

Electronic Supporting Information

Isomer-Driven Polymerization, Depolymerization, and Reconstruction

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1. General Information

General Experimental Procedures: All experiments unless otherwise denoted were performed under a nitrogen or argon atmosphere with the exclusion of air or moisture via standard Schlenk line technique or in a nitrogen glovebox. All glassware was dried prior to use in a 175 °C oven.

Instrumentation: ^1H NMR, $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR, and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker Avance III 400 MHz Spectrometer, a Bruker Avance 300 MHz Spectrometer, and a Bruker Avance 400 MHz Spectrometer. High field NMR was done on a Bruker 14.1 T (600 MHz, ^1H) Avance II spectrometer equipped with a triple resonance cryogenic probe with cold ^1H and ^{13}C cryocooled preamplifier for enhanced sensitivity and equipped with actively shielded z-axis pulsed field gradients. Chemical shifts are reported in parts per million (ppm). Spectra were recorded in chloroform-*d* or benzene-*d*₆ with the residual solvent peak as the internal standard (^1H NMR: CHCl_3 , $\delta = 7.26$ ppm; C_6D_6 , $\delta = 7.16$ ppm. ^{13}C NMR: CHCl_3 , $\delta = 77.16$ ppm; C_6D_6 , $\delta = 128.06$ ppm). $^{29}\text{Si}\{^1\text{H}\}$ DEPT NMR experiments evolution times are correlated to *J* coupling values reported as $^2J_{\text{Si-H}} = 7$ Hz. Multiplicities are as indicated: s (singlet), d (doublet), t (triplet), dd (doublet of doublets), h (heptet), m (multiplet), and br (broad). Coupling constants, *J*, are reported in Hertz (Hz) and integration is provided, along with assignments, as indicated. Attenuated total reflection infrared (ATR-IR) spectroscopy was performed on a Thermo NicoletNexus 670 FTIR spectrometer. Mass spectrometry and high-resolution mass spectrometry were performed in the Department of Chemistry at Johns Hopkins University using a VG Instruments VG70S/E magnetic sector mass spectrometer with electron ionization (EI) (70 eV). The UNlab Plus Glove Box by MBRAUN was maintained under nitrogen atmosphere. Polymer molecular weights were measured by gel permeation chromatography (GPC) on a Tosoh Bioscience EcoSEC GPC workstation using butylated hydroxytoluene stabilized THF as the eluent (0.35 mL min⁻¹, 40 °C) through TSKgel SuperMultipore HZ-M guard column (4.6 mm ID x 2.0 cm, 4 μm, Tosoh Bioscience) and a TSKgel SuperMultipore HZ-M column (4.6 mm ID x 15 cm, 4 μm, Tosoh Bioscience). Polystyrene standards (EasiVial PS-M, Agilent) were used to build a calibration curve. Processing was performed using EcoSEC Data Analysis software (Version 1.14, Tosoh Bioscience). Polymers were dissolved in THF (concentration specified per experiment), filtered (Millex-FG Syringe Filter Unit, 0.20 μm, PTFE, EMD Millipore), and injected using an auto-sampler (10 μL). All silica-gel column chromatography was performed on a Teledyne ISCO Combiflash Rf+ using Redisep Rf silica columns. Recycling size exclusion chromatography was done using the LaboACE LC-5060 PlusII Recycling Preparative HPLC. Further, the stationary phase was JAIGEL 2.5HR and 3HR columns with a BHT-stabilized THF mobile phase.

Materials: Unless otherwise specified, all chemicals were used as purchased without further purification. Solvents used for column chromatography and polymer workup were reagent grade and used as received. Reaction solvent THF, toluene, diethyl ether (Et₂O), dichloromethane (DCM) (Sigma Aldrich, HPLC grade) was dried on a J. C. Meyer Solvent Dispensing System (SDS) using stainless steel columns packed with neutral alumina and

Q5 reactant, a copper (II) oxide oxygen scavenger, following the manufacturer's recommendations for solvent preparation and dispensation.

1,4-butanediol diacrylate, Grubbs 2nd generation catalyst (M204), Grubbs 1st generation catalyst (M102), methanol (99.90%), methyl acrylate, *trans*-1,4-dichloro-2-butene, *cis*-1,4-dichloro-2-butene and benzene (anhydrous), were purchased from Sigma Aldrich. **D1** was synthesized according to the reported procedure.^[25] Grubbs 3rd generation catalyst was synthesized according to the reported.^[48] Ethyl vinyl ether (99.00%) was purchased from Fisher Scientific.

2. Supplemental Figures

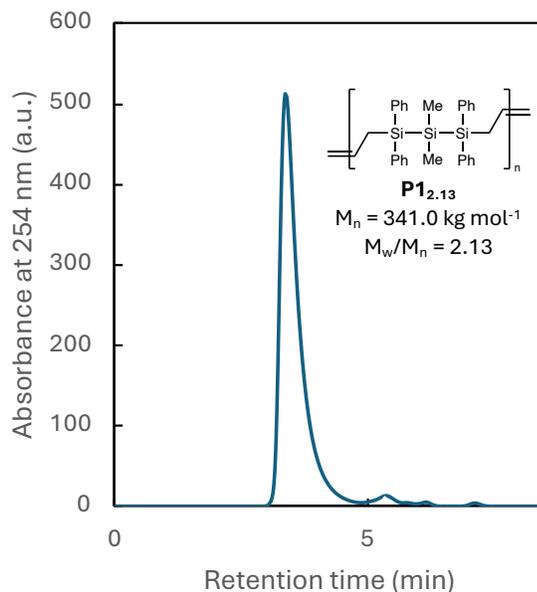


Figure S1. SEC elugram of unimodal **P1_{2.13}** synthesized from recrystallized *trans*-**1** and G3. Molecular weight determined by size exclusion chromatography relative to polystyrene standards at 254 nm (THF, [**P1_{2.13}**] = 0.75 mg mL⁻¹, 40 °C, 0.35 mL min⁻¹, 10 μL injection).

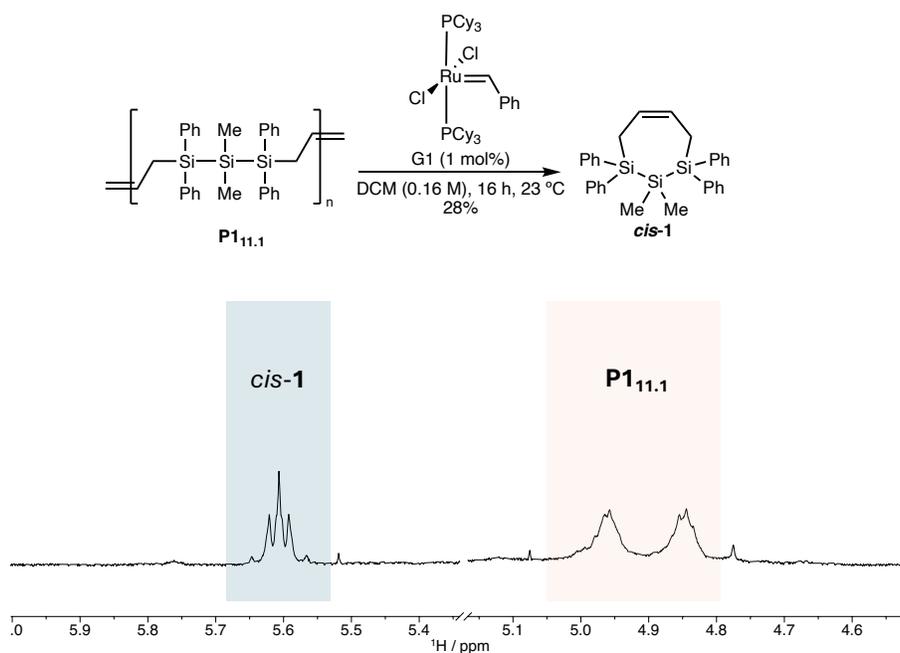


Figure S2. Cropped and annotated crude ¹H NMR spectra (400 MHz, chloroform-*d*) of depolymerization of **P1_{11.1}** to *cis*-**1** (28% conversion). Reaction conditions: 1 mol% **G1**, 0.16 M DCM, 16 h.

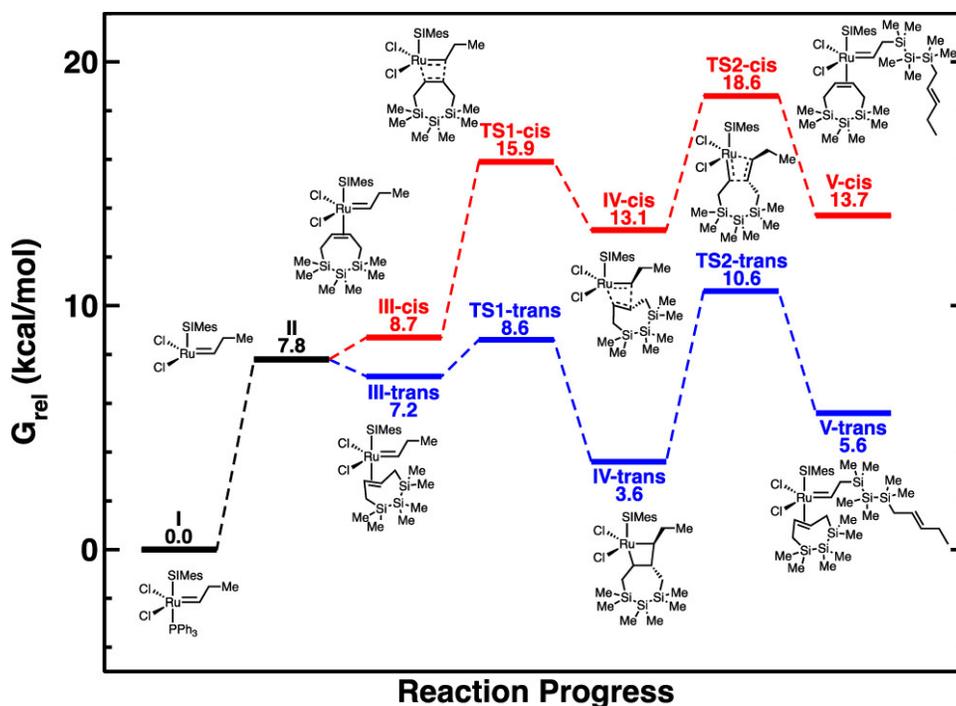


Figure S3. Potential energy surface (in kcal/mol) calculated at the M06/def2-TZVPP-CPCM(DCM)//B3LYP-D4/def2-SVP level of theory for ROMP initiation. All energies refer to Gibbs free energies and are relative to I and two **1** cycles. The *trans*-1 initiation is shown in blue, and the *cis*-1 initiation is shown in red, with common PPh₃ ligated Ru and free Ru catalyst shown in black. Reprinted with permission from J. Am. Chem. Soc. 2023, 145, 10187. Copyright 2023 American Chemical Society.

