SUPPORTING INFORMATION

Direct Restoration of Photocurable Cross-linkers for Repeated Light-based 3D Printing of Covalent Adaptable Networks

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Experiments and methods

Materials

1,6-Hexanediol diacrylate (**1**, 99%) was purchased from Thermo Fisher Scientific, 4,4′-trimethylenedipiperidine (**2**, 97%), 2-hydroxyethyl methacrylate (HEMA, 97%), 2,2-dimethoxy-2-phenylacetophenone (DMPA, photoinitiator, 99%) were purchased from Sigma Aldrich. Chloroform ($CHCl_3$, 99%) was purchased from Thermo Fisher Scientific and used without purification.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Advance Ultrashield 300 MHz spectrometer. Deuterated chloroform ($CDCl_3$) was used as a solvent. Chemical shifts are given in parts per million (ppm).

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) spectra were measured using a Perkin-Elmer Spectrum 1000 FTIR infrared spectrometer with a diamond ATR probe.

Thermogravimetric analyses (TGA) were performed with a Mettler Toledo TGA/SDTA851e instrument under air atmosphere at a heating rate of 10 $K \cdot min^{-1}$ from 25 to 800 °C.

Differential scanning calorimetry (DSC) analyses were performed with a Mettler Toledo instrument 1/700 under a nitrogen atmosphere at a heating rate of 10 $K \cdot min^{-1}$ from −50 to 100 °C.

Mass spectrometry (MS) was performed with LC-MS Agilent Technologies 1100 series LC/MSD system equipped with a soft electrospray source (ESI-MS) and a diode array detector. Acetonitrile was used as a solvent.

Size-exclusion chromatography (SEC) was performed on an Agilent 1260-series system equipped with a 1260 online degasser, a 1260 ISO-pump, a 1260 automatic liquid sampler (ALS), a thermostatted column compartment set at 50 °C, equipped with two PLgel 5 μm mixed-D columns (7.5 mm × 300 mm) and a precolumn in series, a 1260 diode array detector and a 1260 refractive index detector. The used eluent was tetrahydrofuran (THF) at a flow rate of 0.5 mL/min. The chromatograms were analyzed using the Agilent Chemstation software with the SEC add-on. Molar mass values and dispersity (Đ) values were calculated against polystyrene standards.

Rheology experiments were performed on an Anton Paar MCR 302. *Stress-relaxation experiments* were performed in parallel plate geometry using 8 mm sample disks. Experiments were performed at different temperatures (180-120 °C, with intervals of 10 °C) using a constant shear strain within the linear viscoelastic region (LVER) of the samples, and a constant normal force of 1 N. The obtained characteristic relaxation time (τ*) was used to calculate the activation energy. *Amplitude sweep* experiments were performed using a frequency of 1 Hz, a constant normal force of 1 N, and a variable shear strain that was ramped up logarithmically from 0.01% to 10% to determine the LVER.

A time sweep experiment for network decross-linking was performed in parallel plate geometry using an 8 mm swollen network (in HEMA). A strain of 0.1% was applied with a frequency of 1 Hz for a duration of 120 min at 100 °C, storage modulus (G') and loss modulus (G") were recorded over time.

A time sweep experiment for photo-induced curing was performed in parallel plate geometry using 25 mm smooth disks. The lower plate assembly was replaced by a UV light guide accessory, equipped with a disposable acrylic plate and connected to a OmniCure S2000 Spot UV Curing system containing a 200 W Mercury vapor short arc lamp (maximum intensity = 13.23 W cm^{-2}) with a 365 nm filter. A strain of 0.1% was applied with a frequency of 1 Hz at 30 °C, storage (G') and loss modulus (G") were recorded over time. The measurement was first performed without UV for 5 min to determine viscosity, followed by UV exposure for 15 min to determine gel time.

Uniaxial tensile experiments were performed on a Tinius-Olsen H10KT tensile tester, equipped with a 100 N load cell and at a speed of 4 mm/min and a pre-load of 0.02 N. Flat dog bone type samples (3 to 5 specimens) with an effective gage length of 13 mm, a width of 2 mm and uniform thickness were used for the tensile tests. The samples were cut out using a Ray-Ran dog bone cutter.

