

## Supporting Information

### Stretchable, recyclable thermosets via photopolymerization and 3D printing of hemiacetal ester-based resins

You-Chi Mason Wu, Gloria Chyr, Hyunchang Park, Anna Makar-Limanov, Yuran Shi, Joseph M. DeSimone, and Zhenan Bao\*

#### Table of Contents

Section I	General methods	S2
Section II	Synthetic procedures	S4
Section III	Spectral characterization	S7
Section IV	Thermal/mechanical characterization	S14
Section V	Swelling characterization	S17
Section VI	SEC characterization	S18
Section VII	Viscosity characterization	S19
Section VIII	Recycling studies	S20
Section IX	References	S24

## Section I. General methods

### Materials

The following chemicals were purchased from commercial sources and used as received. Polypropylene glycol (MW 2000 and 4000), ethylene glycol vinyl ether, and dibutyltin dilaurate were purchased from Sigma-Aldrich. *rac*-Camphorsulfonic acid and dimethyl sulfoxide were purchased from Acros Organics. Butylated hydroxytoluene and isophorone diisocyanate were purchased from Alfa Aesar. Methanol, dichloromethane, and potassium hydroxide were purchased from Fisher Scientific. Calcium carbide was purchased from Beantown Chemical.

Anhydrous tetrahydrofuran (THF) was dispensed from a J.C. Meyer solvent purification system. Methacrylic acid was purchased from Sigma-Aldrich and dried over 4Å molecular sieves. Amberlyst A-21 was purchased from Supelco (4.6 meq/g, ~60% moisture).

### Instrumentation

<sup>1</sup>H NMR spectra were recorded using Bruker Neo-500 spectrometers at 500 MHz in deuterated solvents as specified, and referenced to the residual solvent signal (7.26 ppm for CDCl<sub>3</sub> and 3.31 ppm for CD<sub>3</sub>OD).

Fourier transform–infrared (FT–IR) spectroscopy was performed on a Thermo Scientific Nicolet iS50 spectrometer using an attenuated total reflectance (ATR) attachment.

Size-exclusion chromatography (SEC) was performed in either CHCl<sub>3</sub> or THF. *CHCl<sub>3</sub>*: Tosoh EcoSEC GPC equipped with 2 TSK gel GPC columns (G3000Hhr and G4000Hhr; 7.8 mm I.D. × 30 cm, 5 μm) calibrated using monodisperse polystyrene standards. CHCl<sub>3</sub> is used as carrier solvent at 40 °C. *THF*: The instrument consists of 2 PolyPore columns connected in series with a 1260 Infinity variable wavelength detector (both from Agilent), a DAWN multi-angle laser light scattering (MALLS) detector, and an Optilab T-rEX differential refractometer (both from Wyatt Technology).

Differential scanning calorimetry (DSC) was performed on a TA Instruments Q2500 instrument at a heating/cooling rate of 10 °C/min under nitrogen flow. Prior to DSC analysis, samples were annealed in a vacuum oven at 100 °C for 1 h to erase thermal history.

Thermogravimetric analysis (TGA) was performed on a TA Instruments Q5500 instrument with a Pt pan at a heating rate of 20 °C/min under nitrogen flow.

Tensile testing and stress–strain cycling tests were performed on a TA Instruments Q800 Dynamic Mechanical Analysis (DMA) instrument on rectangular samples (approx. 2–4-mm width and 0.7-mm thickness) at 25 °C at a strain rate of 50–100%/min.

Swelling measurements were performed by soaking a sample (approx. 2x4x4 mm) in the desired solvent for 1 h. The sample was weighed before and after swelling to determine swelling ratio.

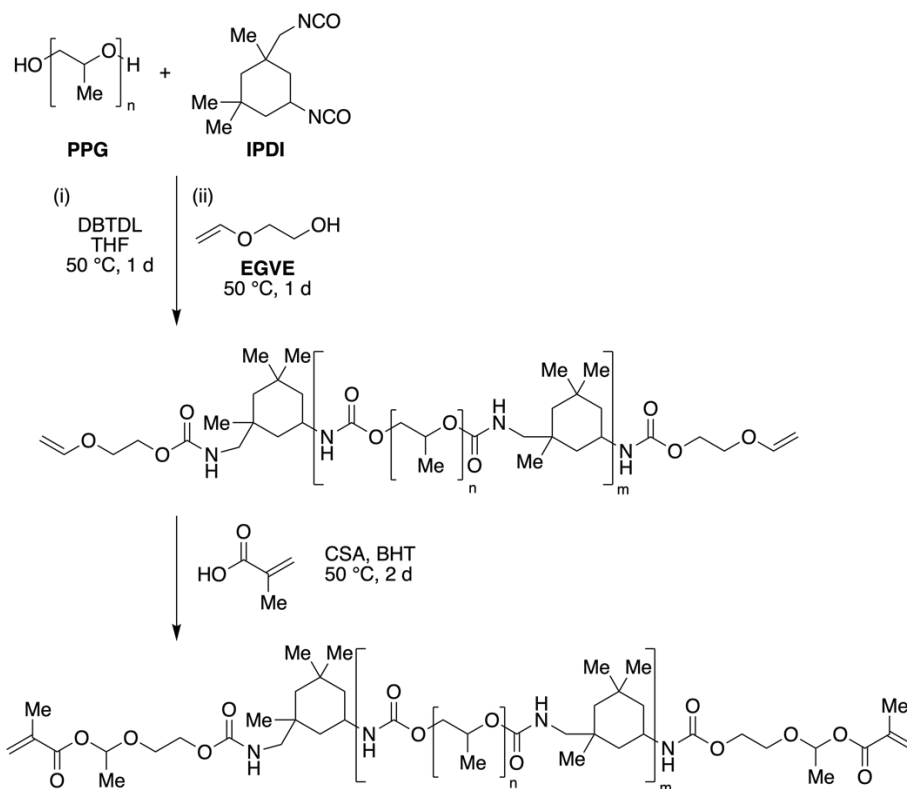
Rheometry was performed on a TA Instruments ARES-G2 instrument using 8-mm stainless steel parallel plates, 0.25N force, and 0.1% oscillation strain. Temperature-sweep measurements were performed at a 5 °C/min heating rate and 1 Hz frequency. Frequency-sweep measurements were performed at 50 °C.

Viscosity was measured using a TA Instruments ARES-G2 rheometer equipped with an 8-mm parallel plate accessory. Measurements were conducted at 25 °C using a steady state algorithm. Shear rates were varied from 0.1–100/s with a maximum equilibration time of 1 minute for steady state flow and 5% tolerance.

3D printing was conducted at room temperature using approximately 3 mL of resin per print, and all resins were printed with the same parameters of 7.8 mW/cm<sup>2</sup>, 1 second light exposure time, and 2 seconds dark time. The thickness of each layer was 10 μm. An initial exposure time of 5 seconds for the first layer is necessary to ensure sufficient adherence of the polymer to the print platform. After 3D printing, the polymer part is rinsed with acetone and submerged in a small beaker of acetone and gently shaken for approximately 10 minutes to remove residual resin. The part is then removed and rinsed again with clean acetone, air-dried, and stored at 4 °C.

## Section II. Synthetic procedures

### Synthesis of PPG-IPDI-HAMA resins



#### *Representative synthesis of PPG-IPDI-HAMA resin (Resin A):*

Polypropylene glycol (PPG) (average molecular weight 2000 g/mol; 10.00 g, 5 mmol, 1 equiv.) was weighed in a Schlenk flask and dried under vacuum for 1 h. Dibutyltin dilaurate (4 mg, cat.), tetrahydrofuran (THF) (10 mL) and isophorone diisocyanate (IPDI) (2.223 g, 10 mmol, 2 equiv.) were added under N<sub>2</sub>. The mixture was stirred at 50 °C for 1 d. Afterwards, ethylene glycol vinyl ether (EGVE) (0.942 mL, 10.5 mmol, 2.1 equiv.) was added and the mixture was stirred for an additional 1 d at 50 °C. The reaction mixture was then evaporated under reduced pressure and dried under vacuum for 1 h. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.49 (dd, 2H), 4.89 (br, 4H), 4.31 (t, 4H), 4.21 (dd, 2H), 4.05 (dd, 2H), 3.87 (t, 4H), 3.7–3.3 (m), 2.91 (m, 3H), 1.22 (d, 6H), 1.13 (t, 103H), 1.06 (s, 9H), 0.92 (s, 6H).

