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Supplementary Information
Temperable dynamic polymeric glasses as tunable and rebondable adhesives

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Materials and Methods

Materials

Chemicals. All chemicals were used as received unless otherwise noted. *m*-xylenediamine (99%), methyl cyanoacetate (99%),1,3-benzenedimethanol (98%), cyanoacetic acid (99%), *p*-toluenesulfonic acid monohydrate (99%), piperidine (99%), glacial acetic acid, 4-nitrobenzaldehyde (98%), benzaldehyde (99%), 4-anisaldehyde (98%), and pentaerythritol tetreakis(3-mercaptopropionate) (> 95%) were purchased from Sigma Aldrich. All solvents (ACS certified) used for synthesis and network casting were purchased from Fisher Scientific.

Plastics and other items. Double-side coated Kapton film backing material (Line-500FN131) used for melt-pressing was purchased from American Durafilm. Kapton tape (Line S-11730) used in lap shear sample preparation was purchased from Uline. Polyetherimide substrates for lap shear tests were obtained from Army Research Laboratory.

Methods

Nuclear Magnetic Resonance (NMR) Spectroscopy. NMR spectroscopy was performed using a 400-MHz Bruker Avance III HD; 9.4 Tesla NMR.

High-Resolution Mass Spectrometry (HRMS). High-resolution mass spectra were performed on Agilent 6244-Tof-MS using ESI (Electrospray Ionization) at the University of Chicago Mass spectroscopy Core Facility.

Thermogravimetric Analysis (TGA). Thermogravimetric analysis was performed using a TA Instruments Discovery Thermogravimetric Analyzer in Soft Matter Characterization Facility at the University of Chicago. Tests were conducted using a ramp rate of 10 °C/min starting from 40 °C to 600 °C.

Differential Scanning Calorimetry (DSC). DSC was performed using a TA Instruments Discovery 2500 Differential Scanning Calorimeter in the Soft Matter Characterization Facility at the University of Chicago. Samples were loaded into aluminum hermetic pans and lids purchased from TA Instruments and were hermetically sealed. Standard DSC curves in Figure 2a and Figure S16 were collected using a heat-cool-heat cycle (160 °C/-30 °C/160 °C) run a 10 °C/min. DSC data for tempered materials were collected using a cool-heat cycle (0 °C/160 °C) run at 10 °C/min.

Atomic Force Microscopy (AFM). AFM measurements showing dynamic reaction-induced phase separation (DRIPS) were taken using an Asylum Research Cypher ES AFM with BlueDrive in NSF Materials Research Science and Engineering Center (MRSEC). Scans were conducted in UHF-Air mode using a FS-1500-AuD cantilevers with resonant frequencies of 1.5 MHz. Images were collected at a scan rate of 4.88 Hz with a 950 mV set point. Samples were imaged near T_g as measured by DSC and were equilibrated for 15 min before scanning. AFM measurements of indented sample surface for crack length calculation were taken using an Asylum Research Cypher S AFM with BlueDrive in NSF Materials Research Science and Engineering Center (MRSEC).

Fracture toughness samples were scanned at ambient temperature using the same cantilevers and parameters as described before. Images were processed using Gwyddion 2.61 to measure the total length of from sample center to the end of crack.

Shear Rheology. Rheology was performed using a TA instruments ARES-G2 shear rheometer which Forced Convection oven (20 °C – 500 °C) attached to an Air Chiller System (-120 °C – 20 °C) and running TA Trios Software in the Soft Matter Characterization Facility at the University of Chicago. An 8 mm parallel plate was used for all tests. Samples were loaded onto the plates, heat to 110 °C and pressed with an axial compression force of 10 N for 10 minutes before running any tests. Amplitude sweep and frequency sweep were done before dynamic temperature ramp to ensure the experimental parameters were within the material's linear viscoelastic regime (LVR).

Fourier transform infrared spectroscopy (FTIR). FTIR of **3H** and **4H** were taken using a Shimadzu IRTracer-100 FT-IR with single bounce attenuated total reflection ATR diamond. Samples were grinded into powder and were placed directly onto the ATR crystal. The spectra were taken at various temperatures above the sample's glass transition temperatures (T_g) and below the temperature that the sample started to flow. The wavenumber shifts at elevated temperatures were used to determine hydrogen bonding in **4H**.

Raman Spectrometry. Raman spectroscopy was performed using a HORIBA LabRAM HR Evolution Confocal Raman Microscope equipped with a 785 nm laser source and HORIBA Synapse OE-CCD. Melt-pressed samples were placed on glass slides, and the spectra were taken at ambient temperature using 785 nm laser, 50X objective at 600 gr/mm grating, 60 s acquisition time and 8 accumulations. Spectra were baselined using polynomial method and smoothed using LabSpec Raman software. It was shown in previous work that the integration of adduct peak over the integration of adduct + free acceptor peak is directly proportional to the amount of thia-Michal adduct within the material.[1] Therefore, the baselined and smoothed spectra were processed in Origin to fit two Voigt peaks, and the peaks were integrated to calculate the fraction of adduct peak using the following equation:

$$Adduct\ peak\ fraction = \frac{Area\ of\ Adduct\ peak}{Area\ of\ Adduct\ peak + Area\ of\ Free\ Acceptor\ Peak}$$

For plotting, the spectra were normalized to the free acceptor peak (peak on the left) using the following equation so that the normalized intensity of that peak is 1.

$$I' = (I - I_{min,freee\ acceptor\ peak})/(I_{max,free\ acceptor\ peak} - I_{min,free\ acceptor\ peak})$$

Nanoindentation. Nanoindentation experiments were performed using a KLA iNano with an InForce 50 actuator. Frequency sweep tests were done with flat punch indenter, and the samples were scanned through 1-200 Hz with harmonic target load of 40 µN, Poisson's ratio of sample of 0.3, and pre-test compression of 1 µm. Fracture toughness tests were performed using Berkovich indenter with Poisson's ratio of sample of 0.3, target depth of 2000 nm, Hardness and Young's modulus was calculated using the Oliver-Pharr method. Upon indentation, AFM imaging of the indentation surface (**Figure S28**) provided geometric parameters for toughness analysis. Indent size was defined from the tip's contact area during indentation, and the crack length was calculated by subtracting indent length from the total measured length from AFM analysis (**Figure S28**). Fracture toughness was then determined using the following relation for a Berkovich-tip geometry:

$$K_c = \frac{1.076X_v\left(\frac{t}{l}\right)^{1/2}\left(\frac{E}{H}\right)^{2/3}P_{\max}}{c^{3/2}}$$

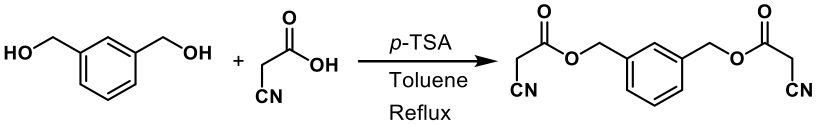
where X_{v} is an empirically fit constant ($X_{\mathrm{v}} = 0.015$), t is the indent size (center to corner), l is the crack length from indent corner to crack tip, c is the crack length from indent center to crack tip, and $P_{\max}$ is load maximum.

Lap shear test with aluminum substrates. Lap shear tests were performed with a Zwick Roell – ZwickLine Z0.5 materials testing machine with a 500 N load cell at ambient conditions. Materials were bonded between aluminum plates; wood chips were glued at gripping sites on both sides of the aluminum plates before sample measurement (details in sample preparation). All experiments were performed at a constant tensile speed of 1 mm/min. Pictures of samples were taken with rulers and sample dimensions were measured through ImageJ.

Lap shear test with polyetherimide substrates. Lap shear tests were performed with an Instron 5640 materials tester equipped with a 50-kN load cell at room temperature with ambient conditions. Samples were bonded between plastic substrates before testing; the area of adhesive samples were controlled by substrate dimension and Kapton tape (details in sample preparation). Sample dimensions (approximately 12 mm x 12.5 mm x 0.17 mm) were measured with caliper before testing. All experiments were performed at a constant tensile speed of 1 mm/min.

Synthesis:

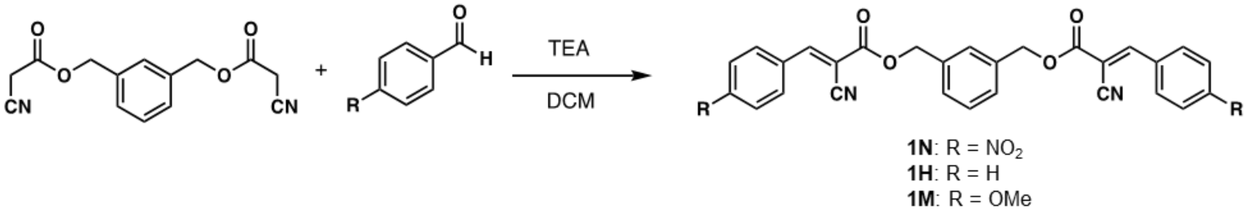
Synthesis of 1,3-phenylenebis(methylene) bis(2-cyanoacetate)



The synthesis of 1,3-phenylenebis(methylene) bis(2-cyanoacetate) was conducted according to a previously reported protocol[2]. 1,3-benzenedimethanol (5.0 g, 0.036 mol) was added to a 250 mL round bottom flask containing cyanoacetic acid (6.77 g, 0.080 mol, 2.2 eq), *p*-toluenesulfonic acid monohydrate (0.1 g, 5 mmol, 0.015 eq), and toluene (100 mL). Dean-stark trap with condenser was attached to the flask and the reaction was refluxed at 135 °C for 16 hr. Upon completion, toluene was removed via rotatory evaporation, and the mixture was dissolved in 100 mL dichloromethane (DCM) and was washed twice with 100 mL water and once with 100 mL brine. The organic phase was dried with magnesium sulfate and DCM was removed via rotatory evaporation. The resulting viscous oil was dried under high vacuum.

NMR: ^{1}H NMR (400 MHz, DMSO) δ 7.45 – 7.37 (m, 4H), 5.21 (s, 4H), 4.10 (s, 4H).

Synthesis of ditopic benzalcyanoacetate (BCA) Michael acceptors (1N, 1H, and 1M)



1,3-phenylenebis(methylene)(2*E*,2'*E*)-bis(2-cyano-3(4-nitrophenyl)acrylate) (1N):

1,3-phenylenebis(methylene) bis(2-cyanoacetate) (2.0 g, 7.3 mmol) was added to a 100 mL round bottom flask with 4-nitrobenzaldehyde (2.44 g, 16.2 mmol, 2.2 eq), triethylamine (TEA) (1.452 g, 14.3 mmol, 2 eq) and DCM (50 mL). The solution was stirred at room temperature for 2 h until yellow-brown precipitation formed. The resulting precipitation was then vacuum filtered, washed twice with 10 mL DCM, and dried under high vacuum (1.5 g, 37 %).

NMR: ^{1}H NMR (400 MHz, DMSO) δ 8.60 (s, 2H), 8.43 – 8.34 (m, 4H), 8.30 – 8.18 (m, 4H), 7.58 (s, 1H), 7.50 (d, *J* = 1.4 Hz, 3H), 5.43 (s, 4H). ^{13}C NMR (101 MHz, DMSO) δ 161.56, 153.52, 149.73, 137.70, 136.10, 132.19, 129.38, 128.55, 127.94, 124.59, 115.34, 106.97, 67.99.

HRMS: HRMS-ESI-APCI mix calcd for C28H18N4O8 [M+Na] 561.1017, found 561.1029.

1,3-phenylehebis(methylene) (2*E*, 2'*E*)-bis(2-cyano-3-phenylacrylate) (1H)

1,3-phenylenebis(methylene) bis(2-cyanoacetate) (3.0 g, 11.0 mmol) was added to a 250 mL round bottom flask with benzaldehyde (2.57 g, 24.2 mmol, 2.2 eq), triethylamine (TEA) (2.23 g, 22.0 mmol, 2 eq) and DCM (100 mL). The solution was stirred under N$_2$ at room temperature for 16 h. DCM was removed via rotatory evaporation, and the crude product was purified using silica gel column chromatography (DCM) (3.2 g, 64 %).

NMR: ^{1}H NMR (400 MHz, DMSO) δ 8.44 (s, 2H), 8.05 (dd, *J* = 7.2, 1.6 Hz, 4H), 7.67 – 7.61 (m, 2H), 7.61 – 7.54 (m, 5H), 7.49 (d, *J* = 1.3 Hz, 3H), 5.40 (s, 4H). ^{13}C NMR (101 MHz, DMSO) δ 162.22, 155.95, 136.24, 133.97, 131.79, 131.35, 129.78, 129.37, 128.48, 127.97, 115.98, 102.86, 67.73.

HRMS: HRMS-ESI-APCI mix calcd for C28H20N2O4 [M+Na] 449.1496, found 449.1499.

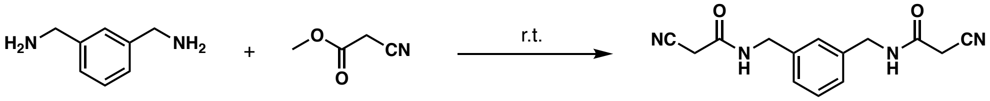
1,3-phenylenebis(methylene) (2E, 2'E)-bis(2-cyano-3-(4-methoxyphenyl) acrylate) (1M)

1,3-phenylenebis(methylene) bis(2-cyanoacetate) (3.0 g, 11.0 mmol) was added to a 250 mL round bottom flask with *p*-anisaldehyde (3.30 g, 24.2 mmol, 2.2 eq), triethylamine (TEA) (2.23 g, 22.0 mmol, 2 eq) and DCM (100 mL). The solution was stirred under N$_2$ at room temperature for 16 h. DCM was removed via rotatory evaporation, and the crude product was purified using silica gel column chromatography (50:1 DCM:EtOAc) (2.86 g, 51%).