Solubility tests were conducted with dry samples with a weight of around 10 - 20 mg and 40 mL of chloroform. Those tests were performed for 24 h at room temperature in chloroform. The solvent was then removed, and the samples were dried under vacuum overnight at 70 °C. The soluble fraction (eq. 1) and swelling ratio (eq. 2) were calculated as follows:

$$\text{soluble fraction (\%)} = \frac{m_i - m_d}{m_i} \text{ (eq. 1)}$$

$$\text{swelling ratio (\%)} = \frac{m_s - m_i}{m_i} \text{ (eq. 2)}$$

with m_i, m_s, and m_d representing the mass of initial samples, the mass of swollen samples, and the remaining mass of dry samples after swelling, respectively.

Synthesis of β-amino ester macromolecular cross-linker (BAEC): A solution of 1,6-hexanediol diacrylate (**1**, 10 g, 1.25 eq.) in 25 ml of chloroform was cooled down in an ice batch. 4,4′-Trimethylenedipiperidine (**2**, 7.44 g, 1.0 eq.) was dissolved in 25 ml of chloroform and added dropwise. After 1 h, the temperature was increased to 50 °C and the mixture was stirred for 16 h. The solvent was subsequently removed under reduced pressure yielding BAEC. Yield: quantitative; Average number molecular weight M_n = 2400 g/mol (Đ = 1.26); ^{1}H NMR (300 MHz, $CDCl_3$, δ): 6.40 (dd, 2H), 6.12 (m, 2H), 5.82 (dd, 2H), 4.16 (t, 4H), 4.07 (t, 16H), 2.96 – 2.79 (m, 16H), 2.74 – 2.60 (m, 16H), 2.51 (m, 16H), 2.07 – 1.83 (m, 16H), 1.66 (m, 20H), 1.40 (m, 10H), 1.20 (m, 26H).

Photocurable resins (PCR): the weight ratio of HEMA as a monomer in BAEC varies from 0 to 80 wt.%. The amount of photoinitiator (DMPA) was 1 wt.% over the total weight. The mixture of BAEC and monomer was first prepared, followed by the addition of DMPA (1 wt.%), yielding homogeneous photocurable resins (PCR).

Photo-curing of networks: the networks were prepared via photo-induced free radical polymerization by exposing PCR, placed between two glass plates separated by a thin silicone rubber spacer (approximately 0.8 mm), to UV light in a custom-built photoreactor, fitted with 9 UV lamps (Philips 9W, λ-range: 320-400 nm, intensity was approximately 2.5 $mW.cm^{-2}$) for 15 min and subsequently post-cured in an oven at 100 °C for 10 min. The obtained dynamic β-amino ester networks were referred to as BENX, where X represents the wt.% of monomer used. For instance, BEN20 corresponds to a β-amino ester network, comprising 20 wt.% of HEMA.

Depolymerization: The networks were placed in a sealable vial and mixed with HEMA, with a weight ratio of HEMA to the network varying from 5:1 to 20:1. The system was then deoxygenated with nitrogen bubbling for 15 min. The depolymerization was performed at 100 °C to enable transesterification between the hydroxyl groups in HEMA and the dynamic β-amino ester present in the cross-links. The resulting depolymerized mixture was used as a feedstock for photocurable resin. The weight concentration of BAEC in the depolymerized mixture was estimated to be approximately equal to the weight ratio of the network used in the depolymerization step.

Thermal treatment of the recycled networks was additionally performed at 120 °C for 2h.

The *reference network* was synthesized by adding 1 wt.% of DMPA to 1,6-hexanediol diacrylate, then cured under UV for 15 min and post-cured in the oven at 100 °C for 10 min.

Thermo-mechanical (re)processability was investigated by breaking the cross-linked material into pieces of about 1-5 mm, which were then placed into a stainless-steel mold for compression molding. This assembly was placed in a preheated compression press (150 °C) for 1 min under 0.5 metric tons of pressure. Then, the pressure was increased to 3 tons and kept constant for an additional 29 min. After 30 min of pressing in total, the sample was carefully removed from the mold.

