Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

3D Printable Non-Isocyanate Polyurethanes with Tunable Material Properties

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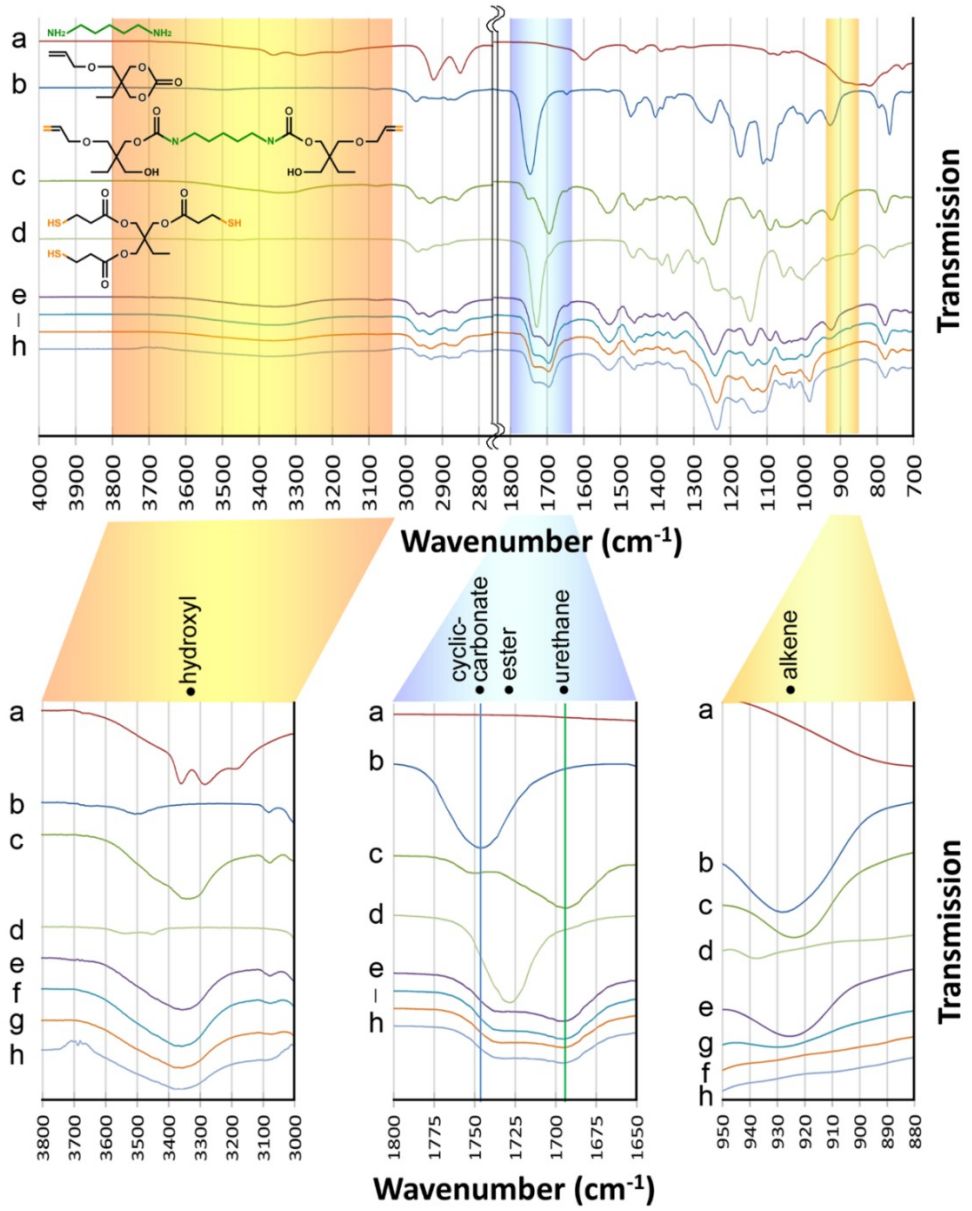
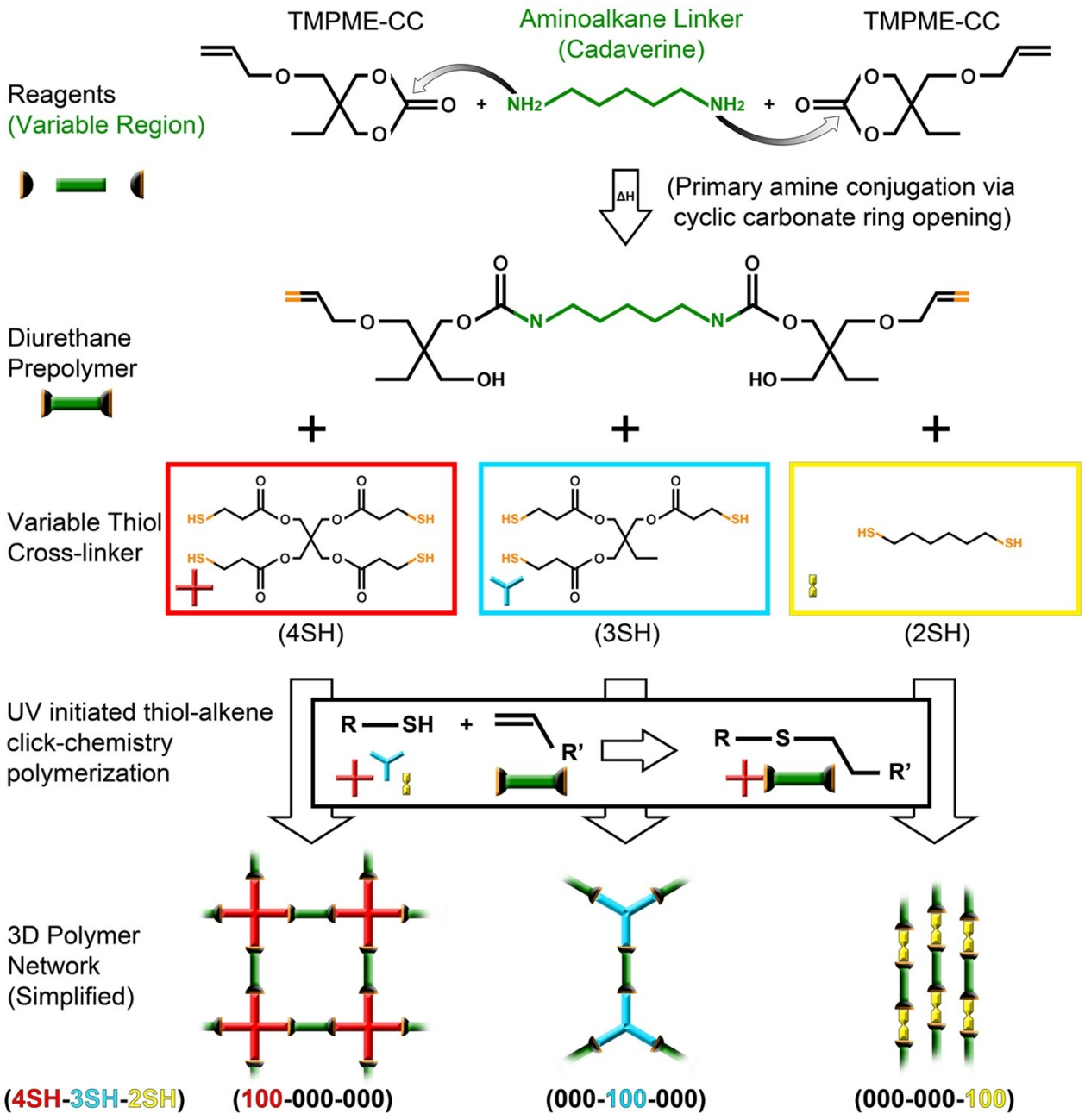
Contents:

FIGURE S1: Continuous FTIR Spectra of Molecular Precursors and Products - Expansion



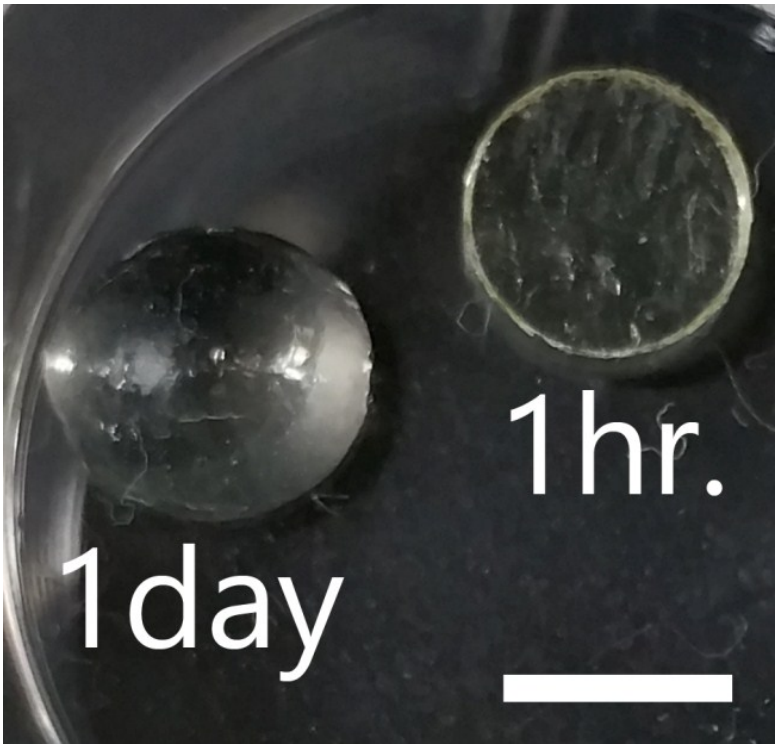
Full FTIR spectra of molecular precursors and products. (a) Cadaverine. (b) TMPMEC [5-allyloxyethyl-5-ethyl-1,3-dioxane-2-one (trimethylolpropane allyl ether–cyclic carbonate)]. (c) Product of heating cadaverine in the presence of TMPMEC. Diallyl urethane product confirmed with replacement of cyclic-carbonate peaks with urethane (O=C-N) and hydroxyl (-OH) peaks. (d) (3SH) = trimethylolpropane tris(3-mercaptopropionate) mixed with the diallyl urethane product (shown in "c"). (e) Mixture of c + d was exposed to 365 nm light for (f) 2.5 min, (g) 5 min, (h) 10.0 min. The peak at 927cm^{-1} indicative of the alkene diminishes with time and shows no difference between (g) and (h). Samples run in triplicate (n=3).

FIGURE S2. Schematic of the NIPU Polymerization System.



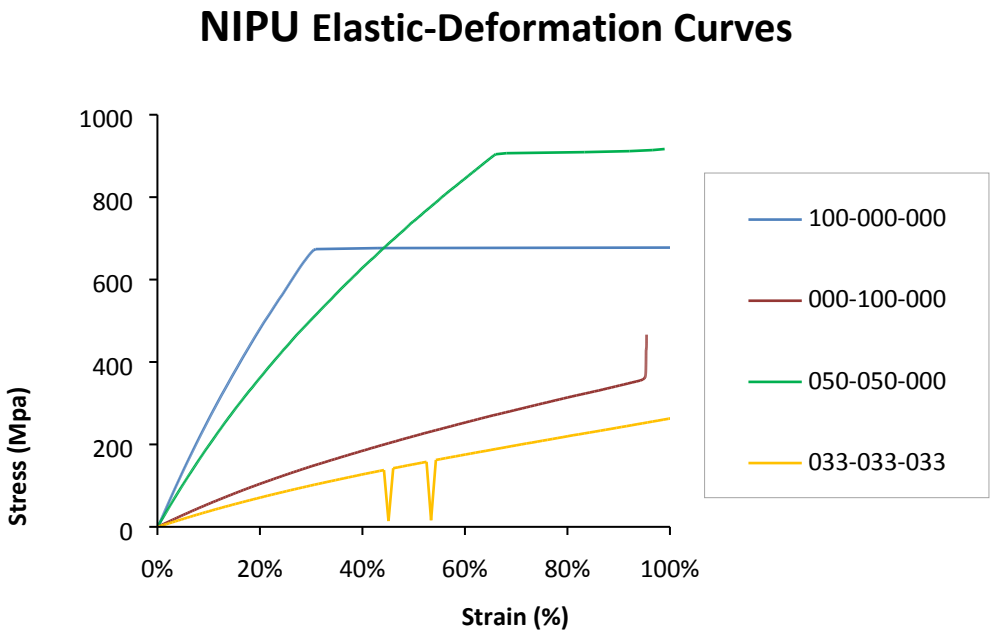
Synthesis of diallyl urethane prepolymer from diamine and TMPME-CC by heating, followed by UV-photoinitiated free radical thiol-ene polymerization with branched variable thiol crosslinkers, to create a 3D polymer network.