NMR: ^{1}H NMR (400 MHz, DMSO) δ 8.35 (s, 2H), 8.14 – 8.03 (m, 4H), 7.53 (d, *J* = 2.0 Hz, 1H), 7.47 (d, *J* = 1.4 Hz, 3H), 7.19 – 7.10 (m, 4H), 5.38 (s, 4H), 3.87 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 164.13, 162.80, 155.33, 136.42, 134.11, 129.34, 128.33, 127.77, 124.42, 116.64, 115.46, 98.76, 67.44, 56.25.

HRMS: HRMS-ESI-APCI mix calcd for C30H24N2O6 [M+Na] 531.1527, found 531.1496.

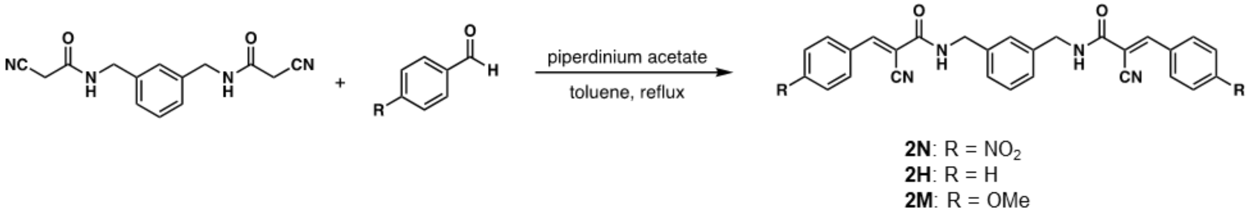
Synthesis of *N,N'*-(1,3-phenylenebis(methylene))bis(2-cyanoacetamide)



m-xylylenediamine (13.6 g, 0.10 mol) was mixed and stirred with methyl cyanoacetate (21.76 g, 0.22 mol, 2.2 eq) in a 250 round bottom flask at room temperature until white crystals formed. The crude product was washed with ethanol for three times and was dried under high vacuum. (37.28 g, 62.8%)

NMR: ^{1}H NMR (500 MHz, DMSO) δ 8.73 (t, *J* = 5.9 Hz, 2H), 7.38 – 7.26 (m, 1H), 7.17 (d, *J* = 5.7 Hz, 3H), 4.28 (d, *J* = 5.8 Hz, 4H), 3.70 (d, *J* = 1.3 Hz, 4H).

Synthesis of ditopic benzalcyanoacetamide (BCAm) Michael acceptors (2N, 2H, and 2M)



(2*E*,2'*E*)-*N*,*N*'-(1,3-phenylenebis(methylene)) bis(2-cyano-3-(4-nitrophenyl)acrylamide) (2N)
N,N'-(1,3-phenylenebis(methylene))bis(2-cyanoacetamide) (4 g, 14.8 mmol) was added to a 250 mL round bottom flask with 4-nitrobenzaldehyde (4.93 g, 32.6 mmol, 2.2 eq), piperidinium acetate (0.1 g) toluene (55 mL), and dimethylformamide (DMF) (45 mL). Dean-stark trap with condenser was attached to the flask and the solution was stirred under N_2 for 10 min before running at reflux (135 °C) for 16 hr. Upon completion, solvents were removed via rotatory evaporation, and the crude product was washed with methanol thrice and dried under high vacuum (3.88 g, 48.9%).

NMR: ^{1}H NMR (400 MHz, DMSO) δ 9.19 (t, *J* = 5.9 Hz, 2H), 8.33 (d, *J* = 8.5 Hz, 6H), 8.11 (d, *J* = 8.6 Hz, 4H), 7.33 (dd, *J* = 9.1, 2.3 Hz, 2H), 7.29 – 7.20 (m, 2H), 4.47 (d, *J* = 6.0 Hz, 4H). ^{13}C NMR (101 MHz, DMSO) δ 160.88, 149.16, 148.84, 139.29, 138.40, 131.44, 128.86, 126.63, 124.60, 124.55, 116.05, 110.52, 43.64.

HRMS: HRMS-ESI-APCI mix calcd for C28H20N6O6 [M+H] 537.1517, found 537.1554.

(2*E*,2'*E*)-*N*,*N*'-(1,3-phenylenebis(methylene)) bis(2-cyano-3-phenylacrylamide) (2H) *N,N'*-(1,3-phenylenebis(methylene))bis(2-cyanoacetamide) (4 g, 14.8 mmol) was added to a 250 mL round bottom flask with benzaldehyde (3.46 g, 32.6 mmol, 2.2 eq), piperidinium acetate (0.1 g) toluene (55 mL), and dimethylformamide (DMF) (35 mL). Dean-stark trap with condenser was attached to the flask and the solution was stirred under N_2 for 10 min before running at reflux (135 °C) for 16 hr. Upon completion, solvents were removed via rotatory evaporation. The resulting yellow oil was crystallized in water, and the crude product was washed with methanol thrice and dried under high vacuum (3.95 g, 59.8%).

NMR: ^{1}H NMR (400 MHz, DMSO) δ 9.07 (t, *J* = 5.9 Hz, 2H), 8.23 (s, 2H), 7.99 – 7.88 (m, 4H), 7.64 – 7.52 (m, 6H), 7.39 – 7.29 (m, 2H), 7.29 – 7.21 (m, 2H), 4.46 (d, *J* = 5.9 Hz, 4H). ^{13}C NMR (101 MHz, DMSO) δ 161.52, 151.23, 139.49, 132.81, 132.38, 130.51, 129.68, 128.84, 126.78, 126.59, 116.81, 106.74, 43.63.

HRMS: HRMS-ESI-APCI mix calcd for C18H22N4O2 [M+H] 447.1816, found 447.1822.

(2E,2'E)-N,N'-(1,3-phenylenebis(methylene)) bis(2-cyano-3-(4-methoxyphenyl)acrylamide) (2M) *N,N'*-(1,3-phenylenebis(methylene))bis(2-cyanoacetamide) (4 g, 14.8 mmol) was added to a 250 mL round bottom flask with *p*-anisaldehyde (4.44 g, 32.6 mmol, 2.2 eq), piperidinium acetate (0.1 g), toluene (60 mL), and DMF (50 mL). Dean-stark trap with condenser was attached to the flask and the solution was stirred under N_2 for 10 min before running at reflux (135 °C) for 16 hr. Upon completion, solvents were removed via rotatory evaporation, and the crude product was washed with methanol thrice and dried under high vacuum (4.97 g, 66.3%).

NMR: ^{1}H NMR (400 MHz, DMSO) δ 8.92 (t, J = 6.0 Hz, 2H), 8.14 (s, 2H), 7.95 (d, J = 8.6 Hz, 4H), 7.36 – 7.27 (m, 2H), 7.27 – 7.19 (m, 2H), 7.10 (d, J = 8.7 Hz, 4H), 4.44 (d, J = 5.9 Hz, 4H), 3.85 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 163.07, 161.91, 150.74, 139.63, 133.01, 132.96, 128.77, 126.60, 126.47, 124.87, 117.42, 115.29, 115.24, 102.93, 56.06, 43.56.

HRMS: HRMS-ESI-APCI mix calcd for C30H26N4O4 [M+H] 507.2027, found 507.2007.

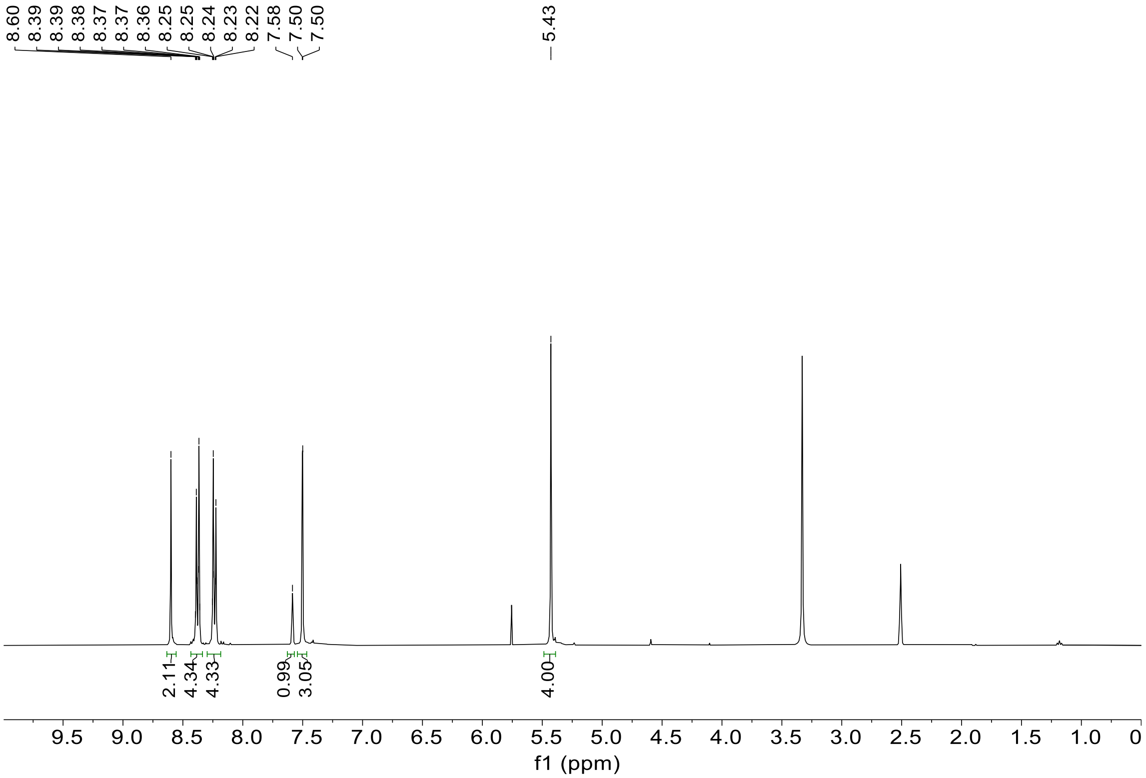


Figure **S1**. ^{1}H NMR (400 MHz) of **1N** in DMSO-d^6.

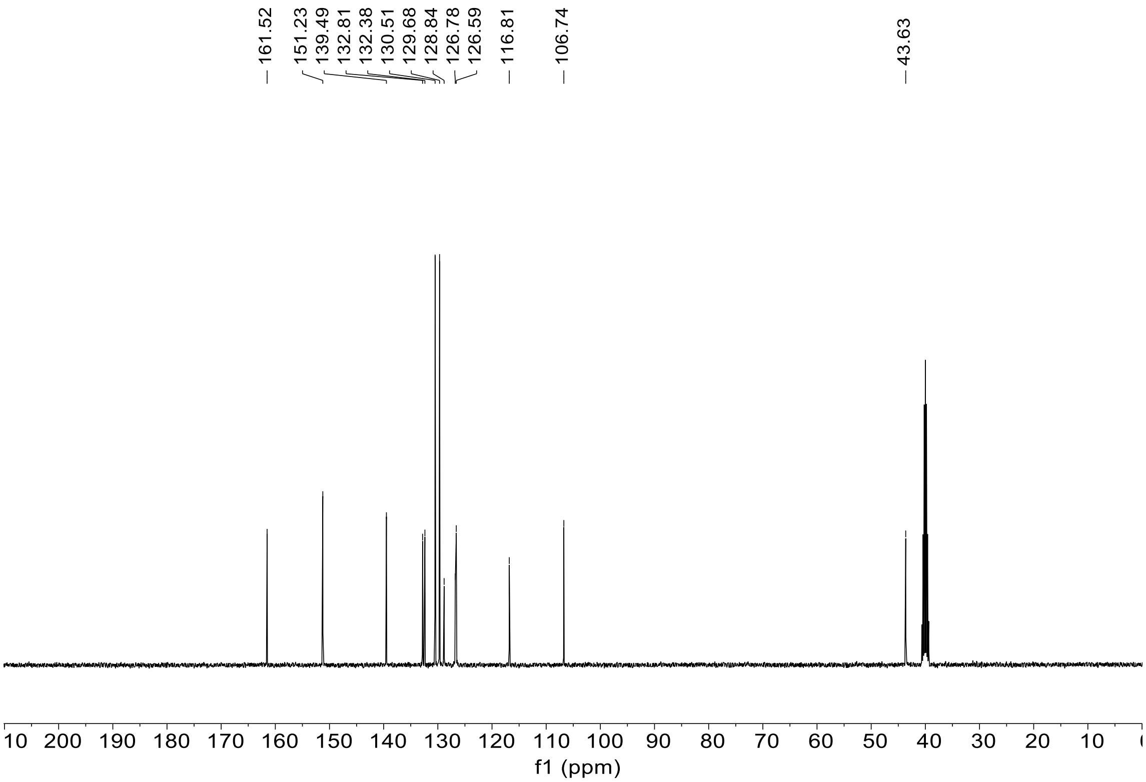


Figure **S2**. ^{13}C NMR (101 MHz) of **1N** in DMSO-d^6.

