Supplementary Information

Homogenizing chain tensions to extend the lifetime of soft materials

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Materials and Methods

Materials

Bis(3-aminopropyl) terminated poly(dimethylsiloxane) (H_2N-PDMS-NH_2, M_n = 5 kDa) were purchased from Gelest. Poly(propylene glycol) bis(2-aminopropyl ether) (H_2N-PPG-NH_2, M_n = 2 kDa), 4,4′-methylenebis(phenyl isocyanate) (MDPI), isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HDI), tricyclo[5.2.1.02,6]decanedimethanol diacrylate (TDDA), 2,2′-(Ethylenedioxy)diethanethiol, trimethylolpropane tris(3-mercaptopropionate), ethyl acrylate, butyl acrylate, methyl methacrylate, hexyl methacrylate, isobornyl acrylate, triethylamine, diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO), 2-Hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone (I-2959), polyethylene glycol (Mn = 2 kDa), ethylene diamine, and Sudan I were purchased from Sigma-Aldrich. 1-[4-(Phenylthio)phenyl]-1,2-octanedione 2-(O-benzoyloxime) (OXE-01) was purchased from BASF. 1,1′-Carbonyldiimidazole (CDI) was purchased from Alfa Aesar. The other chemicals were purchased from TCI. All chemicals were used as received without further purification.

General measurements

All air-sensitive manipulations were carried out under an argon atmosphere by standard Schlenk-line techniques. Dichloromethane (DCM) and tetrahydrofuran (THF) solvents were saturated with argon and purified through activated Al_2O_3 columns under argon (Chembly SPS H4). Solution ^{1}H NMR spectra were recorded on Bruker AVANCE III HD Nanobay (400 MHz), Bruker AVANCE III HD (400 MHz), Bruker AVANCE NEO Nanobay (400 MHz), or Bruker AVANCE NEO (500 MHz) spectrometer, and chemical shifts were referenced to the residual solvent peaks.

Synthetic Protocols

Synthesis of IU oligomer. Synthetic protocol for IU oligomer was identical with that for MPU oligomer except for the use of IPDI (0.45 g, 0.22 g) instead of MDPI (0.50 g, 0.22 g). As a result, IU oligomer (13 g) was obtained. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 6.12 (s, 2H), δ 5.59 (s, 2H), δ 4.46 (br, 6H), δ 4.24 (t, J = 5.5 Hz, 4H), δ 3.51 (m, 4H), δ 3.14 (m, 13H), δ 2.96 (m, 4H), δ 1.95 (s, 6H), δ 1.71 (m, 13H), δ 1.52 (m, 13H), δ 1.06 (m, 15H), δ 0.92 (m, 12H), δ 0.54 (m, 14H), δ 0.07 (s, 1250H).

Synthesis of HU oligomer. Synthetic protocol for HU oligomer was identical with that for MPU oligomer except for the use of HDI (0.40 g, 0.20 g) instead of MDPI (0.50 g, 0.22 g). As a result, HU oligomer (13 g) was obtained. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 6.12 (s, 2H), δ 5.59 (s, 2H), δ 4.51 (br, 10H), δ 4.24 (t, J = 5.5 Hz, 4H), δ 3.51 (m, 4H), δ 3.14 (m, 22H), δ 1.95 (s, 6H), δ 1.51 (m, 24H), δ 1.34 (m, 13H), δ 0.53 (m, 15H), δ 0.07 (s, 1290H).

Synthesis of MPU oligomer with a single sticker. A 250 mL 2-neck round bottom flask was charged with H_2N-PDMS-NH_2 (20.0 g, ~ 4.00 mmol), triethylamine (1.00 mL, 7.17 mmol), and dry DCM (80 mL) under argon atmosphere. To this mixture, DCM (10 mL) solution of MDPI (0.50 g, 2.0 mmol) was added dropwise via syringe over a period of 100 min. The solution was stirred at room temperature for additional 6 hours under argon atmosphere. Then, 2-isocyanatoethyl methacrylate (0.70 mL, 5.0 mmol) was added to the reaction mixture, and

further stirred at room temperature for 6 hours under dark condition. MeOH (1 mL) was added to quench the reaction, and the resulting solution was concentrated in vacuo. The purification protocol (three dissolution–precipitation–decantation processes and solvent drying) was identical with that for MPU oligomer. As a result, MPU oligomer with a single sticker (13 g) was obtained. ^{1}H NMR (400 MHz, THF-*d*8, 298 K): δ 7.28 (d, *J* = 8.6 Hz, 4H), δ 6.97 (d, *J* = 8.5 Hz, 4H), δ 6.06 (m, 2H), δ 5.54 (m, 2H), δ 4.10 (t, *J* = 5.7 Hz, 4H), δ 3.77 (s, 2H), δ 3.37 (m, 4H), δ 3.13 (m, 4H), δ 3.05 (m, 4H), δ 1.90 (s, 6H), δ 1.50 (m, 8H), δ 0.56 (m, 8H), δ 0.11 (s, 1213H).

Synthesis of MPU oligomer without spacer chains. A 250 mL 2-neck round bottom flask was charged with H_2N-PDMS-NH_2 (M_n = 5000 g/mol, 10.0 g, ~ 2.00 mmol), triethylamine (0.5 mL, 3.58 mmol), and dry DCM (40 mL) under argon atmosphere. To this mixture, DCM (10 mL) solution of MDPI (0.75 g, 3.0 mmol) was added quickly. The solution was stirred at room temperature for 1 hour under argon atmosphere. To the reaction mixture, DCM (10 mL) solution of H_2N-PDMS-NH_2 (M_n = 900 g/mol, 1.8 g, 2.0 mmol) was added quickly. The solution was stirred at room temperature for an additional 1 hour under argon atmosphere. Then, 2-isocyanatoethyl methacrylate (0.70 mL, 5.0 mmol) was added and the resulting solution was further stirred at room temperature for 3 hours under dark condition to complete the reaction. Then, MeOH (1 mL) was added to quench the reaction, and the resulting solution was concentrated in vacuo. The residue was dissolved in minimal amount of chloroform and excess amount of MeOH was added to induce precipitation. After 30 min, the supernatant liquid fraction was decanted to afford polymer precipitates. This dissolution–precipitation–decantation process was repeated twice, and the resulting precipitates were completely dried under reduced pressure for three hours at 35 °C to afford MPU oligomer without spacer chains. As a result, MPU oligomer without spacer chains (7 g) was obtained. ^{1}H NMR (400 MHz, THF-*d*8, 298 K): δ 7.29 (d, *J* = 8.0 Hz, 44H), δ 6.96 (d, *J* = 8.3 Hz, 44H), δ 6.06 (m, 2H), δ 5.54 (m, 2H), δ 4.10 (t, *J* = 5.8 Hz, 4H), δ 3.77 (s, 22H), δ 3.38 (m, 4H), δ 3.15 (m, 48H), δ 1.90 (s, 6H), δ 1.53 (m, 49H), δ 0.56 (m, 47H), δ 0.11 (s, 3757H).

Synthesis of MPU oligomer with PPG backbone. A 250 mL 2-neck round bottom flask was charged with H_2N-PPG-NH_2 (10.0 g, ~ 5.00 mmol), triethylamine (1.00 mL, 7.17 mmol), and dry DCM (40 mL) under argon atmosphere. To this mixture, DCM (10 mL) solution of MDPI (1.13 g, 4.52 mmol) was added and the mixture was further stirred at room temperature for 6 hours. Then, 2-isocyanatoethyl methacrylate (0.35 mL, 2.5 mmol) was added and the resulting solution was further stirred at room temperature for 6 hours under dark condition. The purification process for MPU oligomer with PPG backbone was identical with that for MPU oligomer with PDMS backbone except for the use of THF/water combination instead of chloroform/MeOH combination for the dissolution–precipitation–decantation process. As a result, MPU oligomer with PPG backbone (7 g) was obtained. ^{1}H NMR (500 MHz, THF-*d*8 : MeOD = 4 : 1 (v/v), 298 K): δ 7.28 (d, *J* = 8.1 Hz, 26H), δ 6.99 (d, *J* = 8.2 Hz, 26H), δ 6.07 (m, 2H), δ 5.56 (m, 2H), δ 4.10 (t, *J* = 5.6 Hz, 4H), δ 3.77 (s, 14H), δ 3.55-3.22 (br, 700H), δ 1.89 (s, 6H), δ 1.07 (s, 725H).

Synthesis of PEG-diamine (H_2N-PEG-NH_2). This is a precursor polymer used for the synthesis of MPU oligomer with PEG backbone. A 500mL 2-neck round bottom flask was charged with polyethylene glycol (M_n = 2 kDa, 30 g, ~ 15 mmol), CDI (5.8 g, 36 mmol), and dry THF (200 mL) under argon atmosphere. To this mixture, ethylene diamine (17 mL, 250 mmol) was added,

and the resulting mixture was stirred at room temperature for 12 hours. Then, the solution was concentrated in vacuo. The sticky liquid residue was dissolved in a minimal amount of chloroform and precipitations were induced by cold ethanol chilled by liquid nitrogen. The precipitates were collected by centrifugation. This process was repeated twice, and the resulting precipitates were completely dried under reduced pressure for six hours at 35 °C to afford PEG-diamine (10 g). ^{1}H NMR (400 MHz, D_2O, 298 K): δ 4.23 (m, 4H), δ 3.72 (s, 352H), δ 3.28 (m, 4H), δ 2.86 (m, 4H).

