Supporting Information for:
Dynamic Bottlebrush Polymer Networks: Self-Healing in Super-Soft Materials

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Contents

Synthesis and characterization

Reagent and solvent information

Reagents and solvents were used as received except where otherwise noted. 4,4'-bicyclohexanone (≥98%) was purchased from TCI America. Methylene chloride ("DCM", ACS grade, ≥99.5%), methanol ("MeOH", 99%), and ethyl vinyl ether ("EVE", 99%) were purchased from Fischer Scientific and used as received. Tin(II) ethyl hexanoate ($Sn(Oct)_2$, Aldrich, 92.5–100%) was purified by fractional distillation (3×) under reduced pressure (0.05 Torr, 150 °C) and kept in a nitrogen-filled glovebox. 4-Methylcaprolactone ("4MCL") was prepared according to previously reported methods[1] and further purified by three consecutive fractional distillations over calcium hydride (CaH_2, Fisher Scientific, 93%). Crosslinker (4,4'-bioxepane-7,7'-dione, "BD") was prepared according to previously reported methods[2] and further purified by recrystallization from ethyl acetate. Macromonomer initiator (N-(hydroxyethyl)-*cis*-5-norbornene-*exo*-2,3-dicarboximide, "NbOH") was also prepared according to previously reported methods[3] and further purified by recrystallization from chloroform. Grubbs second-generation metathesis catalyst [$(H_2IMes)(PCy_3)_2(Cl)_2Ru$=CHPh, "G2"] was generously provided by Materia. G2 was converted to Grubbs third-generation metathesis catalyst [$(H_2IMes)(pyr)_2(Cl)_2Ru$=CHPh, "G3"] following a previously reported method.[4]

Instrumentation

^{1}H NMR spectra were collected on a Varian Unity Inova AS600 600 MHz using the residual un-deuterated solvent peak as an internal reference ($CHCl_3$ at 7.26 ppm). The following abbreviations (or combinations thereof) were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. FTIR spectra were collected on a Thermo Nicolet iS10 FTIR Spectrometer equipped with a Smart Diamond attenuated total reflectance (ATR) accessory. Size-exclusion chromatography with multi-angle light scattering detection (SEC-MALS) was performed using two Agilent columns (PLgel, 5 μm MiniMIX-D, 250×4.6 mm) connected to a Waters Alliance HPLC System, 2690 separation module pump, Wyatt 18-angle DAWN HELEOS-II light scattering detector, and Wyatt REX differential refractive index detector using THF as the mobile phase. The absolute molar mass was determined by light scattering using online determination of d*n*/d*c* by assuming 100% mass elution under the peak of interest. Mass spectrometry data were collected on a Waters GCT Premier high-resolution time-of-flight mass spectrometer in the electron ionization mode. This instrument has a working mass range up to 800 *m*/*z*.

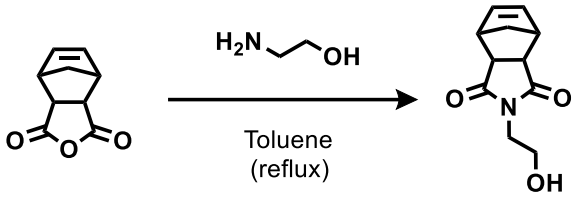
Sample designation

When discussing cured network samples, the sample names are codified to represent the bottlebrush polymer from which each sample was generated (**1A**, **1B**, **2A**, etc) and the equivalents of crosslinker relative to a single bottlebrush polymer (**-5**, **-10**, **-25**, etc). For example, **2A-25** refers to a sample prepared from bottlebrush polymer **2A** with 25 equivalents of crosslinker. In these studies, the amount of Lewis acid catalyst per sample was kept constant at 1.7 wt%.

Synthesis of N-(hydroxyethyl)-cis-5-norbornene-exo-2,3-dicarboximide, "NbOH initiator"

In a 500 mL round-bottom flask charged with a stir bar, 20 g of *cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride (121.8 mmol, 1.0 eq) was combined with 7.8 g (7.8 mL, 127.9 mmol, 1.05 eq) of ethanolamine and 240 mL of toluene. A Dean−Stark trap equipped with a condenser was placed on top of the round-bottom flask, and the reaction was refluxed at 120 °C overnight until all the *cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride was consumed, as determined by NMR. The reaction was then cooled, and the solvent was removed *in vacuo*. The contents were dissolved in 500 mL of DCM, washed three times with 100 mL of 0.1 M HCl, and once with 100 mL of brine before drying over $MgSO_4$. Solvent was removed *in vacuo* and compound was recrystallized from chloroform. ^{1}H NMR (500 MHz, Chloroform-*d*) δ = 6.29 (s, 2H), 3.78 (t, *J* = 5.8, 4.4 Hz, 2H), 3.71 (t, *J* = 5.8, 4.4 Hz, 2H), 3.29 (s, 2H), 2.72 (s, 2H), 1.52 (d, *J* = 10.0, 1.7 Hz, 1H), 1.35 (d, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 178.8, 137.9, 60.6, 47.9, 45.3, 42.8, 41.4. MS for $C_{11}H_{13}NO_3Na$ $[M+Na]^+$, calculated: 230.0793, and found: 230.0783.

Scheme S1. Synthesis of NbOH initiator.



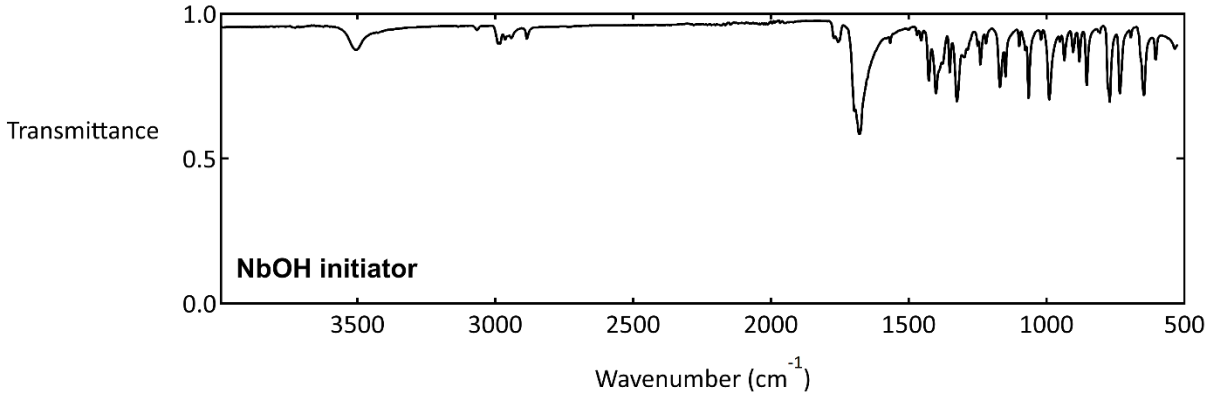
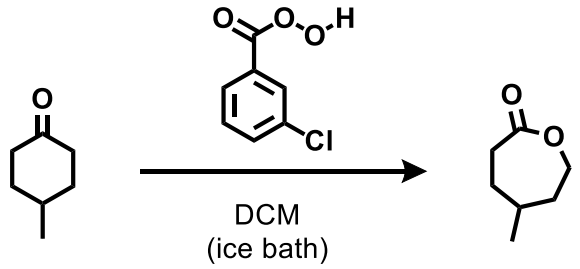


Figure S1. Fourier-transform infrared (FTIR) spectrum of NbOH initiator.

Synthesis of 4-methylcaprolactone,"4MCL monomer"

In a typical reaction, a 250 mL round-bottom flask was charged with a stir bar, 92 g of 3-chloroperoxybenzoic acid (532 mmol, 1.2 eq.), and 500 mL of DCM. Due to impurities in 3-chloroperoxybenzoic acid, an aqueous layer formed on top after complete dissolution and was promptly removed. The reaction vessel was then purged under a flow of Ar gas for 10 minutes while stirring, after which it was cooled to 0 °C. To this stirred solution, 50 g of 4-methylcyclohexanone (444 mmol, 1.0 eq.) was added dropwise, and the resulting solution was left stirring for 16 hours. After completion, the reaction was diluted with 250 mL of DCM and washed with the following aqueous solutions: 750 mL of 10% sodium bisulfite (twice), 750 mL of saturated sodium bicarbonate (four times), and 750 mL of saturated brine (once). The organic layer was dried over magnesium sulfate, filtered, and dried *in vacuo* to give a colorless liquid. This crude product was distilled three times from calcium hydride to give 46 g of 4-methylcaprolactone with an isolated yield of 81% and >95% purity (359 mmol). ^{1}H NMR (600 MHz, Chloroform-*d*) δ = 4.22 (ddd, *J* = 12.9, 5.8, 1.9 Hz, 1H), 4.14 (dd, *J* = 12.9, 10.4 Hz, 1H), 2.60 (m, 2H), 1.89 (dt, *J* = 15.3, 4.0 Hz, 1H), 1.83 (m, 1H), 1.73 (m, 1H), 1.45 (dtd, *J* = 15.3, 10.8, 1.9 Hz, 1H), 1.28 (dtd, *J* = 14.0, 11.3, 2.6 Hz, 1H), 0.95 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 176.1, 68.1, 37.2, 35.2, 33.2, 30.8, 22.1. MS for $C_7H_{12}O_2Na$ $[M+Na]^+$, calculated: 151.0735, and found: 151.0730.

Scheme S2. Synthesis of 4MCL monomer.



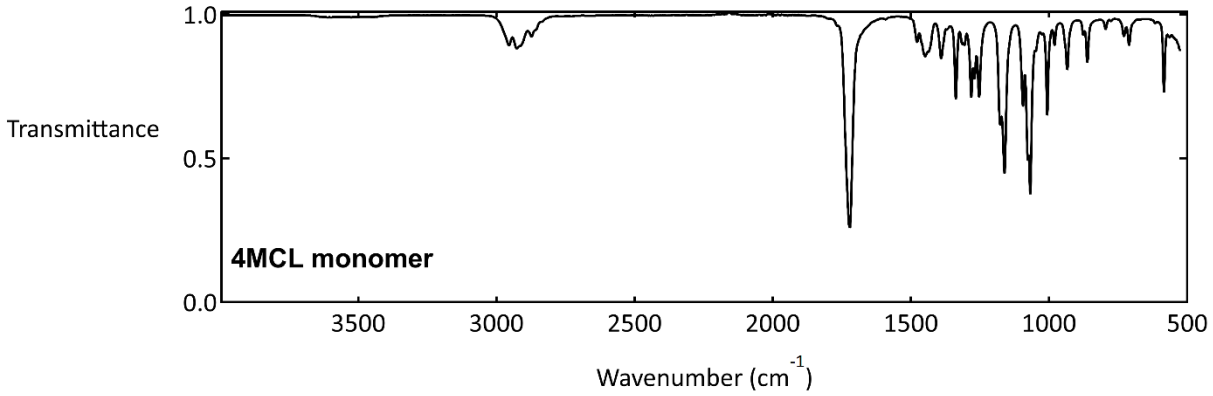
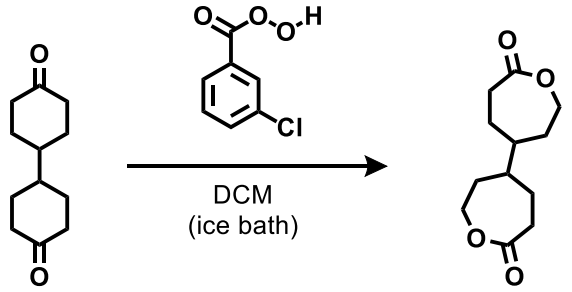


Figure S2. Fourier-transform infrared (FTIR) spectrum of 4MCL monomer.

Synthesis of 4,4'-bioxepane-7,7'-dione, "BD crosslinker"

In a typical reaction, a 250 mL round-bottom flask was charged with a stir bar, 11 g of 3-chloroperoxybenzoic acid (46 mmol, 3 eq.), and 150 mL of DCM. Due to impurities in 3-chloroperoxybenzoic acid, an aqueous layer formed on top after complete dissolution and was promptly removed. The reaction vessel was then purged under a flow of Ar gas for 10 minutes while stirring, after which it was cooled to 0 °C. To this was added 3.0 g of 4,4'-bicyclohexanone (15 mmol, 1 eq.) dissolved in a minimal amount of DCM, and the resulting solution was left stirring for 16 hours. After completion, the reaction was diluted by 150 mL of DCM and washed with the following aqueous solutions: 400 mL of 10% sodium bisulfite (twice), 400 mL of saturated sodium bicarbonate (four times), and 400 mL of saturated brine (once). The organic layer was dried over magnesium sulfate, filtered, and dried *in vacuo* to give 2.6 g of a white solid (11.1 mmol) with an isolated yield of 74% and >95% purity. ^{1}H NMR (600 MHz, Chloroform-*d*) δ = 4.33 (dd, *J* = 5.1, 7.2 Hz, 2H), 4.15 (dd, *J* = 13.1, 9.2 Hz, 2H), 2.72 (ddd, *J* = 14.2, 7.4, 1.6 Hz, 2H), 2.59 (ddt, *J* = 14.5, 12.5, 2.3 Hz, 2H), 1.89 (m, 2H), 1.84 (m, 2H), 1.4 (m, 4H), 1.48 (q, *J* = 12.1 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 176.1, 68.1, 37.2, 35.2, 33.2, 30.8, 22.1. MS for $C_{12}H_{18}O_4Na$ $[M+Na]^+$, calculated: 249.1103, and found: 249.1105.

Scheme S3. Synthesis of BD crosslinker.



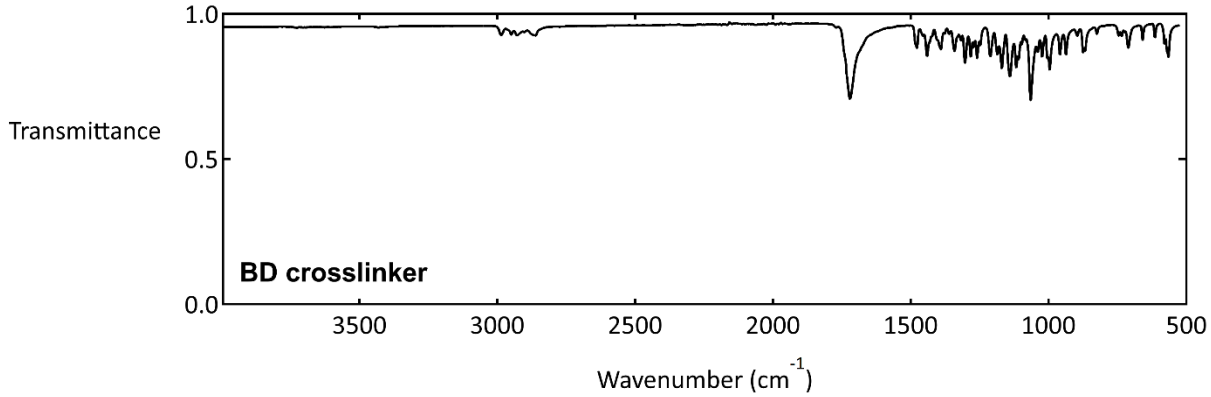
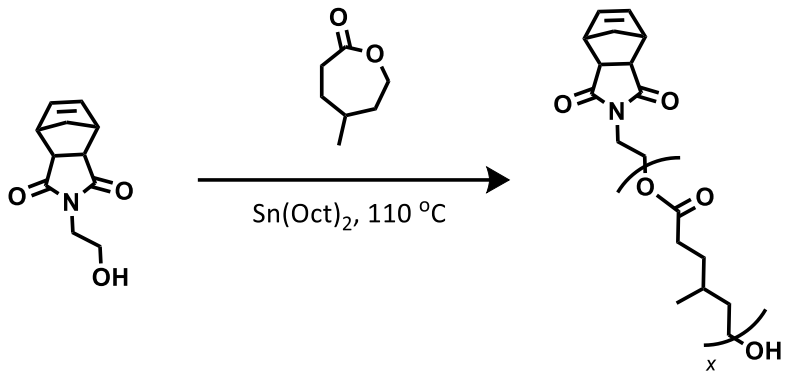


Figure S3. Fourier-transform infrared (FTIR) spectrum of BD crosslinker.

