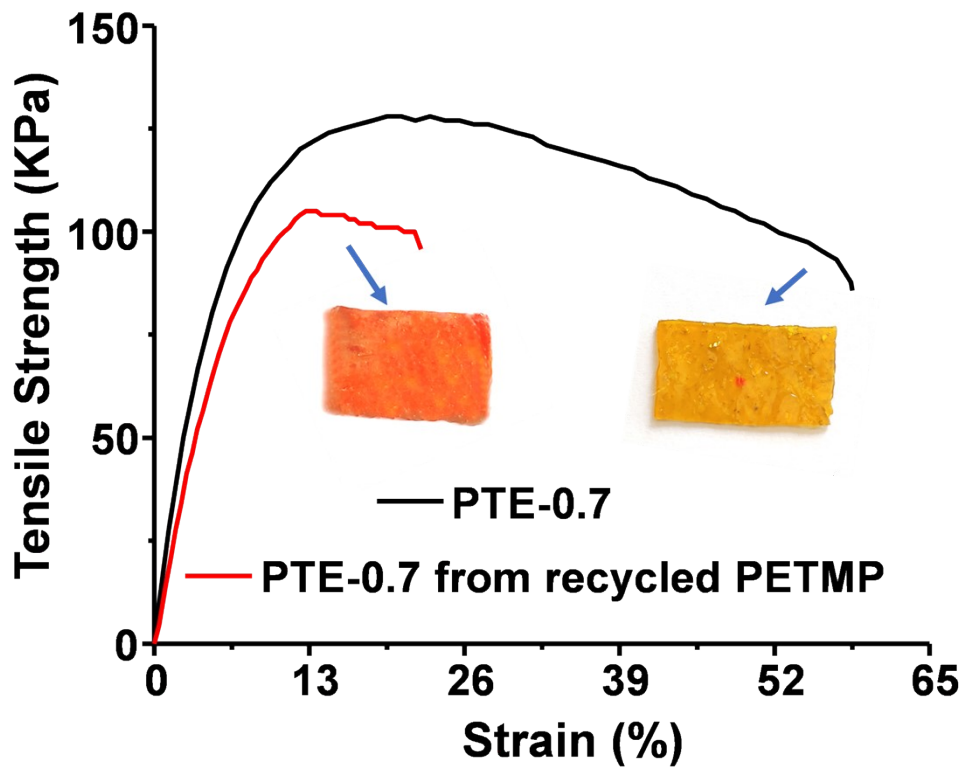


Figure S11: The tensile plots of PTE-0.7 and PTE-0.7 synthesized from recycled PETMP.

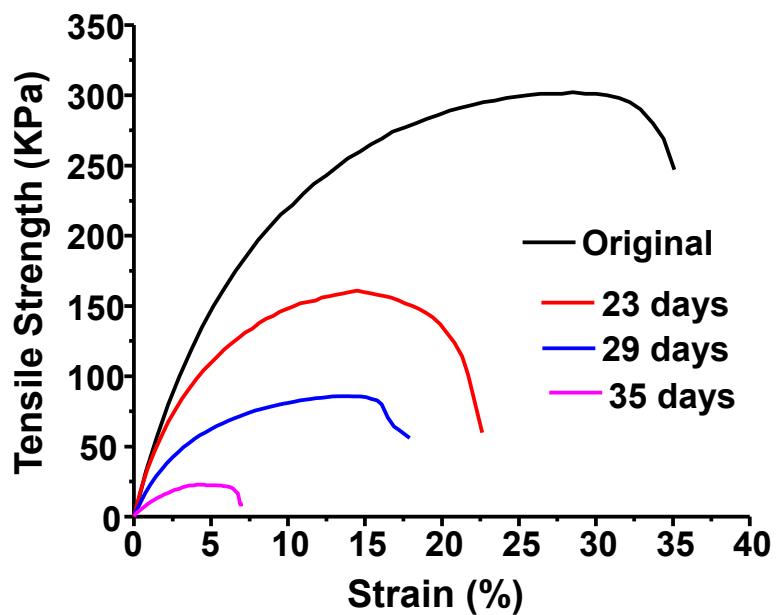


Figure S12: The tensile plots of the pristine PTE-0.5 and the samples after different biodegradation periods.