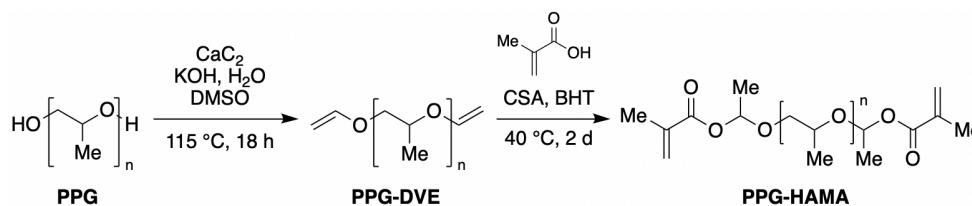
To the crude product in the same flask were added camphorsulfonic acid (CSA) (5.8 mg, 0.025 mmol, 0.5 mol%), 2,6-di-tert-butyl-4-methylphenol (BHT) (2.8 mg, 0.0125 mmol, 0.25 mol%), and methacrylic acid (10 mL, 120 mmol, 24 equiv.) under N<sub>2</sub>, and the mixture was stirred at 50 °C for 2 d. Afterwards, the reaction was diluted with CH<sub>2</sub>Cl<sub>2</sub>, and saturated aqueous NaHCO<sub>3</sub> was added and the mixture was stirred until bubbling stopped. The organic phase was separated, and the aqueous phase was extracted twice more with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic extract was dried

with MgSO<sub>4</sub> and evaporated to obtain a colorless, viscous liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.16 (s, 2H), 6.01 (q, 2H), 5.61 (s, 2H), 4.87 (br, 4H), 4.21 (br, 4H), 3.7–3.3 (m), 2.91 (m, 3H), 1.95 (s, 6H), 1.46 (d, 6H), 1.22 (d, 6H), 1.12 (t, 103H), 1.06 (s, 9H), 0.92 (s, 6H).

Representative amounts of reagents for Resins A, B, and C:

	A	B	C
PPG	10.00 g	12.00 g	12.00 g
IPDI	2.223 g	2.001 g	1.000 g
Dibutyltin dilaurate	4 mg	4 mg	4 mg
THF	10 mL	12 mL	18 mL
EGVE	0.942 mL	0.556 g	278 mg
Methacrylic acid	10 mL	8 mL	6 mL
CSA	5.8 mg	7.0 mg	3.5 mg
BHT	2.8 mg	3.3 mg	1.7 mg
Yield	74%	96%	96%

### Synthesis of PPG-HAMA resin (PPG-only control)



The vinylation reaction was performed according to an adapted literature procedure.<sup>1</sup> PPG (average molecular weight 4000 g/mol; 5.00 g, 1.25 mmol, 1 equiv.), ground KOH (140 mg, 2.5 mmol, 2 equiv.), water (0.27 mL, 15 mmol, 12 equiv.), and DMSO (5 mL) were added to a flask. Ground CaC<sub>2</sub> (673 mg, 10.5 mmol, 8.4 equiv.) was added to the flask, which was fitted with a reflux condenser and balloon. The mixture was heated at 115 °C for 18 h. Afterwards, the mixture was diluted with diethyl ether and filtered through basic alumina. The organic phase was washed with 3x brine, dried with MgSO<sub>4</sub>, and evaporated to give a viscous liquid. Vinylation was confirmed by NMR. The product, PPG divinyl ether, was used for the next step without further purification.

PPG divinyl ether was dried under vacuum in a flask prior to the reaction. CSA (1.74 mg, 0.0075 mmol, 0.6 mol%) and BHT (0.55 mg, 0.0025 mmol, 0.2 mol%) were added to the flask, and the flask was evacuated and backfilled with N<sub>2</sub> 3 times. Methacrylic acid (1.6 mL, 18.8 mmol, 15 equiv.) was added, and the vessel was sealed and stirred under N<sub>2</sub> at 40 °C for 2 d. Afterwards, the mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> and aqueous NaHCO<sub>3</sub> was added, and the mixture was stirred until bubbling stopped. The organic phase was separated, and the aqueous phase was extracted twice more with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic extract was dried with MgSO<sub>4</sub> and evaporated to obtain a light brown, viscous liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.16–6.05 (m, 4H), 5.57 (m, 2H), 3.7–3.3 (m), 1.93 (s, 6H), 1.42 (t, 6H), 1.13 (t, 205H).

### **Photocrosslinking of resin**

1 wt% of diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) was dissolved in a small amount of  $\text{CH}_2\text{Cl}_2$  and added to the resin, mixed thoroughly, and the mixture was evaporated under reduced pressure. The photoinitiator-containing resin was stored in the dark.

To crosslink the resin into thermoset, three methods were used according to desired form factor: (1) the resin was poured into a Teflon mold (approx. 1x4 cm) and irradiated with UV light (365 nm) for 5 min in the glovebox; (2) the resin was sandwiched between OTS-treated Si wafer and a glass slide, with a spacer of  $\sim 0.7$  mm thickness, and irradiated with UV light (365 nm) for 10 min; (3) the resin was 3D-printed using the CLIP system (see Section I).

### Section III. Spectral characterization

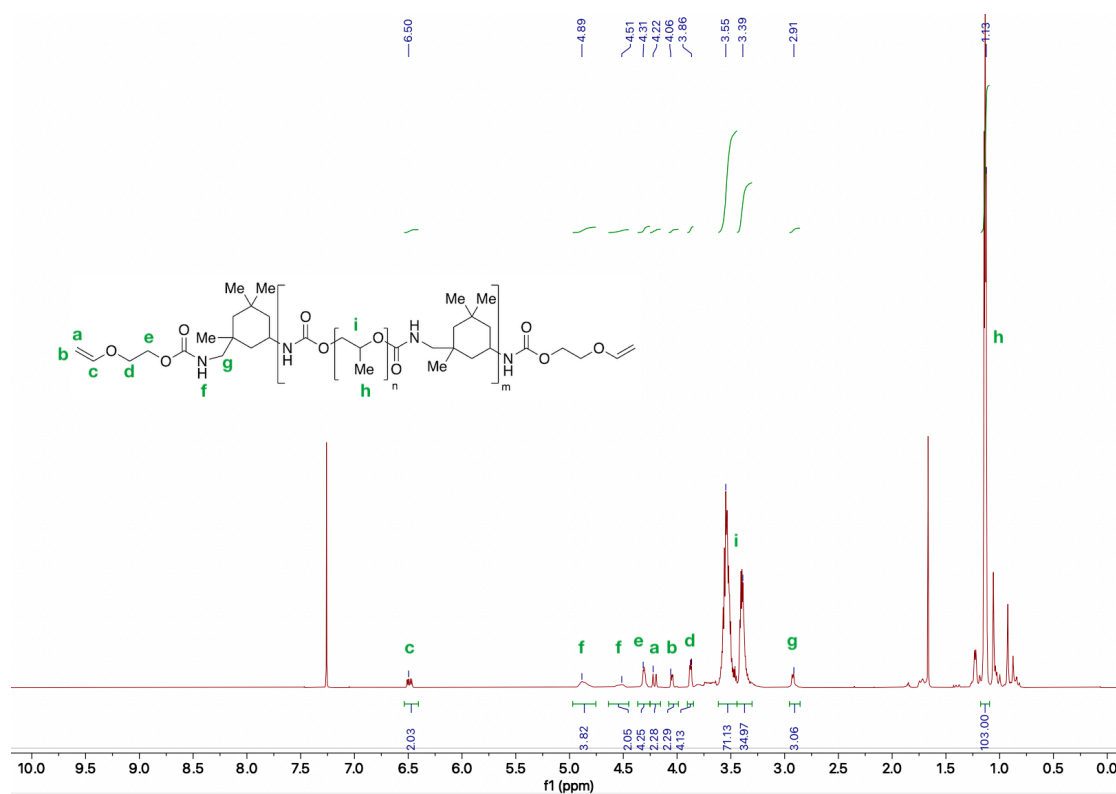


Figure S1.  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) of Resin A after end-capping reaction with EGVE.