Macromonomer by ring-opening polymerization (ROP)

The following procedure was used to prepare both macromonomer batches (**A** and **B**); the representative spectroscopic characterization reported is for macromonomer **B**.

Scheme S4. Synthesis of P4MCL macromonomer.



In a nitrogen-filled glovebox, 50 g of 4MCL monomer (390 mmol, 40 eq.) were added to an oven-dried round-bottom flask equipped with a stir bar. To this reaction vessel, initiator NbOH (9.76 mmol, 1 eq.) and catalyst $Sn(Oct)_2$ (0.97 mmol, 0.1 eq.) were also added before sealing the reaction vessel. This mixture was then removed from the glovebox and stirred in a pre-heated oil bath at 110 °C, during which the initiator rapidly dissolved to form a homogeneous reaction solution. An aliquot was periodically extracted to determine the conversion of monomer by ^{1}H NMR. Once the desired conversion was achieved, the vessel was immediately removed and quenched to 0 °C in an ice bath. DCM was added to dilute the polymerization after which it was precipitated into cold MeOH (−78 °C). The cold methanol was then decanted off to yield a concentrated and viscous polymer. This dissolution/precipitation process was repeated twice more to thoroughly remove unreacted monomer and catalyst. The final P4MCL was then rigorously dried under high vacuum (10 mTorr) for 24 hours to ensure adequate removal of residual DCM and MeOH. The product was isolated as 46.2 g of a clear oil (92% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ = 6.26 (s, 2H), 4.27 – 4.12 (m, 4H), 4.11 – 4.03 (m, 56H), 3.73 – 3.70 (m, 2H), 3.25 (p, *J* = 1.7 Hz, 2H), 2.67 (d, *J* = 1.4 Hz, 2H), 2.66 – 2.55 (m, 2H), 2.34 – 2.21 (m, 58H), 1.70 – 1.60 (m, 60H), 1.58 – 1.50 (m, 31H), 1.49 – 1.39 (m, 59H), 1.32 – 1.25 (m, 2H), 0.89 (d, *J* = 6.6 Hz, 88H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 177.8, 174.0, 173.7, 173.7, 173.2, 137.8, 68.0, 62.6, 62.5, 60.6, 47.8, 45.2, 42.6, 39.4, 37.6, 37.2, 35.2, 33.2, 31.9, 31.7, 31.5, 31.4, 30.8, 29.5, 29.4, 29.1, 22.1, 19.3, 19.0. M_n (^{1}H NMR) = 4.0 kg mol^{-1}. MALS SEC (d*n*/d*c* = 0.071): M_n = 4.5 kg mol^{-1}, $Đ$ = 1.06.

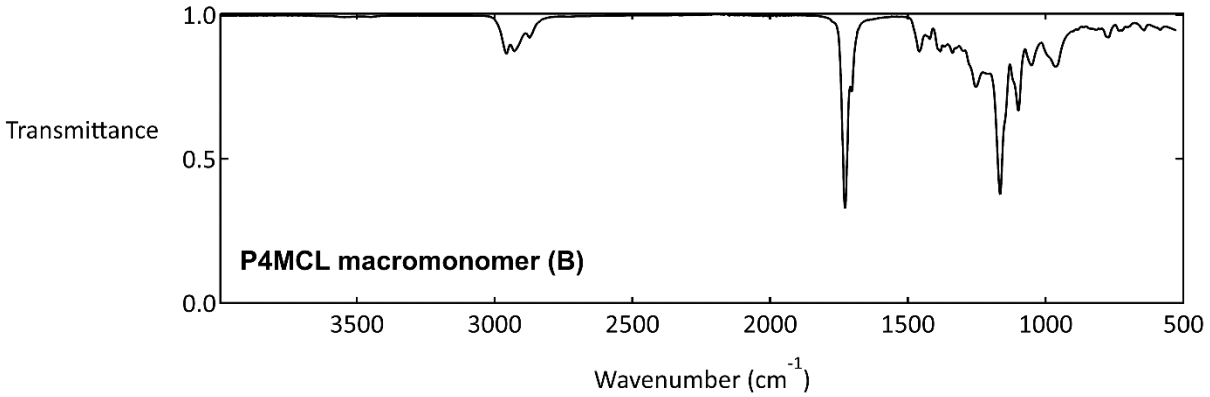
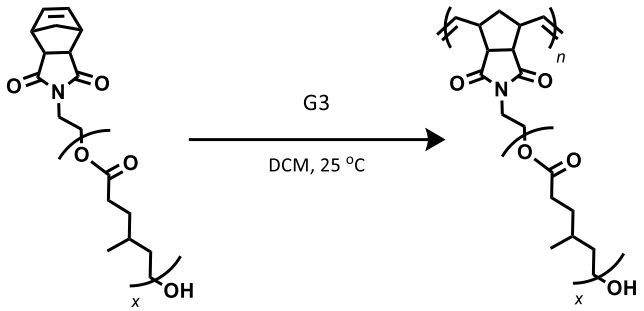


Figure S4. Fourier-transform infrared (FTIR) spectrum of P4MCL macromonomer (**B**).

Bottlebrush polymer by ring-opening metathesis polymerization (ROMP)

The following procedure was used to prepare all bottlebrush polymers (**1A**, **1B**, **2B**, **3B**, and **4B**); the representative spectroscopic characterization reported is for bottlebrush polymer **1B**.

Scheme S5. Synthesis of P4MCL bottlebrush polymer.



In a nitrogen-filled glovebox, 20 g of P4MCL macromonomer (50 eq., 4.4 mmol) were added to an oven-dried round-bottom flask equipped with a stir bar. DCM was added until a concentration of 20 wt% macromonomer was reached. Separately, 65 mg of G3 (1 eq., 0.1 mmol) was added to a scintillation vial and dissolved in a minimal amount of solvent (typically, <0.5 mL DCM). The solution with macromonomer was stirred vigorously to ensure full dissolution and to promote rapid mixing upon the addition of catalyst. To the stirring solution, G3 was quickly added. As the reaction progressed, the color of the solution changed from its initial green to a dull brown. After an hour of stirring, a large excess of EVE (approximately 1 mL, 120 eq.) was added to quench the G3. The reaction was then stirred an additional two hours to ensure sufficient quenching and precipitated into cold methanol three times, with the precipitate being centrifuged, filtered, and redissolved between each precipitation. To ensure complete removal of solvent, the bottlebrush polymer was dried in a vacuum oven for 24 hours at room temperature. The final material was isolated as 16.6 g of a clear, slightly yellow oil (83% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ = 5.74 (br, s, 2H), 4.08 (br, tt, *J* = 11.0, 5.5 Hz, 154H), 3.98 – 3.88 (br, m, 1H), 3.76 – 3.58 (br, m, 7H),

2.52 – 2.02 (br, m, 163H), 1.67 (br, ddt, *J* = 20.6, 14.4, 6.4 Hz, 168H), 1.60 – 1.50 (br, m, 89H), 1.52 – 1.34 (br, m, 162H), 1.27 – 1.06 (br, m, 5H), 0.91 (br, d, *J* = 6.5 Hz, 242H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.8, 62.6, 60.8, 50.8, 39.5, 35.2, 31.9, 31.8, 29.6, 29.1, 19.0.

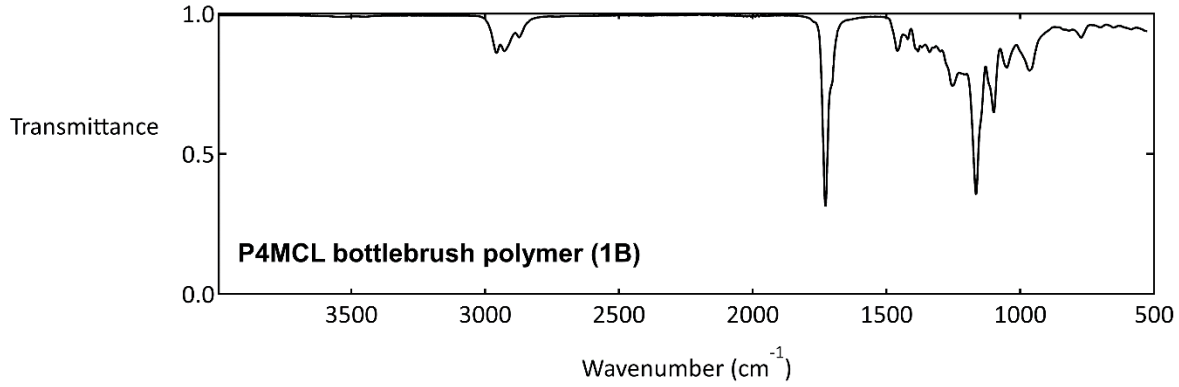
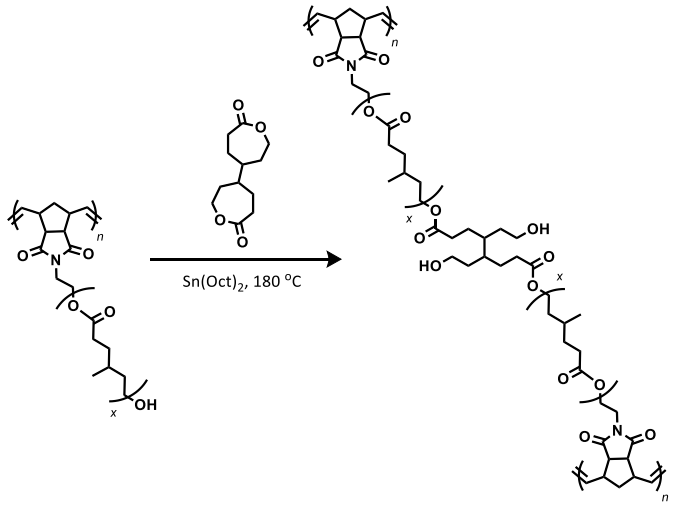


Figure S5. Fourier-transform infrared (FTIR) spectrum of P4MCL bottlebrush polymer (**1B**).

Network curing

Scheme S6. Synthesis of P4MCL bottlebrush polymer network.



The procedure for network generation was the same across all sample sets used, but the values in the following representative procedure were calculated based on the molecular weight for bottlebrush polymer **1B**. First, 300 mg of bottlebrush polymer (1 eq., 1.3 μmol) were weighed out in a dram vial. Next, a stock solution of 20 mg mL^{-1} was made for both the crosslinker and catalyst. From the crosslinker stock solution, 215 μL (4.3 mg, 15 eq., 19 μmol) of solution were added to the bottlebrush. Next, from the catalyst stock solution, 256 μL (5.1 mg, 10 eq., 12.7 μmol) of solution were added to the bottlebrush. Another approximate 0.5 mL of DCM was then added to ensure good mixing. After mixing to homogeneity, the solution was then dried under vacuum (approximately 25 mTorr) for 48 hours. The resulting homogeneous paste was loaded into a mold and heated at 180 °C for five hours to yield a cured network.

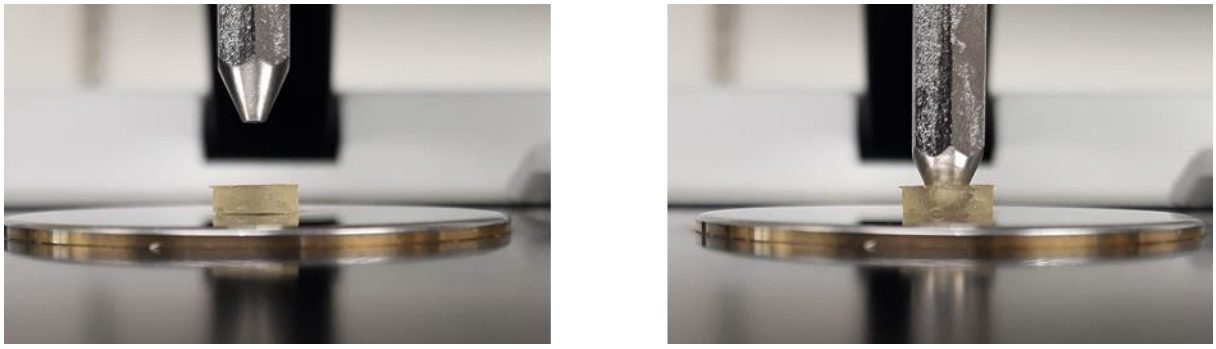


Figure S6. Experimental setup for Fourier-transform infrared (FTIR) spectral analysis of P4MCL bottlebrush polymer networks. The piston was hand-tightened to form good contact, also demonstrating the compliance of dynamic bottlebrush polymer networks.

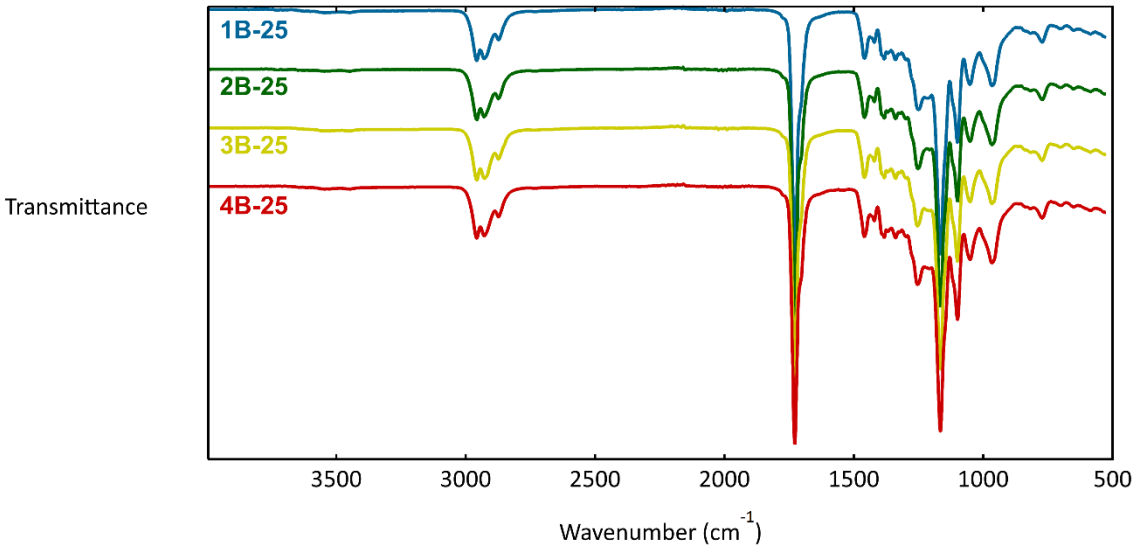


Figure S7. Fourier-transform infrared (FTIR) spectrum of P4MCL bottlebrush polymer networks formed from bottlebrush polymers **1B**, **2B**, **3B**, and **4B**, and cured with n_{cl} = 25.