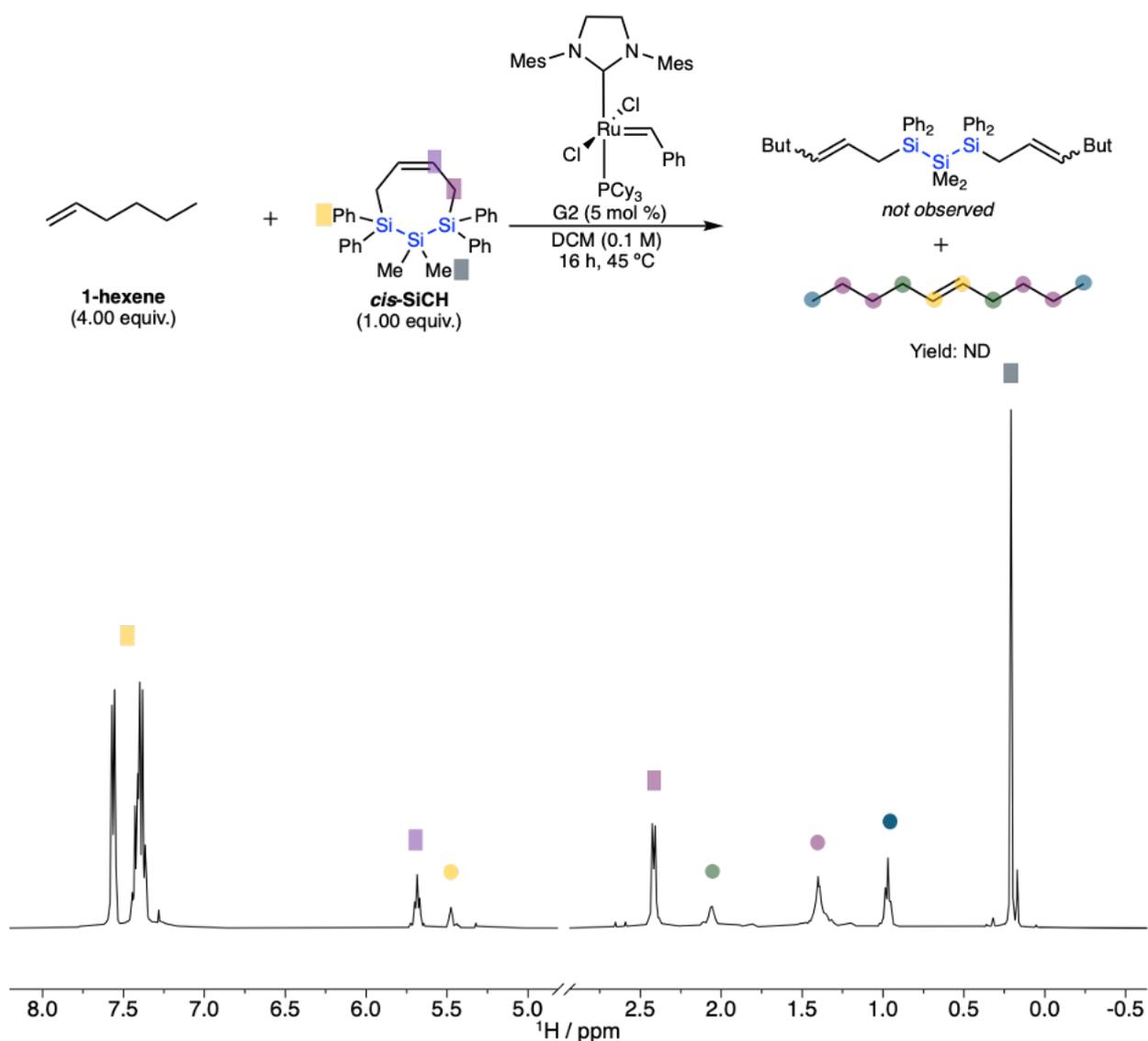


Figure S4. Cropped crude ¹H NMR spectrum (400 MHz, chloroform-*d*) from the unsuccessful CM of *cis*-1 and 1-hexene. The reaction proceeded to give 5-decene and *cis*-1.

Table S1. Maximum concentration of *cis*-1 in organic solvents.

Solvent	Amount <i>cis</i> -1 (mg)	Solvent Added (mL)	Concentration of dilution (M)
Dioxane	16.1	1.20	0.028
CHCl ₃	16.2	0.190	0.178
Toluene	20.9	0.900	0.048
THF	18.6	0.260	0.150

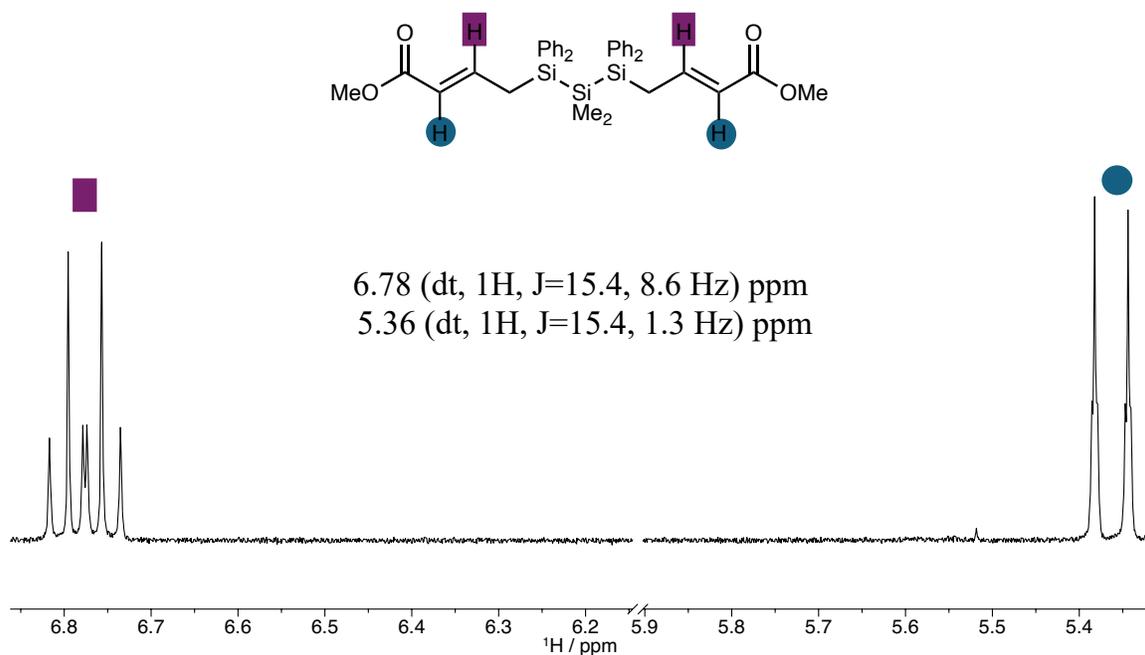


Figure S5. Cropped ^1H NMR spectra (400 MHz, chloroform- d) of the RO-CM product, **2**. The olefinic region shown only indicates the *trans* isomer.

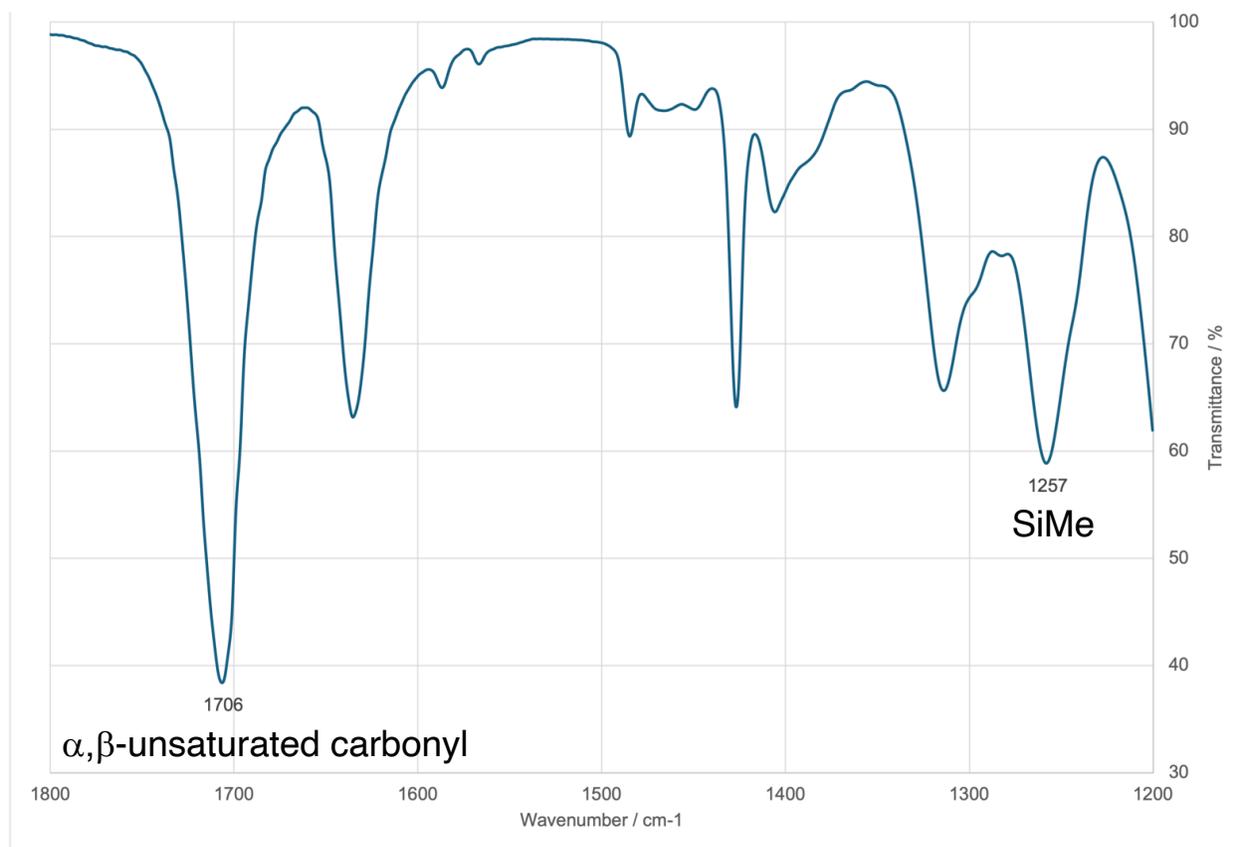


Figure S6. Cropped ATR-IR spectra of **P2** indicating the α,β -unsaturated carbonyl at 1706 cm^{-1} , as well as a SiMe functional group at 1257 cm^{-1} .

