Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Chemically Recycling Poly(thiourethane) Thermosets Enabled by Dynamic Thiourethane Bonds

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Experimental

Materials Trimethylolpropane tris(3-mercaptopropionate) (TMPTMP), cyclopentanethiol, 1-octanethiol, methyl 3-mercaptopropionate, methyl thioglycolate, ethyl 2-mercaptopropionate, cyclohexyl isocyanate, 4,4′-methylenebis(cyclohexyl isocyanate) (CHDI), 1,3-Bis(1-isocyanato-1-methylethyl)benzene (TXMDI), m-xylylene diisocyanate (XDI), Tolylene-2,4-diisocyanate (TDI), 1,1,3,3-Tetramethylguanidine (TMG), (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO), pyrogallol (PYL), and 1,3,5-triazine-2,4,6-trione (TATATO) were purchased from Sigma-Aldrich. Ethoxilated-trimethylolpropan tri(3-Mercaptopropionate) (ETTMP 700 and ETTMP 1300) were donated from Bruno Bock. Irgacure 2022 were purchased from BASF. All reactants and solvents were used as received.

Equilibrium constants determination Cyclohexyl isocyanate and cyclopentane thiol were dissolved in $CDCl_3$ (0.25 M) with 4 mol% TMG and transferred to the NMR tubes. ^1H NMR spectra were collected 12 hrs after the monomers were mixed at room temperature. The concentration of each species was calculated based on the integral ratios of the ^1H NMR signals and the initial concentration of thiol and isocyanate groups. The equilibrium constants were calculated[31] as:

$$K_{eq} = \frac{[3]_{eq}}{[1]_{eq} \times [2]_{eq}}$$

Determination of dissociation rates of modeled thiourethane bonds. Small molecule thiourethanes were synthesized by mixing thiol with equal moles of isocyanate in $CDCl_3$ (0.25 M) with 4 mol% TMG. After 1hr, after confirming equilibrium was reached, 4-fold excess of isocyanate was added into the solution. The consumption rates of the corresponding thiourethane were monitored by ^1H NMR at room temperature at varied time intervals. The dissociation rate constant was calculated[31] as

$$k_d = \frac{\log\left(\frac{[3]_t}{[3]_0}\right)}{t} .$$

Sample preparation. Stoichiometric mixtures of a thiol and isocyanate based on functionality were prepared with 2 wt% TEMPO as an initiator. The resin was casted between glass slides with 0.25 mm thickness spacers. The resins were cured at 80^{o}C for 4 h follow by postcuring at 100^{o}C overnight. To recycle the thiourethane network, 0.5g film was cut into small pieces and mixed with 9 molar equivalent excess of thiol monomers and solvent (5 mL acetone and 4 wt% TMG). The thiourethane film completely depolymerized within 6 hours at ambient temperature. The organic layer was washed with 1M HCl solution twice followed by washing with brine water. The combined organic layer was then dried over anhydride Na_2SO_4 and can be used after removing all the volatiles.

Dynamic mechanical analysis. Mechanical performance (modulus and glass transition temperature) of the pristine and recycled polymers was characterized using a DMA Q800 (TA Instruments) in multifrequency strain mode with a sinusoidal stress of 1 Hz frequency and a heating rate of 3 ºC min^{-1}. The glass transition temperature (Tg) was determined as the peak of the tan delta curve.

Tensile Tensile stress-strain curves were measured via a tensile test (MTS 858 Mini Bionix II) with a strain rate of 5 mm min^{-1}. Dog-bone samples of the size 0.25 × 3.8 × 15 mm (t × w × l) were used. Three replicates were made for each sample.

3D printing. A stoichiometric ratio of recycled thiol oligomers and triallyl monomer, TATATO, were mixed with 2 wt.% Irgacure 819 and 0.02 wt.% pyrogallol. All objects were printed on a PRUSA SL1 using a blue-light LED projector ($\lambda = 405$ nm, $J_e = 0.4$ mW·cm^{-2}). Each layer was exposed for an equivalent time period (t = 13s). The CAD model was obtained from Thingiverse.com. PrusaSlicer software sliced the CAD models into discrete 0.1 mm layers and created a corresponding black and white image stack.

Fourier Transform Infrared Spectroscopy. Polymerization kinetics were monitored in situ using a FTIR instrument (Nicolet 6700). Irradiation was performed with a light guide connected to a 405 nm LED source (Thorlabs). The light intensity was kept at 0.4 mW/cm2, which was measured by a radiometer (Model 100, Demetron Research Corp.). Samples were irradiated for 5 min until the monitored group absorption peak no longer decreased. The final resin conversions were calculated based on the absorbance peak area of vinyl functional group around 3000 cm^{-1} and thiol functional group around 2600 cm^{-1}.

Thermogravimetric analysis (TGA). The TGA curves of the pristine and recycled polymers were measured via a PerkinElmer Pyris 1. All samples were heated from 50 ºC to 600 ºC at 10 ºC/min under nitrogen flow.