Digital light processing (DLP) 3D printings were performed with a LumenX DLP printer from Cellink. An intensity of 75% (30 mW cm^{-2}) was applied. Printable dynamic photocurable resins were prepared by using ethyl (2,4,6-trimethyl benzoyl) phenyl phosphinate (TPO-L) photo-initiator (2.5 wt%) and quinoline yellow photo-absorber (0.05 wt%).

Characterization results

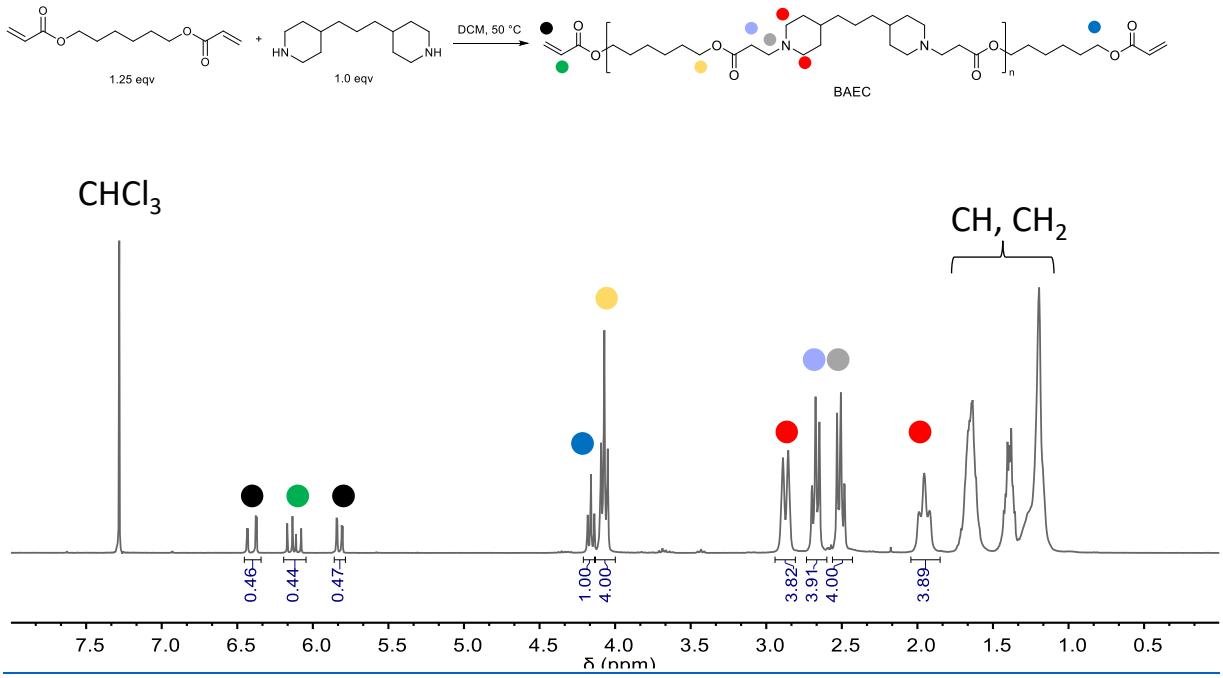

Figure S1. ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of synthesized BAEC.

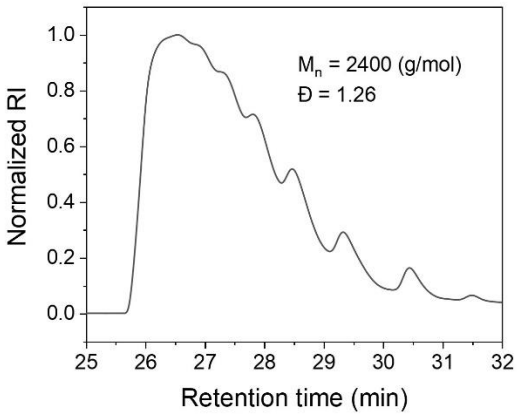

Figure S2. SEC chromatogram of BAEC cross-linker in THF, polystyrene (PS) standards were used for calibration.

