Electronic Supplementary Material (ESI) for Polymer Chemistry.


**Supporting Information**

# Rapidly-cured Isosorbide-based Cross-linked Polycarbonate Elastomers

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## Experimental

### Materials

Isosoribe (98%), allyl chloroformate (97%), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%) and trimethylolpropane tris(3-mercaptopropionate) (TMPTMP, ≥95%) were purchased from Sigma Aldrich. *N*,*N*,*N′*,*N′*-Tetramethylethylenediamine (TMEDA, 99%) was purchased from Alfa Aesar. Anhydrous solvents were purchased from Fisher Scientific and further dried and degassed using a SciMatCo solvent purification system. All other reagents were used as received.

### Characterization

$^{1}H$ and $^{13}C$ NMR spectra were recorded on a Varian 500 spectrometer interfaced to a UNIX computer using Mercury software. The monomer was purified by Medium Pressure Liquid Chromatography (MPLC) using a CombiFlash $R_f$ (Teledyne Isco) (80:20 hexanes:ethylacetate). Chemical shifts were referenced to the solvent nuclei resonances. IR spectra were obtained on a Shimadzu IR Prestige Attenuated Total Reflectance Fourier-transform Infrared Spectrometer (ATR-FTIR). Spectra were analysed using IRsolution software package (Shimadzu). Raman Spectroscopy was recorded using the B&W Tek iRaman system operating at 785 nm over the range of 700 to 3400 $cm^{-1}$ and were analyzed by BW Spec 3.27 software.

Differential scanning calorimetric (DSC) studies were performed on a DSC822$^{e}$ (Mettler-Toledo), with a heating rate of 10 ºC/min to determine the glass transition ($T_g$) of the thermosets. The $T_g$ was taken as the midpoint of the inflection tangent upon the third heating scan. Thermogravimetric analysis was performed under Ar atmosphere using a model TGA/DSC 1 Star$^{e}$ system (Mettler-Toledo), with a heating rate of 10 ºC/min measured at the onset. Measurements were analyzed using Star$^{e}$ software version 10.00d (Mettler-Toledo).

### Static water contact angle measurements

Contact angles were measured as static contact angles using the sessile drop technique with an Attension Theta optical tensiometer (Biolin Scientific). Drops were fitted with a Young–Laplace formula to calculate the static contact angle in the Theta software (Biolin Scientific). Each measurement was performed five times with reported value being the average of these runs and was taken 3 seconds from the time that the drop was placed on the thermoset. After each run, the sample was picked up by a set of tongs and the surface was dried with a Kimwipe.

### Mechanical Measurements

Dynamic mechanical analysis (DMA) was performed on a Mettler Toledo TT-DMA system. Samples were *ca.* 7 x 5 x 0.6 mm. DMA data were obtained from Triton Laboratory software and exported to Origin Pro 9.0 for analysis. Dynamic mechanical analysis (Mettler-Toledo TT-DMA, Columbus, OH) was measured in tension via thermal scan (3 °/min) from -80 to 120 °C, under a dynamic force of 1 N, a static/dynamic force ratio of 1.5, and a frequency of 1 Hz.

To determine toughness values, ultimate tensile strengths, and failure strains, tensile testing experiments were conducted to failure on ASTM D638 type IV, with a thickness of 0.60 mm ± 0.05 mm. dog bone samples (n = 5) using a dual-column Instron model 5965 tensile tester with a 500 N load cell, 1000 N high temperature pneumatic grips, and a temperature chamber thermally controlled by forced convection heating. Tests were run at a speed of 5 mm/min to obtain elastic modulus, tensile strength and elongation at break at room temperature. The dog bone samples were cut with a 40 W Gravograph LS100 $CO_2$ laser and edges were smoothed with 180 grit sandpaper. Pneumatic grips were used to affix the sample in the testing frame at a compressed air pressure of 50 psi. Each measurement was repeated with 5 test specimens minimum, with each sample examined after testing to ensure the break occurred in the neck segment.

### Cell culture

MC3T3 cells were purchased from the American Type Culture Collection (ATCC, Manassas, VA) and subcultured according to ATCC protocol. Briefly, cells were cultured in MEM-alpha medium supplemented with 10% fetal bovine serum (Sigma-Aldrich, St. Louis, MO) and 1% antibiotic (Lonza, Walkersville, MD). Confluent cells were treated with Trypsin:EDTA (Sigma-Aldrich, St. Louis, MO) and counted with a Countess II cell counter (ThermoFisher Scientific, Waltham, MA). Prior to plating cells on glass-bottomed cell culture dishes and incubated at 37 °C with 5 % $CO_2$. Polymer-coated dishes were sterilized under UV in the biosafety cabinet and washed with sterile DPBS (Life Technologies, Carlsbad, CA) before plating cells on them.