Swelling Test and Soluble Fraction Test. The degree of swelling and the soluble fraction of pristine and recycled polymers have been determined in a variety of solvents (toluene, methanol, and acetone). Square shaped samples of the size 0.25 × 3 × 3 mm (t × w × l) were used. The sample (initial weight, m_i) was immersed in the solvent at ambient temperature for 24 hours. Once the swelling equilibrium was reached, the weight of the sample was measured after wiping dry the surface solvent (m_s). Sample was further dried in a vacuum oven at 70°C until constant weight after desorption (m_d) was achieved. The equilibrium degree of swelling, s, and sorption, w, are calculated using the following equations:

$$s = \frac{m_i - m_s}{m_i},\ w = \frac{m_i - m_d}{m_i}$$

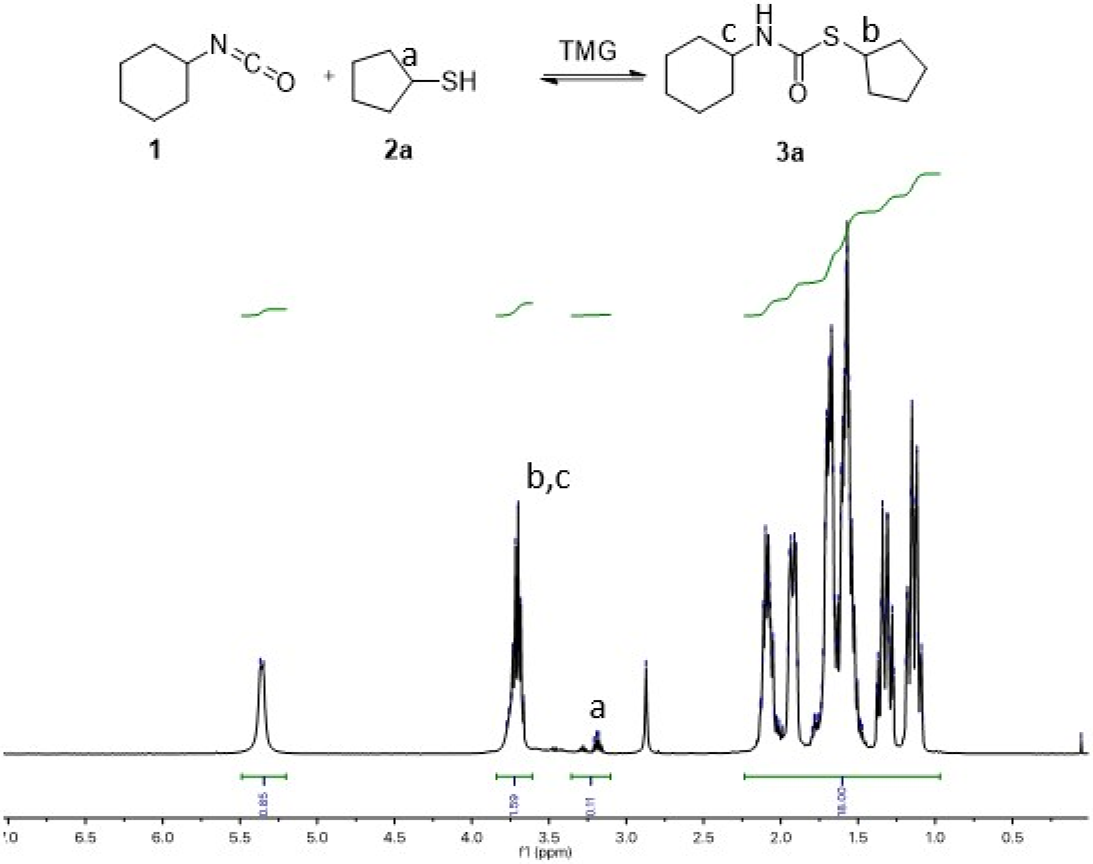


Fig S1. Determination of equilibrium constant of the thiourethane 3a. ^{1}H NMR spectrum of 1 and 2a at initial ratio of 1:1 and the product 3a in $CDCl_3$ (0.25 M). 4 mol% TMG was added in the mixture. The spectrum was taken 12 hr after TMG were added.

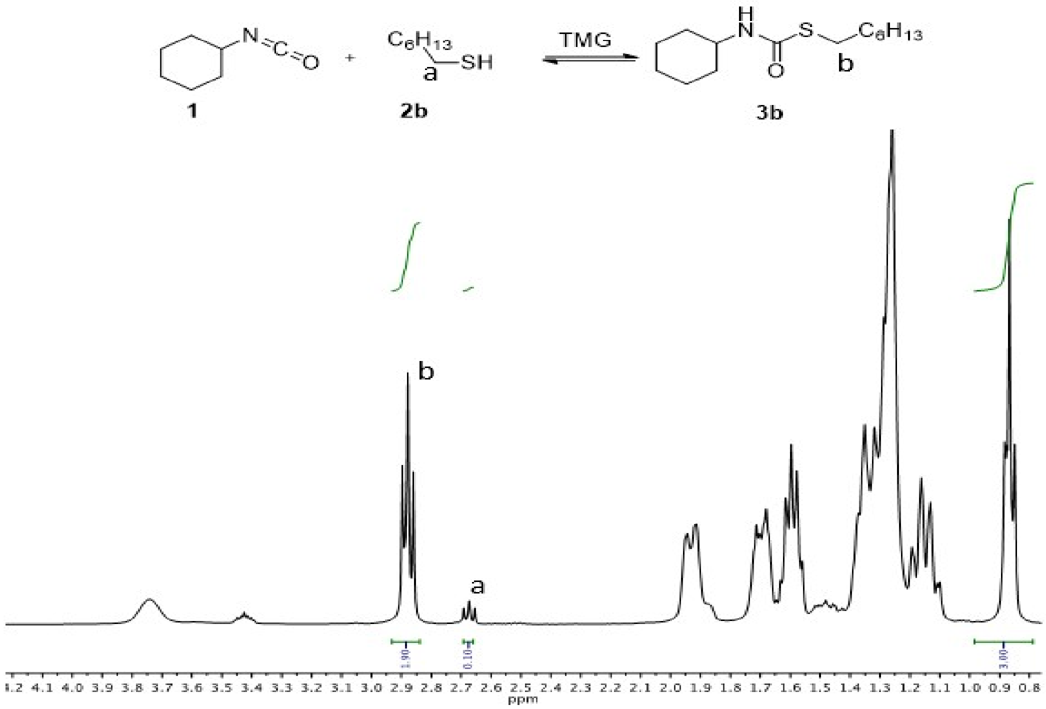


Fig S2. Determination of equilibrium constant of the thiourethane 3b. ^{1}H NMR spectrum of 1 and 2b at initial ratio of 1:1 and the product 3a in $CDCl_3$ (0.25 M). 4 mol% TMG was added in the mixture. The spectrum was taken 12 hr after TMG were added.