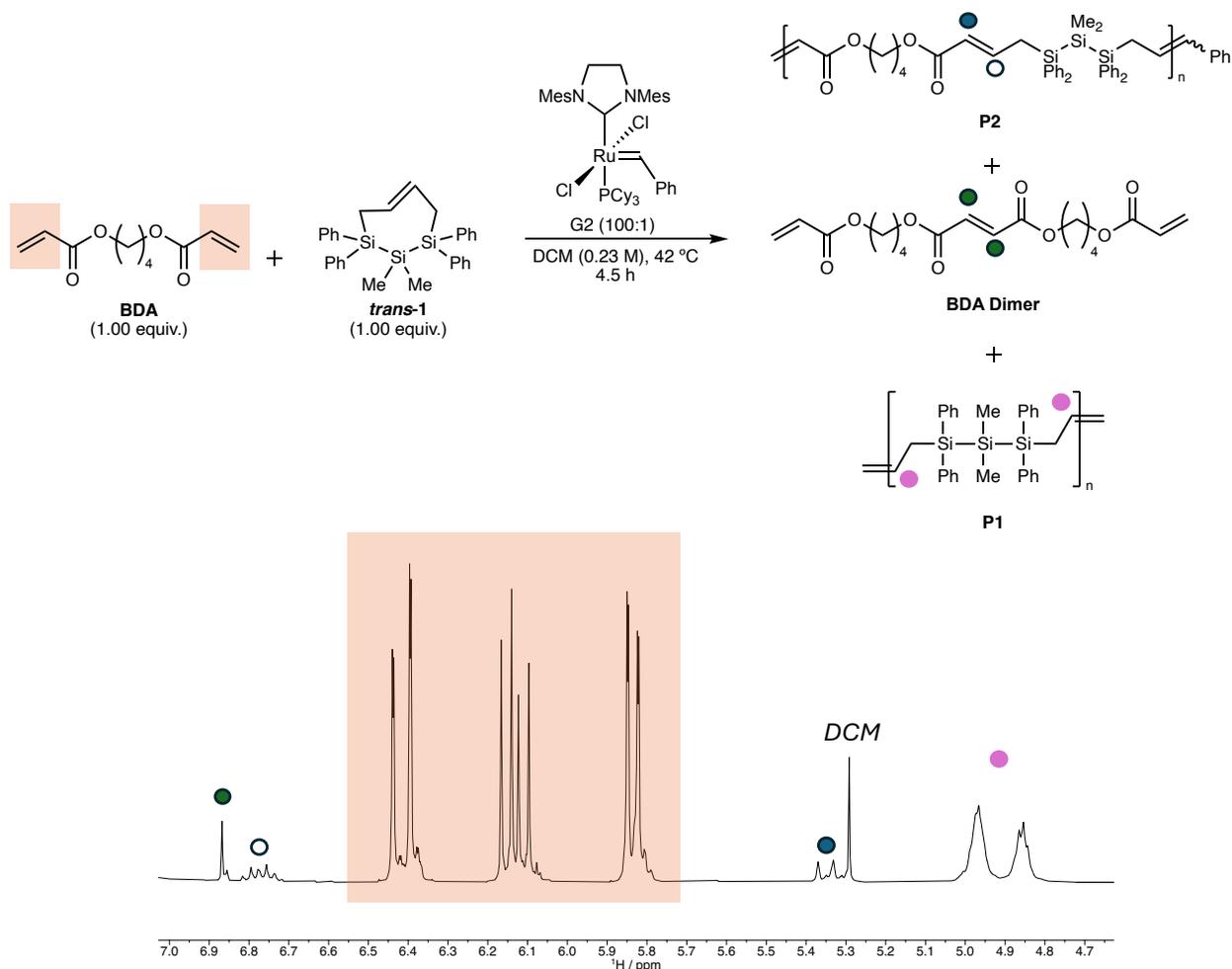


Figure S7. Cropped $^1\text{H-NMR}$ spectra (400 MHz, chloroform-*d*) highlighting the olefinic region of a 4.5 h aliquot of the ROIMP of **trans-1** and **BDA**. Present are the olefinic peaks of **P1**, **P2** as well as the **BDA dimer**.

Sample: 20240905 poly-alt(BDA-SiCH)
Size: 4.5240 mg
Method: Ramp

DSC-TGA

File: \\...20240905 poly-alt(BDA-SiCH).001
Operator: FF
Run Date: 05-Sep-2024 12:02
Instrument: SDT Q600 V20.9 Build 20

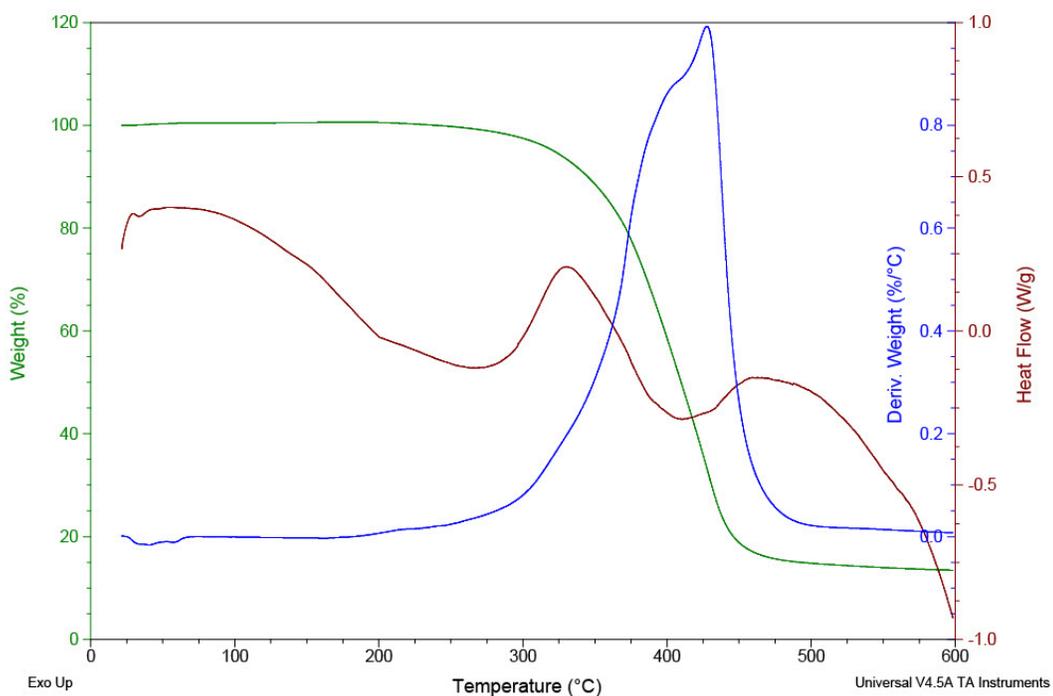
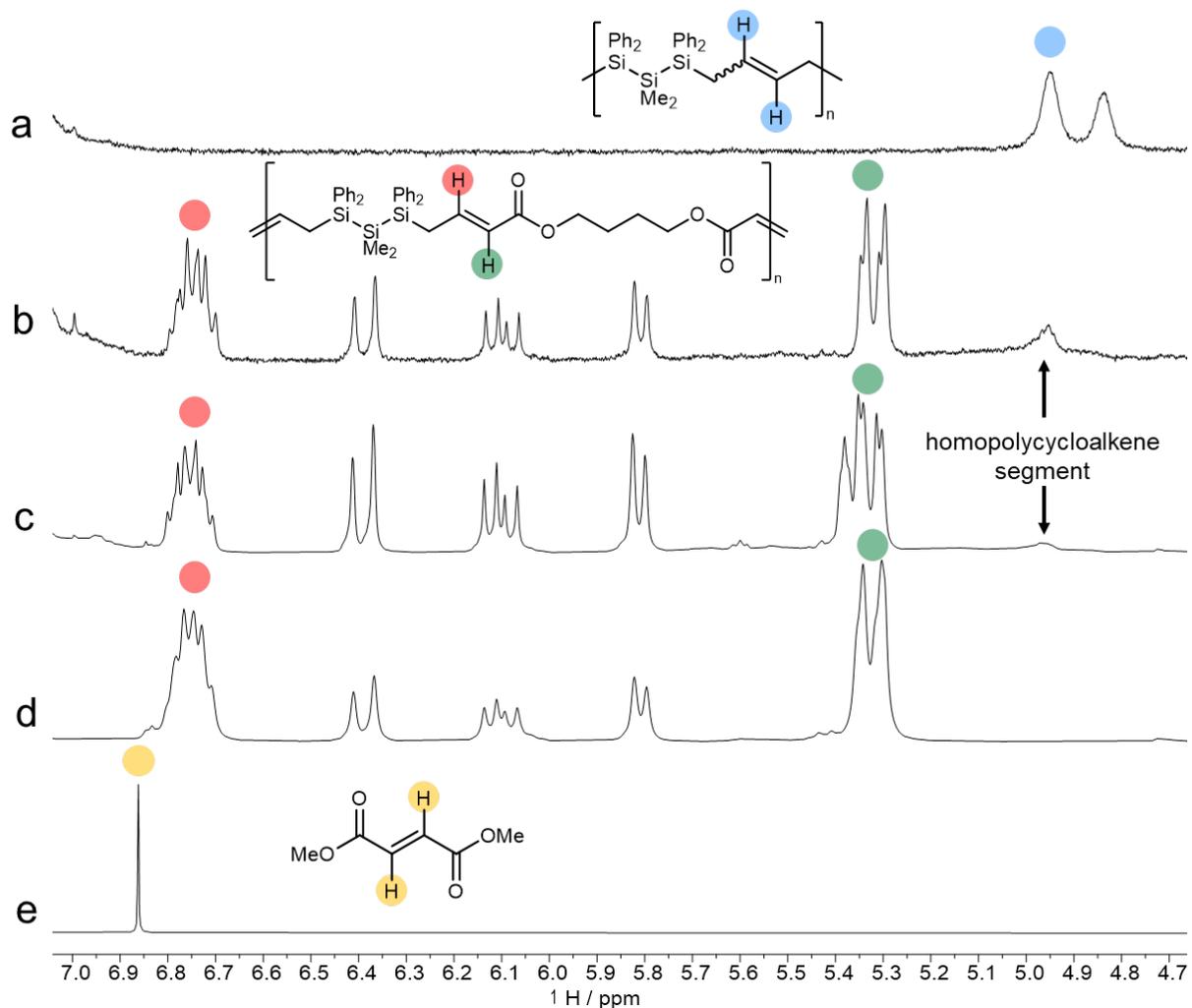


Figure S8. Thermogravimetric analysis (TGA) of **P2**.



f

[<i>cis</i> -1]:[BDA]:[G2]	%Alternation ^a	M _n (g mol ⁻¹) ^b	M _w /M _n ^b
100:100:1	>99%	3310	1.52
105:100:1	>99%	3091	1.48
125:100:1	91.5%	2285	1.42
150:100:1	76.6%	4062	1.47

^a Determined by ¹H NMR spectroscopy. ^b Molecular weight determined by size exclusion chromatography relative to polystyrene standards at 254 nm (THF, [Sample] = 1.00 mg mL⁻¹, 40 °C, 0.35 mL min⁻¹, 10 μL injection).

Figure S9. Cropped ¹H-NMR spectra (400 MHz, chloroform-*d*) of the olefinic region of **a**) pure **P1**, **b**) alternating polymer **P2** made with feed ratio of [*cis*-1]:[BDA]:[G2] = [150]:[100]:[1], **c**) alternating polymer **P2** made with feed ratio of [*cis*-1]:[BDA]:[G2] = [125]:[100]:[1], **d**) alternating polymer **P2** made with feed ratio of [*cis*-1]:[BDA]:[G2] = [105]:[100]:[1], and **e**) pure dimethyl fumarate. Panel **f**) summarizes the %alternation and molecular weight characteristics.

