Supporting Information for

Controlled Polymerization of β-Pinadiene: Accessing Unusual Polymer Architectures with Biomass-Derived Monomers

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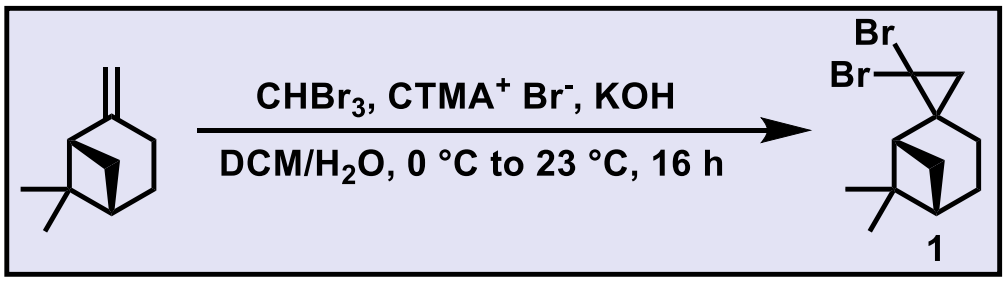
1 General Considerations

1.1 Materials and Methods

Unless otherwise noted, solvents were dried on an MBraun solvent purification system with 3Å molecular sieves and degassed with three freeze pump thaw cycles. All other reagents were obtained from commercial sources and used without further purification. Oxygen and water sensitive manipulations were performed in a nitrogen filled MBraun glovebox or using standard Schlenk techniques. All polymerizations were performed in a N_2 filled glovebox. ^1H and ^{13}C NMR data were collected on a Varian 600 MHz NMR, Varian 500 MHz NMR, or Varian 300 MHz NMR spectrometer. Chemical shifts (δ) are reported in ppm using the residual solvent as reference. Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA Q500 and Dynamic Mechanical Analysis (DMA) data was collected on a TA Instruments DMA Q800 with a powder clamp. Gel Permeation Chromatography (GPC) data was collected on an Omnisec Resolve and Omisec Reveal System using triple detection with detectors in series: UV, light scattering, viscometer, and refractive index and three Viscotek styrene divinylbenzene copolymer columns (in series T3000, T4000, and T5000) at a flow rate of 1 mL/min and thermostatted to 30 °C using either tetrahydrofuran (THF) or chloroform ($CHCl_3$) as the eluent. Molecular weight and dispersity data were determined using triple detection. Wide angle X-ray scattering (WAXS) of powder samples was performed on a Malvern Panalytical Empyrian X-ray diffractometer with a Cu anode and k(α) wavelength of 1.5406 Å.

2 Monomer Synthesis

2.1 Synthesis of 1[1,2]

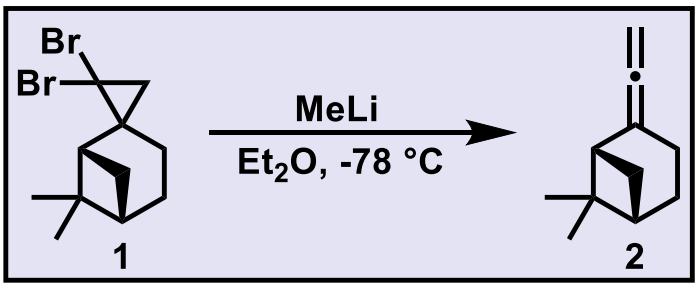


Scheme S1: Synthesis of **1**

A 500 mL round bottom flask was charged with a Teflon stir bar, (1*S*)-(-)-β-pinene (8.71 g, 63.86 mmol), dichloromethane (DCM, 100 mL), bromoform ($CHBr_3$, 12.27 mL, 127.72 mmol), and cetyltrimethylammonium bromide ($CTMA^+$ Br^-, 465.5 mg, 1.28 mmol). The mixture was cooled to 0 °C, and KOH (50% w/w in water) was added dropwise (21.5 g, 383.16 mmol). The resulting mixture was left to stir for 16 h while warming to room temperature. The reaction mixture was then neutralized with 2 M HCl and diluted with water (75 mL). The organic phase was separated, and the aqueous phase was extracted with DCM (2 x 50 mL). The combined organic layers were washed with brine (2 x 100 mL), dried over sodium sulfate, and filtered. The solvent was removed under vacuum,

after which the crude product was dissolved in hexanes and filtered through a plug of silica gel. Subsequent solvent removal under vacuum afforded **1** as a colorless oil (18.35 g, 93% yield). **^{1}H NMR (300 MHz, $CDCl_3$):** δ 2.51-2.36 (1H, m), 2.26 (1H, dt, J = 10 Hz, J = 6 Hz), 2.00-1.86 (4H, m), 1.58-1.48 (3H, m), 1.43-1.31 (1H, m), 1.24 (3H, s), 0.91 (3H, s). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 50.13, 40.24, 40.08, 39.72, 26.88, 24.41, 26.06, 23.82, 21.78. Spectral data are shown in Figures S15 and S16.

2.2 Synthesis of 2

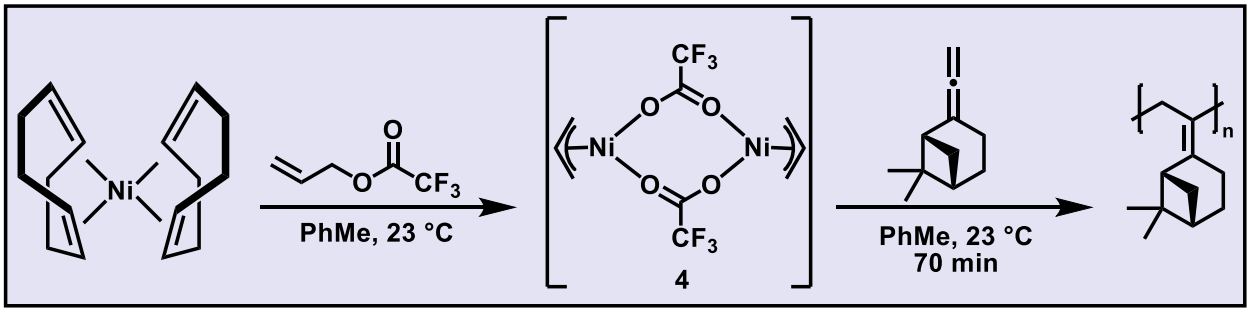


Scheme S2: Synthesis of **2**

A 100 mL flame dried Schlenk flask was charged with a Teflon stir bar, **1** (6.16 g, 20.00 mmol), and diethyl ether (Et_2O, 40 mL) before cooling the solution to -78 °C (10 min isotherm). Methyllithium (1.6 M in Et_2O, 14.40 mL, 23.04 mmol) was then added dropwise, and the reaction was stirred at -78 °C for 45 min. The reaction mixture was then warmed to 0 °C and quenched with water (15 mL). The mixture was then warmed to room temperature and further diluted with water (10 mL). The organic phase was separated, and the aqueous layer was extracted with Et_2O (3 x 15 mL). The combined organic layers were washed with brine (2 x 20 mL), dried over sodium sulfate, filtered, and concentrated under vacuum. Vacuum distillation at 65 °C afforded **2** as a colorless oil (2.51 g, 84.7% yield). Spectral data were consistent with literature reports.[1,2] **2** was further characterized by ^{13}C, ^{1}H-^{1}H COSY, and ^{1}H-^{13}C HSQC NMR spectroscopy (see section 3.1.1 for additional details). Spectral data are shown in Figures S17 – S20.

3 Polymerization Studies and Material Characterization

3.1 General Procedure for the Vinyl-Addition Polymerization of 2 Using 4



Scheme S3: Generation of **4** *in situ* and Synthesis of **3**

In an N_2 filled glovebox, bis(1,5-cyclooctadiene)nickel(0) (10 mg, 0.036 mmol) was dissolved in toluene (1.38 mL). To this solution was added allyltrifluoroacetate (4.7 µL, 0.036 mmol), which generated **4** *in situ*. This freshly prepared stock solution of **4** ([Ni] = 0.026 M) was subsequently used in polymerization studies. An aliquot of the catalyst stock solution was added to a solution of **2** in toluene (0.25 M). The amount of catalyst solution added was dictated by the desired $[\mathbf{2}]_0$:$[\mathbf{Ni}]_0$ ratios (Table S1). Polymerizations were conducted at 23 °C for 70 min unless otherwise noted in Table 1. Polymerizations were quenched by precipitation into methanol. The precipitated solids were filtered and then dried under vacuum. GPC data for the isolated polymers are reported in Figure S1. ^{1}H and ^{13}C NMR spectra for the precipitated material were collected in $CDCl_3$ (Figures S21 and S22).

Table S1: Selected Molecular Weight Data for **3**.

Entry	$[2]_0$:$[Ni]_0$	M_n (Da)$^{(a)}$	Target $M_n^{(b)}$	Đ$^{(c)}$
1	34:1	7,504	5,040	1.37
2	86:1	18,920	12,750	1.19
3	169:1	26,420	25,050	1.13
4	337:1	52,030	49,960	1.23
5	503:1	66,270	74,570	1.23
6	688:1	99,580	102,000	1.31

(a) Determined by GPC. (b) Calculated using $[\mathbf{2}]_0$:$[\mathbf{Ni}]_0$ X 148.25 (rounded values shown). (c) Calculated using M_W/M_n.

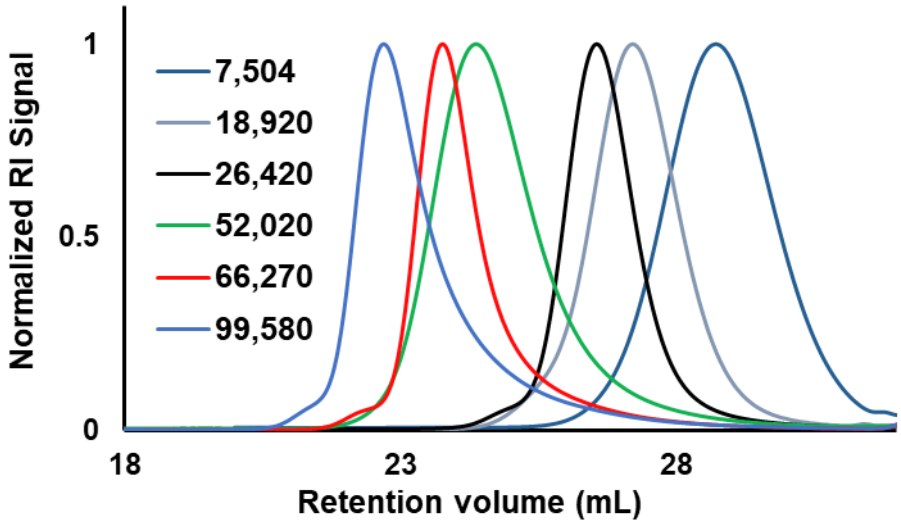


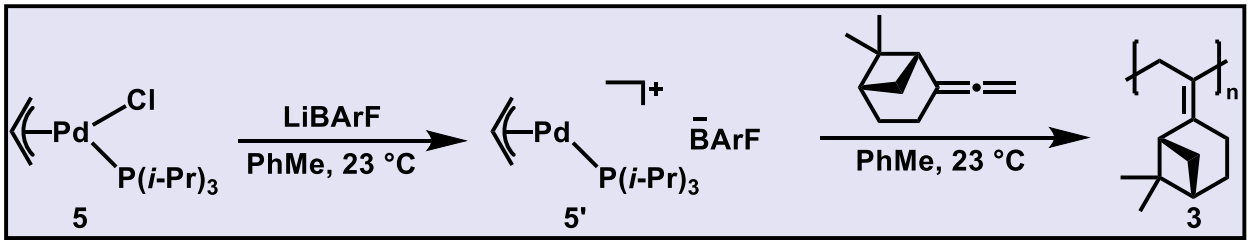
Figure S1: Selected GPC Data for **3.**

3.1.1 Confirmation of Fused-Ring Structure of 3

The HSQC spectrum of **2** (Figure S19) shows the ^{1}H resonances at δ = 2.57 and 2.21 (each of which integrates to 1H) correlate to the same ^{13}C resonance at δ = 19.60; therefore, these protons represent a methylene set. The ^{1}H resonances at δ = 2.34 and 1.51 (each of which integrates to 1H) correlate to the same ^{13}C resonance at δ = 26.14; therefore, these protons represent another methylene set. Finally, the ^{1}H resonances at δ = 1.89 and 1.82 (each of which integrates to 1H) correlate to the same ^{13}C resonance at δ = 23.67; therefore, these protons represent another methylene set. The ^{1}H resonances at δ = 2.47 and 1.92 each integrate to 1H and correlate to separate ^{13}C resonances (δ = 47.73 and 40.31, respectively); thus, these correspond to two methines. The COSY spectrum of **2** (Figure S20) shows a correlation between the methylene set at δ = 2.57 and 2.21 with the vinylic protons of the allene unit which can therefore be assigned as the methylene vicinal to the allene. The two methine protons were found to have correlations with the remaining two methylene sets, making the determination of the bridging methylene difficult. As such, the HSQC spectrum of **2** was found to be more diagnostic.

Due to significant broadening and overlap in the ^{1}H and ^{13}C NMR spectra of **3** (M_n = 79,910 Da), COSY correlations were not as informative (Figure S23). However, the HSQC spectrum of **3** (Figure S24) clearly shows the retention of two methine protons (correlating to ^{13}C resonances at δ = 46.39 and 40.73, respectively); these correlations and chemical shifts are not consistent with the presence of an endocyclic olefin. Three methylene sets are also observed in the HSQC spectrum of **3**.

3.2 Procedure for the Vinyl-Addition Polymerization of 2 Using 5



Scheme S4: Vinyl-Addition Polymerization of **2** Using **5**

In an N_2 filled glovebox, (η^3-allyl)Pd(*i*-Pr_3P)Cl (**5**; 0.8 mg, 0.0022 mmol) and LiBArF (1.5 mg, 0.0022 mmol) were taken up in toluene (0.2 mL) and allowed to stir for 15 min to generate **5'** *in situ* ([Pd] = 0.011 M). The solution of **5'** was then added to a solution of **2** (66 mg, 0.443 mmol). The reaction was allowed to stir at 23 °C for 70 min, at which time the solution was added to methanol to precipitate any polymeric material. GPC data for the isolated polymer is reported in Figure S2. ^{1}H NMR spectroscopic data for the precipitated material (collected in $CDCl_3$; Figure S25) was consistent with that observed for the material prepared using **4**.

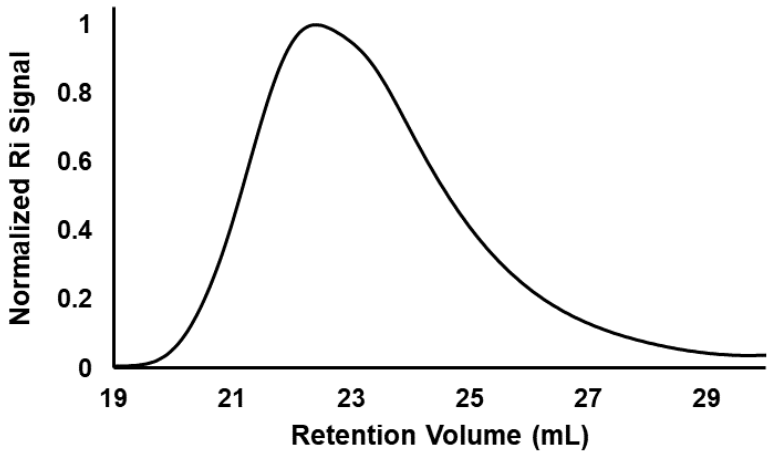
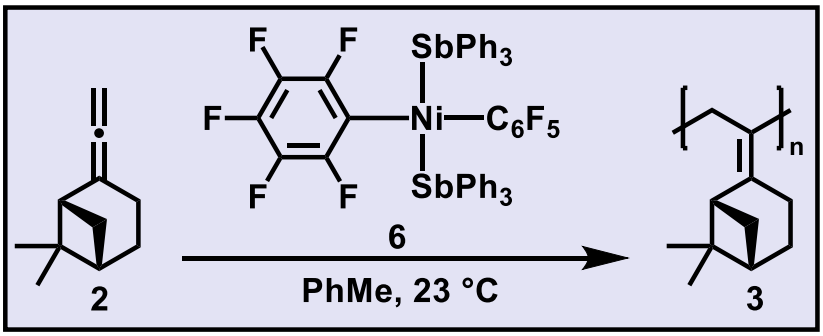


Figure S2: GPC Data for the Vinyl-Addition Polymerization of **2** Using **5'**

3.3 Procedure for the Vinyl-Addition Polymerization of 2 Using 6



Scheme S5: Vinyl-Addition Polymerization of **2** Using **6**

In an N_2 filled glovebox, *trans*-[Ni(C6F5)$_2$(SbPh3)$_2$] (2.6 mg, 0.0024 mmol) was taken up in toluene (0.2 mL). The solution of **6** ([Ni] = 0.012 M) was then added to a solution of **2** (73 mg, 0.489 mmol). The reaction was allowed to stir at 23 °C for 70 minutes, at which point polymer product was recovered by precipitation in methanol. GPC data for the isolated polymer is reported in Figure S3. ^{1}H NMR spectroscopic data for the precipitated material (collected in $CDCl_3$; Figure S26) was consistent with that observed for the material prepared using **4**.