Synthesis of MPU oligomer with PEG backbone. A 100 mL 2-neck round bottom flask was charged with H_2N-PEG-NH_2 (1.9 g, ~ 0.56 mmol), triethylamine (0.16 mL, 1.1 mmol), and dry DCM (10 mL) under argon atmosphere. To the reaction mixture, DCM (5 mL) solution of MDPI (0.13 g, 0.50 mmol) was added, and the solution was stirred at room temperature for 6 hours. Then, 2-isocyanatoethyl methacrylate (0.05 mL, 0.3 mmol) was added and the resulting solution was further stirred at room temperature for 6 hours under dark condition. The purification process for MPU oligomer with PEG backbone was identical with that for MPU oligomer with PDMS backbone except for the use of THF/hexane combination instead of chloroform/MeOH combination for the dissolution–precipitation–decantation process. As a result, MPU oligomer with PEG backbone (1.4 g) was obtained. ^{1}H NMR (400 MHz, D_2O, 298 K): δ 8.22 (s, 6H), δ 8.06 (d, J = 8.3 Hz, 12H), δ 7.88 (d, J = 8.3 Hz, 12H), δ 6.94 (m, 2H), δ 6.42 (m, 2H), δ 4.99 (m, 15H), δ 4.45 (s, 921H), δ 2.75 (s, 6H), δ 2.18 (t, J = 7.3 Hz, 8H).

Preparation of polymer networks (Fig. 3)

ESS-PEA. MPU oligomer (0.4 g) was dissolved in ethyl acrylate (1984 μL) along with 222 μL aliquot of MeOH. Photoinitiator stock solution was independently prepared by dissolving OXE-01 photoinitiator (0.1 g) in THF (1 mL), from which 91 μL of was taken and added to the first solution. The mixed solution was then poured onto a 65 mm diameter Teflon mold and cured using a 40 W 365 nm UV lamp (VILBER, Bio-Link) for 10 min. The entire process was carried out in a glove box charged with argon gas. The resulting photocured polymer film showed a thickness ranging from 300 to 400 μm.

PEAs with IU oligomers. Preparation of PEA with IU oligomers was identical with that of ESS-PEA except for the use of IU oligomer (0.4 g) instead of MPU oligomer (0.4 g).

PEAs with HU oligomers. Preparation of PEA HUC was identical with that of ESS-PEA except for the use of HU oligomer (0.4 g) instead of MPU oligomer (0.4 g).

ESS-PMMA. Preparation of ESS-PMMA was identical with that of ESS-PEA except for the use of methyl methacrylate (1694 μL) instead of ethyl acrylate (1984 μL). For this case, MPU oligomer (0.7 g) was used.

ESS-PHMA. Preparation of ESS-PHMA was identical with that of ESS-PEA except for the use of hexyl methacrylate (2242 μL) instead of ethyl acrylate (1984 μL). For this case, MPU oligomer (0.5 g) was used.

ESS-PBA. Preparation of ESS-PBA was identical with that of ESS-PEA except for the use of butyl acrylate (2281 μL) instead of ethyl acrylate (1984 μL). For this case, MPU oligomer (0.7 g) was used.

ESS_{PPG}-PHEA. Preparation of ESS_{PPG}-PHEA was identical with that of ESS-PEA except for the use of 2-hydroxyethyl acrylate (2000 μL) and MPU oligomer with PPG backbone (0.27 g) instead of ethyl acrylate (1984 μL) and MPU oligomer with PDMS backbone (0.4 g), respectively.

PEA. TDDA (0.05 g) was dissolved in ethyl acrylate (1000 μL), and 168 μL of this mixture was taken and added into 2830 μL of ethyl acrylate. To this solution, OXE-01 stock solution (0.1 mg/mL in THF, 138 μL) was added. The mixed solution was then poured onto a 65 mm diameter Teflon mold and cured using a 40 W 365 nm UV lamp (VILBER, Bio-Link) for 10 min. The entire process was carried out in a glove box charged with argon gas.

Preparation of hydrogels

ESS_{PEG}-PAAm hydrogel. MPU oligomer with PEG backbone (0.28 g) and acrylamide (1.4 g) was dissolved in deionized (DI) water (2 mL). Photoinitiator stock solution was independently prepared by dissolving I-2959 photoinitiator (4.5 mg) in ethanol (1 mL), from which 50 μL of was taken and added to the first solution. The mixed solution was charged in a 30-mL glass vial (crosslinker : monomer molar ratio was 1:1000). The solution was purged with argon for more than 30 min and cured using a 40 W 365 nm UV lamp (VILBER, Bio-Link) for 3 hours.

PAAm hydrogel. Preparation of PAAm hydrogel was identical with that of ESS_{PEG}-PAAm hydrogel except for the use of *N*,*N'*-methylenebisacrylamide (MBAA, 3.1 mg) instead of MPU oligomer with PEG backbone (0.28 g). The amount of MBAA was set to maintain the crosslinker : monomer molar ratio to 1:1000.

Mechanical characterization

Tensile, fracture, fatigue and puncture tests were conducted using a universal testing machine (UTM) (Instron 68SC-1).

Puncture tests. The polymer films were cut into square shape (45 mm × 45 mm) and positioned between two steel holders having central holes of 35 mm diameter. A sharp steel blade (0.76 mm × 7 mm) was equipped to the UTM and positioned on the center of the polymer films. Puncture tests were performed by pushing down the blade to the polymer films with a loading rate of 100 mm min^{-1}.

Compression tests. Compression tests were performed with a universal testing machine (UTM) (Instron 5982). Samples were 3D-printed into cylindrical shapes with dimensions of 15 mm × 10 mm (diameter × height). The printing conditions for rigid photocurable resins (FDB and TC 85) included a layer thickness of 100 μm, UV intensity of 4.5 mW cm^{-2}, and an exposure time of 4 s for each layer. The printing conditions for ESS photopolymers are provided in the 3D printing section. Compression rate was set to 1 mm min^{-1}.

FT-IR spectra

FT-IR spectra were recorded using a spectrometer (PerkinElmer, Frontier FT-IR) in the range of 400–4000 cm^{-1} with an average of 16 scans. For stretching experiments, samples were elongated on a holder and subsequently fixed with adhesive tape prior to recording.

Viscosity measurements

Viscosity was measured using a rheometer (Anton Paar, MCR 302) with a 50 mm-diameter parallel plate and a Peltier temperature control system. Oligomers were dissolved in p-xylene at varying concentrations. The resulting solutions were placed on the stage, and the upper plate was lowered until the gap between the plate and stage reached 0.1 mm. Viscosity was measured at 25 °C over a shear rate range of 100–1000 s^{-1}.

AFM imaging

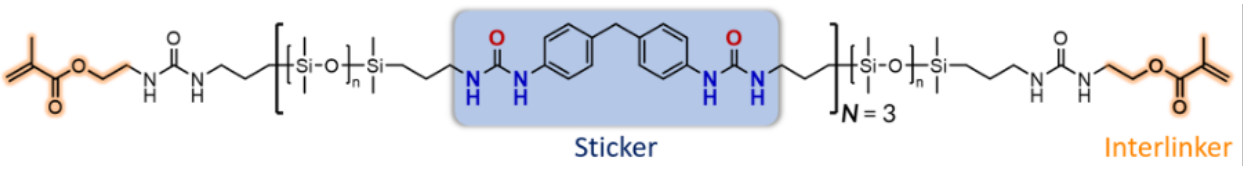
Height and phase images of the polymer networks were obtained using an AFM (Park Systems, NX10) in tapping mode. For the images shown in Figure 2, polymer films were cured using a 1 mm spacer, then cut to obtain a cross-sectional view. For stretching experiments, samples were elongated on a holder and subsequently fixed with adhesive tape prior to imaging. For the images shown in Figure 3, polymer solutions were dropped onto 1 cm × 1 cm silicon oxide wafers and spin-coated at 3000 rpm for 30 s under an Ar atmosphere. The spin-coated samples were then cured using a 40 W, 365 nm UV lamp (VILBER, Bio-Link) for 10 min before AFM imaging.