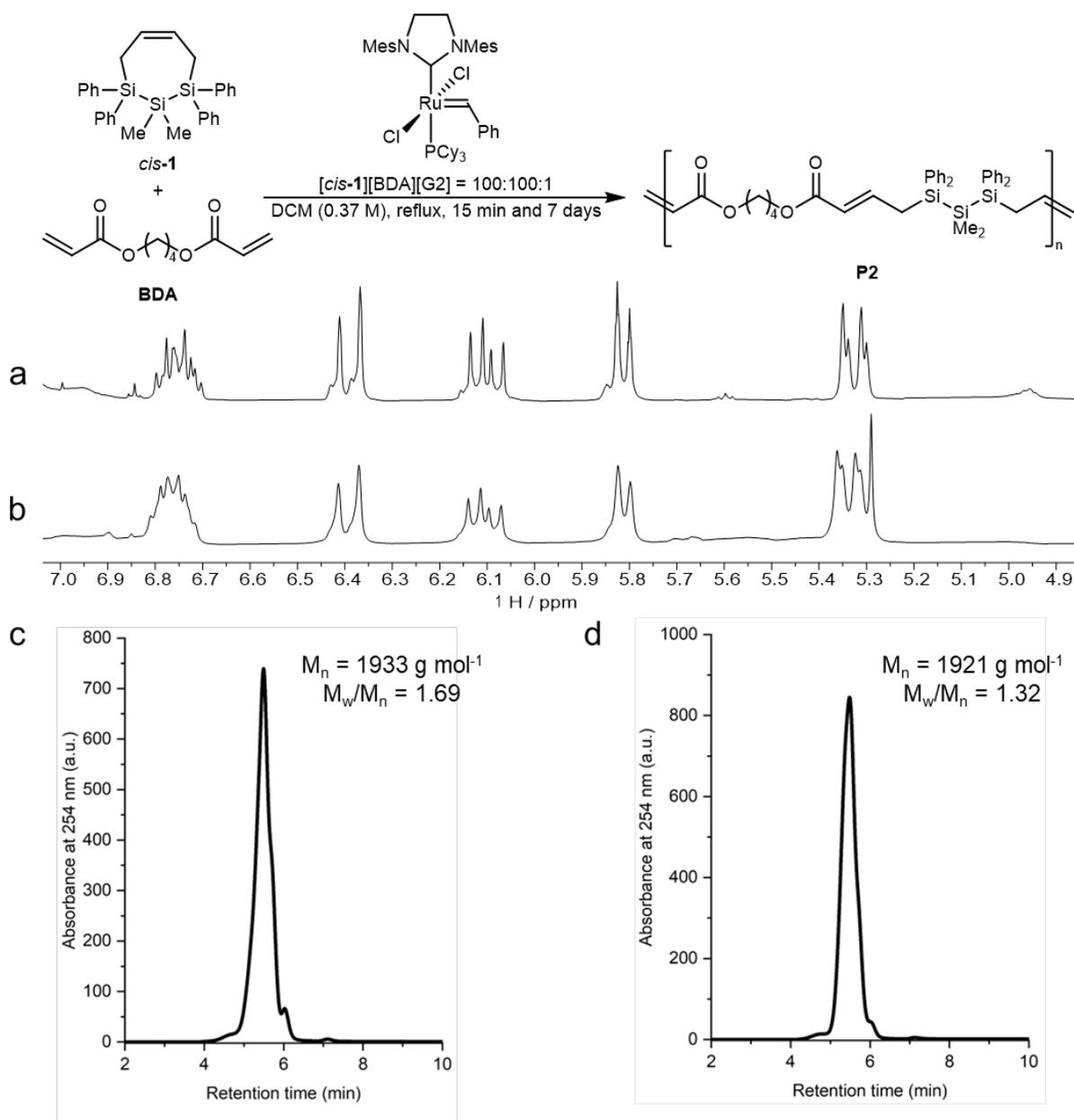
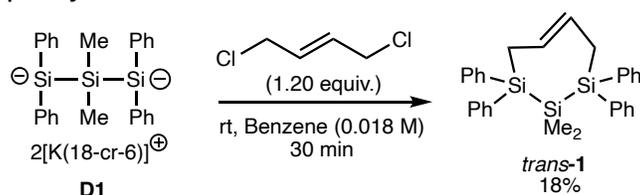


Figure S11. Synthesis of alternating polymer **P2** with the associated cropped ¹H NMR spectrum (400 MHz, chloroform-*d*) of the olefinic region of reactions quenched after **a**) 15 minutes and **b**) 7 days, as well the associated SEC elugram of reactions quenched after **c**) 15 minutes and **d**) 7 days. Molecular weight determined by size exclusion chromatography relative to polystyrene standards at 254 nm (THF, [Sample] = 1.00 mg mL⁻¹, 40 °C, 0.35 mL min⁻¹, 10 μL injection).

3. Experimental Procedures and Tabulated Characterization

3.1 Synthesis of high purity *trans*-1



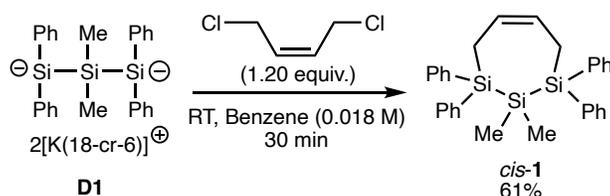
Caution - **D1** is air and moisture-reactive and should be handled in an inert and dry atmosphere. Benzene is a known carcinogen and exposure should be minimized.

Trans-1 was synthesized following a modified procedure from Wakefield (2023)^[25]

In a nitrogen-filled glovebox, an oven-dried 250 mL Schlenk flask equipped with a stir bar was charged with the **D1** (2.00 g, 1.94 mmol, 1.00 equiv.) and sealed with a rubber septum and stopcock. 0.3 mL of (E)-1,4-dichlorobutene was added to a 25 mL oven-dried round bottom flask. The Schlenk flask containing the dianion and the flask of dichlorobutene were removed from the glove box and transported to the hood, where they were placed under an argon atmosphere. **D1** was dissolved in benzene (107 mL) and began to stir at room temperature. The 1,4-dichlorobutene was diluted with 3 mL to prepare a stock 0.32 mM solution. 0.766 mL (0.242 mmol, 1.00 equiv.) was added to the dianion solution to initiate the reaction. The reaction color was observed to change from deep burgundy to a clear light-yellow solution. The reaction was allowed to stir at room temperature for 30 minutes and then quenched with 50 mL of deionized H₂O (added slowly with a pipette then completed with a funnel) and 50 mL of a saturated aqueous solution of NH₄Cl (added slowly with a pipette first then completed with a funnel). The biphasic mixture was transferred to a 250 mL separatory funnel and the aqueous layer was separated from the organic layer. The organic layer was dried over NaSO₄ before being concentrated by rotatory evaporation. The crude material was recrystallized by dissolving in 1.50 mL of hot toluene. The solution was cooled to room temperature before crystallizing in a -10 °C freezer. After 3 days, the crystals were washed and isolated with cold hexanes and dried under vacuum for 2 hours yielding *trans*-1 as clear-white crystals (169.0 mg, 18%). ¹H and ¹³C spectra are consistent with those previously reported for this compound and no further characterization was performed.^[25]

All *trans*-1 was wrapped in foil and stored in a -10 °C lab freezer for further use.

3.2 Synthesis of *cis*-1



Caution - **D1** is air and moisture-reactive and should be handled in an inert and dry atmosphere. Benzene is a known carcinogen and exposure should be minimized.

cis-1 was synthesized following a modified procedure from Wakefield (2023).^[25]

In a nitrogen-filled glovebox, an oven-dried 250 mL Schlenk flask equipped with a stir bar was charged with the **D1** (2.37 g, 2.30 mmol, 1.00 equiv.) and sealed with a rubber septum and stopcock. 0.750 mL of (*Z*)-1,4-dichlorobutene was added into a 25 mL oven-dried round bottom flask. The Schlenk flask containing the dianion and the flask of dichlorobutene was sealed, removed from the glove box, and transported to the hood where they were placed under an argon atmosphere. **D1** was dissolved in benzene (175 mL) and began to stir at room temperature. The 1,4-dichlorobutene was diluted with 5.15 mL to prepare a stock 1.38 mM solution. 2.00 mL (2.76 mmol, 1.20 equiv.) was added to the dianion solution to initiate the reaction. The reaction color was observed to change from deep burgundy to a clear light-yellow solution. The reaction was allowed to stir at room temperature for 30 minutes and then quenched with 65 mL of deionized H₂O (added slowly with a pipette first then completed with a funnel). The reaction was transferred into a 500 mL Erlenmeyer flask and 75 mL of a saturated aqueous solution of NH₄Cl (added slowly with a pipette first then completed with a funnel). The biphasic mixture was transferred to a 500 mL separatory funnel and the aqueous layer was separated from the organic layer. The organic layer was dried over NaSO₄ before being concentrated by rotary evaporation. The crude *cis*-1 was recrystallized using 1 mL of hot toluene. The solution was left to cool to room temperature before cooling in a -10 °C freezer overnight. The next day the crystals were washed and isolated with cold hexanes and dried under vacuum for 2 hours yielding *cis*-1 as clear-white crystals (667.0 mg, 61%). ¹H and ¹³C spectra are consistent with those previously reported for this compound and no further characterization was performed.^[25]

3.3 ROMP of *trans*-1

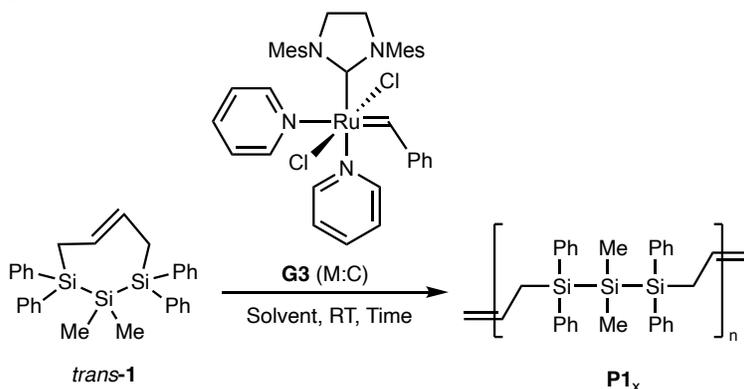


Table S2. Reaction parameters of *trans*-1 ROMP. Products are named after the dispersity, M_w/M_n .

Entry	Monomer	M:C	Solvent	Concentration	Time	Yield (%)
P1 _{1.23}	<i>trans</i> -1	100:1	DCM	2.40 M	10 min	68 ^a
P1 _{11.1}	<i>trans</i> -1	500:1	THF	1.37 M	30 min	59
P1 _{2.13}	<i>trans</i> -1	250:1	DCM	2.40 M	10 min	78
P1 _{1.14}	<i>trans</i> -1	250:1	DCM	1.78 M	10 min	84

^a pre-recycling yield post-precipitation. 330 mg of **P1** was purified further via recycling size exclusion chromatography.

Synthesis of **P1**_{1.23}

To an oven dried microwave vial (MV) equipped with a stir bar, 1.128 g (2.36 mmol, 100 equiv.) of *trans*-1 was added. The MV was sealed with a cap, purged, and backfilled 3 times with argon. In a nitrogen filled glovebox. A stock solution of G3 was prepared dissolving 43 mg of G3 in 0.500 mL of dry DCM. *trans*-1 was diluted with 0.780 mL of dry DCM and then 0.200 mL (0.02366 mmol, 1.00 equiv.) of the G3 solution was added to *trans*-1 to initiate the reaction. The reaction stirred for 10 minutes at room temperature until the solution became viscous. 0.500 mL of ethyl vinyl ether was added to quench the reaction and allowed to stir for 10 minutes. Volatiles were removed under reduced pressure. The crude was redissolved in 4 mL of DCM and precipitated in 40 mL of MeOH. The polymer was filtered and dried for 3 hours on the filter then overnight on the Schlenk line vacuum after being transferred to a tared vial yielding pre-RSEC P1 (767.0 mg, 68%). 330 mg of **P1**_{1.23} was further purified via recycling size exclusion chromatography yielding **P1**_{1.23} as a white glassy polymer (130 mg). ¹H and ¹³C spectra are consistent with those previously reported for this compound and no further characterization was performed.^[25]

Synthesis of **P1**_{11.1}

In a nitrogen-filled glovebox, an oven dried vial equipped with a stir bar was charged with 457. mg (0.958 mmol, 500 equiv.) of *trans*-1 and diluted with 0.700 mL of dry THF. To a

separate oven-dried 1-dram vial, a G3 stock solution was prepared by dissolving 4 mg of G3 in 0.287 mL of THF. Both vials were sealed, brought out of the glovebox and placed under argon on the Schlenk line. 0.100 mL of the G3 stock solution was added to the now stirring solution of *trans*-**1** at room temperature to initiate the reaction. The reaction stirred at room temperature for 30 minutes. After 30 min the reaction was quenched with 0.200 mL of ethyl vinyl ether. Volatiles were removed under reduced pressure. The crude was redissolved in 2 mL of DCM and precipitated in 20 mL of MeOH. The precipitate was filtered and reprecipitated following the same steps. The precipitated polymer was dried on the filter for 3 hours before being transferred to a tared vial and dried under vacuum overnight yielding **P1**_{11.1} as a glassy off-white polymer (270 mg, 59%). ¹H and ¹³C spectra are consistent with those previously reported for this compound and no further characterization was performed.^[25]