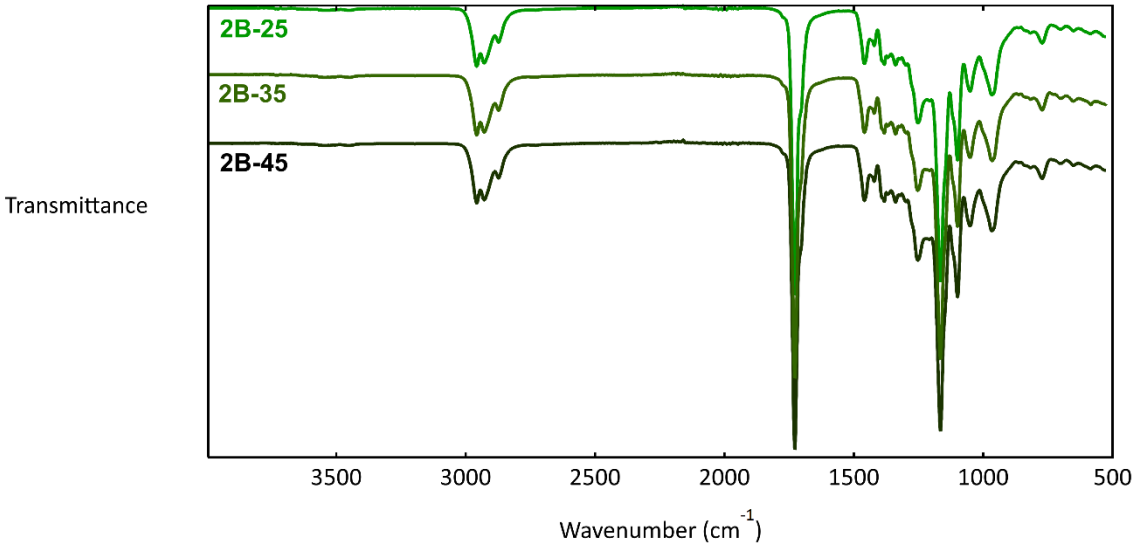


Figure S8. Fourier-transform infrared (FTIR) spectrum of P4MCL bottlebrush polymer networks formed from bottlebrush polymer **2B** and cured with n_{cl} = 25, 35, and 45.

Mechanical testing

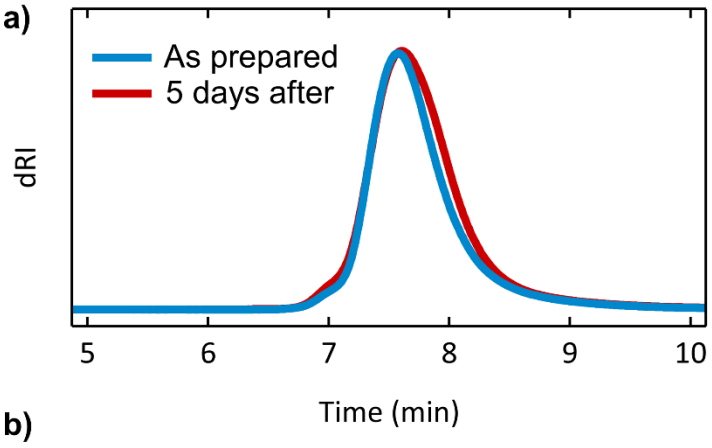
Instrumentation

Frequency and strain sweeps were run on a TA Instruments AR-G2 with an 8 mm parallel-plate geometry. After running strain sweeps from 0.1% to 100%, frequency sweeps were collected at a sufficiently low strain to ensure they were within the linear viscoelastic regime (with a typical value being 1% strain). The plateau modulus was taken to be the modulus at the lowest measured frequency (0.01 Hz).

In situ curing experiments were run on a TA Instruments ARES-G2 equipped with a nitrogen-purged forced convection oven. The advanced sensitivity of the instrument allowed for high-resolution characterization of the uncured polymer melt while also enabling *in situ* monitoring of the entire curing process. A room-temperature frequency sweep was collected on both the cured and uncured material from 0.01 Hz to 10 Hz and a strain of 1%. Curing was monitored during a rapid temperature ramp from 25 to 180 °C (<3 minutes) followed by holding at 180 °C until completion.

Stress-relaxation experiments were conducted on a TA Instruments DMA 850 in compression mode with a sample diameter of 8 mm to allow for the same specimens to be used from the rheology experiments. For the stress-relaxation experiments, samples were first brought to thermal equilibrium for 20 minutes at the desired testing temperature, after which a preload force of 0.2 N was first applied and the sample was subjected to a 1% strain.

Characterization of bottlebrush polymers before and after curing



b)

Sample ID*	N_{SC}	N_{BB}	M_n (kDa)	$Đ$
As prepared	35	260	1,300	1.11
5 days after	35	283	1,400	1.12

Figure S9. a) SEC traces (normalized differential refractive index signal) and **b)** characterization results from a formulation stability experiment wherein a sample was prepared (N_{SC} = 35, N_{BB} = 260, n_{cl} = 15, 0.2 wt% catalyst) and left at room temperature for 5 days. The before and after traces show negligible differences in their molecular weight distribution, indicating adventitious curing at room temperature is not an issue for these materials.

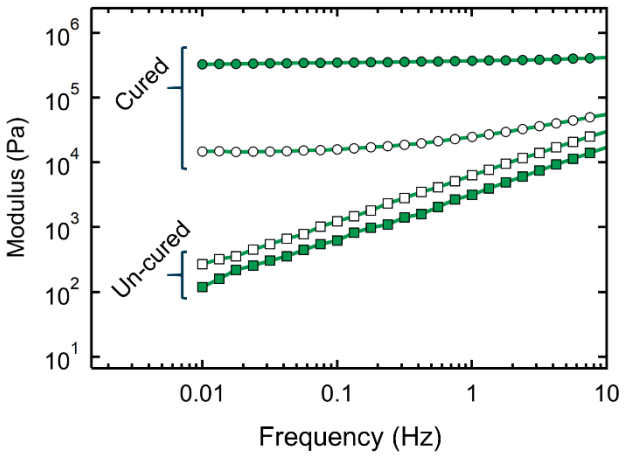


Figure S10. Room-temperature frequency sweeps of sample **1B-15** with 1.7 wt% catalyst both before and after curing. As shown by the storage (closed symbols) and loss (open symbols) moduli, the sample behaves as a typical polymer melt before curing. After drying for 48 hours (25 °C) and curing for 5 hours (180 °C), the mechanical response is dominated by the storage modulus and a clear plateau is evident, indicating a well-crosslinked network.

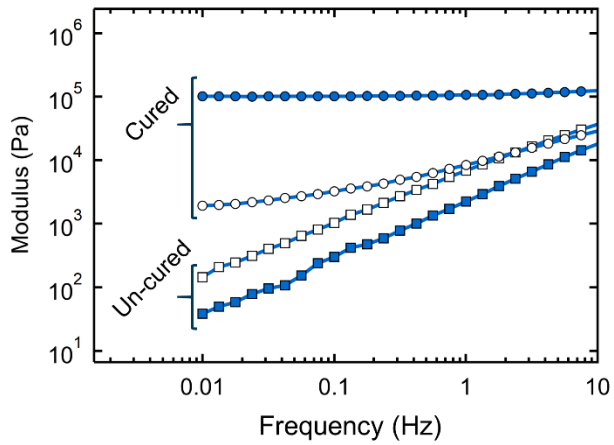


Figure S11. Room-temperature frequency sweeps sample **1B-15** with 0.8 wt% catalyst both before and after the curing. As shown by the storage (closed symbols) and loss (open symbols) moduli, the sample behaves as a typical polymer melt before curing. After drying for 48 hours (25 °C) and curing for 5 hours (180 °C), the mechanical response is dominated by the storage modulus and a clear plateau is evident, indicating a well-crosslinked network.

Raw curing curves

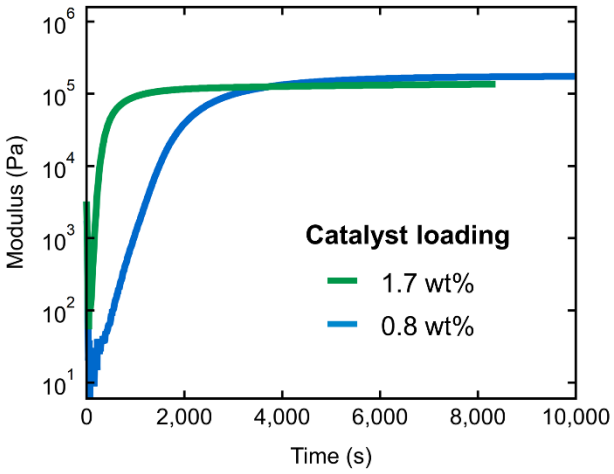


Figure S12. *In situ* curing curves illustrate the timescale and relative rates at 180 °C as a function of catalyst loading. Samples with the formula **1B-15** and two different concentrations of catalyst.

Stress-relaxation fitting

To fit stress-relaxation data, a modified stretched exponential equation (**Eq. S1**) was used. The first two terms are typical of exponential decays with a prefactor *A* and a characteristic relaxation time τ^* in seconds. The β term has been introduced to account for a distribution of relaxation modes as is expected in crosslinked networks with a spectrum of local chemical environments. β is always a dimensionless value between 0 and 1.[2,5] Finally, as these measurements were run in compression, a preload force is required to ensure good contact and an experimental "zero" plane.

As these samples are particularly soft, this preload force is enough to shift the final modulus by a non-negligible amount but can be corrected during fitting with the offset *b*.

$$G'(t) = Ae^{\left(\frac{-t}{\tau*}\right)^{\beta}} + b \qquad \textbf{Eq. S1}$$

Raw data

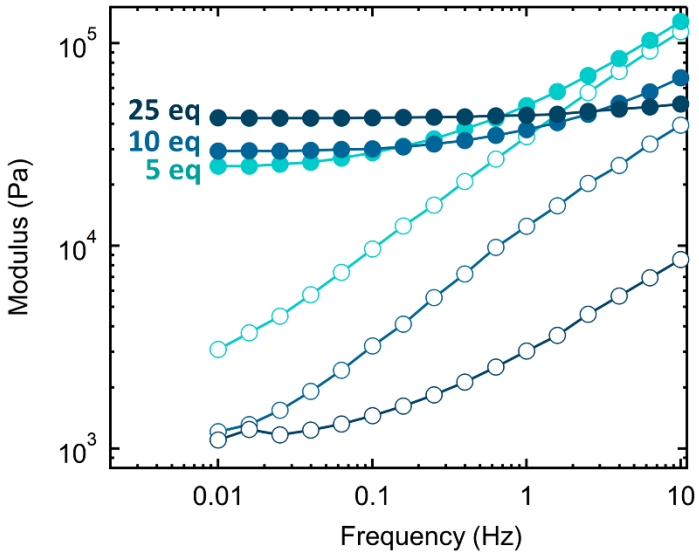


Figure S13. Frequency sweeps of samples **1A-5**, **1A-10**, and **1A-25**, demonstrating the tunability of bottlebrush polymer properties through formulation. Filled circles are storage modulus values and empty circles are loss modulus values.

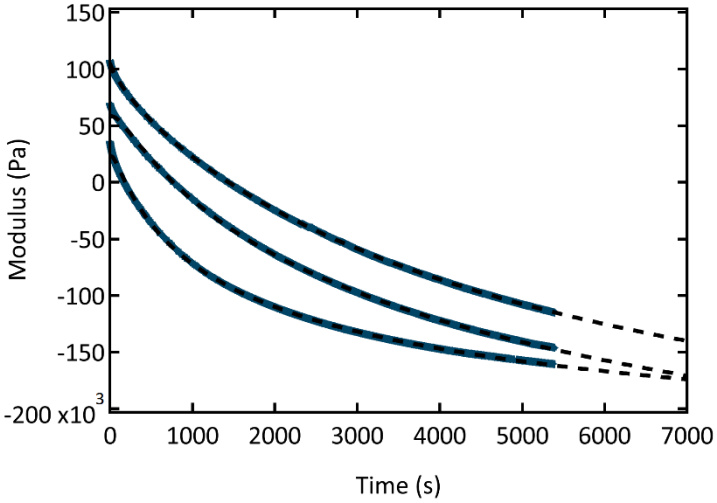


Figure S14. Raw stress-relaxation data for sample **1A-25** with superimposed fits.

Table S1. Fit parameters for sample **1A-25**

T (°C)	A (Pa)	τ^* (sec)	β	b (Pa)	$(RT)^{-1}$	ln(τ^*)
180	221,000	1,720	0.71	−183,000	0.266	7.45
170	270,000	3,150	0.87	−201,000	0.272	8.05
160	341,000	5,130	0.78	−236,000	0.278	8.54

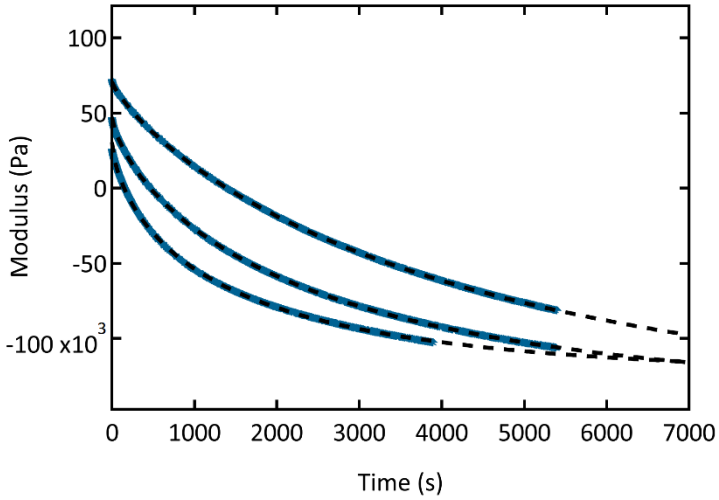


Figure S15. Raw stress-relaxation data for sample **1A-10** with superimposed fits.

