Electronic Supporting Information

Dynamic reaction-induced phase separation in tunable, adaptive covalent networks

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EXPERIMENTAL DETAILS

Materials

All reagents were purchased from Sigma-Aldrich. Solvents for reactions and film casting were purchased from Fisher-Scientific. Deuterated solvents were purchased from ACROS Organics. All chemicals were used as received without further purification unless otherwise noted. All dynamic tM films were tested within a week of preparation and stored below T_g.

Instrumentation

Nuclear Magnetic Resonance (NMR). General Nuclear Magnetic Resonance Spectroscopy were performed using either 500 MHz Bruker AVANCE II+ 500; 11.7 Tesla NMR or Bruker AVANCE III HD 500; 11.7 Tesla NMR at the NMR facilities at the University of Chicago.

For experimental temperatures ranging 25–40 °C, a standard plastic sample spinner was used; for equilibrium measurements at 50 °C and up, the sample was held in a ceramic spinner (to avoid warpage). Sample temperatures were measured by proxy through the use of a neat ethylene glycol standard, using relationships published previously[1], namely

$$T = 466.5 - 102\Delta\delta$$

Where T is measured in K and $\Delta\delta$ is the difference between ethylene glycol peaks in ppm (suitable for temperatures between 273 and 416 K).
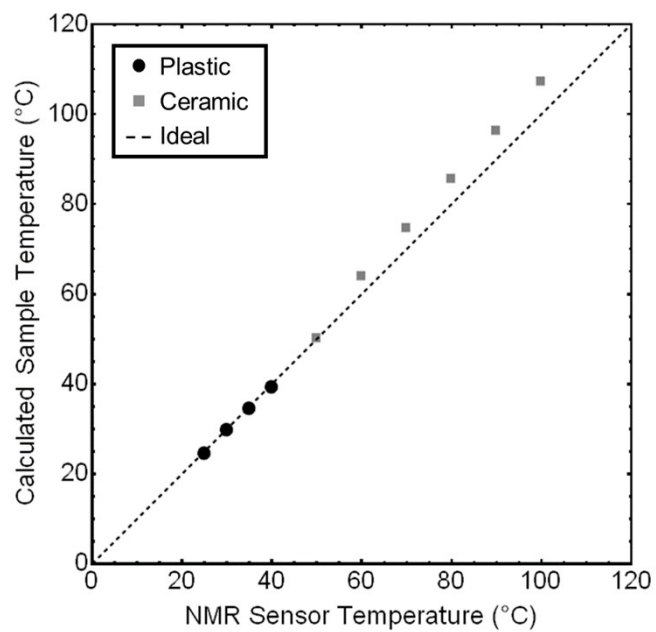
Figure S1. Measured sample temperatures (using neat ethylene glycol) for relevant NMR temperatures used in equilibrium studies.

Gas Chromatography-Mass Spectrometry (GC-MS). GC Mass Spectrometry was collected using an Agilent 7890B GC equipped with an Agilent HP-5MS column coupled to an Agilent 5977A EI/PCI-MS.

Matrix Assisted Laser Desorption/Ionization Mass Spectrometry (MALDI-MS). MALDI-TOF was measured by Bruker Ultraflextreme MALDI-TOF-TOF spectrometer using dithranol as matrix and sodium trifluoroacetate as ionizer.

Thermogravimetric Analysis (TGA). Thermogravimetric analysis was performed using a TA Instruments Discovery Thermogravimetric Analyzer in the Soft Matter Characterization Facility at the University of Chicago. Samples were tested under nitrogen atmosphere using platinum pans. Tests were conducted using a ramp of 10 °C/min from starting operating temperature (ca. 35 °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 prepared in aluminum hermetic pans from TA Instruments and were hermetically sealed. Typical test conditions involved a heat-cool-heat procedure (200 °C/-80 °C/200 °C) run at 10 °C/min.

Tensile Analysis. Tensile analysis was performed using a Zwick-Roell zwickiLine Z0.5 Materials Testing Instrument with a 100 N load cell in the Soft Matter Characterization Facility at the University of Chicago. Samples were cut into rectangular strips (length x width x thickness = 25

mm x 3.5 mm x 0.5 mm) and pulled uniaxially at a strain rate of 10 mm/min (ca. 100 %/min). Specimens were clamped using silicon rubber clamps to prevent tearing of the soft material.

Atomic Force Microscopy (AFM). Atomic force microscopy was performed using an Asylum Research Cypher ES AFM with BlueDrive in the University of Chicago's Materials Preparation and Measurement Laboratory as part of the NSF Materials Research Science and Engineering Center (MRSEC). Scans were conducted in tapping mode using a NanoWorld Arrow™ Ultra High Frequency (UHF) AFM probe.

As-Cast Film Preparation: AFM samples were prepared on 15 mm round glass coverslips following procedures that mirrored the film preparation (see page S15). Samples were drop-cast onto the coverslip from the same chloroform solution used to prepare the equivalent film. Drop-cast samples were dried overnight at room temperature, then further dried at 60 °C for 24 hours.

Annealed Film Preparation: As cast samples were placed onto a 25 mm stainless steel parallel plate geometry on the ARES-G2 rheometer. The top plate was lowered to protect the sample, but was never put in direct contact with the sample surface. After loading the sample, the attached FCO oven was heated to 200 °C and the sample was held isothermally for 30 minutes. Following the annealing process, the sample was either quenched by quickly removing the hot sample and dropping into a dewar of liquid nitrogen or slowly cooled using the temperature ramp function on the ARES-G2 (1 °C/min).

Dynamic Mechanical Analysis (DMA). DMA was performed using the TA Instruments RSA-GA DMA with 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. Pressed films were cut on a warm plate (temperature slightly above T_g of the network) into strips ca. 4 mm wide and ca. 10 mm long, then cooled back to room temperature on a flat surface. The strips were loaded into the tensile geometry above the T_g of the network (for example, 60 °C for **4N$_{100}$** or 40 °C for **4N$_{50}$H$_{50}$**) and finger tightened to prevent film breakage and ensure good contact with the tensile geometry. A typical procedure included an amplitude sweep (0.01% – 5%) above T_g at a frequency of 1Hz to define the linear viscoelastic region (LVR) as well as maximize the oscillatory force signal being picked up by the instrument. After the amplitude sweep, the samples were cooled to -20 °C using an IsoForce Temperature Ramp (0.01 N tension, 3.0 °C/min). Samples were soaked for 1 minute at -20 °C and a second amplitude sweep (0.01% - 5%) was conducted at a frequency of 1 Hz to optimize conditions below T_g. The samples were quite brittle at low temperatures and as such, it was important to closely monitor both the cooling process and the amplitude sweep for critically high force values (> 15 N) that could break the films.

Once parameters had been identified for optimal amplitude and frequency, temperature ramps could be conducted. Samples were loaded as previously described. A typical procedure included cooling to -20 °C using the IsoForce temperature ramp (0.01 N tension, 3.0 °C/min) and holding at -20 °C for 1 minute. Following the cooling step, conditioning options were enabled to account for automatic axial force adjustment (0.01 N ± 0.5 N tension, Set Initial Value box unchecked) and automatic strain adjustment set to the minimum oscillatory force for LVR above T_g and maximum oscillatory force for LVR below T_g as determined by the amplitude sweeps.

Samples were then heated using the oscillatory temperature ramp procedure from -20 °C to 150 °C (or until failure) at a rate of 3.0 °C/min with an amplitude set in the LVR of the -20 °C amplitude sweep and a frequency of 1 Hz.

Shear Rheology. Rheology was performed using the TA Instruments RSA-G2 ARES with 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.

As the thia-Michael films softened significantly during DMA studies, it was useful to probe the plateau regime via shear rheology which is more suited to evaluating soft, viscoelastic solids. Pressed films were cut into 8 mm circles using a die on a warm surface (just above T_g of the sample). The circular samples were loaded onto the parallel plate geometries warmed above T_g, centered, and heated further to pressing temperatures (70 °C or 90 °C) with an axial compression force of 0.1 N. Samples were held at pressing temperatures for 1-5 minutes until geometry gap was no longer increasing indicating an equilibrated sample. Compression force was adjusted to 0.01 N and sample was cooled to 80 °C for amplitude and frequency sweeps to establish a linear viscoelastic region (LVR). The LVR amplitude and frequency were used to parameterize the temperature sweeps.