Synthesis of **P1**_{2.13}

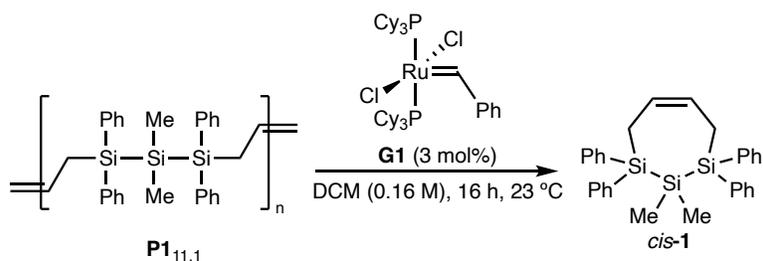
In a nitrogen-filled glovebox, an oven dried vial equipped with a stir bar was charged with 169.2 mg (0.355 mmol, 250 equiv.) of recrystallized *trans*-**1** and diluted with 0.148 mL of dry DCM. To a separate oven-dried 1-dram vial, a G3 stock solution was prepared by dissolving 20 mg of G3 in 1.00 mL of DCM. Both vials were sealed, brought out of the glovebox, and placed under argon on the Schlenk line. 0.0515 mL of the G3 stock solution was added to the now stirring solution of *trans*-**1** at room temperature to initiate the reaction. The reaction stirred at room temperature for 10 minutes. After 10 min the reaction was quenched with 0.200 mL of ethyl vinyl ether. Volatiles were removed under reduced pressure. The crude was redissolved in 3 mL of DCM and precipitated in 30 mL of MeOH. The precipitate was filtered and reprecipitated following the same steps. The precipitated polymer was dried on the filter for 3 hours before being transferred to a tared vial and dried under vacuum overnight yielding **P1**_{2.13} as a glassy off-white polymer (128 mg, 78%). ¹H and ¹³C spectra are consistent with those previously reported for this compound and no further characterization was performed.^[25]

Synthesis of **P1**_{1.14}

In a nitrogen filled glovebox, an oven dried 1-dram vial was equipped with a stir bar was charged with 164.1 mg (0.344 mmol, 250 equiv.) of *trans*-**1** along with 0.143 mL of dry DCM. To a separate oven dried 1-dram vial, a 0.0275 M stock solution of G3 was made by dissolving 13.6 mg of G3 in 0.68 mL of DCM. To the solution of *trans*-**1** was added 0.050 mL (1.38 μmol, 1 equiv.) of the prepared G3 stock solution. The vial was sealed, removed from the glovebox, and allowed to stir at room temperature for 10 minutes. The reaction was quenched with 0.200 mL of ethyl vinyl ether. The reaction stirred for another 10 minutes prior to removing volatiles under reduced pressure. The crude was dissolved in 2 mL of warm DCM and precipitated into 30 mL of methanol stirring in an ice bath. The precipitate was filtered and reprecipitated two more times. The polymer was transferred to a tared vial and dried overnight under vacuum yielding glassy off-white **P1**_{1.14} (138 mg,

84%). ^1H and ^{13}C spectra are consistent with those previously reported for this compound and no further characterization was performed.^[25]

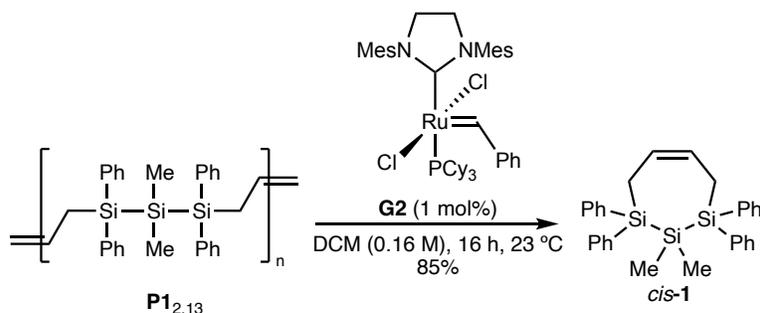
3.4 General procedure for depolymerization



Below is a specific example for the general procedure to conduct the depolymerization experiments of **P1**, from Table 2, entry 6.

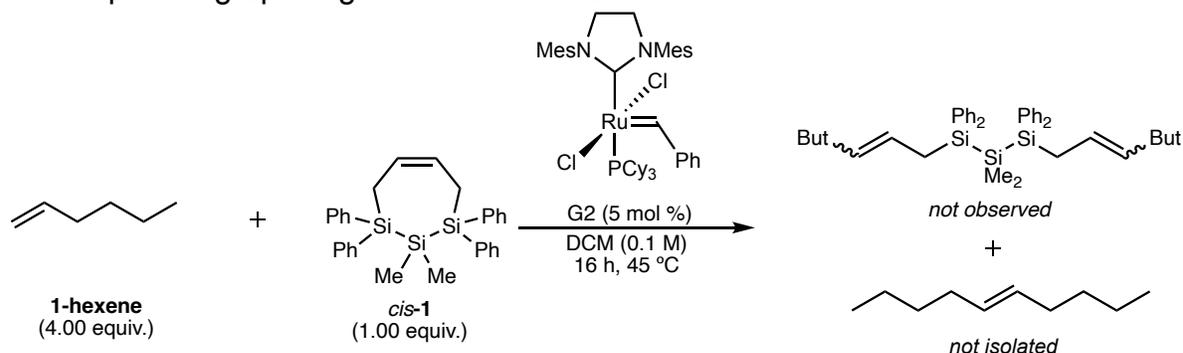
In a nitrogen-filled glovebox, stock solutions of **P1_{11.1}** (60 mg in 0.600 mL of DCM) and **G1** (12 mg in 0.500 mL of DCM) were made. To an oven-dried 1-dram vial equipped with a stir bar, 0.160 mL (0.03355 mmol, 1.00 equiv.) of **P1_{11.1}** stock solution, 0.030 mL of DCM, and 0.070 mL (1.01×10^{-3} mmol, 0.03 equiv.) of **G1** stock solution were added. The vial was sealed and brought out of the glove box, to stir overnight. The next day, the reaction was quenched with 0.150 mL of ethyl vinyl ether. The volatiles were removed under reduced pressure and the reaction was analyzed by ¹H-NMR.

3.5 Depolymerization of **P1**_{2.13} and isolation of *cis*-**1**



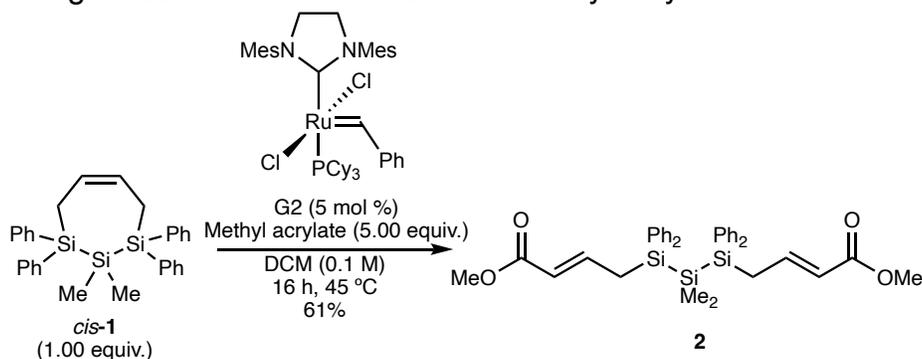
In a nitrogen-filled glovebox, a microwave vial was charged with **P1**_{2.13} (80 mg, 0.168 mmol, 1.00 equiv.). **P1**_{2.13} was diluted with 1.00 mL of dry DCM. Also in the glovebox, a stock solution of **G2** was made in an oven-dried round bottom flask by diluting 10.2 mg of **G2** with 0.874 mL of DCM (13.7 mM). 0.120 mL (0.00168 mmol, 0.01 equiv.) of the **G2** stock solution was added to **P1**_{2.13} via syringe. The reaction was sealed and brought out of the glovebox to stir at room temperature overnight. The next day, the reaction was quenched with 0.200 mL of ethyl vinyl ether, and the volatiles were removed under reduced pressure. The quenched reaction was redissolved with 5 mL of DCM and 150 mg of celite was added. The mixture was sealed and allowed to stir for 1 hour. The celite was removed via vacuum filtration and the filtrate was concentrated under reduced pressure yielding *cis*-**1** as a white solid 67.8 mg (85%). ¹H and ¹³C spectra are consistent with those previously reported for this compound and no further characterization was performed.^[25]

3.6 Attempted ring-opening cross-metathesis of *cis*-1 and 1-hexene



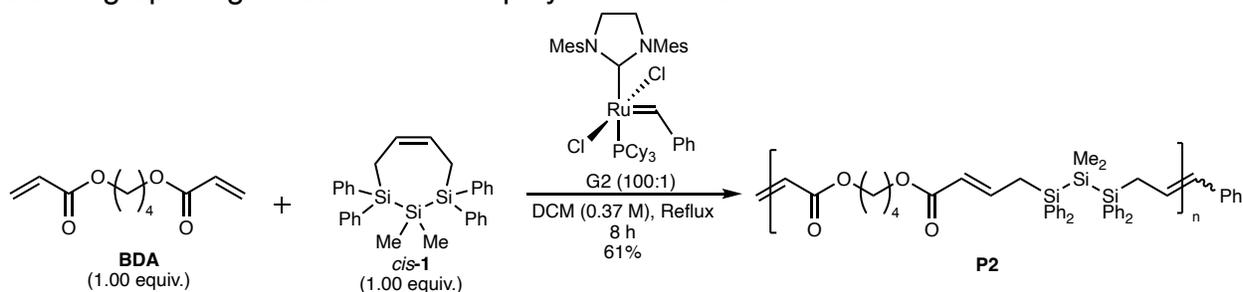
In a glove box, an oven-dry microwave vial was charged with *cis*-1 (95.3 mg, 0.200 mmol, 1.00 equiv.) and diluted with dry DCM (1 mL). A stock solution of G2 was prepared by dissolving 20 mg of G2 in 0.603 mL of DCM. The microwave vial and the G2 solution were sealed and brought out of the glove box. 1-hexene (0.100 mL, 0.800 mmol, 4.00 equiv.) was added to the solution of *cis*-1 and stirred at room temperature. 0.250 mL of the G2 solution was added to the microwave vial to initiate the reaction. The reaction solution was stirred at room temperature for 15 minutes before being heated to 45 °C to stir overnight. The next day the reaction was cooled to room temperature and concentrated under reduced pressure. The crude was analyzed by ¹H-NMR and only the 1-hexene homodimer was observed.