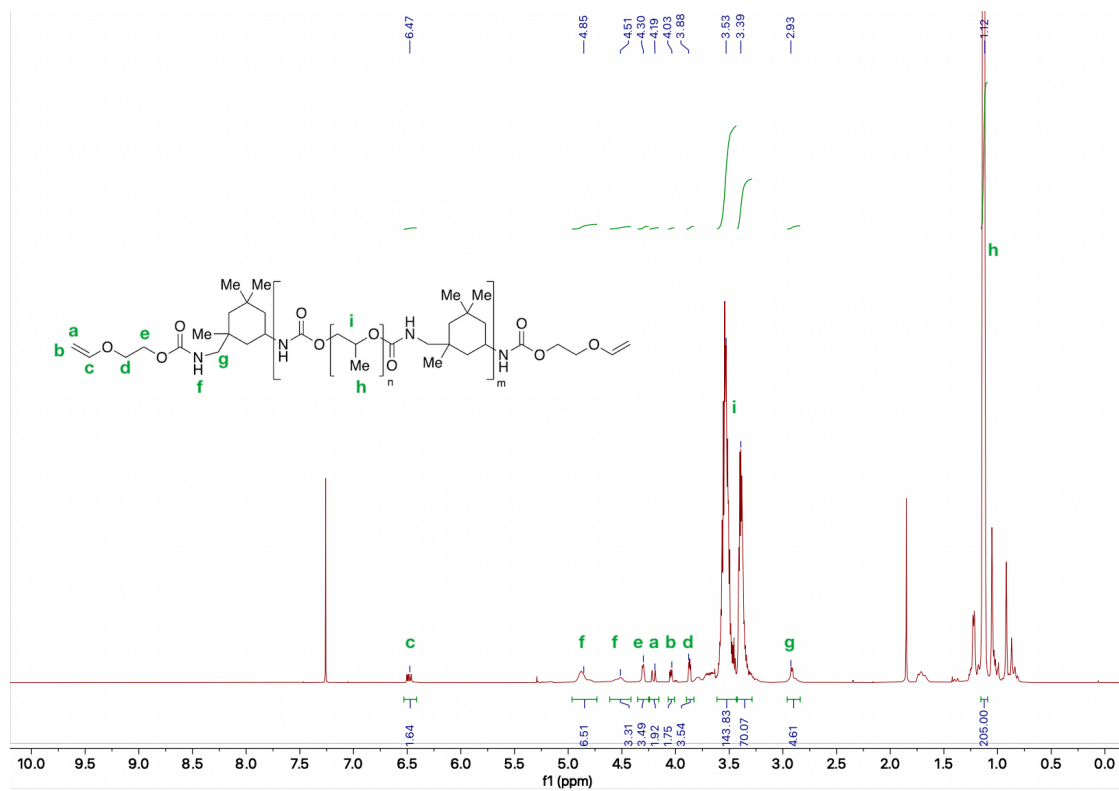


Figure S2. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of Resin B after end-capping reaction with EGVE.

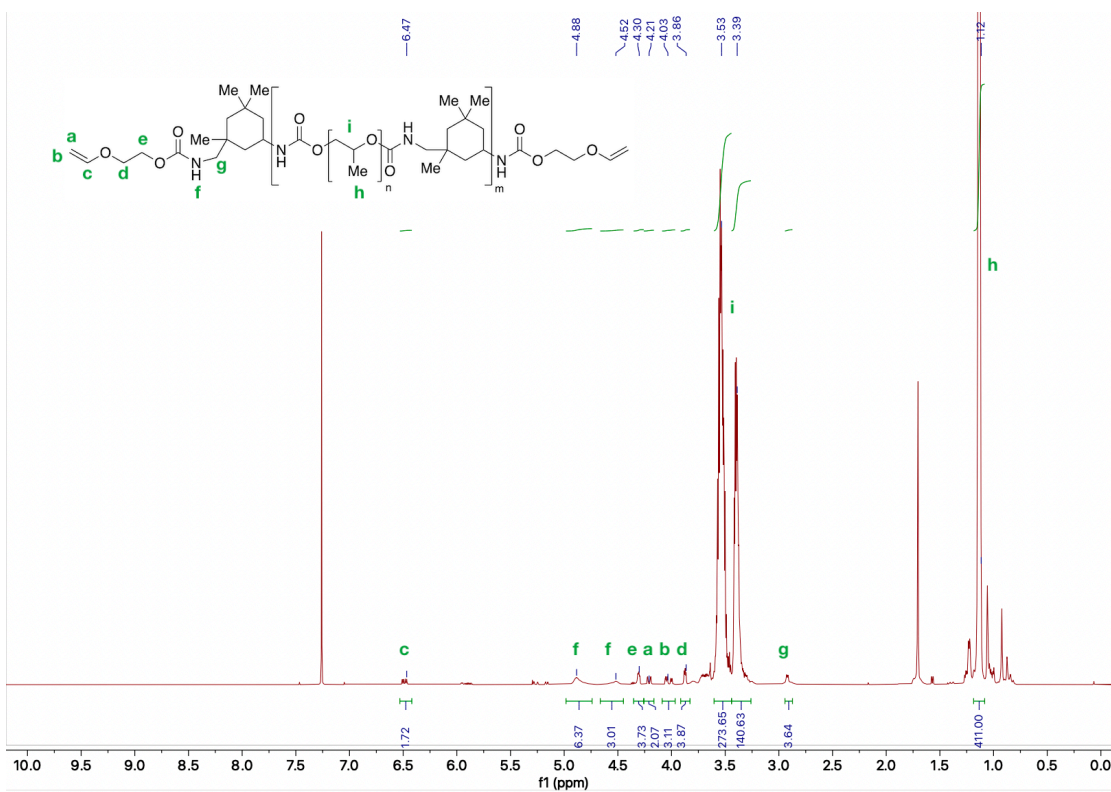


Figure S3. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of Resin C after end-capping reaction with EGVE.



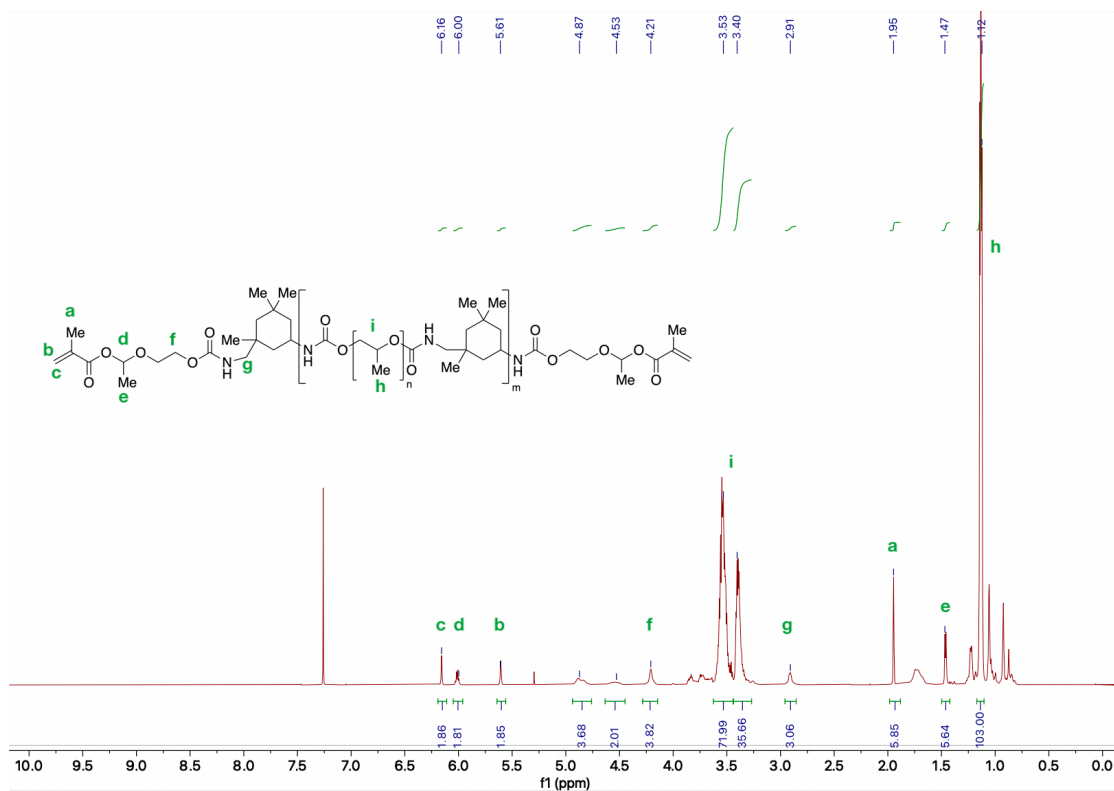


Figure S4. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of PPG-IPDI-HAMA Resin A.