### Fixation and immunofluorescence

Cells were fixed after 24hr from cell plating with 2% paraformaldehyde (Electron microscopy sciences, Hatfield, PA) and co-stained with Phalloidin-Alexa488 (Life Technologies, Carlsbad, CA) and anti-vinculin antibody (Sigma-Aldrich, St. Louis, MO) followed by secondary antibody conjugated with Alexa 647 (Life Technologies, Carlsbad, CA).

## Confocal imaging

Fluorescence images were acquired with a laser scanning confocal microscope (Olympus, Japan) with default excitation and emission filter settings for each fluorophore. Overall cell population was identified from large filter view with 10x objective (image size 1271.81 x 1271.81 µm). Details of cell morphology were investigated from the images acquired with 20x objective with 2x zoom (image size 317.44 x 317.44 µm).

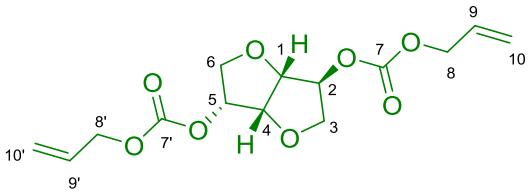
## Cytotoxicity assays

IDA-*co*-TMPTMP film polymer was plated with MC3T3-E1 mouse preosteoblast cells (5 x 103 cells/well) in 96-well plate in MEMα medium (10% fetal bovine serum and 1% penicillin/streptomycin). Cells with films were incubated at 37 □C in a humidified atmosphere containing 5% $CO_2$ for 72 h. MTS combined reagent (20 µL) was added to each well (Cell Titer 96® Aqueous Non-Radioactive Cell Proliferation Assay, Promega Co., Madison, WI). The cells were incubated with the reagent for 2 h at 37 °C in a humidified atmosphere containing 5% $CO_2$ protected from light. Absorbance was measured at 490 nm using SpectraMax M5 (Molecular Devices Co., Sunnyvale, CA). The cell viability was calculated based on the relative absorbance to the control-untreated cells.

## Synthetic Procedure

Monomer Synthesis, isosorbide dialloc, IDA. In a 500-mL round bottom flask, oven dried (100 °C for ~1 h) under $N_2$ (degassing by vacuuming and back filling with $N_2$ 4 times at room temperature) and in an ice bath above a stir plate (c.a. 500 rpm) isosorbide (10.0 g, 68.4 mmol), dry $CH_2Cl_2$ (250 mL) and TMEDA (24.0 mL, 150 mmol) were combined and cooled to 0 °C. Allyl chloroformate (25.0 mL, 235 mmol) was added via syringe pump at a rate of 20 mL/h. The reaction was allowed to warm to room temperature and proceed over the following 24 h. The solution was washed with water (250 mL x 3), 0.5 M HCl (250 mL x 2), saturated solution of sodium bicarbonate (250 mL x 2) and brine (250 mL x 2). The organic phase was dried over anhydrous $MgSO_4$ and concentrated in vacuo to a slightly viscous pale yellow oil. The crude oil was purified by an automatic flash column chromatography system eluded with a gradient of ethyl acetate in hexanes (0 to 20%) and concentrated to afford a clear oil (18.5 g, 86.1% yield, isosorbide dialloc, IDA). $R_f$ = 0.7 $^1$H-NMR (500 MHz, $CDCl_3$): δ 5.99-5.91 (m, 2H, H9, H9'), 5.39 (m, 2H, H10-trans, H10'-trans), 5.31 (m, 2H, H10-cis, H10'-cis), 5.13 (d, *J* = 3.4 Hz, 1H, H2), 5.10 (app q, *J* = 5.4 Hz, 1H, H5), 4.92 (app t, *J* = 5.2 Hz, 1H, H4), 4.68-4.65 (m, 4H, H8, H8'), 4.57 (app d, *J* = 4.8 Hz, 1H, H1), 4.11 (d, *J* = 11.1 Hz, 1H, H6), 4.05 (dd, *J* = 11.0, 3.4 Hz, 1H, H3'), 3.94-3.92 (m, 2H, H3 and H6'); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 154.3 (C7 or C7'), 154.0 (C7' or C7), 131.30 (C9 or C9'), 131.17 (C9' or C9), 119.3 (C10 or C10'), 119.0 (C10' or C10), 85.9 (C1), 81.3 (C2), 80.9 (C4), 76.8 (C5), 73.2 (C6 or C3), 70.5 (C3 or C6), 68.82 (C8 or C8'), 68.79 (C8' or C8); FTIR (ATR) 3060-2860, 1740, 1650, 1450, 1430, 1370, 1350, 1290, 1240, 1170, 1100, 1050, 1000, 970, 940 $cm^{-1}$; HRMS ($ESI^+$, m/z): $[M+Li]^{+1}$ calculated for $C_{14}H_{18}O_8Li$, 321.1162, found 321.1163.