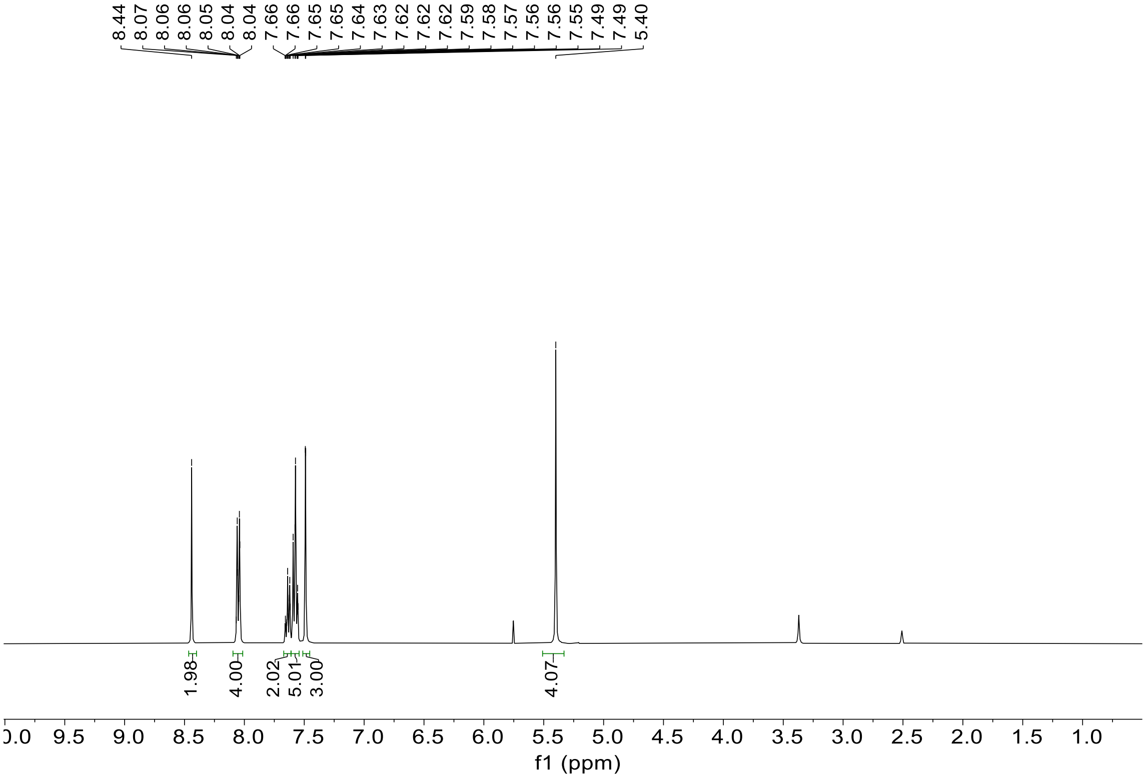


Figure **S3**. ^{1}H NMR (400 MHz) of **1H** in DMSO-d^6.

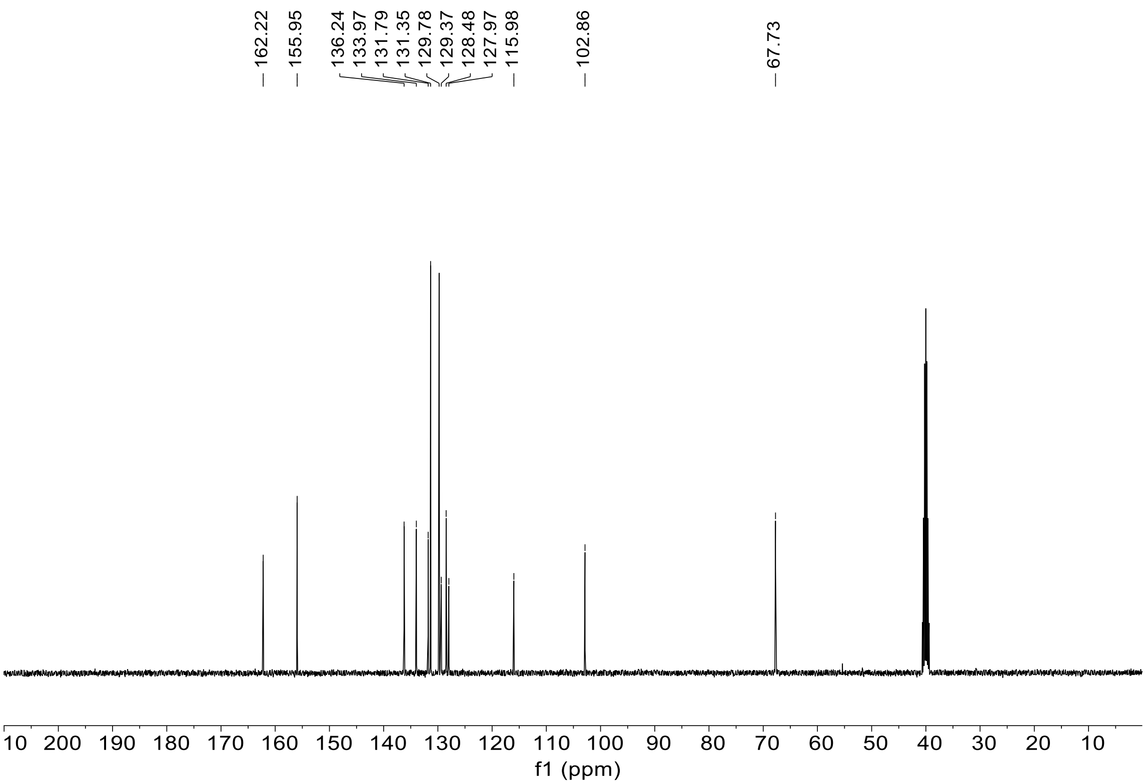


Figure **S4**. ^{13}C NMR (101 MHz) of **1H** in DMSO-d^6.

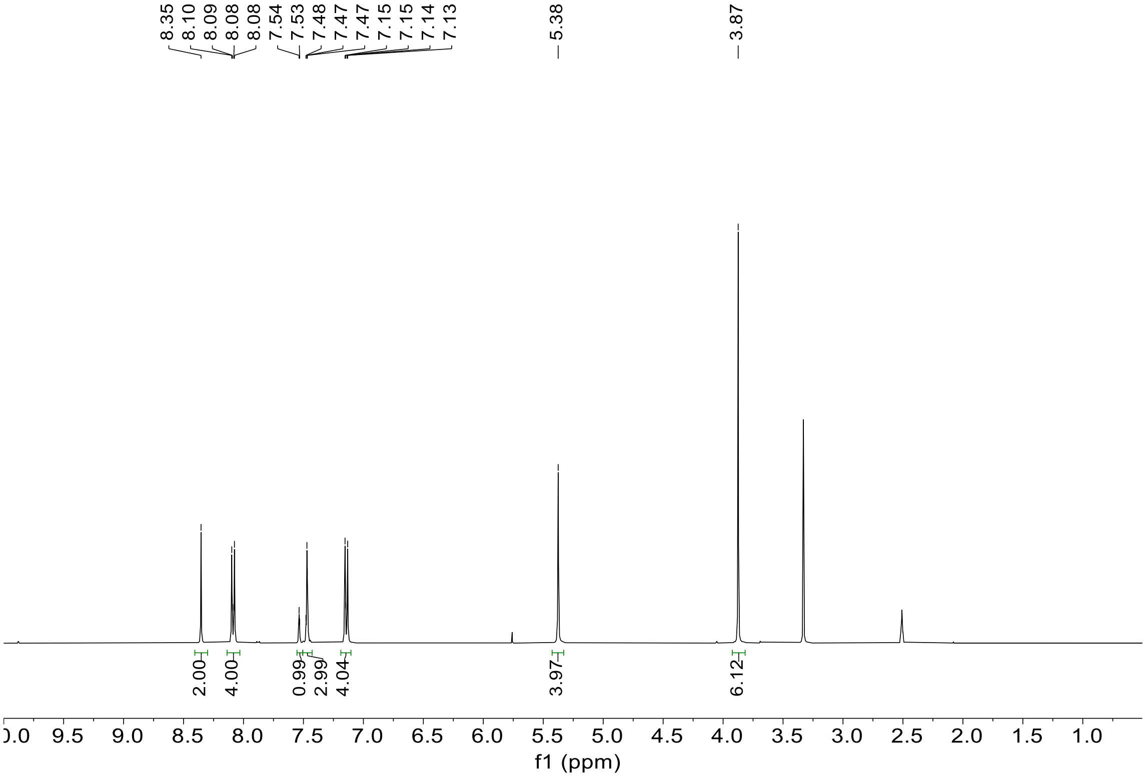


Figure **S5**. ^{1}H NMR (400 MHz) of **1M** in DMSO-d^6.

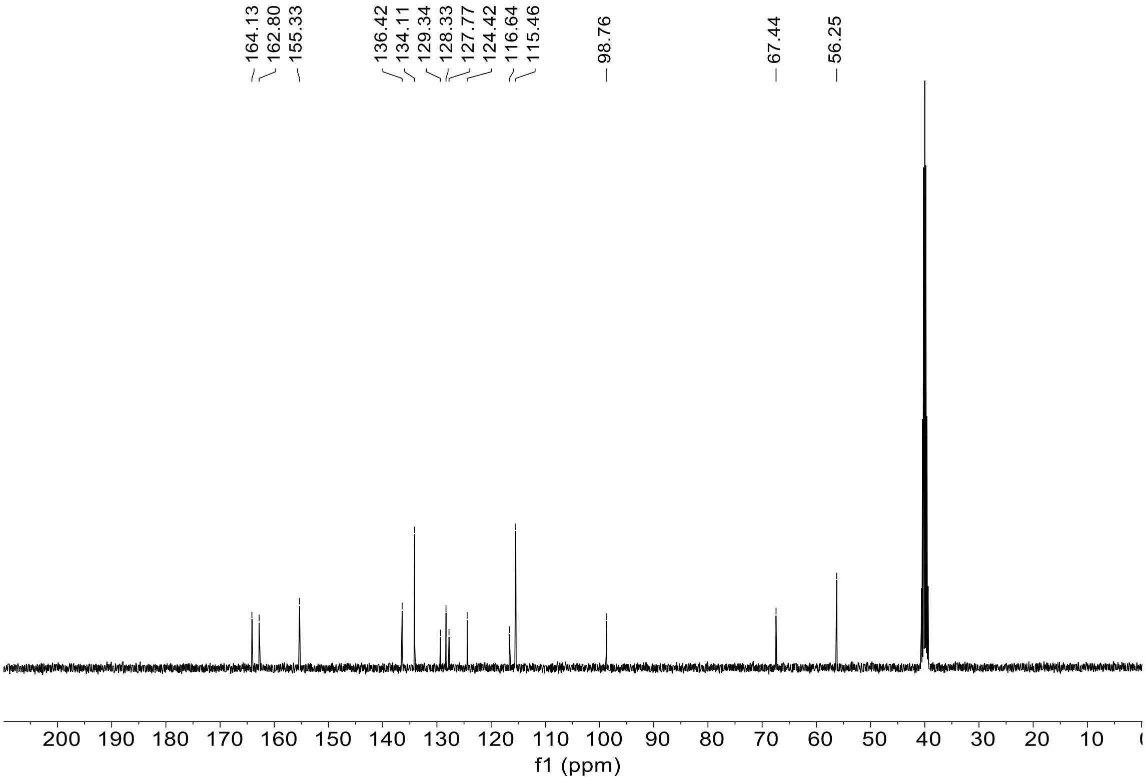


Figure **S6**. ^{13}C NMR (101 MHz) of **1M** in DMSO-d^6.

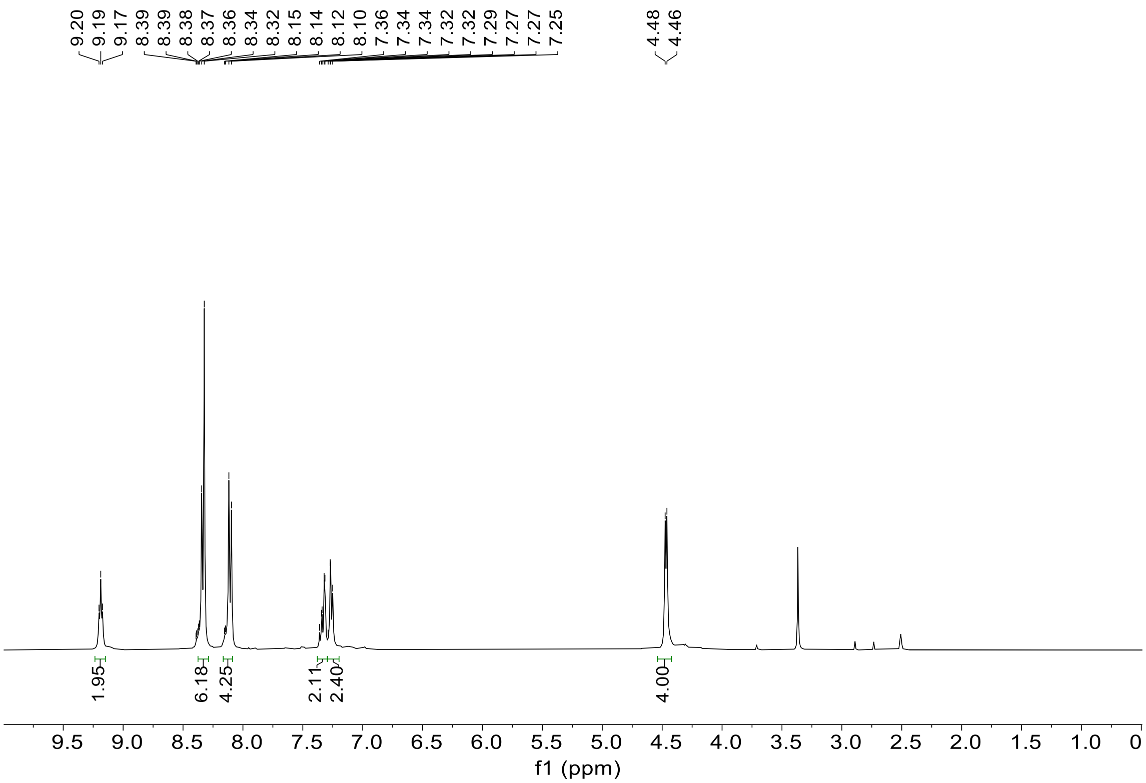


Figure **S7**. ^{1}H NMR (400 MHz) of **2N** in DMSO-d^6.