Samples were cooled to 60 °C, held for 5 minutes, and temperature ramp studies were conducted. Conditioning options were set to 0.01 N axial compression force and strain adjustments were disabled. Temperature sweeps were conducted at 3 °C/min from 60 °C to 150 °C, held at 150 °C for 10 minutes, then ramped down to 60 °C again at the same rate. After holding isothermally at 60 °C for 10 minutes, the sample was ramped once again to 150 °C. The second heating was used for reported measurements.

Synthetic methods

Synthesis of benzalcyanoacetate *mono*-X

R-Benzalcyanoacetates (***mono*-X**)
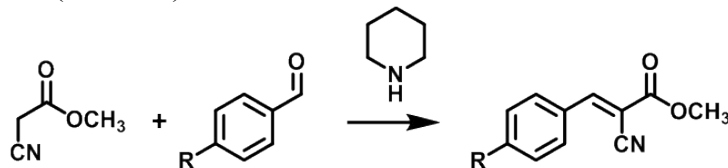
Methyl cyanoacetate (2 mg, 2.01 mmol, 0.16 M) and R-benzaldehyde (2.01 mmol) were combined in a round bottom flask with methanol and catalytic piperidine. The reaction was stirred at room temperature for three hours. After 3 hours, the solution was placed in the freezer for 24 hours and the precipitate was collected via vacuum filtration. Nitro- (***mono*-N**), bromo- (***mono*-B**), hydrogen- (***mono*-H**), and methoxy-substituted (***mono*-M**) electrophiles were synthesized using this method.

4-Nitrobenzalcyanoacetate (*mono*-N): ^{1}H NMR (500 MHz in CDCl$_3$; δ ppm:). ^{13}C NMR (126 MHz in CDCl$_3$; δ ppm: 162.11, 152.22, 149.94, 136.98, 131.75, 124.52, 114.68, 107.06, 54.06). GC-MS (232.20, [M]). Yield by mass = 70%.

4-Bromobenzalcyanoacetate (*mono*-B). ^{1}H-NMR (500 MHz in d_6-DMSO; δ ppm: 3.88 (*s*, 3H), 7.84 (*d*, 2H), 8.00 (*d*, 2H), 8.43 (*s*, 1H)). ^{13}C-NMR (101 MHz in CDCl$_3$; δ 162.91, 153.98, 132.88, 132.46, 130.35, 128.59, 103.31, 53.73). GC-MS (MW = 266.09). Yield by mass = 25%.

Benzalcyanoacetate (*mono*-H): ^{1}H NMR (500 MHz in CDCl$_3$; δ ppm:). ^{13}C NMR (126 MHz in CDCl$_3$; δ ppm: 163.06, 155.41, 133.53, 131.48, 131.21, 129.40, 115.57, 105.62, 53.53). GC-MS (187.20, [M]). Yield by mass = 75%.

4-Methoxybenzalcyanoacetate (*mono*-M): ^{1}H NMR (500 MHz in CDCl$_3$; δ ppm:). ^{13}C NMR (126 MHz in CDCl$_3$; δ ppm: 164.06, 163.83, 154.86, 133.91, 124.48, 116.41, 114.98, 99.01, 55.84, 53.40). GC-MS (217.22, [M]). Yield by mass = 70%.
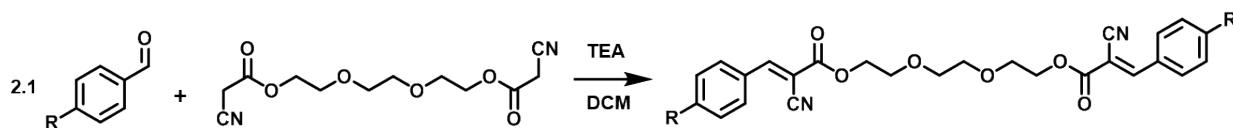
Synthesis of triethylene glycol bis(cyanoacetate)
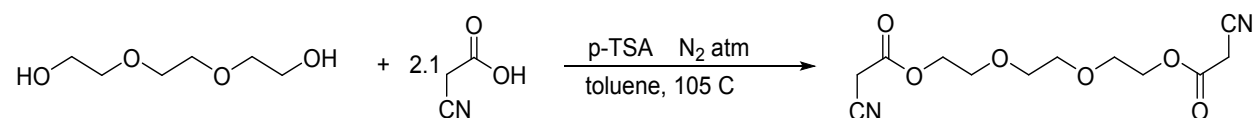
The ditopic compounds were synthesized in two steps as previously reported by Sassi and Gupta.[2] In the first step, building the bis-cyanoacrylate core, triethylene glycol (TEG, 20.0 g, 0.13 mol, 0.78 M) and cyanoacetic acid (23.2 g, 0.27 mol) were combined in a 500 mL round bottom flask with 0.12 molar equivalents of catalytic *p*-toluenesulfonic acid monohydrate (3.0 g, 0.016 mol) in toluene (166.7 mL). The setup was equipped with a waterless condenser and Dean-Starks trap, heated to 105 °C under nitrogen atmosphere, and stirred using a magnetic stir bar for ca. 18 hours (overnight). Once complete, the solvent was removed via rotary evaporation. The resulting yellow oil was diluted with ca. 300 mL methylene chloride (DCM) and remaining salts were filtered out. The filtrate was washed thoroughly (3 or more times) with brine (sodium chloride - saturated water) and dried with magnesium sulfate. DCM was removed from the solution via rotary evaporation and the resulting yellow oil was dried overnight under high vacuum (MW = 284.15 g/mol, yield = 70% by mass). ^{1}H NMR (500 MHz in CDCl$_3$; δ ppm: 3.54 (*s*, 2H), 3.68 (*s*, 2H), 3.76 (*t*, 2H), and 4.39 (*t*, 2H)). ^{13}C NMR (101 MHz in CDCl$_3$; δ 163.11, 112.99, 70.68, 68.62, 65.77, 24.73). This TEG bis(cyanoacetate) product routinely contained some contaminate of

starting material, however the contaminate did not affect the second step and was sufficiently removed in the workup of the final product.

Triethylene glycol bis(4-nitrobenzalcyanoacetate) (1N). TEG bis(cyanoacetate) (5 g, 0.018 mol. 0.14 M) and 4-nitrobenzaldehyde (5.74 g, 0.038 mol) were added a 250 mL flask round bottom flask with dichloromethane (DCM, 130 mL) and 0.15 molar equivalents of catalytic triethylamine (TEA, 0.3 mL, 0.003 mol). The flask was then placed under a nitrogen atmosphere and allowed to stir using a magnetic stir bar overnight. DCM was removed using rotary evaporation and the resultant oil was triturated in MeOH two hours. The solution was filtered and a solid powder was collected. This trituration process was repeated until the filtrate was clear and colorless, leaving behind a reddish, clumpy powder. ^{1}H NMR (500 MHz in CDCl$_3$; δ ppm: 3.77 (s, 2H), 3.89 (t, 2H), 4.54 (t, 2H), 8.16 (d, 2H), 8.34 (s, 1H), and 8.37 (d, 2H)), ^{13}C NMR (126 MHz in CDCl$_3$; δ 161.95, 152.06, 149.78, 136.82, 131.59, 124.36, 114.36, 106.90, 53.90). MALDI-MS (573.46, [M]+Na$^+$). Yield by mass = 45%.

Triethylene glycol bis(4-bromobenzalcyanoacetate) (1B). TEG bis(cyanoacetate) (5.00 g, 0.018 mol. 0.14 M) and 4-bromobenzaldehyde (7.03 g, 0.038 mol) were added to a 250 mL flask round bottom flask with dichloromethane (DCM, 130 mL) and 0.15 molar equivalents of catalytic triethylamine (TEA, 0.3 mL, 0.003 mol). The flask was then placed under a nitrogen atmosphere and allowed to stir using a magnetic stir bar overnight. DCM was removed using rotary

evaporation and the resultant oil was triturated in MeOH two hours. The solution was filtered and a solid powder was collected. This trituration process was repeated until the filtrate was clear and colorless. ^{1}H NMR (500 MHz in CDCl$_3$; δ ppm: 3.76 (*s*, 2H), 3.87 (*t*, 2H), 4.50 (*t*, 2H), 7.66 (*d*, 2H), 7.87 (*d*, 2H), and 8.21 (*s*, 1H)), ^{13}C NMR (101 MHz in CDCl$_3$; δ 162.25, 153.81, 132.71, 132.30, 130.23, 128.42, 115.14, 103.39, 70.90, 68.76, 65.92). Yield by mass = 64%.