FIGURE S3: NIPU Material:0%$_{4SH}$-50%$_{3SH}$-50%$_{2SH}$ Shape Reversion



NIPU Material: 0%$_{4SH}$-50%$_{3SH}$-50%$_{2SH}$ solidified with 5 minutes of UV exposure and cut into 6 mm x 1 mm (D x H) disks, seen at one hour. After 1 day, the disk structure reverted to a drop-like dome appearance. This sample was not mechanically tested, but illustrates a viscous liquid shape deformation over time. (Scale bar = 5mm).

FIGURE S4: NIPU Stress-Strain Curves of Key Mixtures



Stress-strain curves of key NIPU mixtures used. Data curves were used to determine Young's Modulus values for comparing NIPU material property variations (Figure 4). The curves are derived from probe force/displacement curves combined with measurements from the NIPU thin film samples. Format is NIPU: $\%_{4SH}$-$\%_{3SH}$-$\%_{2SH}$.

FIGURE S5: Gel content (%) of (1) NIPU:100%$_{4SH}$, (2) NIPU:100%$_{3SH}$ and (3) NIPU:50%$_{4SH}$-50%$_{3SH}$

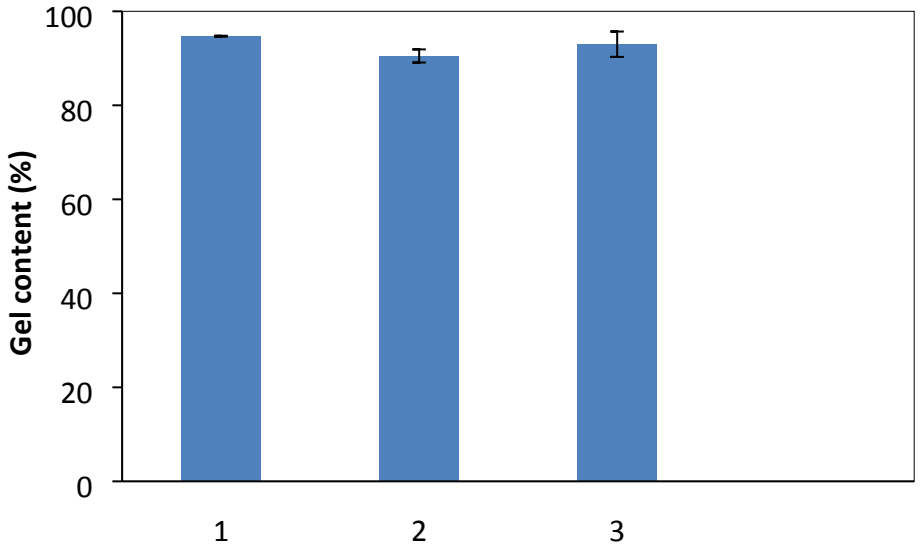


FIGURE S6: (A) Differential scanning calorimetry (DSC) and (B) Thermogravimetric analysis (TGA) for (1) NIPU:100%$_{4SH}$, (2) NIPU:100%$_{3SH}$ and (3) NIPU:50%$_{4SH}$-50%$_{3SH}$.