TEM imaging

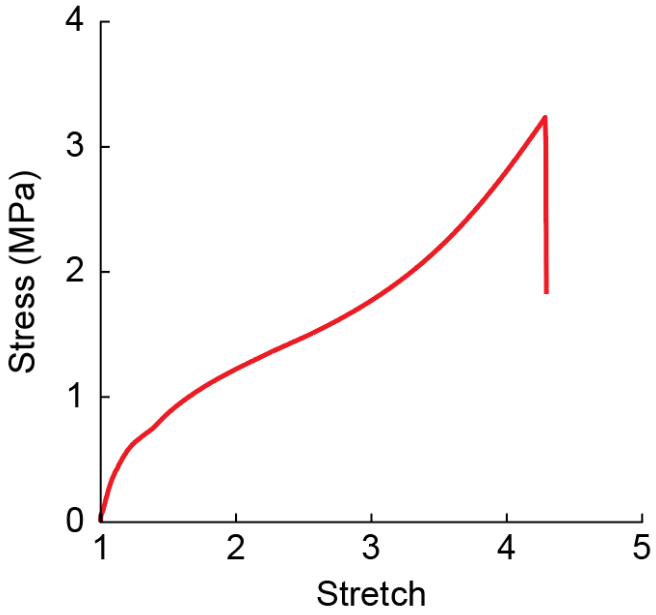
To prepare TEM samples, each polymer film was first embedded in an acrylate resin and cured into acrylate blocks at 70 C for 5 h. Each block was then cut into a ~150 nm thick slice using an ultramicrotome (Leica, EM UC7). The resultant sample was placed on a Cu grid and observed by TEM (JEOL, JEM-2100).

Contact angle analysis

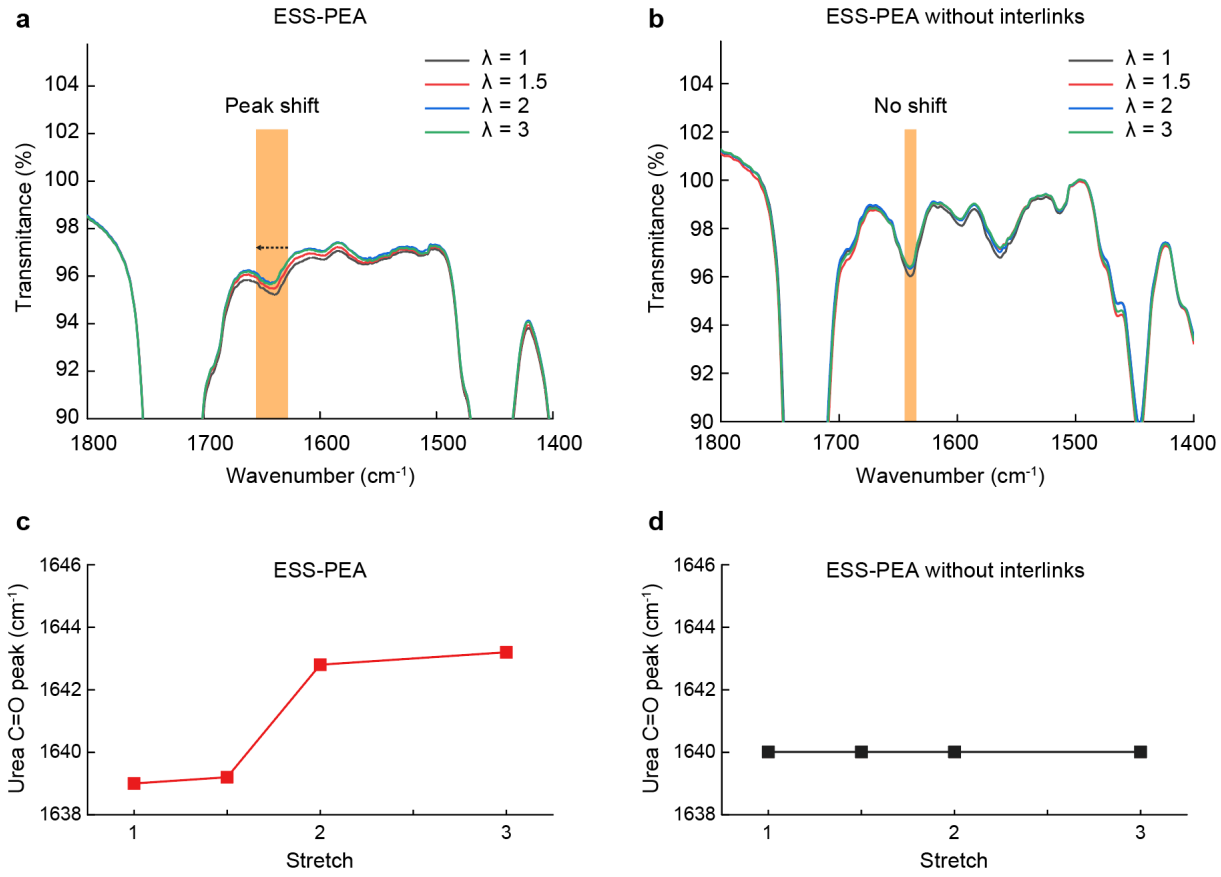
Contact angle was measured using sessile drop method with a contact angle analyzer (SEO, Phoenix 300). A 5 μL drop of deionized water was deposited on the polymer film surface using micropipette, and the contact angle was measured within 10 s. All processes were repeated three times and the contact angle values were determined by averaging the results from each experiment.



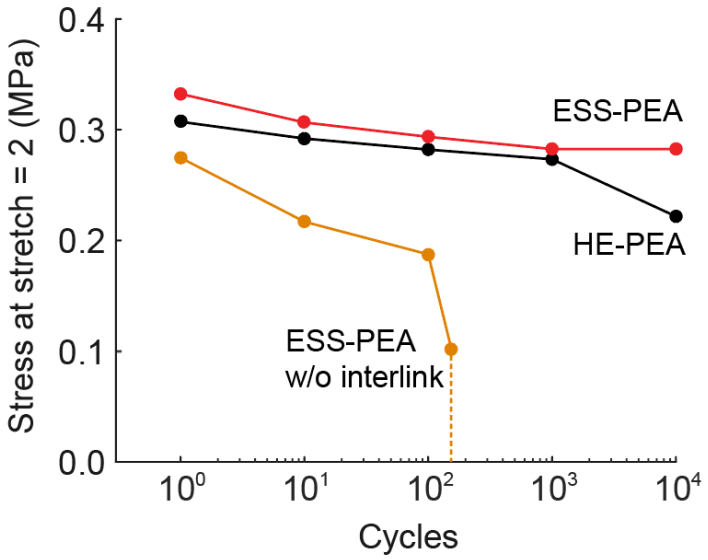
Supplementary Fig. 1 | Chemical structure of MPU oligomers. MPU supramolecular sticker and two interlinkers are highlighted by a blue box and orange lines, respectively.



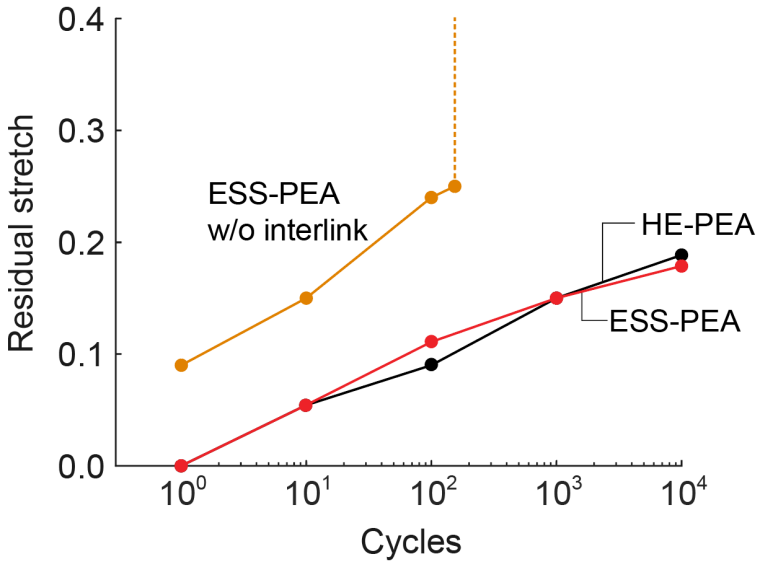
Supplementary Fig. 2 | Stress-stretch curve of self-crosslinked MPU oligomer. MPU oligomers can be self-crosslinked to make a polymer network because of the two interlinks. Despite the short chain length (~21 kDa), the crosslinked MPU oligomers exhibit high stretchability (> 4) and strength (> 3 MPa), which show robust but deformable nature of ESS domains.



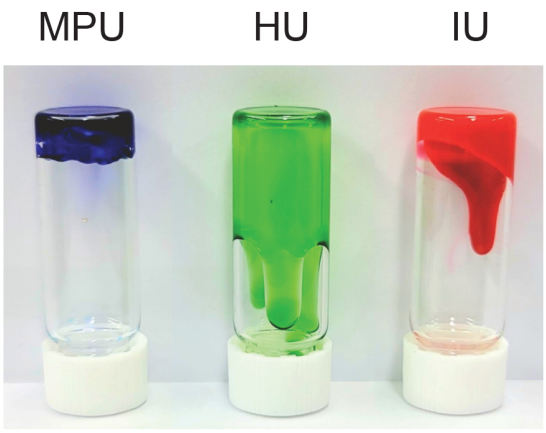
Supplementary Fig. 3 | Deformation of ESS probed by FT-IR spectra. FT-IR spectra recorded under stretch of **a,** ESS-PEA and **b,** ESS-PEA without interlinks. The orange box indicates the IR absorption peaks from C=O bond stretching and their shift. The urea C=O bond stretching wavenumber of **c,** ESS-PEA and **d,** ESS-PEA without interlinks as a function of stretch. In the ESS composites, only ESS domains have the urea C=O bonds. Therefore, the change of the urea C=O bond stretch wavenumber reflects the deformation of ESS.