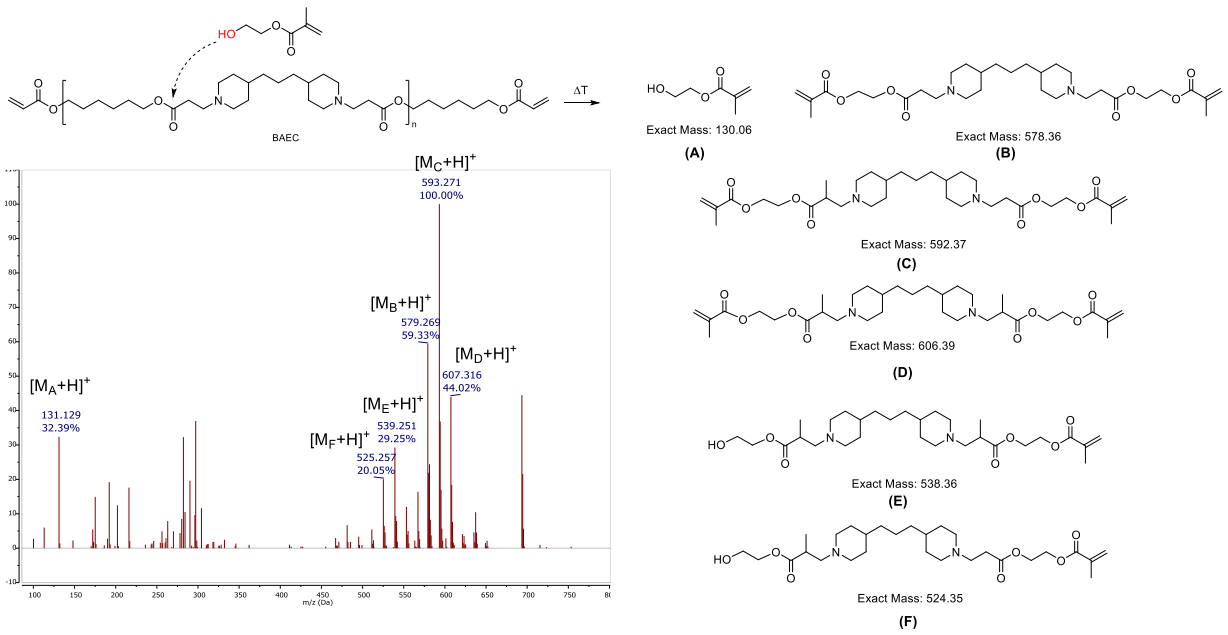

Figure S3. Mass spectrometry analysis (ESI-MS) of depolymerized mixture indicates the formation of methacrylate-containing compounds applicable for photocured CAN.

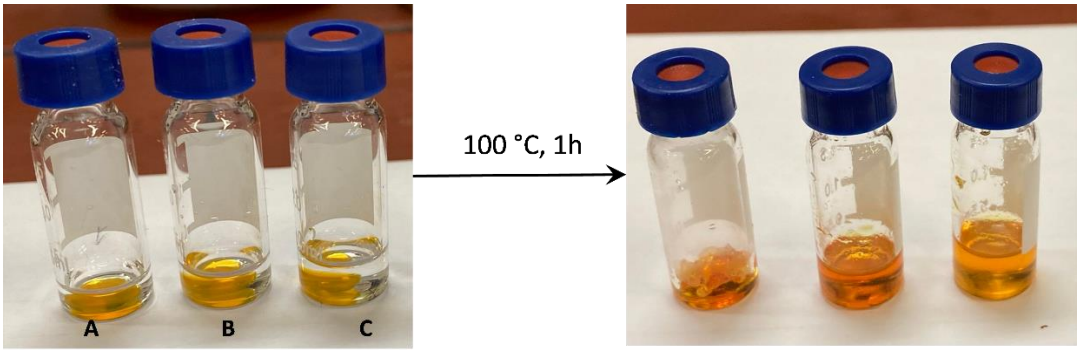

Figure S4. Visualization of the decross-linking of BEN network in HEMA: The vials A to C correspond to 10, 20, and 30 equiv. of HEMA used over the BAE moieties in the network, respectively.