Figure S13: A remolded strip of PTE-0.5 stretched against 205 gm load.

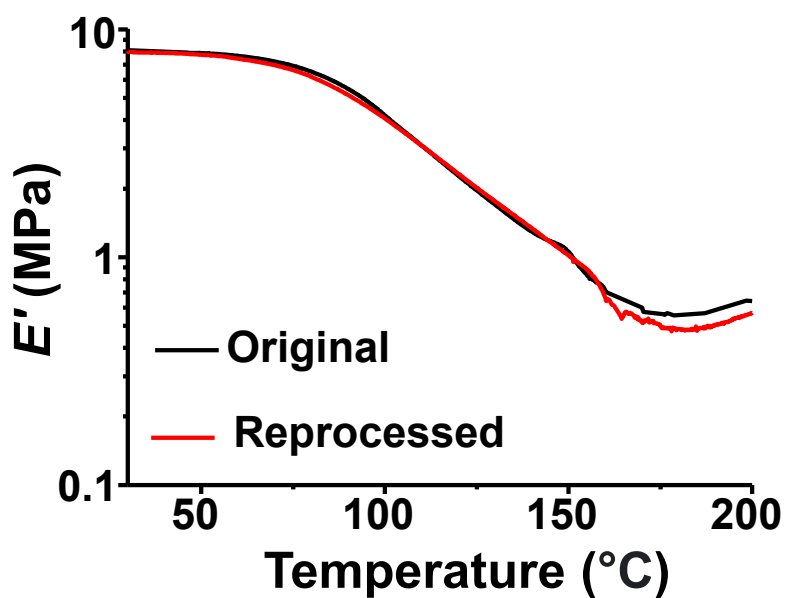


Figure S14: DMTA Traces of PTE-0.5 (original and reprocessed) samples recorded over the temperature range of 30 to 200 $^{\circ}\text{C}$.

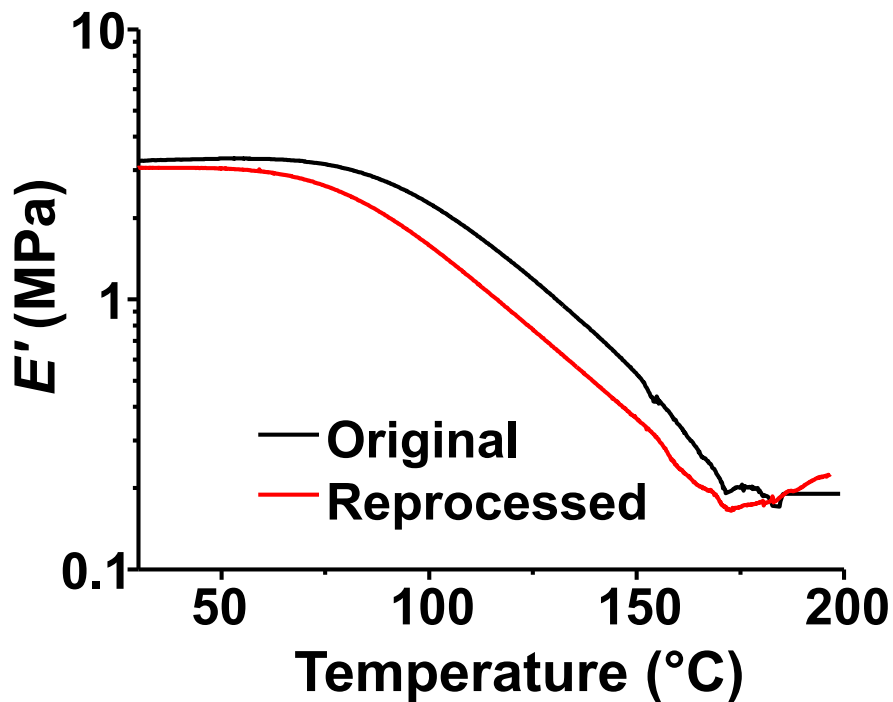


Figure S15: DMTA Traces of PTE-0.6 (original and reprocessed) samples recorded over the temperature range of 30 to 200 °C.