Table S2. Fit parameters for sample **1A-10**

T (°C)	A (Pa)	τ^* (sec)	β	b (Pa)	$(RT)^{-1}$	ln(τ^*)
180	157,000	1,450	0.65	−125,000	0.266	7.28
170	188,000	2,580	0.72	−140,000	0.272	7.86
160	220,000	4,420	0.82	−149,000	0.278	8.39

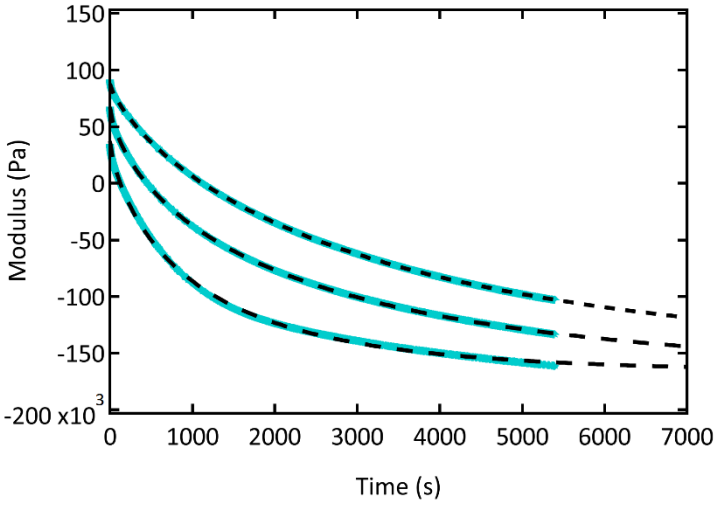


Figure S16. Raw stress-relaxation data for sample **1A-5** with superimposed fits.

Table S3. Fit parameters for sample **1A-5**

T (°C)	A (Pa)	τ^* (sec)	β	b (Pa)	$(RT)^{-1}$	ln(τ^*)
180	205,000	1,090	0.73	−167,000	0.266	7.00
170	240,000	2,240	0.68	−172,000	0.272	7.71
160	247,000	3,230	0.77	−159,000	0.278	8.08

*Sol–gel results for samples prepared from **4B***

Table S4. Sol–gel analysis of samples derived from the largest N_{BB} bottlebrush polymer (**4B**).

Sample	M_n (kDa)	n_{cl}	G_x (kPa)	Gel (%)
4B-15	1,680	15	11.3	91
4B-25	1,680	25	15.0	92
4B-35	1,680	35	22.6	89

Linear comparison for mechanical studies

To showcase the effect of polymer architecture, an analogous P4MCL linear network was synthesized. The target molecular weight between crosslinks (M_x) for this sample is above the entanglement molecular weight,[1] so its modulus should approach the lowest modulus feasible for these linear materials. As with the macromonomer synthesis, this formulation was combined without solvent and heated to 110 °C, a temperature at which the crosslinker readily dissolves. The samples were heated at 110 °C for 24 hours to reach high conversion and minimize plasticization from unreacted monomer.

Table S5. Formulation for linear sample comparison ($M_{x,theo}$ = 9.6 kDa)

Role	Compound	Formula weight	Eq.	Mass (g)
Initiator	Benzyl alcohol	108.1	1	0.002
Monomer	4-methyl-caprolactone	128.2	150	0.350
Crosslinker	4,4'-bioxepane-7,7'-dione	226.3	2	0.008
Catalyst	Tin(II) 2-ethylhexanoate	409.1	0.8	0.006

Thermal analysis

Instrumentation

Differential scanning calorimetry (DSC) data were collected on a liquid-nitrogen-cooled TA Instruments Q2000 Differential Scanning Calorimeter with an indium standard calibration. The samples were measured under a nitrogen environment and in a temperature range from −100 to 100 °C at a ramp rate of 10 °C per minute with a sensitivity <0.2 μW and a baseline drift <10 μW. Thermo-gravimetric analysis (TGA) was collected on a TA Instruments Discovery Thermo-Gravimetric Analyzer. The measurements were taken under a nitrogen environment from an initial thermally equilibrated state at 50 °C ramping up to 600 °C at 10 °C per minute.

DSC results

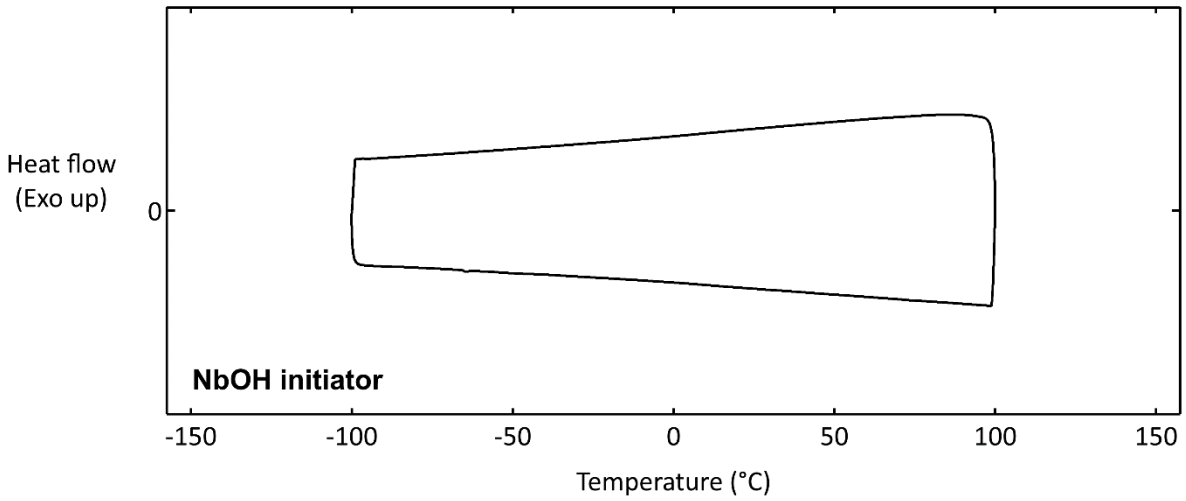


Figure S17. DSC trace of NbOH initiator.

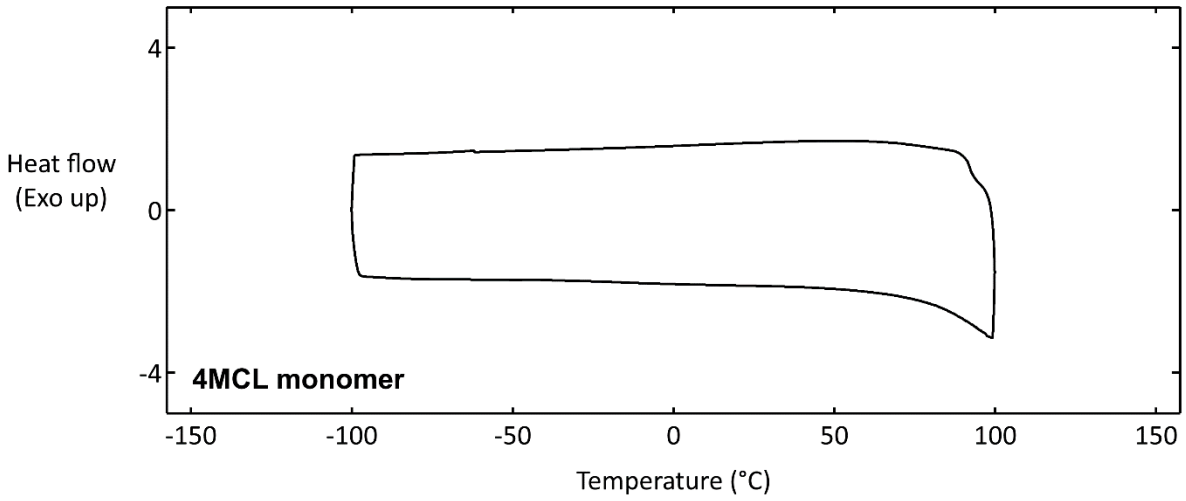


Figure S18. DSC trace of 4MCL monomer.

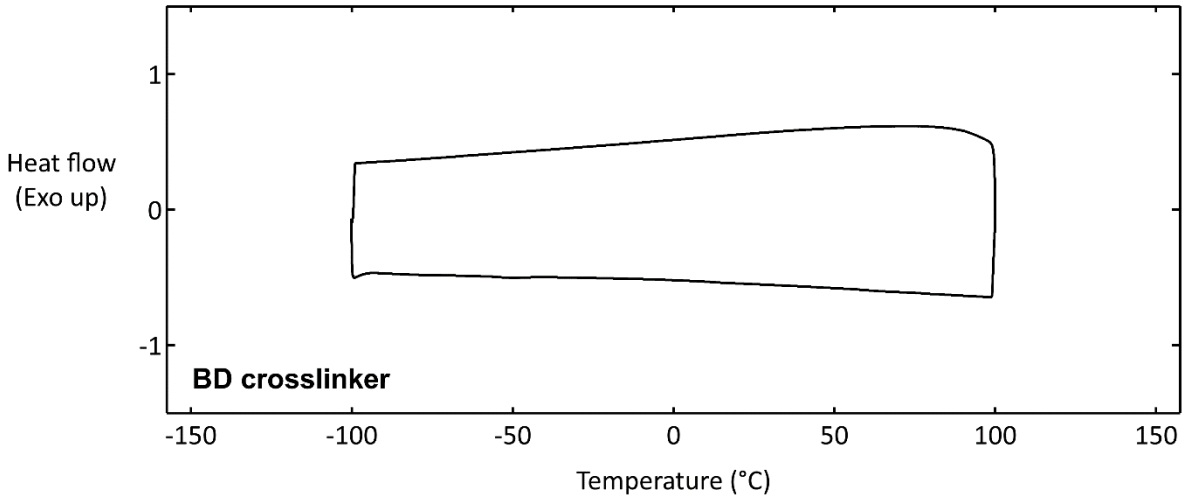


Figure S19. DSC trace of BD crosslinker.

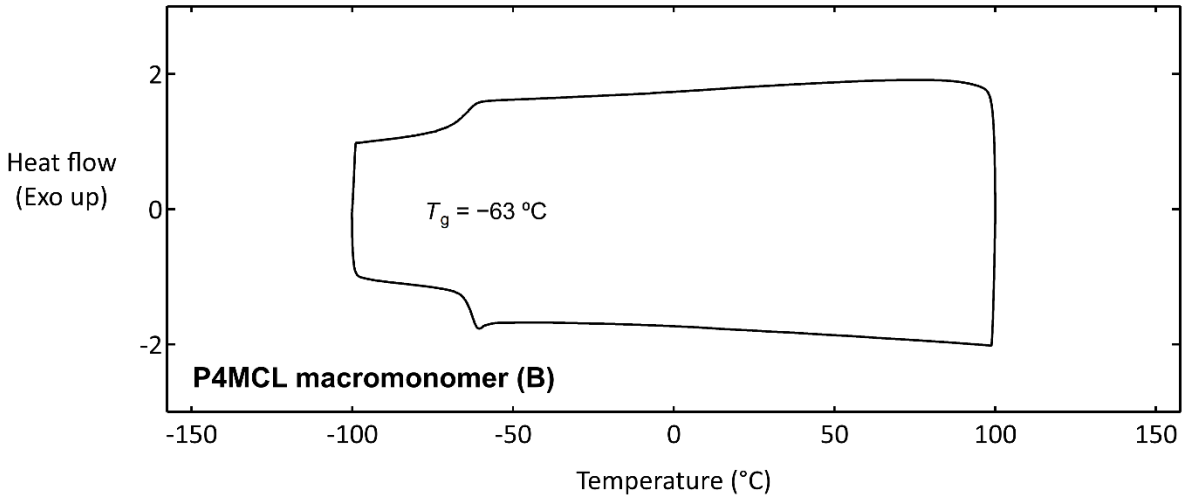


Figure S20. DSC trace of P4MCL macromonomer **B**.

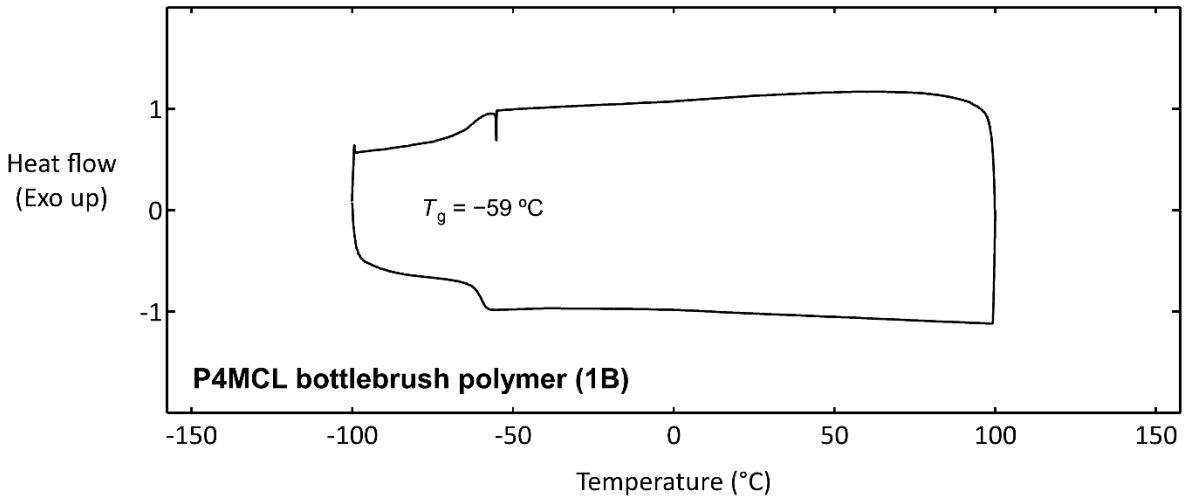


Figure S21. DSC trace of P4MCL bottlebrush polymer **1B**.

