Electronic Supplementary Material (ESI) for Polymer Chemistry.
This journal is © The Royal Society of Chemistry 2017

Supporting Information

Reprocessable Polyhydroxyurethane Network Exhibiting Full Property Recovery and Concurrent Associative and Dissociative Dynamic Chemistry via Transcarbamoylation and Reversible Cyclic Carbonate Aminolysis

Xi Chen[1], Lingqiao Li[1], Kailong Jin[1], and John M. Torkelson[1,2]*

[1]*Dept. of Chemical and Biological Engineering, Northwestern University, Evanston, IL 60208 USA*

[2]*Dept. of Materials Science and Engineering, Northwestern University, Evanston, IL 60208 USA*

*Correspondence to: Prof. John M. Torkelson (Email: *j-torkelson@northwestern.edu*)

1. Experimental

Materials

Poly(propylene glycol) diglycidyl ether (average M_n = ~640 g/mol), tris(4-hydroxyphenyl)methane triglycidyl ether, tris(2-aminoethyl)amine (96%), cyclohexylamine (CYCHA, *ReagentPlus*®*,* ≥99%), 4-(dimethylamino)pyridine (DMAP, *ReagentPlus*®*,* ≥99%), tetrabutylammonium iodide (TBAI, reagent grade, 98%), 1,4-butanediol, anhydrous N,N-dimethylformamide (DMF, 99.8%), dimethyl sulfoxide-d_6 (DMSO, 99.9 atom% D) and chloroform-d (99.8 atom% D) were purchased from Sigma-Aldrich. JEFFAMINE® D-400 polyoxypropylenediamine (average M_n = ~430 g/mol) was supplied by The Huntsman Corporation. Divinyl benzene dioxide was supplied by The Dow Chemical Company, Freeport, TX.

Synthesis

Synthesis of Poly(propylene glycol) Dicyclocarbonate (PPGDC)

Poly(propylene glycol) diglycidyl ether (100 g, 156.25 mmol) and TBAI (5.771 g, 15.625 mmol) were added to a round bottom flask. The flask was placed into an oil bath set at 80 °C, and CO_2 gas was bubbled through the mixture continuously until the reaction reached full conversion. The progress of reaction was monitored using ^1H NMR spectroscopy by examining the disappearance of peaks (~2.62, 2.79, and 3.15 ppm) associated with epoxy moiety. After the reaction was completed, 40 mL acetone and 60 mL deionized water were added to the flask to dissolve and precipitate the product. Then the mixture was transferred into a separatory funnel for phase separation, and the lower layer was collected. The acetone-water wash was repeated several times until TBAI was completely removed from the product. The product was dried in a vacuum oven at 80 °C.

Synthesis of Tris(4-hydroxyphenyl)methane Tricyclocarbonate (THPMTC)

Tris(4-hydroxyphenyl)methane triglycidyl ether (25 g, 54.29 mmol) and TBAI (2.005 g, 5.429 mmol) were added to a test tube. The tube was placed into an oil bath set at 80 °C, and CO_2 gas was bubbled through the mixture continuously until the reaction reached full conversion. Anhydrous dimethylacetamide was added to the test tube when the mixture became too viscous for CO_2 to flow through. The progress of reaction was monitored using ^1H NMR spectroscopy by examining the disappearance of peaks (~2.72, 2.87, and 3.32 ppm) associated with epoxy moiety. After the reaction was completed, the mixture was dissolved in 25 mL acetone and poured into a beaker. Then 75 mL deionized water was added to precipitate the product. The liquid phase was decanted and the solid product collected. The acetone-water wash was repeated several times until TBAI was completely removed from the product. The product was dried in a vacuum oven at 80 °C.

Synthesis of Divinyl Benzene Dicyclocarbonate (DVBDC)

Divinylbenzene dioxide (25 g, 15.4 mmol) and TBAI (5.69 g, 1.54 mmol) were added to a round bottom flask. The flask was placed into an oil bath set at 80 °C, and CO_2 gas was bubbled through the mixture continuously until the reaction reached full conversion. Anhydrous dimethylacetamide was added to the flask when the mixture became solid. The progress of reaction was monitored using ^1H NMR spectroscopy by examining the disappearance of peaks (~2.76, 3.12, and 3.83 ppm) associated with epoxy moiety. After the reaction was completed, the solid mixture was dissolved in 30 mL acetone and then precipitated with 100 mL water. The slurry was filtrated, and the solid paste was collected. The acetone-water wash was repeated several times until TBAI was completely removed from the product. The product was dried in a vacuum oven at 80 °C.

Synthesis of PHU Networks

In a typical synthesis of PPGDC-TAEA networks, 2 g (2.75 mmol) PPGDC and 33.56 mg (0.275 mmol) DMAP were added to a Flacktek Max-10 mixing cup and heated at 80 °C. After the catalyst was fully dissolved, 0.2678 g (1.83 mmol) tris(2-aminoethyl)amine was added and mixed using a FlackTek DAC 150.1 FVZ-K SpeedMixer™ at 2800 rpm for 40 sec. The cup was then sealed with a piece of parafilm and the mixture was reacted at 80 °C for 2 h. Then the cup was placed in an oven set at 80 °C for 12 h to achieve higher conversion. In a typical synthesis of THPMTC-JEFFAMINE® D-400 networks, 2.757 g (4.65 mmol) THPMTC and 85.23 mg (0.699 mmol) DMAP were added to a 20-mL scintillation vial and dissolved in 2.0 mL anhydrous DMF. Then 3 g (6.99 mmol) JEFFAMINE® D-400 was added to the vial and mixed with other components by shaking. The mixture was reacted at 80 °C for 5 h and then poured into a mold. The material was cured at 80 °C for 12 h using a compression mold. Then the gel was cut into small pieces and placed in a vacuum oven at 80 °C for 48 h to remove DMF and achieve higher conversion.