Triethylene glycol bis(benzalcyanoacetate) (1H). TEG bis(cyanoacetate) (5.00 g, 0.018 mol. 0.14 M) and benzaldehyde (4.03 g, 0.038 mol) were added to a 250 mL flask round bottom flask with dichloromethane (DCM, 130 mL) and 0.15 molar equivalents of catalytic triethylamine (TEA, 0.3 mL, 0.003 mol). The flask was then placed under a nitrogen atmosphere and allowed to stir using a magnetic stir bar overnight. DCM was removed using rotary evaporation and the resultant oil was triturated in MeOH two hours. The solution was filtered and a solid powder was collected.
 This trituration process was repeated until the filtrate was clear and colorless. ^{1}H NMR (500 MHz in CDCl$_3$; δ ppm: 3.77 (*s*, 2H), 3.88 (*t*, 2H), 4.51 (*t*, 2H), 7.53 (*t*, 2H), 7.58 (*t*, 1H), 8.01 (*d*, 2H) and 8.28 (*s*, 1H)). ^{13}C NMR (101 MHz in CDCl$_3$; δ 162.51, 155.35, 133.40, 131.45, 131.15, 129.30, 115.36, 102.80, 70.91, 68.80, 65.81). MALDI-MS (483.47, [M]+Na$^+$). Yield by mass = 51%.

Triethylene glycol bis(4-methoxybenzalcyanoacetate) (1M). TEG bis(cyanoacetate) (5.00 g, 0.018 mol. 0.14 M) and 4-methoxybenzaldehyde (5.17 g, 0.038 mol) were added to a 250 mL flask round bottom flask with dichloromethane (DCM, 130 mL) and 0.15 molar equivalents of catalytic triethylamine (TEA, 0.3 mL, 0.003 mol). The flask was then placed under a nitrogen atmosphere and allowed to stir using a magnetic stir bar overnight. DCM was removed using rotary evaporation and the resultant oil was triturated in MeOH two hours. The solution was filtered and

a solid powder was collected. This trituration process was repeated until the filtrate was clear and colorless. ^{1}H NMR (500 MHz in CDCl$_3$; δ ppm: 3.77 (*s*, 2H), 3.87 (*t*, 2H), 3.91 (*s*, 3H), 4.48 (*t*, 2H), 7.01 (*d*, 2H), 8.02 (*d*, 2H), and 8.20 (*s*, 1H)). ^{13}C NMR (101 MHz in CDCl$_3$; δ 163.86, 163.14, 154.66, 133.74, 124.36, 116.08, 114.79, 99.14, 70.90, 68.87, 65.54, 55.64). MALDI-MS (543.53, [M]+Na$^+$). Yield by mass = 51%.

Preparation of disulfide-crosslinked films

CAUTION—Reaction is exothermic and may release steam and splatter as network forms if peroxide is added too quickly.

4 g (0.0219 mol) of 2,2′-(Ethylenedioxy)diethanethiol and 0.107 g (0.219 mmol) of PTMP were dissolved in 25 mL of THF and added to a 250 mL beaker with a stir bar. At this point, 0.065 g of sodium iodide was dissolved in a minimal amount of deionized-water and, while stirring, added to the mixture in the beaker. Slowly, drop-wise, ~7 mL (>1.5x molar excess relative to thiol functional groups) of 30% aq. H_2O_2 solution was added to the beaker, gelation was observed as peroxide was added (white milky fluid). Following gelation, solution abruptly turned yellow (formation of I_2 in situ) as network precipitated out of solution. Network is yellow due to trapped I_2 side-product. Solid network material was isolated from beaker and added to a clean 500 mL beaker with stirrer for washing and iodine removal. The network was rinsed of unused reagents using 5 x 100 mL of THF. To remove Iodine I_2, 100 mL of THF was first added and stirred for 30 minutes until the networks fully swelled. A 20 mL aqueous solution of 70 mg sodium thiosulfate (slight molar excess w.r.t. sodium iodide) was added. After network is no longer visibly yellow, network chunks are further rinsed using 5 x 100 mL of acetone. Finally, the material is rinsed with 10 x 200 mL DI-water in order to remove sodium iodide, acetone, THF, and other remaining impurities. Networks were then freeze-dried using a lyophilizer in order to remove as much water as possible prior to compression molding. Finally, the polymer was molded using a Carver laboratory press at 135 °C using an applied force of 10,000 psi for 30 minutes, which produced homogenous, transparent and rubbery films with a thickness of ~600 μm.

Preparation of thia-Michael films

The electrophile(s), **1**, (100 mg/mL) and PTMP (300 mg/mL) were dissolved separately in chloroform, then combined and stirred for two hours at 50 °C, allowing the system to homogenize. It is important to note here that heat is not required for this reaction to take place (as demonstrated by the initial NMR studies at room temperature), however, the samples were heated in order to ensure that all components were sufficiently soluble. After two hours, the solution was poured onto a Teflon dish and dried, overnight, at room temperature. An additional 24 hours of drying in a vacuum oven at 60 °C under vacuum was carried out, followed by a final drying step under vacuum at 150 °C for 30 minutes to complete the drying process, as confirmed by TGA. The dried films were compression molded at 90 °C (70 °C for films containing only **1H** or **1M**) for ten minutes under 10,000 psi with a 400 µm steel spacer and Kapton®/Teflon® blend substrates.

Overview of film properties

Table S1. Dynamic thia-Michael films and corresponding material properties.

Sample Name	T_g [a,†] (°C)	T_{high} [b] (°C)	$G'_{25\,°C}$ [c] (MPa)	$G'_{80\,°C}$ [d] (kPa)	Strain at break (%)[†]	Stress at break (MPa)[†]
2N$_{100}$	19.5 ± 3.7	133	2100	342.3	1.5 ± 0.3	20 ± 3
2B$_{100}$	-0.5 ± 1.6	n/a	n/a	n/a	n/a	n/a
2H$_{100}$	-10.8 ± 4.9	114	0.64	46.0	500 ± 200	$0.17 \pm .03$
2M$_{100}$	-20.9	113	n/a	n/a	n/a	n/a
2N$_{50}$B$_{50}$	14.0 ± 0.8	135	2200	180.7	38 ± 6	21 ± 3
2N$_{50}$H$_{50}$	1.7 ± 2.9	109	1800	110.6	150 ± 40	2.5 ± 0.4
2N$_{50}$M$_{50}$	1.0 ± 2.0	110	150	10.4	680 ± 70	0.5 ± 0.1

[†] Error calculated as standard deviation of $n \geq 3$,
[a] Calculated from onset of glass transition,
[b] Calculated from onset of second thermal transition,
[c] Determined by observed tensile storage modulus (E') at 25 °C,
[d] Determined by observed shear storage modulus (G') at 80 °C.

CHARACTERIZATION

Equilibrium NMR measurements

Titration of *mono*-X with 1-octanethiol. The benzalcyanoacetate species (***mono*-X**) were titrated with 1-octanethiol in anhydrous deuterated methyl sulfoxide (d_6-DMSO) (Figure S7A). The DMSO was treated with activated molecular sieves before use in the titration experiments to reduce the amount of water present. Stock solutions of ***mono*-X** (0.025 M in d_6-DMSO, **T1**) were prepared in 5 mL batches. The **T1** solution (0.782 mL) was added to 0.218 mL (50 molar equivalents to ***mono*-X**) of 1-octanethiol, resulting in a concentrated solution (**T2**) with total concentrations of ***mono*-X** and 1-octanethiol at 0.0195 M and 1.25 M, respectively. The **T2** solution was allowed to equilibrate for 18 hours.

Following the equilibration of **T2**, the titration study commenced. In an NMR tube, 0.782 mL **T1** and 0.218 mL of d_6-DMSO were combined, ensuring that the concentration of ***mono*-X** remained the same throughout the titration experiment. To this sample, **S2** was added followed by an 18 hour equilibration. After the equilibration period, the sample was analyzed via ^{1}H NMR spectroscopy (Figure S2), then additional **S2** was added to the NMR tube and the process was repeated.