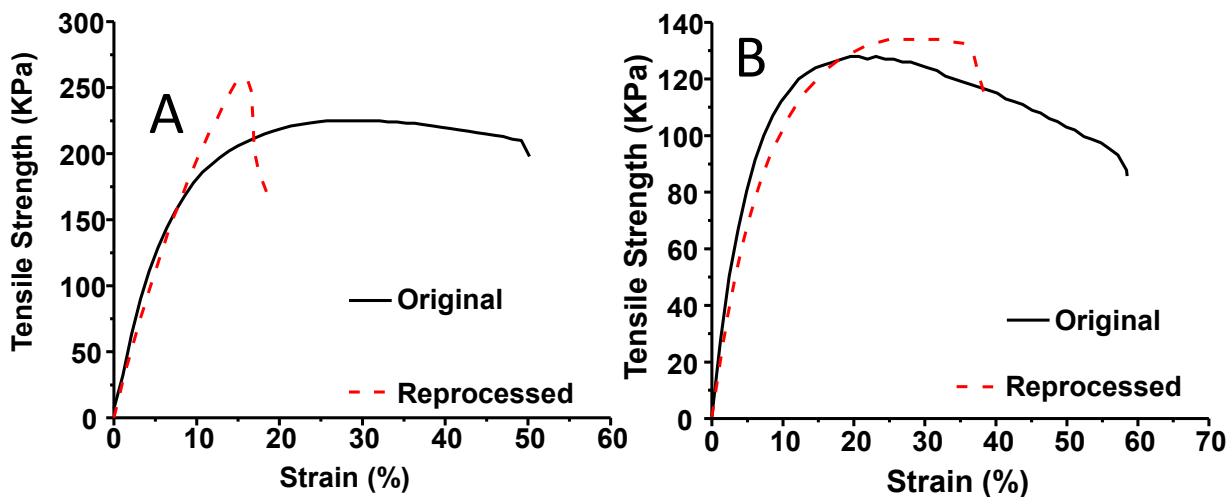


Figure S16: The tensile data of original and reprocessed (A) PTE-0.6 and (B) PTE-0.7 samples.