Synthesis of Model Molecule

In a typical synthesis of DVBDC-CYCHA model molecule, 0.2 g (0.8 mmol) DVBDC and 9.77 mg (0.08 mmol) DMAP were added to a 7-mL scintillation vial and dissolved in 0.5 mL deuterated DMSO. Then 0.1587 g (1.6 mmol) cyclohexylamine was added to the vial, and the mixture was reacted at 80 °C for 36 h until the peaks associated with cyclic carbonate (~4.42, 4.90, and 5.91 ppm) disappeared completely in ^{1}H NMR spectra.

Reprocessing Procedure

Reprocessing of the PHU networks was performed using a PHI press (Model 0230C-X1). The as-synthesized PHU networks were cut into small pieces and pressed into ~0.8 mm-thick sheets at 140 °C with a 7-ton ram force (generating a pressure of ~11 MPa). The reprocessing time was 2 h for PPGDC-TAEA networks and 1 h for THPMTC-JEFFAMINE® D-400 networks. These were the minimum times required to yield an intact film which could hold its shape in swelling tests. After reprocessing the original materials, a uniform film was obtained, which was considered as the 1st reprocessed sample. The 1st reprocessed sample was then cut into small pieces and pressed again to give the 2nd reprocessed sample. Similarly, the same procedure was performed to obtain a 3rd reprocessed sample.

Decross-linking Procedure

THPMTC-JEFFAMINE® D-400 networks were first ground into fine powder, and then 50 mg of the powder was added to each of the two test tubes. In tube 1, 1.8 ml 1,4-butanediol and 0.6 ml DMSO was added. In tube 2, 2.4 ml DMSO was added. The test tubes were kept in an oil bath at 140 °C for 24 h with stirring. The appearance of mixture in each tube was compared before and after this process.

Characterization

Swelling tests were carried out for all reprocessed samples to verify the effective healing of networks. Samples measuring ~10 mm x ~10 mm x ~0.8 mm were immersed in anhydrous DMF and chloroform, which are considered as good solvents for linear PHUs. The samples were left to swell for 1 day, and then the container was shaken to determine whether the sample broke into small pieces.

Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy was performed using a Bruker Tensor 37 MiD IR FTIR spectrophotometer equipped with an attenuated total reflectance (ATR) diamond/ZnSe attachment. All samples were scanned at a resolution of 2 cm^{-1}, and 64 scans were collected in the range of 4000-600 cm^{-1}. The cyclic carbonate group peaks at ~1800 cm^{-1} were examined for PHU network samples with the spectra normalized with respect to the ether group peak at ~1100 cm^{-1}. ^{1}H NMR spectra were obtained using a Bruker Avance III 500 MHz NMR spectrometer with a direct cryoprobe at room temperature. Deuterated chloroform or dimethyl sulfoxide was used as solvent, and the samples were scanned 128 times.

Dynamic mechanical analysis (DMA) was performed using a TA Instruments Rheometrics Stress Analyzer-GIII. Rectangular specimens measuring ~30 mm x ~7 mm x ~0.8 mm were mounted on the fixture and underwent temperature sweeps from -50 °C to 70 °C (for PPGDC-TAEA networks) or -10 °C to 130 °C (for THPMTC-JEFFAMINE® D-400 networks). The measurement was carried out under tension mode at a frequency of 1 Hz and a heating rate of 3 °C/min. The storage modulus (E'), loss modulus (E") and tan δ value (E"/E') were recorded. At least three measurements were performed for each sample.

The mechanical properties of reprocessed PHU networks were measured according to ASTM D1708-10 using an MTS Sintech 20/G tensile tester. Dog-bone-shaped samples were cut from reprocessed films and were mounted on the fixture to undergo extension at a rate of 130 mm/min until break. The data were acquired at a frequency of 350 Hz, and the values of ultimate tensile strength and strain at break were reported as average values of at least five specimens. Errors were reported as standard deviations.

Differential scanning calorimetry (DSC) was performed using a Mettler Toledo DSC 822e. Samples were annealed at 80 °C for 15 min and then cooled to -50 °C (PPGDC-TAEA networks) or -10 °C (THPMTC-JEFFAMINE® D-400 networks) at a rate of -40 °C/min. Sample T_gs were obtained from a second heating ramp at 10 °C/min. The values of T_g were determined using ½ ΔC_p method.

Thermogravimetric analysis (TGA) was performed using a simultaneous thermal analyzer NETZSCH STA 449 F3 Jupiter®. In a helium flow, samples were ramped from 25 °C to 140 °C at a rate of 10 °C/min. The temperature was then held at 140 °C for 150 min. The thermal analyzer was coupled to an Agilent 7890A gas chromatography-mass spectrometry (GC-MS) system to analyze the mass of any volatile fragment. Gases generated during the measurement were condensed in a cryogenic trap using liquid nitrogen and heated to 400 °C rapidly to pass through the GC-MS system after the TGA measurement.