Thermoset Synthesis, IDA-*co*-TMPTMP. In a vial wrapped in aluminum foil (to protect from undesired UV radiation), IDA (1.26 g, 4.00 mmol) and trimethylolpropane tris(3-mercaptopropionate) (TMPTMP) (1.07 g, 2.67 mmol) were combined in reactive end functionality stoichiometric ratio along with DMPA (0.0236 g, 1 wt%), stirred for 10 minutes over a stir plate, placed on the vortex for 2 minutes then sonicated for 10 minutes. Immediately, the mixture was pipetted between two glass slides in-between three glass cover slips and placed under a 365 nm light for 1 minute. Post cross-linking the sample was placed in a vacuum oven at 100 °C and 125 mm Hg for various times (0, 6, 12, 18 or 24 h) to afford the desired product, IDA-*co*-TMPTMP as a transparent, colorless film. FTIR (ATR) 3050-2810, 1740, 1730, 1250, 1140, 1000, 970 $cm^{-1}$.




IDA

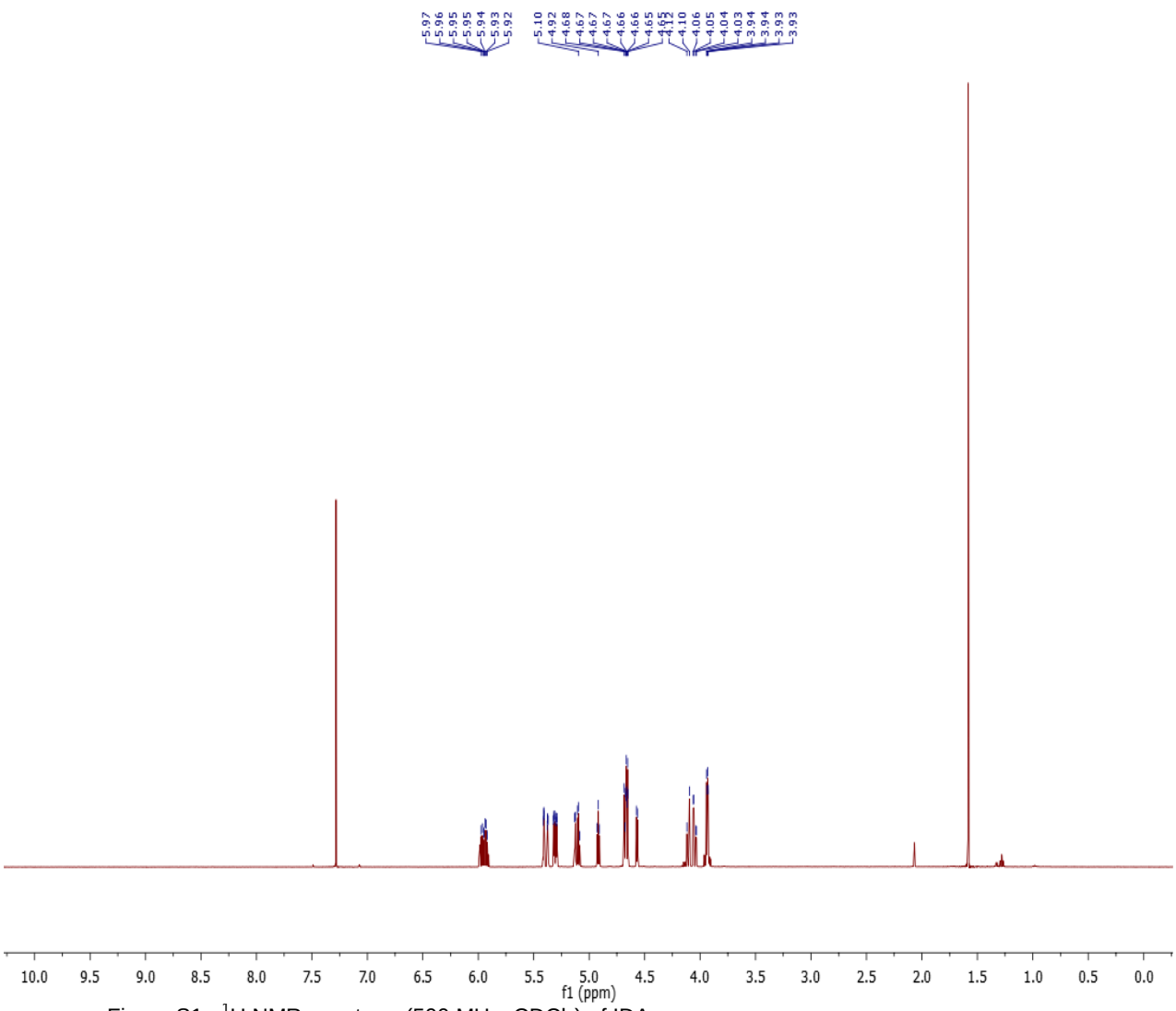



Figure S1: $^{1}H$ NMR spectrum (500 MHz, $CDCl_3$) of IDA.