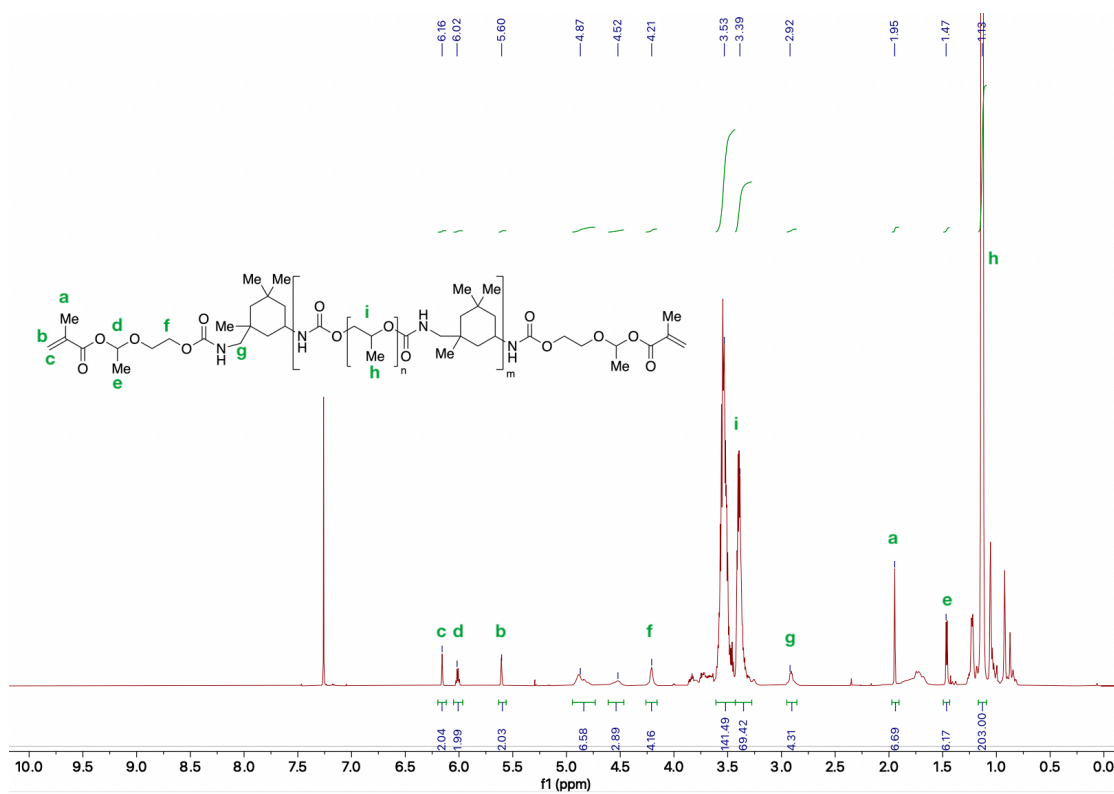


Figure S5. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of PPG-IPDI-HAMA Resin B.

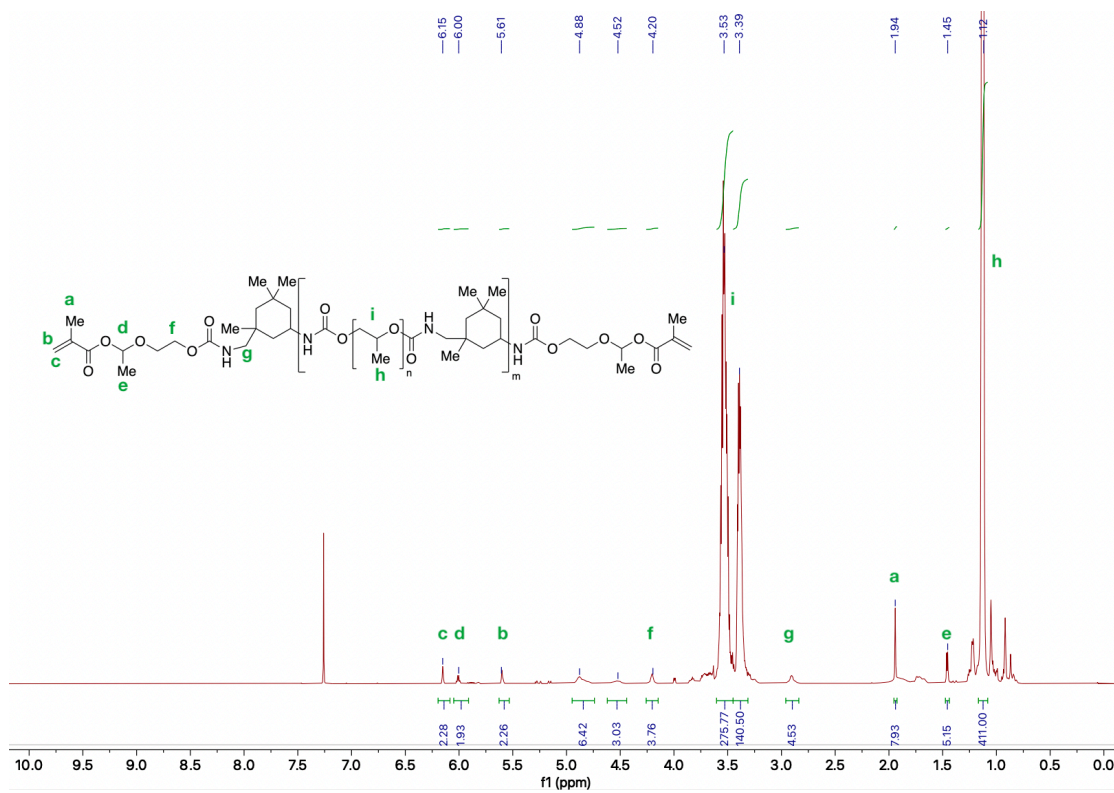


Figure S6. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of PPG-IPDI-HAMA Resin C.

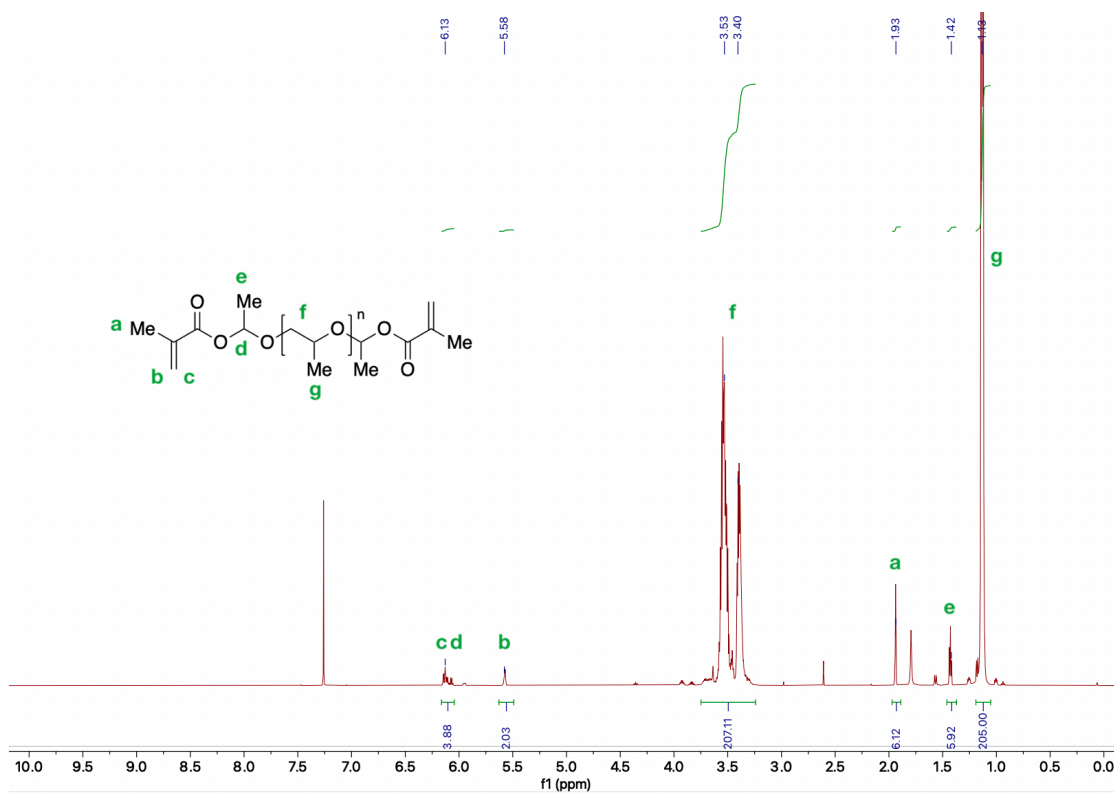
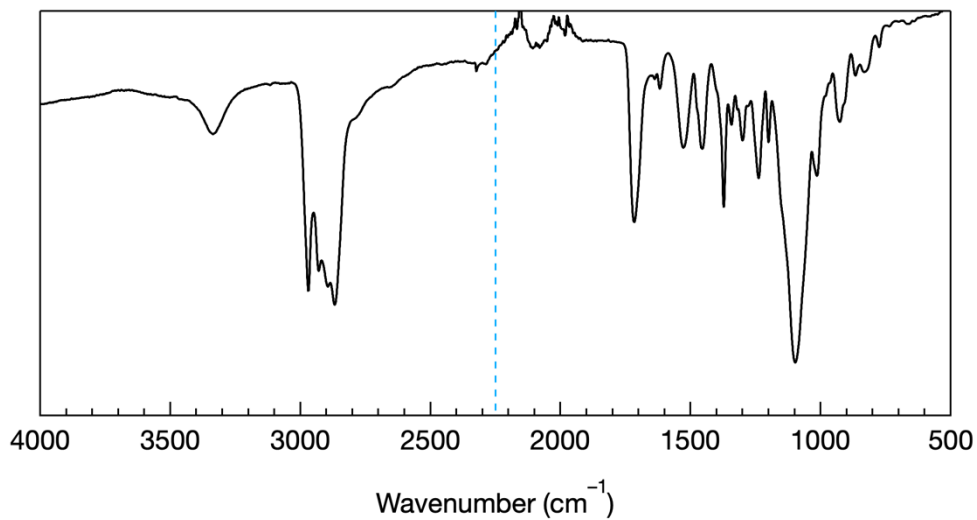
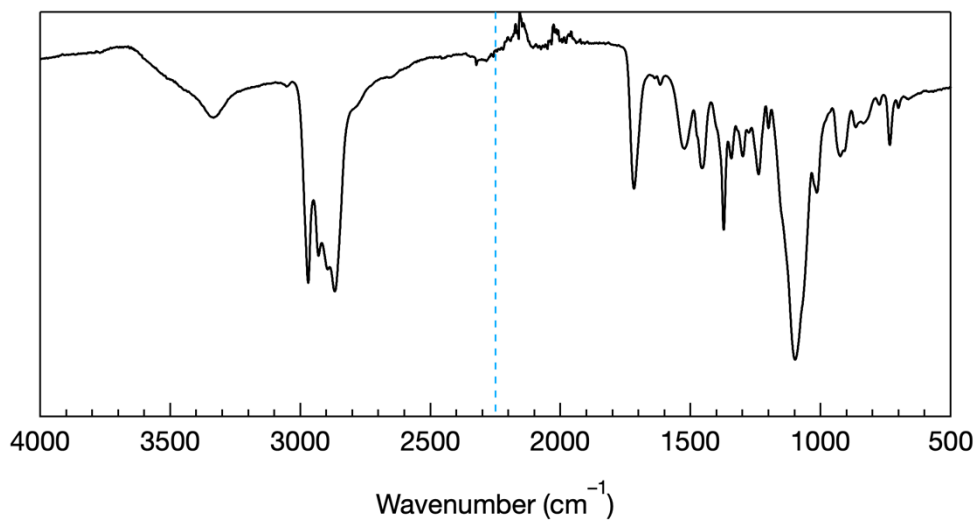