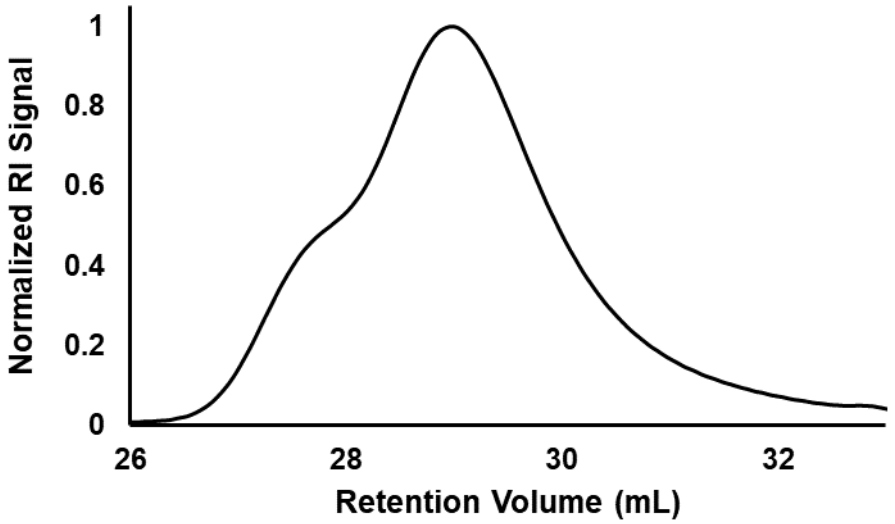


Figure S3: GPC Data for the Vinyl-Addition Polymerization of **2** Using **6**

3.4 Initiator Screen for Other Polymerizations of 2

Polymerization of **2** was also attempted under uncontrolled radical (section 3.4.1), controlled radical (section 3.4.2), anionic (section 3.4.3), and cationic conditions (sections 3.4.4 and 3.4.5). All reactions were performed outside of the glovebox using standard Schlenk techniques.

3.4.1 General Procedure for the Uncontrolled Radical Polymerization of 2

A flame dried, septum capped 2-dram vial was charged with a Teflon stir bar, **2** (100 mg 0.675 mmol), THF (2.0 mL), and AIBN (0.17 mg, 0.001 mmol). The resulting solution was subjected to three freeze-pump-thaw cycles and allowed to warm to room temperature under an atmosphere of N_2. Polymerizations were attempted under a variety of temperatures and times (Table S2); however, no polymeric product was recovered upon addition of the reaction mixtures to methanol.

3.4.2 General Procedure for the Controlled Radical Polymerization of 2

A flame dried, septum capped 2-dram vial was charged with a Teflon stir bar wrapped in copper wire, **2** (100 mg, 0.675 mmol), DMSO (2.0 mL), ethyl α-bromoisobutyrate (0.20 mg, 0.001 mmol), and PMDETA (50 µL, 7.19 mmol). The resulting solution was subjected to three freeze-pump-thaw cycles and allowed to warm to room temperature under an atmosphere of N_2. Polymerizations were attempted under a variety of temperatures and times (Table S2); however, no polymeric product was recovered upon addition of the reaction mixtures to methanol.

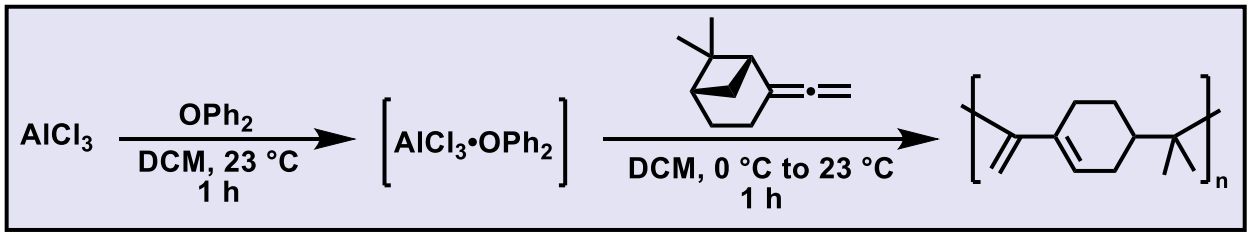
3.4.3 General Procedure for the Anionic Polymerization of 2

A flame dried 10 mL Schlenk flask was charged with a Teflon stir bar, **2** (150 mg, 1.01 mmol), and Et_2O (4 mL). The solution was cooled to 0 °C, and an alkyl lithium solution in Et_2O (0.0075 mmol lithiate; Table S2) was added. The reaction was then allowed to stir under an atmosphere on N_2 for 1 h. Polymerizations were attempted with a variety of alkyl lithiates under various temperatures (Table S2); however, no polymeric product was recovered upon addition of the reaction mixtures to methanol.

3.4.4 General Procedure for the Cationic Polymerization of 2

A flame dried, septum capped 2-dram vial was charged with a Teflon stir bar, 2 (150 mg, 1.01 mmol), and solvent (4 mL; see Table S2). In a separate flame dried, septum capped 2-dram vial, a 0.15 M stock solution of cationic initiator was prepared (Table S2). The solution of **2** was cooled to 0 °C, and the initiator solution was added via syringe. Reactions were carried out under an atmosphere of N_2 while warming from 0 → 23 °C over the course of 1 h. Polymeric product was recovered from methanol precipitation only in the case of polymerizations mediated by $AlCl_3$•OPh_2 (Table S2, entry 12; see section 3.4.5 for additional details).

3.4.5 Cationic Ring-Opening Polymerization of 2 with $AlCl_3$•OPh_2



Scheme S6: Cationic Ring-Opening Polymerization of **2** with $AlCl_3$•OPh2

The cationic ring-opening polymerization of **2** was performed according to a modification of the procedure developed by Kostjuk.[3] A flame dried, septum capped 2-dram vial was charged with a Teflon stir bar and $AlCl_3$ (74 mg, 0.55 mmol). The $AlCl_3$ was suspended in DCM (3.7 mL), and diphenyl ether (87.5 µL, 0.55 mmol) was added dropwise. The mixture was stirred for 1 h to generate a 0.15 M solution of the $AlCl_3$•OPh_2 complex. In a separate vial, **2** (140 mg, 0.94 mmol) was taken up in DCM (0.25 M) and cooled to 0 °C. The $AlCl_3$•OPh_2 solution (50 µL, 0.075 mmol) was then added via syringe to the solution of **2**, and the mixture was allowed to stir from 0 °C → 23 °C over a period of 1 h. The polymer product was recovered by precipitation in methanol (26.3 mg, 18.8% yield). GPC data for the isolated polymer is reported in Figure S4. ^{1}H NMR spectroscopic analysis of the precipitated material (collected in $CDCl_3$; Figure S27) revealed two sets of vinyl signals (δ = 5.61 and δ = 6.56), which was interpreted as evidence of ring-opening during the polymerization.

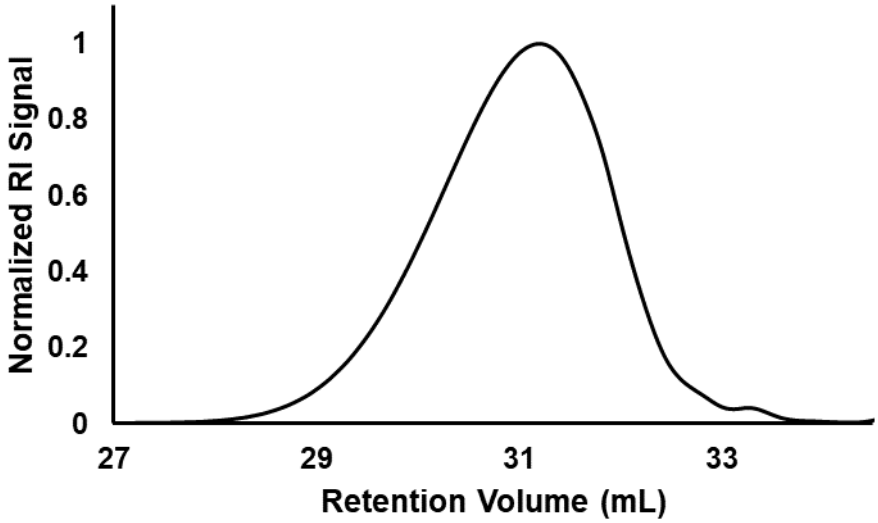
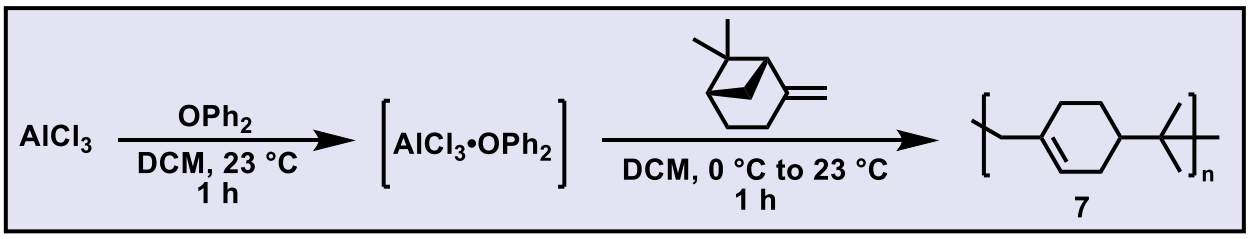


Figure S4: GPC Data for the Cationic Ring-Opening Polymerization of **2**

Table S2: Initiator Screen for the Ring-opening Polymerization of **2**

Entry	Initiator	Solvent	$[2]_0$:$[Initiator]_0$	Time (h)	Temperature (°C)	Yield (%)
1	AIBN	THF	650:1	16	80	0
2	AIBN	THF	650:1	24	80	0
3	AIBN	THF	650:1	16	90	0
4	Bromoisobutyrate (Cu/PMDETA)	DMSO	650:1	16	23	0
5	Bromoisobutyrate (Cu/PMDETA)	DMSO	650:1	16	50	0
6	MeLi	Et_2O	130:1	1	0	0
7	MeLi	Et_2O	130:1	1	23	0
8	n-BuLi	Et_2O	130:1	1	0	0
9	n-BuLi	Et_2O	130:1	1	23	0
10	BF_3OMe_2	Et_2O	140:1	1	0 – 23	0
11	$AlCl_3$	DCM	12.5:1	1	0 – 23	0
12	$AlCl_3$•OPh_2	DCM	12.5:1	1	0 – 23	18.8

3.5 Procedure for the Preparation of 7



Scheme S7: Preparation of **7**

7 was prepared according to a modification of the procedure developed by Kostjuk.[3] $AlCl_3$•OPh_2 was prepared according to the procedure described in section 3.4.5. In a separate flame dried Schlenk flask, (1*S*)-(-)-β-pinene (6.54 g, 36.7 mmol) was taken up in DCM/hexanes (21 mL:14 mL) and cooled to 0 °C. The $AlCl_3$•OPh_2 solution (0.75 mL, 0.11 mmol) was then added to via syringe, and the resulting mixture was allowed to stir at 0 °C for 2 min. After warming to room temperature, the solution was added to methanol to precipitate any polymeric material. Filtration of these solids afforded **7** as a white powder (1.08 g, 21.6% yield). GPC data for the isolated polymer is reported in Figure S5. ^{1}H and ^{13}C NMR spectra of the precipitated material was consistent with literature values[3–5] (Figures S28 and S29).

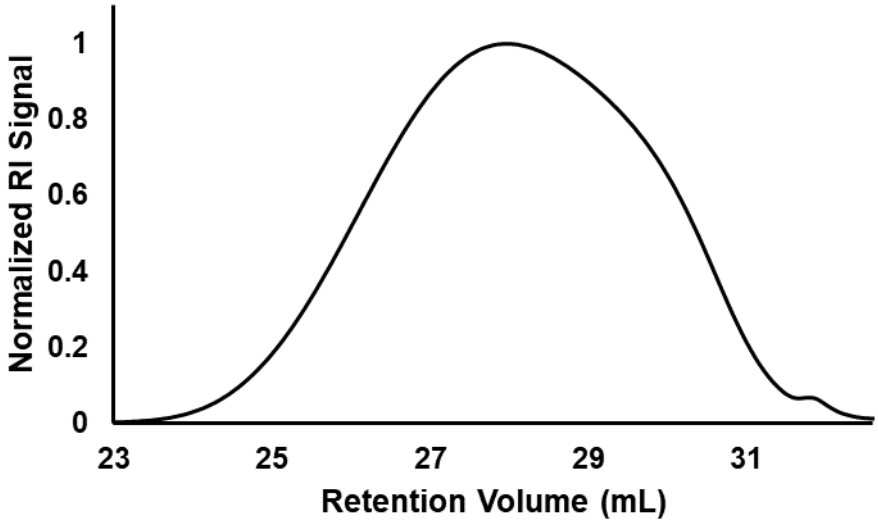


Figure S5: GPC Data for **7**

3.6 Thermomechanical Data

TGA thermograms were collected using powder samples of **3** and **7** (10 °C/min heating rate). Powder samples of **3** and **7** were analyzed by DMA using a powder clamp attachment. Samples were heated at a rate of 2 °C/min at 1.00 Hz.

3.6.1 TGA and DMA Data for 3

Representative thermomechanical data for **3** (M_n = 7,504 Da) are shown in Figures S6 and S7. The TGA thermogram of a powdered sample revealed an initial decomposition onset temperature of 294 °C (Figure S6). Negligible mass loss was observed below this temperature. A powder sample of the same polymer exhibited a peak in Tanδ at 160 °C (Figure S7) when analyzed by DMA.

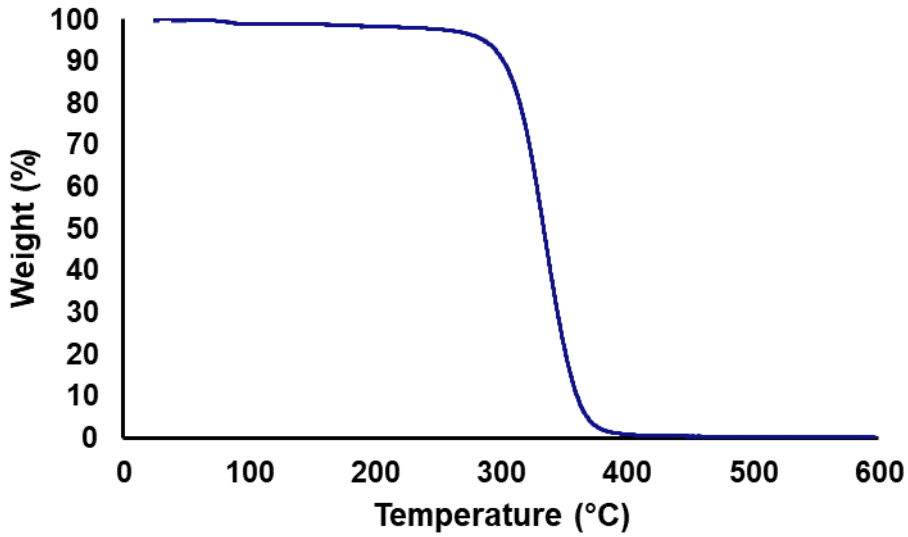


Figure S6: Representative TGA Thermogram of **3** (10 °C/min heating rate)

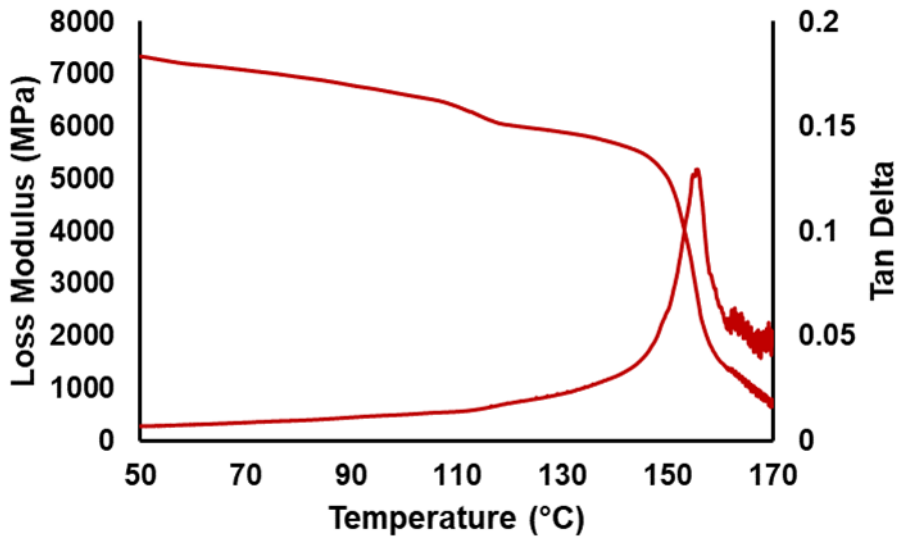


Figure S7: Representative Powder DMA of **3** (2 °C/min; 1.00 Hz)

3.6.2 TGA and DMA Data for 7

Representative thermomechanical data for **7** (M_n = 5,812 Da) are shown in Figures S8 and S9. The TGA thermogram of a powdered sample indicated an initial decomposition onset temperature of 303 °C (Figure S8). Negligible mass loss was observed below this temperature. A powder sample of the same polymer revealed a peak in Tanδ at 82 °C when analyzed by DMA (Figure S9).