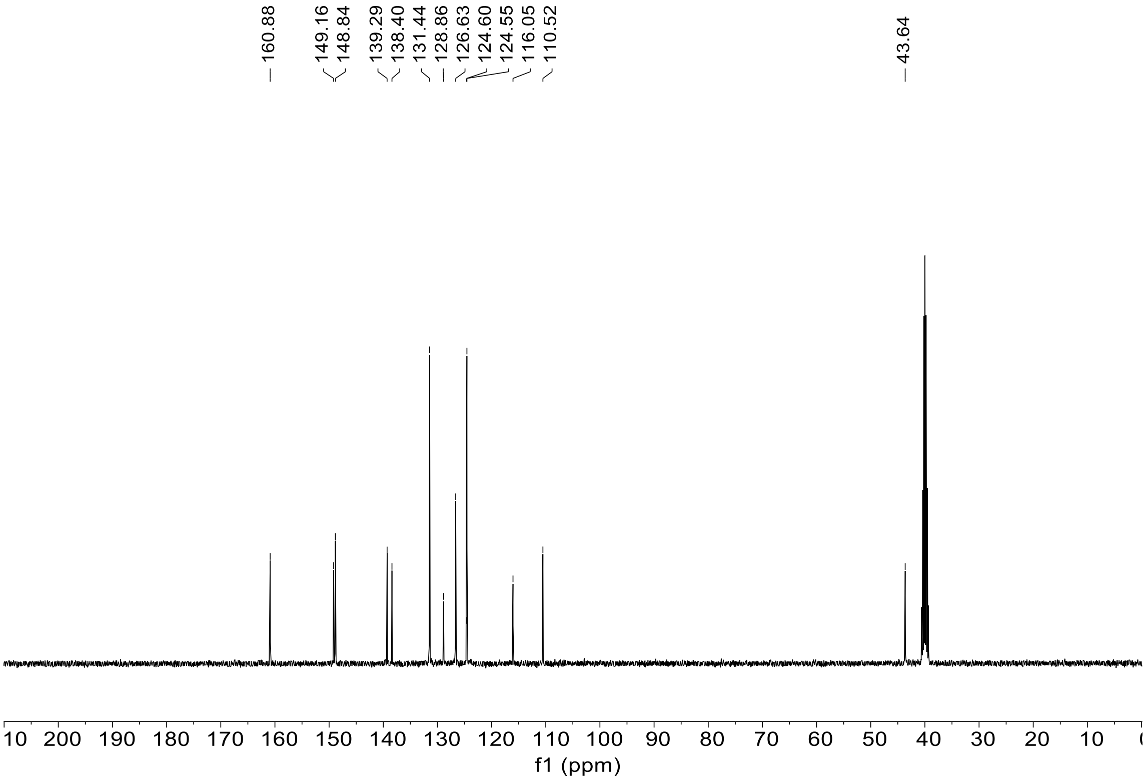


Figure **S8**. ^{13}C NMR (101 MHz) of **2N** in DMSO-d^6.

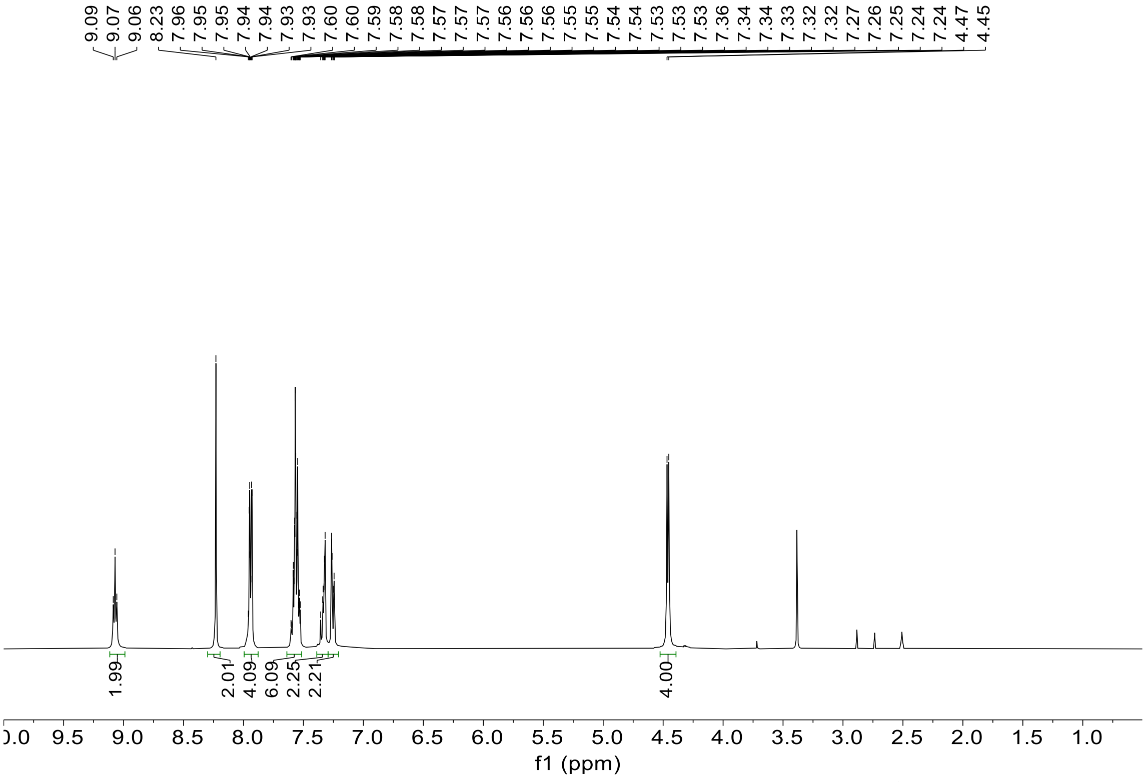


Figure **S9**. ^{1}H NMR (400 MHz) of **2H** in DMSO-d^6.

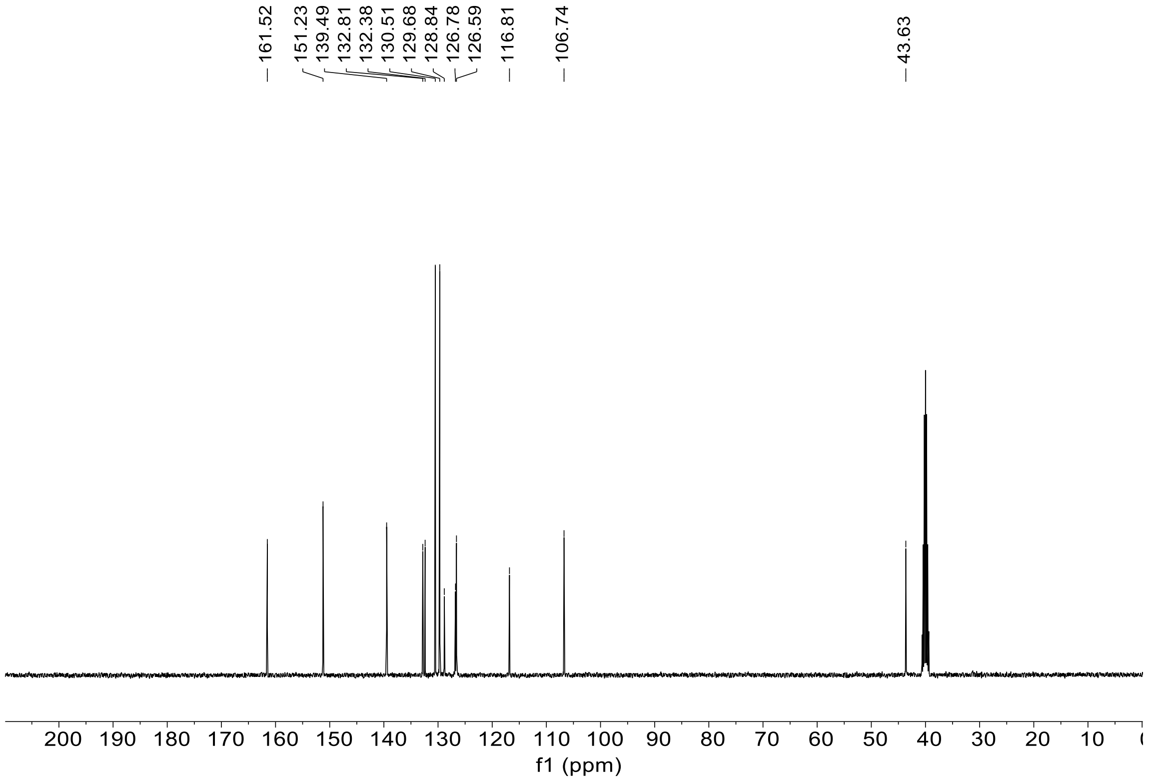


Figure **S10**. ^{13}C NMR (101 MHz) of **2H** in DMSO-d^{6}.

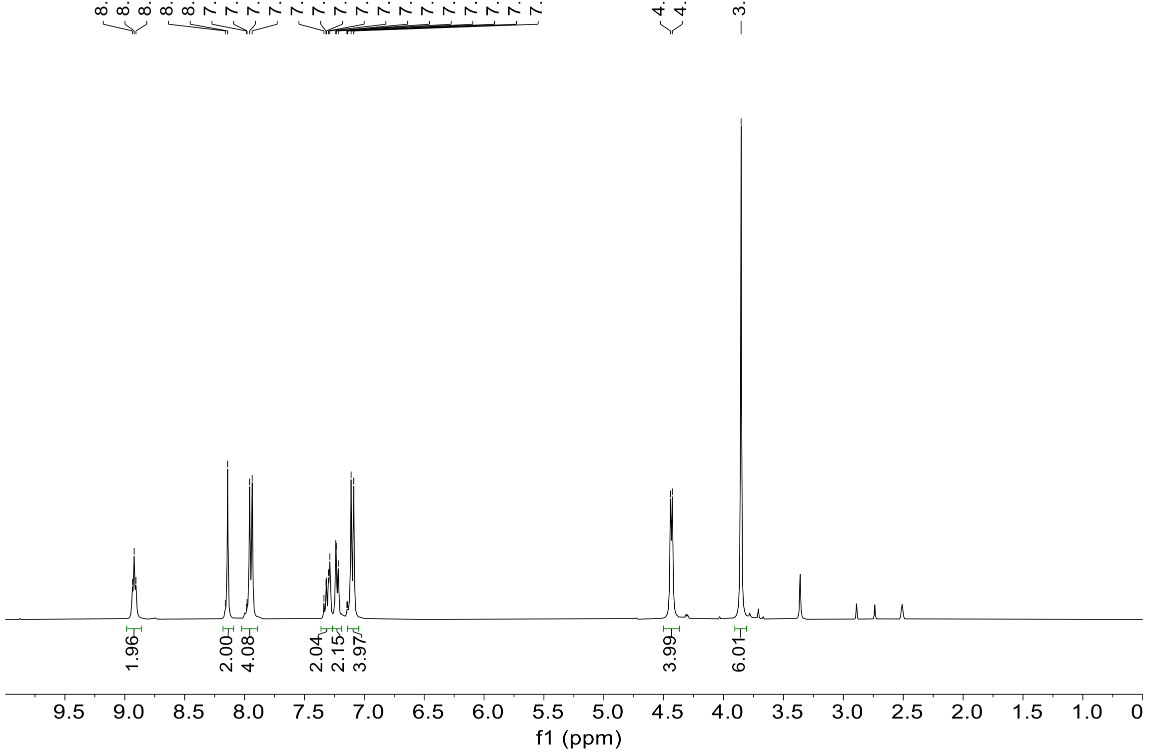


Figure **S11**. ^{1}H NMR (400 MHz) of **2M** in DMSO-d^{6}.

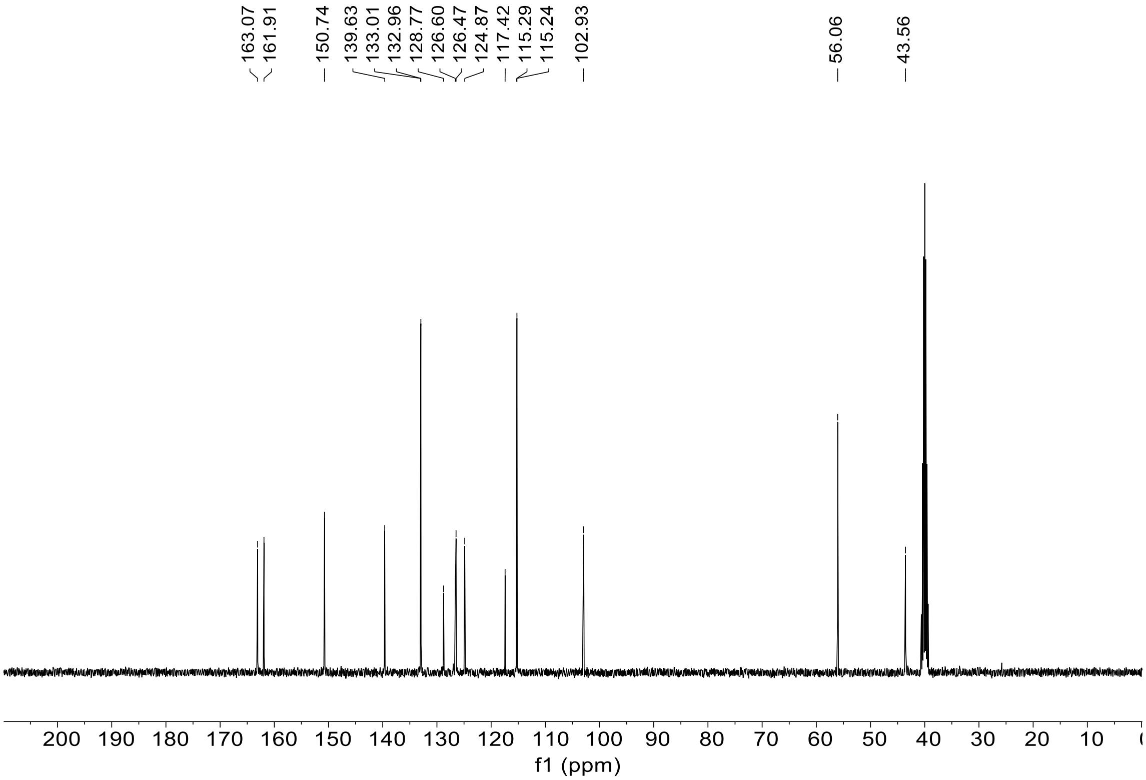


Figure **S12**. ^{13}C NMR (101 MHz) of **2M** in DMSO-d^6.