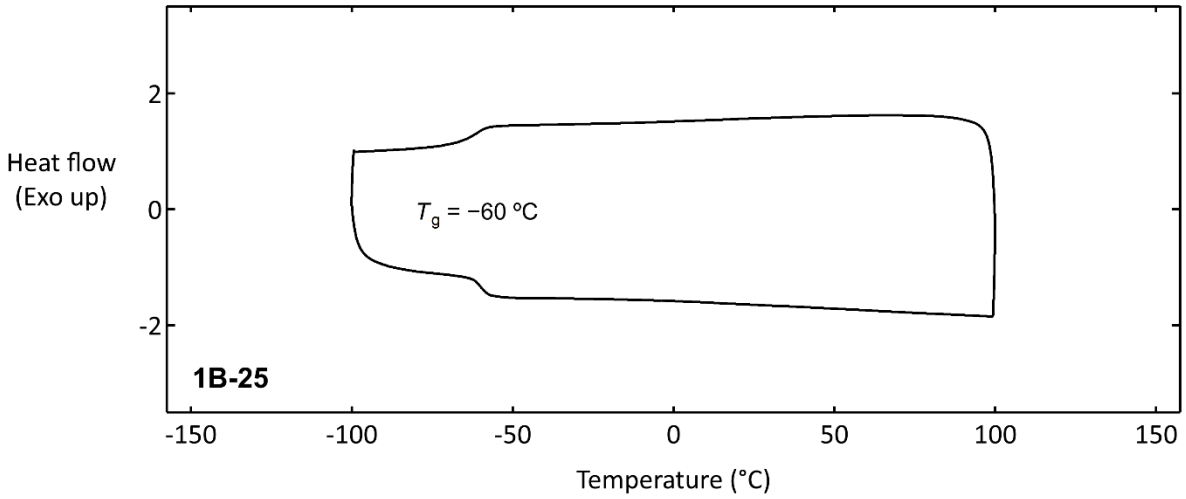


Figure S22. DSC trace of P4MCL bottlebrush polymer network **1B-25**.

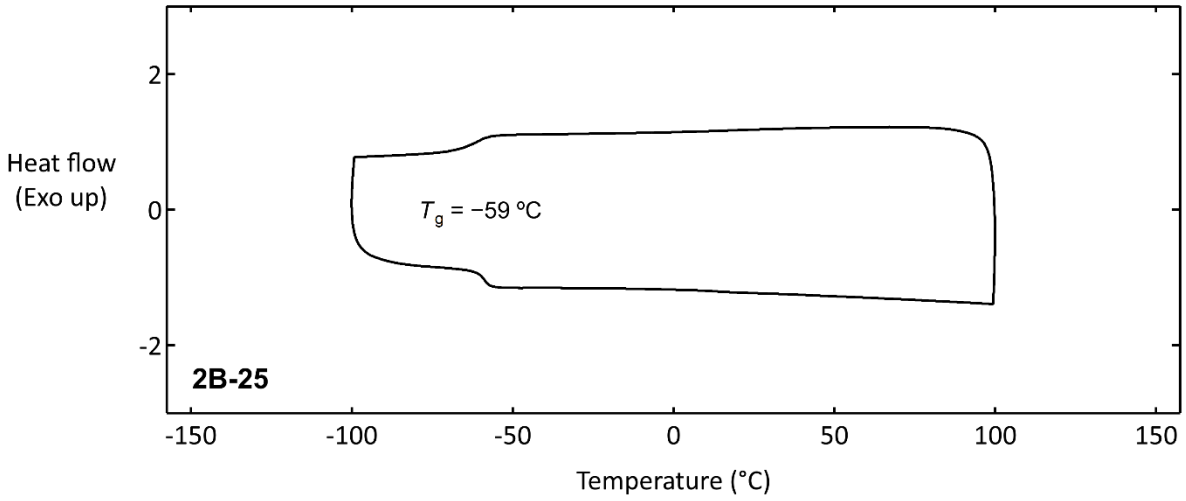


Figure S23. DSC trace of P4MCL bottlebrush polymer network **2B-25**.

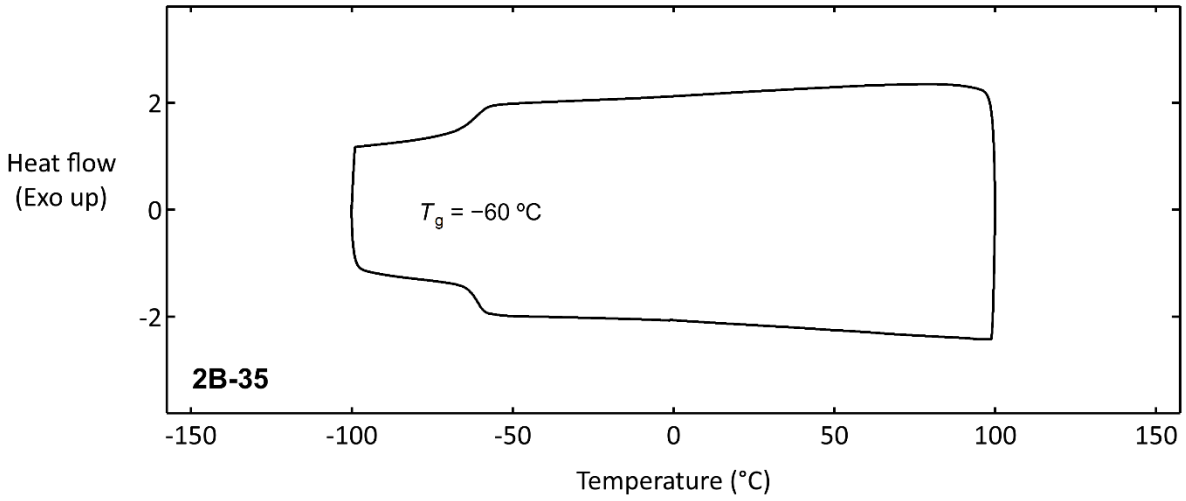


Figure S24. DSC trace of P4MCL bottlebrush polymer network **2B-35**.

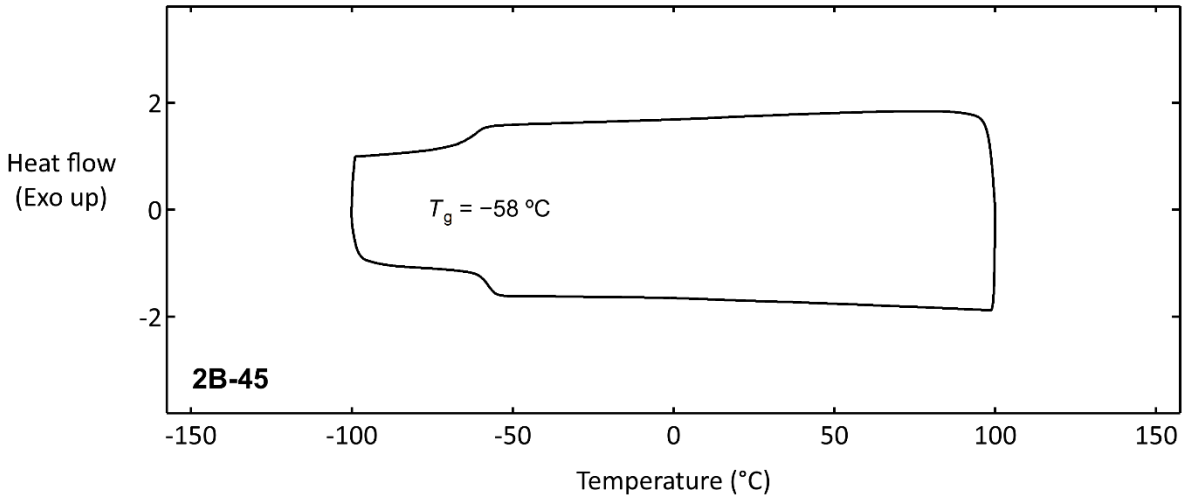


Figure S25. DSC trace of P4MCL bottlebrush polymer network **2B-45**.

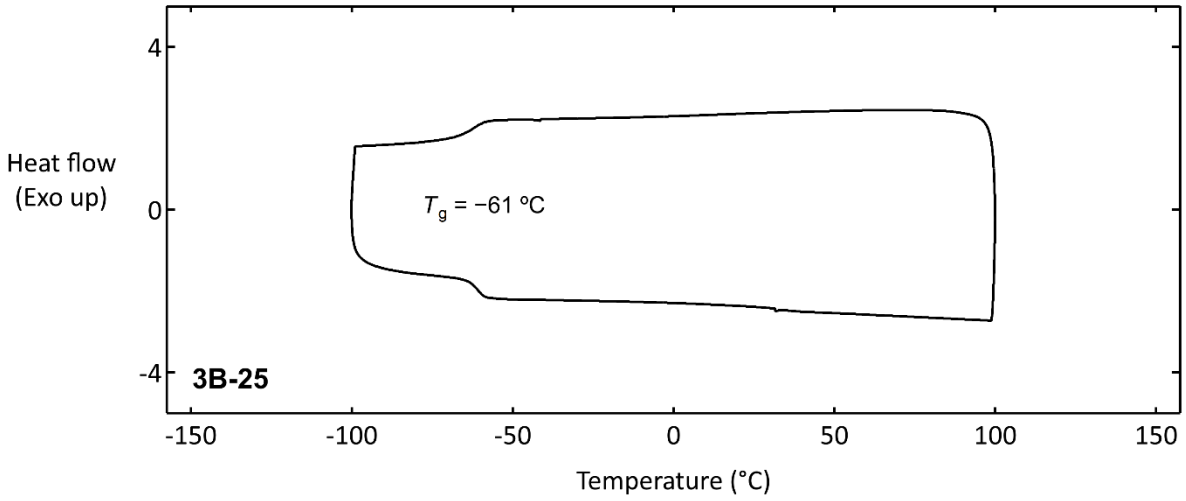


Figure S26. DSC trace of P4MCL bottlebrush polymer network **3B-25**.

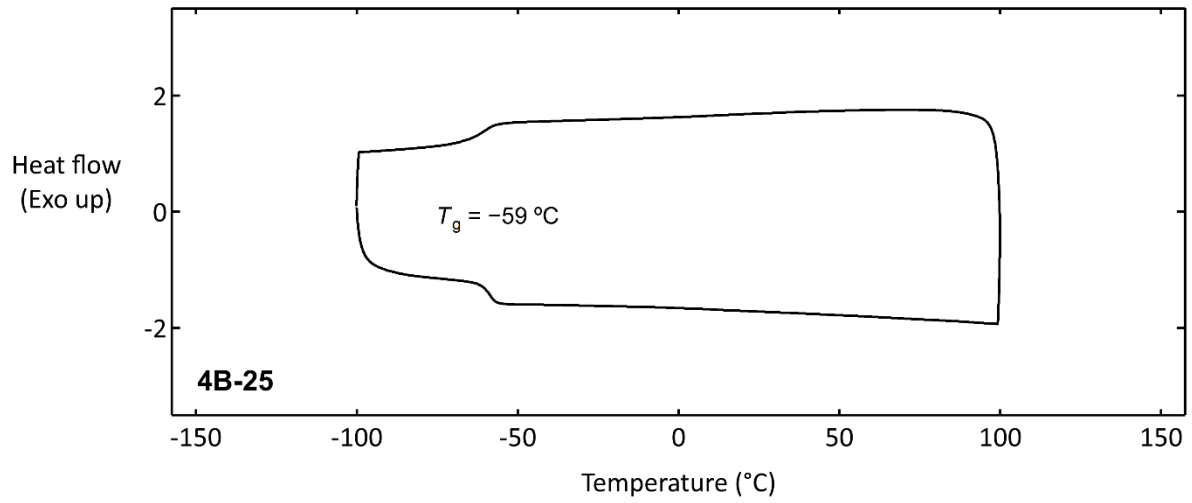


Figure S27. DSC trace of P4MCL bottlebrush polymer network **4B-25**.

TGA results

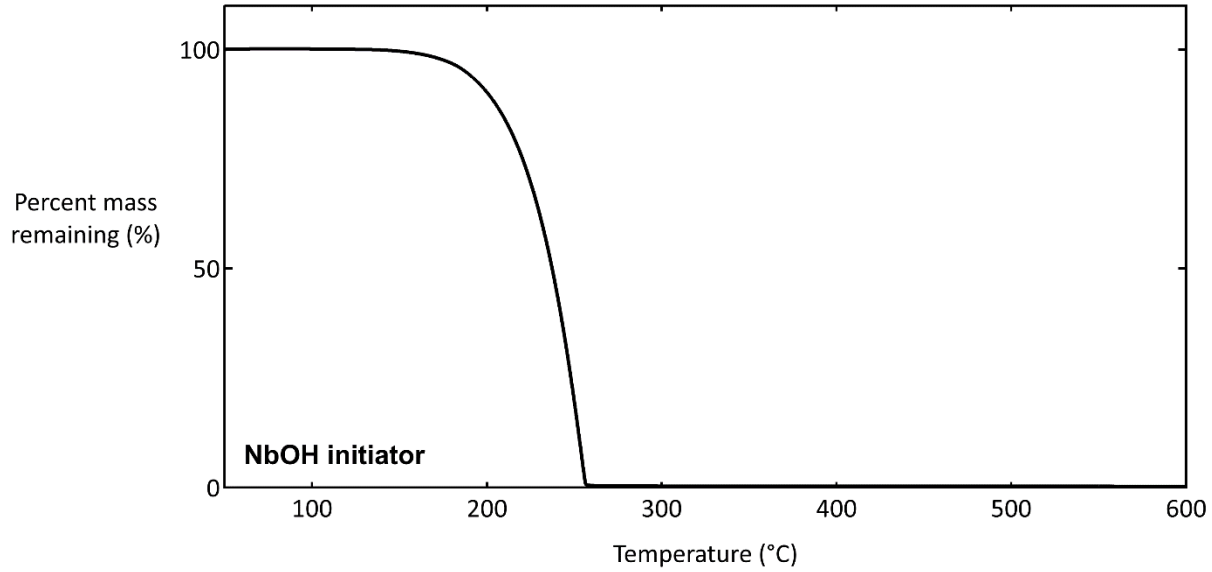


Figure S28. TGA of NbOH initiator.

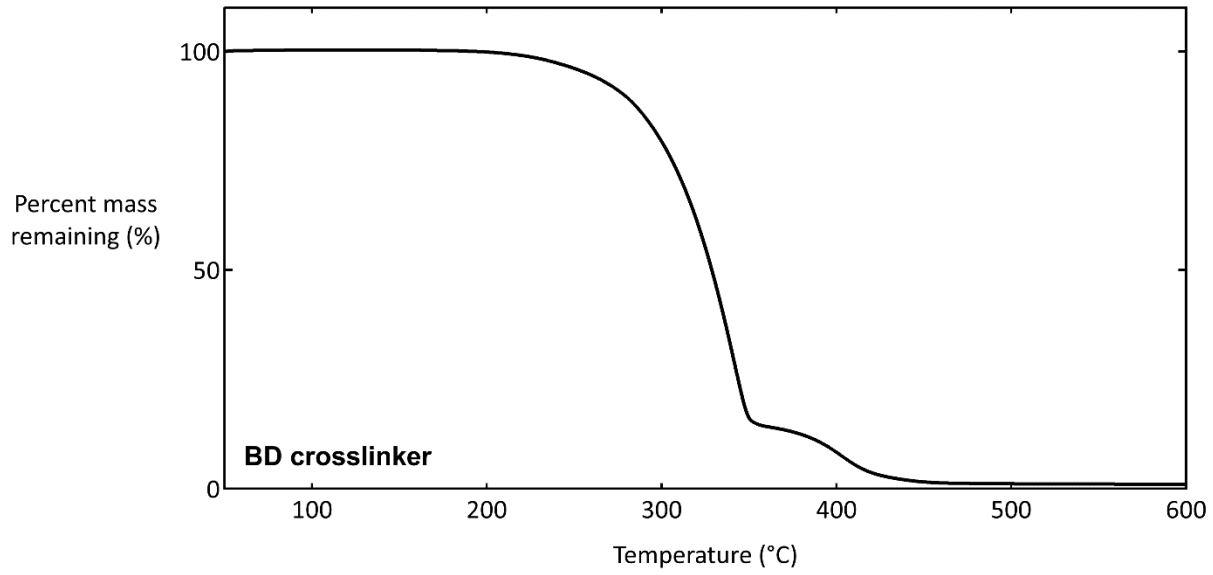


Figure S29. TGA of BD crosslinker.