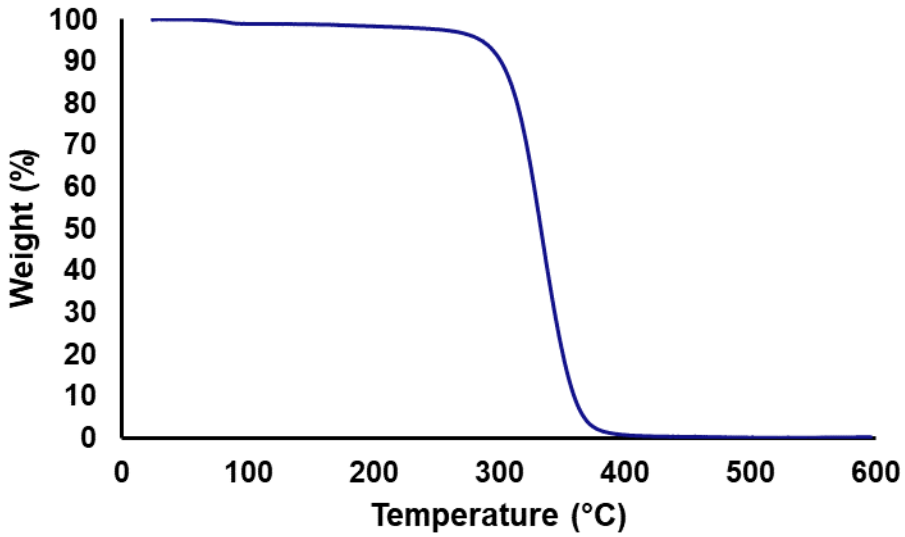


Figure S8: Representative TGA Thermogram of **7** (10 °C/min heating rate)

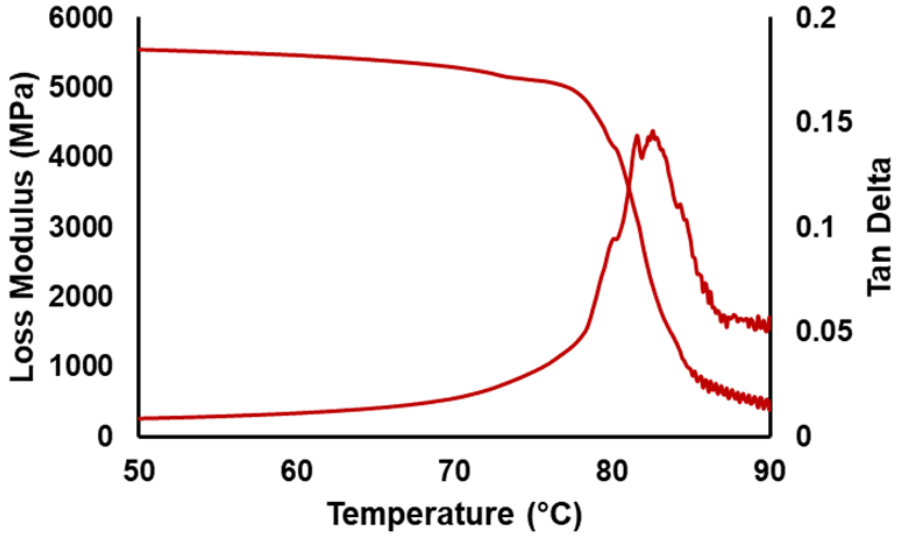


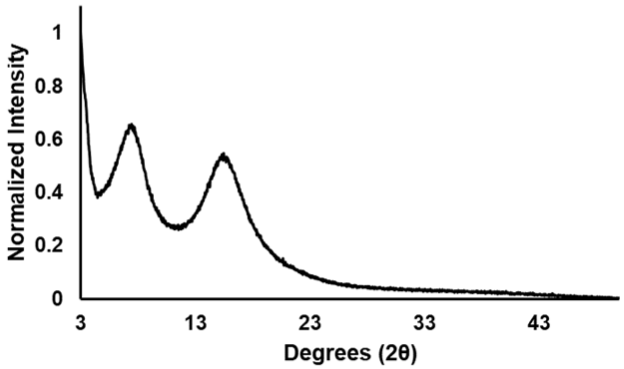
Figure S9: Representative Powder DMA of **7** (2 °C/min; 1.00 Hz)

3.6.3 WAXS Measurements of 3

WAXS was performed on low molecular weight (M_n = 7,504 Da) and high molecular weight (M_n = 79,910 Da) powder samples of **3**. WAXS was also performed on a powder sample of **7**, as well as annealed samples of **3** and **7**. WAXS measurements typically required 75 mg of polymer sample; comprehensive measurement parameters are given in Figures S10–12 and S13–14.

Freshly precipitated powder samples of **3** (both low and high molecular weight materials; Figures S10 and S11, respectively) displayed semi-crystalline peaks at 2θ = 7.45° and 15.52° (averaged from low and high molecular weight materials). A sample of **3** (M_n =

66,090 Da) was annealed for 1 h at 185 °C in a vacuum oven (Figure S12); WAXS analysis revealed similar semi-crystalline peaks at 2θ = 7.71° and 15.64°. The d-spacing values for all materials were calculated using Bragg's law. Crystallite sizes were calculated using the Scherrer equation (shape factor value of 0.9 and instrumental line broadening of 0.026°; results are summarized in Table S3). All calculations were performed following a baseline correction of the raw data file (second derivatives used as anchor points for baseline correction).



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Generator voltage	45	
Tube current 40		
Unit cell		
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Scan axis	Gonio	
Scan range	2.994799997	50.00121198
Scan step size	0.0262606	
No. of points 1790		
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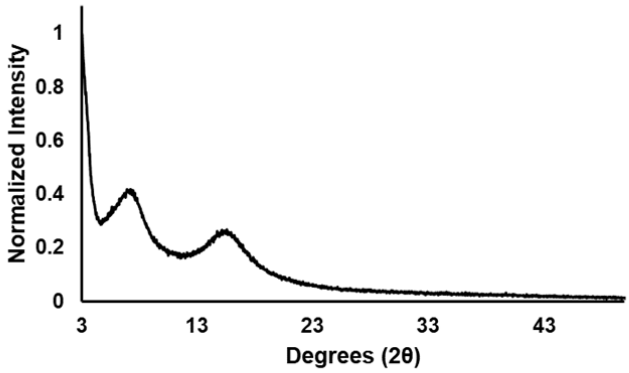
Figure S10: WAXS Spectrum of Low Molecular Weight (M_n = 7,504 Da) **3**



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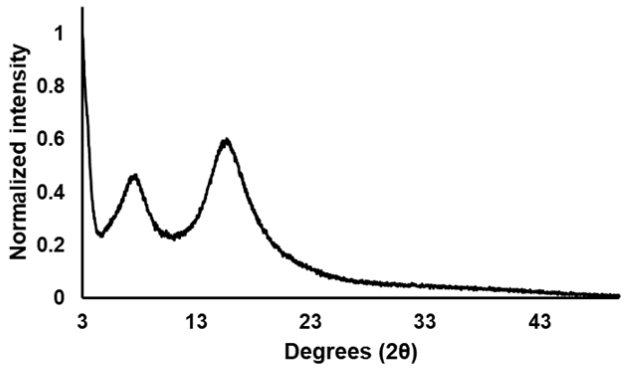
Divergence slit	Fixed	0.25
Monochromator used	NO	
Generator voltage	45	
Tube current 40		
Unit cell		
h k l	0 0 0	
Scan axis	Gonio	
Scan range	2.994799997	50.00121198
Scan step size	0.0262606	
No. of points 1790		
Scan type	CONTINUOUS	
Phi	170.1	
Time per step	46.665	

Figure S11: WAXS Spectrum of High Molecular Weight (M_n = 79,910 Da) **3**



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Comment - 4 Diffractometer system=EMPYREAN
Comment - 5 Measurement program=C:\PANalytical\Data Collector\Programs\Alan Fried\PDS + PASS - Pixcel - 3-50 deg - 0.026 deg step - 50 sec - 6 minutes.xrdmp, Identifier={AE262BF2-69C2-4DE7-9468-26D0DFFEC50F}

Anode material	Cu
K-Alpha1 wavelength	1.540598
K-Alpha2 wavelength	1.544426
Ratio K-Alpha2/K-Alpha1	0.5
Divergence slit	Fixed
Monochromator used	NO
Generator voltage	45
Tube current	40
Unit cell	
h k l	0 0 0
Scan axis	Gonio
Scan range	2.994799997
Scan step size	0.0262606
No. of points	1790
Scan type	CONTINUOUS
Phi	0
Time per step	46.665

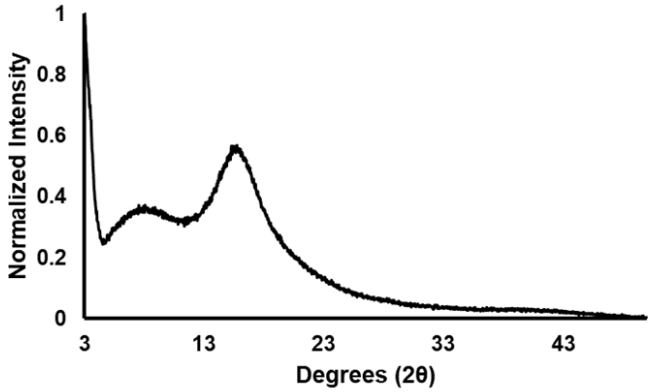
Figure S12: WAXS spectrum of Annealed **3** (M_n = 66,090 Da)

Table S3: WAXS Data for **3**

	Low angle peak			High angle peak		
	Angle (2θ)	**d-spacing (nm)**	**Crystallite (Å)**	**Angle (2θ)**	**d-spacing (nm)**	**Crystallite (Å)**
3 (7.5 kDa)	**7.45**	**11.86**	**32.4**	**15.48**	**5.72**	**22.6**
3 (79.9 kDa)	**7.45**	**11.85**	**33.4**	**15.57**	**5.69**	**21.7**
Annealed 3	**7.71**	**11.46**	**34.3**	**15.64**	**5.66**	**23.0**

3.6.4 WAXS Measurements of 7

WAXS analysis of a powder sample of **7** (M_n = 5,812 Da; Figure S13) displayed an amorphous peak at 2θ = 7.52° and a semi-crystalline peak at 15.74°. A separate sample of **7** (M_n = 6,151 Da) was annealed for 1 h at 105 °C in a vacuum oven (Figure S14); WAXS analysis revealed an amorphous peak at 2θ = 6.34° and a semi-crystalline peak at 15.85°. The d-spacing values for all materials were calculated using Bragg's law. Crystallite sizes were calculated using the Scherrer equation (shape factor value of 0.9 and instrumental line broadening of 0.026°; results are summarized in Table S4). All calculations were performed following a baseline correction of the raw data file (second derivatives used as anchor points for baseline correction)



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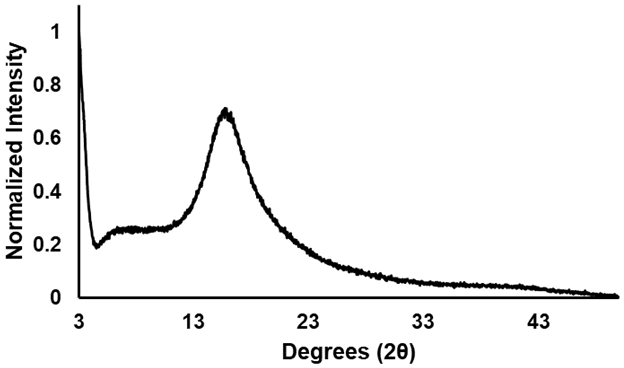
Comment - 3 Sample stage=Reflection-transmission spinner; Minimum step size Phi:0.1
Comment - 4 Diffractometer system=EMPYREAN
Comment - 5 Measurement program=C:\PANalytical\Data Collector\Programs\Alan Fried\PDS + PASS - Pixcel - 3-50 deg - 0.026 deg step - 50 sec - 6 minutes.xrdmp, Identifier={AE262BF2-69C2-4DE7-9468-26D0DFFEC50F}

Anode material	Cu	
K-Alpha1 wavelength	1.540598	
K-Alpha2 wavelength	1.544426	
Ratio K-Alpha2/K-Alpha1	0.5	
Divergence slit	Fixed	0.25
Monochromator used	NO	
Generator voltage	45	
Tube current 40		
Unit cell		
h k l	0 0 0	
Scan axis	Gonio	
Scan range	2.994799997	50.00121198
Scan step size	0.0262606	
No. of points 1790		
Scan type	CONTINUOUS	
Phi	21	
Time per step	46.665	

Figure S13: WAXS Spectrum of **7** (M_n = 5,812 Da)



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Comment - 3 Sample stage=Reflection-transmission spinner; Minimum step size Phi:0.1
Comment - 4 Diffractometer system=EMPYREAN
Comment - 5 Measurement program=C:\PANalytical\Data Collector\Programs\Alan Fried\PDS + PASS - Pixcel - 3-50 deg - 0.026 deg step - 50 sec - 6 minutes.xrdmp, Identifier={AE262BF2-69C2-4DE7-9468-26D0DFFEC50F}

Anode material	Cu	
K-Alpha1 wavelength	1.540598	
K-Alpha2 wavelength	1.544426	
Ratio K-Alpha2/K-Alpha1	0.5	
Divergence slit	Fixed	0.25
Monochromator used	NO	
Generator voltage	45	
Tube current 40		
Unit cell		
h k l	0 0 0	
Scan axis	Gonio	
Scan range	2.994799997	50.00121198
Scan step size	0.0262606	
No. of points 1790		
Scan type	CONTINUOUS	
Phi	221.4	
Time per step	46.665	

Figure S14: WAXS Spectrum of Annealed **7** (M_n = 6,151 Da)

Table S4: WAXS Data for **7**

	Low angle peak			High angle peak		
	Angle (2θ)	d-spacing (nm)	Crystallite (Å)	Angle (2θ)	d-spacing (nm)	Crystallite (Å)
7 (5.81 kDa)	7.52	11.74	21.4	15.74	5.62	23.6
Annealed 7	6.34	13.92	n/a	15.85	5.59	20.5

4 Determination of Living Character for the Polymerization of 2 Using 4

4.1 Molecular Weight as a Function of Monomer Conversion

In an N_2 filled glovebox, a stock solution of **4** was prepared according to the procedure outlined in section 3.1 ([Ni] = 0.026 M). In a separate vial, **2** (200 mg, 1.35 mmol) and mesitylene (as an internal standard; 188 µL, 1.35 mmol) were taken up in toluene-d8 (4.05 mL). A 0.26 mL (0.007 mmol in Ni) aliquot of the stock solution of **4** was added, and the reaction was allowed to stir at 23 °C. Aliquots (0.15 mL) of the reaction mixture were removed every 5 minutes, quenched by exposure to air, and analyzed using ^{1}H NMR spectroscopy. The aliquots were then concentrated to dryness and analyzed by GPC to determine the number average molecular weight (M_n) of any polymeric species (Table S5). The calculated M_n data were plotted as a function of monomer conversion, which revealed a linear correlation (Figure 2A).

Table S5: Living Plot Molecular Weight and Conversion Data

Entry	Reaction Time (min)	Conversion (%)	M_n (Da)	Đ
1	0	0	-	-
2	5	36	8,734	1.27
3	10	42	13,110	1.20
4	15	49	15,150	1.20
5	20	58	16,160	1.21
6	25	64	17,260	1.23
7	30	72	20,060	1.20
8	35	76	20,690	1.20
9	40	80	22,120	1.22
10	45	86	23,170	1.20

4.2 Chain Extension Experiment

In an N_2 filled glovebox, a stock solution of **4** was prepared according to the procedure in section 3.1([Ni] = 0.026 M). In a separate vial, **2** (150 mg, 1.01 mmol) and mesitylene (as an internal standard; 140.5 µL; 1.01 mmol) were taken up in toluene (7.0 mL). To the solution of **2,** a 0.385 mL aliquot of the stock solution of **4** was added (0.01 mmol Ni), and

the reaction was allowed to stir at 23 °C. After 70 min, a 0.2 mL aliquot of the reaction mixture was removed to confirm complete consumption of **2** by ^{1}H NMR spectroscopy. At this point, a 150 mg (1.01 mmol) portion of **2** in 0.2 mL of toluene was added to the polymerization mixture and allowed to stir. Another 0.2 mL aliquot was taken after 70 min, and ^{1}H NMR spectroscopic analysis revealed complete consumption of **2**. Finally, a second 150 mg (1.01 mmol) portion of **2** in 0.2 mL of toluene was added to the polymerization mixture and allowed to stir. Another 0.2 mL aliquot was taken after 70 min, and ^{1}H NMR spectroscopic analysis revealed complete consumption of **2**. All NMR aliquots were concentrated under vacuum and analyzed by GPC to determine the number average molecular weight (M_n) of any polymeric species (Table S6). Note: we calculated mmol Ni removed in each aliquot and iteratively subtracted this from the original total (0.01 mmol Ni). For each extension, we used this calculated mmol Ni, the measured M_n from the previous extension, and the amount of added monomer to determine target M_n. The observed data were consistent with successful chain extension (Figure 2B).