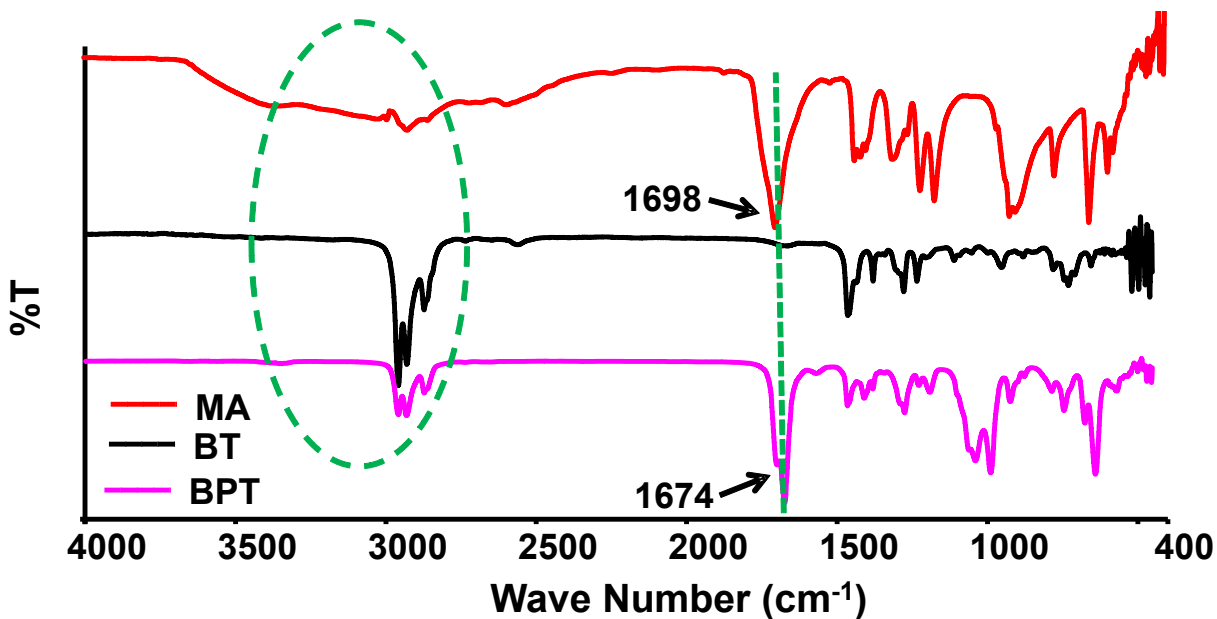


Figure S17: FT-IR Data of Malonic Acid (MA), BT, and BPT (Precursor