3.7 Ring-opening cross-metathesis of *cis*-1 and methyl acrylate



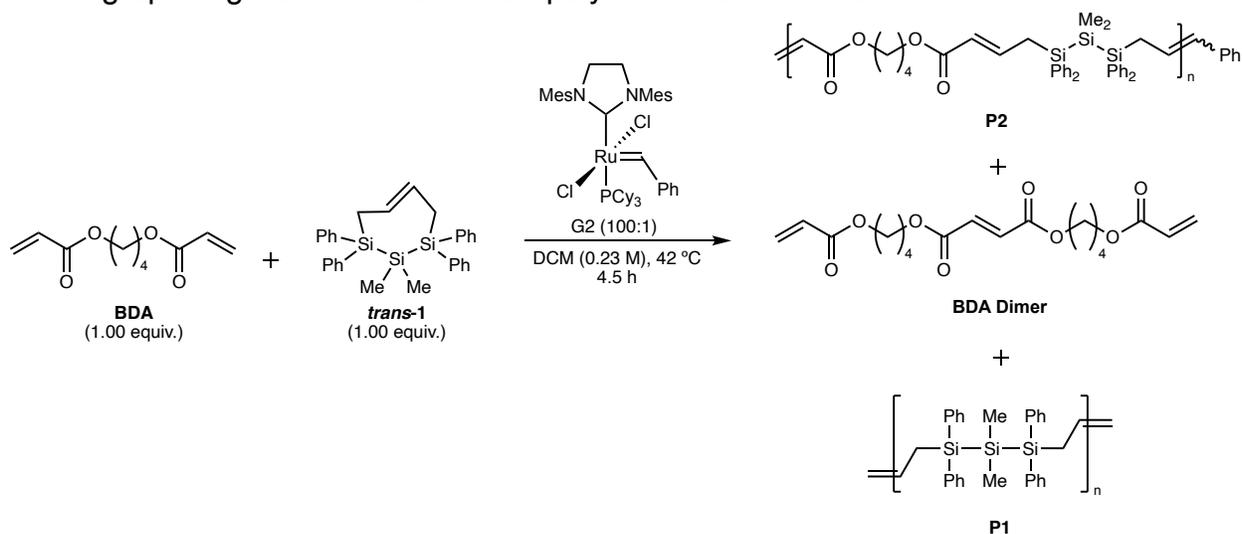
In a nitrogen-filled glove box, an oven-dried microwave vial (MV) was charged with *cis*-1 (100 mg, 0.219 mL, 1.00 equiv.), diluted with 2.10 mL of DCM, and sealed. Also in the glove box, A stock solution of G2 was prepared by dissolving 18.1 mg of G2 in 0.195 mL of DCM into a 1-dram vial with a septa cap. Both solutions were sealed and brought out of the glove box. 0.095 mL (1.05 mmol, 5.00 equiv.) of methyl acrylate was quickly added to the MV and allowed to stir. 0.097 mL (0.0105 mmol, 5 mol%) of the G2 stock solution was added to the MV to initiate the reaction. The MV was submerged in a 45 °C oil bath and left to stir overnight. The next day the reaction was cooled to room temperature and concentrated under reduced pressure. The residue looked like brown oil. The crude oil was purified by silica gel chromatography. DiMA-1 eluted in from a fraction of 25% ethyl acetate and 75% hexanes. The fractions were concentrated under reduced pressure and stored on the bench top as a colorless oil. (79.4 mg, 61%). ¹H-NMR (CDCl₃, 400 MHz) 7.48 – 7.27 (m, 20H), 6.92 – 6.71 (m, 2H), 5.39 (d, 2H, *J*=15.5 Hz), 3.62 (s, 6H), 1.97 (d, 4H, *J*=8.7 Hz), 0.43 (s, 6H) ppm. ¹³C-NMR (101 MHz, CDCl₃) 166.81, 146.67, 135.42, 134.00, 129.53, 128.16, 128.14, 120.06, 51.17, 20.76, -4.10. ²⁹Si-NMR (79 MHz, CDCl₃) -18.64, -45.54. ATR-IR Spectroscopy (cm⁻¹) 3068, 1715, 1639, 1485, 1427, 1320, 1265, 1125, 839, 696. Preliminary attempts at obtaining HRMS were unsuccessful.

3.8 Ring-opening cross-metathesis polymerization of *cis*-1 and BDA



A 10 mL Schlenk flask, reflux condenser, and 2 10 mL round bottom flasks (RBF) were oven-dried overnight. The next day the Schlenk flask and reflux condenser (fit with a dummy flask) were cooled under vacuum. One 10 mL RBF was cooled under vacuum in the glovebox antechamber. In a nitrogen-filled glovebox, a stock solution of G2 was prepared by dissolving 13.6 mg of G2 in 0.866 mL of DCM into the 10 mL RBF sealed and brought out of the glovebox. 176.0 mg (0.370 mmol, 1.00 equiv.) was weighed into the 10 mL Schlenk flask and then purged and backfilled 3 times with argon. The Schlenk flask was diluted with 0.802 mL of dry DCM. BDA (0.070 mL, 0.370 mmol, 1.00 equiv.) and G2 (0.200 mL, 0.00370 mmol, 0.01 equiv.) from the prepared stock solution were added to the Schlenk flask under heavy argon flow. The reflux condenser and dummy flask were purged and backfilled 3 times with argon. Then under heavy argon flow, the reflux condenser was fit to the Schlenk flask, and the reaction stirring began. Water was flowed through the condenser and the apparatus was submerged in a 48 °C oil bath. The reaction stirred at reflux for 8 h. After 8 h, the reaction was cooled to room temperature, and the volatiles were removed under reduced pressure. The crude was dissolved in 2 mL precipitated in 20 mL MeOH twice. The polymer creates a cloudy solution but crashes out as a goo that sticks to the beaker. The polymer was decanted away from the methanol yielding a brown oily and sticky polymer. The polymer was redissolved in 8 mL of DCM and 50 mg of celite was added to the solution and stirred for 15 min. The celite was filtered off, removing any residual catalyst, and the solution was concentrated under reduced pressure to yield P2 as a colorless sticky white solid. (151.0 mg, 61% gravimetric yield). ¹H-NMR(CDCl₃, 400 MHz): δ = 8.31 – 6.87 (m, 25H), 6.75 (ddd, 1H, *J*=14.8, 9.2, 7.8 Hz), 6.39 (dd, 1H, *J*=17.3, 1.5 Hz), 6.10 (dd, 1H, *J*=17.3, 10.4 Hz), 5.81 (dd, 1H, *J*=10.4, 1.5 Hz), 5.32 (d, 1H, *J*=15.5 Hz), 4.23 – 3.89 (m, 6H), 1.93 (d, 4H, *J*=8.5 Hz), 1.67 (t, 2H, *J*=3.2 Hz), 1.54 (s, 4H), 0.41 (s, 6H) ppm. ¹³C-NMR (101 MHz, CDCl₃) δ 166.29, 146.59, 135.41, 133.97, 133.94, 130.71, 129.52, 128.46, 128.11, 120.19, 64.06, 63.31, 25.28, 20.65, -4.12, -4.14. ²⁹Si NMR (79 MHz, CDCl₃) δ -18.57, -45.57. ATR-IR Spectroscopy (cm⁻¹) 3068, 1707, 1635, 1427, 1258, 1123, 1102, 839, 696.

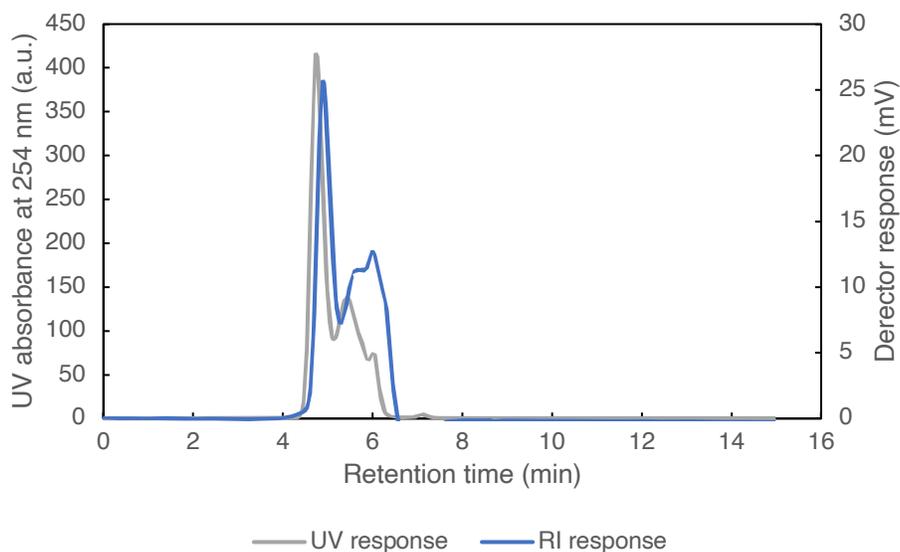
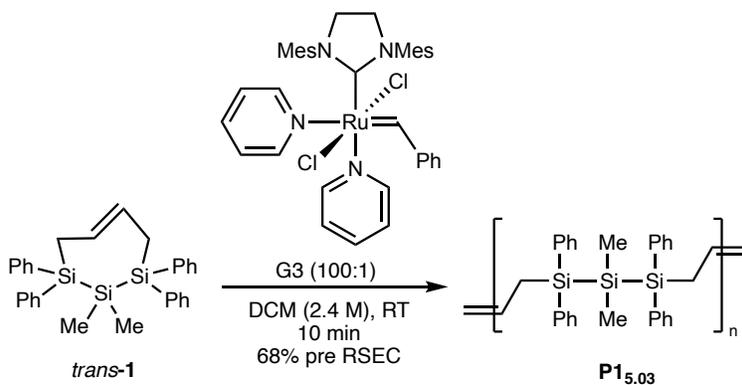
3.9 Ring-opening insertion-metathesis polymerization of *trans*-1 and BDA



A 10 mL Schlenk flask, reflux condenser, and 2 10 mL round bottom flasks (RBF) were oven-dried overnight. The next day the Schlenk flask and reflux condenser (fit with a dummy flask) were cooled under vacuum. One 10 mL RBF was cooled under vacuum in the glovebox antechamber. In a nitrogen-filled glovebox, a stock solution of G2 was prepared by dissolving 10.8 mg of G2 in 0.607 mL of DCM into the 10 mL RBF sealed and brought out of the glovebox. 200.0 mg (0.419 mmol, 1.00 equiv.) was weighed into the 10 mL Schlenk flask and then purged and backfilled 3 times with argon. The Schlenk flask was diluted with 1.48 mL of dry DCM. BDA (0.079 mL, 0.419 mmol, 1.00 equiv.) and G2 (0.200 mL, 0.00419 mmol, 0.01 equiv.) from the prepared stock solution were added to the Schlenk flask under heavy argon flow. After G2 was added, the headspace was evacuated with a dynamic vacuum and then backfilled with Argon. The reflux condenser and dummy flask were purged and backfilled 3 times with argon. Then under heavy argon flow, the reflux condenser was fit to the Schlenk flask, and the reaction stirring began. Water was flowed through the condenser and the apparatus was submerged in a 42 °C oil bath. The reaction stirred at reflux for 4.5 h. After 4.5 h, the reaction was cooled to room temperature, and the volatiles were removed under reduced pressure. The crude was dissolved in 2 mL precipitated in 20 mL hexanes. The polymer creates a cloudy solution but crashes out as a goo that sticks to the beaker. The polymer was decanted away from the hexanes yielding a brown oily and sticky polymer. The polymer was redissolved in 3 mL of DCM and precipitated into 30 mL of MeOH. The polymer was filtered through a fine-fitted funnel and dried under vacuum. The dried polymer was analyzed by ¹H-NMR spectroscopy.

4. Gel Permeation Chromatography (GPC) Spectra

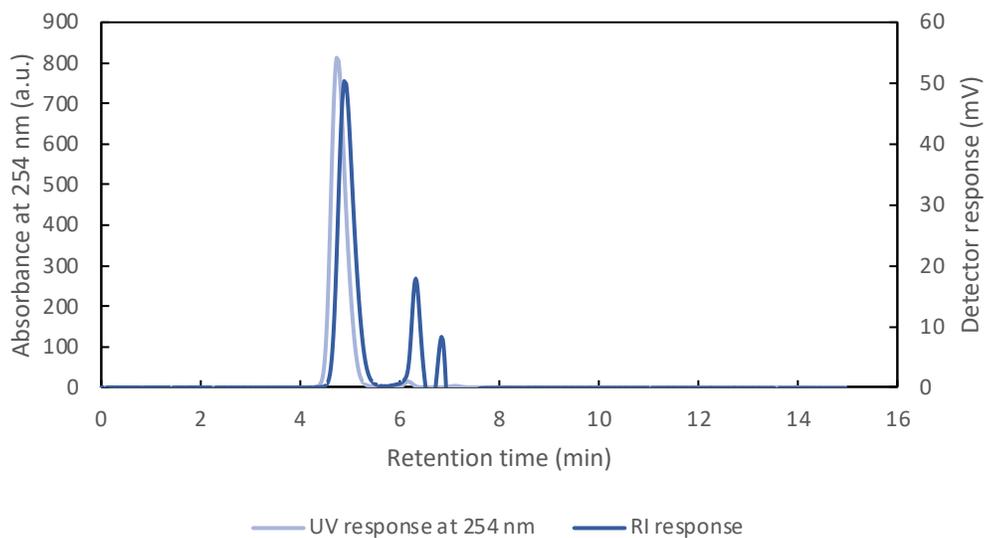
4.1 P1_{5.03} GPC spectra of polymer taken before RSEC.