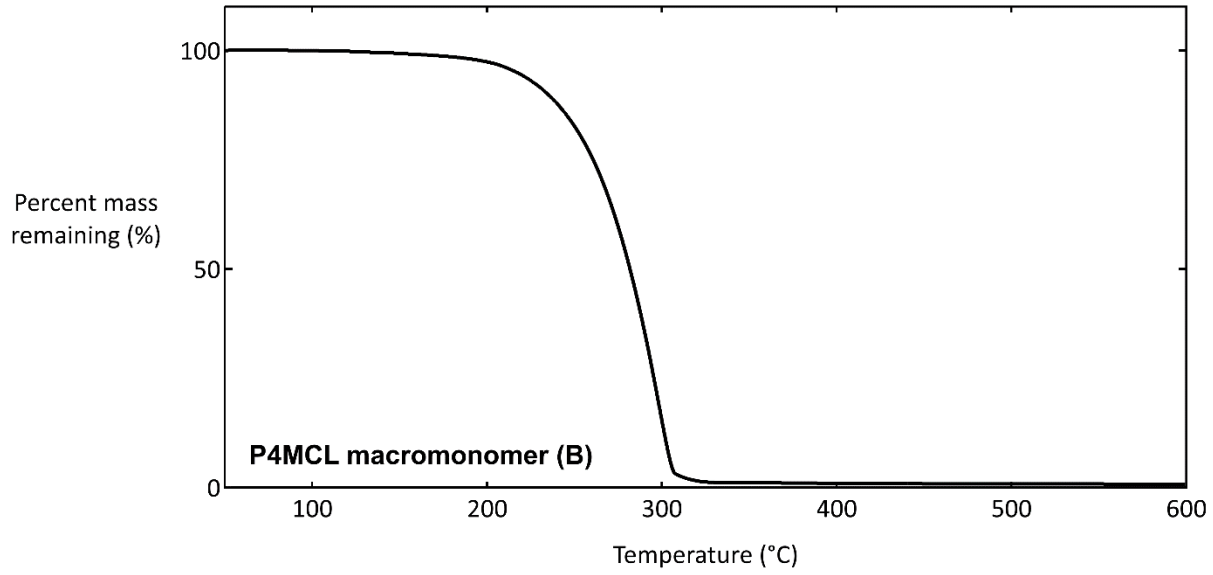


Figure S30. TGA of P4MCL macromonomer **B**.

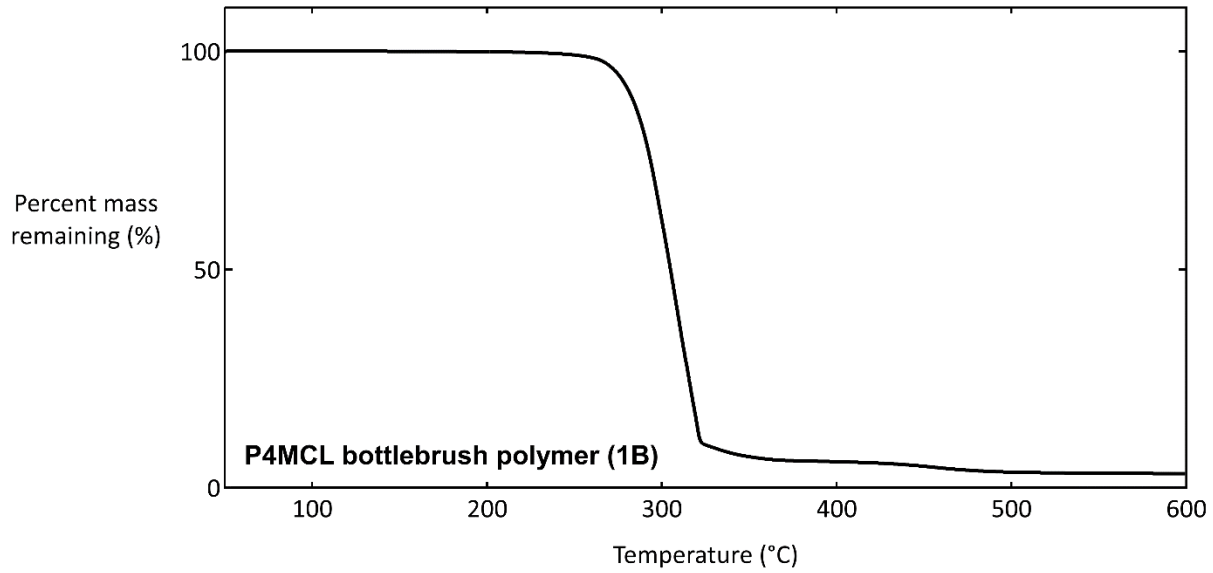


Figure S31. TGA of P4MCL bottlebrush polymer **1B**.

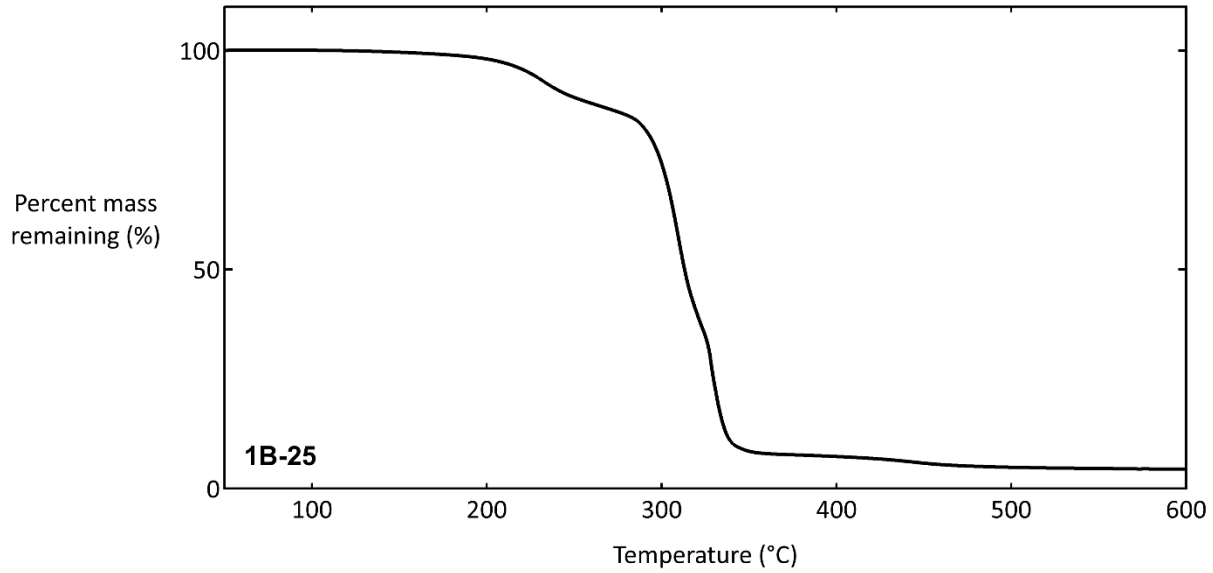


Figure S32. TGA of P4MCL bottlebrush polymer network **1B-25**.

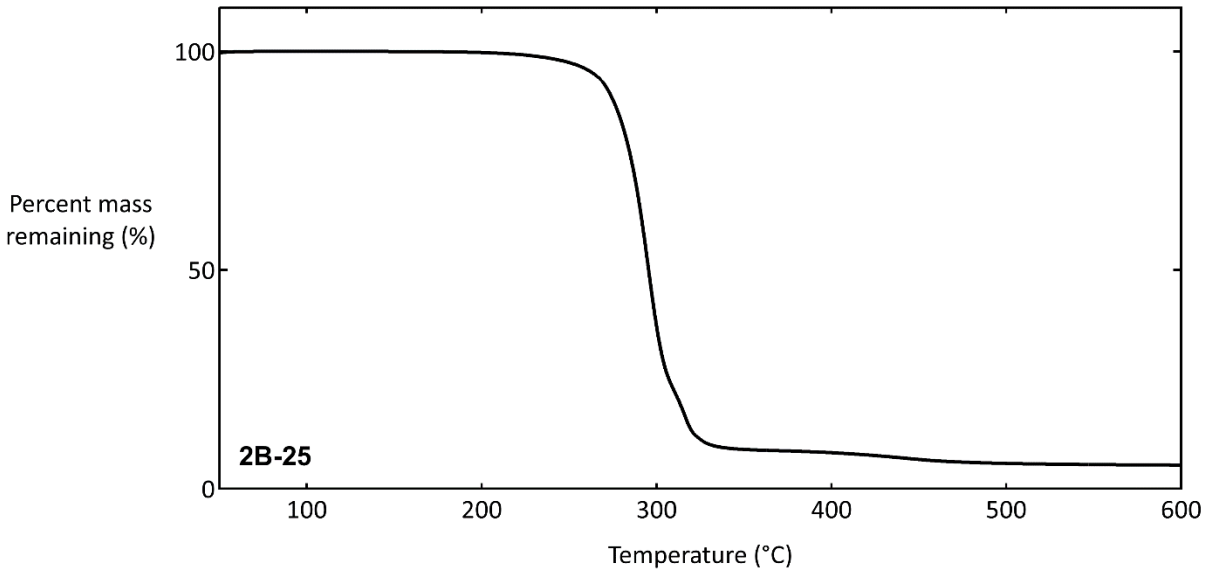


Figure S33. TGA of P4MCL bottlebrush polymer network **2B-25**.

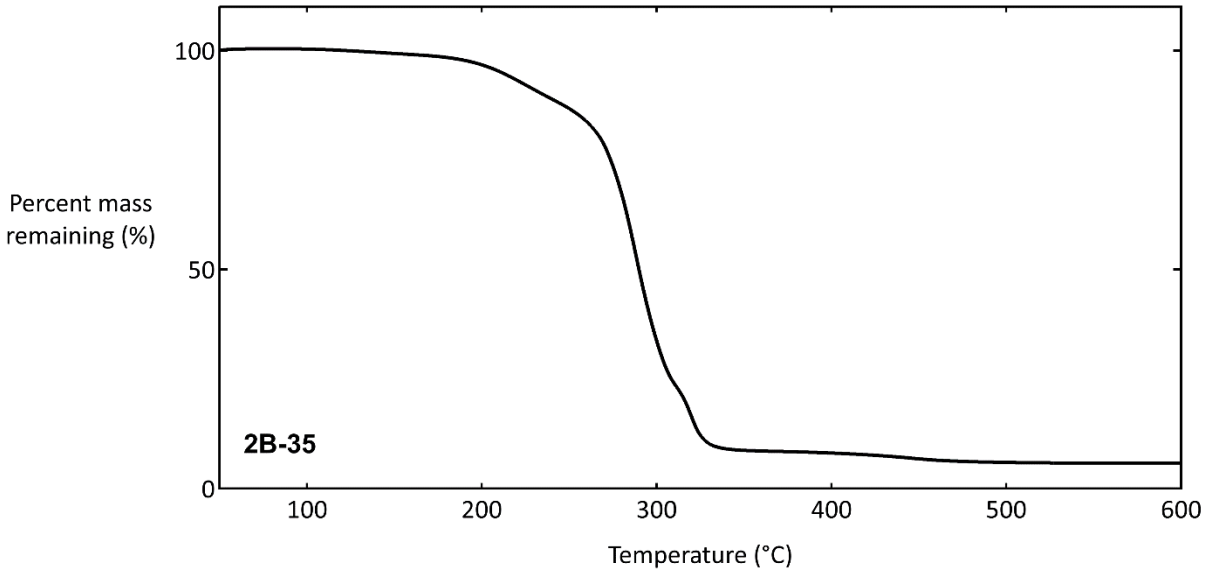


Figure S34. TGA of P4MCL bottlebrush polymer network **2B-35**.

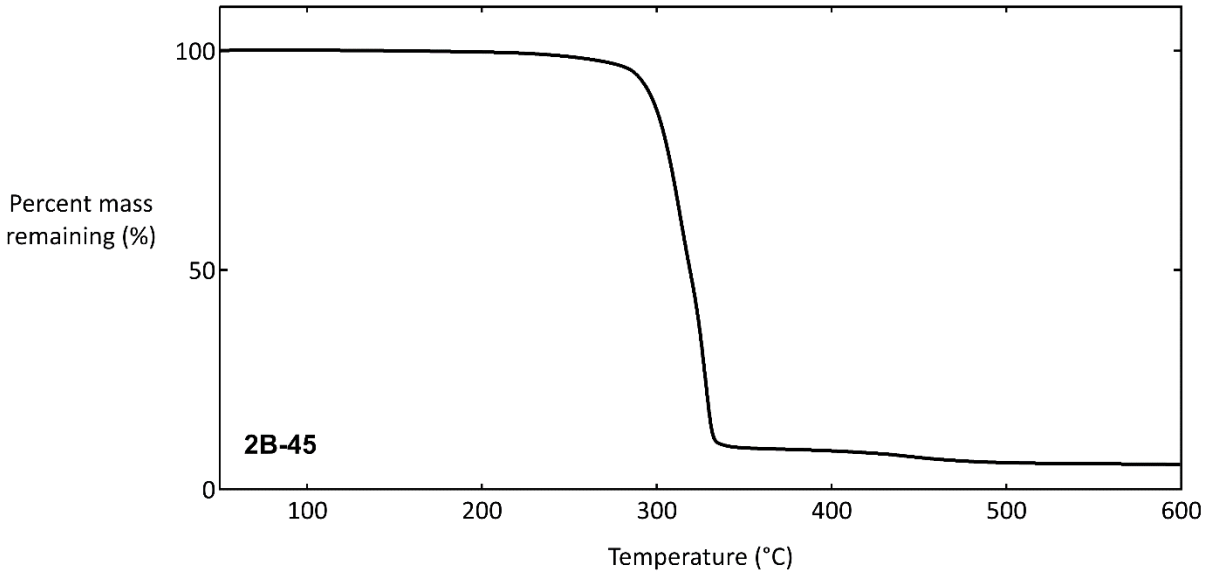


Figure S35. TGA of P4MCL bottlebrush polymer network **2B-45**.