Table S6: Molecular Weight Data for Chain Extension of **3**

Entry	Extensions	M_n (Da)	Target M_n (Da)	Đ
1	0	28,530	14,973	1.30
2	1	45,420	43,920	1.30
3	2	59,590	61,238	1.36

5 NMR Spectroscopic Data

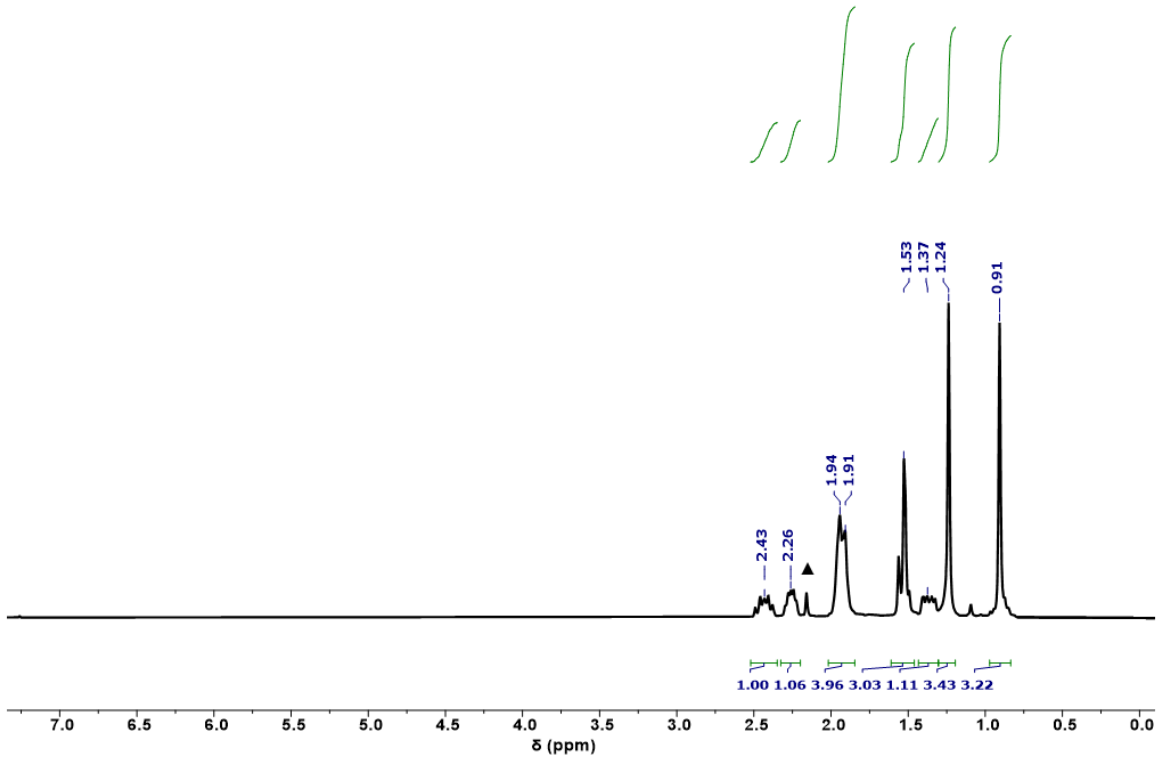


Figure S15: ^{1}H NMR Spectrum of **1**. Residual Acetone Represented by ▲.