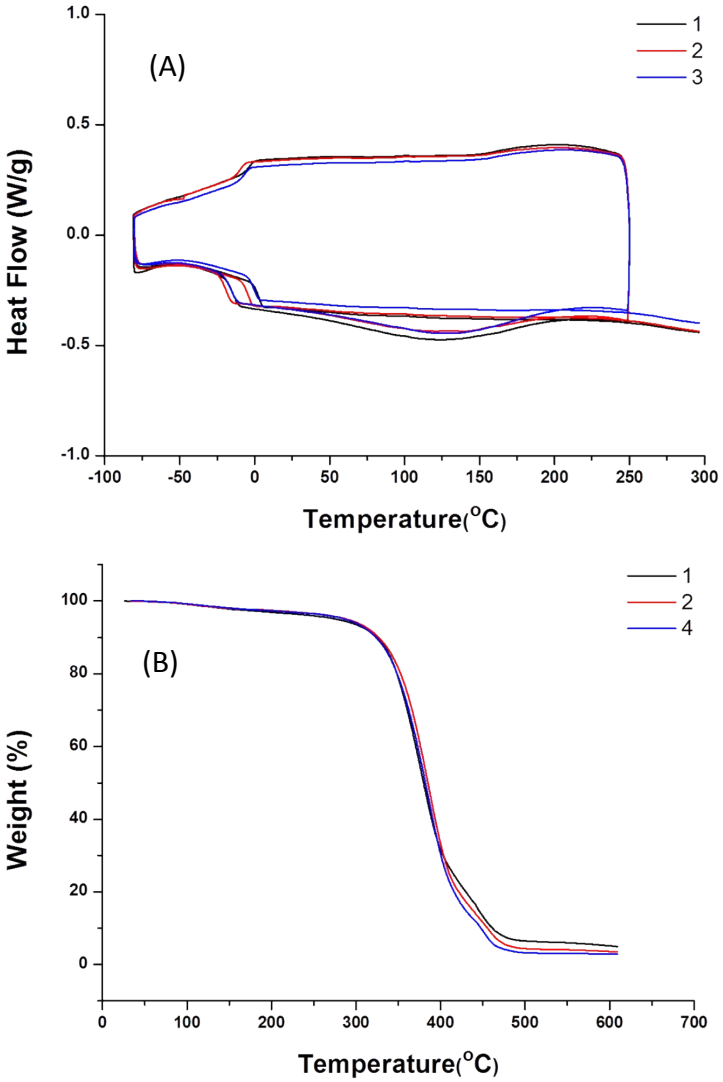
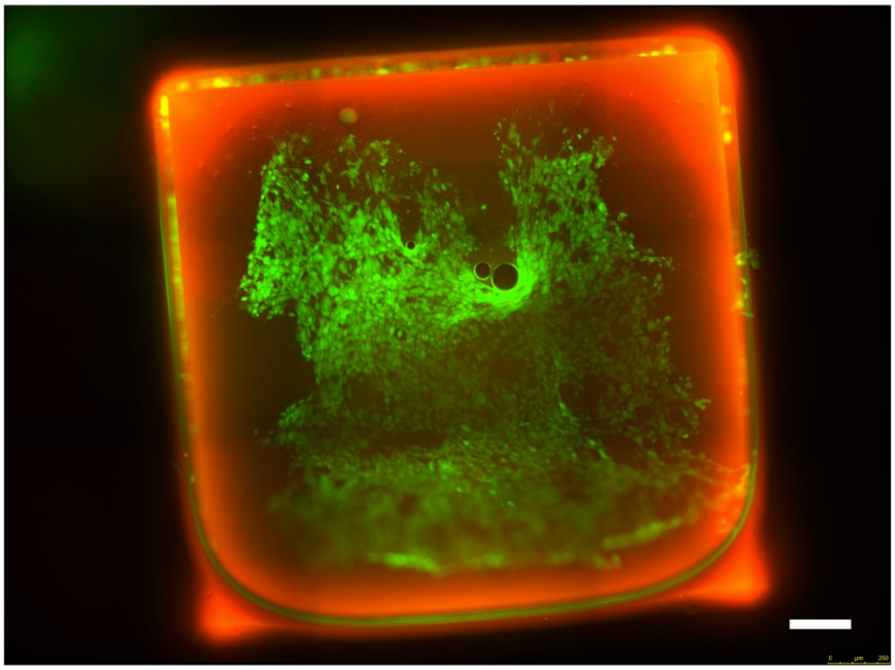