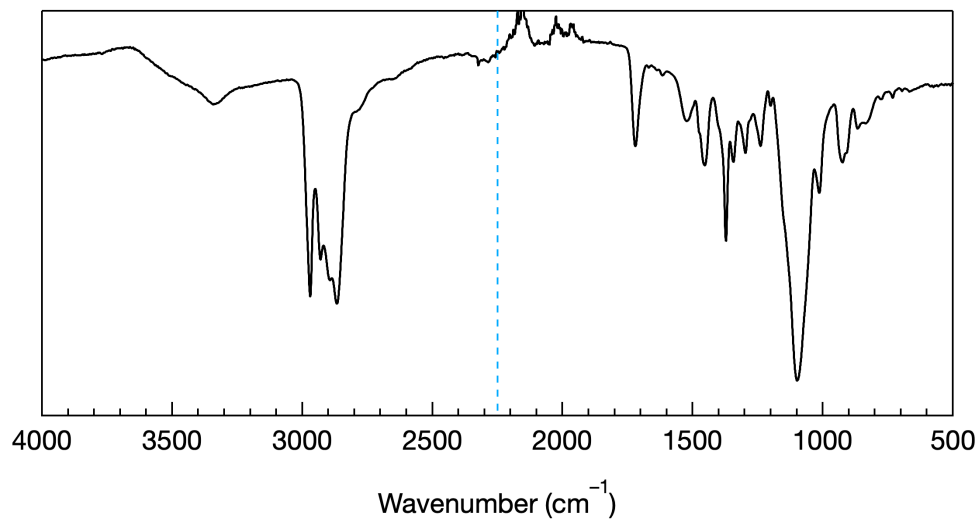
Figure S7. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of PPG-HAMA.



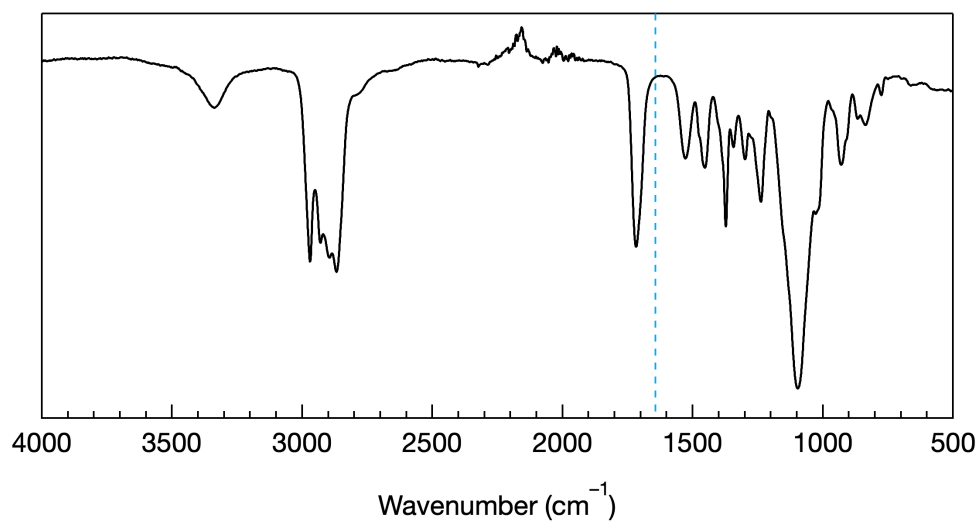
**Figure S8.** FT-IR spectrum of Resin **A** after EGVE reaction, showing full conversion of isocyanate groups (disappearance of C=O stretch expected at  $\sim 2260\text{ cm}^{-1}$ ).



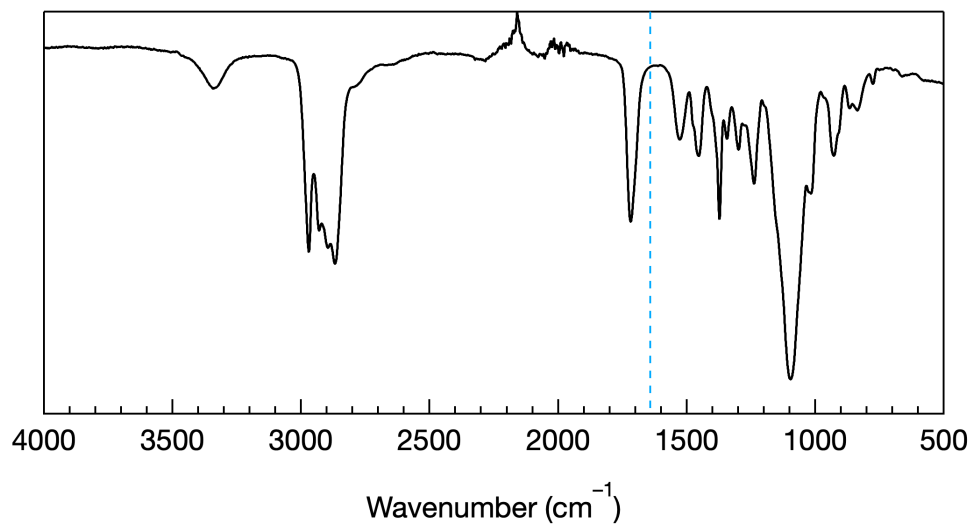
**Figure S9.** FT-IR spectrum of Resin **B** after EGVE reaction, showing full conversion of isocyanate groups (disappearance of C=O stretch expected at  $\sim 2260\text{ cm}^{-1}$ ).



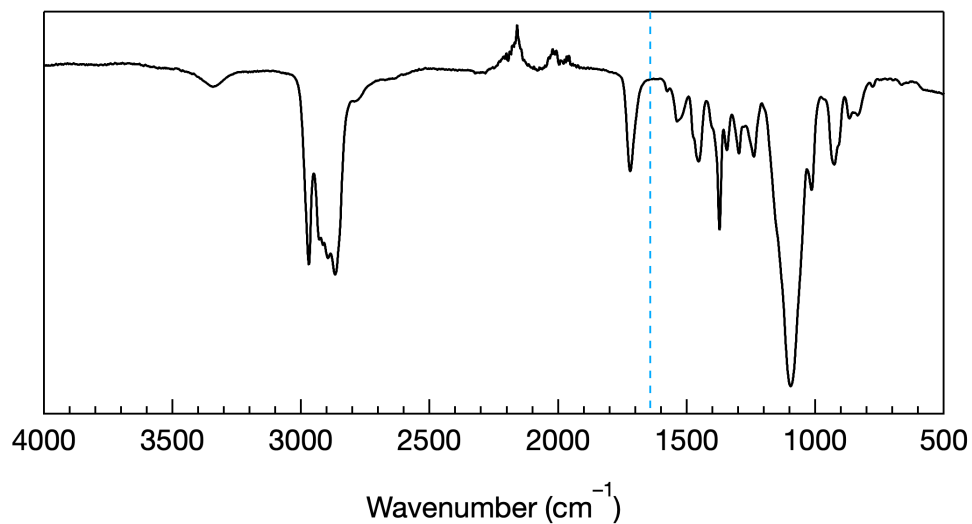
**Figure S10.** FT-IR spectrum of Resin C after EGVE reaction, showing full conversion of isocyanate groups (disappearance of C=O stretch expected at  $\sim 2260\text{ cm}^{-1}$ ).



**Figure S11.** FT-IR spectrum of Thermoset A after photocrosslinking, showing full conversion of methacrylate groups (disappearance of C=C stretch expected at  $\sim 1640\text{ cm}^{-1}$ ).