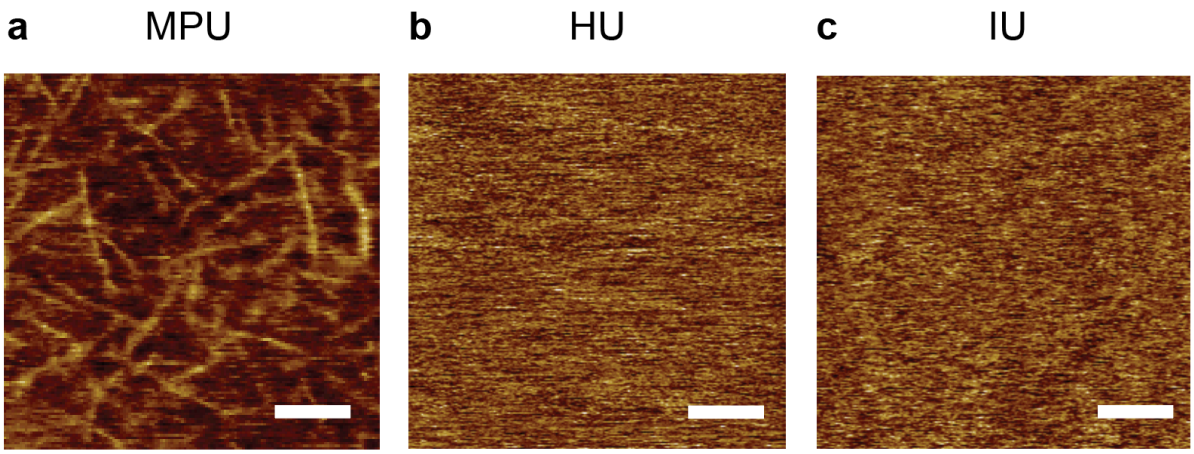
Supplementary Fig. 4 | Stress at λ = 2 as a function of the number of cycles. ESS-PEA, PEA, and ESS-PEA without interlink are subjected to cyclic loading with the stretch amplitude λ = 2, and the maximum stress values at λ = 2 are plotted as a function of the number of cycles. Note that the ESS-PEA remains intact after 10^3 cycles and the stress plateaus whereas ESS-PEA without interlink fails before 200 cycles.



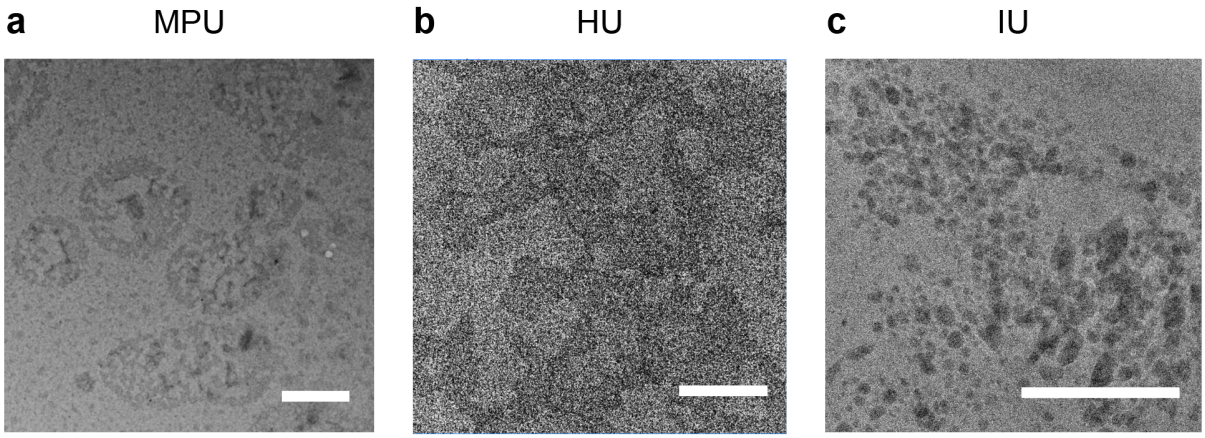
Supplementary Fig. 5 | Residual stretch as a function of the number of cycles. ESS-PEA, PEA, and ESS-PEA without interlink are subjected to cyclic loading with the stretch amplitude $\lambda = 2$, and the residual stretches are plotted as a function of the number of cycles. Note that ESS-PEA has similar residual stretch with that of PEA after 10^4 cycles whereas ESS-PEA without interlink fails before 200 cycles.



Supplementary Fig. 6 | Flowability of MPU, HU and IU oligomers. Flip test is performed for supramolecular oligomers with different stickers. The MPU, HU, and IU oligomers are stained by blue, green, and red dyes, respectively. At room temperature, the MPU oligomer does not flow due to the strong interchain hydrogen bonding, while the HU oligomer and IU oligomer flow.

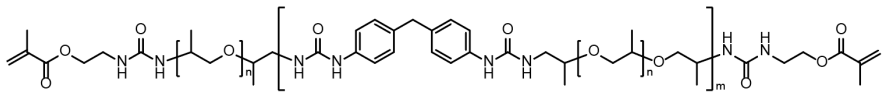


Supplementary Fig. 7 | Effect of the supramolecular sticker on the self-assembly of the oligomers. AFM images of PEA with **a,** MPU oligomers (ESS-PEA), **b,** HU oligomers, and **c,** IU oligomers. Note that MPU oligomers self-assemble to form nanofibers while other oligomers do not. Scale bars, 100 nm.

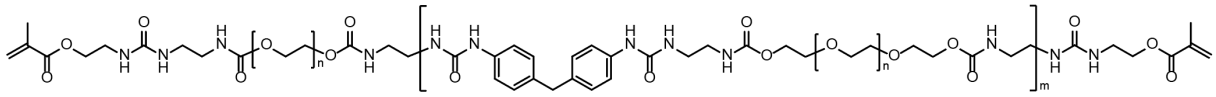


Supplementary Fig. 8 | TEM images of PEA with various oligomers. Cross-sectional images of PEA with **a,** MPU oligomers (ESS-PEA), **b,** HU oligomers, and **c,** IU oligomers. Scale bars, 500 nm.