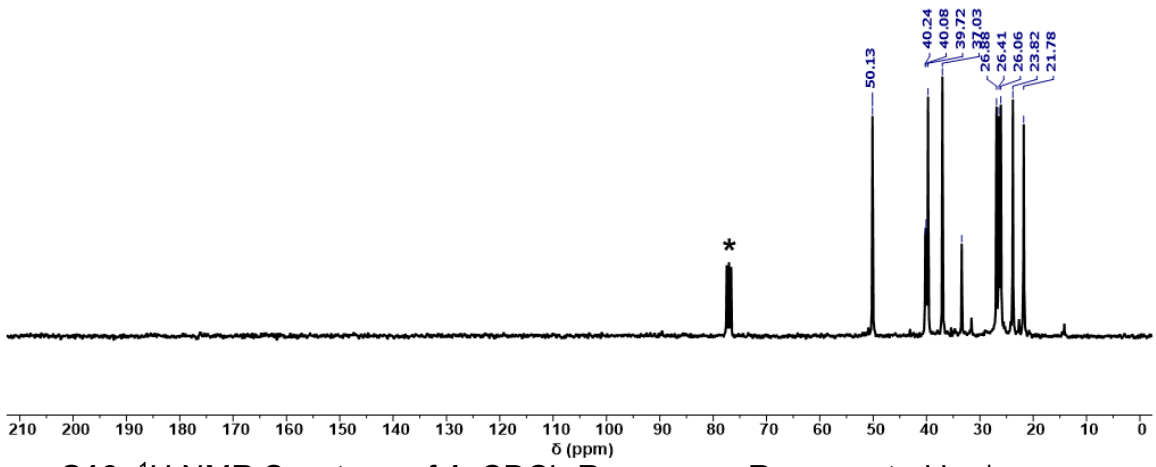


Figure S16: ^{1}H NMR Spectrum of **1**. $CDCl_3$ Resonance Represented by *

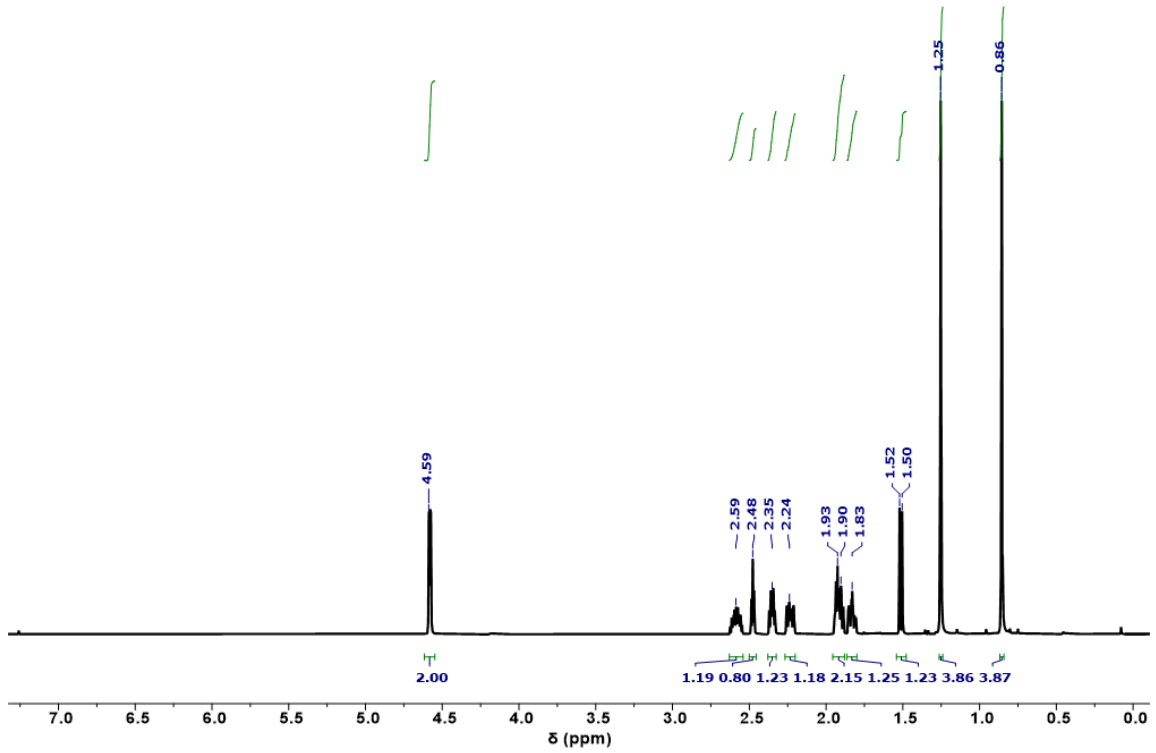


Figure S17: ^{1}H NMR Spectrum of **2**

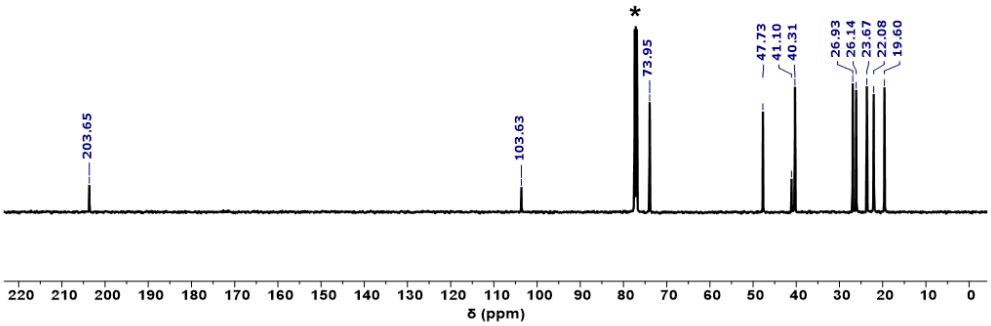


Figure S18: ^{13}C NMR Spectrum of **2**. $CDCl_3$ Resonance Represented by *

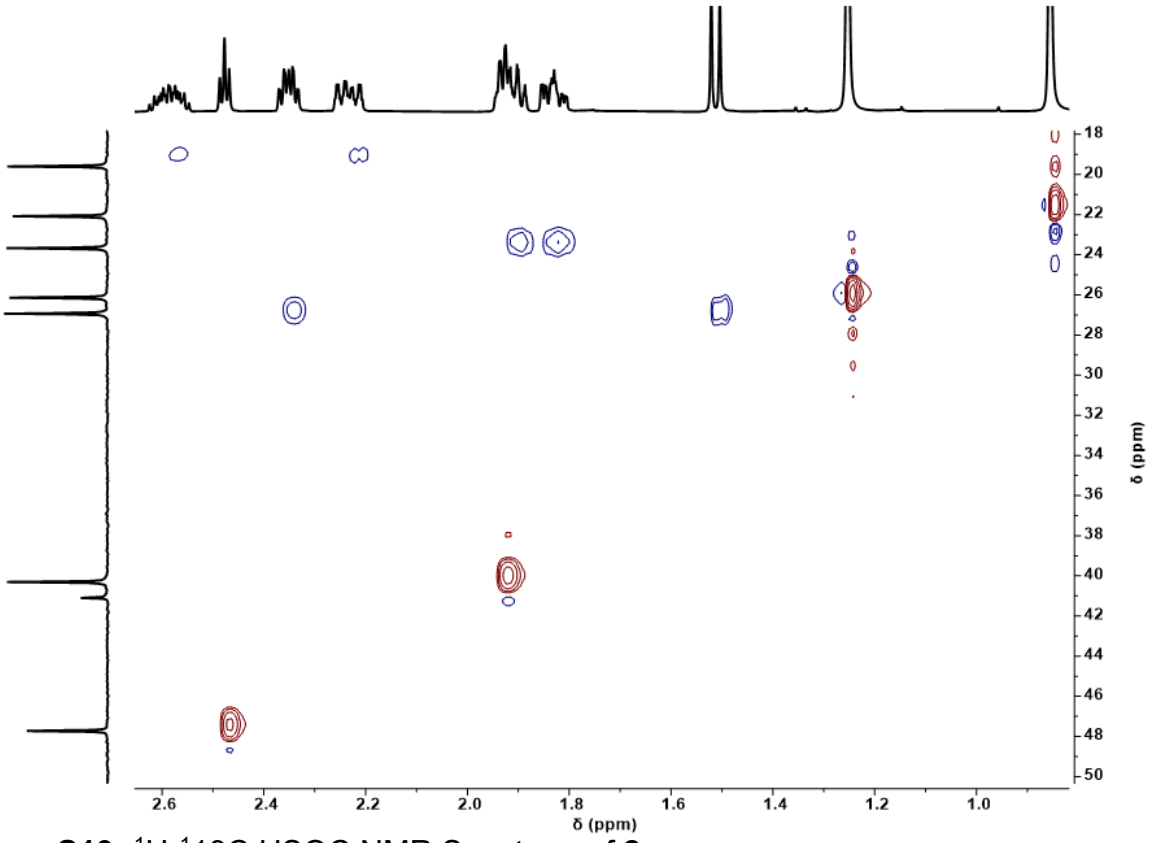


Figure S19: ^{1}H-$^{1}13C$ HSQC NMR Spectrum of **2**

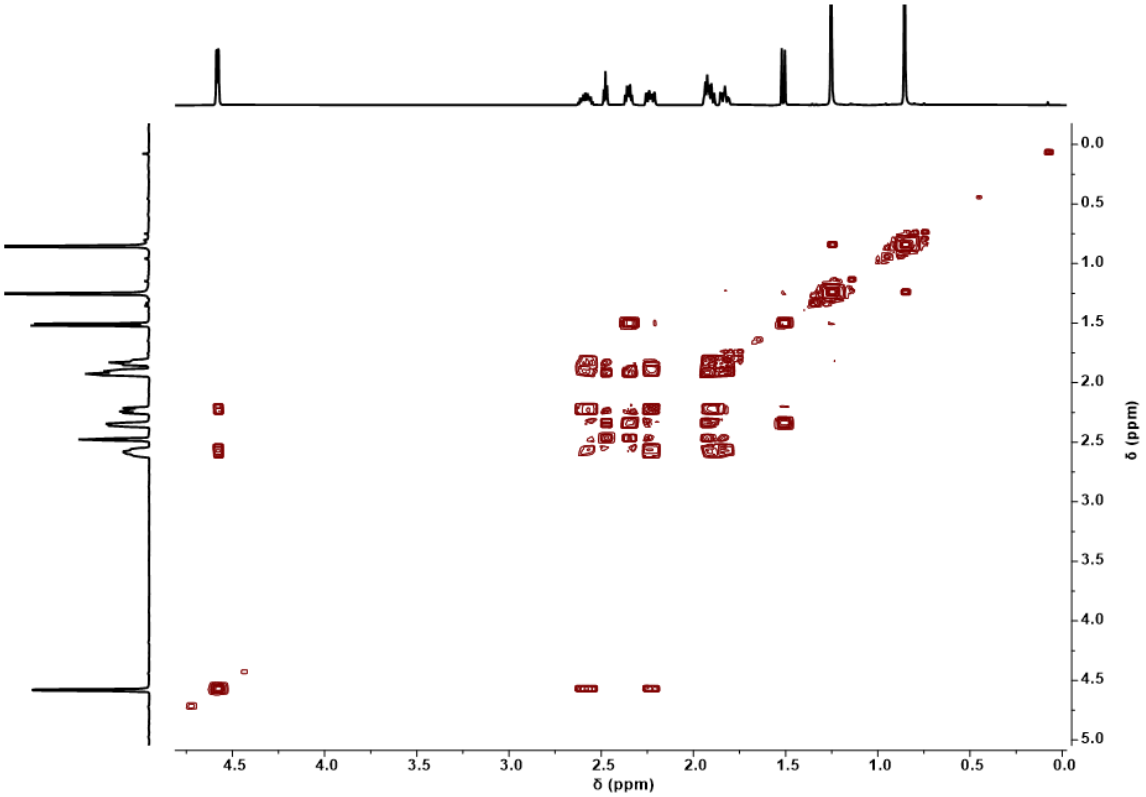


Figure S20: ^{1}H-^{1}H COSY NMR Spectrum of **2**

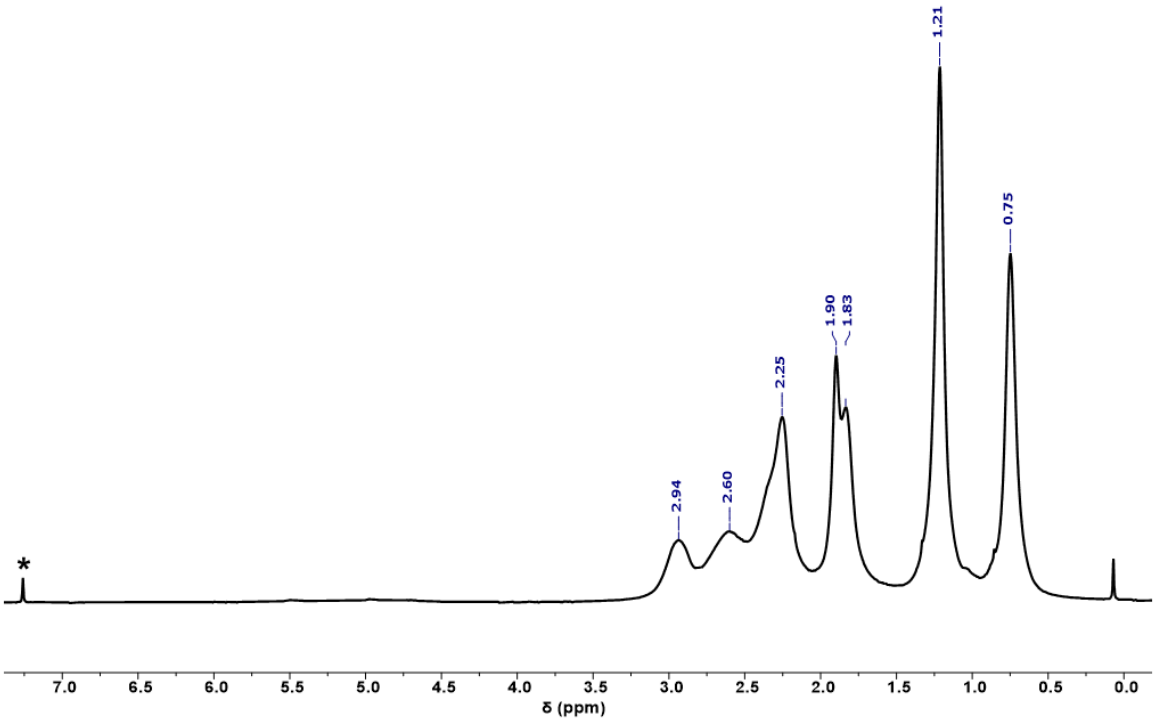


Figure S21: ^{1}H NMR Spectrum of **3**. Residual $CHCl_3$ Represented by *

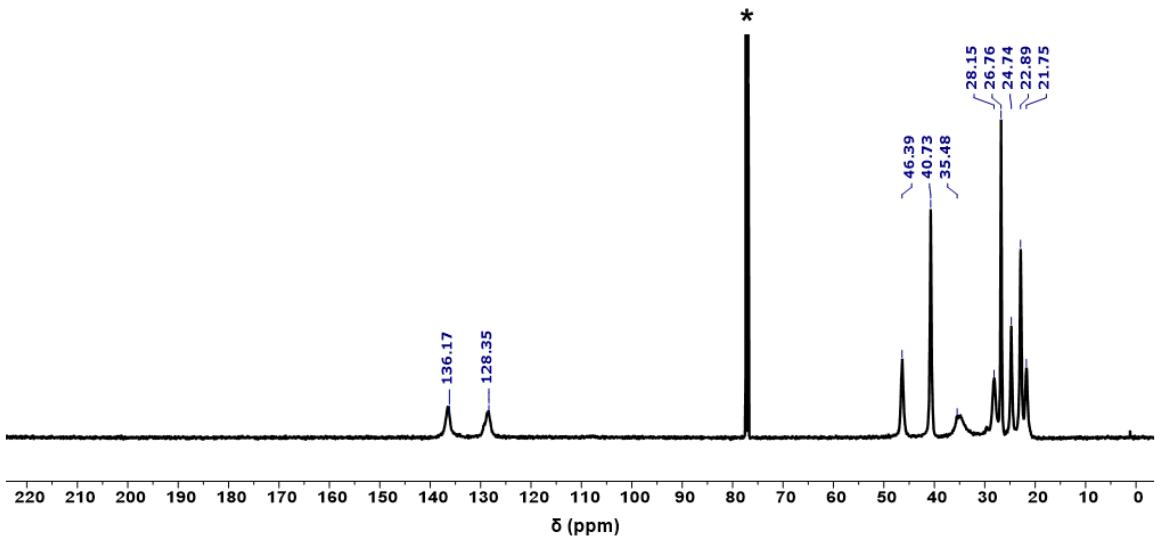


Figure S22: ^{13}C NMR Spectrum of **3**. $CDCl_3$ Resonance Represented by *

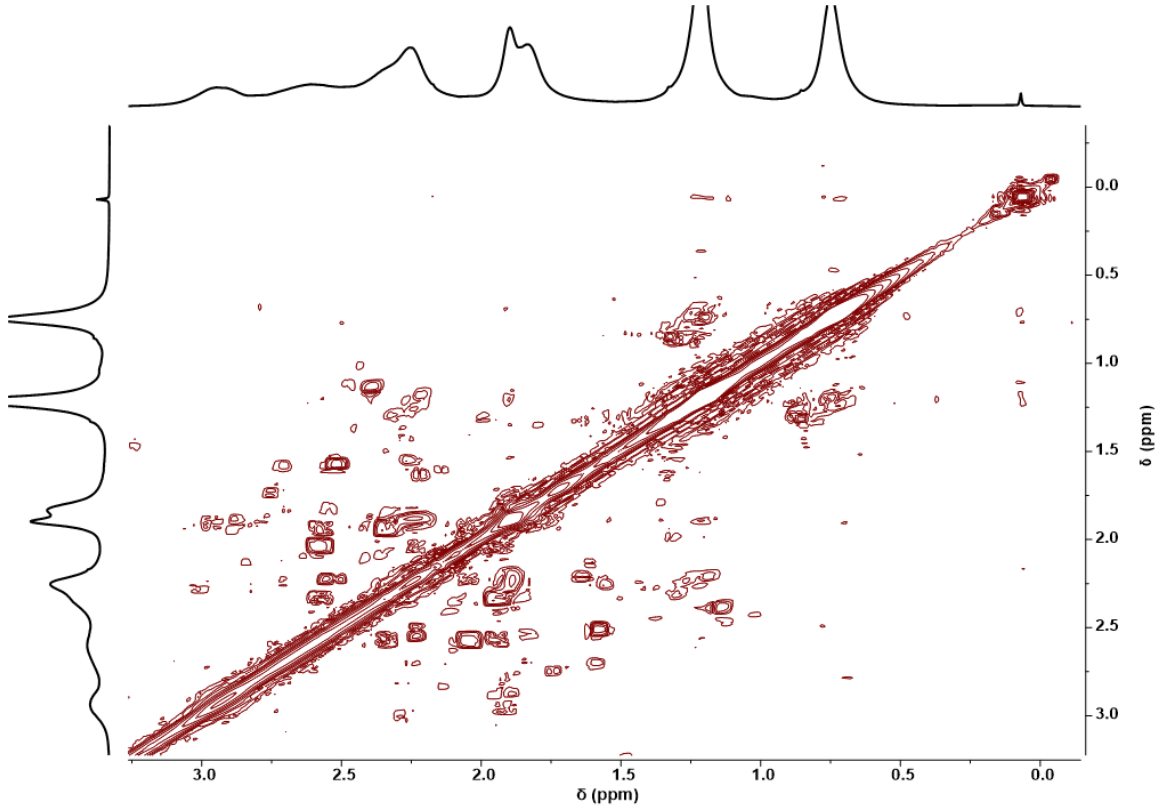


Figure S23: ^{1}H-^{1}H COSY NMR Spectrum of **3**

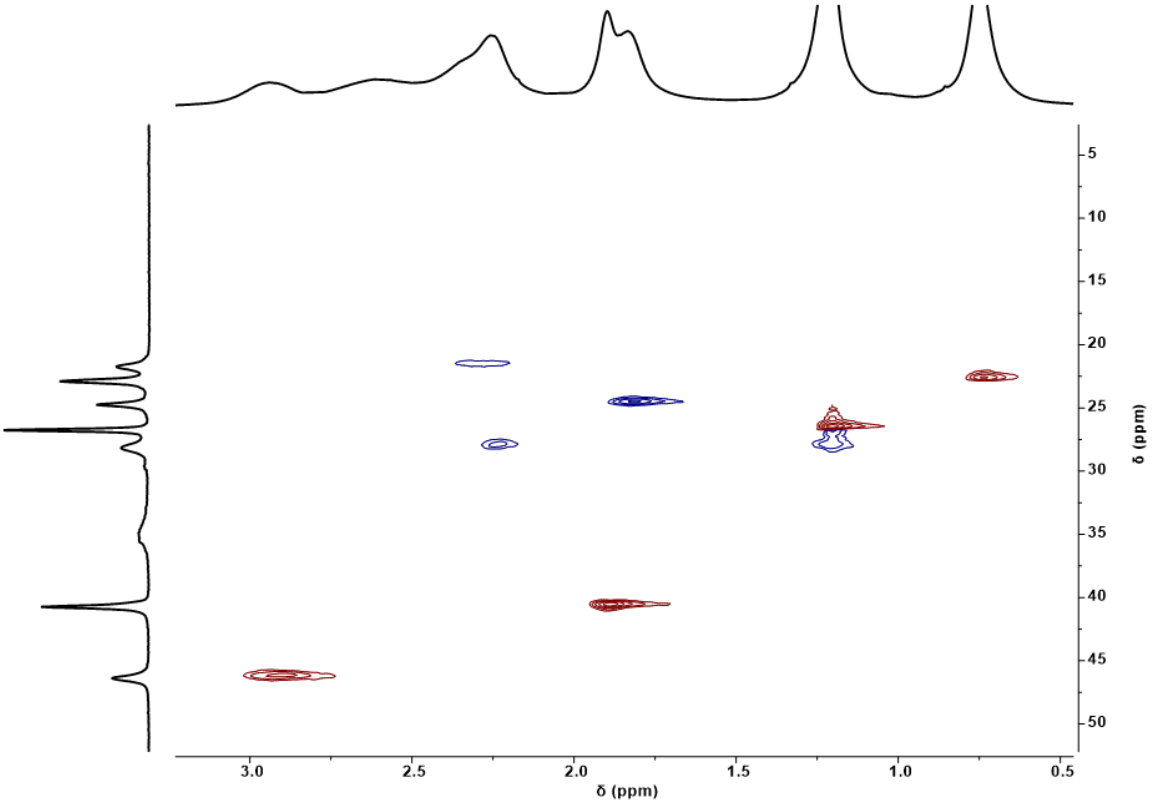


Figure S24: ^{1}H-^{13}C HSQC NMR Spectrum of **3**

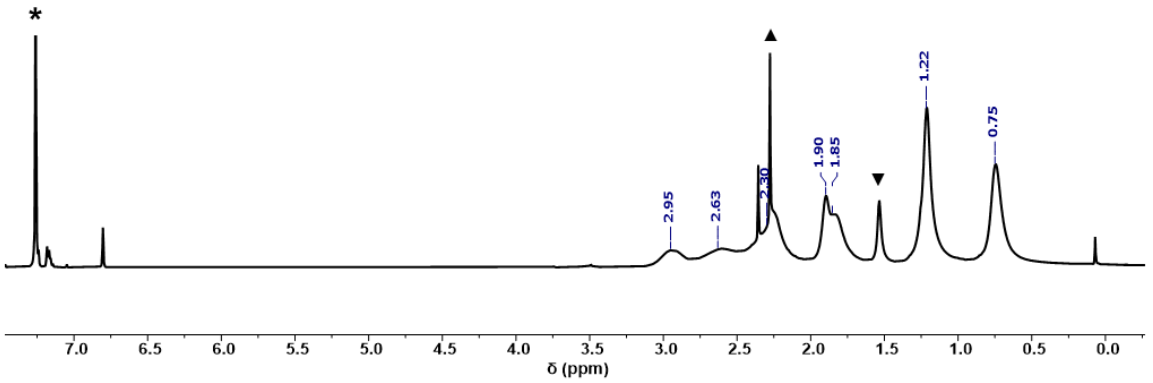


Figure S25: ^{1}H NMR Spectrum of **2** Polymerized with **5**. Residual $CHCl_3$, Acetone, and Water Represented by *, ▲, and ▼ Respectively

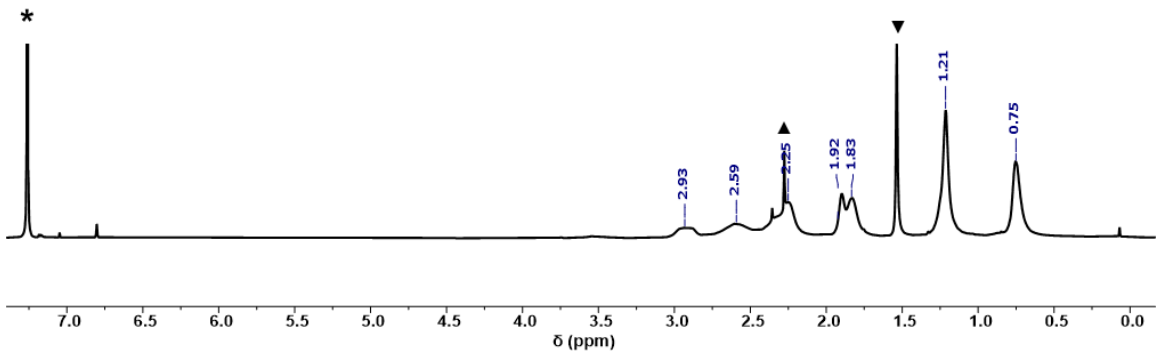


Figure S26: 1H NMR Spectrum of **2** Polymerized with **6**. Residual $CHCl_3$, Acetone, and Water Represented by *, ▲, and ▼ Respectively

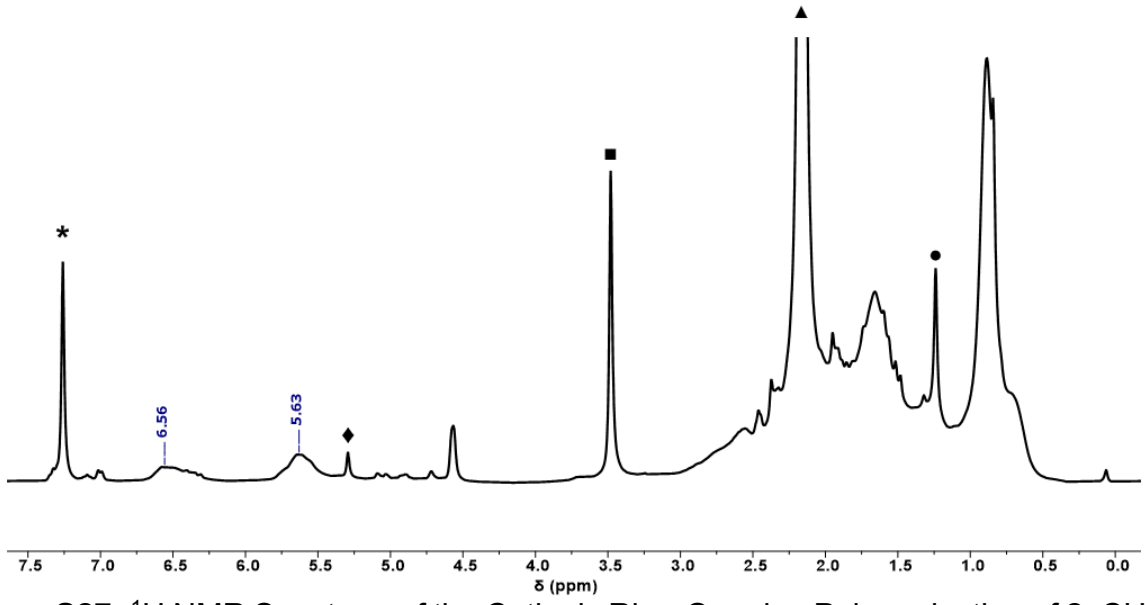


Figure S27: ^{1}H NMR Spectrum of the Cationic Ring-Opening Polymerization of **2**. $CHCl_3$, DCM, Methanol, Acetone, and Et_2O represented by *, ♦, ■, ▲, and ●, respectively

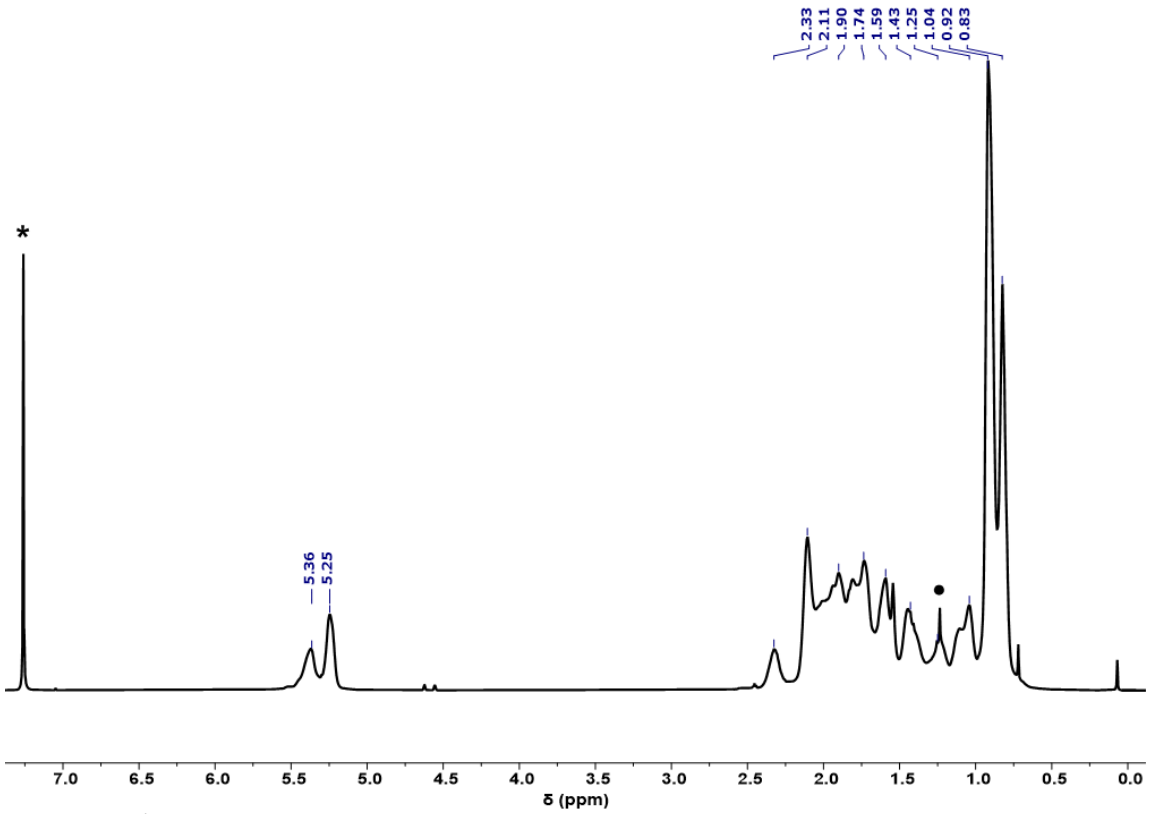


Figure S28: ^{1}H NMR Spectrum of **7**. Residual $CHCl_3$ and Et_2O Represented by * and ●, Respectively