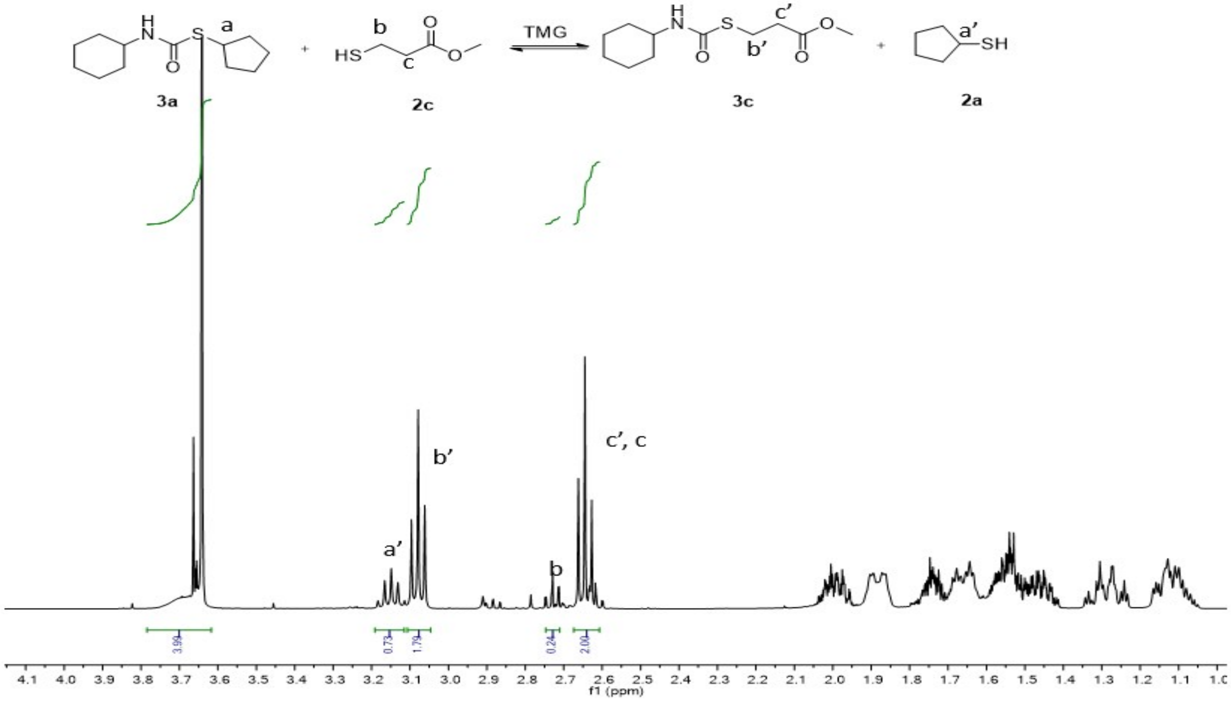


Fig S3. Determination of equilibrium constant of the thiourethane 3c. ^{1}H NMR spectrum of 1, 2a, and 2c at initial ratio of 1:1:1 and the product 3a and 3c in $CDCl_3$ (0.25 M). 4 mol% TMG was added in the mixture. The spectrum was taken 12 hr after TMG were added.