Peak No.	Retention Time (min)	M _n ^a (kg mol ⁻¹)	M _w ^a (kg mol ⁻¹)	M _w /M _n ^a
RI				
1	4.90	1.13	8.56	7.57
2	6,87	0.032	0.041	1.27
UV				
1	4.74	2.03	10.2	5.03
2	7.11	0.014	0.022	1.55

^a Determined by size exclusion chromatography relative to polystyrene standards at 254 nm (THF, [P1_{5.03}] = 1.00 mg mL⁻¹, 40 °C, 0.35 mL min⁻¹, 10 μL injection).

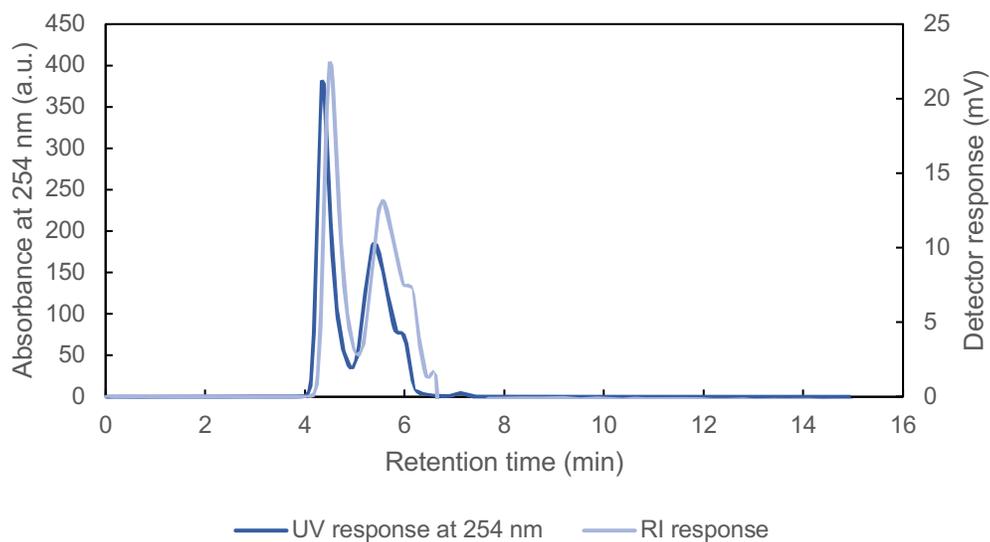
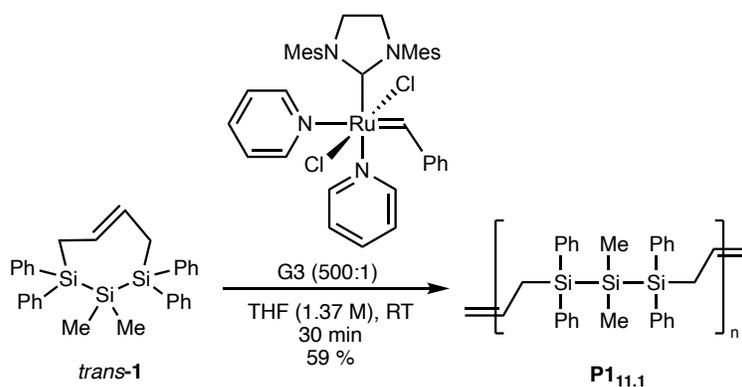
4.2 P1_{1.23} GPC spectra post RSEC



Peak No.	Retention Time (min)	M_n^a (kg mol ⁻¹)	M_w^a (kg mol ⁻¹)	M_w/M_n^a
RI				
1	4.90	12.6	15.8	1.25
2	6.32	0.245	0.280	1.14
3	6.62	0.100	0.101	1.02
4	6.84	0.053	0.054	1.02
5	7.07	0.019	0.022	1.15
UV				
1	4.74	13.0	15.9	1.23
2	6.17	0.238	0.275	1.16
3	7.11	0.013	0.015	1.14

^a Determined by size exclusion chromatography relative to polystyrene standards at 254 nm (THF, [P1_{1.23}] = 1.00 mg mL⁻¹, 40 °C, 0.35 mL min⁻¹, 10 μL injection).

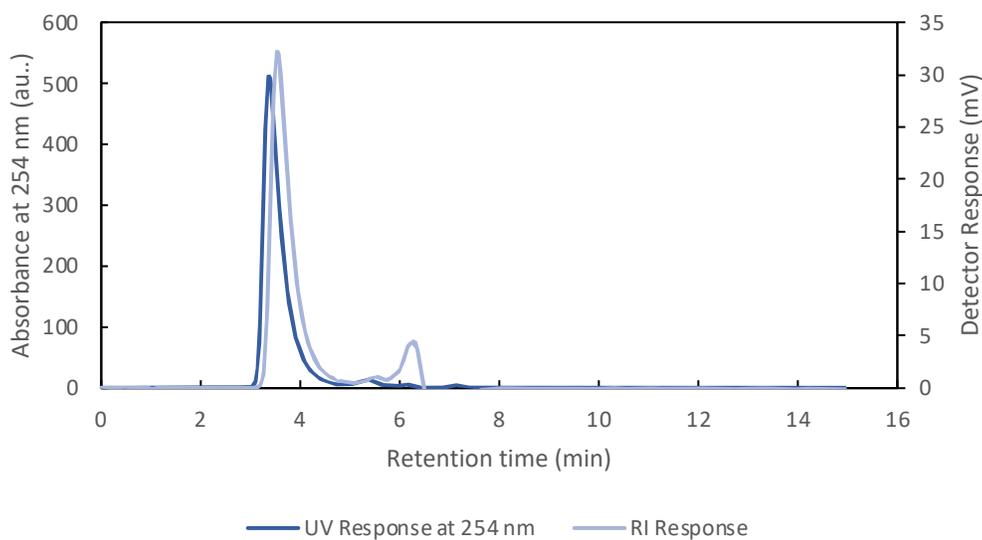
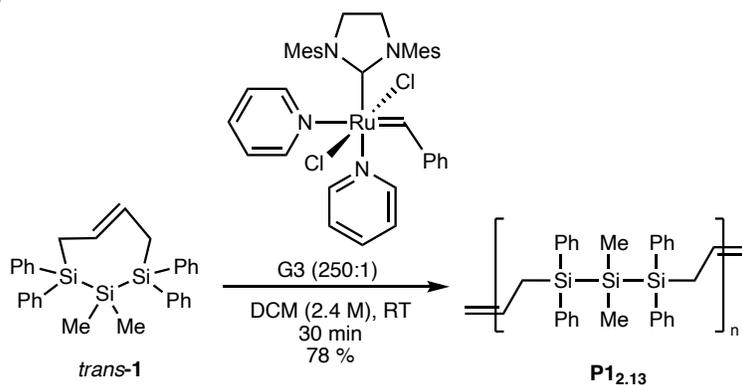
4.3 P1_{11.1} GPC spectra



Peak No.	Retention Time (min)	M _n ^a (kg mol ⁻¹)	M _w ^a (kg mol ⁻¹)	M _w /M _n ^a
RI				
1	4.51	1.65	21.7	13.1
2	7.01	0.027	0.036	1.34
UV				
1	4.35	2.21	24.6	11.1
2	7.10	0.017	0.039	2.38

^a Determined by size exclusion chromatography relative to polystyrene standards at 254 nm (THF, [P1_{11.1}] = 1.00 mg mL⁻¹, 40 °C, 0.35 mL min⁻¹, 10 μL injection).

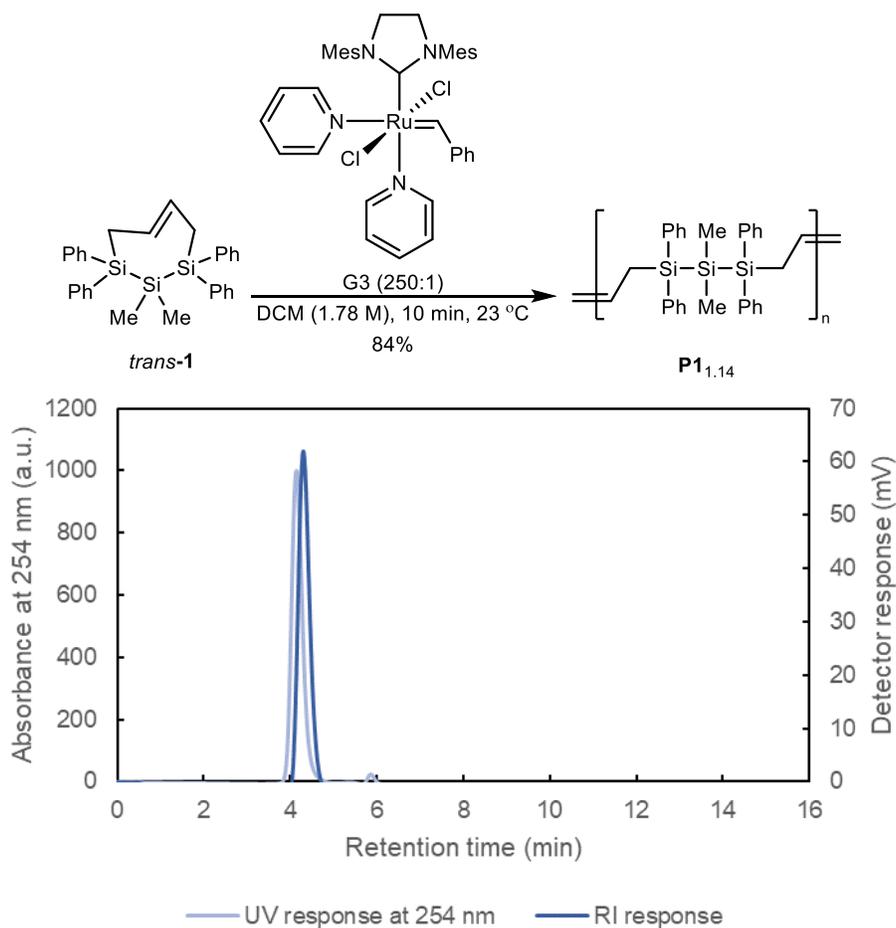
4.4 **P1**_{2.13} GPC Spectra



Peak No.	Retention Time (min)	M_n^a (kg mol ⁻¹)	M_w^a (kg mol ⁻¹)	M_w/M_n^a
RI				
1	3.55	364.	705.	1.94
UV				
1	3.38	341	727	2.13
2	5.36	2.68	3.73	1.39