Quantitatively, the extent of adduct formation was defined by monitoring the growing doublets between 4.50 – 5.20 ppm (H_a and H_b, respectively in Figure S2) in conjunction with the subsequent loss of ***mono*-X** by the shrinking singlet at ca. 8.50 ppm (D, in Figure S2). As the total integration of these peaks accounts for the total amount of benzalcyanoacetate moiety (reacted and unreacted) in the system, the extent of reaction at each titration step could be calculated by comparing the area under each peak. For example, during the titration of ***mono*-H** (Figures S2), if the integral of the singlet at 8.44 ppm was one and the integral of the doublets at 4.52 ppm was

also one, then half of the original electrophile in the solution was reacted with 1-octanethiol and the concentration of both **mono-X** and the adduct at that point would be 9.75 x 10^{-3} M (0.0195 M **mono-H** in the starting solution divided by two). The equilibrium constant (K_{eq}) could then be extrapolated from the titration experiments by plotting the concentration of the product, [P], versus the thiol concentration, [SH], and fitting the data using a 1:1 binding isotherm where $[E]_0$ is the starting electrophile concentration.

$$[P] = \frac{[E]_0[SH]}{K_{eq}^{-1} + [SH]}$$

In reactions with 1-octanethiol, **mono-N**, **mono-H**, and **mono-M** were determined to possess a K_{eq} of 470 M^{-1}, 58 M^{-1}, and 9 M^{-1}, respectively. The solution-based experiments revealed that the K_{eq} of the thia-Michael reaction did, in fact, scale with changes in electron-donating/withdrawing capabilities of the *para*-substituent, as demonstrated by the positive linear trend (ρ = 1.46) in the resulting Hammett plot.
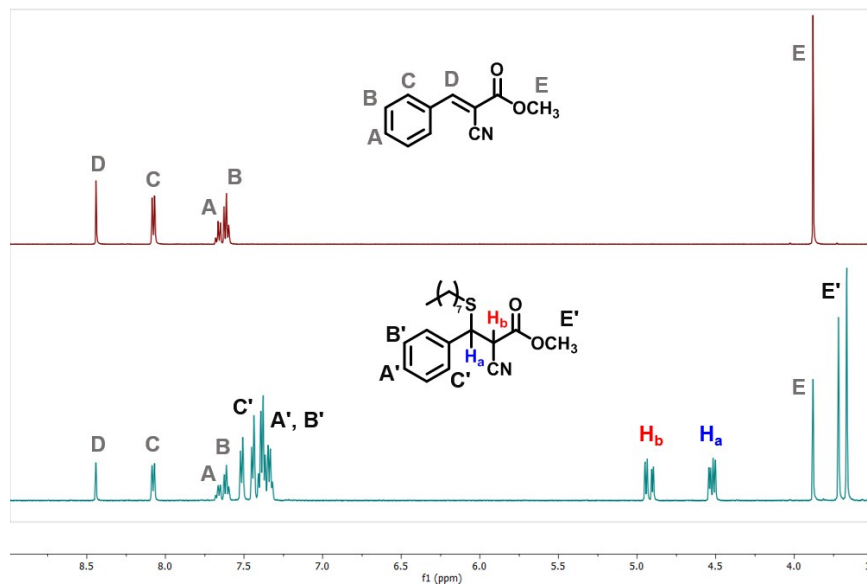
Figure S2. *Top* ^{1}H NMR (500 MHz, CDCl$_3$) spectrum of **mono-H** prior to titration. *Bottom* ^{1}H-NMR of **mono-H**+thiol adduct following titration procedure with key peaks highlighted.
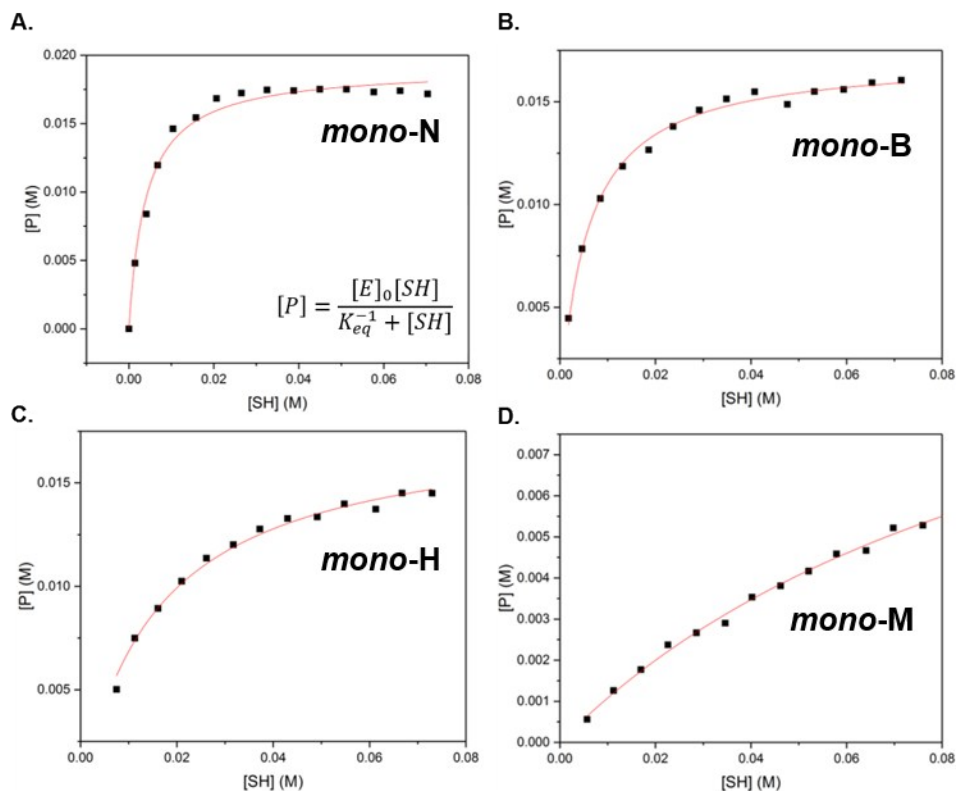
A.

B.

C.

D.

$$[P] = \frac{[E]_0[SH]}{K_{eq}^{-1} + [SH]}$$

Figure S3. Plot of product concentration ([P]) versus free thiol concentration ([SH]) during the titration of A) *mono*-N, B) *mono*-B, C) *mono*-H, and D) *mono*-M with 1-octanethiol. Result were fit with the 1:1 binding isotherm (red line, equation inset in A).

Table S2. Summary of experimental equilibrium constants measure at room temperature in d_6-DMSO.

	mono-M	*mono*-H	*mono*-B	*mono*-N
σ_{para}	-0.27	0	0.23	0.78
K_{eq} (M^{-1})	9.4 ± 1.0	58.0 ± 3.8	160.0 ± 20.0	470.0 ± 150.0

Equilibrium association of mono-X and 1-octanethiol. Individual stock solutions (200 mM, ~1.5 mL) of benzalcyanoacetate species (*mono-X)* and 1-octanethiol were prepared in d6-DMSO that had been treated with molecular sieves. Equal volumes of each solution (typically 0.25 mL) were then added to a mixing vial (resulting in 100 mM concentrations of both species) and the contents were quickly added to an NMR tube via a syringe. The sample was then introduced into a preheated NMR and allowed to equilibrate for 5 minutes before collecting data to ensure homogeneous sample temperature. Samples were monitored until equilibrium was reached (typically 1-3 hours at 25 ºC).