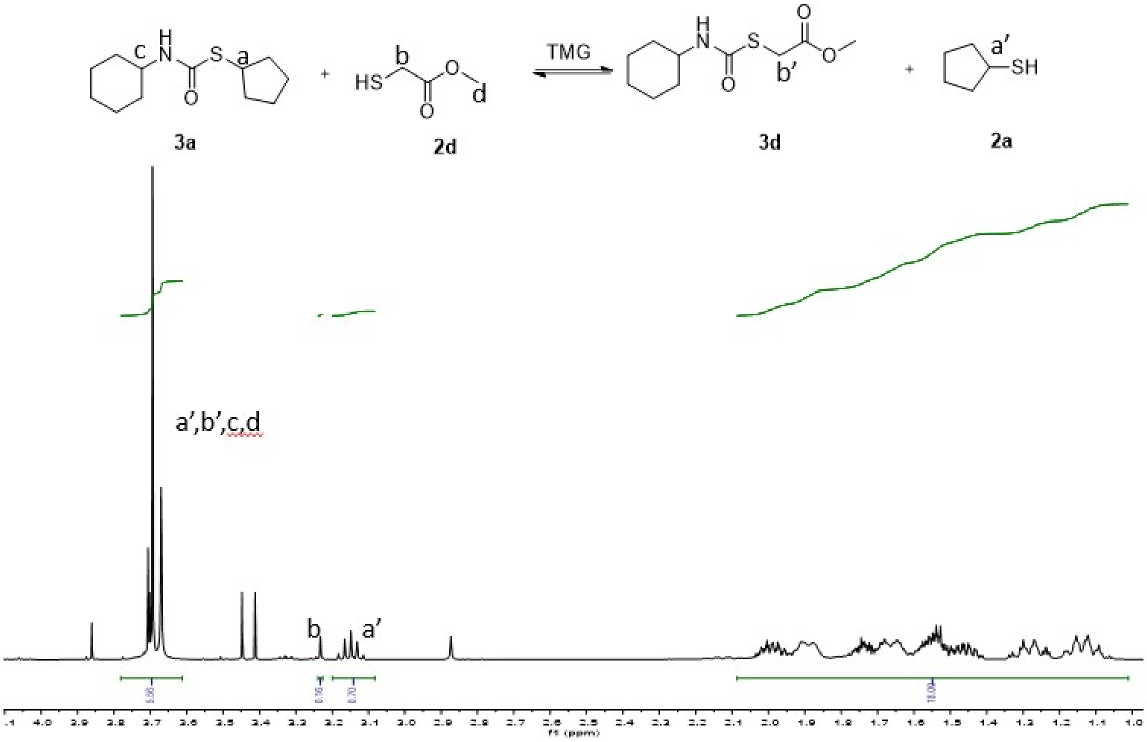


Fig S4. Determination of equilibrium constant of the thiourethane 3d. ^{1}H NMR spectrum of 1, 2a, and 2d at initial ratio of 1:1:1 and the product 3a and 3d in $CDCl_3$ (0.25 M). 4 mol% TMG was added in the mixture. The spectrum was taken 12 hr after TMG were added.

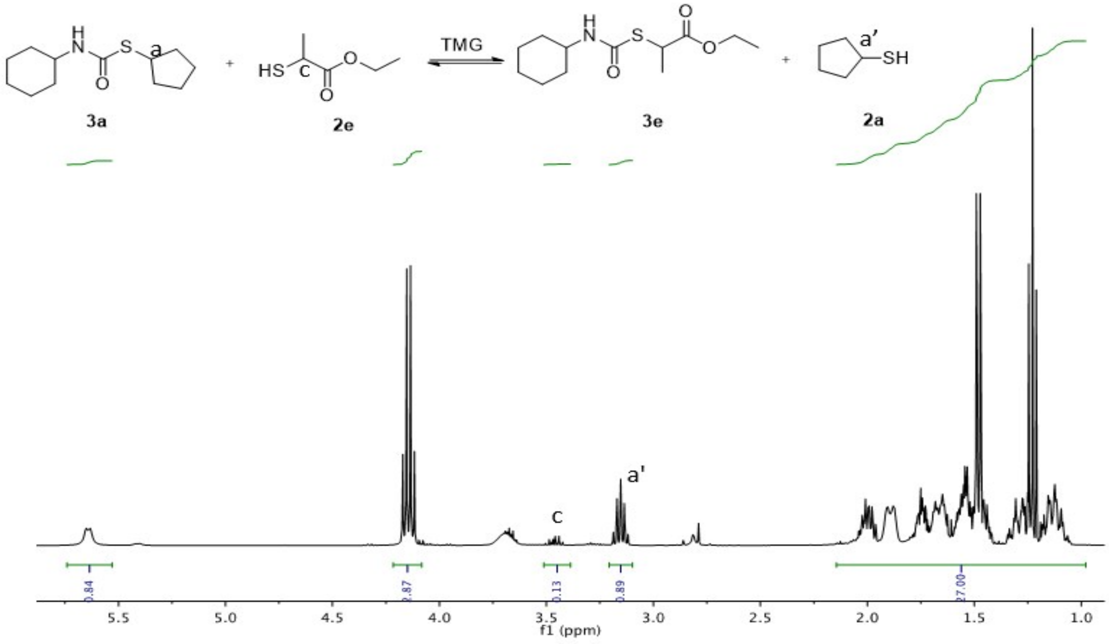
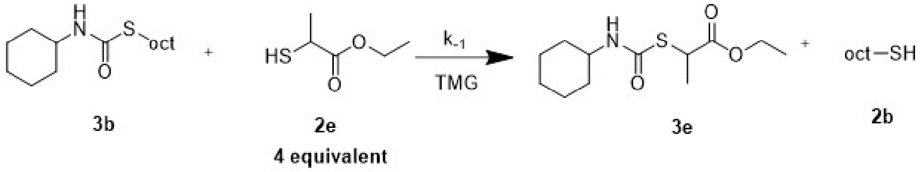


Fig S5. Determination of equilibrium constant of the thiourethane 3e. ^{1}H NMR spectrum of 1, 2a, and 2e at initial ratio of 1:1:1 and the product 3a and 3e in $CDCl_3$ (0.25 M). 4 mol% TMG was added in the mixture. The spectrum was taken 12 hr after TMG were added.