2. Supporting Figures

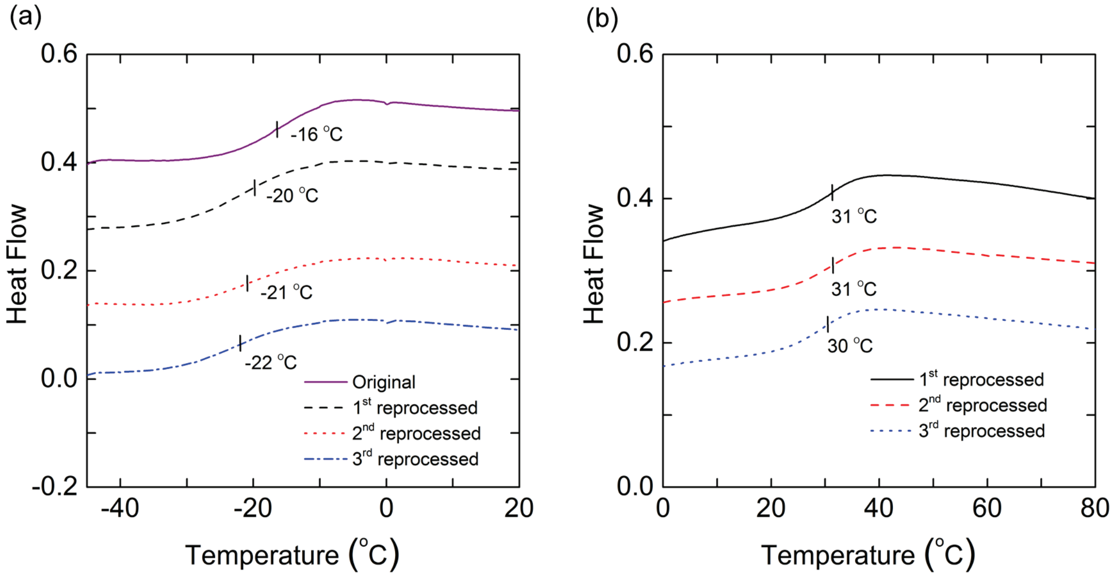

Figure S1. (a) DSC heat flow curves of original, 1st reprocessed, 2nd reprocessed and 3rd reprocessed PPGDC-TAEA PHU samples. (b) DSC heat flow curves of 1st reprocessed, 2nd reprocessed and 3rd reprocesssed THPMTC-JEFFAMINE® D-400 PHU samples. Values shown are $T_{g,\mathrm{midpoint}}$ determined using ½ ΔC_p method.

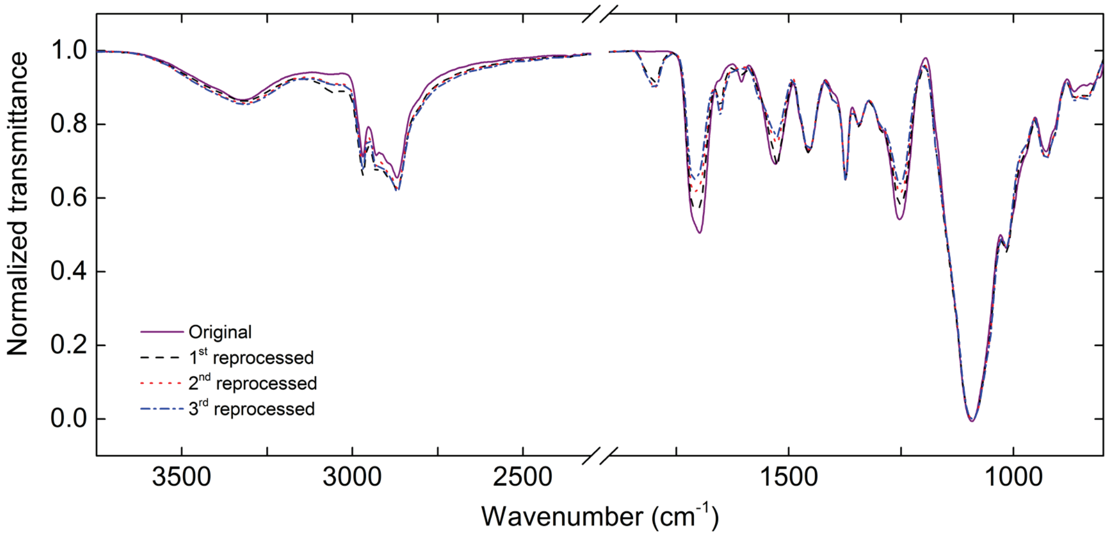

Figure S2. Normalized FTIR spectra of original, 1st reprocessed, 2nd reprocessed and 3rd reprocessed PPGDC-TAEA PHU samples.

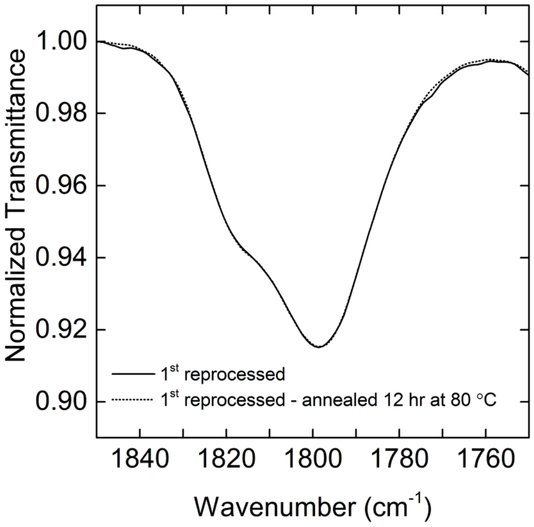

Figure S3. Normalized FTIR transmittance of 1st reprocessed PPGDC-TAEA sample and 1st reprocessed PPGDC-TAEA sample after 12-h anneal at 80 ˚C.