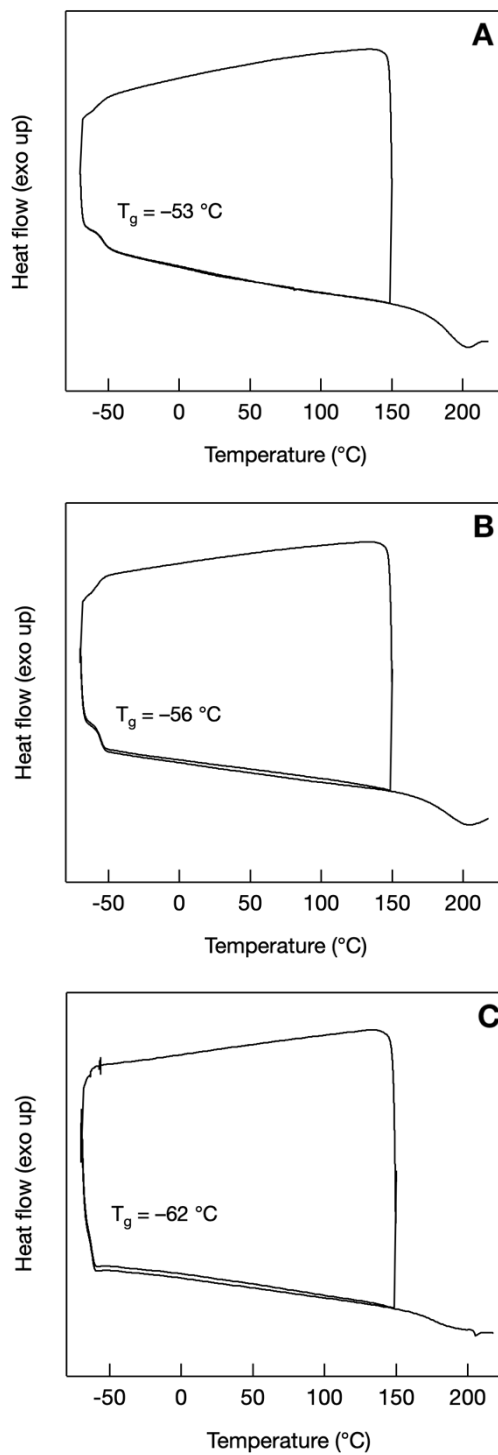


**Figure S12.** FT-IR spectrum of Thermoset **B** after photocrosslinking, showing full conversion of methacrylate groups (disappearance of C=C stretch expected at  $\sim 1640\text{ cm}^{-1}$ ).

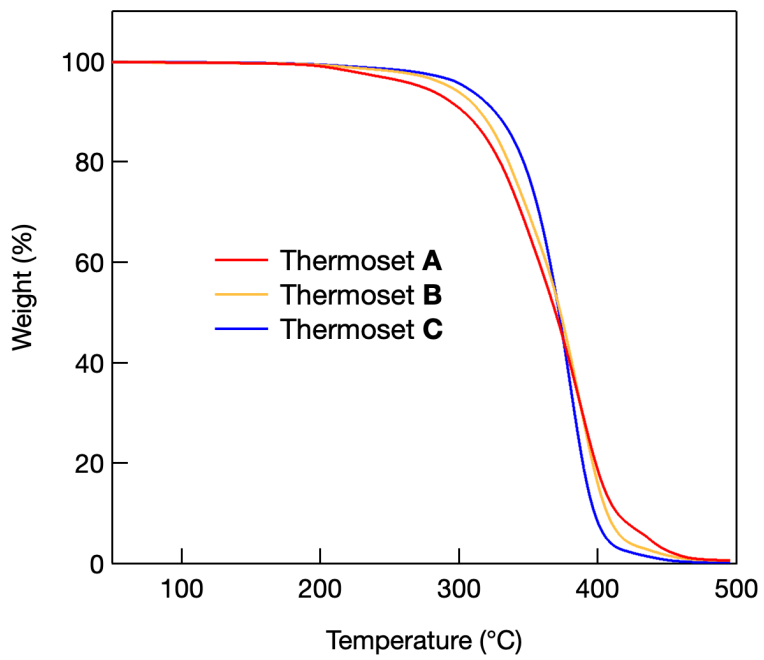


**Figure S13.** FT-IR spectrum of Thermoset **C** after photocrosslinking, showing full conversion of methacrylate groups (disappearance of C=C stretch expected at  $\sim 1640\text{ cm}^{-1}$ ).

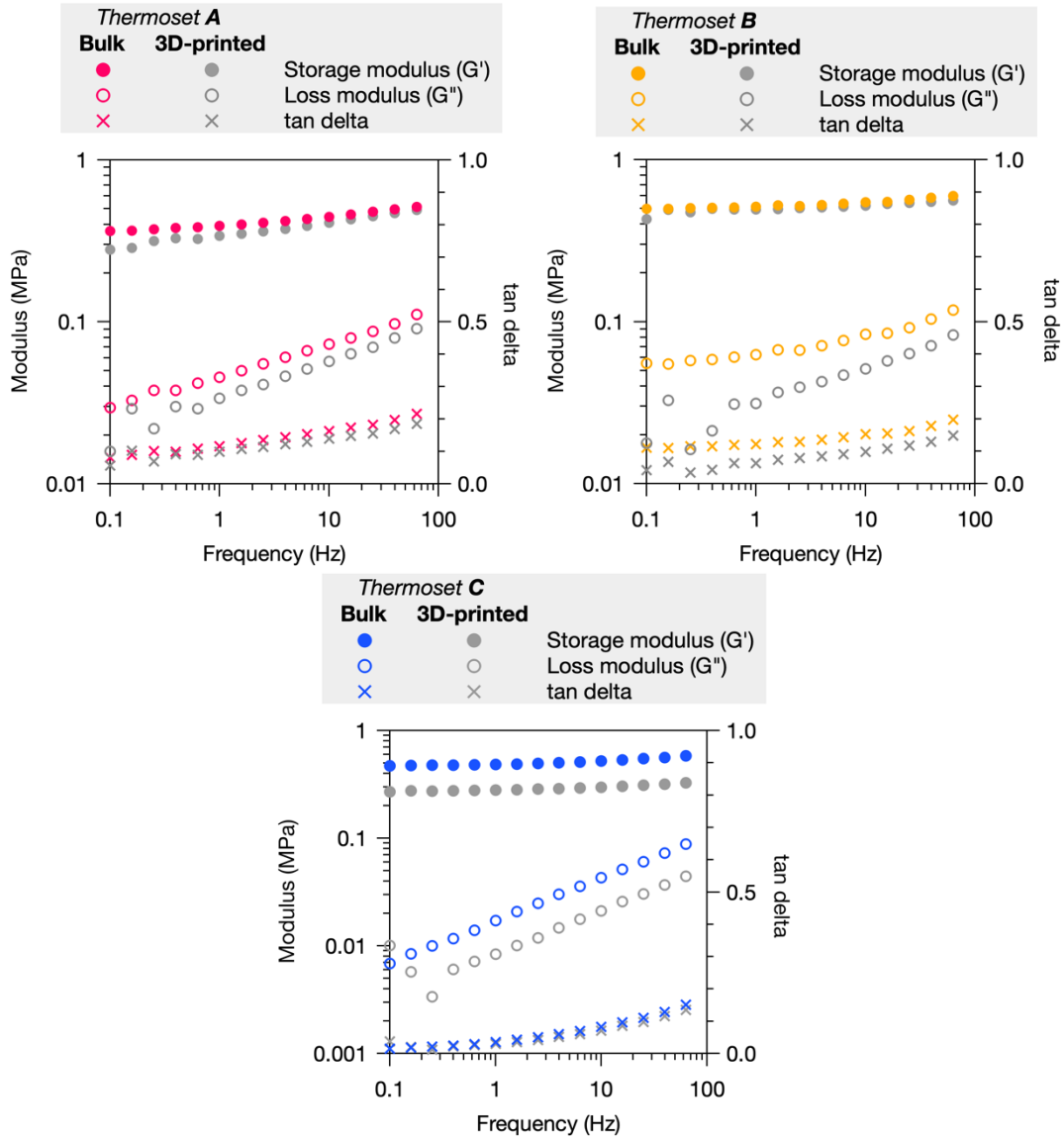
**Section IV.**  
**Thermal characterization.**



**Figure S14.** DSC characterization of Thermosets **A**, **B**, and **C**.



**Figure S15.** TGA characterization of Thermosets **A**, **B**, and **C**.



**Figure S16.** Frequency-sweep rheometric measurements comparing mechanical properties of Thermosets **A**, **B**, and **C** obtained by bulk UV curing vs. 3D printing (CLIP).