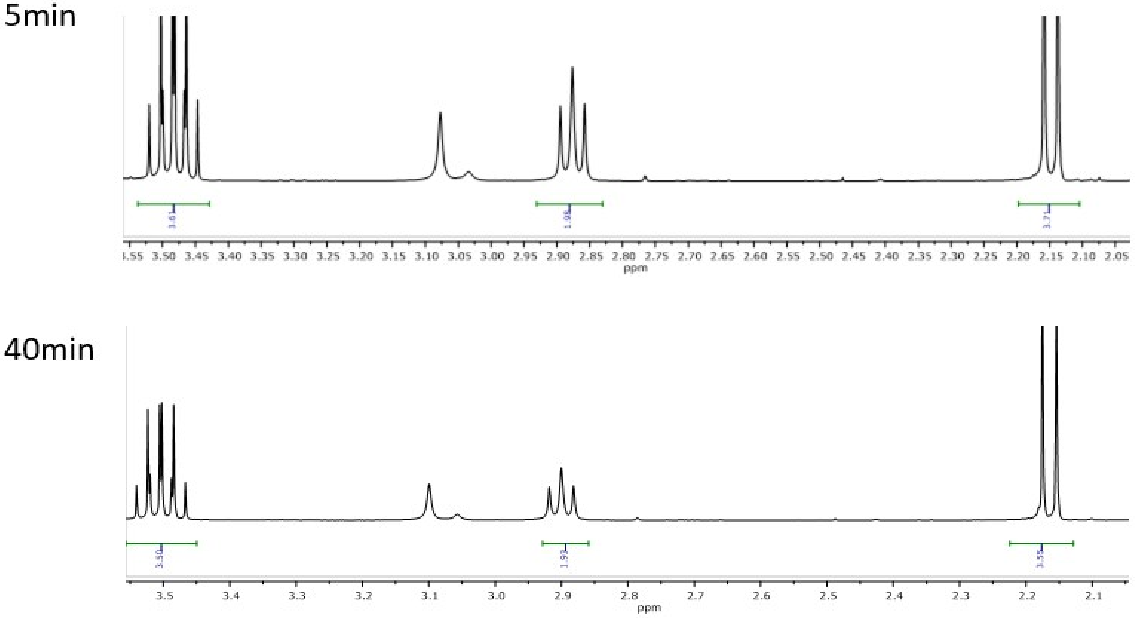


Fig S6. The exchange kinetics of the thiourethane 3b bond. ^{1}H NMR spectrum of 3b (0.25 M) and 2e, at initial ratio of 1:4 and the product 3e and 2b in $CDCl_3$. 4 mol% TMG was added in the mixture. The spectrum was taken 40 min after 2e were added. All the reaction conducted at ambient temperature.

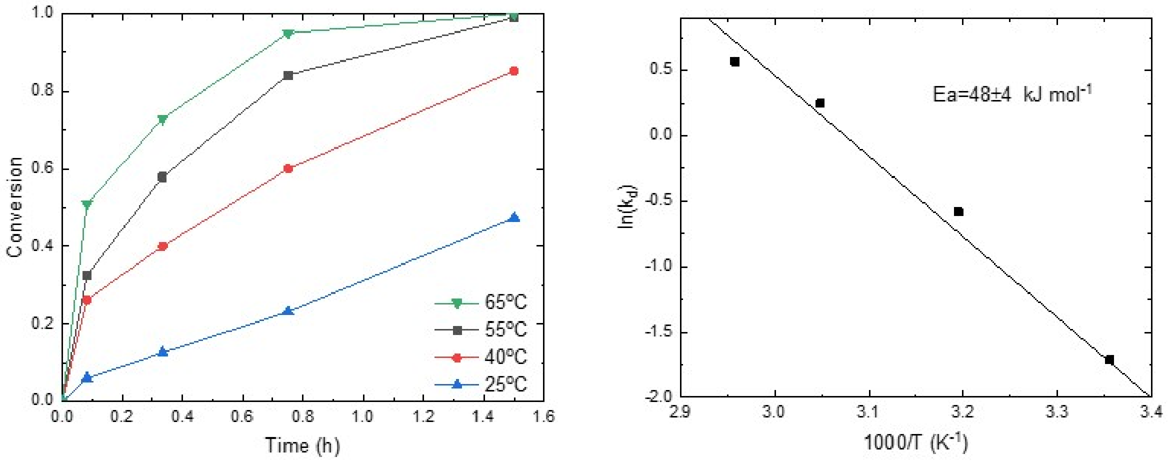


Fig S7. The exchange kinetics of the thiourethane 3b bond at varied temperature. ^{1}H NMR spectrum of 3b (0.25 M) and 2e, at initial ratio of 1:4 and the product 3e and 2b in $CDCl_3$. 4 mol% TMG was added in the mixture. The activation energy was calculated based on linear regression of dissociation kinetic parameter and temperature.