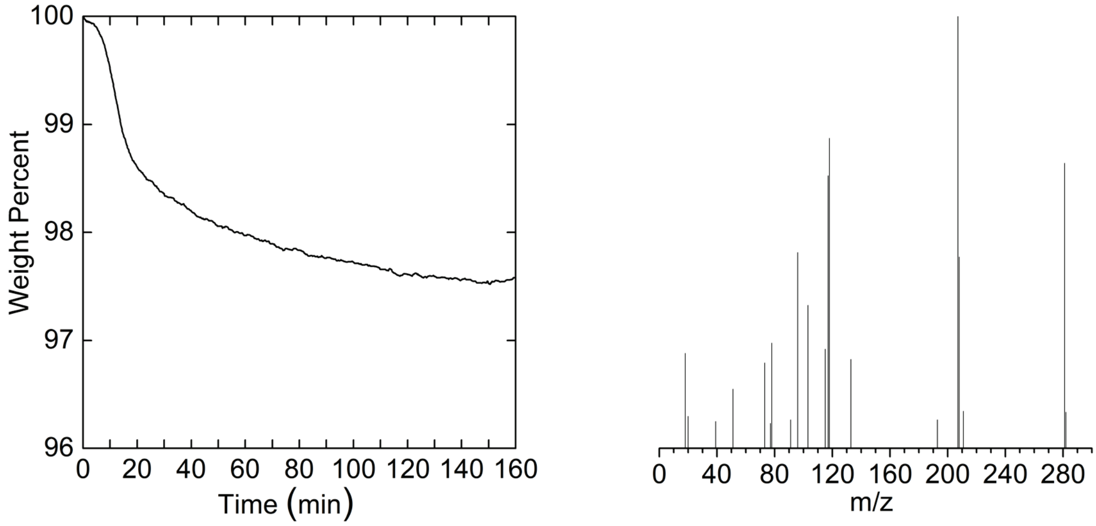

Figure S4. (a) TGA result of the original PPGDC-TAEA PHU sample with 140 ˚C isothermal heating in helium flow. (b) Mass spectrum of volatile fragments from TGA measurement.

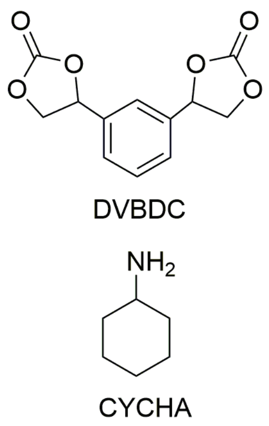

Figure S5. Chemical structures of DVBDC and CYCHA.

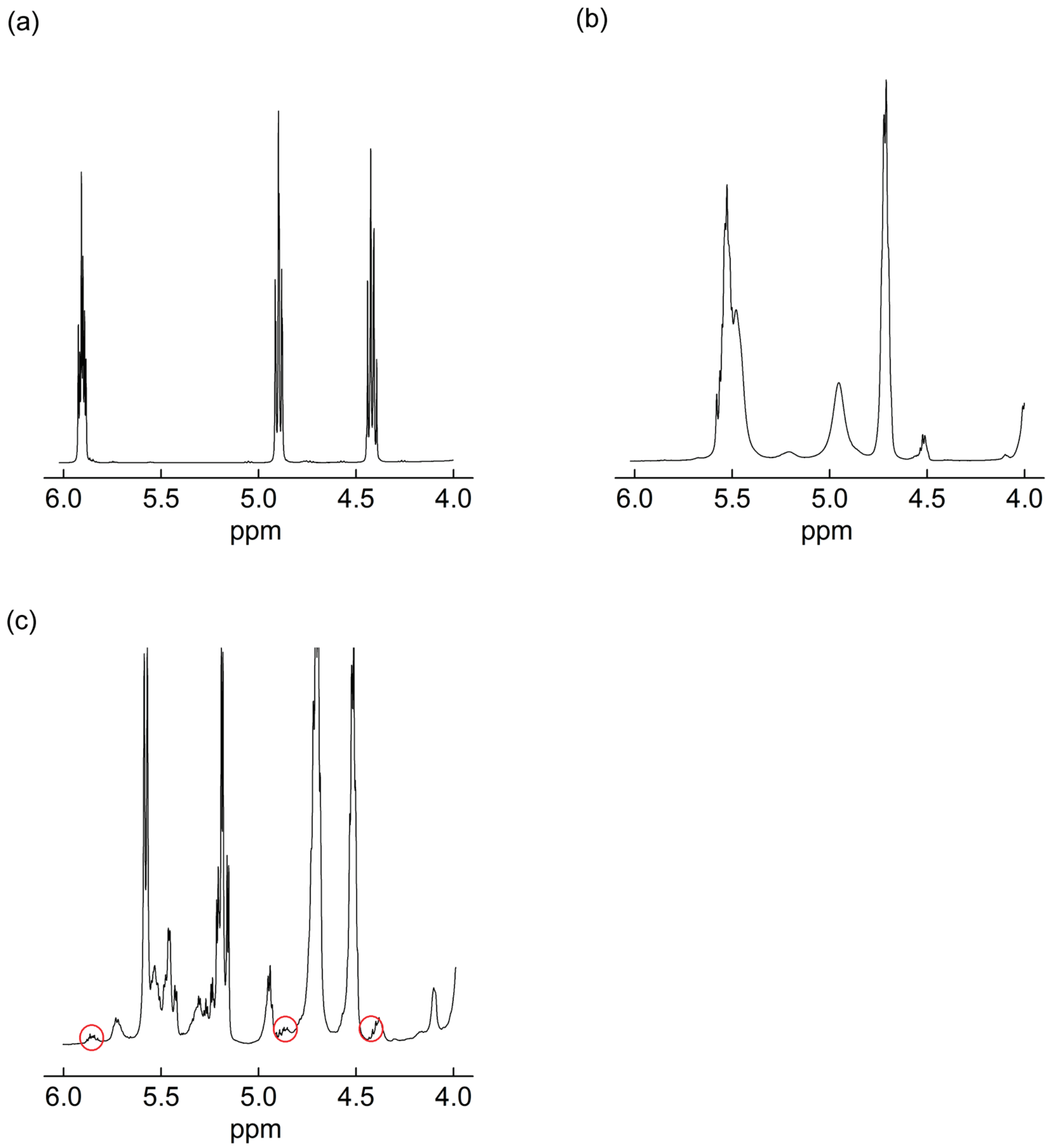

Figure S6. NMR spectra of reactant mixture (a) at the beginning of reaction; (b) after 36 h of reaction at 80 °C; (c) after 36 h of reaction and then 8 h of annealing at 140 °C. Circled regions are peaks associated with cyclic carbonate moiety.