Sample Preparation

Casting/Drying Bulk Dynamic Network Films. In a 20 mL glass vial, ditopic Michael acceptors were dissolved in dimethylformamide (DMF) (1 ml per 100 mg acceptor). Pentaerythritol tetreakis(3-mercaptopropionate) (PTMP) was added and the solution was heated to 60 °C, sonicated, and vortexed until clear and homogenous. The solution was then transferred to a Teflon ® dish and covered with perforated aluminum foil, dried on hot plate at 60 °C for 48 hours and in a vacuum oven under a preset heating profile (ramp from room temperature to 120 °C in 48 hours, isothermal at 120 °C for 72 hours). High temperatures were avoided during the DMF drying procedure to prevent possible degradation of the thia-Michael networks.

Melt pressing. Dried films were melt-pressed at 2 tons of force for 15 minutes. **3H** was pressed at 90 °C, while **3N**, **4H**, **4M** were pressed at 110 °C.

AFM samples. From the solution made in preparation of the bulk dynamic network films, ~ 15 μL was cast onto 12 mm round glass coverslips. Drying procedure was the same as the bulk film preparation.

Raman, storage modulus, and fracture toughness samples. Bulk films of **3N** and **4H** were melt-pressed to a thickness of 0.64 mm and cut to ~ 3mm x 3 mm squares. Samples were tempered at designated temperatures for 24 hr, quenched on a cold surface (0 °C) and were allowed to return to room temperature before these tests. All tests were conducted at room temperature.

Lap shear samples.
Samples with aluminum substrates: Melt-pressed **3N** and **4H** films were cut into 3 mm x 3 mm squares and were placed in between aluminum plates (75 mm x 20 mm x 1.5 mm), two aluminum plates were clamped with 2 binder clips to exert ~30 N force on the samples (binder clips force was measured by Zwick). Clamped samples were then transferred to an oven and heated (130 °C for **4H**, 150 °C for **3N**) for 24 h to soften the samples and bond them onto aluminum substrate surfaces. After bonding the binder clips were taken off and the samples were tempered at designated temperatures for 24 h and quenched in fridge (~4 °C) for 5 min after tempering. Tensile tests were performed after the sample temperature returned to ambient temperature.
Rebonding tests with aluminum substrates. Melt-pressed **3N** and **4H** films were cut into 3 mm x 3 mm squares and were placed in between aluminum plates (75 mm x 20 mm x 1.5 mm), two aluminum plates were clamped with 2 binder clips to exert ~30 N force on the samples (binder clips force was measured by Zwick). Clamped samples were then transferred to an oven and heated (130 °C for **4H**, 150 °C for **3N**) for 24 h to soften the samples and bond them onto aluminum substrate surfaces. After bonding the binder clips were taken off and the samples were tempered at designated temperatures for 24 h and quenched in fridge (~4 °C) for 5 min after tempering. Tensile tests were performed after the sample temperature returned to ambient temperature. The lap shear substrates were then clamped together using two binder clips (exert a force of ~30N) at the same location and were heated in the oven (130 °C for **4H**, 150 °C for **3N**) for 24 h for them to rebond. Binder clips were removed after rebonding and the samples were then tempered at designated temperatures for 24 h, quenched to room temperature and performed another set of lap shear tests.

Samples with polyetherimide substrates: Due to poor contact between dry samples and polymer surfaces, DMF plasticized samples that were softer and more flexible were used in sample preparation. DMF solutions of Michael acceptor (**1N** and **2H**) and PTMP were prepared in the same way as bulk film preparation (100 mg acceptor per 1 mL of DMF). The solution was transferred into a Teflon ® dish and was heated at 80 °C until it formed a swollen gel at room temperature (~30 % DMF in weight checked by TGA). The swollen gel was cut to square shape of 12 mm x 12 mm and were put in between polyetherimide substrates (62 mm x 12 mm x 3.2 mm). Spacing bars (same substrates with one side taped with a 0.3 mm thickness tape) were placed and taped with Kapton tapes on top and bottom to fix the sample during bonding. Two binder clips were clamped along the length of substrates which gave the samples compression force around 30 N (as measured by Zwick). After that, the sample was transferred to the oven and was heated with a preset heating profile (ramp from ambient temperature to 90 °C in 48 h, isothermal at 90 °C for 48 h, ramp to 120 °C in 24 h and isothermal at 120 for 48 h). Vacuum was turned on when sample temperature reached 120 °C to further pull off residual DMF. After that the binder clips and spacing bars were removed, and the sample was placed in the oven for tempering at designated temperatures for 24 hours and it was transferred to freezer (-20 °C) to be quenched to room temperature for lap shear tests. Before loading the sample to Instron, two short pieces cut from the same substrates were attached to both ends of the sample using double-sided tape so that the sample can be clamped vertically.

Materials Characterization

Thermal Gravimetric Analysis (TGA)

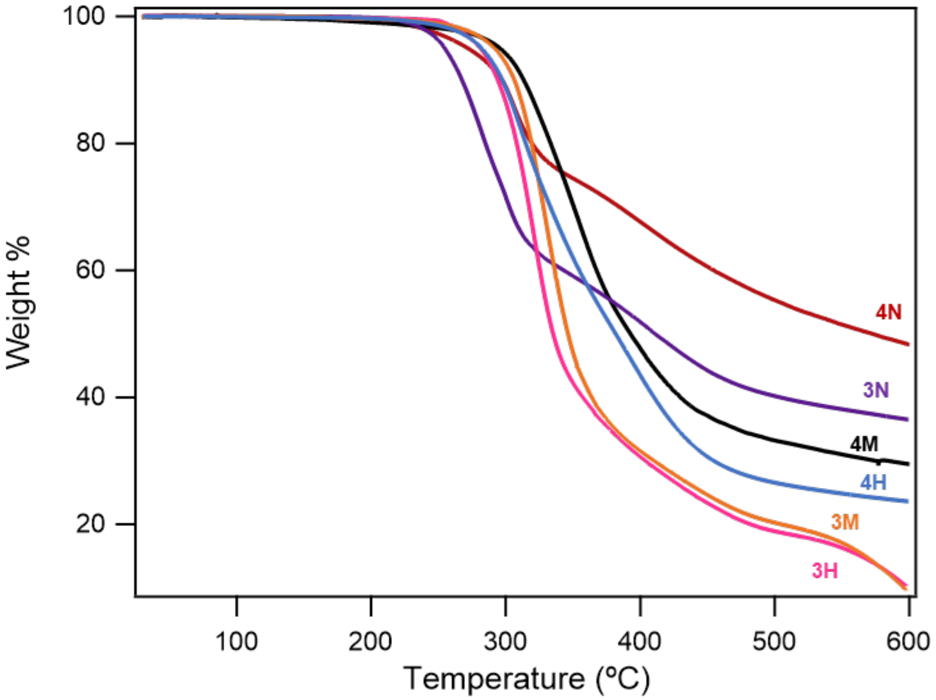


Figure S13. Thermal gravimetric analysis (TGA) data for **BCA** and **BCAm** materials (ramp rate = 10 °C/min to 600 °C) showing films are solvent-free.

Fourier Transform Infrared Spectroscopy (FTIR) of **3H** and **4H**.

FTIR of **3H** and **4H** were taken to demonstrate hydrogen bonding between benzalcyanoacetamide (BCAm) acceptor units. **3H** used benzalcyanoacetate (BCA) Michael acceptors with no ability to form amide-based hydrogen bonding the film. FTIR for both films were taken at various temperatures above their T_g. Previous studies showed that at higher temperatures the peak position of N-H stretch without H bonding shifted due to dissociation of hydrogen bonding.[3] Figure **S14** showed that as temperature increased there was no shift in peak positions in **3H**, while Figure **S15** showed that major peaks for **4H** all shifted to the left at higher temperatures, including the peak at ~3300 cm^{-1}, corresponding to N-H group without H-bonding.

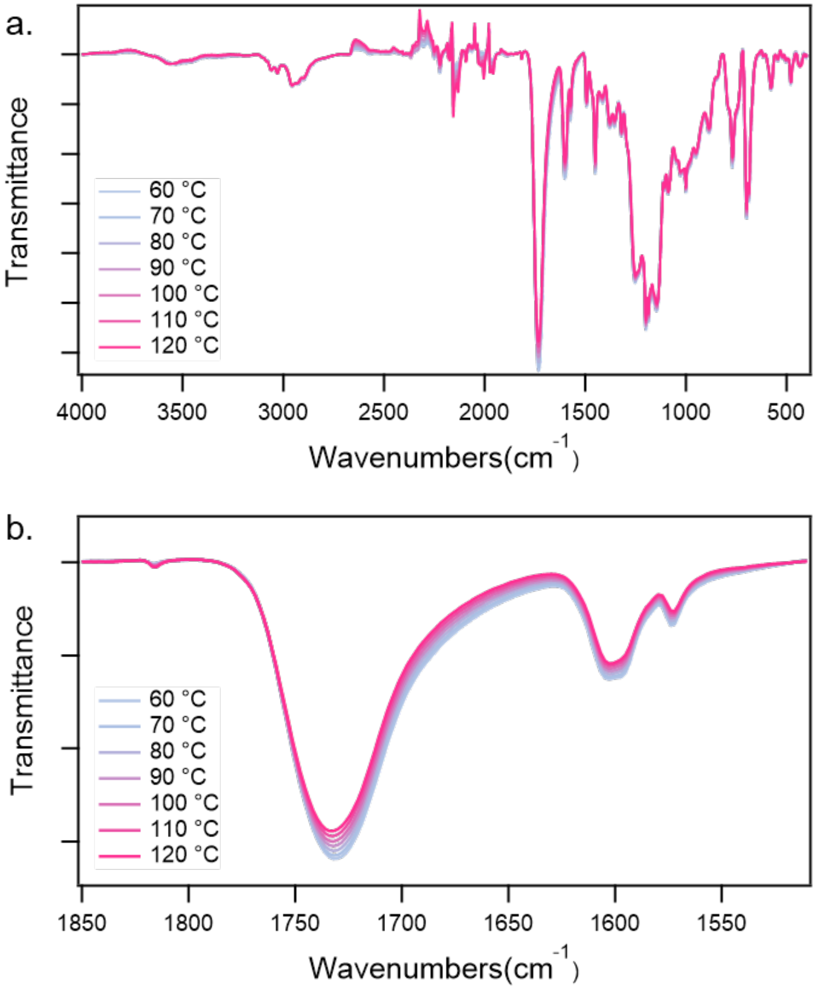


Figure S14. FT-IR spectra of **3H** taken at various temperatures. (a) Full spectrum from 4000 cm^{-1} to 400 cm^{-1}. (b) Zoomed in spectrum from 1500 cm^{-1} to 1850 cm^{-1} showing no significant peak shifting on the C=O stretch.

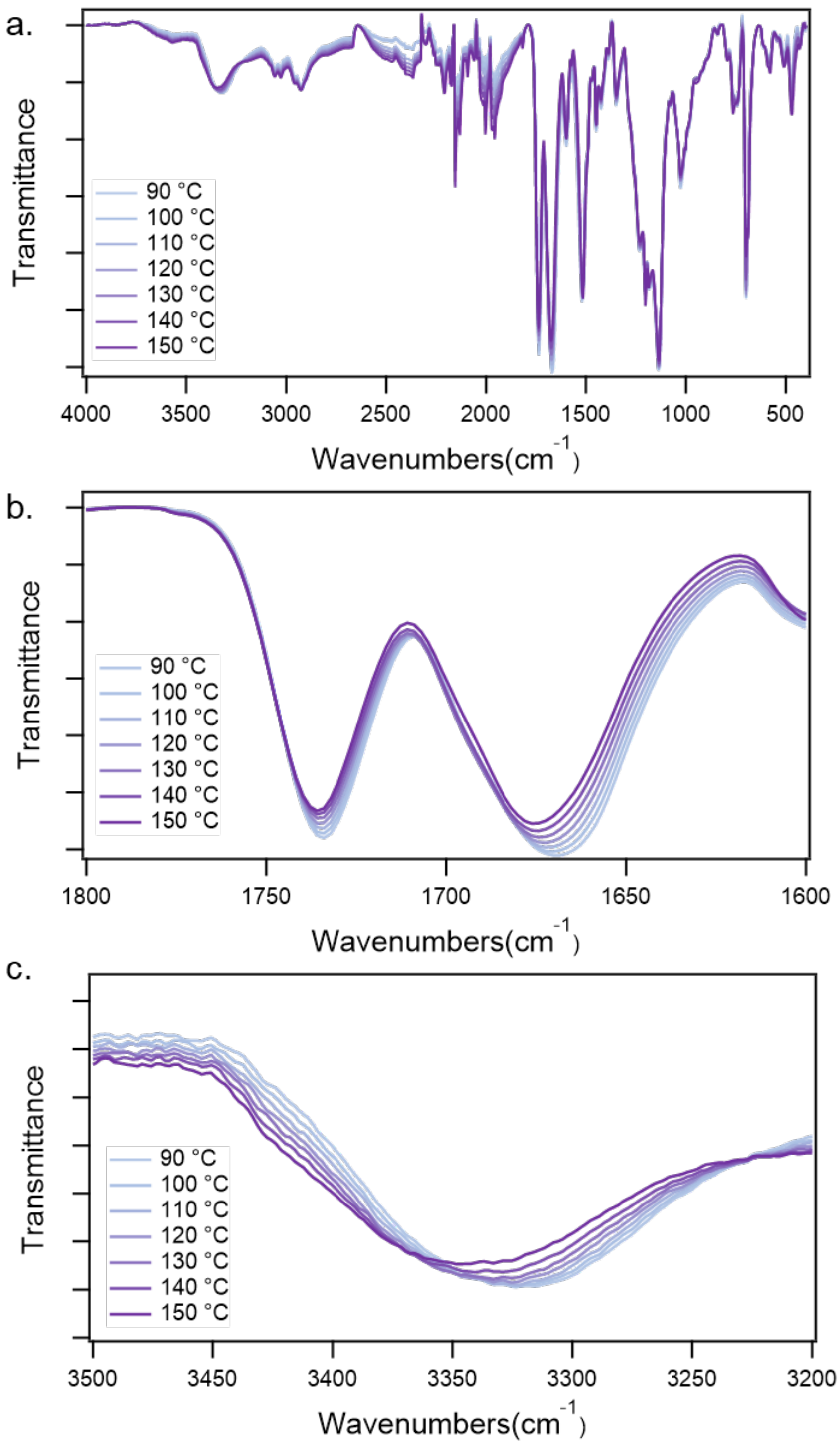


Figure S15. FT-IR spectra of **4H** taken at various temperatures. (a) Full spectrum from 4000 cm^{-1} to 400 cm^{-1}. (b) Zoomed in spectrum from 1600 cm^{-1} to 1800 cm^{-1} showing peak shifts on the C=O stretch. (c) Zoomed in spectrum from 3200 cm^{-1} to 3500 cm^{-1} showing peak shifts in N-H group peak.