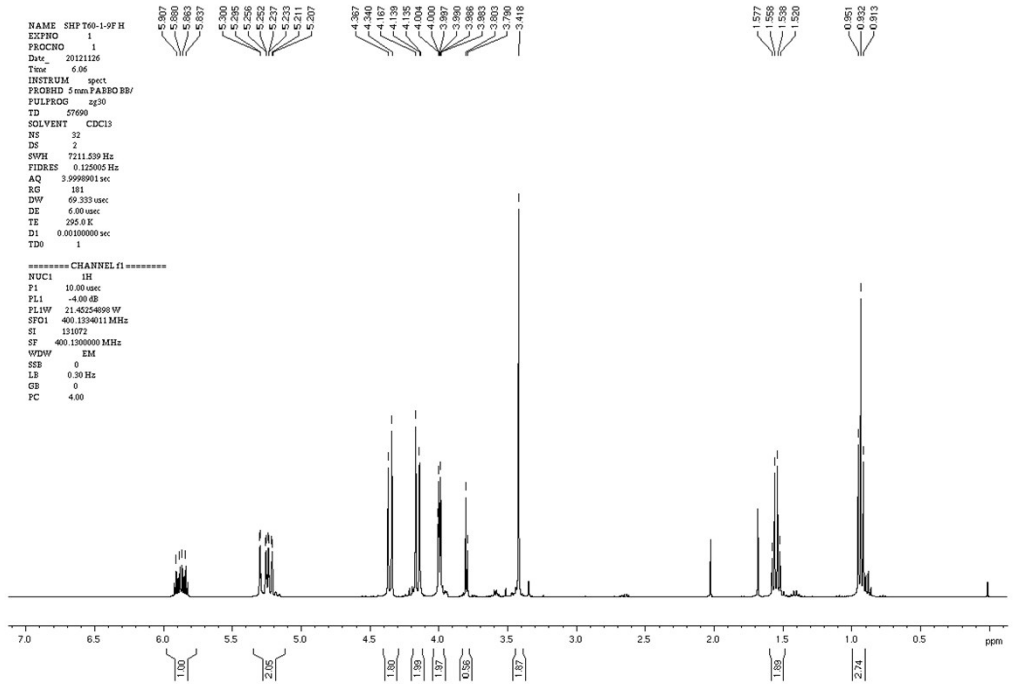
FIGURE S7: Uncoated NIPU Material 100% $_{4SH}$ shows low cell adhesion via bubble displacement and cytocompatability



Cell Live/Dead Assay: Murine C3H C2C12 myoblasts grown on NIPU for 5 days. Green = Calcein AM, Red = Ethidium Bromide. NIPU: 100%$_{4SH}$ were tested (uncoated). Structures were inverted for imaging. Image shows low cell adhesion and cytocompatibility. Bottom of image shows cell sheet falling toward viewer. Air bubbles displace the cell sheet. (Scale bar = 250 μm).

FIGURE S8: (A) ^{1}H- and (B) ^{13}C-NMR (400 MHz, $CDCl_3$) spectrum of 2-(allyloxymethyl)-2-ethyl-trimethylene carbonate (TMPMEC) (S. H. Pyo and R. Hatti-Kaul, *Adv. Synth. Catal.*, 2016, **358**, 834–839)[30].

(A)



(B)