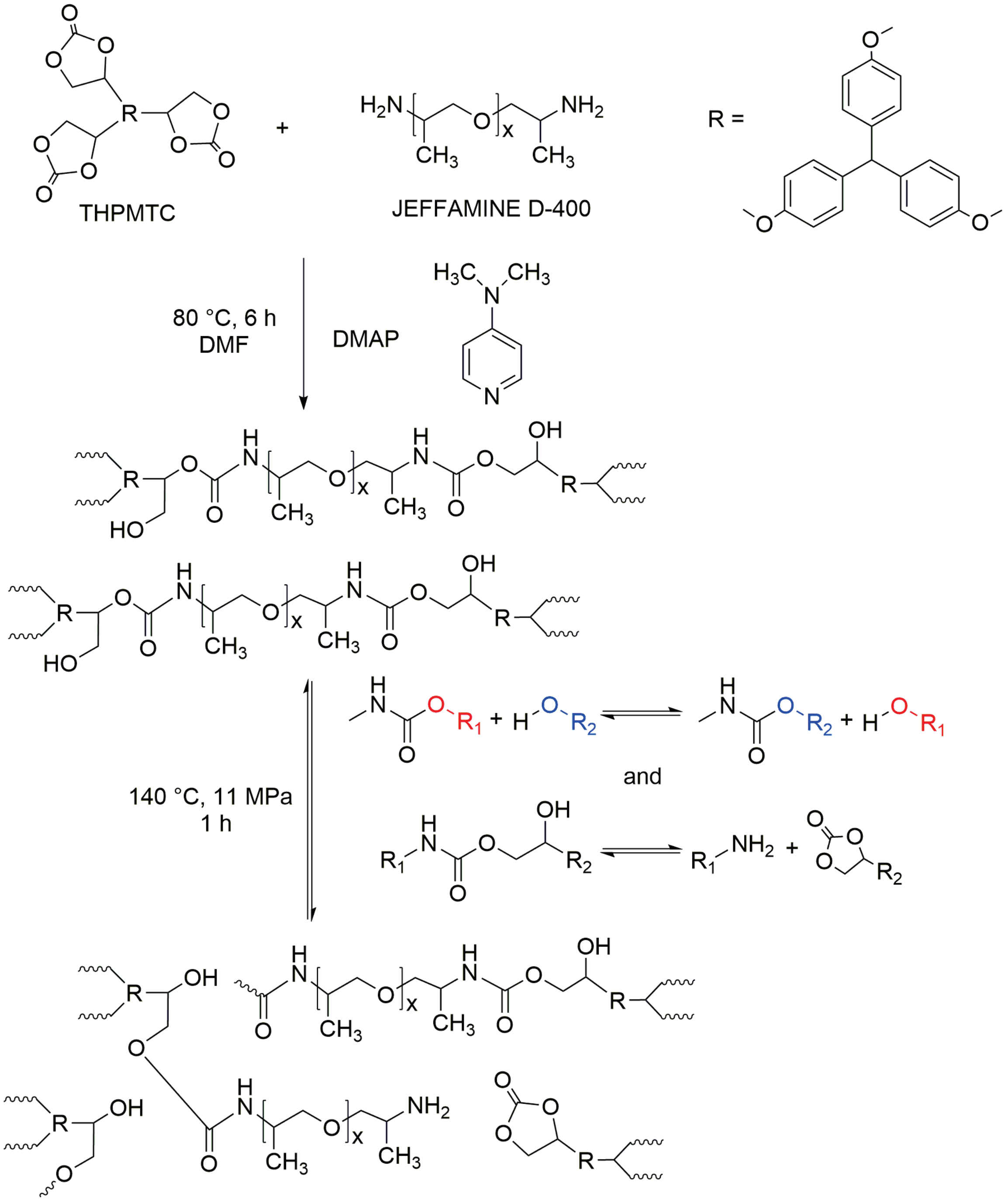

Figure S7. Mechanism of synthesis and rearrangement of THPMTC-JEFFAMINE® D-400 PHU networks.