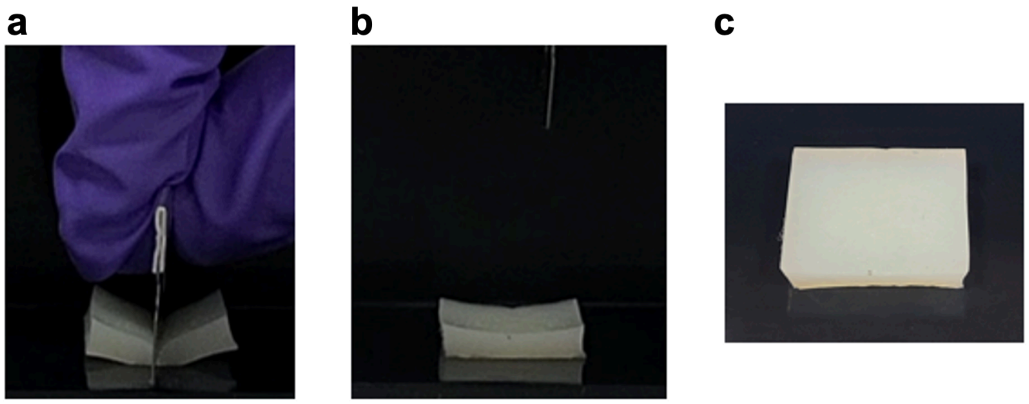
a



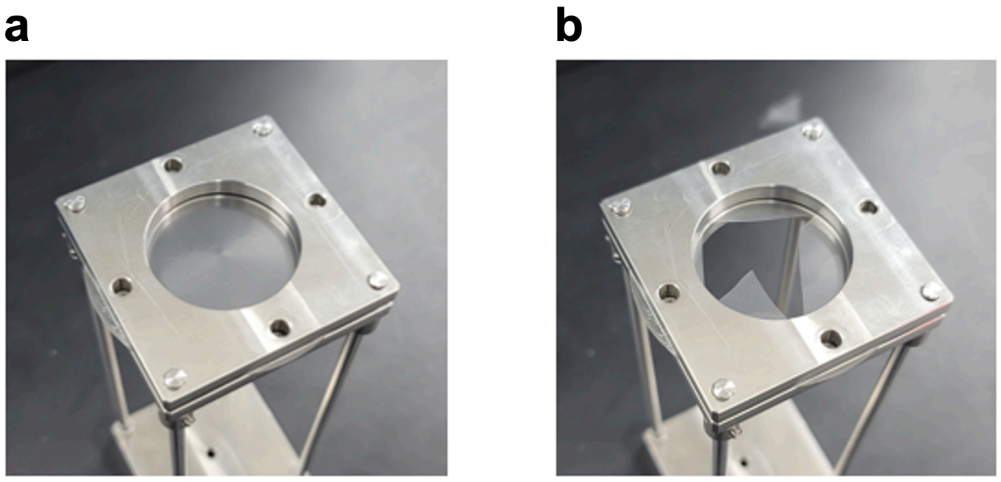
b



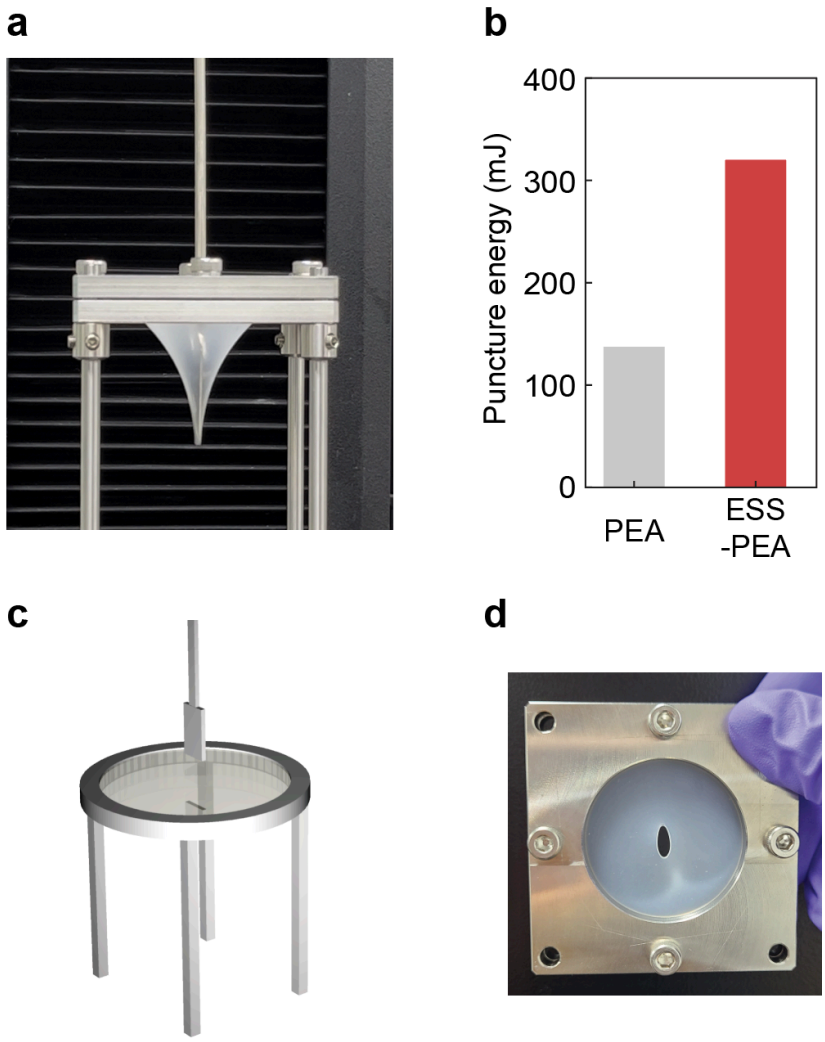
Supplementary Fig. 9 | Hydrophilic MPU oligomers. Chemical structures of **a,** MPU oligomer with PPG backbone, and **b,** MPU oligomer with PEG backbone.



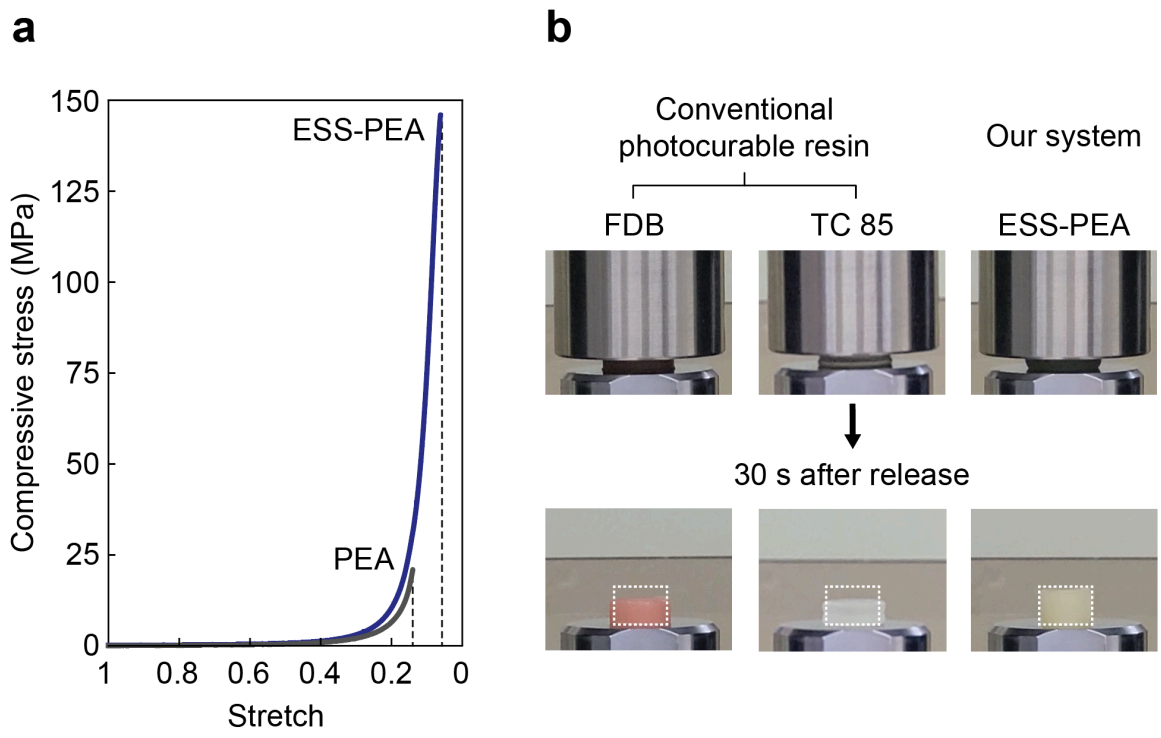
Supplementary Fig. 10 | ESS_{PEG} toughens hydrogel. a, Optical image of an ESS_{PEG}-PAAm hydrogel pressed by a razor blade. **b,** With the pressure applied by our hand, the razor blade cannot cut the hydrogel, which highlights the high toughness of the hydrogel. **c,** An optical image of ESS_{PEG}-PAAm hydrogel after being pressed by the razor blade.



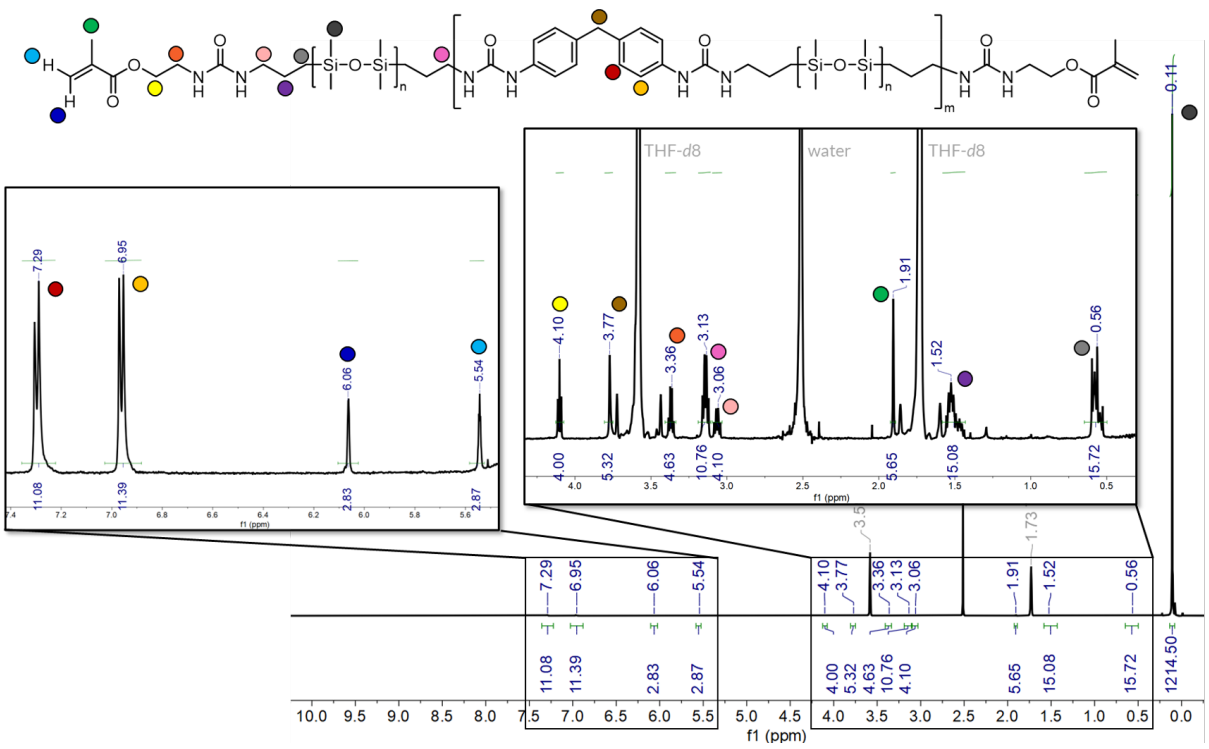
Supplementary Fig. 11 | Ball drop test. Images of **a,** ESS-PMMA and **b,** PMMA specimens after the ball drop test. The ball drop test was performed by dropping the ball of 12 g at the height of 15 cm.