Differential Scanning Calorimetry (DSC)

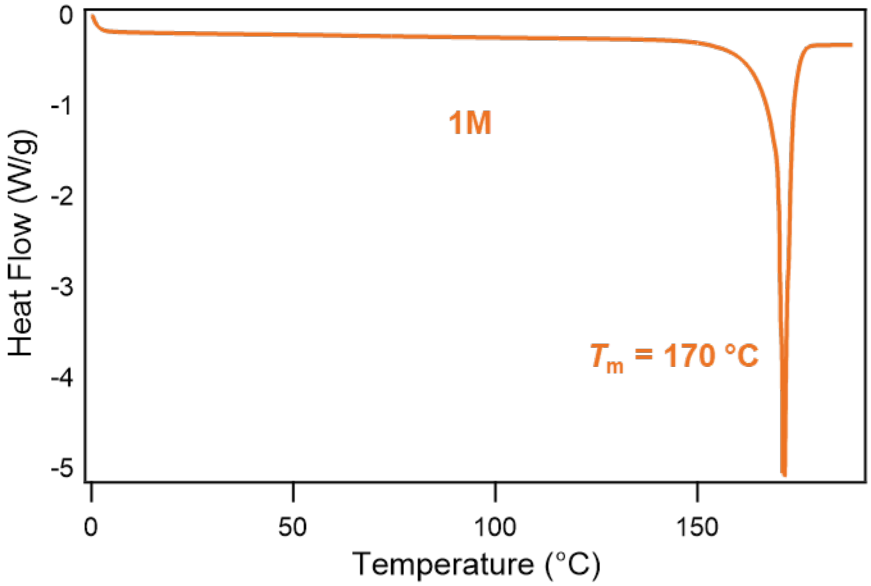


Figure S16. DSC data for **1M**.

Table S1. As cast T_g, T_{UT}, and T_m obtained from DSC thermogram (Figure 2A) for 4N, 4H, 4M, 3N, 3H, and 3M.

	T_g (as cast) (°C)	T_{UT} (as cast) (°C)	T_m (°C)
4N	74	112	NA
4H	66	110	NA
4M	50	107	NA
3N	61	115	NA
3H	7	125	NA
3M	5	NA	166

Atomic Force Microscopy (AFM)

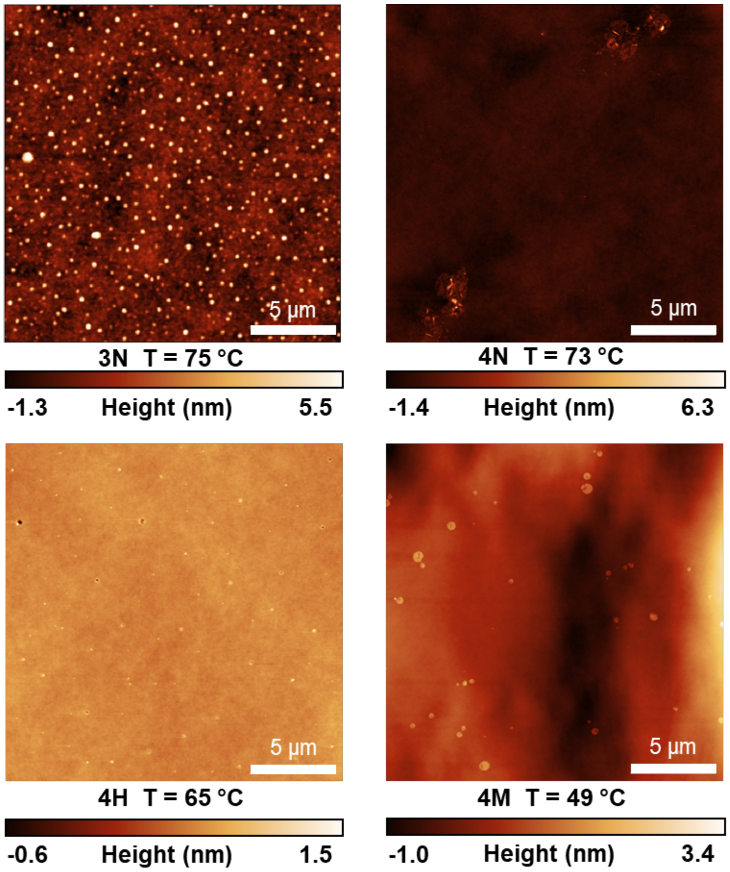


Figure S17. AFM height images corresponding to AFM phase images shown in Figure **2b**.

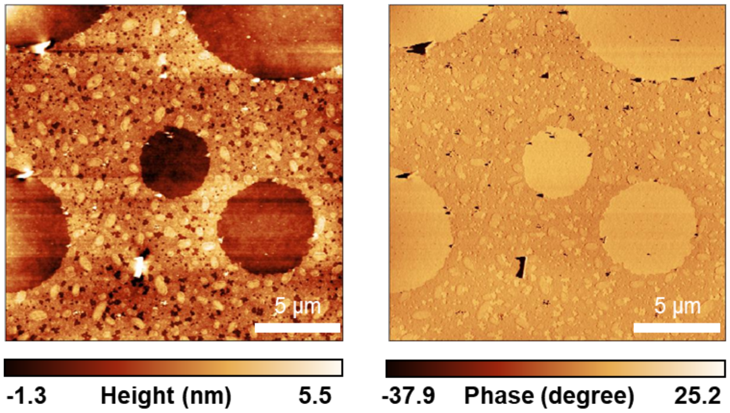


Figure S18. AFM height(left) and phase(right) images of **3H** taken at 10 °C.

Dynamic Temperature Ramps

Glass transition temperatures from rheology data were determined by Tan δ peaks, upper transition temperatures were determined at the point that the storage modulus curve deviated from the extended line of storage modulus in the rubbery plateau.

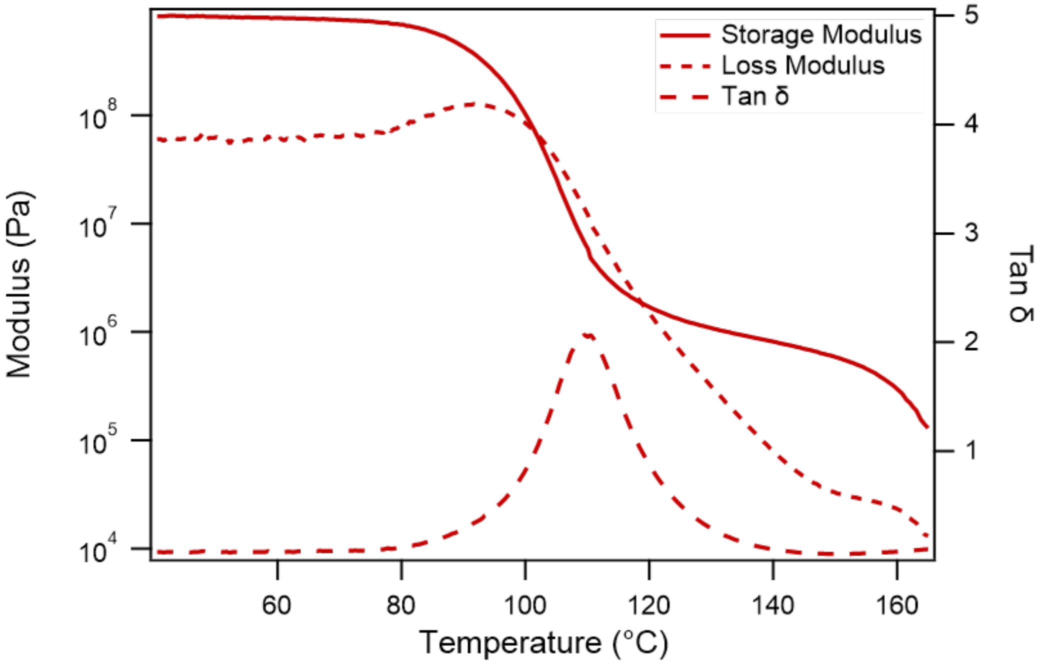


Figure S19. Dynamic temperature ramps of **4N**.

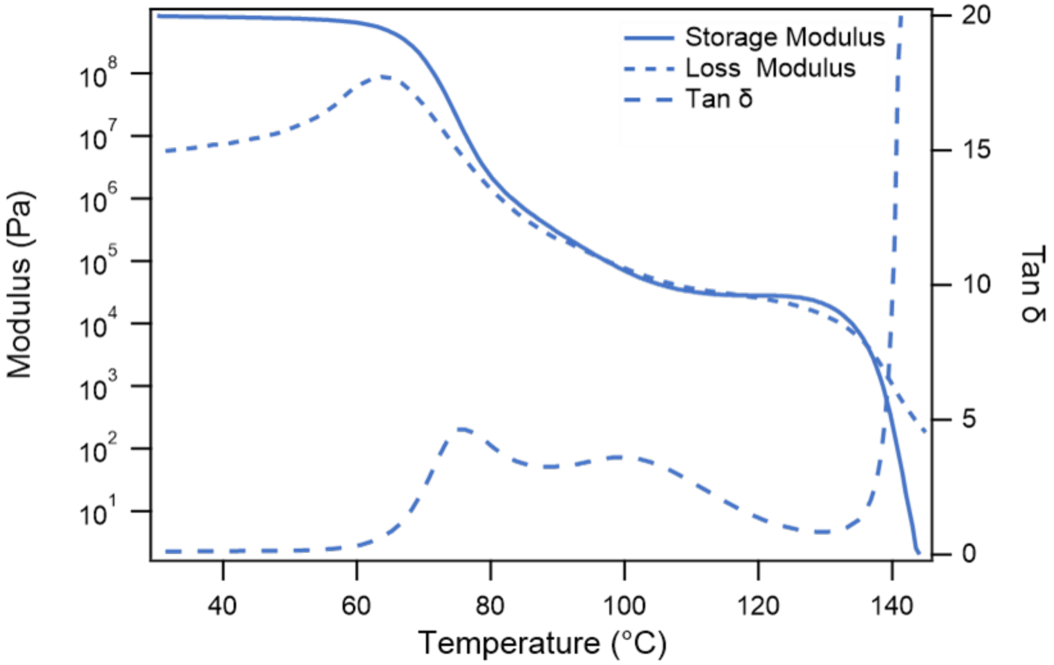


Figure S20. Dynamic temperature ramps of **4H**.

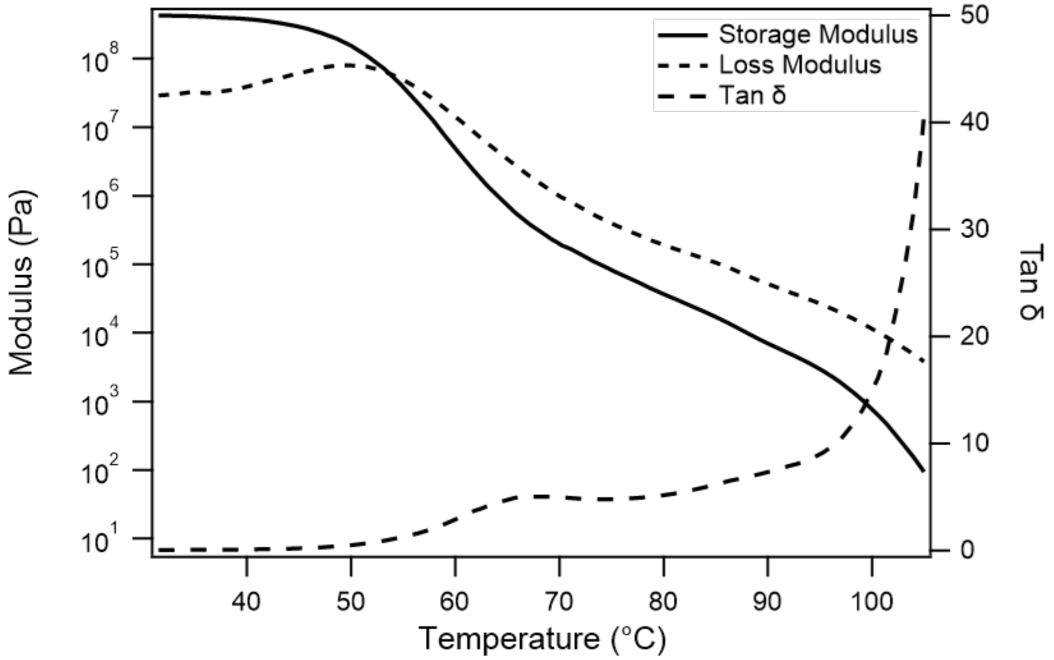


Figure S21. Dynamic temperature ramps of **4M**.