Representative peaks of interest and the governing equation for monitoring adduct formation are displayed below in Figure S4.
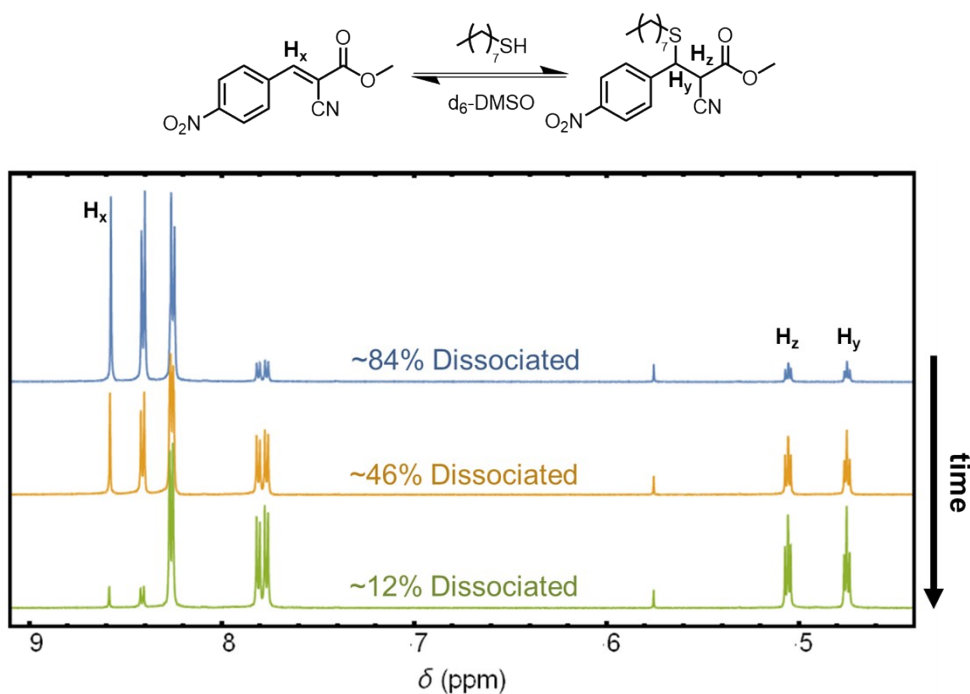
$$\frac{[Dissociated]_t}{[Dissociated]_0} = \frac{[Dissociated]_t}{[Associated]_t + [Dissociated]_t} = \frac{\int H_x}{\int H_x + 0.5(\int H_y + \int H_z)}$$

Figure S4. Representative NMR scans obtained during an equilibrium experiment and the integrations used to monitor association, in this case mono-N is used as the Michael acceptor in 25 °C conditions.
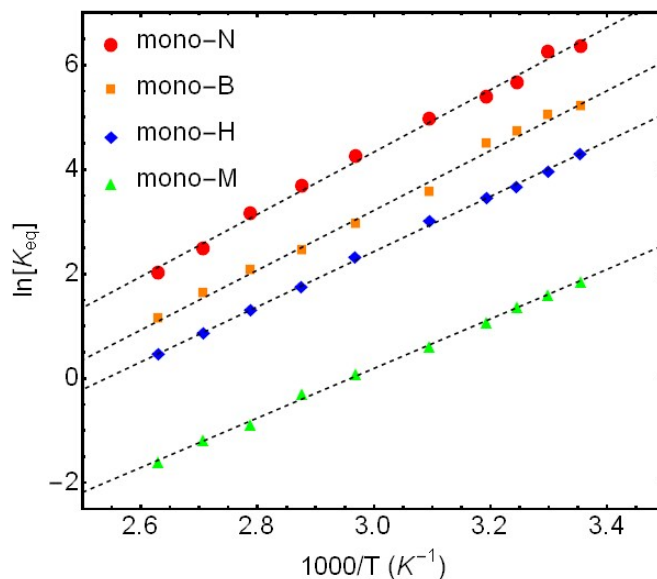
Figure S5. Van't Hoff plot of calculated K_{eq} values from main manuscript Figure 2b.

The K_{eq} values shown in Figure S5 were calculated by the following formula (assuming second order association and first order dissociation). C_0 was fixed at 0.1 M for all experiments

$$K_{eq} = \frac{[Associated]}{[mono-X]*[thiol]} = \frac{\%Associated}{C_0*(1-\%Associated)^2}$$

Table S3: Results of linear fits to the van't Hoff data (error reported from standard error of fit)

Compound	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
mono-N	-49.6 ± 1.3	-113 ± 4
mono-B	-47.6 ± 1.3	-116 ± 4
mono-H	-43.9 ± 0.5	-112 ± 1
mono-M	-39.4 ± 0.6	-117 ± 2

Raman spectroscopic measurements

The thiol/disulfide content in the thia-Michael films was evaluated by comparing the Raman spectra of the networks to both the starting thiol component (PTMP) and a network formed via disulfide bonds. A free thiol appears at 2570 cm^{-1} in the spectra of neat PTMP (black, Figure S5A), however, this peak is eliminated as the reactive thiol groups participate in the thia-Michael reaction. As the elimination of thiols from the spectra could equally be attributed to disulfide formation within the network, the spectra were compared to a control sample composed of diethylene glycol dithiol and PTMP crosslinked via disulfide bonds (sample prepared and donated by Arvin Sookezian). As shown in Figure S6B, while a broad disulfide peak is clearly visible at ca. 510 cm^{-1} in the control sample, no notable peaks were found in any of the thia-Michael networks that could be definitively characterized as a disulfide bond.
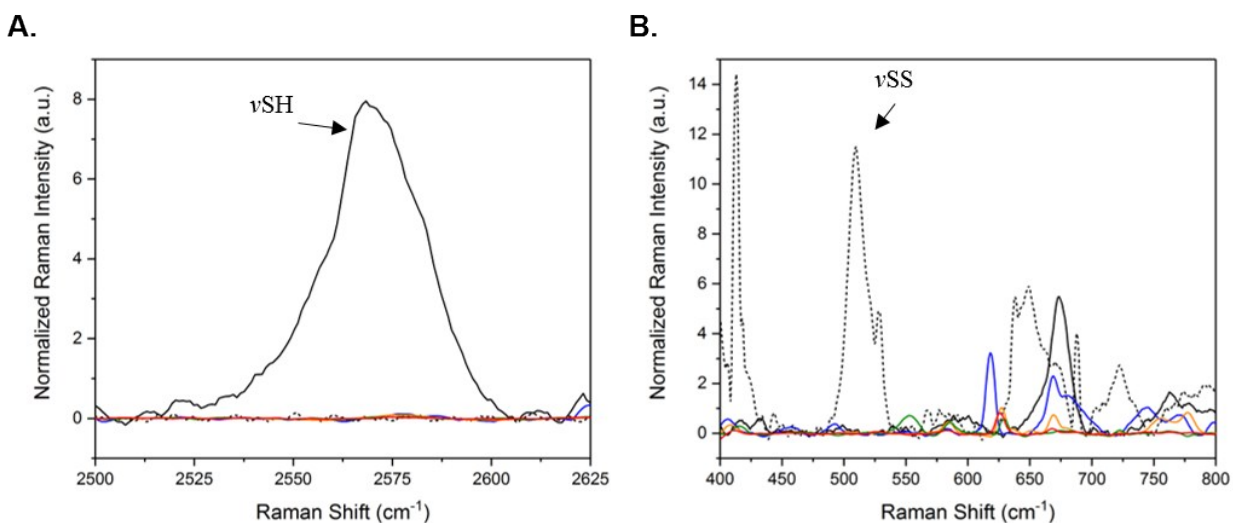
Figure S6. Raman spectra of A) thiol regime and B) disulfide regime highlighting the disappearance of the thiol peak as well as the absence of disulfide formation within the thia-Michael networks. PTMP (black), disulfide network (dotted line), **2N$_{100}$** (red), **2H$_{100}$** (blue), **2B$_{100}$** (orange), **2M$_{100}$** (green).
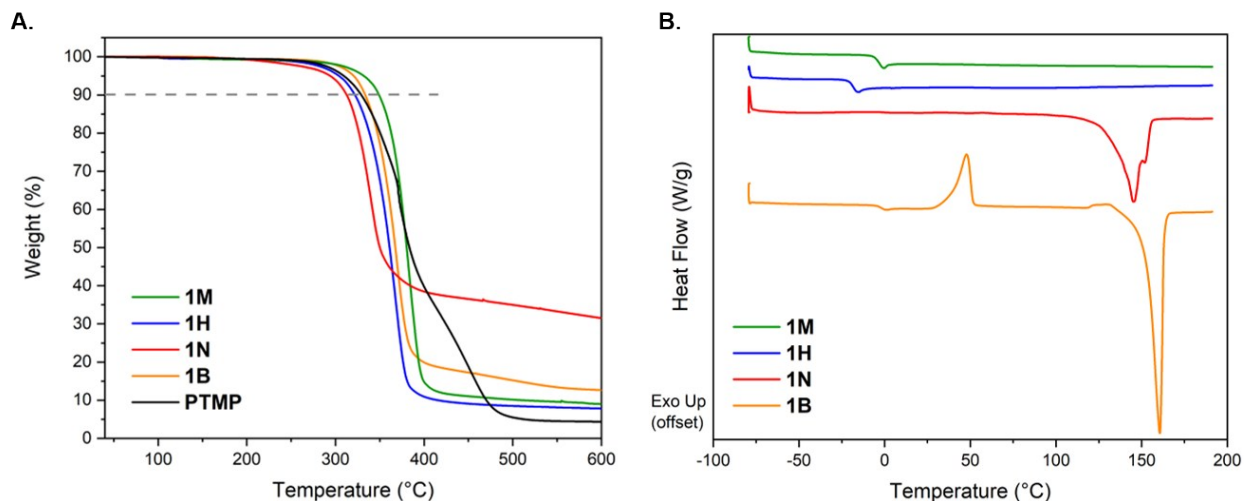
Thermal characterization