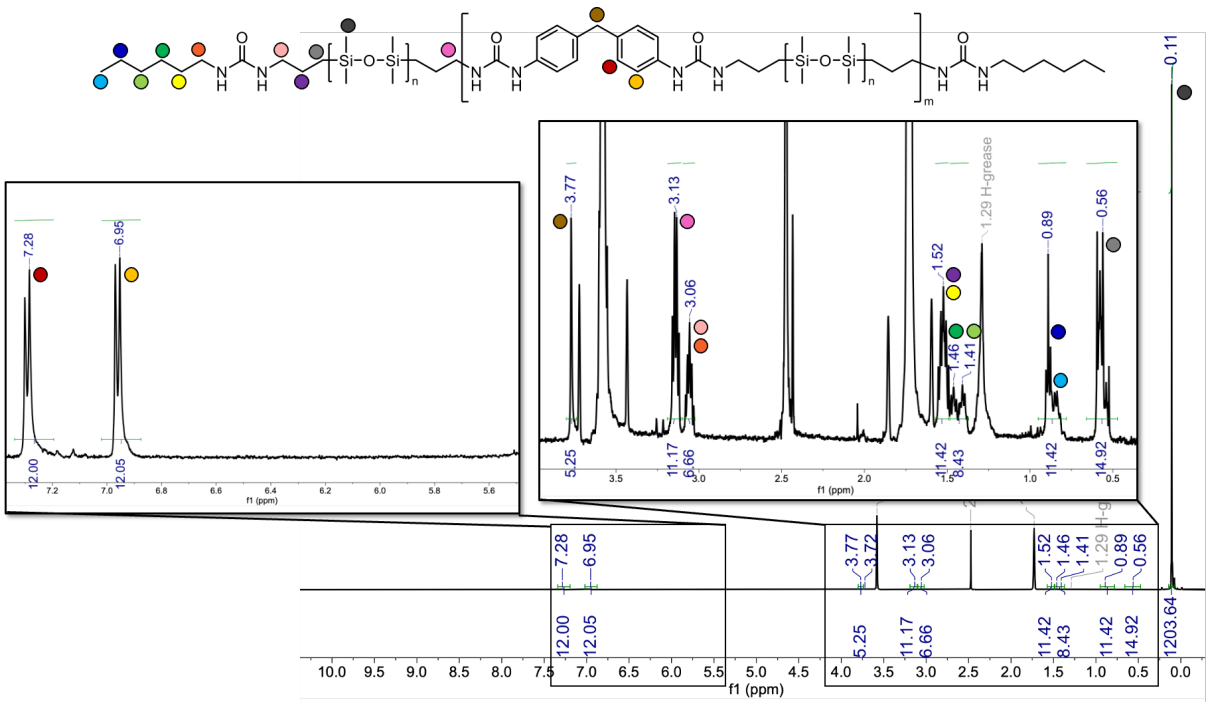
Supplementary Fig. 12 | Puncture test of 3D printed ESS-PEA. a, Optical image of an ESS-PEA under puncture test. **b,** Puncture energy of ESS-PEA and PEA. **c,** Schematic illustration of puncture test setup. **d,** Optical image of the punctured ESS-PEA specimen.



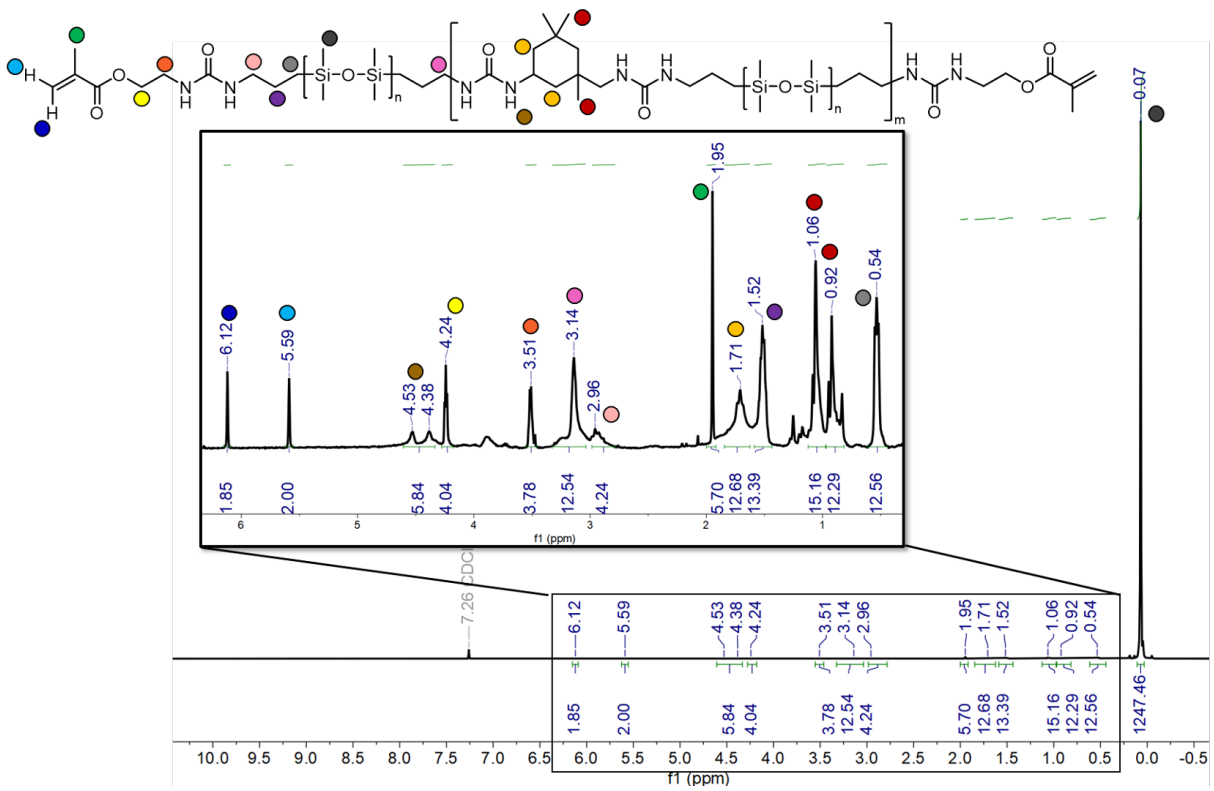
Supplementary Fig. 13 | Compression test of 3D printed blocks of ESS-PEA and commercial photoresins. a, Compressive stress-stretch curves for ESS-PEA (blue) and PEA (grey). **b,** Optical images of FDB, TC85, and ESS-PEA blocks under the compression test (top) and the recovery of their shapes after 30 s (bottom).



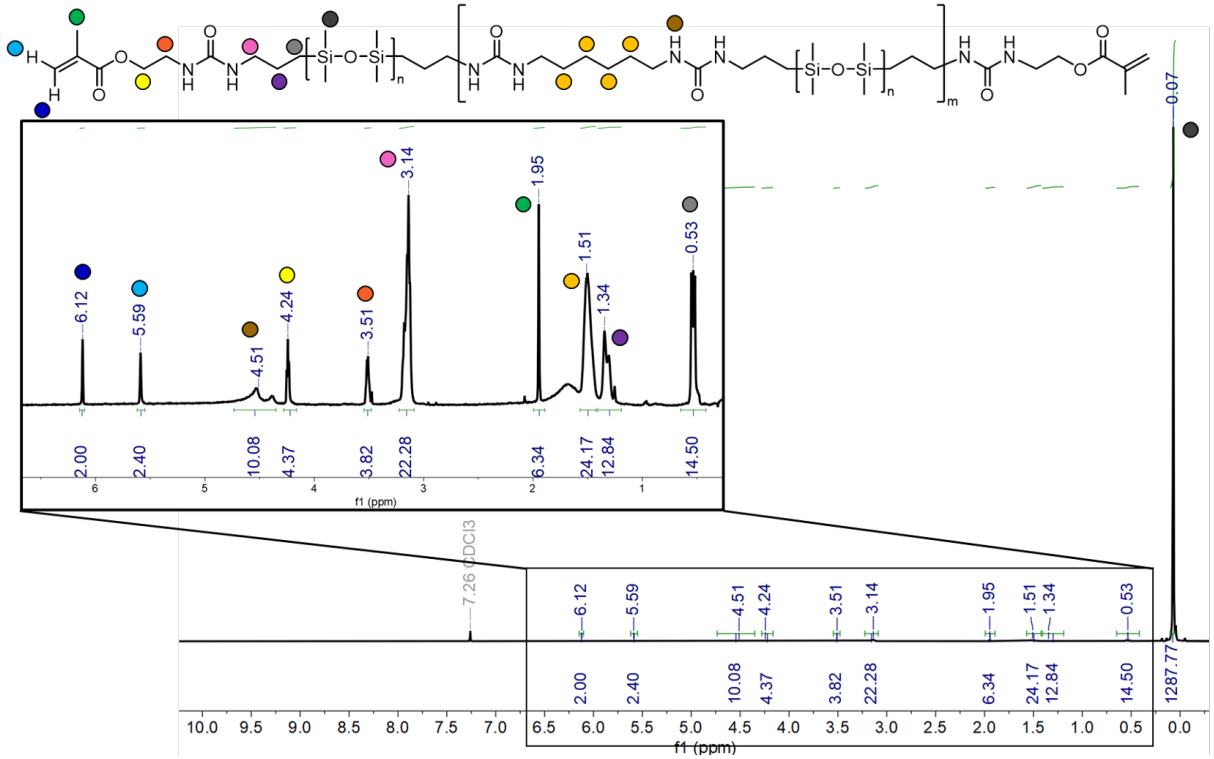
Supplementary Fig. 14 | ^{1}H NMR spectrum (500 MHz) of MPU oligomer measured in THF-*d*8 (*T* = 297 K).