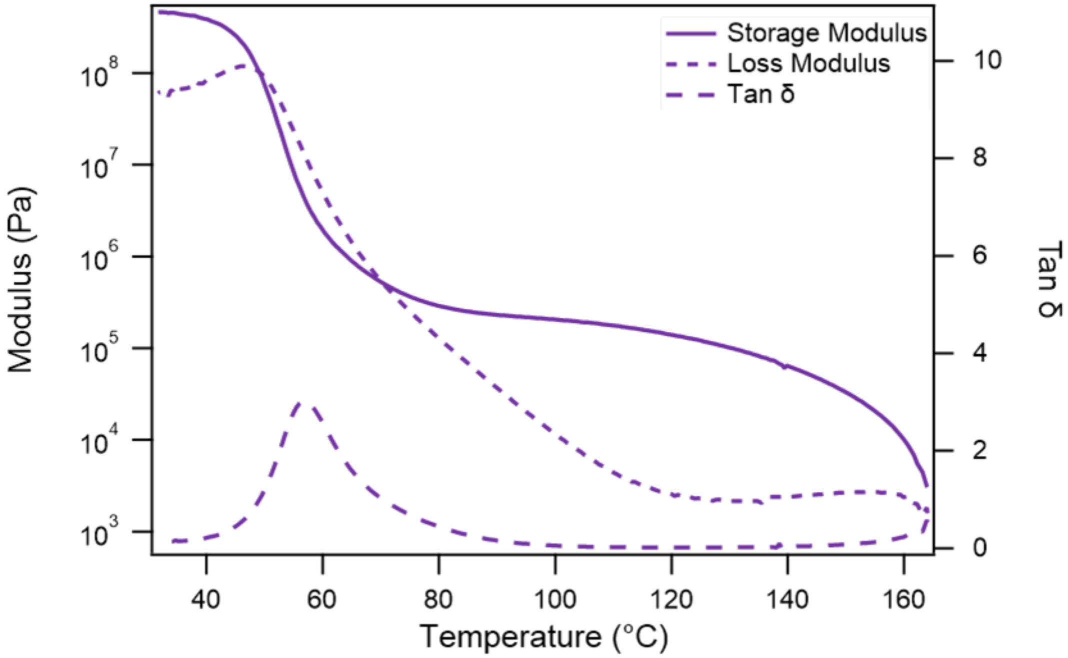


Figure S22. Dynamic temperature ramps of **3N**.

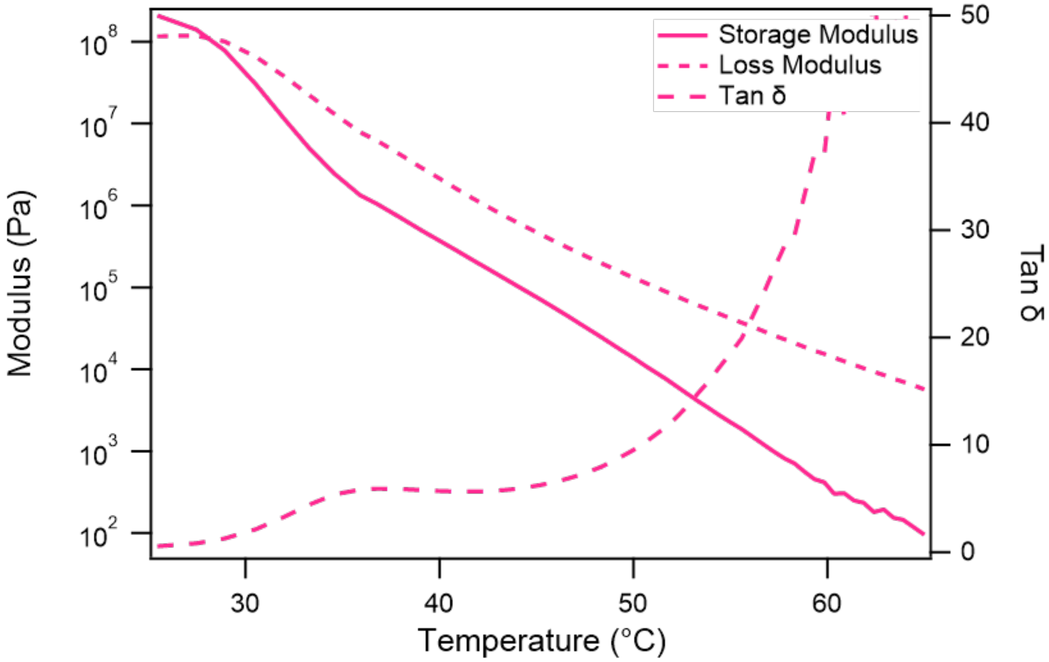


Figure S23. Dynamic temperature ramps of **3H**.

Time-resolved Shear Rheometry Growth Curves

8 mm diameter samples were loaded on a shear rheometer, and the thermal history was erased by heating at 150 °C for 10 min before the temperature was rapidly lowered to T_t. All samples were collected within the linear viscoelastic region (LVR) at 1 Hz.

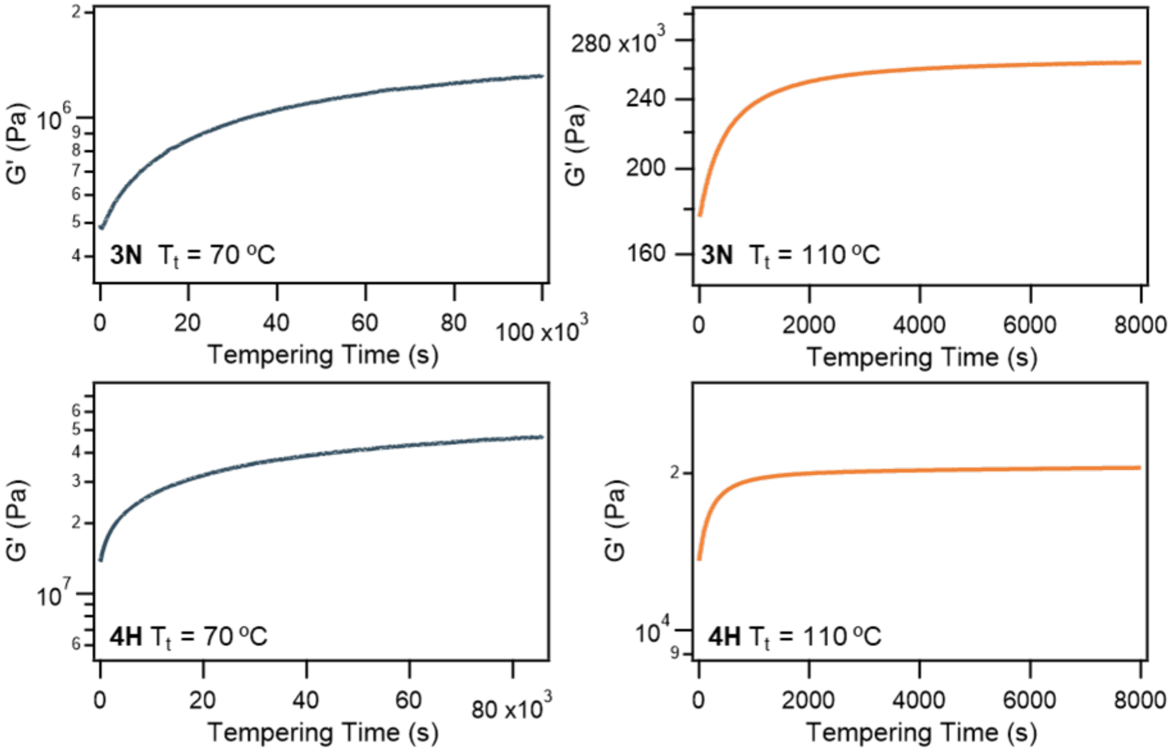


Figure S24. Shear rheometry, time resolved isothermal growth curves for **3N** and **4H** tempered at 70 °C and 110 °C.

DSC of tempered films

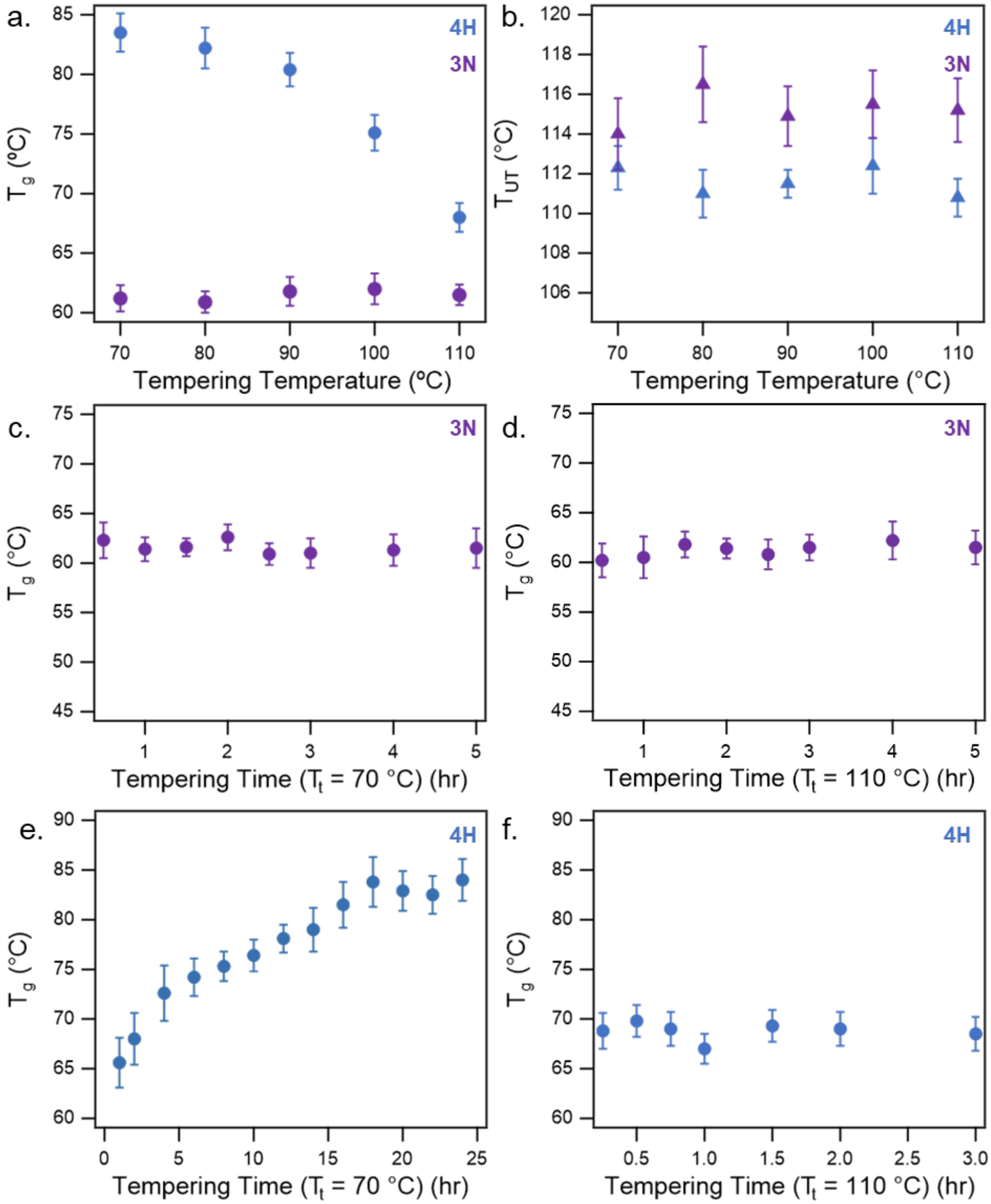


Figure S25. (a) T_g of tempered **3N** and **4H** at various temperatures (n = 5), tempering time at all tempering temperatures is 24 h. (b) T_{UT} of tempered **3N** and **4H** at various tempering temperatures (n = 5), tempering time at all tempering temperatures is 24 h. (c) T_g of **3N** tempered at 70 °C for variable amount of tempering time (n = 5). DSC samples were tempered in the oven, after the desired amount of tempering time, the samples were quenched in ice bath to room temperature, transferred to DSC and ran a cool-heat procedure (0 °C/160 °C) at a 10 °C/min. (d) T_g of **3N** tempered at 110 °C for variable amount of tempering time (n = 5). (e) T_g of **4H** tempered at 70 °C for variable amount of tempering time (n = 5). (f) T_g of **4H** tempered at 110 °C for variable amount of tempering time (n = 5).

Raman Spectroscopy

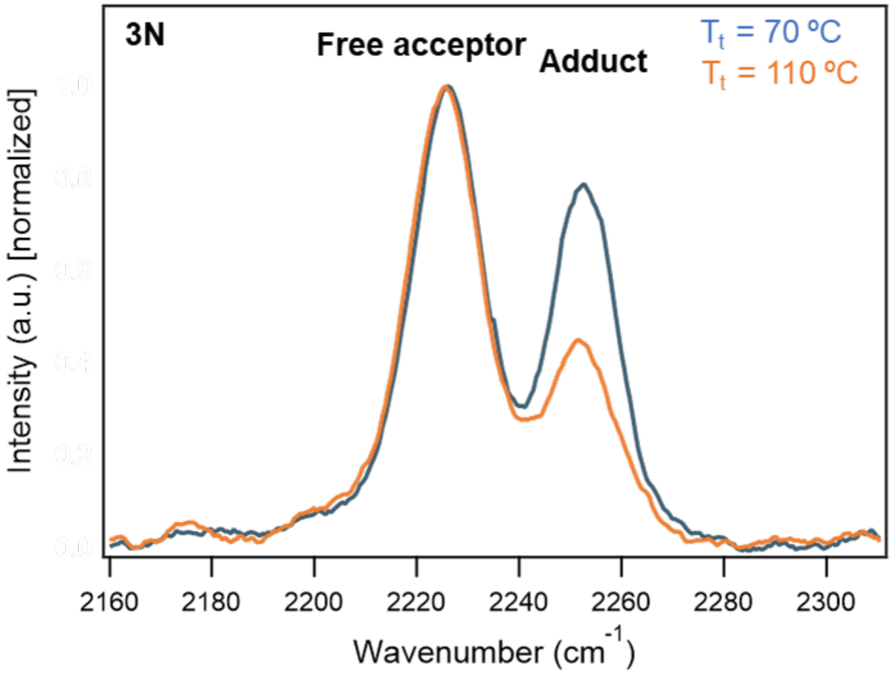


Figure S26. Room temperature partial Raman of the **3N** films tempered at various temperatures, with the nitrile stretch of the free acceptor peak at 2226 cm^{-1} and the nitrile stretch of the adduct peak at 2253 cm^{-1}, data were baselined and smoothed using LabSpec6. Peaks were normalized to the free acceptor peak.