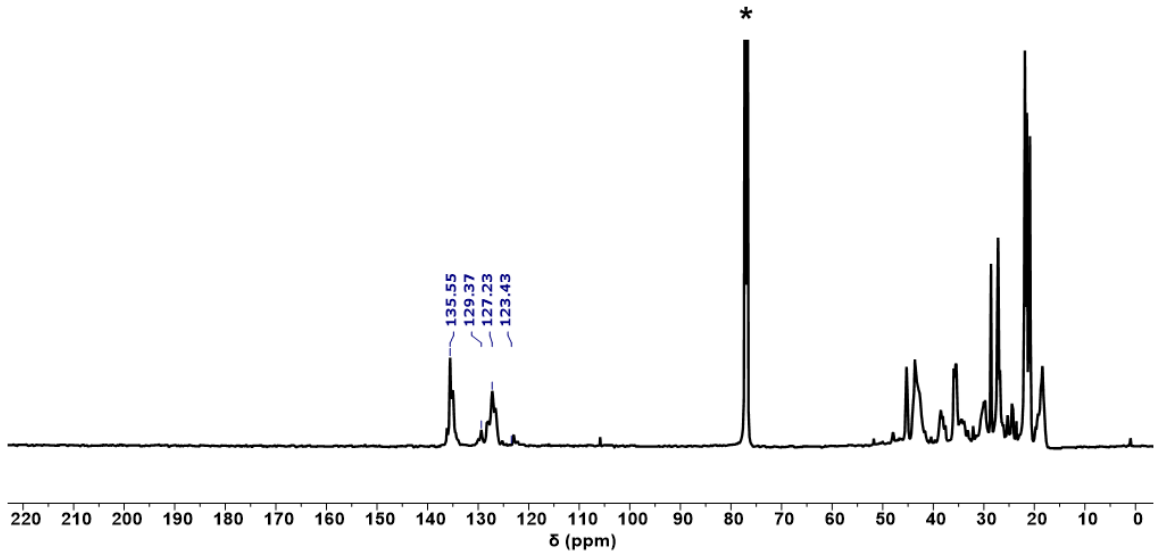
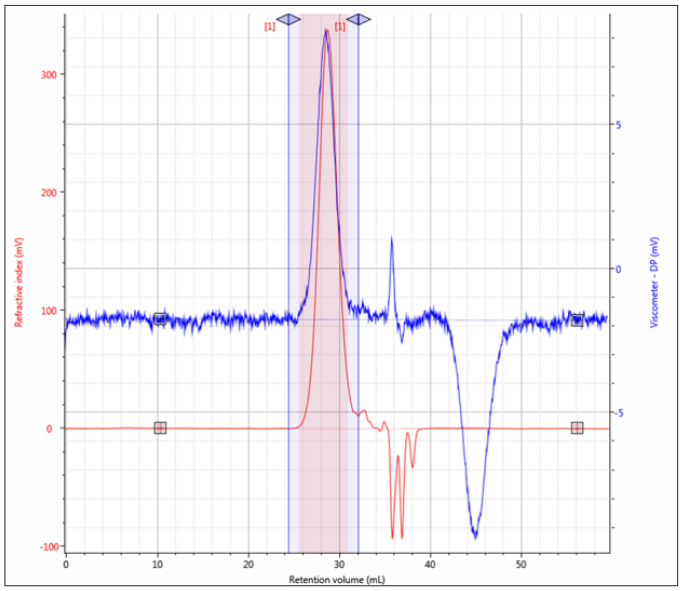


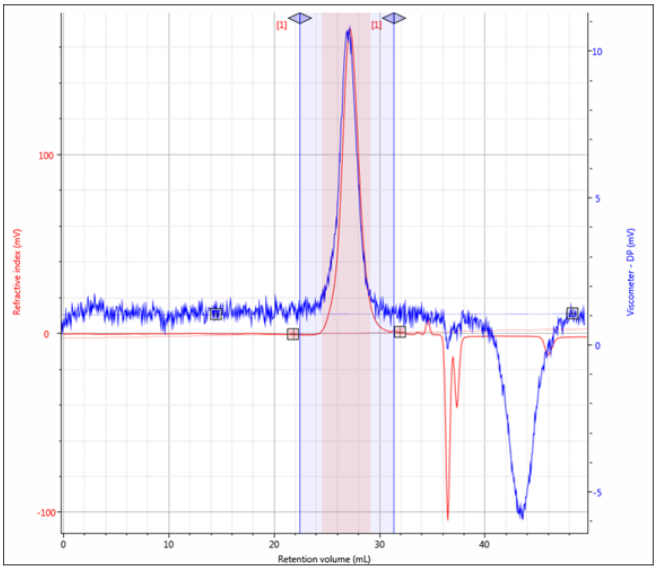
Figure S29: ^{13}C NMR Spectrum of **7**. $CDCl_3$ Resonance Represented by *

6 Raw GPC Data



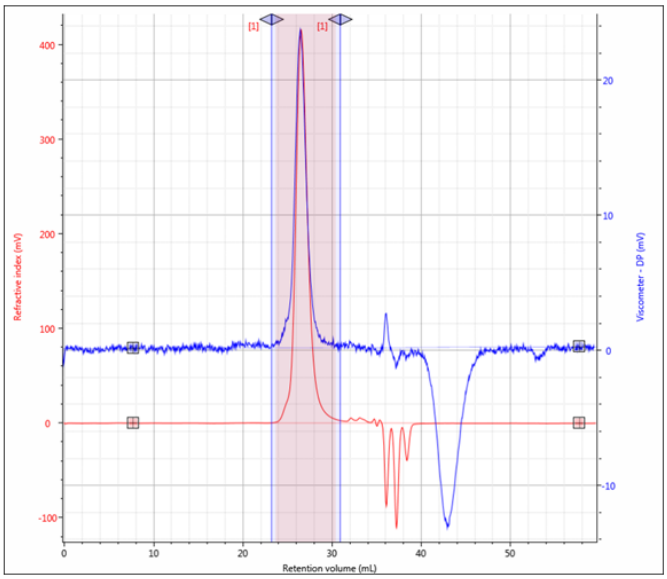
RV (mL)	28.72
Mn (g/mol)	7,504
Mw (g/mol)	10,290
Mz (g/mol)	13,420
Mw/Mn	1.371
IVw (dL/g)	0.05437
Rh(η)w (nm)	2.021
Rgw (nm)	N/C
M-H a	0.4446
M-H log K (dL/g)	-3.034
RI peak (mV·mL)	830.6
RALS peak (mV·mL)	26.55
LALS peak (mV·mL)	19.13
DP peak (mV·mL)	24.3
MALS peak (mV·mL)	N/C
Calc. dn/dc	0.1431
Recovery (%)	N/C

Figure S30: Raw GPC Data for Table S1 Entry 1



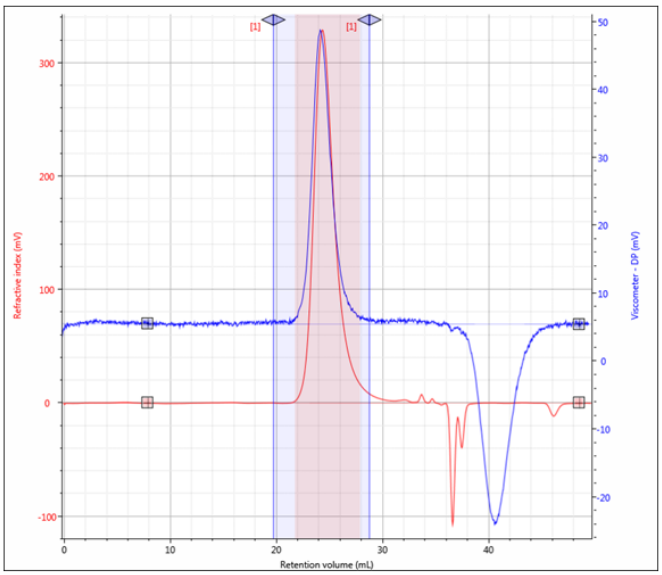
RV (mL)	27.22
Mn (g/mol)	18,920
Mw (g/mol)	22,540
Mz (g/mol)	45,450
Mw/Mn	1.192
IVw (dL/g)	0.06982
Rh(η)w (nm)	2.843
Rgw (nm)	N/C
M-H a	0.686
M-H log K (dL/g)	-4.13
RI peak (mV·mL)	340.2
RALS peak (mV·mL)	17.72
LALS peak (mV·mL)	14
DP peak (mV·mL)	20.51
MALS peak (mV·mL)	N/C
Calc. dn/dc	0.1137
Recovery (%)	N/C

Figure S31: Raw GPC Data for Table S1 Entry 2



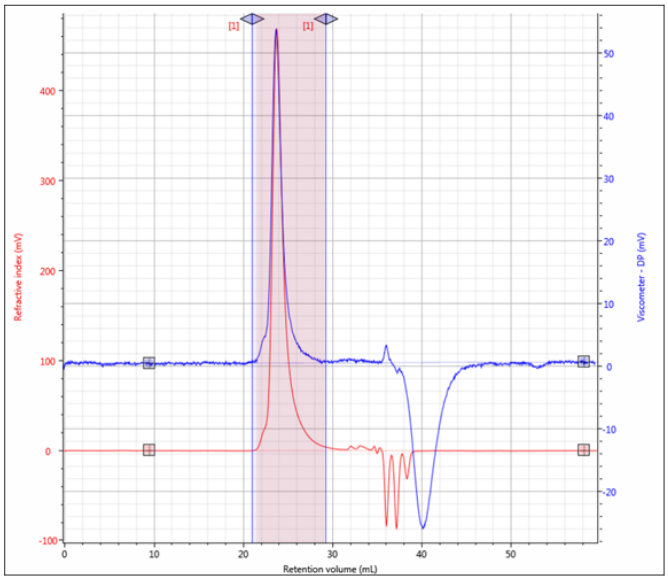
RV (mL)	26.56
Mn (g/mol)	26,420
Mw (g/mol)	29,720
Mz (g/mol)	33,750
Mw/Mn	1.125
IVw (dL/g)	0.1055
Rh(η)w (nm)	3.625
Rgw (nm)	N/C
M-H a	0.652
M-H log K (dL/g)	-3.888
RI peak (mV·mL)	674.6
RALS peak (mV·mL)	62.56
LALS peak (mV·mL)	45.57
DP peak (mV·mL)	37.58
MALS peak (mV·mL)	N/C
Calc. dn/dc	0.1437
Recovery (%)	N/C

Figure S32: Raw GPC Data for Table S1 Entry 3



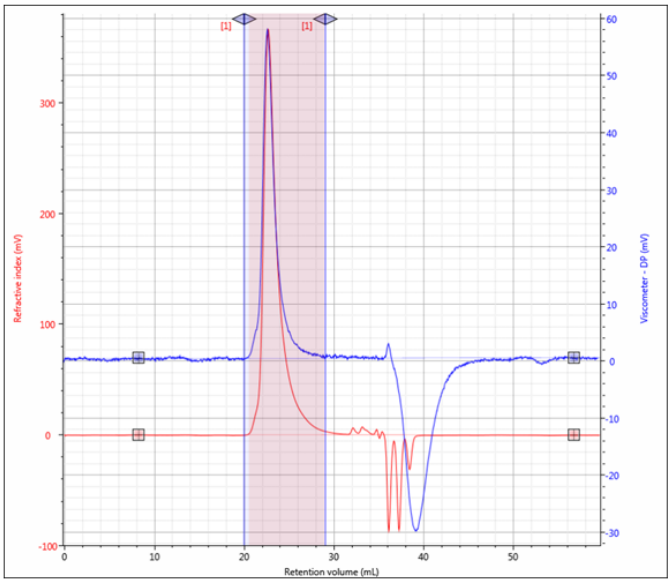
RV (mL)	24.37
Mn (g/mol)	52,030
Mw (g/mol)	64,050
Mz (g/mol)	78,070
Mw/Mn	1.231
IVw (dL/g)	0.1352
Rh(η)w (nm)	5.069
Rgw (nm)	N/C
M-H a	0.6352
M-H log K (dL/g)	-3.912
RI peak (mV·mL)	767.6
RALS peak (mV·mL)	112.2
LALS peak (mV·mL)	86.02
DP peak (mV·mL)	95.43
MALS peak (mV·mL)	N/C
Calc. dn/dc	0.1152
Recovery (%)	N/C

Figure S33: Raw GPC Data for Table S1 Entry 4



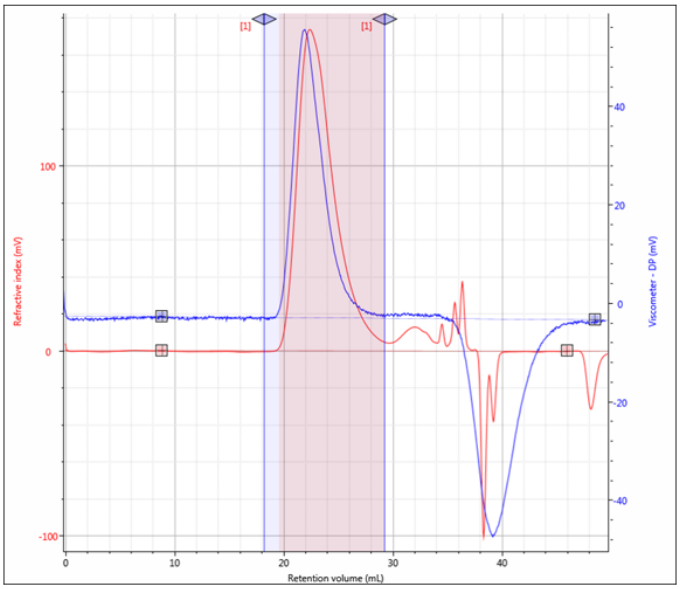
RV (mL)	23.77
Mn (g/mol)	66,270
Mw (g/mol)	81,440
Mz (g/mol)	95,160
Mw/Mn	1.229
IVw (dL/g)	0.2254
Rh(η)w (nm)	6.526
Rgw (nm)	N/C
M-H a	0.5149
M-H log K (dL/g)	-3.17
RI peak (mV·mL)	743.2
RALS peak (mV·mL)	208.1
LALS peak (mV·mL)	152.8
DP peak (mV·mL)	80.24
MALS peak (mV·mL)	N/C
Calc. dn/dc	0.1583
Recovery (%)	N/C

Figure S34: Raw GPC Data for Table S1 Entry 5



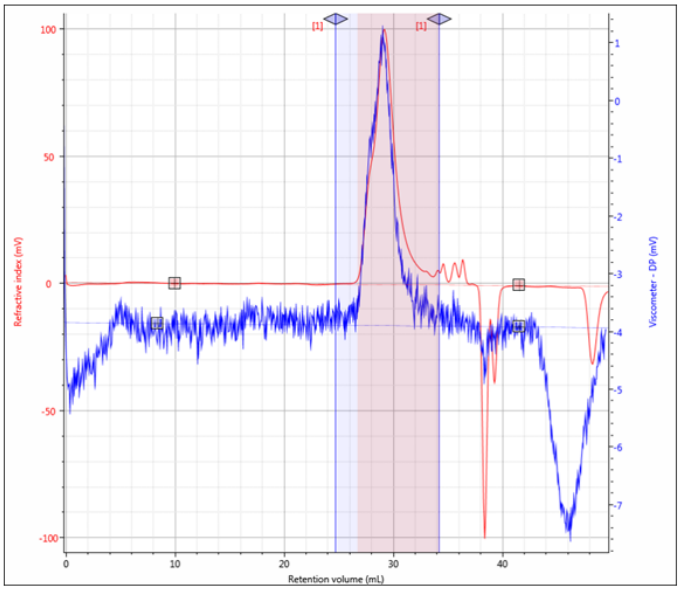
RV (mL)	22.7
Mn (g/mol)	99,580
Mw (g/mol)	130,200
Mz (g/mol)	158,300
Mw/Mn	1.308
IVw (dL/g)	0.2885
Rh(η)w (nm)	8.252
Rgw (nm)	N/C
M-H a	0.5731
M-H log K (dL/g)	-3.465
RI peak (mV·mL)	695.3
RALS peak (mV·mL)	307.8
LALS peak (mV·mL)	227.1
DP peak (mV·mL)	97.68
MALS peak (mV·mL)	N/C
Calc. dn/dc	0.1566
Recovery (%)	N/C

Figure S35: Raw GPC Data for Table S1 Entry 6



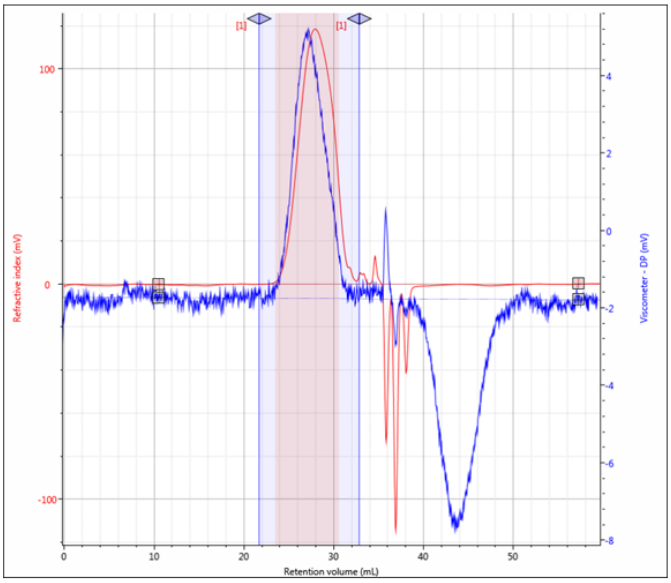
RV (mL)	22.41
Mn (g/mol)	159,300
Mw (g/mol)	271,000
Mz (g/mol)	416,500
Mw/Mn	1.701
IVw (dL/g)	0.2866
Rh(η)w (nm)	10.28
Rgw (nm)	7.607
M-H a	0.6363
M-H log K (dL/g)	-3.977
RI peak (mV·mL)	674.8
RALS peak (mV·mL)	371.6
LALS peak (mV·mL)	290.9
DP peak (mV·mL)	185.5
MALS peak (mV·mL)	N/C
Calc. dn/dc	0.1052
Recovery (%)	N/C

Figure S36: Raw GPC Data for the Vinyl-Addition Polymerization of **2** With **5**