Figure S7. A) TGA data for **1N** (red), **1B** (orange), **1H** (blue), and **1M** (green) and PTMP (black). 10% weight loss is marked by the gray dashed line (Heating rate = 10 °C/min). B) DSC curves of **1N** (red), **1B** (orange), **1H** (blue), and **1M** (green) showing results of second heating (exotherm up, second heating shown, ramp rate = 10 °C/min, curves offset for ease of viewing).
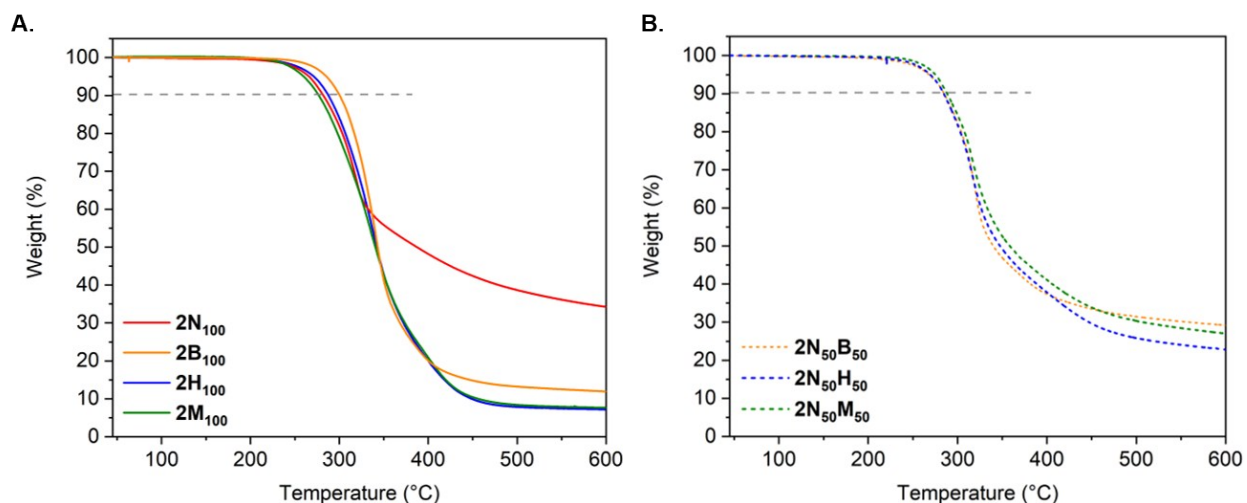

Figure S8. A) TGA data for $2N_{100}$ (red), $2B_{100}$ (orange), $2H_{100}$ (blue), and $2M_{100}$ (green). B) TGA data for $2N_{50}B_{50}$ (dashed orange), $2N_{50}H_{50}$ (dashed blue), and $2N_{50}M_{50}$ (dashed green). (Heating rate = 10 °C/min).
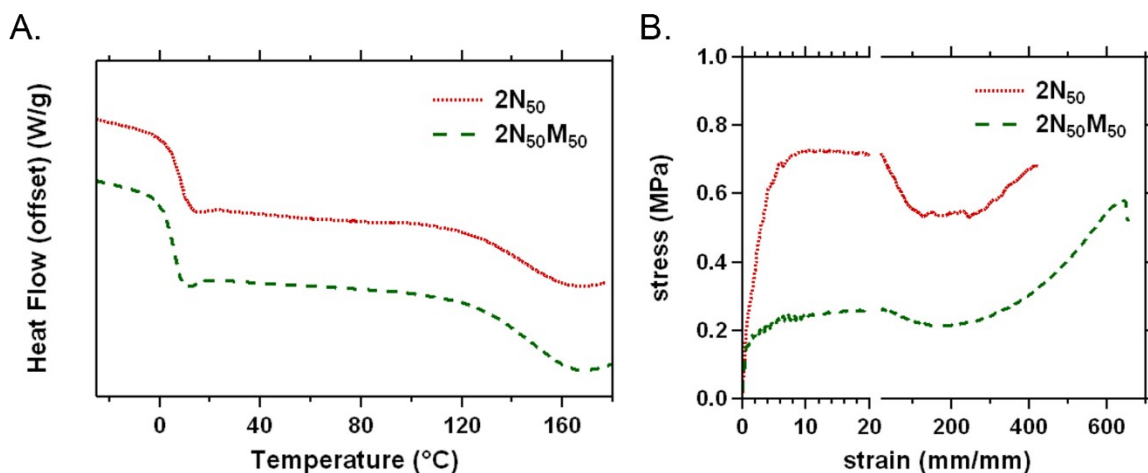
Figure S9. a) Differential scanning calorimetry (DSC) curves for **2N$_{50}$** and **2N$_{50}$M$_{50}$**, showing similar thermal behaviours. b) Stress-strain curves (strain rate = 10 mm/min, 25 °C) for **2N$_{50}$** and **2N$_{50}$M$_{50}$**.
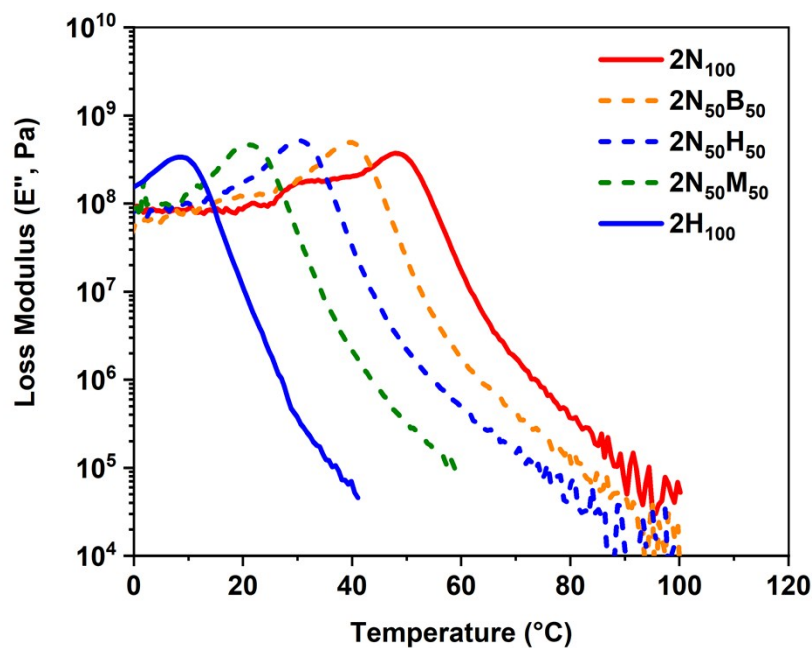
Figure S10. DMA loss modulus results for **2N$_{100}$** (red), **2N$_{50}$B$_{50}$** (dashed orange), **2N$_{50}$H$_{50}$** (dashed blue), **2N$_{50}$M$_{50}$** (dashed green), and **2H$_{100}$** (blue).
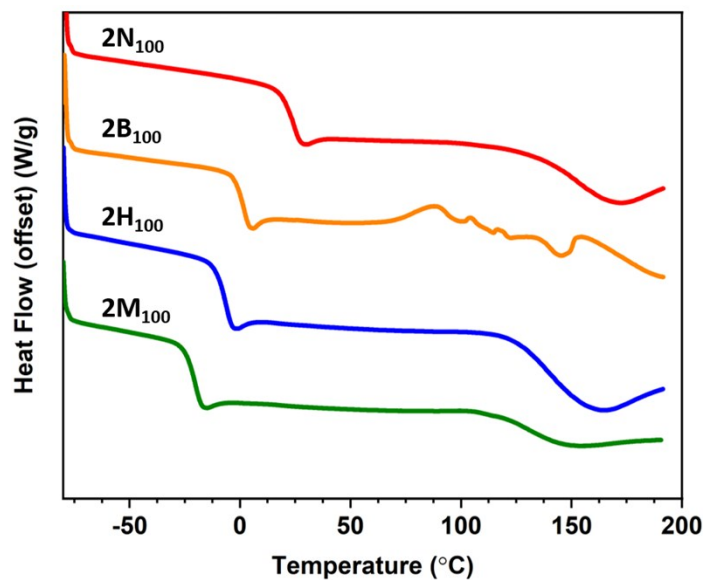
Figure S11. Differential scanning calorimetry (DSC, exotherm up) 2nd heating curve of **2N$_{100}$** (red), **2B$_{100}$** (orange), **2H$_{100}$** (blue), and **2M$_{100}$** (green). Ramp rate = 10 °C/min; DSC plots offset for ease of viewing.
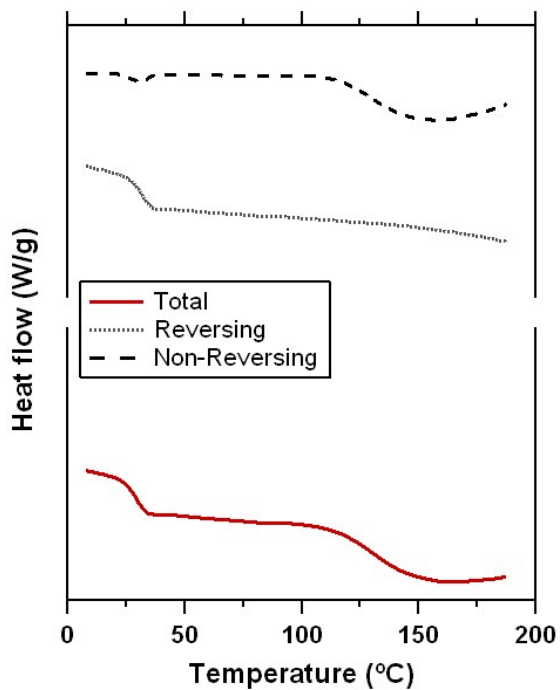