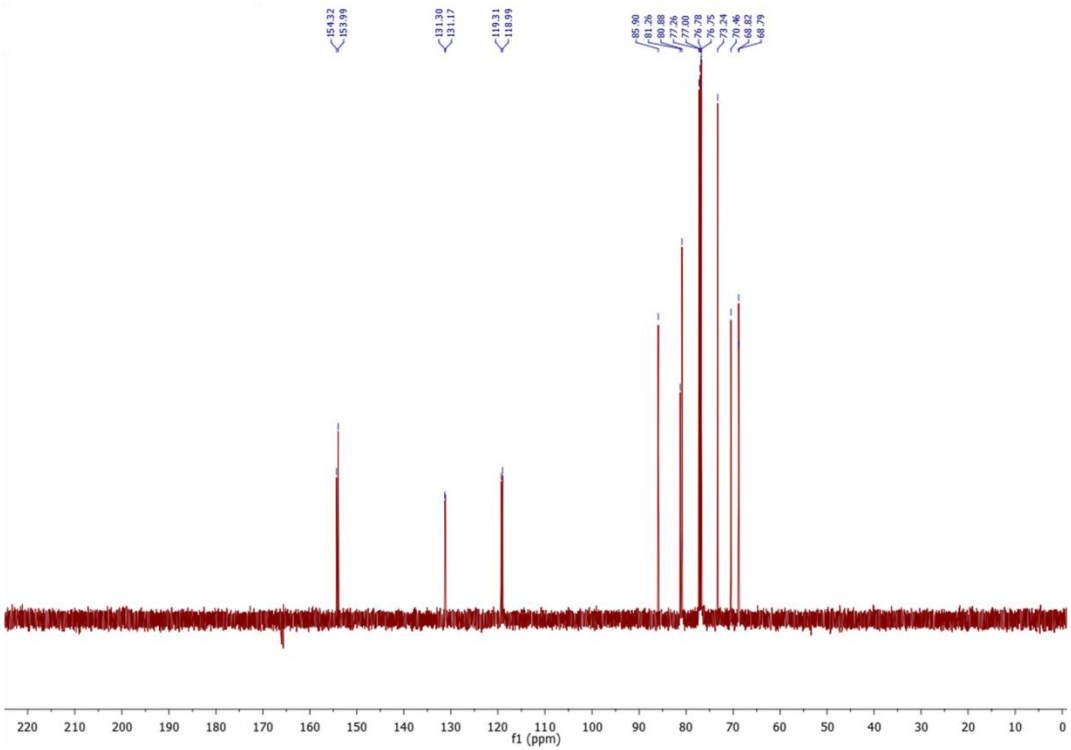



Figure S2: $^{13}C$ NMR spectrum (125 MHz, $CDCl_3$) of IDA.