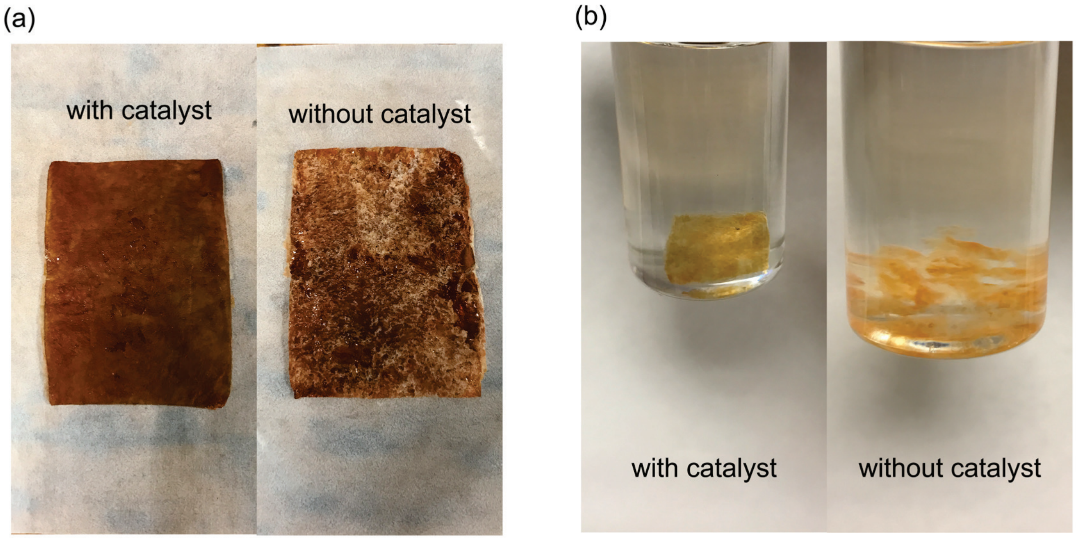

Figure S8. (a) Compression molding results of THPMTC-JEFFAMINE® D-400 PHU networks synthesized with catalyst (on the left) and without catalyst (on the right). (b) Swelling of compression molded THPMTC-JEFFAMINE® D-400 PHU networks in DMF.

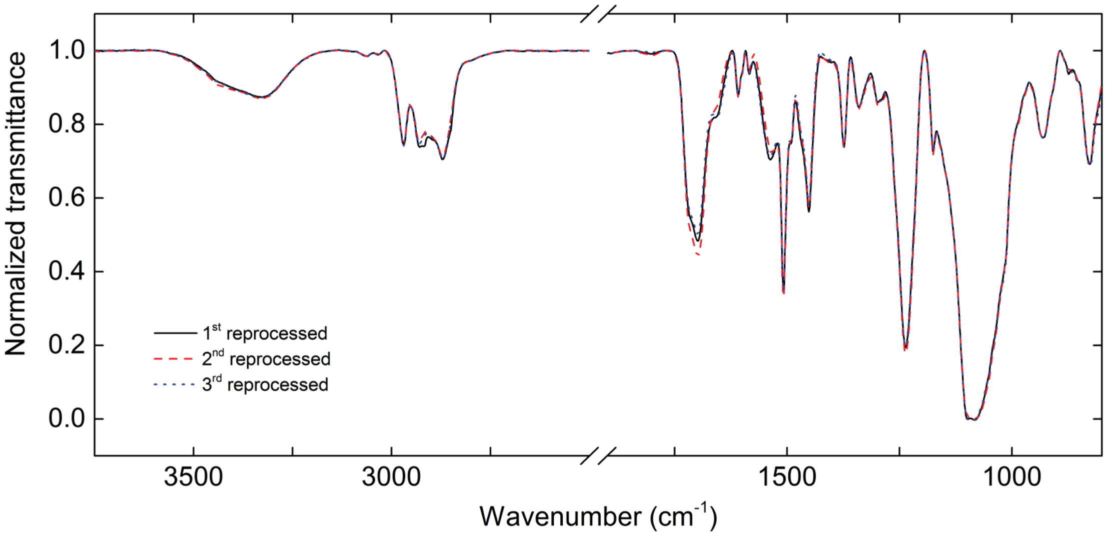

Figure S9. Normalized FTIR spectra of 1st reprocessed, 2nd reprocessed and 3rd reprocessed THPMTC-JEFFAMINE® D-400 PHU samples.

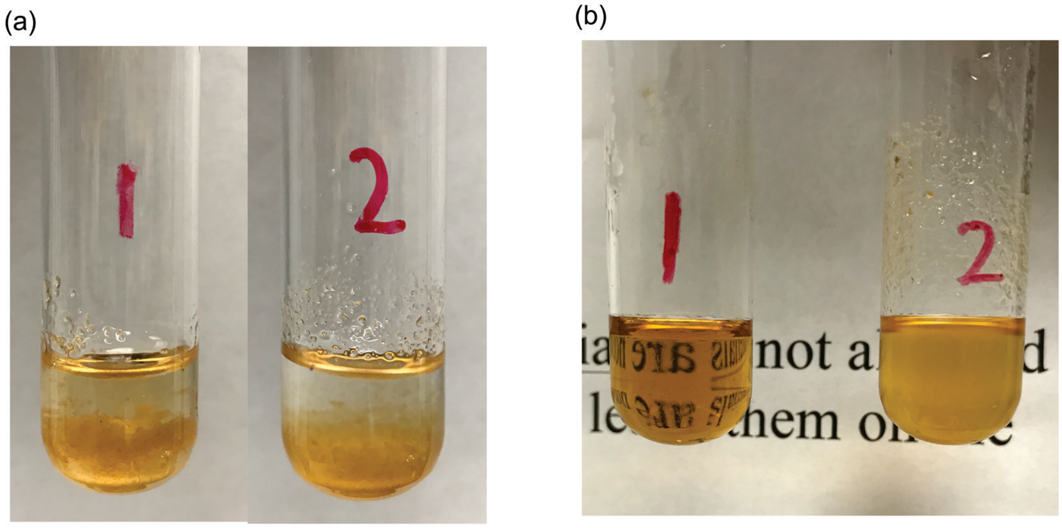

Figure S10. 1st reprocessed THPMTC-JEFFAMINE® D-400 PHU network (a) before and (b) after decross-linking. Tube 1 contains 1,4-butanediol and DMSO. Tube 2 contains only DMSO.