of Exchange reaction).

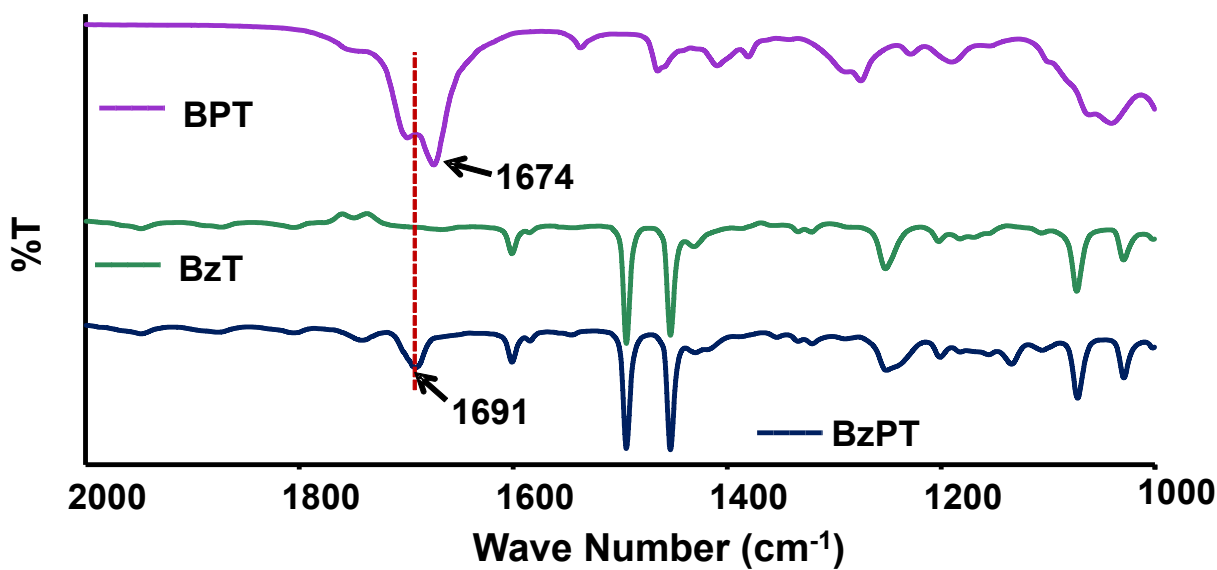
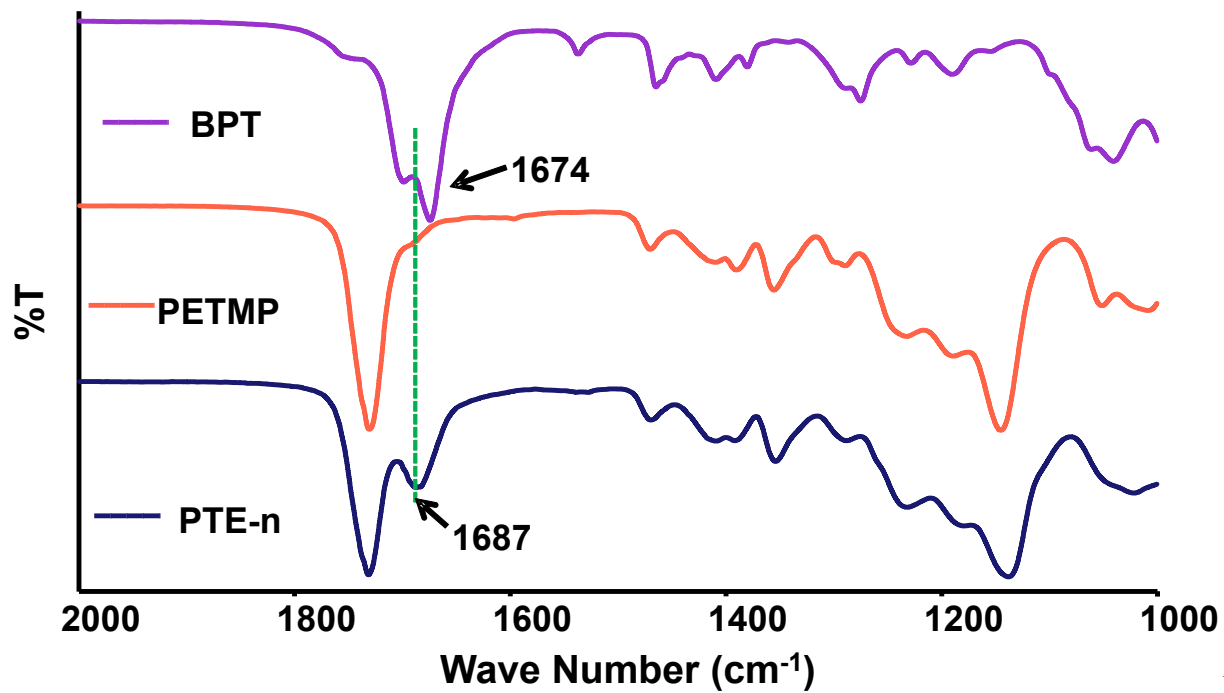