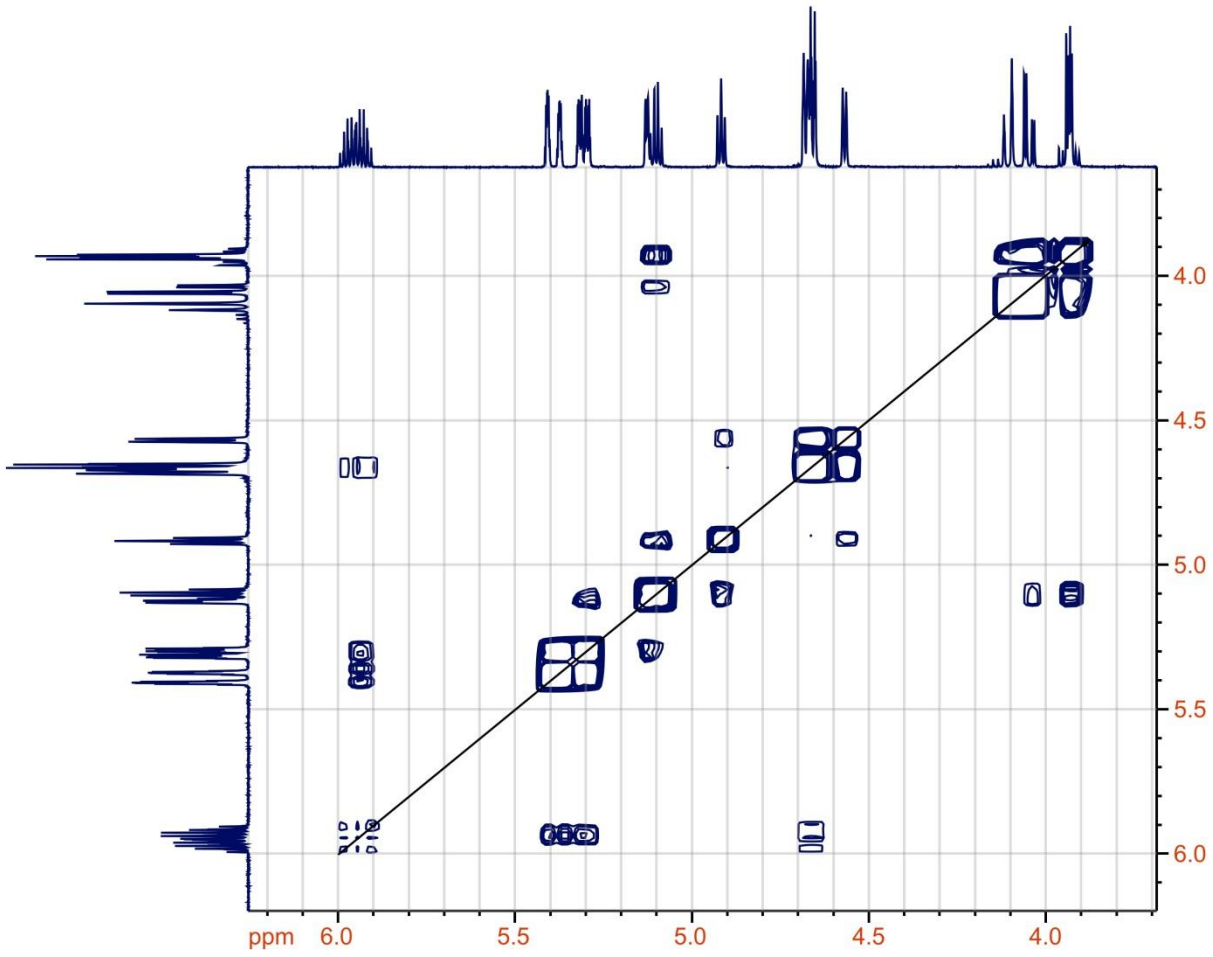
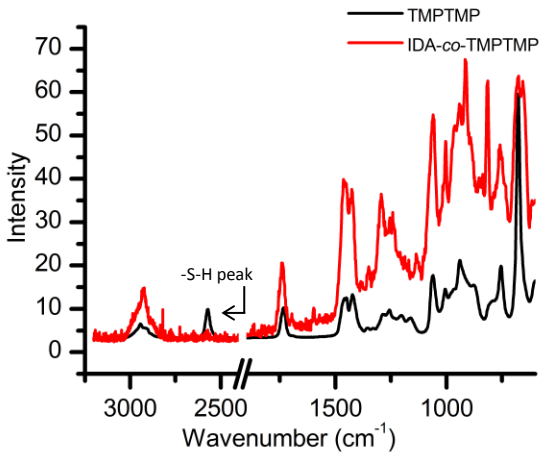



Figure S3: COSY Spectrum for IDA.

A.




B.

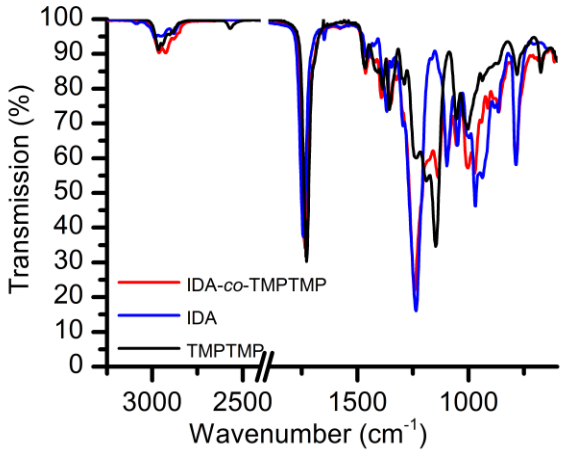



Figure S4: Raman (A) and IR (B) spectra of starting materials and films (IDA-*co*-TMPTMP) with no post-cure.