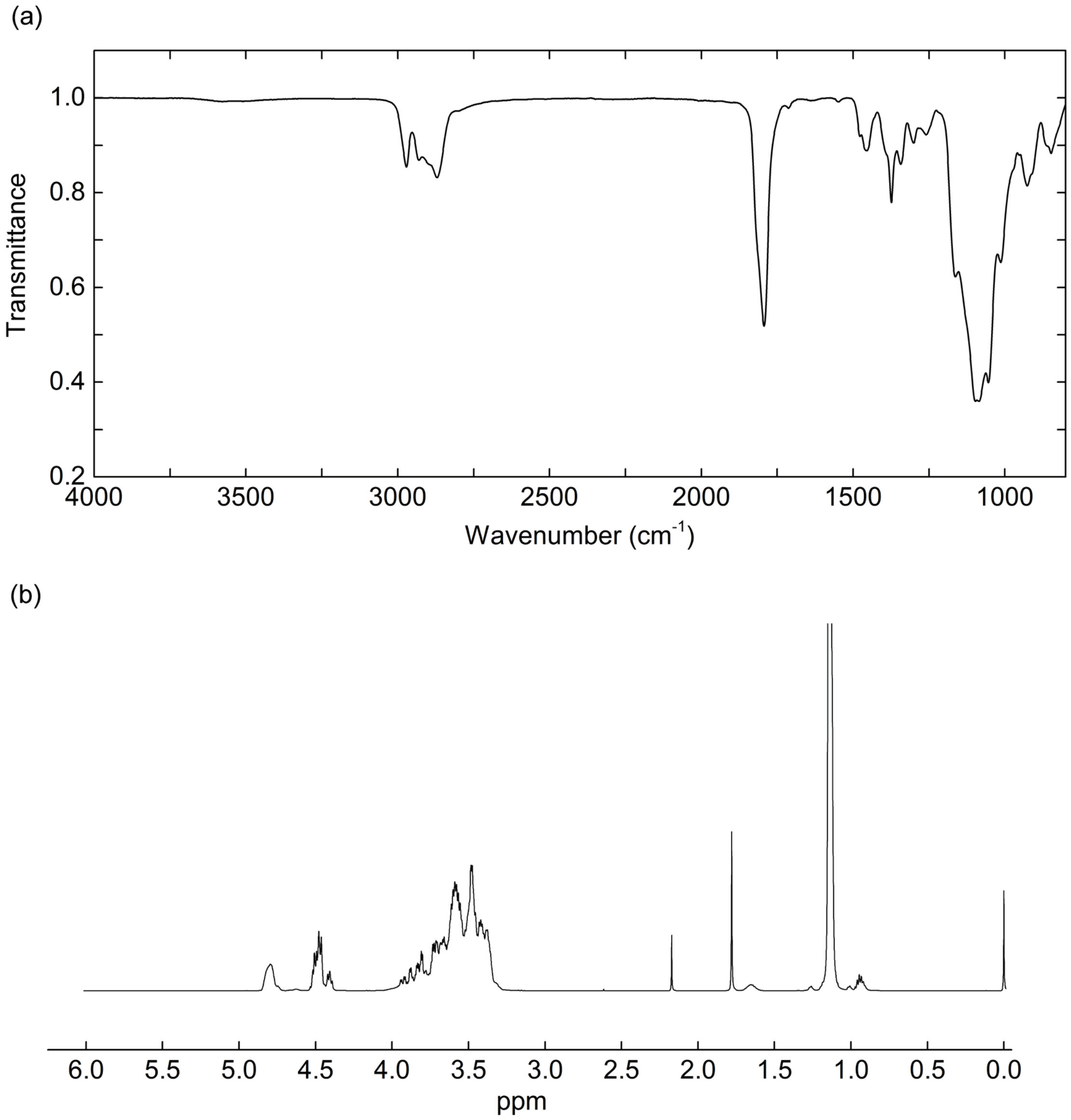

Figure S11. (a) FTIR spectrum of PPGDC. (b) ^{1}H NMR spectrum of PPGDC.