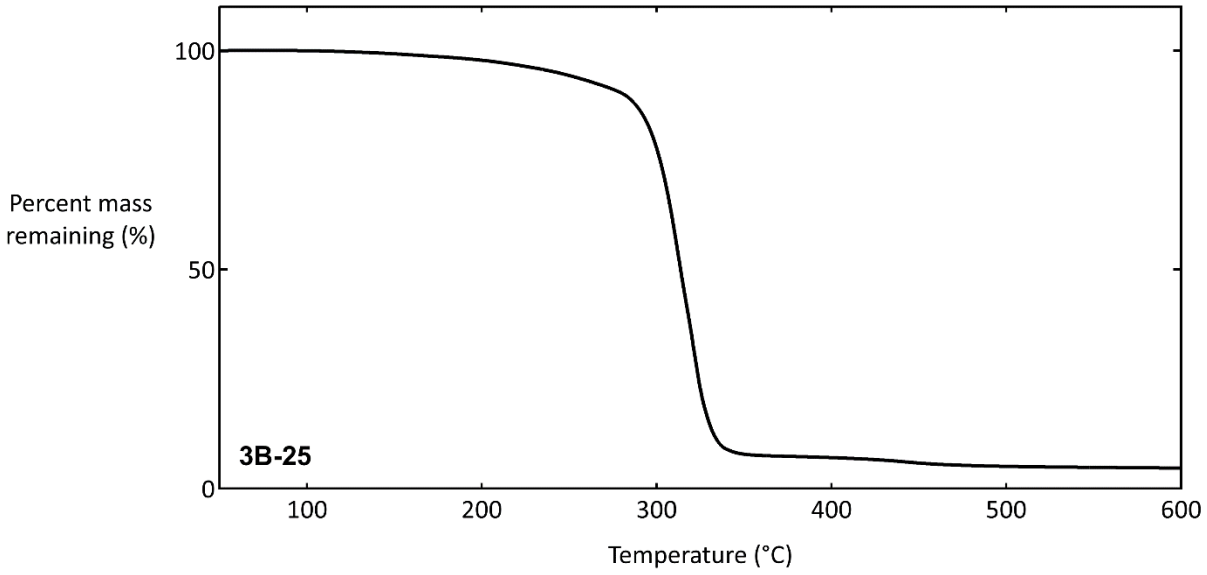


Figure S36. TGA of P4MCL bottlebrush polymer network **3B-25**.

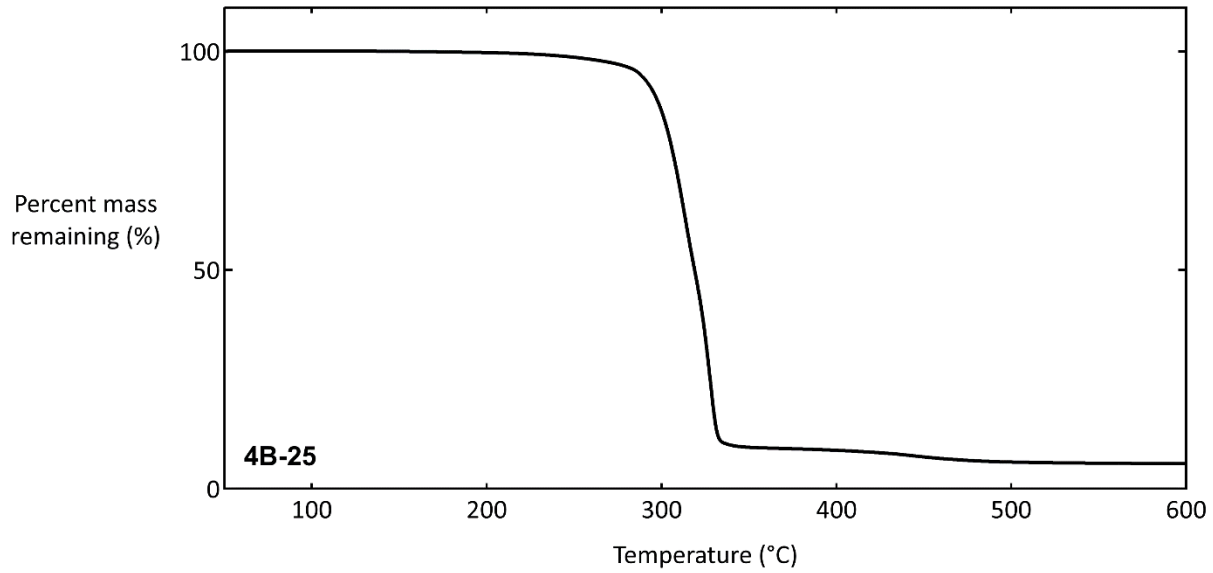


Figure S37. TGA of P4MCL bottlebrush polymer network **4B-25**.

Summary of thermal analysis

Table S6. Compiled results of thermal analysis for all measured solid small molecules, representative polymers, and networks samples.

Sample	T_g (°C)	T_{d5} (°C)
NbOH initiator	n/a	188
BD crosslinker	n/a	257
P4MCL macromonomer (**B**)	−63	217
P4MCL bottlebrush polymer (**1B**)	−59	274
1B-25	−60	224
2B-25	−59	264
2B-35	−60	211
2B-45	−58	266
3B-25	−61	243
4B-25	−59	287

NMR spectra

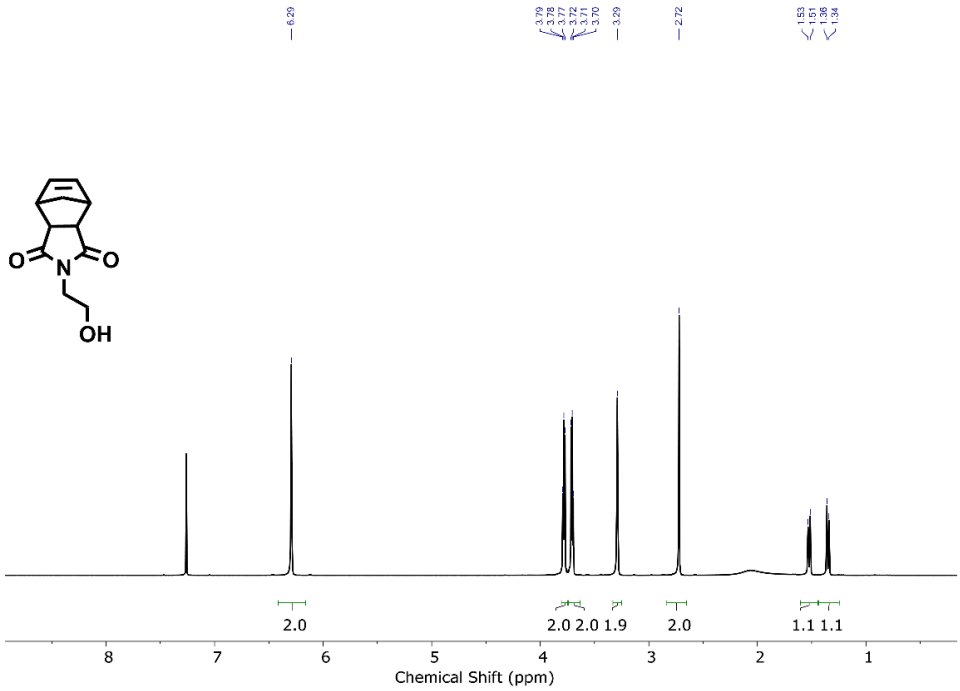


Figure S38. ^{1}H NMR spectrum of NbOH initiator.

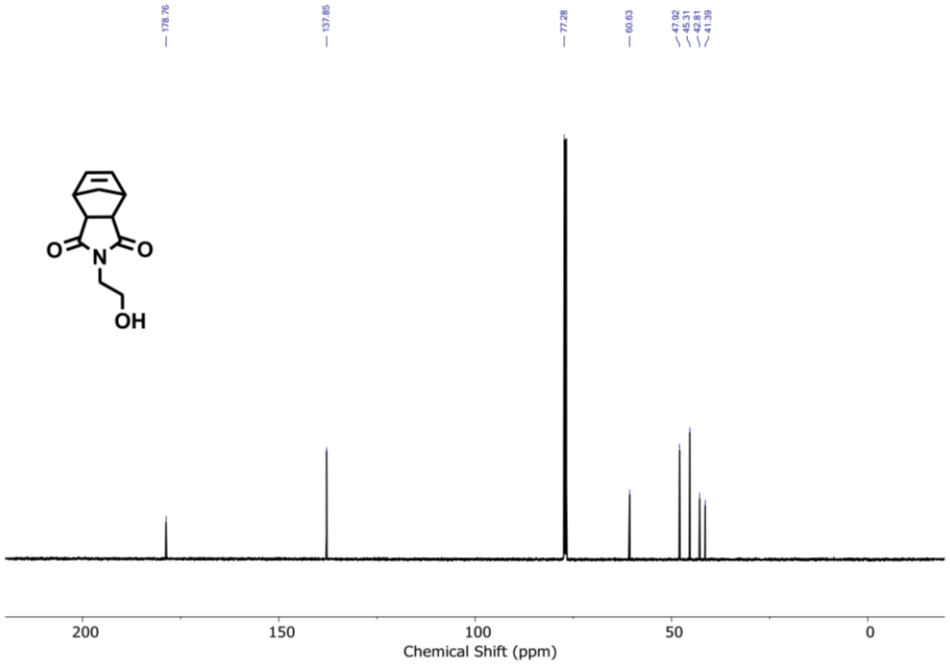


Figure S39. ^{13}C NMR spectrum of NbOH initiator.

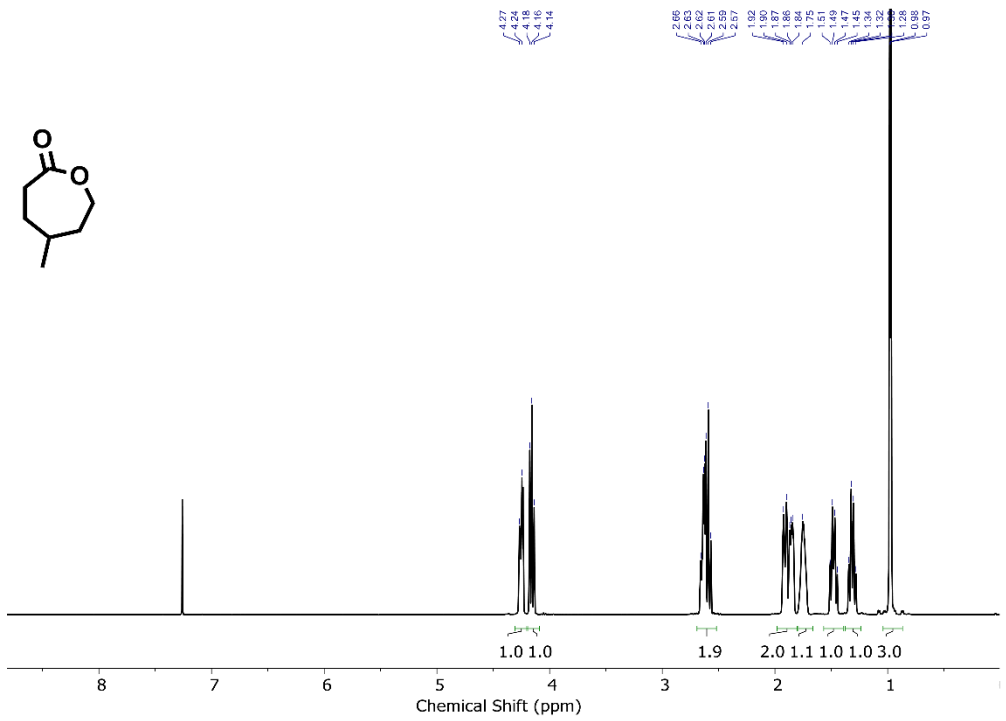


Figure S40. ^{1}H NMR spectrum of 4MCL monomer.

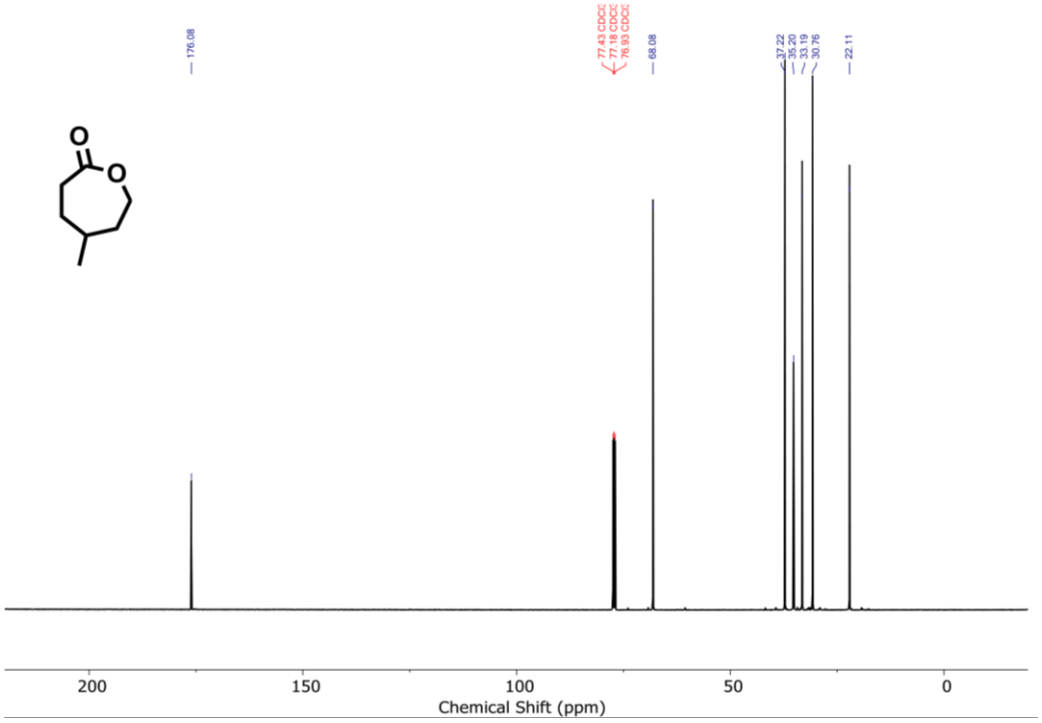


Figure S41. ^{13}C NMR spectra of 4MCL monomer.