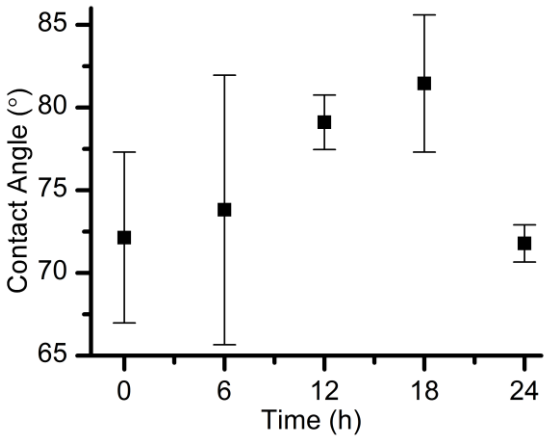
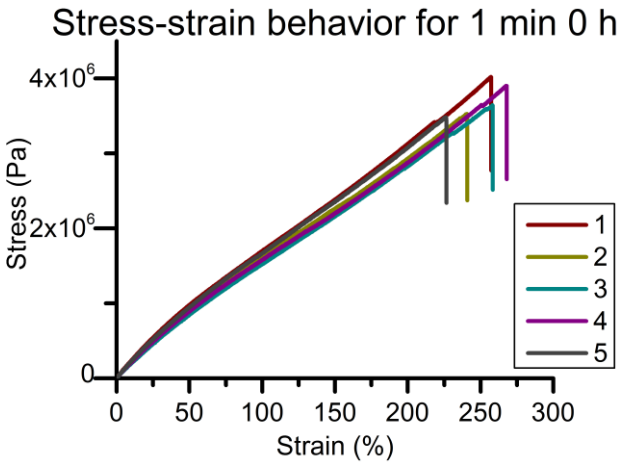



Figure S5: Water contact angle values of films with 1 minute UV curing time and various post-cure heating times.

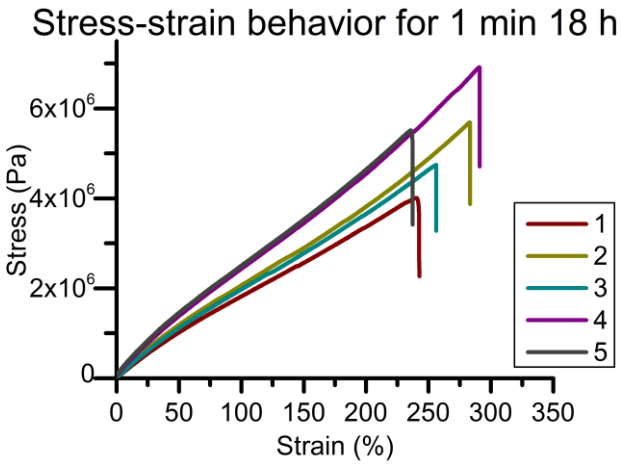
Table S1: Storage moduli at various temperatures.

| *Time* | *E' @ 0 °C (MPa)* | *E' @ 25 °C (MPa)* | *E'@ 50 °C (MPa)* | *E'' 0°C (MPa)* | *E'' @ 50 °C (MPa)* |
|---|---|---|---|---|---|
| 0 h | 1700 | 79 | 6.5 | 120 | 0.6 |
| 6 h | 1700 | 280 | 5.8 | 90 | 1.1 |
| 12 h | 1500 | 430 | 6.2 | 67 | 1.3 |
| 18 h | 2000 | 550 | 6.9 | 130 | 1.1 |
| 24 h | 1700 | 350 | 7.1 | 110 | 1.2 |

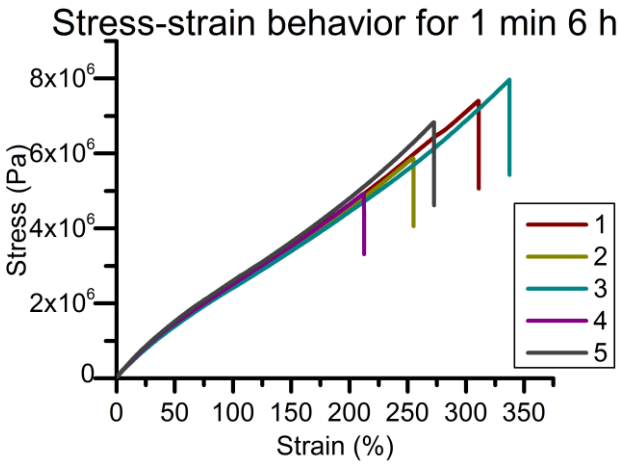
A.