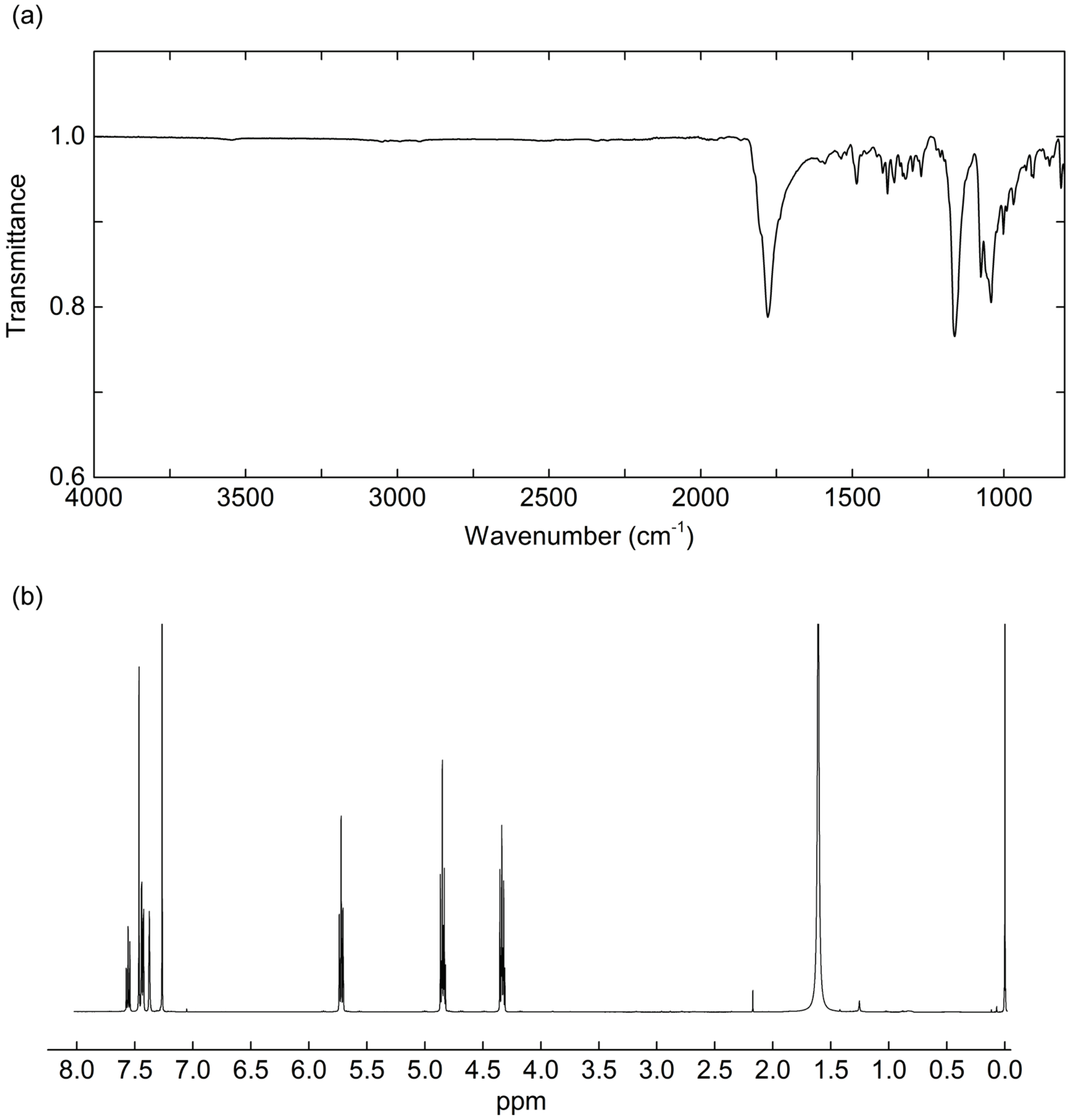

Figure S12. (a) FTIR spectrum of DVBDC. (b) ^{1}H NMR spectrum of DVBDC.

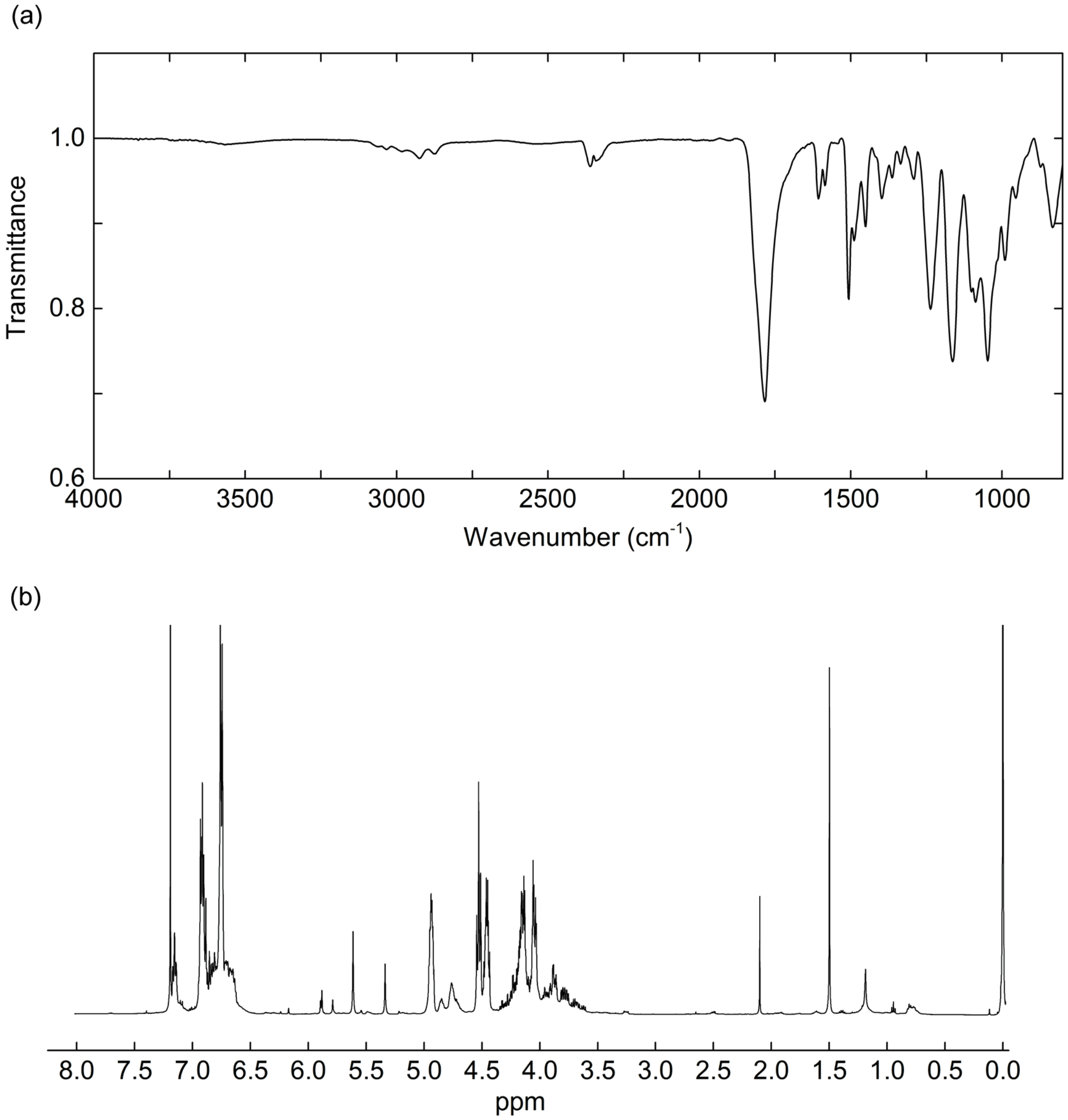

Figure S13. (a) FTIR spectrum of THPMTC. (b) ^{1}H NMR spectrum of THPMTC.