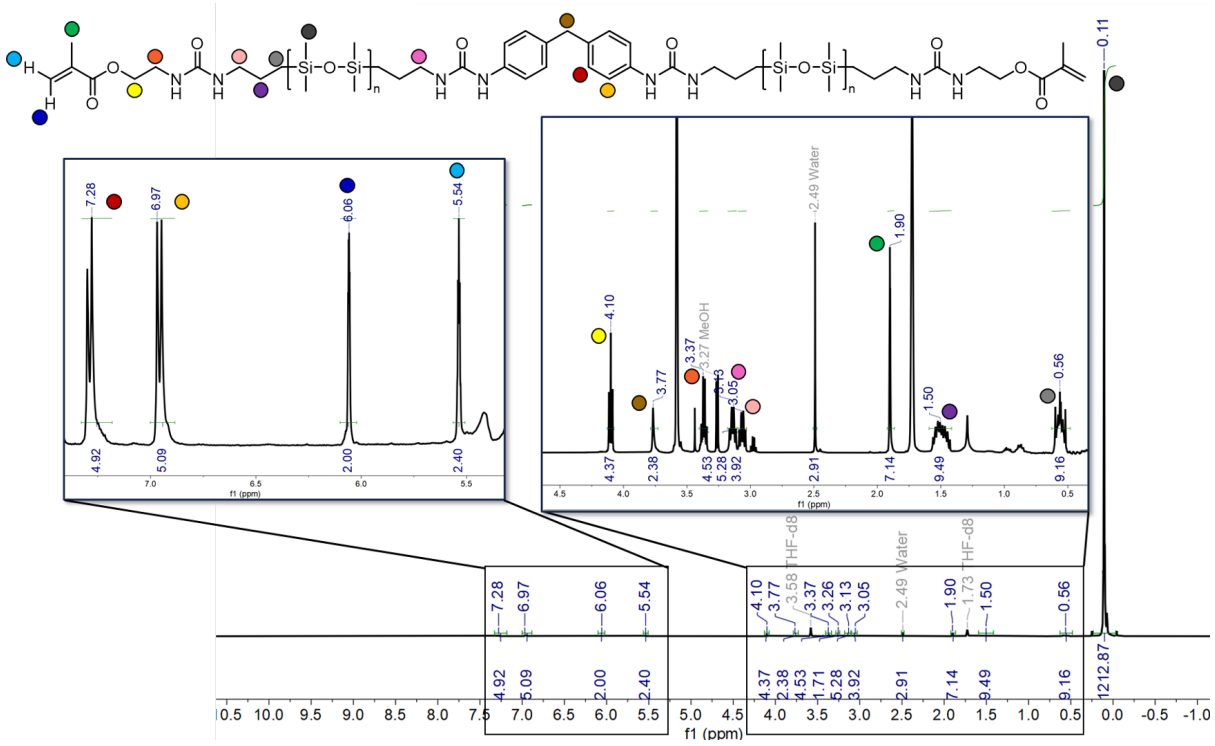
Supplementary Fig. 15 | ^{1}H NMR spectrum (500 MHz) of MPU oligomer without interlink measured in THF-*d*8 (*T* = 297 K).



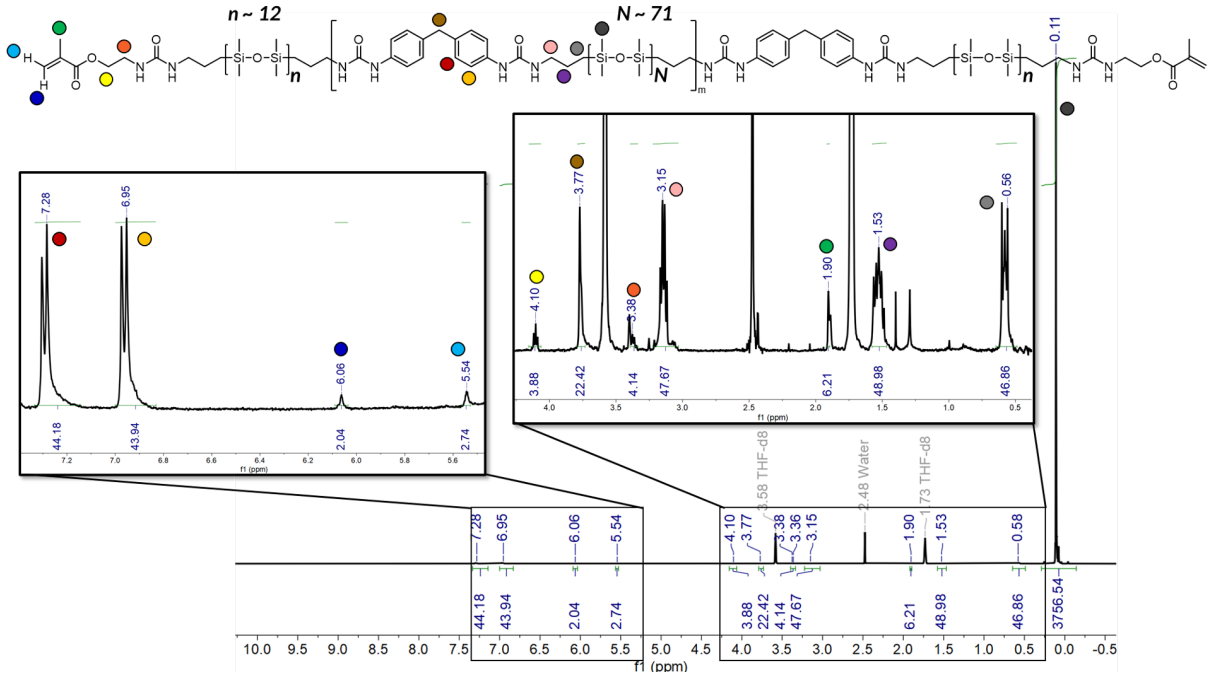
Supplementary Fig. 16 | ^{1}H NMR spectrum (500 MHz) of IU oligomer measured in $CDCl_3$ (T = 297 K).