Figure S12. Modulated DSC of **2N$_{100}$** (5 °C/min, 1 °C amplitude, 60 s period) showing T$_g$-like behavior for the lower thermal transition (strong reversing character) and strongly non-reversing character for the upper thermal transition.
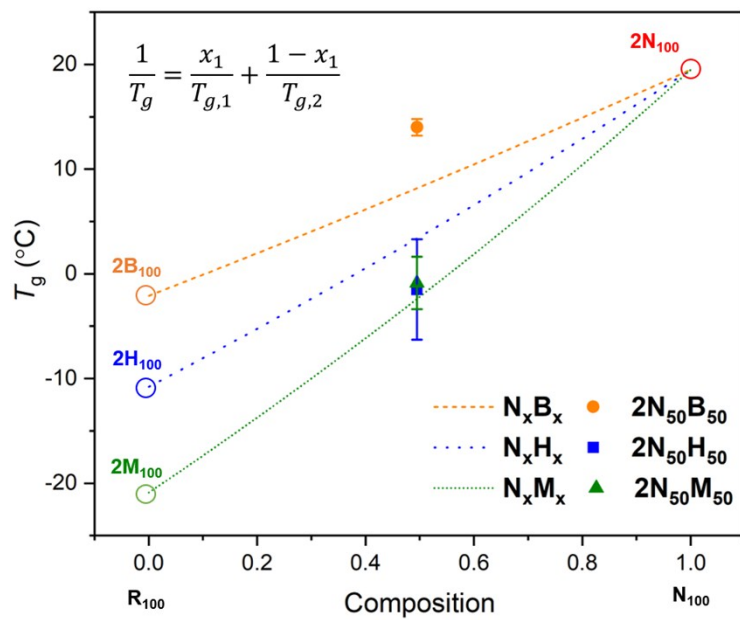
Figure S13. Fit of **2N$_{50}$B$_{50}$** (orange), **2N$_{50}$H$_{50}$** (blue), and **2N$_{50}$M$_{50}$** (green) to Fox equation (dotted lines, equation inset) for polymer blends.
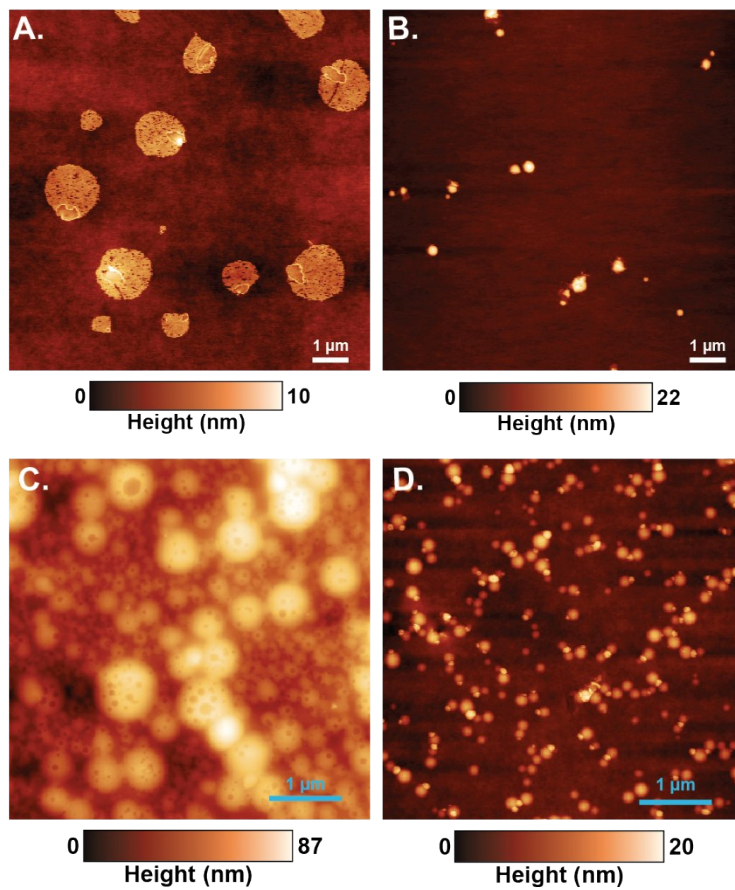
Atomic Force Microscopy

Figure S14. AFM height images for A) **2H$_{100}$**, B) **2M$_{100}$**, C) **2N$_{50}$H$_{50}$**, D) **2N$_{50}$M$_{50}$**.
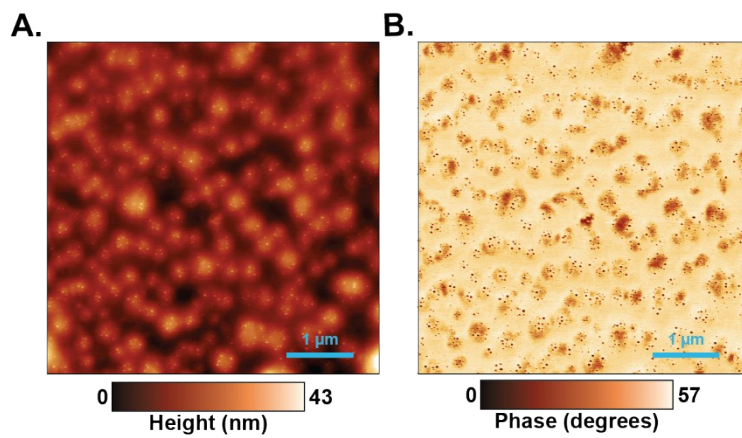
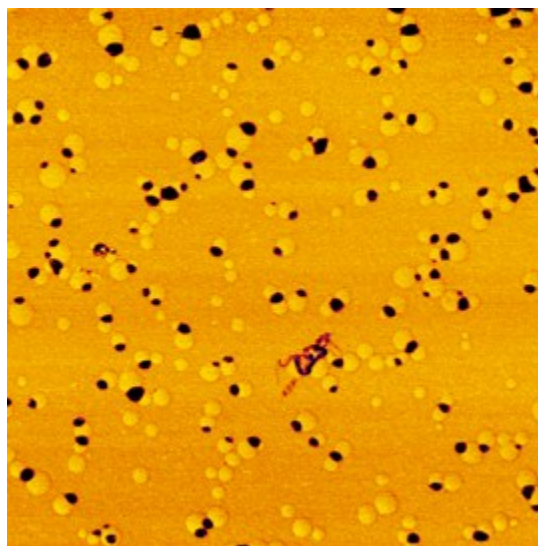Figure S15. AFM A) height and B) phase images for $2N_{50}B_{50}$.