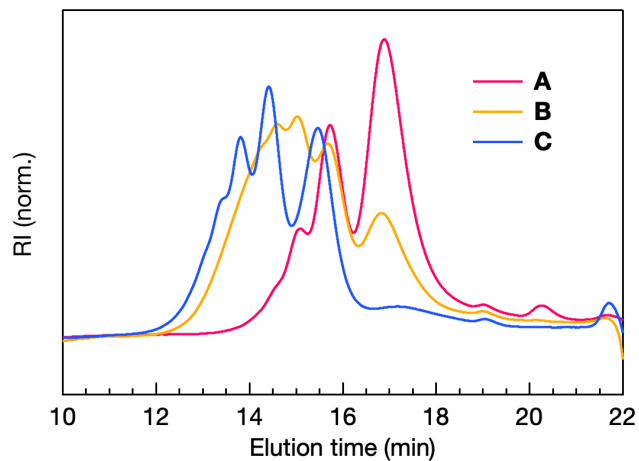


**Section V.**  
**Swelling characterization**

**Table S1.** Swelling ratio of Thermosets **A**, **B**, and **C** in water and methanol.

	Water	Methanol
<b>A</b>	1.6%	46%
<b>B</b>	1.6%	65%
<b>C</b>	1.7%	119%

## Section VI. SEC characterization

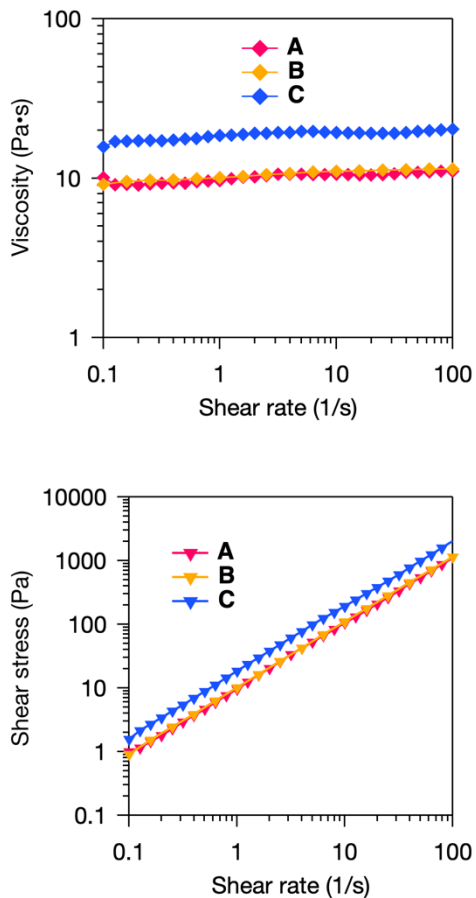


**Figure S17.** SEC ( $\text{CHCl}_3$ ) chromatographs of the polyurethanes **A**, **B**, and **C** after EGVE addition reaction. SEC was performed on the polymers after EGVE addition and not HAMA formation in order to avoid side reactions possibly occurring with the methacrylate end-group during analysis.  $M_n$  and  $D$  values are tabulated in Table S1 below.

**Table S2.**  $M_n$  and  $D$  of polyurethanes **A**, **B**, and **C** based on SEC ( $\text{CHCl}_3$ ).

	$M_n$ (kDa)	$D$
<b>A</b>	2.2	2.0
<b>B</b>	5.4	2.2
<b>C</b>	9.7	1.8

## Section VI. Viscosity characterization



**Figure S18.** Resins **A**, **B**, and **C** exhibit Newtonian characteristics as indicated by the linear relationship between shear stress and shear rate, as well as the near-constant viscosity across three orders of magnitude of shear rate.

**Table S3.** Viscosities of Resins **A**, **B**, and **C**.

	Viscosity (Pa·s)
<b>A</b>	$10.1 \pm 0.6$
<b>B</b>	$10.5 \pm 0.7$
<b>C</b>	$18.7 \pm 1.1$

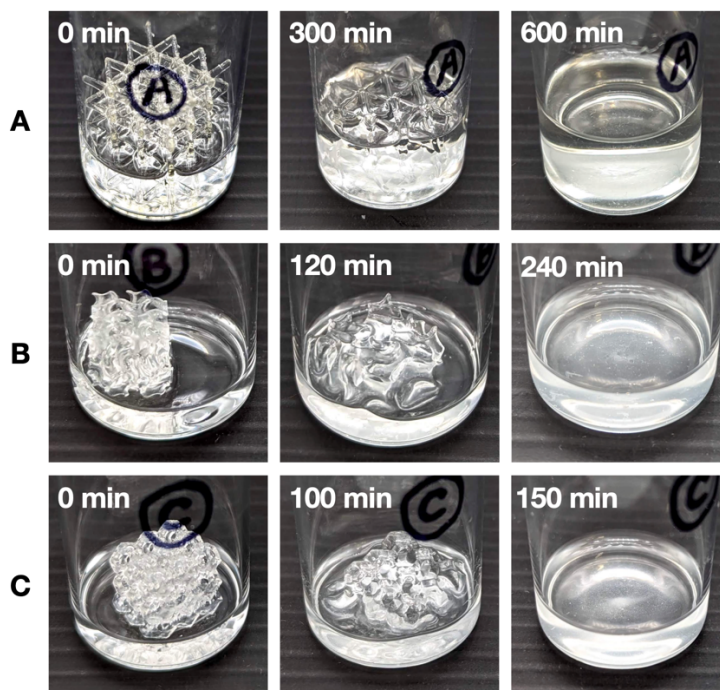
## Section VII. Recycling studies

### Degradation timepoint studies

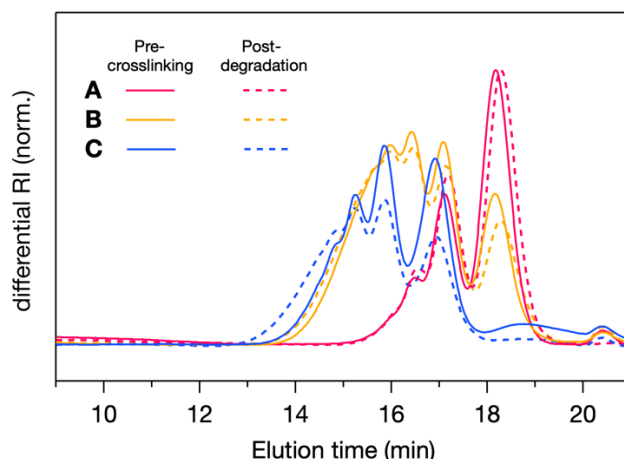
Small pieces of thermosets (approx. 2x4x4 mm) were placed into vials, and the appropriate solvent (0.05M HCl in methanol, pure methanol, 0.05 M HCl in water, water) was added to each. The vial was left for the desired time, then the solution was removed and the remaining solid was rinsed with methanol, dried under high vacuum, and weighed.

### Recycling

The HAE-based thermoset was soaked in 0.05M HCl in methanol for 24 h, upon which it fully dissolved to produce a clear solution. Figure S17 shows timelapse photographs of the degradation process of the 3D-printed thermosets. Figure S18 shows SEC analysis pre-crosslinking and post-degradation, showing minimal change in molecular weights of the polyurethanes.



**Figure S19.** Timelapse photographs of the acid-catalyzed degradation of 3D-printed thermosets.



**Figure S20.** SEC (THF) analysis pre-crosslinking and post-degradation.

Following degradation, one of the following purification methods was used to remove the small amount of poly(methacrylic acid) side product. The results are tabulated in Table S2.

*Ion-exchange resin method:* 1M NaOH was added (0.8 equiv. for each 1 equiv. of HCl used). Amberlyst A-21 was added (~3 equiv. of amine for 1 equiv. of carboxylic acid theoretically produced) and left to stand overnight. The Amberlyst resin was filtered off for regeneration, and the filtrate was evaporated. Diethyl ether was added to dissolve the recycled polyurethane, and the solution was dried using MgSO<sub>4</sub>, filtered, and evaporated to give a colorless, viscous liquid polyurethane.

*Aqueous NaHCO<sub>3</sub> method:* The mixture was evaporated under reduced pressure. The crude material was then dissolved in diethyl ether and washed with 3x aqueous NaHCO<sub>3</sub>. Brine was used to break up any emulsions. The organic phase was dried with MgSO<sub>4</sub>, filtered, and evaporated to give a colorless, viscous liquid polyurethane.