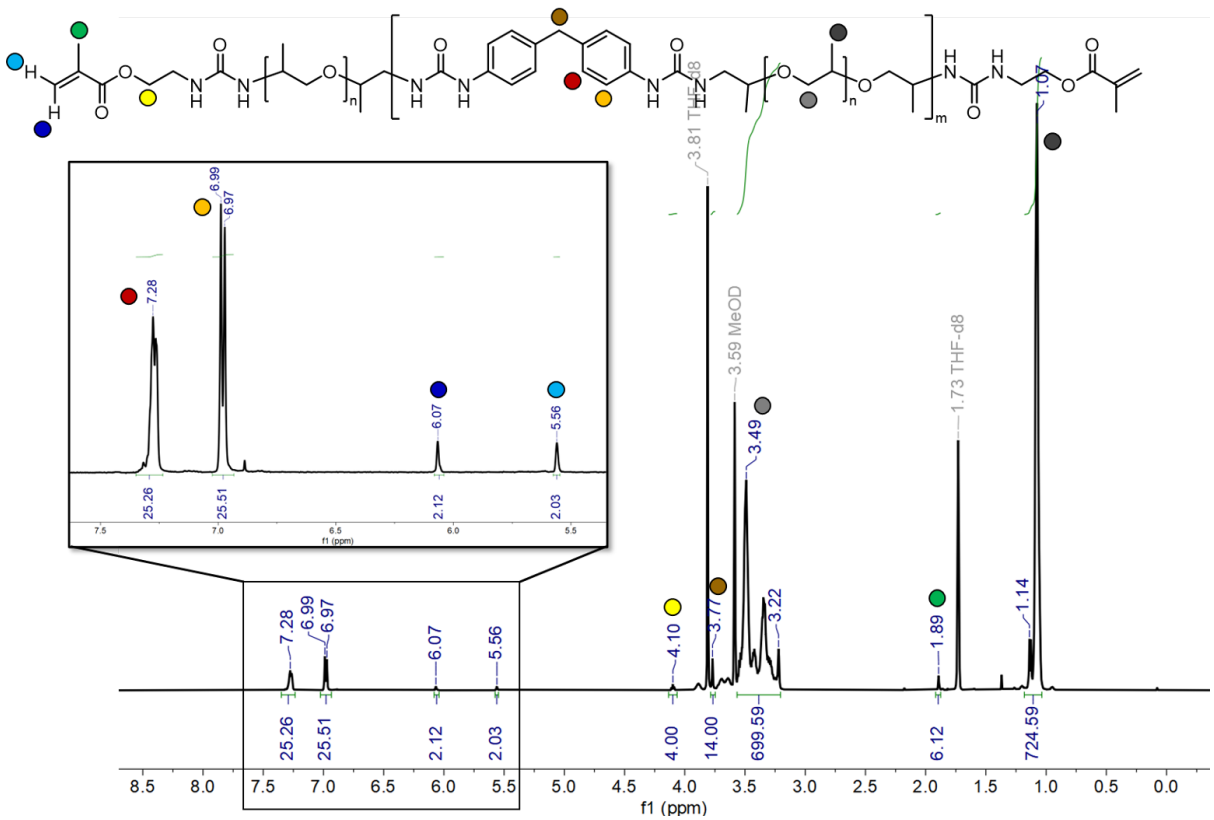
Supplementary Fig. 17 | ^{1}H NMR spectrum (500 MHz) of HU oligomer measured in $CDCl_3$ (T = 297 K).



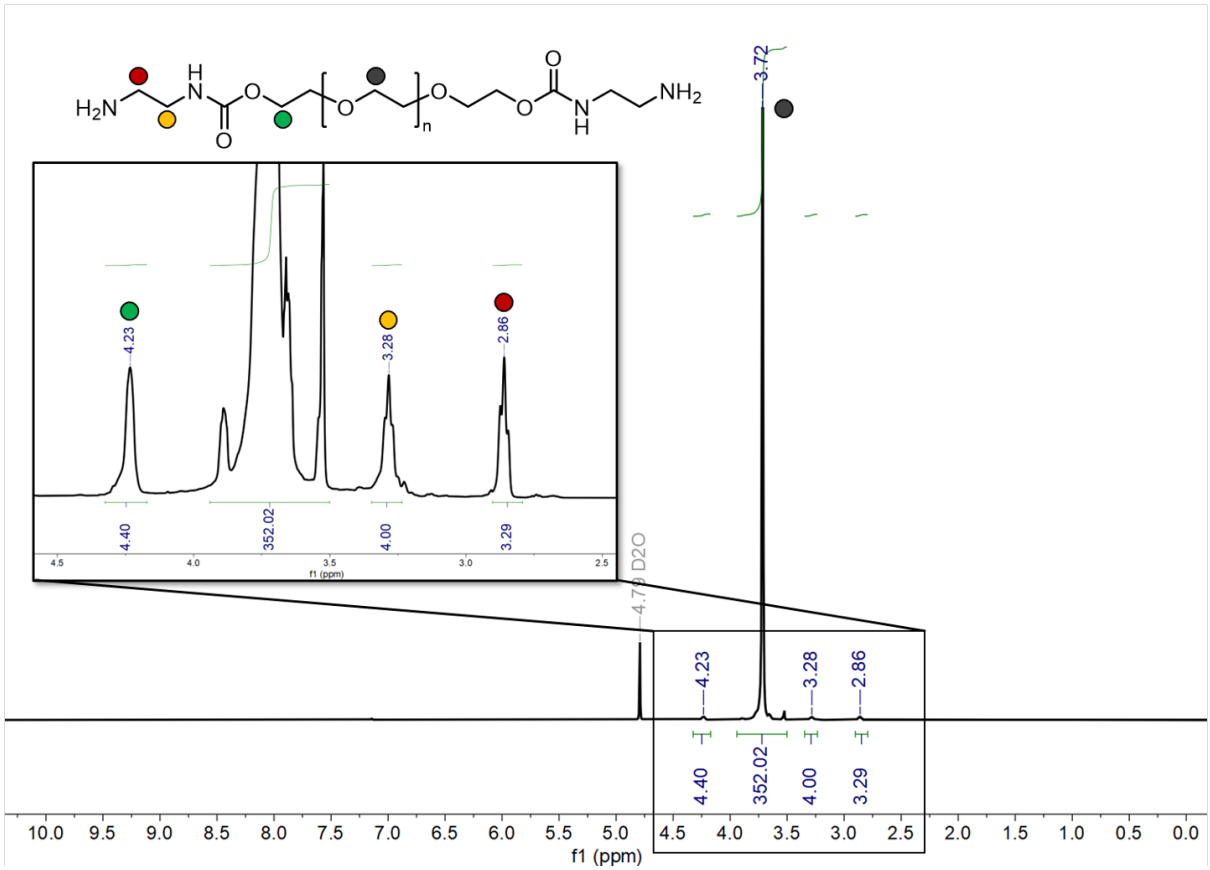
Supplementary Fig. 18 | ^{1}H NMR spectrum (400 MHz) of MPU oligomer with a single sticker measured in THF-*d*8 (*T* = 297 K).



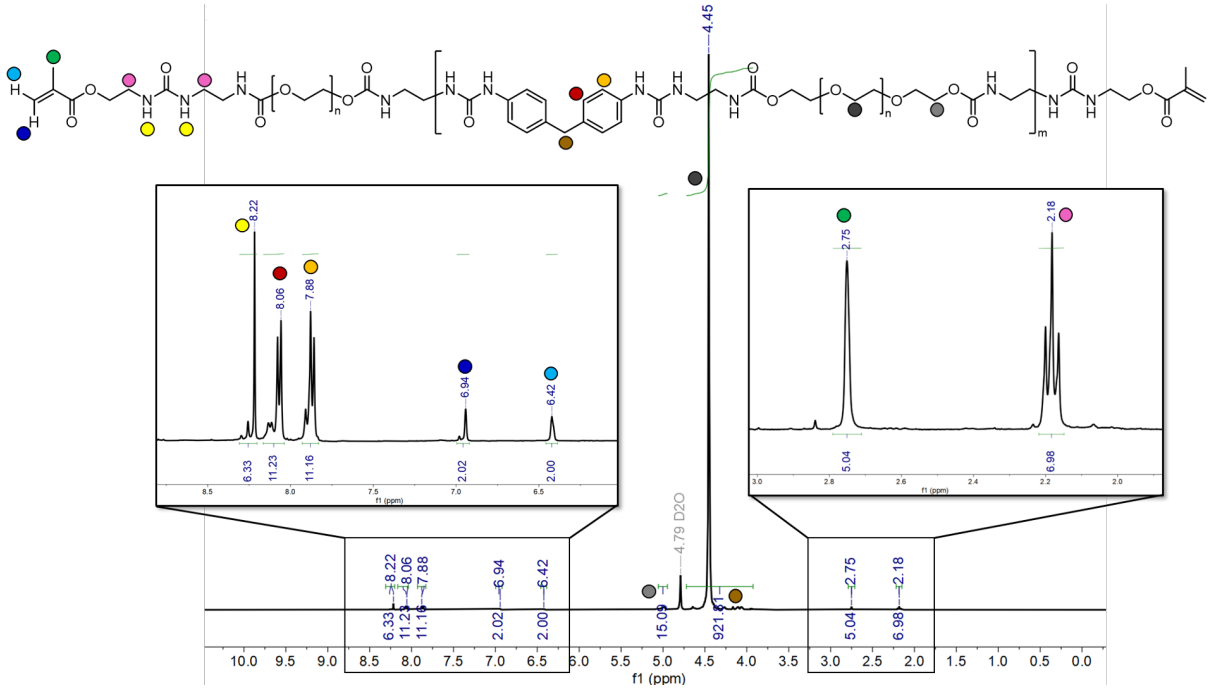
Supplementary Fig. 19 | ^{1}H NMR spectrum (400 MHz) of MPU oligomer without spacer chains measured in THF-*d*8 (*T* = 297 K).



Supplementary Fig. 20 | ^{1}H NMR spectrum (500 MHz) of MPU oligomer with PPG backbone measured in THF-*d*8 : MeOD = 4 : 1 (v/v) (*T* = 297 K).



Supplementary Fig. 21 | ^{1}H NMR spectrum (400 MHz) of PEG-diamine measured in D_2O (T = 297 K).



Supplementary Fig. 22 | ^{1}H NMR spectrum (400 MHz) of MPU oligomer with PEG backbone measured in D_2O (T = 297 K).