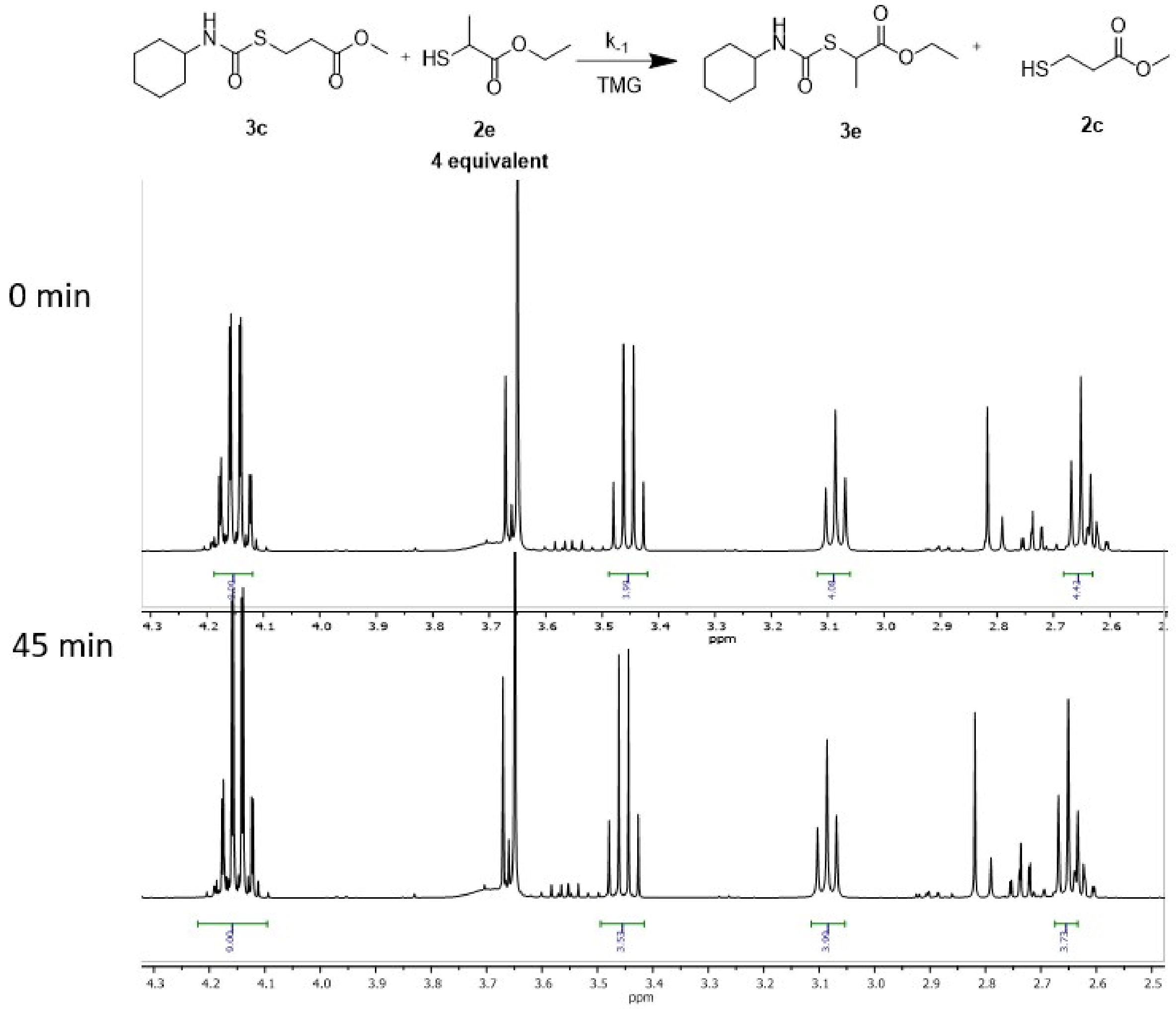
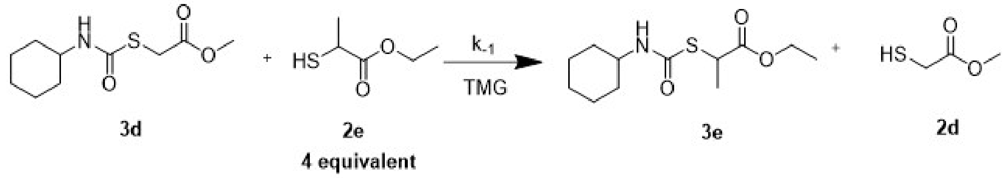


Fig S8. The exchange kinetics of the thiourethane 3c bond. ^{1}H NMR spectrum of 3c (0.25 M) and 2e, at initial ratio of 1:4 and the product 3e and 2c in $CDCl_3$. 4 mol% TMG was added in the mixture. The spectrum was taken 45 min after 2e were added. All the reaction conducted at ambient temperature.



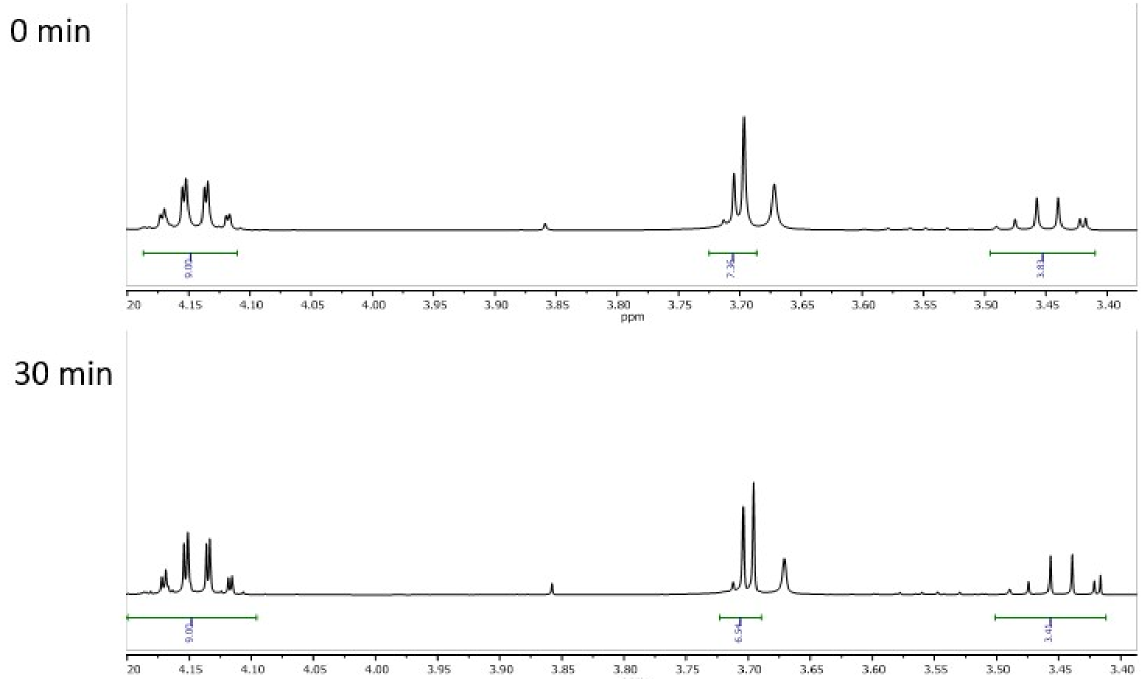


Fig S9. The exchange kinetics of the thiourethane 3d bond. ^{1}H NMR spectrum of 3d (0.25 M) and 2e, at initial ratio of 1:4 and the product 3e and 2d in $CDCl_3$. 4 mol% TMG was added in the mixture. The spectrum was taken 30 min after 2e were added. All the reaction conducted at ambient temperature.