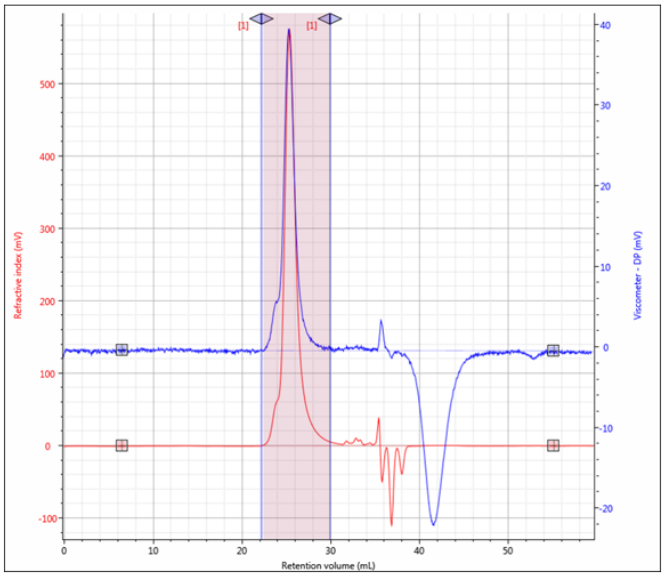
RV (mL)	29.2
Mn (g/mol)	15,490
Mw (g/mol)	19,510
Mz (g/mol)	34,020
Mw/Mn	1.26
IVw (dL/g)	0.06348
Rh(η)w (nm)	2.51
Rgw (nm)	N/C
M-H a	0.6582
M-H log K (dL/g)	-3.983
RI peak (mV·mL)	249.4
RALS peak (mV·mL)	12.24
LALS peak (mV·mL)	10.05
DP peak (mV·mL)	13.48
MALS peak (mV·mL)	N/C
Calc. dn/dc	0.1231
Recovery (%)	N/C

Figure S37: Raw GPC Data for the Vinyl-Addition Polymerization of **2** With **6**



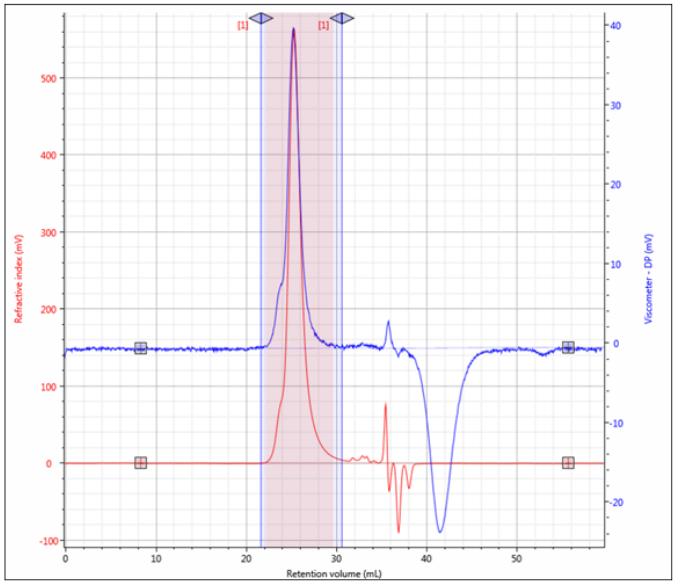
RV (mL)	27.97
Mn (g/mol)	5,812
Mw (g/mol)	11,110
Mz (g/mol)	19,400
Mw/Mn	1.912
IVw (dL/g)	0.09343
Rh(η)w (nm)	2.417
Rgw (nm)	N/C
M-H a	0.5315
M-H log K (dL/g)	-3.148
RI peak (mV·mL)	524.1
RALS peak (mV·mL)	16.93
LALS peak (mV·mL)	12.13
DP peak (mV·mL)	28.14
MALS peak (mV·mL)	N/C
Calc. dn/dc	0.1335
Recovery (%)	N/C

Figure S38: Raw GPC Data for the Cationic Ring-Opening Polymerization of (1*S*)-(-)-β-pinene



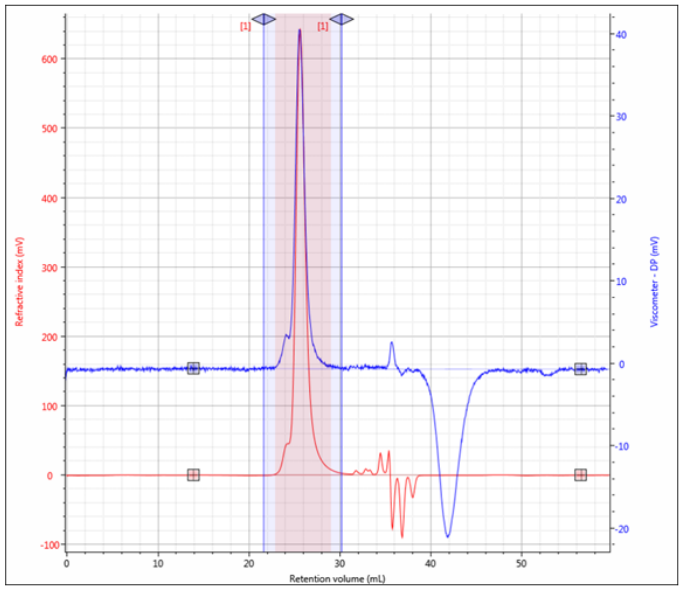
RV (mL)	25.39
Mn (g/mol)	39,210
Mw (g/mol)	45,530
Mz (g/mol)	53,710
Mw/Mn	1.161
IVw (dL/g)	0.129
Rh(η)w (nm)	4.46
Rgw (nm)	N/C
M-H a	0.5725
M-H log K (dL/g)	-3.549
RI peak (mV·mL)	939.1
RALS peak (mV·mL)	131.3
LALS peak (mV·mL)	95.92
DP peak (mV·mL)	63.82
MALS peak (mV·mL)	N/C
Calc. dn/dc	0.1428
Recovery (%)	N/C

Figure S39: Raw GPC Data for the Polymerization of **2** With **4** in Toluene (for Solvent Screen)



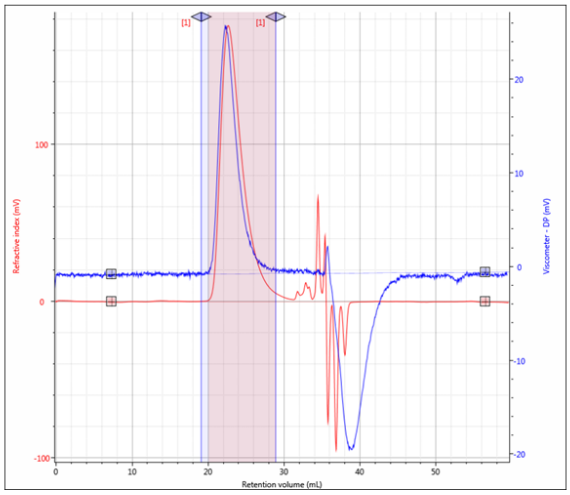
RV (mL)	25.32
Mn (g/mol)	36,500
Mw (g/mol)	46,450
Mz (g/mol)	56,760
Mw/Mn	1.272
IVw (dL/g)	0.1338
Rh(η)w (nm)	4.539
Rgw (nm)	N/C
M-H a	0.4978
M-H log K (dL/g)	-3.187
RI peak (mV·mL)	1,037
RALS peak (mV·mL)	149.5
LALS peak (mV·mL)	109.4
DP peak (mV·mL)	72.42
MALS peak (mV·mL)	N/C
Calc. dn/dc	0.1444
Recovery (%)	N/C

Figure S40: Raw GPC Data for the Polymerization of **2** With **4** in Toluene at 35 °C (for Solvent Screen)



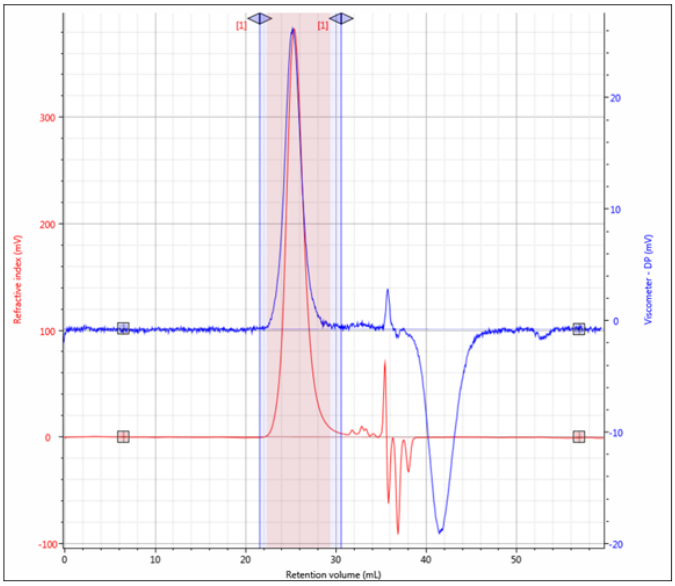
RV (mL)	25.67
Mn (g/mol)	33,840
Mw (g/mol)	39,300
Mz (g/mol)	45,390
Mw/Mn	1.161
IVw (dL/g)	0.1234
Rh(η)w (nm)	4.202
Rgw (nm)	N/C
M-H a	0.5701
M-H log K (dL/g)	-3.522
RI peak (mV·mL)	877.8
RALS peak (mV·mL)	107.6
LALS peak (mV·mL)	78.52
DP peak (mV·mL)	56.19
MALS peak (mV·mL)	N/C
Calc. dn/dc	0.1449
Recovery (%)	N/C

Figure S41: Raw GPC Data for the Polymerization of **2** With **4** in Et_2O (for Solvent Screen)



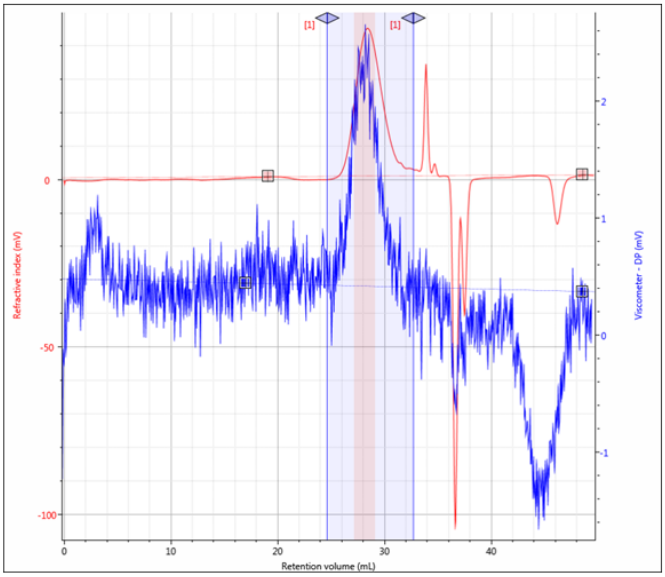
RV (mL)	22.68
Mn (g/mol)	95,400
Mw (g/mol)	148,400
Mz (g/mol)	204,800
Mw/Mn	1.556
IVw (dL/g)	0.2151
Rh(η)w (nm)	7.716
Rgw (nm)	N/C
M-H a	0.5683
M-H log K (dL/g)	-3.587
RI peak (mV·mL)	591
RALS peak (mV·mL)	242.3
LALS peak (mV·mL)	179.3
DP peak (mV·mL)	74.12
MALS peak (mV·mL)	N/C
Calc. dn/dc	0.1289
Recovery (%)	N/C

Figure S42: Raw GPC Data for the Polymerization of **2** With **4** in THF (for Solvent Screen)



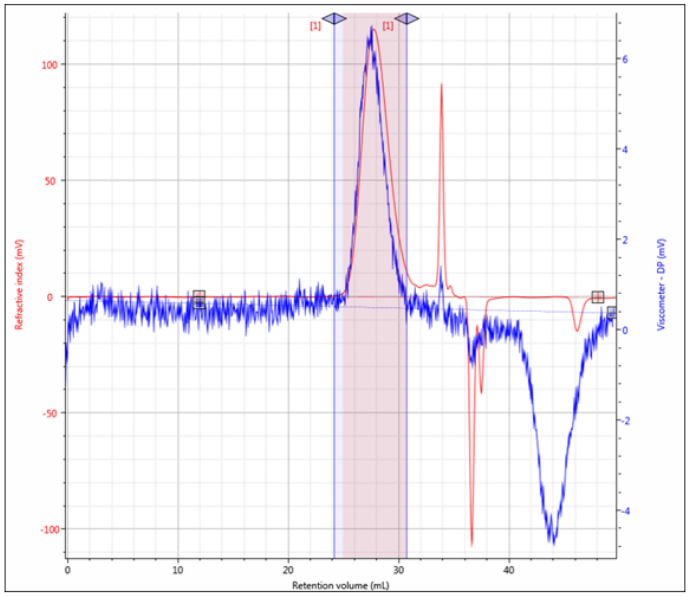
RV (mL)	25.41
Mn (g/mol)	35,300
Mw (g/mol)	45,500
Mz (g/mol)	56,650
Mw/Mn	1.289
IVw (dL/g)	0.1293
Rh(η)w (nm)	4.447
Rgw (nm)	N/C
M-H a	0.5585
M-H log K (dL/g)	-3.479
RI peak (mV·mL)	901.5
RALS peak (mV·mL)	125.9
LALS peak (mV·mL)	92.21
DP peak (mV·mL)	61.47
MALS peak (mV·mL)	N/C
Calc. dn/dc	0.1427
Recovery (%)	N/C

Figure S43: Raw GPC Data for the Polymerization of **2** With **4** in DCM (for Solvent Screen)



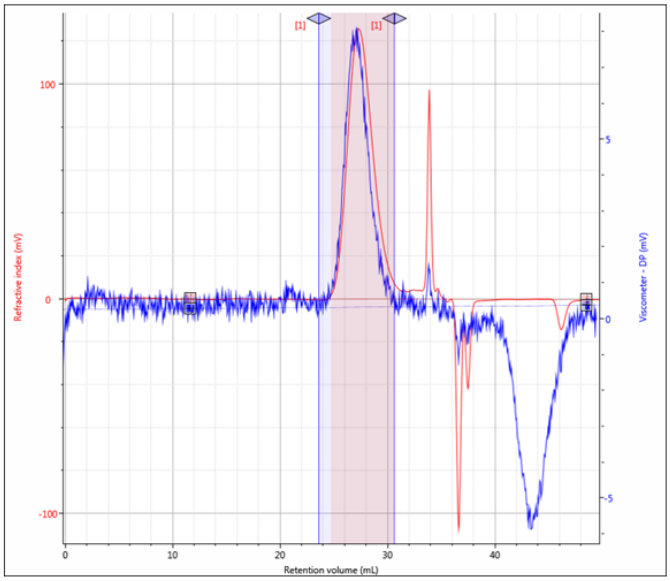
RV (mL)	28.45
Mn (g/mol)	8,734
Mw (g/mol)	11,090
Mz (g/mol)	14,260
Mw/Mn	1.27
IVw (dL/g)	0.06282
Rh(η)w (nm)	2.097
Rgw (nm)	N/C
M-H a	-1.337
M-H log K (dL/g)	4.078
RI peak (mV·mL)	127.3
RALS peak (mV·mL)	5.028
LALS peak (mV·mL)	4.288
DP peak (mV·mL)	5.605
MALS peak (mV·mL)	N/C
Calc. dn/dc	0.1372
Recovery (%)	N/C

Figure S44: Raw GPC Data for Table S5 Entry 2



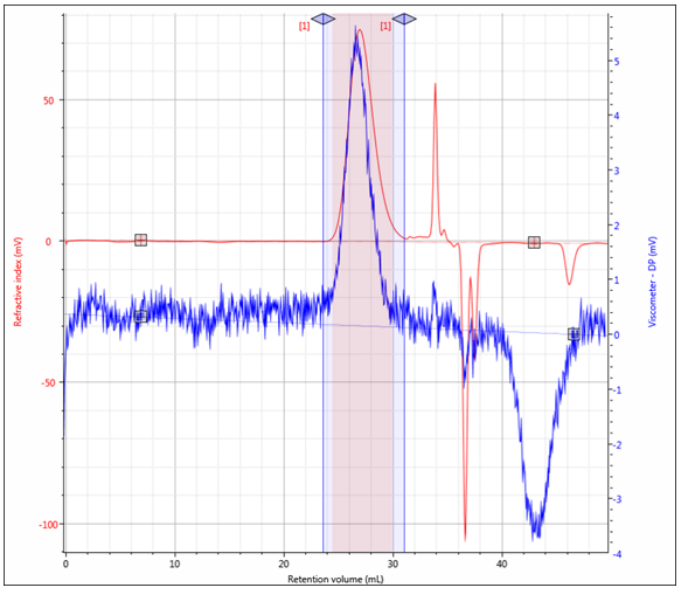
RV (mL)	27.79
Mn (g/mol)	13,110
Mw (g/mol)	15,750
Mz (g/mol)	22,370
Mw/Mn	1.202
IVw (dL/g)	0.06212
Rh(η)w (nm)	2.414
Rgw (nm)	N/C
M-H a	0.9581
M-H log K (dL/g)	-5.167
RI peak (mV·mL)	327.9
RALS peak (mV·mL)	13.7
LALS peak (mV·mL)	10.9
DP peak (mV·mL)	16.1
MALS peak (mV·mL)	N/C
Calc. dn/dc	0.134
Recovery (%)	N/C