Figure S16. AFM phase image of $2N_{50}M_{50}$ (same as Figure 5d) recolored to highlight phase shapes.

Shape memory experiments

Shape memory test procedure. A sample was cut into a strip (ca. 10 mm x 3 mm x 0.4 mm) and mounted onto the tensile geometry in the DMA instrument. During the course of the one-way shape memory experiment, the samples were equilibrated at 60 °C for 10 minutes under no tensile force. After equilibration, an instantaneous tensile force of 0.5 N was applied to the sample and held while the internal oven temperature was cooled to 20 °C at a rate of 5 °C/minute. The sample was held under 0.5 N force for 10 additional minutes after cooling and the strain was recorded as the maximum strain, ε_m. The force was removed, revealing the sample's new, temporary shape and the unloading strain, ε_u, was measured. The fixing ratio (sample's capacity to hold its shape in the absence of applied force, R_f) was determined by calculating the percent strain change after unloading, $(\varepsilon_u/\varepsilon_m)*100$. After 10 minutes at 20 °C under no tensile force, the sample was reheated to 60 °C at 5 °C/minute and the strain after recover, ε_r, was evaluated. Finally, the recovery ratio (extent to which the sample returns to its original shape, R_r) was determined as the percent strain recovered from the maximum strain, $(\varepsilon_m - \varepsilon_r/\varepsilon_m)*100$.

The reprogrammable shape memory experiment was conducted in a similar fashion. A **2N$_{50}$H$_{50}$** strip was equilibrated in the tensile fixture of a DMA at 90 °C (just below the second phase transition temperature) for 10 minutes. At this temperature, the film creep can be seen as the instrument moves to keep the force on the material at zero. After ten minutes, an instantaneous 0.1 N tensile force was applied to the strip and the film was cooled to 20 °C at a rate of 5 °C/minute. Once cooled, the force was removed from the film and the first fixing ratio of the new, permanent shape was determined ($R_{f,1} = 100\%$). Then the sample was reheated to 60 °C to set a temporary shape. Upon reheating, some recovery of the original shape was observed ($R_{r,1} = 31\%$). Once equilibrated at 60 °C, 0.5 N tensile force was applied (same force as used in the one-way shape

memory experiments) and the sample was once again cooled to 20 °C. Once the force was removed, the fixing ratio of new, temporary shape was determined ($R_{f,2} = 100\%$). The sample was reheated to 60 °C and the temporary Shape 2 recovered back to the programmed Shape 1.
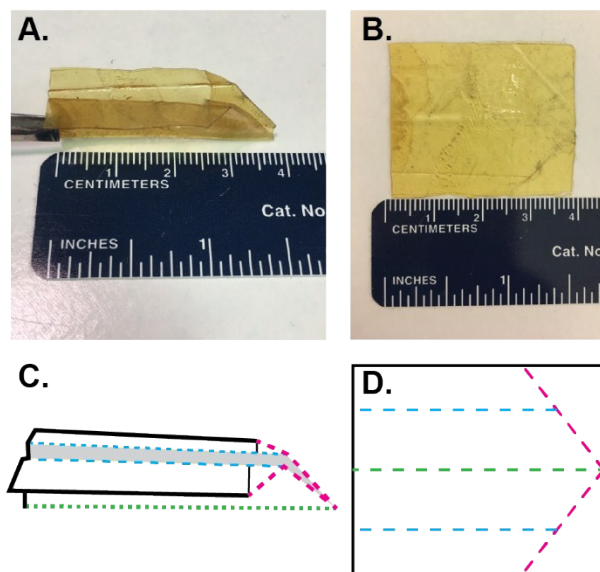

Figure S17. A) **2N$_{50}$H$_{50}$** film folded into an airplane geometry, B) film from image A unfolded showing creases where folds were made, C) cartoon showing plane with creases highlighted, D) 2D cartoon of airplane-forming creases as they appear on a flat surface.
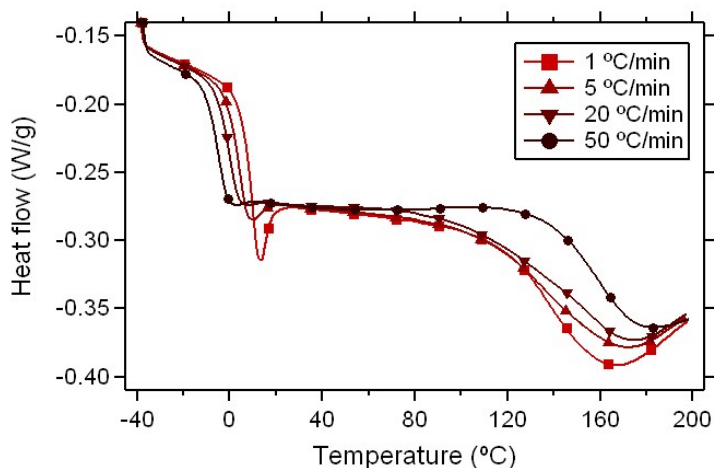
Cooling rate experiments

Figure S18. DSC heating curves (10 °C/min) of a single $2N_{50}H_{50}$ sample cooled at different rates from 200 °C to -40 °C. Notably, slow cooling rates correspond to an increased amount of hard phase as evinced by the increased peak intensity at elevated temperatures. Additionally, slower cooling rates also result in higher transition temperatures for the lower temperature transition, in agreement with typical glass transition behavior.
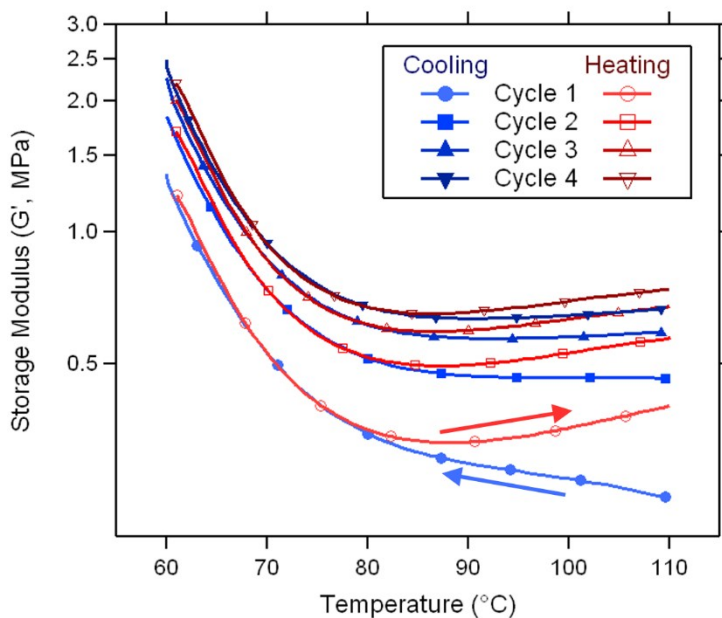

Figure S19. Rheological data of thermal cycling for a $2N_{100}$ sample in the plateau region. The cooling and heating curves show a significant increase in storage modulus, likely through the growth of the hard phase during cycling. (temperature ramp rate = 3 °C/min, frequency = 2 Hz, parallel plate geometry).

References

1   C. Ammann, P. Meier and A. E. Merbach, *J. Magn. Reson.*, 1982, **46**, 319–321.
2   Patent WO2010056452 A2, May 20, 2010