Figure S18: FT-IR Data of BPT (Precursor), BzT, and BzPT (Exchange Product).



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Figure S19: FT-IR Data of BPT (Precursor), PETMP, and PTE-n (thin film).

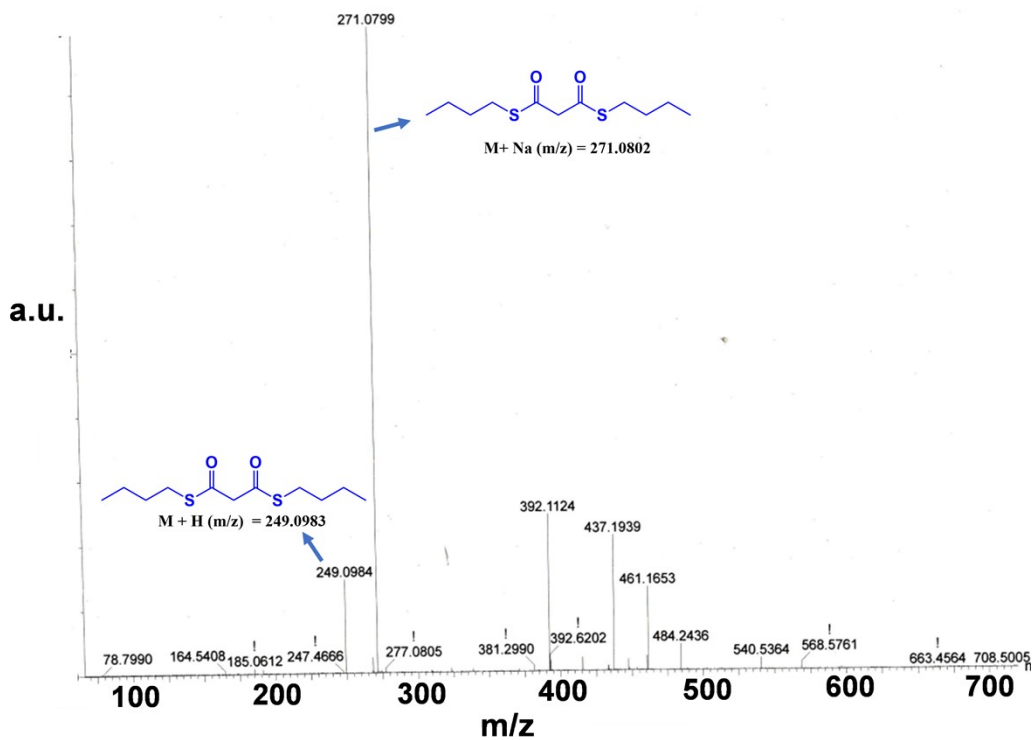


Figure S20: High-Resolution Mass spectra of BPT (Precursor of the thioesterification reaction).

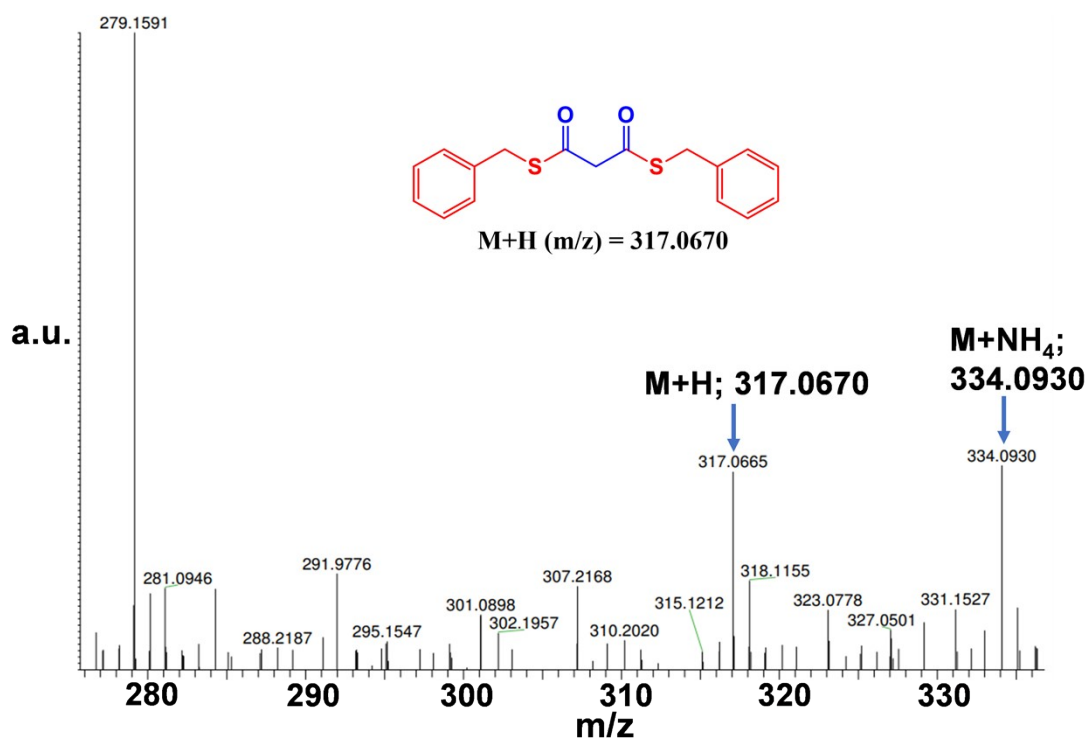


Figure S21: High-Resolution Mass spectra of BzPT (transthioesterification reaction product).