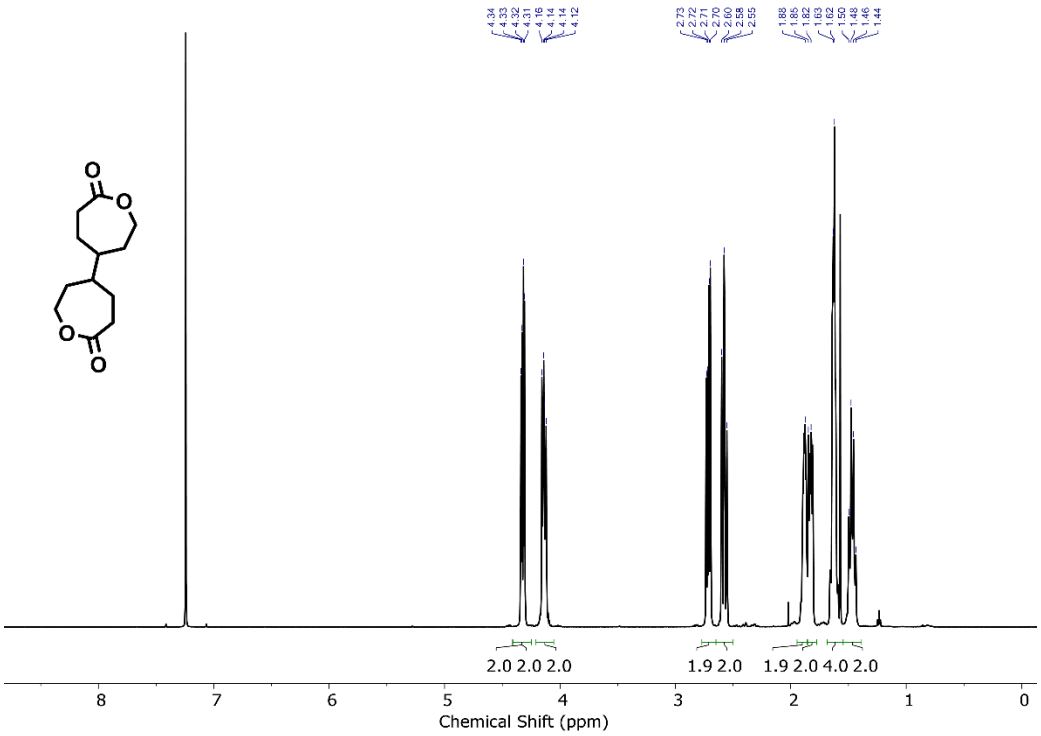


Figure S42. ^{1}H NMR spectrum of BD crosslinker.

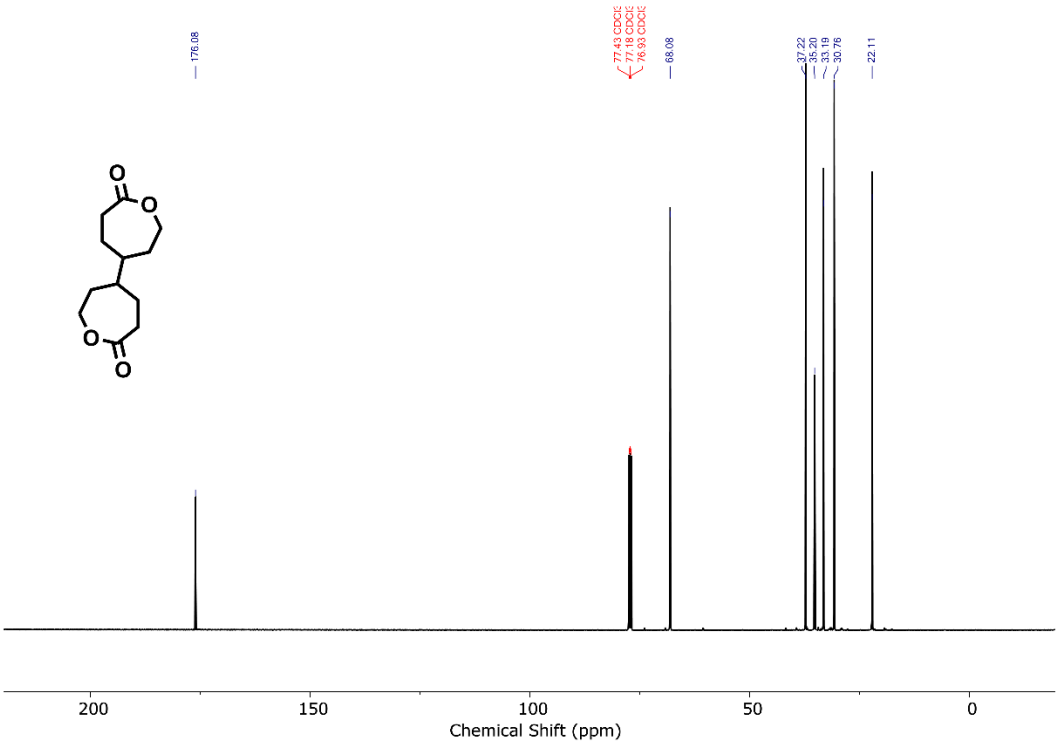


Figure S43. ^{13}C NMR spectrum of BD crosslinker.

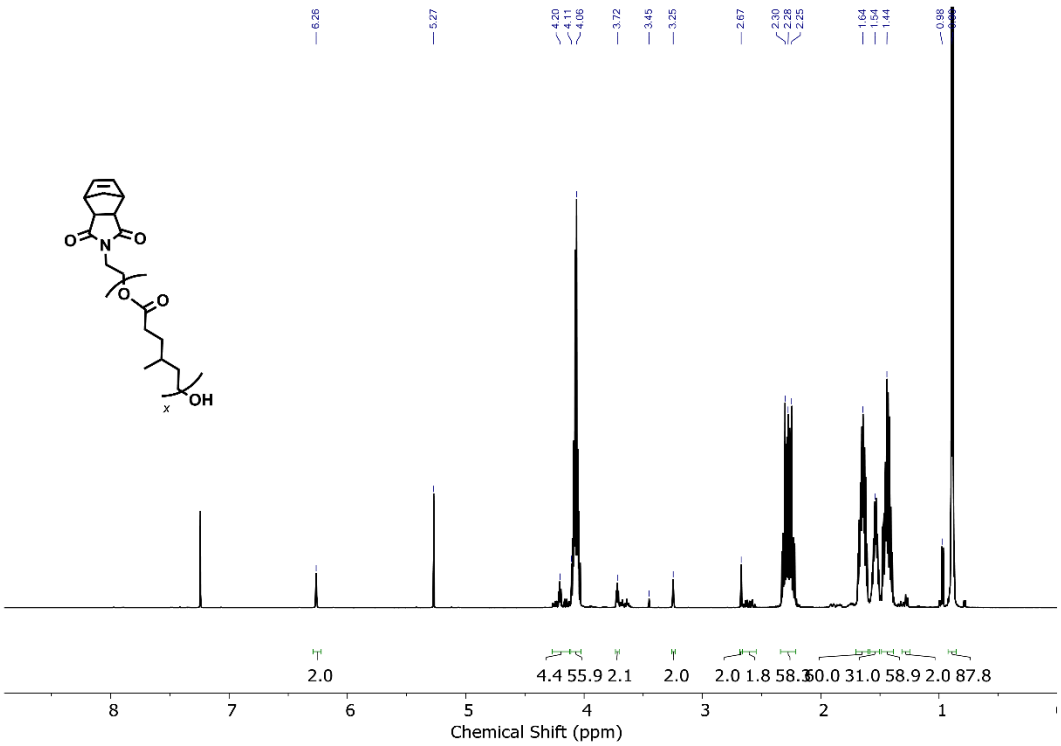


Figure S44. ^{1}H NMR spectrum of P4MCL macromonomer **B**.

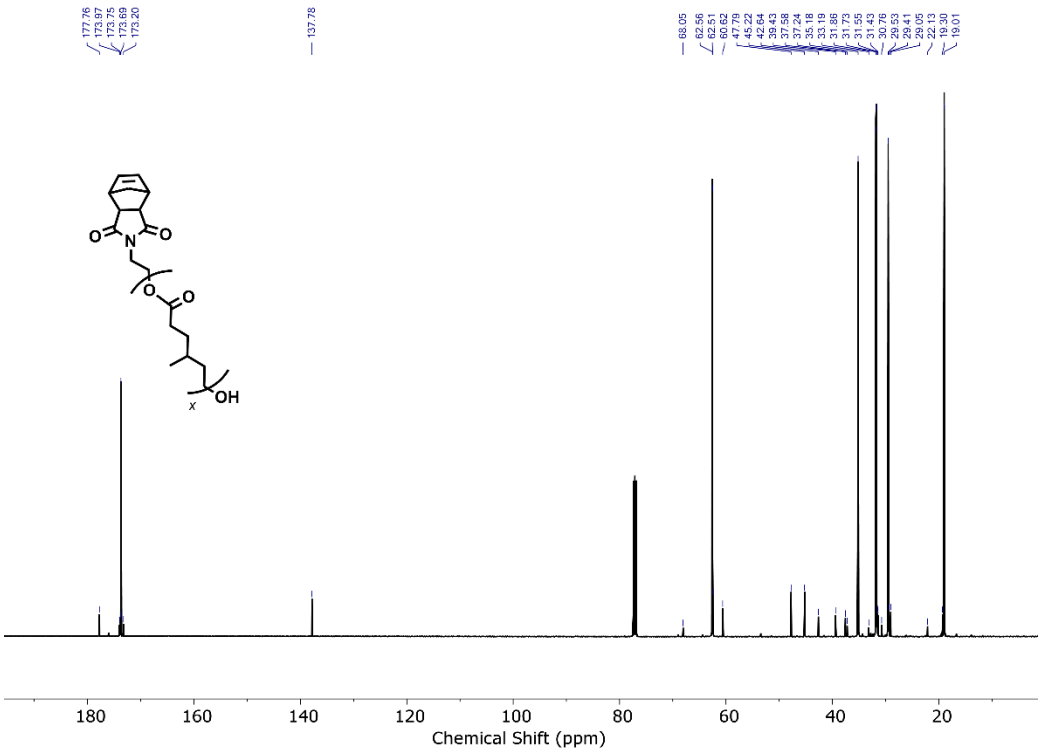


Figure S45. ^{13}C NMR spectrum of P4MCL macromonomer **B**.

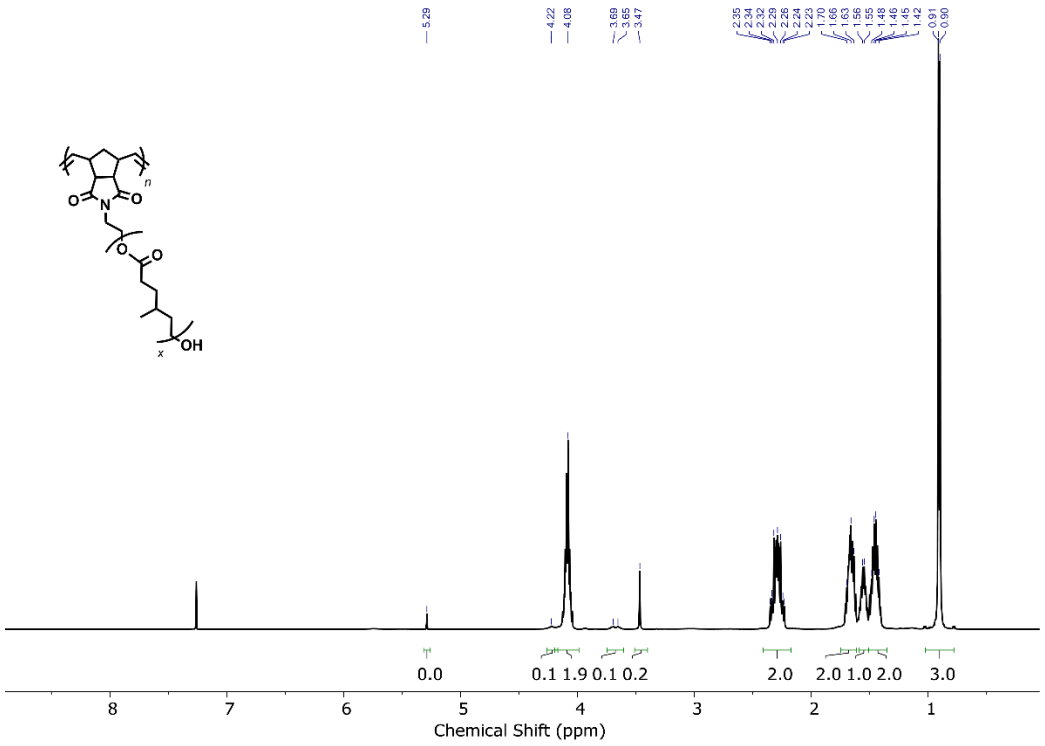


Figure S46. ^{1}H NMR spectrum of P4MCL bottlebrush polymer **1B**.

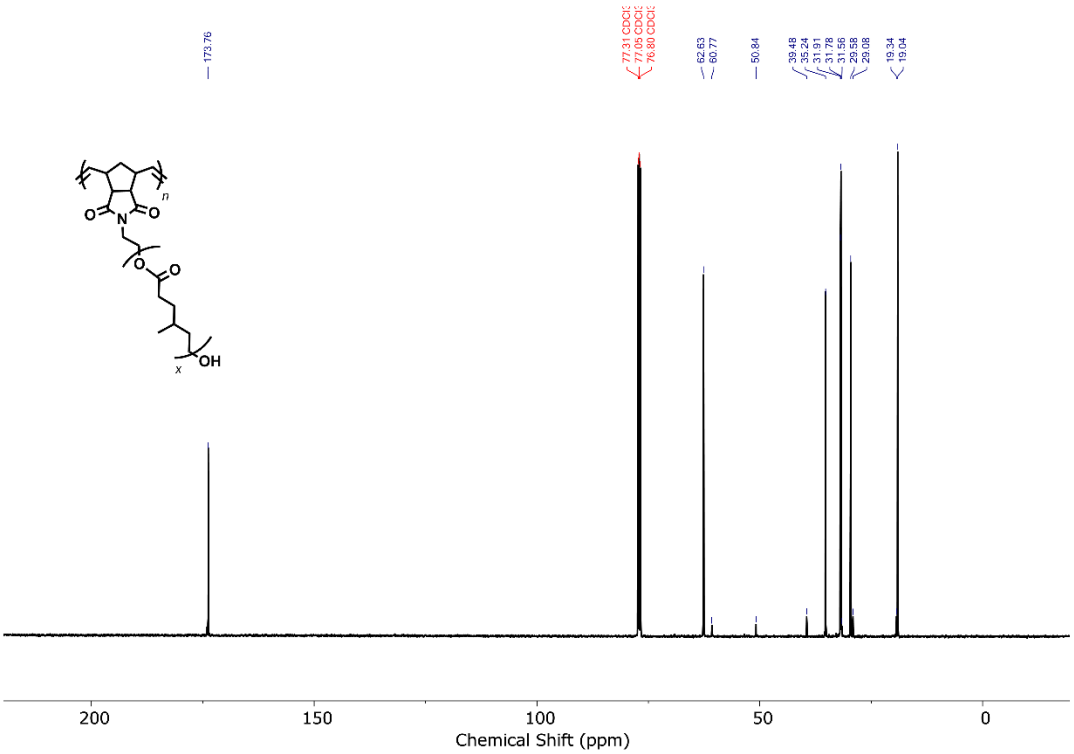


Figure S47. ^{13}C NMR spectrum of P4MCL bottlebrush polymer **1B**.

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