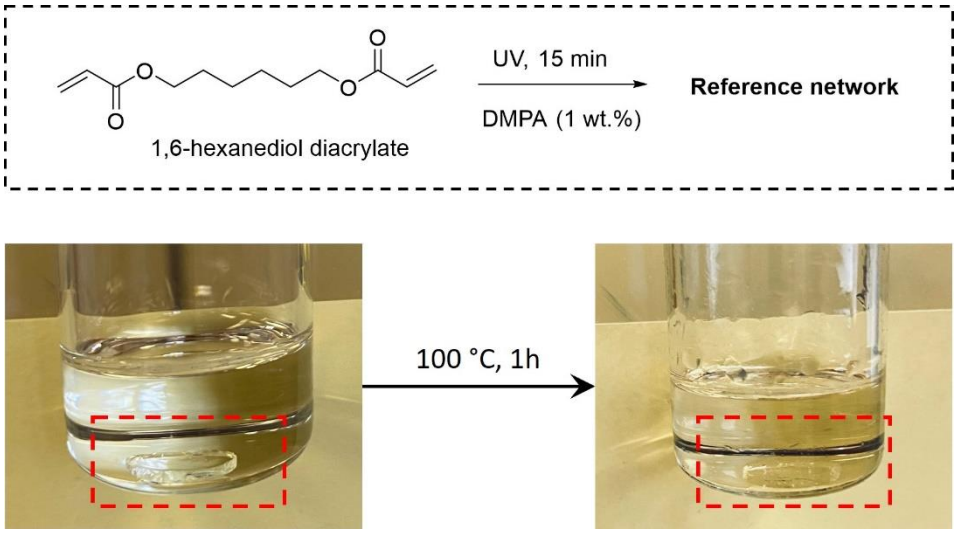

Figure S5. The synthesis of the reference polyacrylate network by photocuring without BAE moieties (top). Visualization of the reference network, which maintained its structure in the same decross-linking conditions as the one used for BEN (100 ºC, 1h) (bottom).

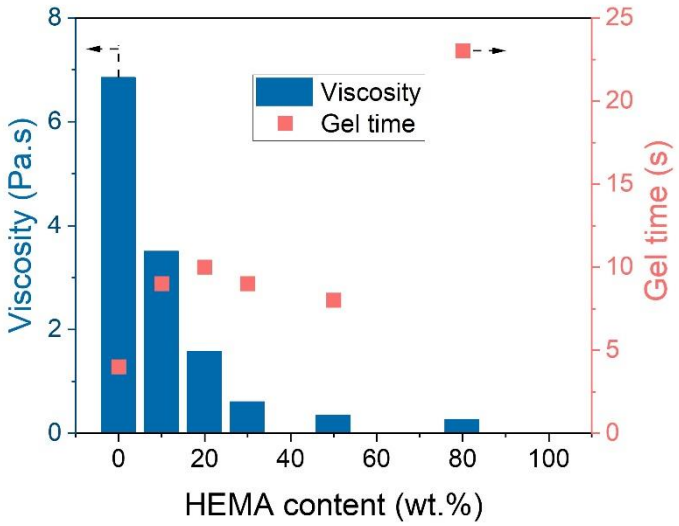

Figure S6. Effect of HEMA composition on viscosity and gel time of PCR (1 wt.% of DMPA as photoinitiator).

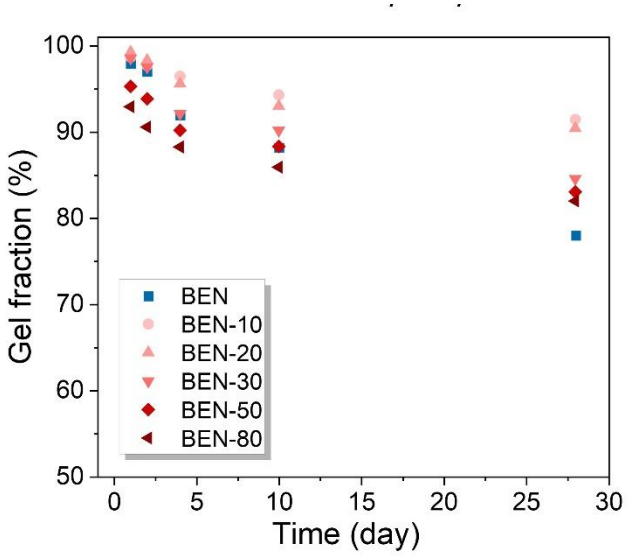

Figure S7. Effect of varying HEMA composition on the hydrolytic properties of the networks. BEN to BEN-80 correspond to networks comprising 0 to 80 wt.% of HEMA. Hydrolysis tests were performed in deionized water at room temperature.