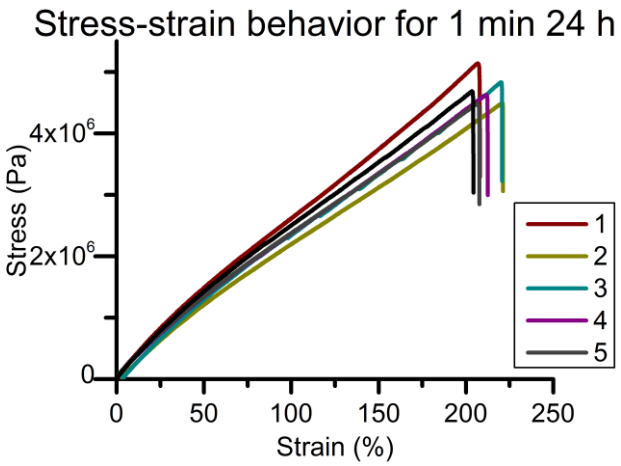

D.




B.




E




C.

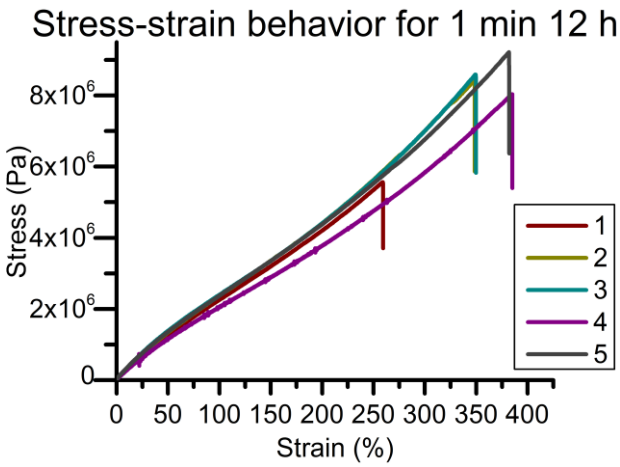



Figure S6: Stress-strain curves for all trials of each IDA-*co*-TMPTMP, following 1 min UV-irradiation and various post-cure heating times, as noted in the headings.