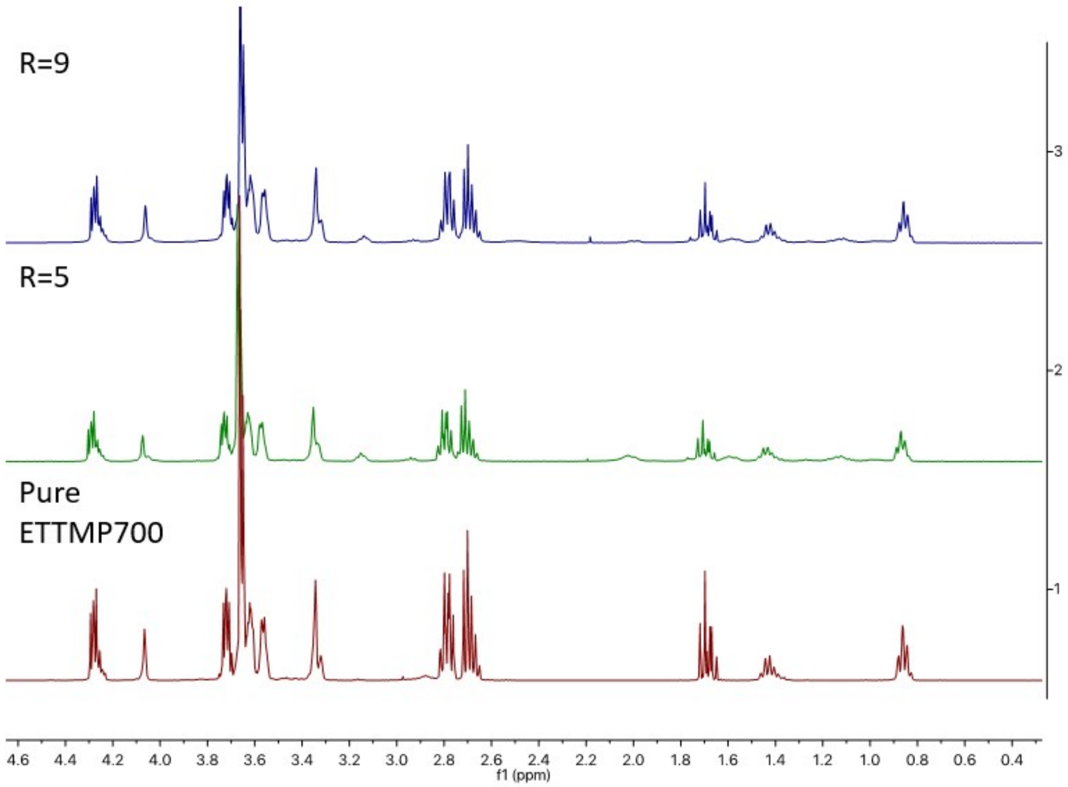


Fig S10. ^{1}H NMR spectrum of recycled oligomers (R=5 and R=9) in CDC_{l3}. The oligomers were obtained by depolymerized with excess thiol in acetone and TMG as catalyst at ambient temperature.

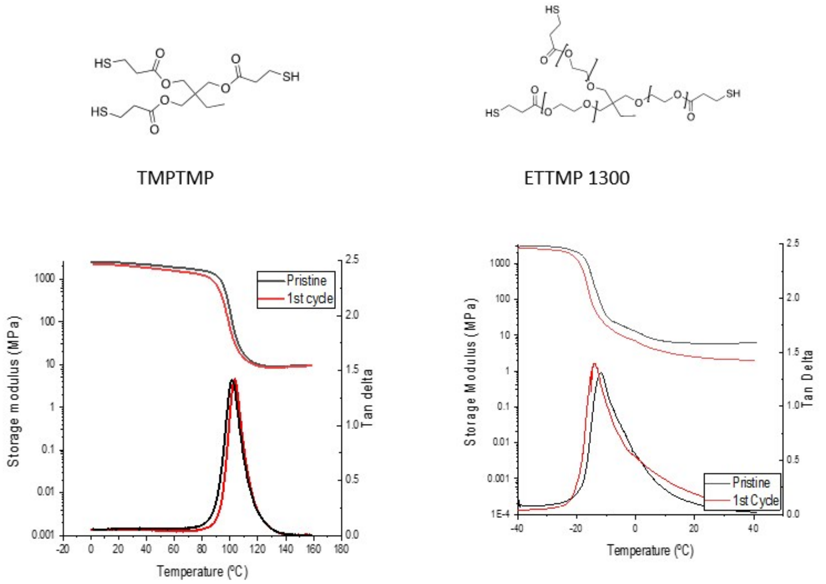


Fig S11. DMA curve of pristine and recycled thiourethane films. The samples were made with CHDI reacting with different trithiol with stoichiometric ratio of 1:1 with 2 wt% TEMPO. The mechanical properties change from glassy material to rubbery material base on the chain length of the trithiol monomers. The recycled film shows similar mechanical properties with its pristine sample.