Figure S8. The lack of processability of the reference network (comprising no BAE bonds) was observed through compression molding (2 tons of pressure, at 150 °C, for 30 min).

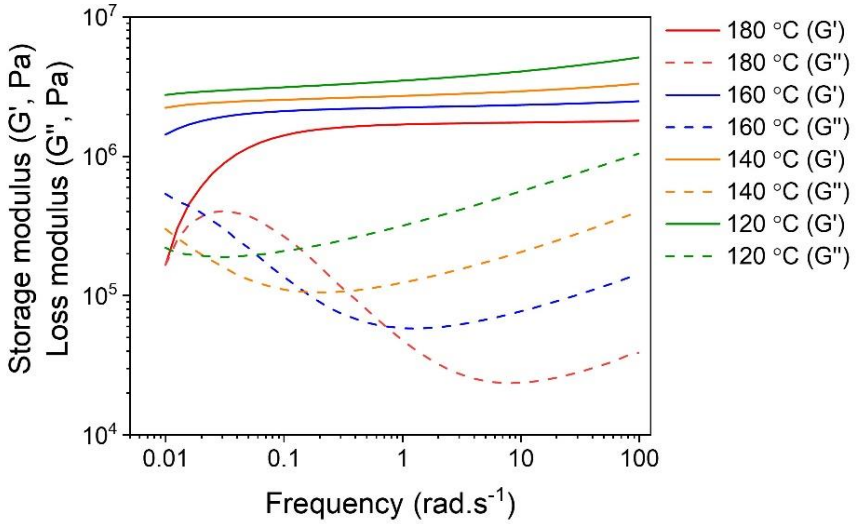

Figure S9. Frequency sweep of BEN-20 shows a drop in storage modulus with increased temperature, indicating the contribution of a dissociative exchange.

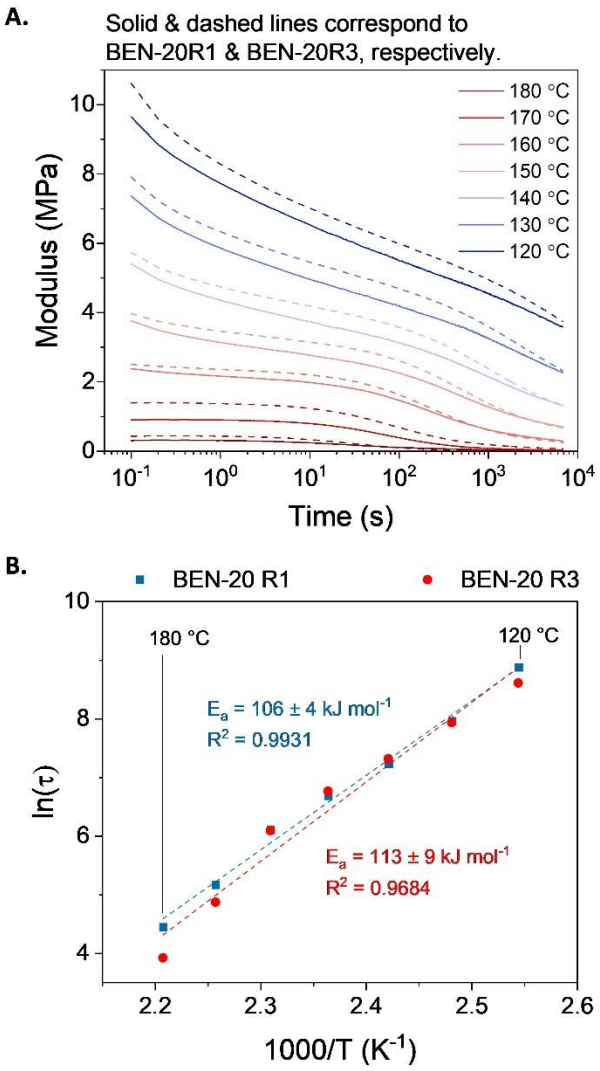

Figure S10. **(A)** Stress-relaxation curves and **(B)** Arrhenius plots of the first and third (re)molded samples corresponding to BEN-20R1 and BEN-20R3, respectively.