Figure S45: Raw GPC Data for Table S5 Entry 3



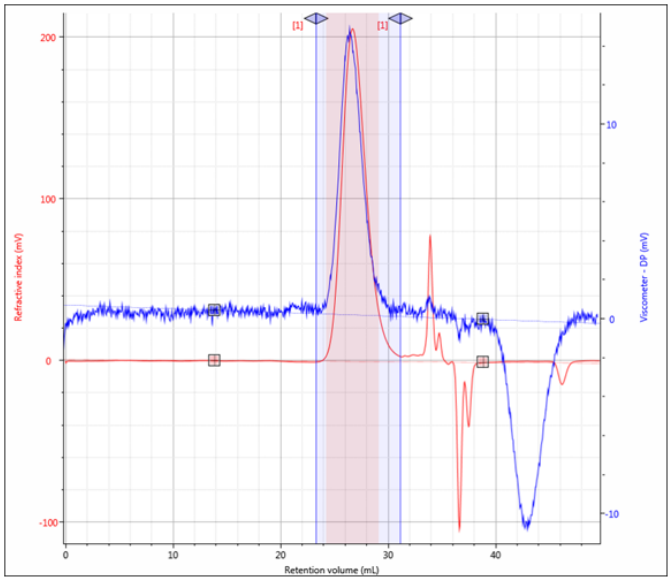
RV (mL)	27.34
Mn (g/mol)	15,150
Mw (g/mol)	18,140
Mz (g/mol)	25,200
Mw/Mn	1.197
IVw (dL/g)	0.0737
Rh(η)w (nm)	2.691
Rgw (nm)	N/C
M-H a	0.7635
M-H log K (dL/g)	-4.386
RI peak (mV·mL)	348.5
RALS peak (mV·mL)	16.87
LALS peak (mV·mL)	13.01
DP peak (mV·mL)	20.32
MALS peak (mV·mL)	N/C
Calc. dn/dc	0.1333
Recovery (%)	N/C

Figure S46: Raw GPC Data for Table S5 Entry 4



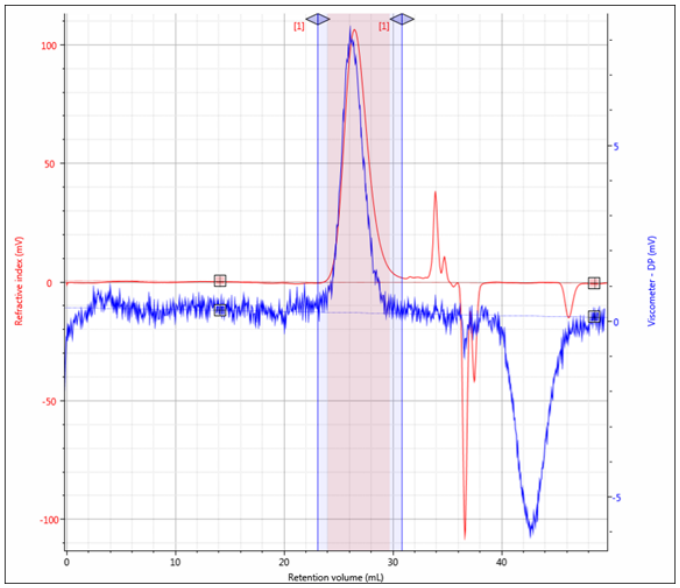
RV (mL)	26.99
Mn (g/mol)	16,160
Mw (g/mol)	19,540
Mz (g/mol)	25,210
Mw/Mn	1.209
IVw (dL/g)	0.0854
Rh(η)w (nm)	2.892
Rgw (nm)	N/C
M-H a	0.6796
M-H log K (dL/g)	-3.973
RI peak (mV·mL)	205
RALS peak (mV·mL)	10.81
LALS peak (mV·mL)	8.287
DP peak (mV·mL)	14.25
MALS peak (mV·mL)	N/C
Calc. dn/dc	0.135
Recovery (%)	N/C

Figure S47: Raw GPC Data for Table S5 Entry 5



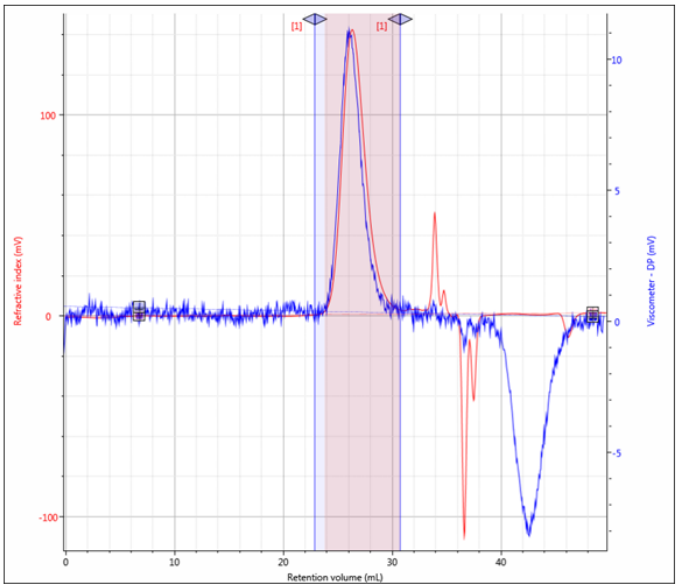
RV (mL)	26.72
Mn (g/mol)	17,260
Mw (g/mol)	21,240
Mz (g/mol)	27,560
Mw/Mn	1.231
IVw (dL/g)	0.08682
Rh(η)w (nm)	3.016
Rgw (nm)	N/C
M-H a	0.7006
M-H log K (dL/g)	-4.08
RI peak (mV·mL)	544.6
RALS peak (mV·mL)	31.97
LALS peak (mV·mL)	25.07
DP peak (mV·mL)	36.88
MALS peak (mV·mL)	N/C
Calc. dn/dc	0.1373
Recovery (%)	N/C

Figure S48: Raw GPC Data for Table S5 Entry 6



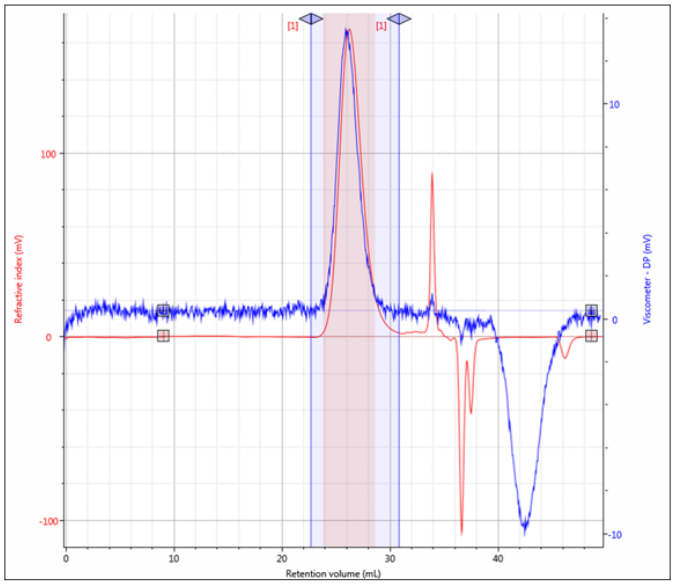
RV (mL)	26.49
Mn (g/mol)	20,060
Mw (g/mol)	24,060
Mz (g/mol)	30,490
Mw/Mn	1.199
IVw (dL/g)	0.08775
Rh(η)w (nm)	3.14
Rgw (nm)	N/C
M-H a	0.6954
M-H log K (dL/g)	-4.093
RI peak (mV·mL)	274.1
RALS peak (mV·mL)	17.41
LALS peak (mV·mL)	13.56
DP peak (mV·mL)	19.43
MALS peak (mV·mL)	N/C
Calc. dn/dc	0.1326
Recovery (%)	N/C

Figure S49: Raw GPC Data for Table S5 Entry 7



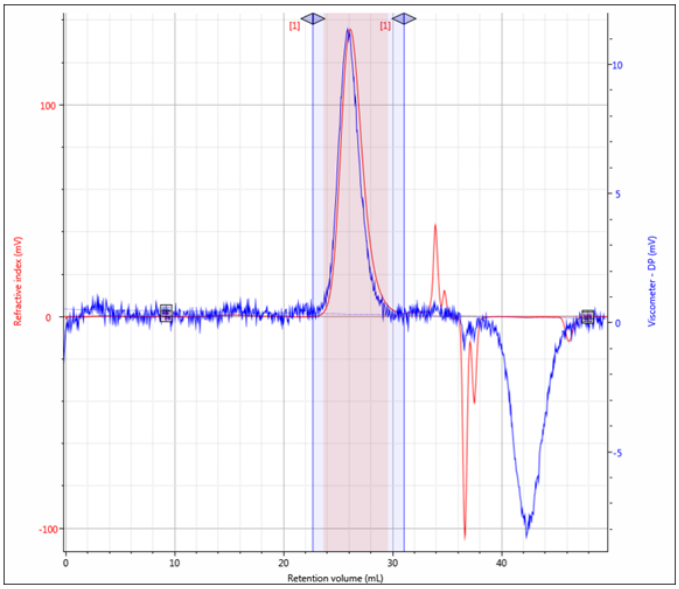
RV (mL)	26.36
Mn (g/mol)	20,690
Mw (g/mol)	24,760
Mz (g/mol)	31,150
Mw/Mn	1.197
IVw (dL/g)	0.09111
Rh(η)w (nm)	3.213
Rgw (nm)	N/C
M-H a	0.7518
M-H log K (dL/g)	-4.331
RI peak (mV·mL)	359.4
RALS peak (mV·mL)	24.22
LALS peak (mV·mL)	18.75
DP peak (mV·mL)	25.15
MALS peak (mV·mL)	N/C
Calc. dn/dc	0.1374
Recovery (%)	N/C

Figure S50: Raw GPC Data for Table S5 Entry 8



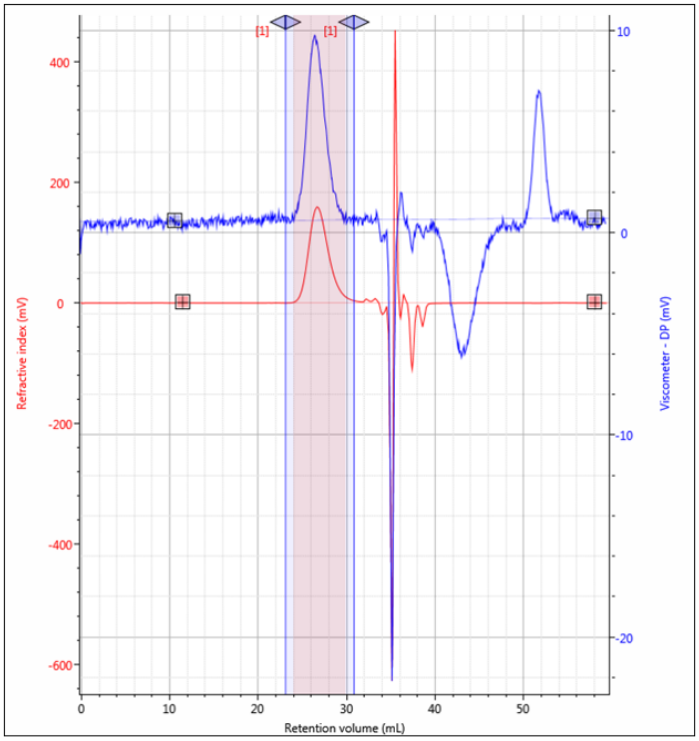
RV (mL)	26.26
Mn (g/mol)	22,120
Mw (g/mol)	26,870
Mz (g/mol)	35,200
Mw/Mn	1.215
IVw (dL/g)	0.0912
Rh(η)w (nm)	3.317
Rgw (nm)	N/C
M-H a	0.9472
M-H log K (dL/g)	-5.247
RI peak (mV·mL)	416.9
RALS peak (mV·mL)	29.62
LALS peak (mV·mL)	23.16
DP peak (mV·mL)	29.91
MALS peak (mV·mL)	N/C
Calc. dn/dc	0.1318
Recovery (%)	N/C

Figure S51: Raw GPC Data for Table S5 Entry 9



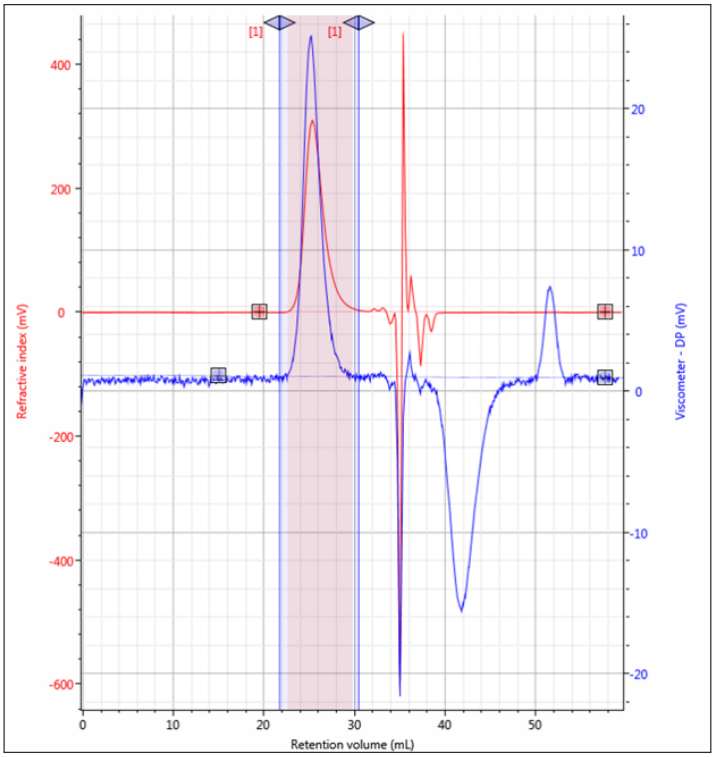
RV (mL)	26.14
Mn (g/mol)	23,170
Mw (g/mol)	27,780
Mz (g/mol)	34,740
Mw/Mn	1.199
IVw (dL/g)	0.09502
Rh(η)w (nm)	3.392
Rgw (nm)	N/C
M-H a	0.7161
M-H log K (dL/g)	-4.186
RI peak (mV·mL)	333.9
RALS peak (mV·mL)	24.34
LALS peak (mV·mL)	18.76
DP peak (mV·mL)	25.47
MALS peak (mV·mL)	N/C
Calc. dn/dc	0.1319
Recovery (%)	N/C

Figure S52: Raw GPC Data for Table S5 Entry 10



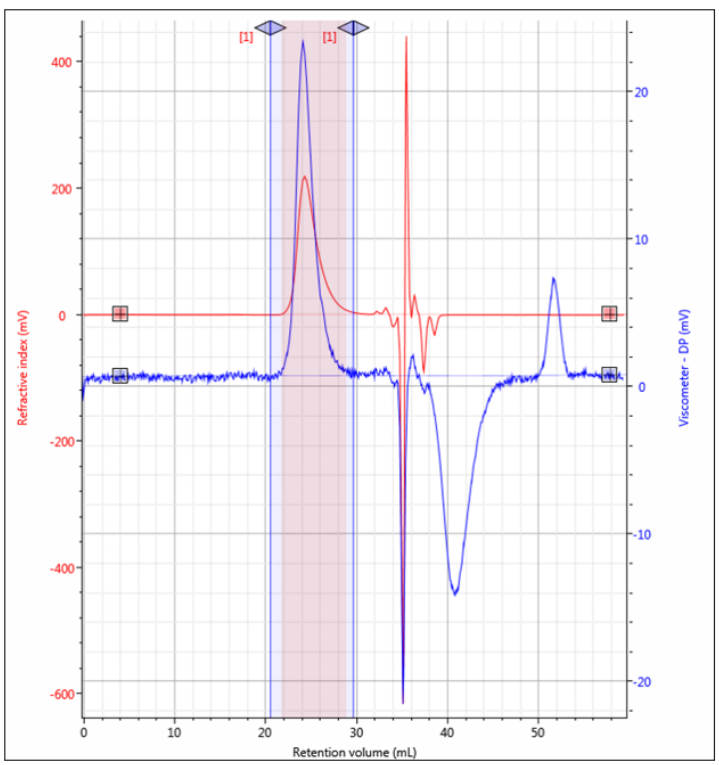
RV (mL)	26.71
Mn (g/mol)	28,530
Mw (g/mol)	37,210
Mz (g/mol)	46,590
Mw/Mn	1.304
IVw (dL/g)	0.07822
Rh(η)w (nm)	3.512
Rgw (nm)	N/C
M-H a	0.6233
M-H log K (dL/g)	-3.952
RI peak (mV·mL)	418.9
RALS peak (mV·mL)	37.76
LALS peak (mV·mL)	27.6
DP peak (mV·mL)	22.14
MALS peak (mV·mL)	N/C
Calc. dn/dc	0.1115
Recovery (%)	N/C

Figure S53: Raw GPC Data for Table S6 Entry 1



RV (mL)	25.39
Mn (g/mol)	45,420
Mw (g/mol)	58,940
Mz (g/mol)	72,720
Mw/Mn	1.298
IVw (dL/g)	0.1085
Rh(η)w (nm)	4.573
Rgw (nm)	N/C
M-H a	0.6183
M-H log K (dL/g)	-3.905
RI peak (mV·mL)	764.9
RALS peak (mV·mL)	113.9
LALS peak (mV·mL)	83.22
DP peak (mV·mL)	54.47
MALS peak (mV·mL)	N/C
Calc. dn/dc	0.1164
Recovery (%)	N/C

Figure S54: Raw GPC Data for Table S6 Entry 2



RV (mL)	24.32
Mn (g/mol)	59,590
Mw (g/mol)	81,240
Mz (g/mol)	103,700
Mw/Mn	1.363
IVw (dL/g)	0.1539
Rh(η)w (nm)	5.699
Rgw (nm)	N/C
M-H a	0.5577
M-H log K (dL/g)	-3.536
RI peak (mV·mL)	566.8
RALS peak (mV·mL)	128.9
LALS peak (mV·mL)	94.43
DP peak (mV·mL)	52.16
MALS peak (mV·mL)	N/C
Calc. dn/dc	0.1289
Recovery (%)	N/C

Figure S55: Raw GPC Data for Table S6 Entry 3

7 References

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