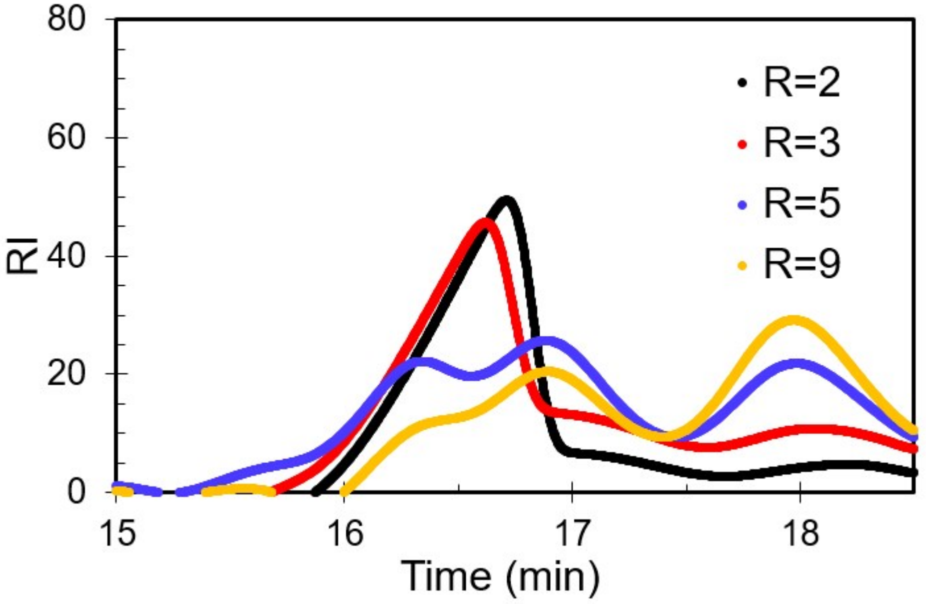


Fig S12. Refractive index profiles of recycled oligomer from thiouretane film. The oligomers were obtained by depolymerizing thiourethane film with excess of ETTMP700 at varied stoichiometric ratio r=2,3,5 and 9 in acetone and TMG at ambient temperature. Samples were prepared with a concentration of 10 mg/ml in dry DMSO and analyzed at 0.35 mL/min at 50^{o}C.

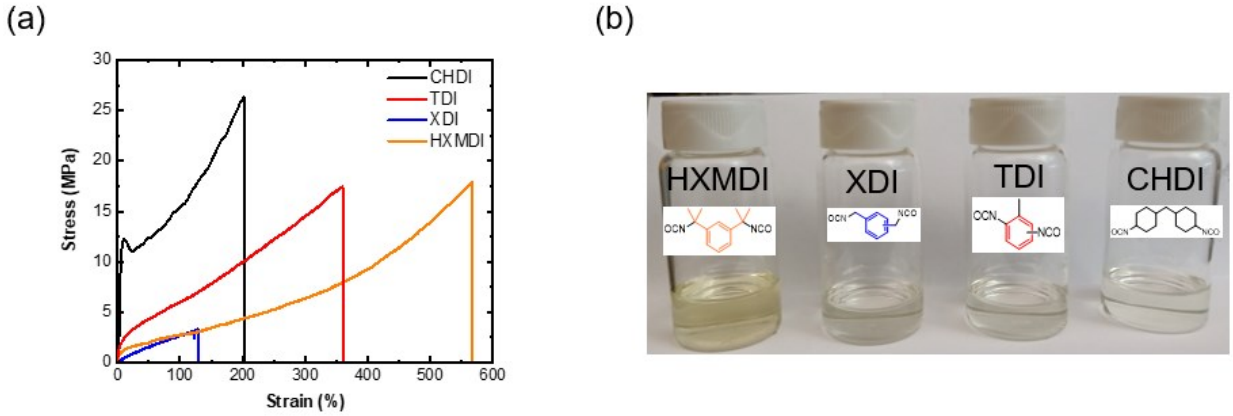


Fig S13. (a) Tensile stress-strain curves of ETTMP700 with a variety of diisocyanate monomers. (b) a photo of depolymerized networks.

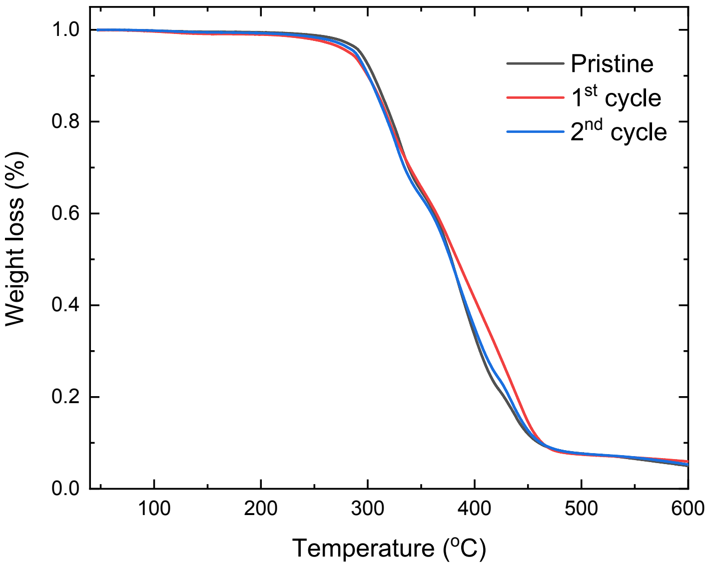


Fig S14. TGA curves of pristine and recycled thiourethane films. The recycled film shows similar thermogravimetric properties with its pristine sample.

Table S1. The solvent equilibrium degree of swelling of the pristine and recycled thiourethane polymers. (SD in parentheses).

	Toluene	Methanol	Acetone
Pristine	0.34 (0.02)	0.26 (0.01)	0.40 (0.03)
1st cycle	0.36 (0.01)	0.26 (0.02)	0.48 (0.09)
2nd cycle	0.32 (0.04)	0.27 (0.02)	0.43 (0.06)

Table S2. Solvent sorption results for the pristine and recycled thiourethane polymers. (SD in parentheses).

	Toluene	Methanol	Acetone
Pristine	0.05 (0.01)	0.02 (0.01)	0.02 (0.01)
1st cycle	0.02 (0.02)	0.01 (0.01)	0.01 (0.01)
2nd cycle	0.03 (0.02)	0.02 (0.01)	0.01 (0.01)