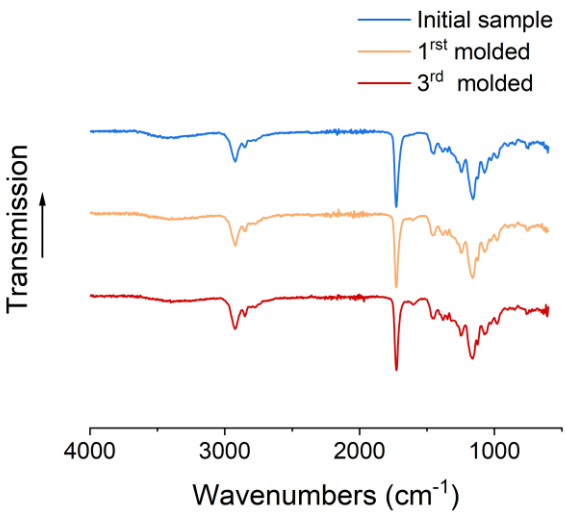

Figure S11. ATR-FTIR spectrum of BEN-20 network, showing no significant change in chemical characteristics after (re)molding three times.

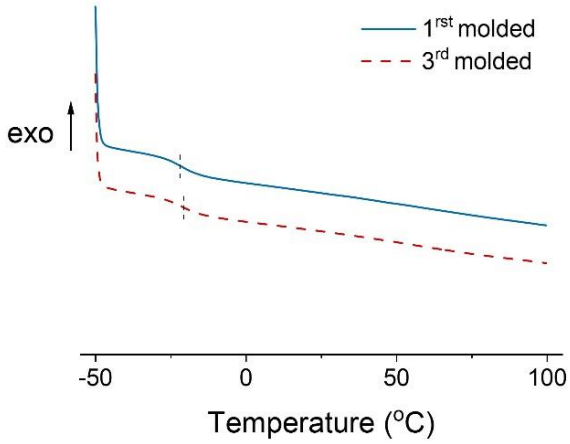

Figure S12. DSC thermogram of BEN-20 after the first and the third (re)molding did not show considerable change in thermal behavior.

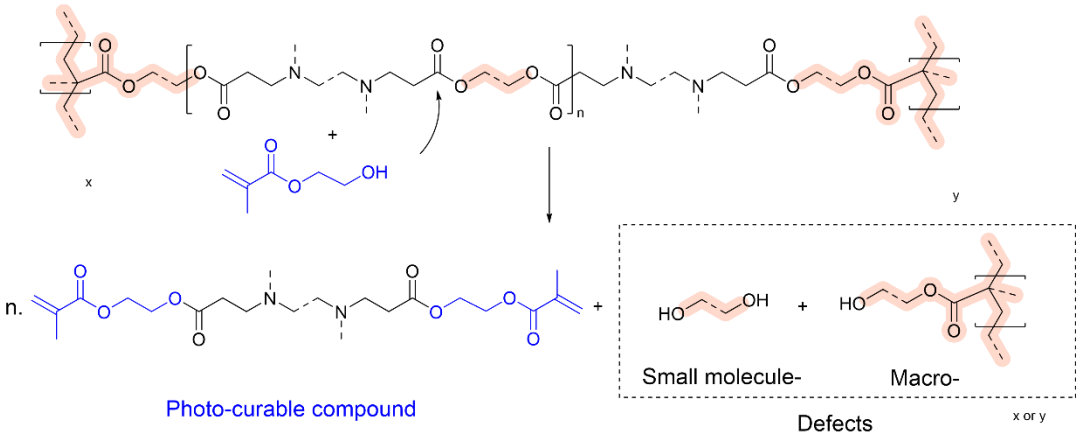

Figure S13. The possibility of generating defects without photocurable methacrylate groups obtained from depolymerization.