**Table S4.** Purification and recycling of HAE-based thermosets.

	Mass of thermoset (mg)	Method	Mass of recovered polyurethane (mg)	Yield of polyurethane (%)
<b>A</b>	405	Amberlyst	360	97
<b>B</b>	414	Amberlyst	371	94
<b>B</b>	113	NaHCO <sub>3</sub>	92	85
<b>C</b>	564	Amberlyst	542	97

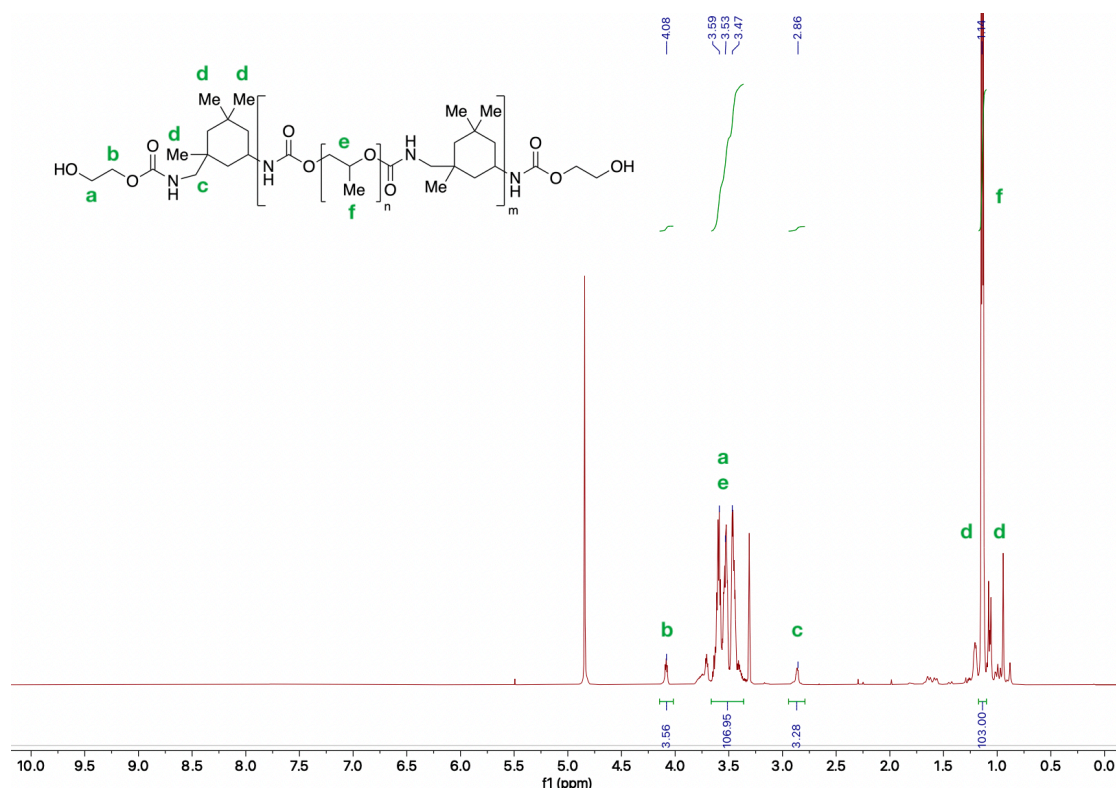


Figure S21. <sup>1</sup>H NMR of recycled polyurethane A in CD<sub>3</sub>OD.

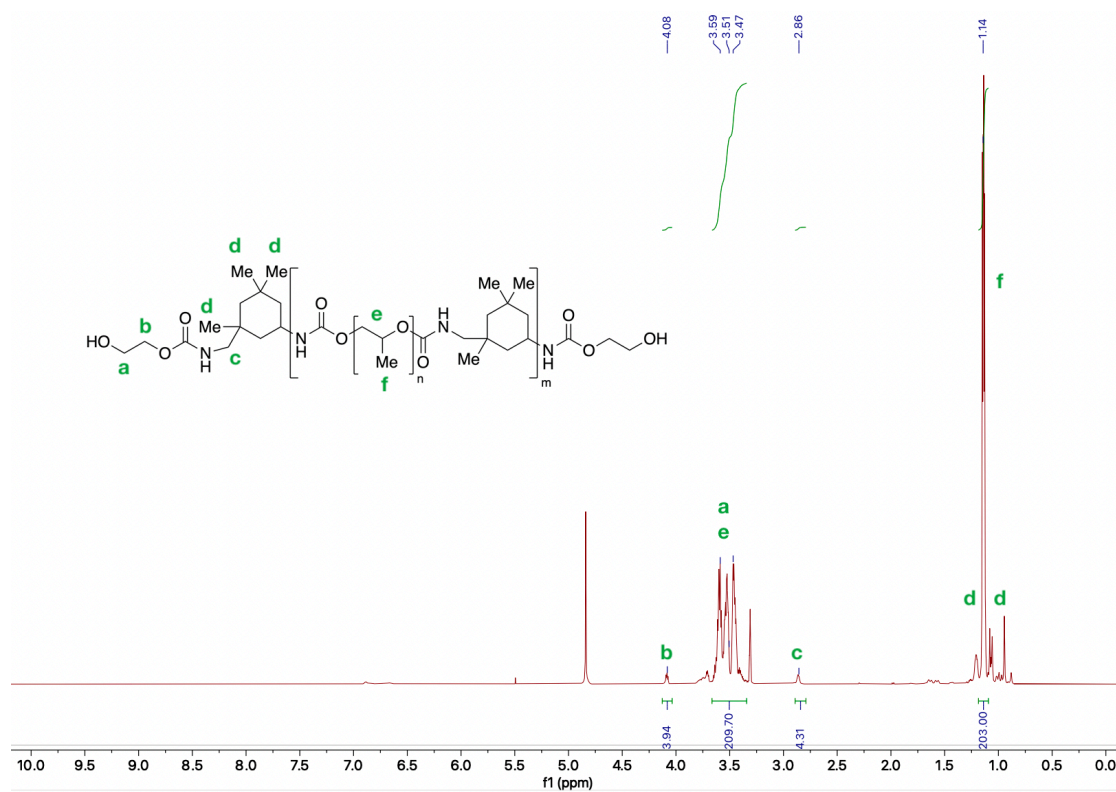
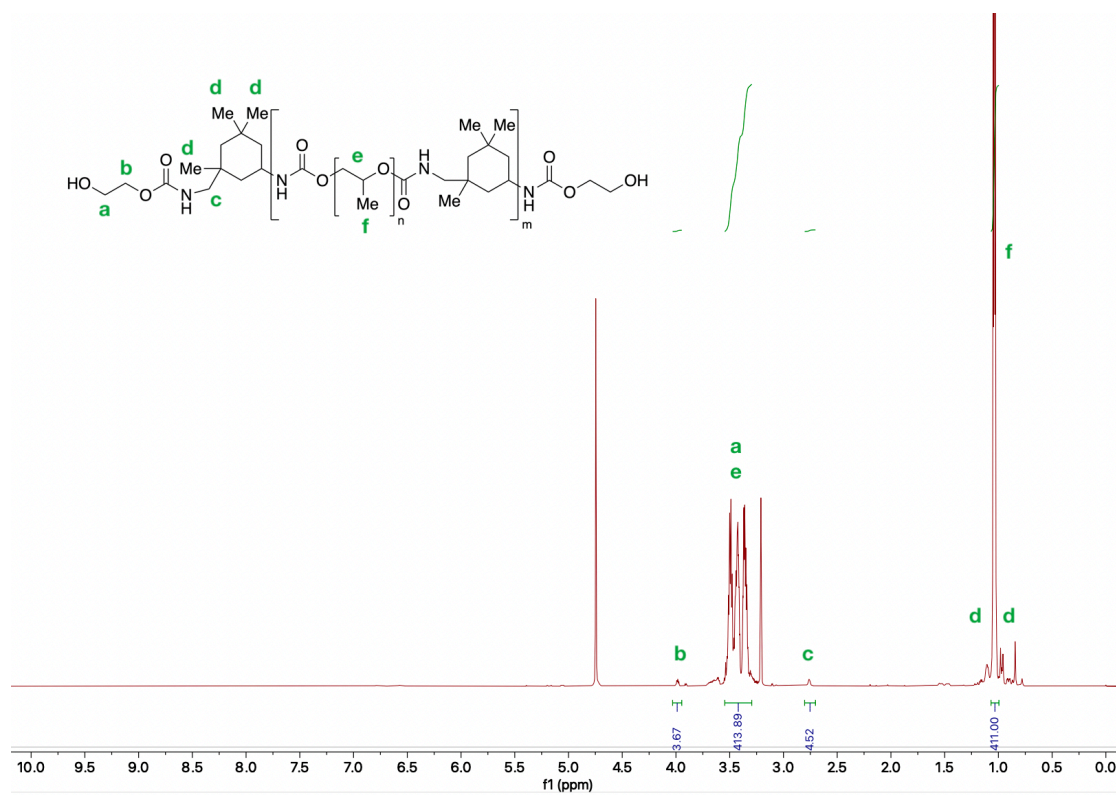


Figure S22. <sup>1</sup>H NMR of recycled polyurethane B in CD<sub>3</sub>OD.



**Figure S23.** <sup>1</sup>H NMR of recycled polyurethane C in CD<sub>3</sub>OD.

## Section VIII. References

- [1] Ryosuke Matake, Yusuke Adachi, and Hiroshi Matsubara. Synthesis of vinyl ethers of alcohols using calcium carbide under superbasic catalytic conditions (KOH/DMSO). *Green Chem.* **2016**, *18*, 2614–2618.