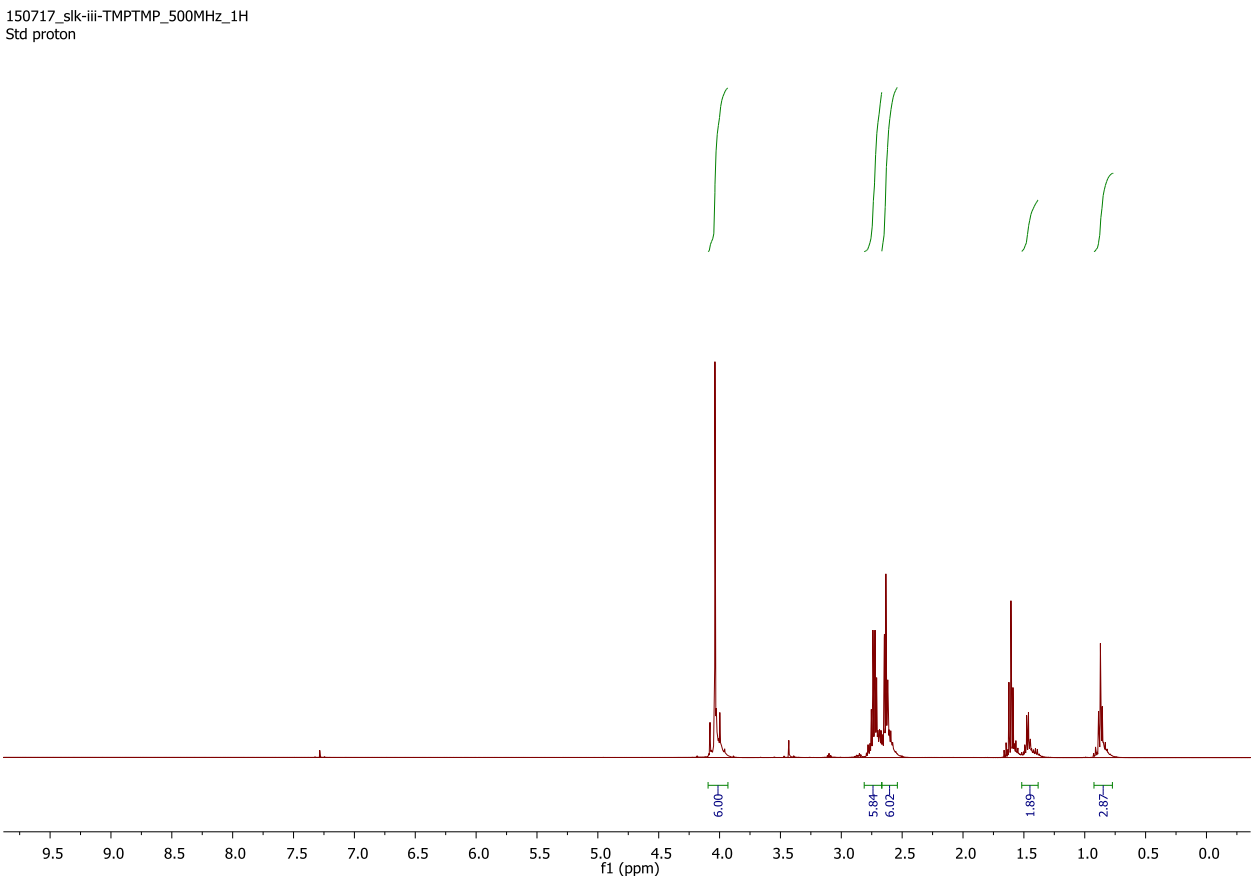



Figure S7: $^{1}$H NMR of the commercially available starting material, TMPTMP. Spectra agrees with literature[1].

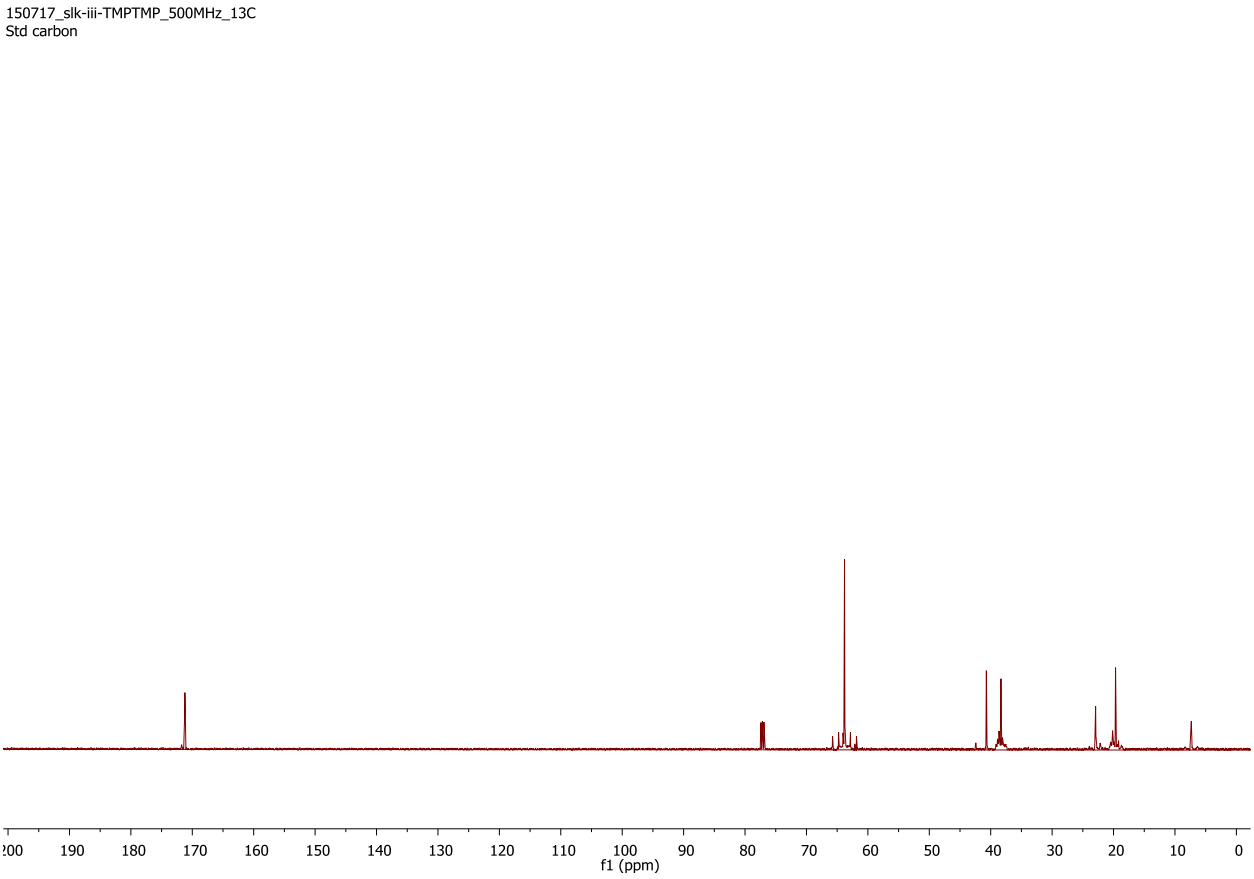



Figure S8: $^{13}C$ NMR of the commercially available starting material, TMPTMP. Spectra agrees with literature[1].

Reference:

[1] Olofsson, K.; Malkoch, M.; Hult, A. Soft hydrogels from tetra-functional PEGs using UV-induced thiol–ene coupling chemistry: a structure-to-property study. *RSC Advances* **2014**, *4* (57), 30118.