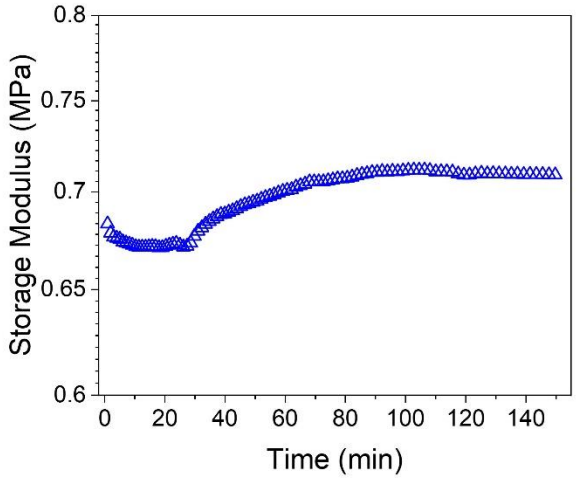

Figure S14. Time sweep experiment of BEN-20U1 (neat) at 120 ºC showing that the storage modulus increased and reached a plateau after approximately 2 h.

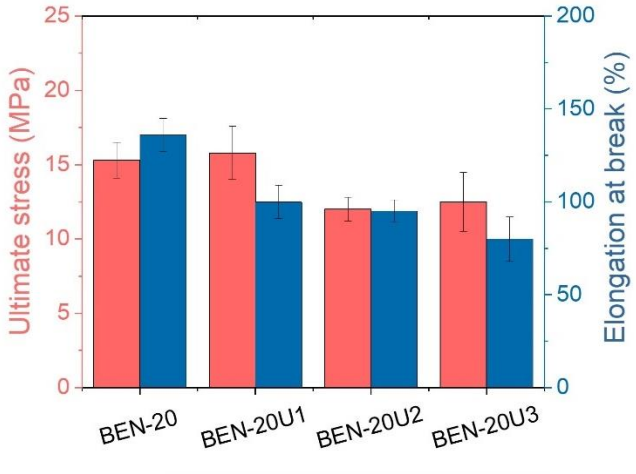

Figure S15. Ultimate stress and elongation at break of the initial network (BEN-20) and the ones after 1 to 3 cycles of the recycling process (BEN-20U1 to BEN-20U3, respectively).

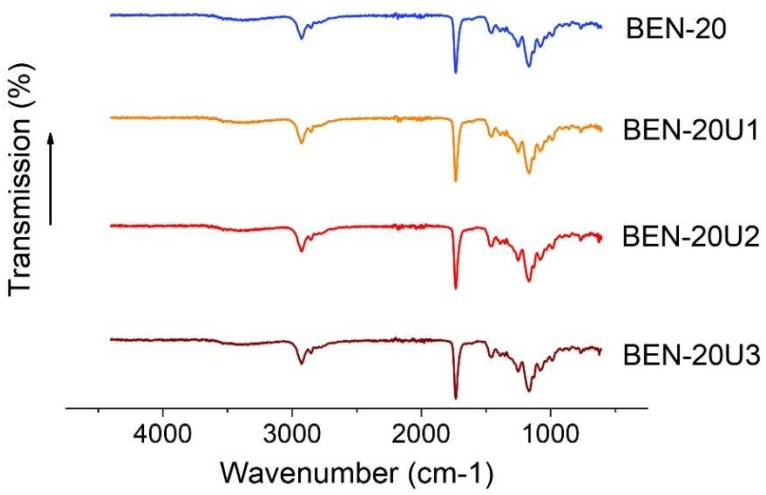

Figure S16. ATR-FTIR spectrum of the initial BEN-20 and chemically recycled networks shows no considerable changes in chemical characteristics. BEN-20U1 to BEN-20U3 correspond to the networks after 1 to 3 times of chemical recycling.

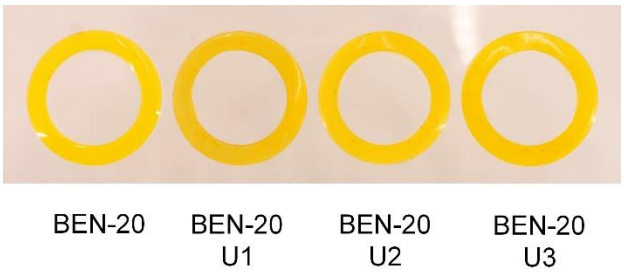

Figure S17. Visualization of DLP 3D printed structures using dynamic photocurable resins (PCR). BEN20 and BEN-20U1 to BEN-20U2 correspond to the original PCR and the first to the third recycled PCR, respectively.