Storage Modulus of tempered films

Table S2. Absolute values of storage modulus of 3N and 4H films tempered at 70 °C and 110 °C at 1 Hz (n =5, 6 indentations were done on each sample).

	3N	**4H**
T_t = 70 ºC	2040 ± 108 MPa	3052 ± 148 MPa
T_t = 90 ºC	1680 ± 117 MPa	2601 ± 135 MPa
T_t = 110 ºC	1498 ± 125 MPa	2111 ± 121 MPa

Fracture toughness

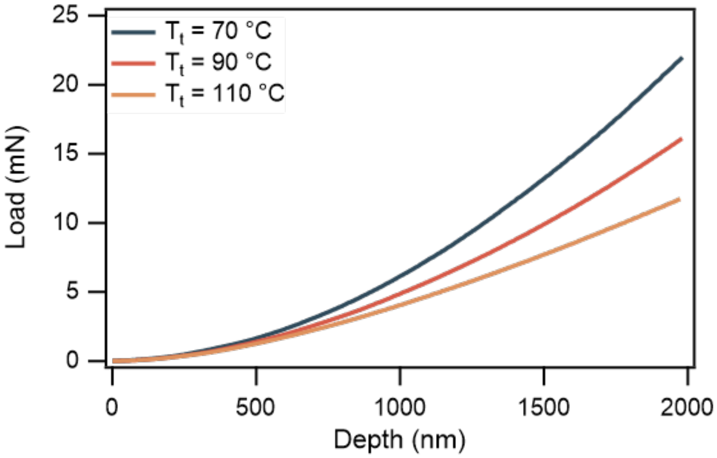


Figure S27. Representative load-depth curves obtained by nanoindentation of **4H** films tempered at various temperatures.

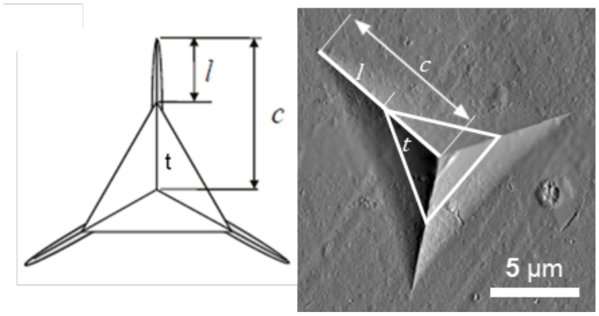


Figure S28. (Left) A schematic of an indentation created using a Berkovich tip, where *t* and *l* were determined by the tip contact area obtained through nanoindentation. (Right) Representative AFM height images of **4H** post indentation. The total length of each indentation *c* was the average distance from the center to each corner.

Table S3. Absolute values of fracture toughness parameters of 3N and 4H tempered at 70 °C, 90 °C, and 110 °C (n = 5, 6 indentations were done on each sample with 75 µm spacing).

Sample	**E (MPa)**	**P_{max} (mN)**	**H (MPa)**	**c (µm)**	**t (µm)**	**l (µm)**	**Kc (MPa·m$^{1/2}$)**
4H T_t = 70 ºC	4370 ± 376	13.01	230 ± 57	6.31	4.73	1.67	7.253 ± 0.61
4H T_t = 90 ºC	3610 ± 364	16.20	214 ± 35	6.16	4.32	2.16	6.504 ± 0.49
4H T_t = 110 ºC	2700 ± 339	15.34	176 ± 38	6.53	3.83	2.57	5.279 ± 0.41
3N T_t = 70 ºC	4530 ± 387	22.42	288 ± 62	7.95	3.66	4.26	5.233 ± 0.39
3N T_t = 90 ºC	4210 ± 355	21.42	279 ± 49	7.77	3.51	4.50	4.655 ± 0.47
3N T_t = 110 ºC	4010 ± 349	18.43	236 ± 35	7.55	3.42	5.31	4.254 ± 0.37

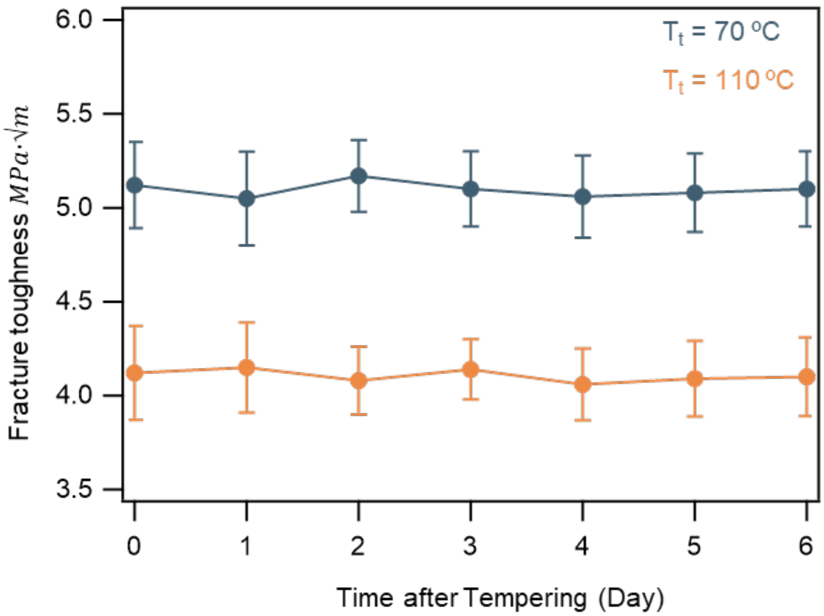


Figure S29. Aging study. Fracture toughness of **3N** tempered at 70 °C and 110 °C were measured over a course of a week (n = 3, 6 indentations were done on each sample with 75 µm spacing).

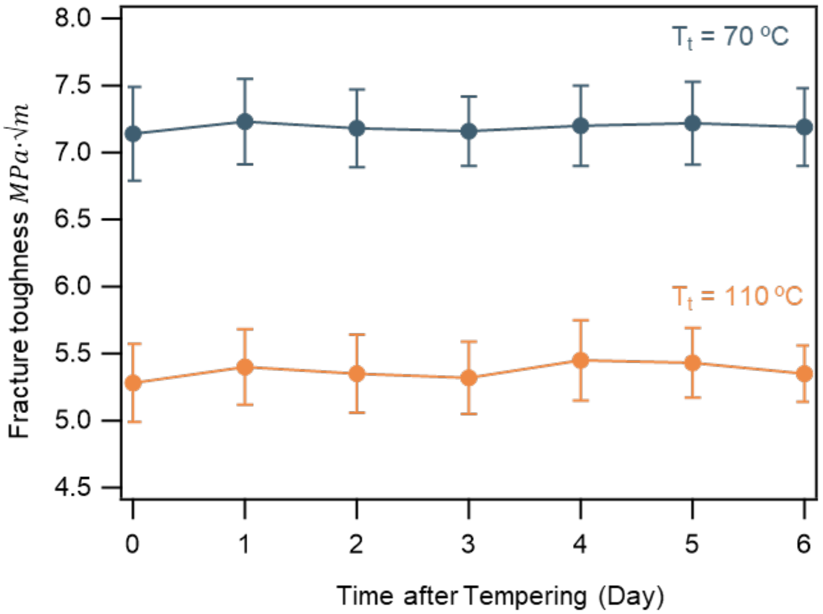


Figure S30. Aging study. Fracture toughness of **4H** tempered at 70 °C and 110 °C were measured over a course of a week (n = 3, 6 indentations were done on each sample with 75 µm spacing).

Lap shear tests

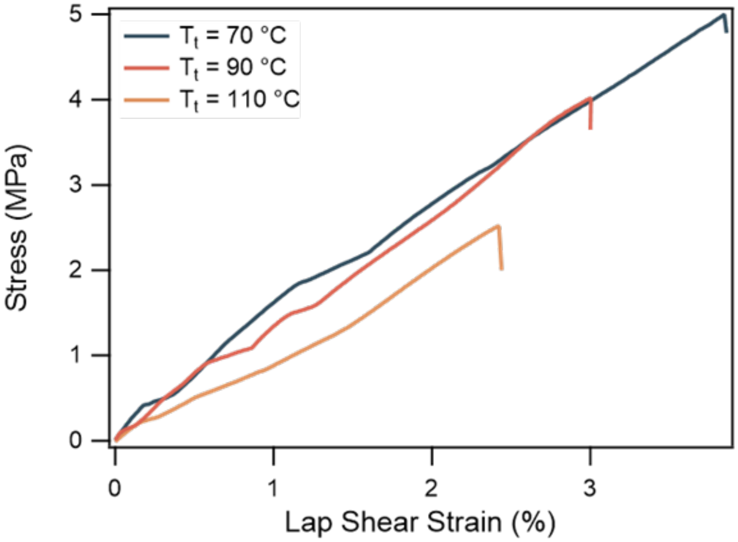


Figure S31. Representative stress-strain curves of **3N** tempered at various temperatures with aluminum substrates.

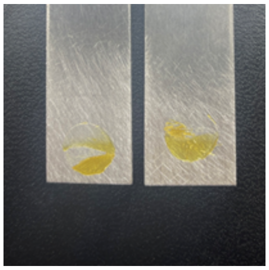


Figure S32. Representative photo of lap shear samples of **4H** after lap shear tests with aluminum substrates, showing cohesive failures.

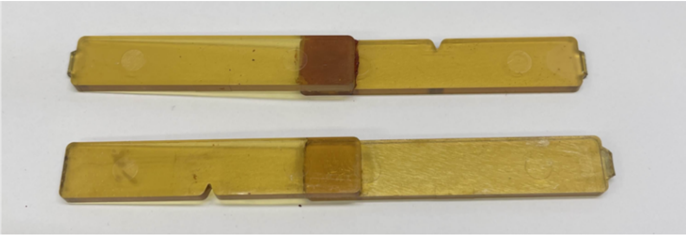


Figure S33. Pictures of lap shear samples of **3N** and **4H**. After DMF removal the samples remained clear and bubble free.

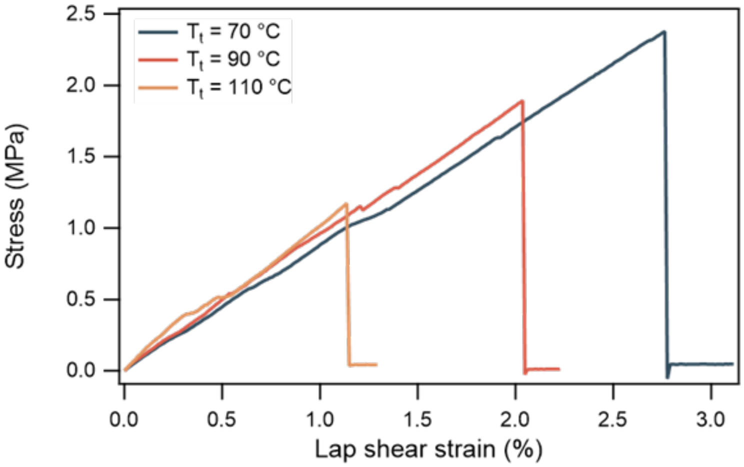


Figure S34. Representative stress-strain curves of **3N** tempered at various temperatures with polyetherimide substrates.

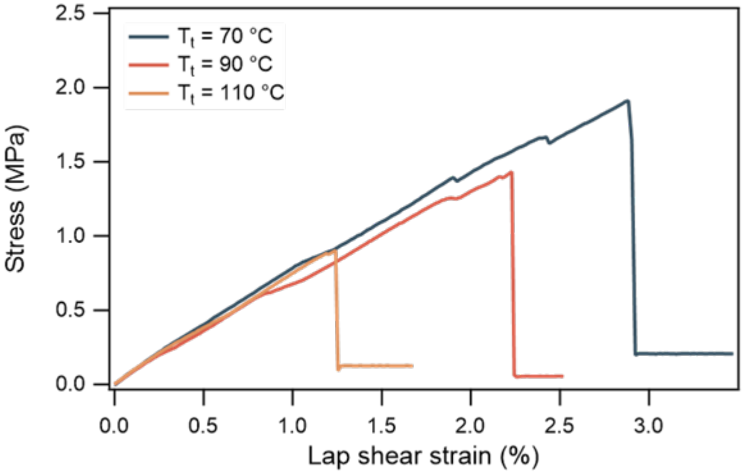


Figure S35. Representative stress-strain curves of **4H** tempered at various temperatures with polyetherimide substrates.

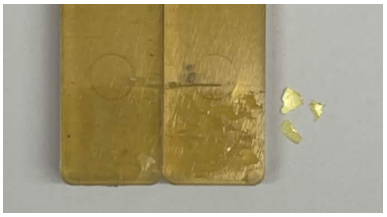


Figure S36. Representative photo of lap shear samples of **4H** after lap shear tests with polyetherimide substrates, showing mixed-mode failure surface.

References:

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