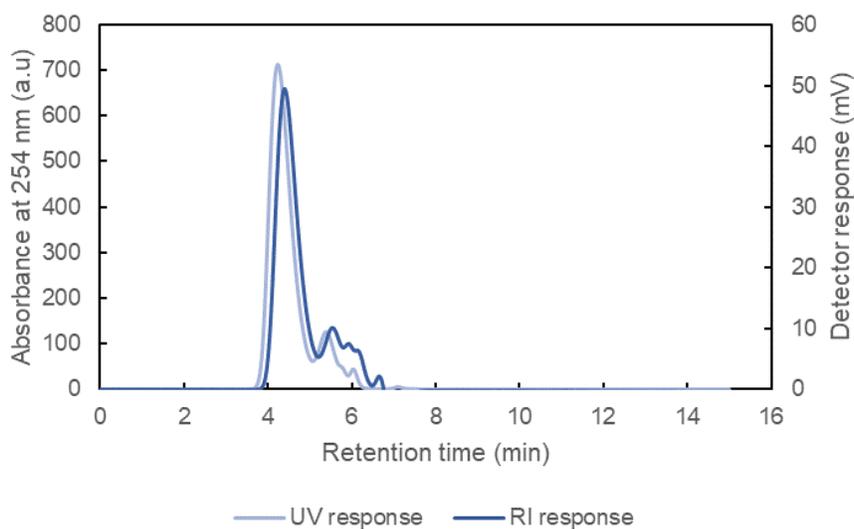
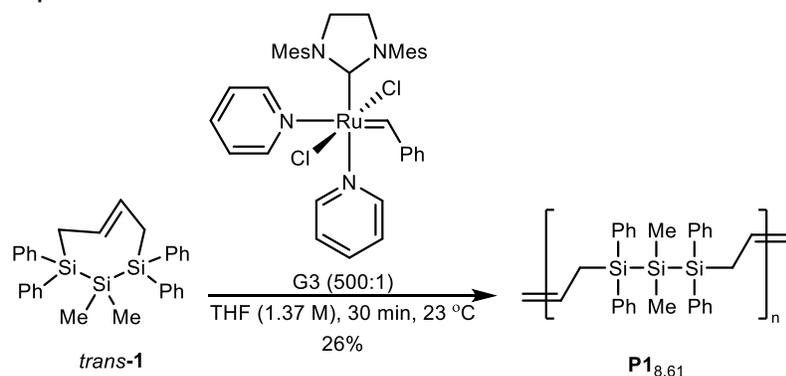
^a Determined by size exclusion chromatography relative to polystyrene standards at 254 nm (THF, [**P1**_{2.13}] = 0.75 mg mL⁻¹, 40 °C, 0.35 mL min⁻¹, 10 μL injection).

4.5 P1_{1,14} GPC Spectra



Peak No.	Retention Time (min)	M _n ^a (kg mol ⁻¹)	M _w ^a (kg mol ⁻¹)	M _w /M _n ^a
RI				
1	4.30	92.0	105.7	1.15
2	6.03	0.470	0.548	1.17
UV				
1	4.14	92.9	105.7	1.14
2	5.36	0.656	0.693	1.06

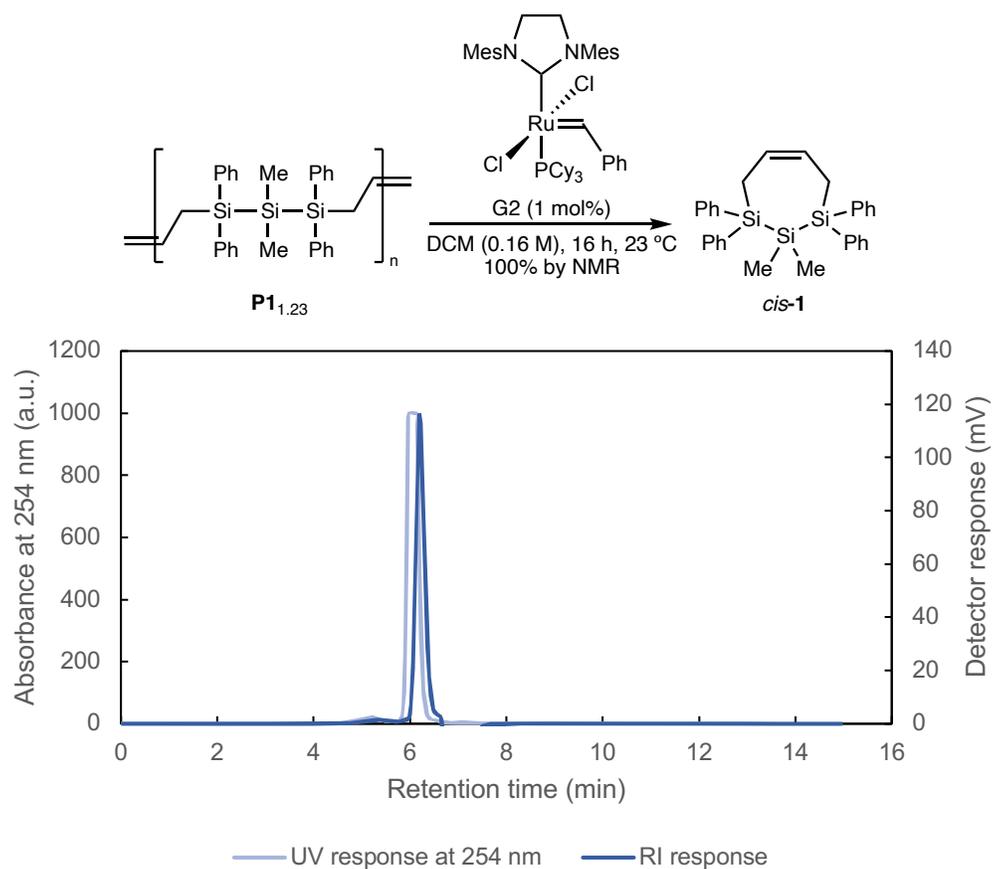
4.6 P1_{8.61} GPC Spectra



Peak No.	Retention Time (min)	M _n ^a (kg mol ⁻¹)	M _w ^a (kg mol ⁻¹)	M _w /M _n ^a
RI				
1	4.39	4.57	64.2	14.0
2	6.65	0.167	0.168	1.00
UV				
1	4.233	7.98	68.8	8.61

^a Determined by size exclusion chromatography relative to polystyrene standards at 254 nm (THF, [P1_{8.61}] = 1.00 mg mL⁻¹, 40 °C, 0.35 mL min⁻¹, 10 μL injection).

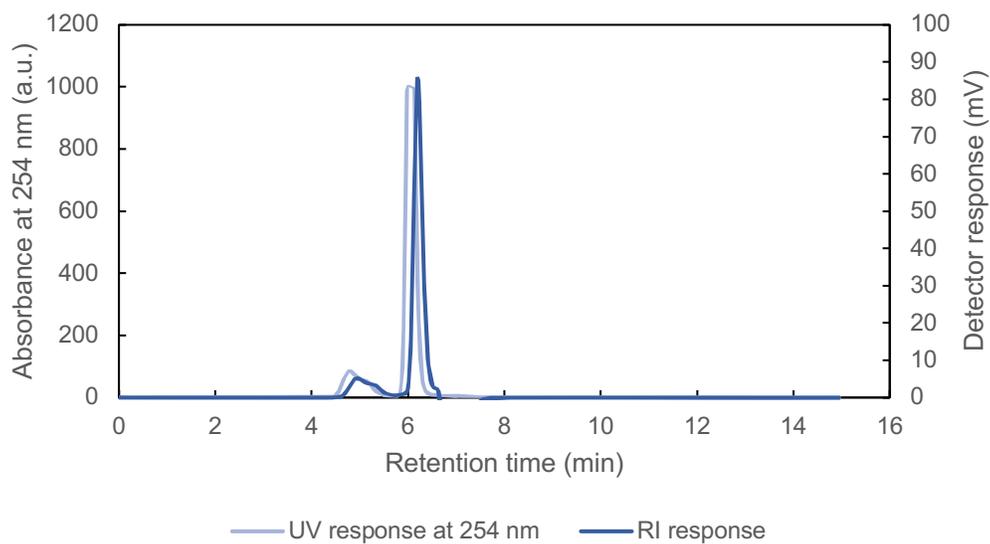
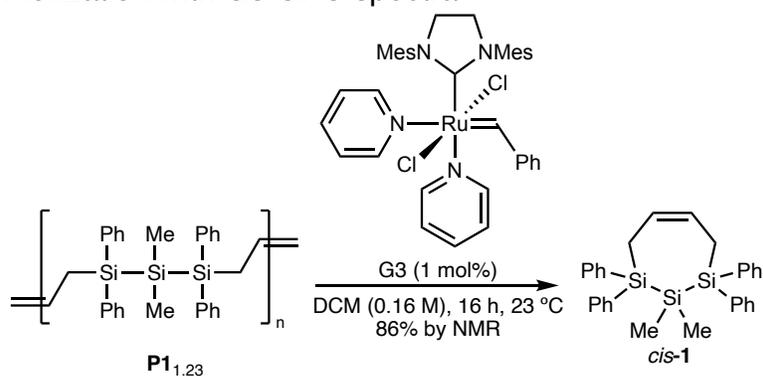
4.7 P1_{1,2,3} depolymerization with G2 GPC spectra



Peak No.	Retention Time (min)	M _n ^a (kg mol ⁻¹)	M _w ^a (kg mol ⁻¹)	M _w /M _n ^a
RI				
1	5.34	4.62	8.46	1.83
2	6.20	0.306	0.341	1.11
3	6.89	0.031	0.039	1.26
UV				
1	5.01	11.8	13.3	1.12
2	5.18	2.50	3.64	1.46
3	5.96	0.302	0.335	1.11
4	7.11	0.009	0.015	1.69

^a Determined by size exclusion chromatography relative to polystyrene standards at 254 nm (THF, [Sample] = 1.00 mg mL⁻¹, 40 °C, 0.35 mL min⁻¹, 10 μL injection).

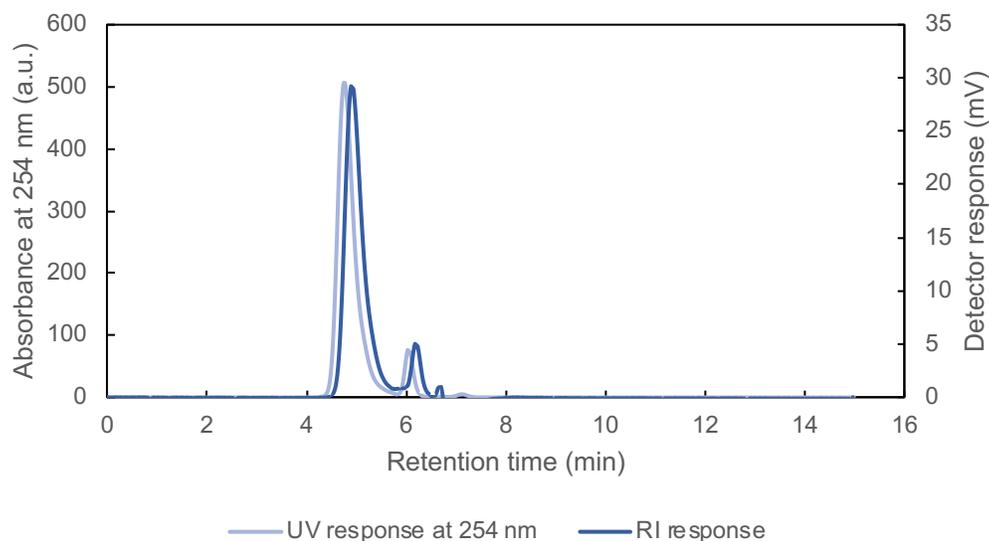
4.8 P1_{1,23} depolymerization with G3 GPC spectra



Peak No.	Retention Time (min)	M _n ^a (kg mol ⁻¹)	M _w ^a (kg mol ⁻¹)	M _w /M _n ^a
RI				
1	4.93	13.1	15.2	1.16
2	5.17	3.88	4.53	1.17
3	6.20	0.306	0.338	1.11
4	6.89	0.030	0.038	1.26
UV				
1	4.79	13.5	15.3	1.14
2	5.01	3.88	4.69	1.21
3	5.98	0.308	0.337	1.09
4	7.10	0.017	0.024	1.43

^a Determined by size exclusion chromatography relative to polystyrene standards at 254 nm (THF, [Sample] = 1.00 mg mL⁻¹, 40 °C, 0.35 mL min⁻¹, 10 μL injection).

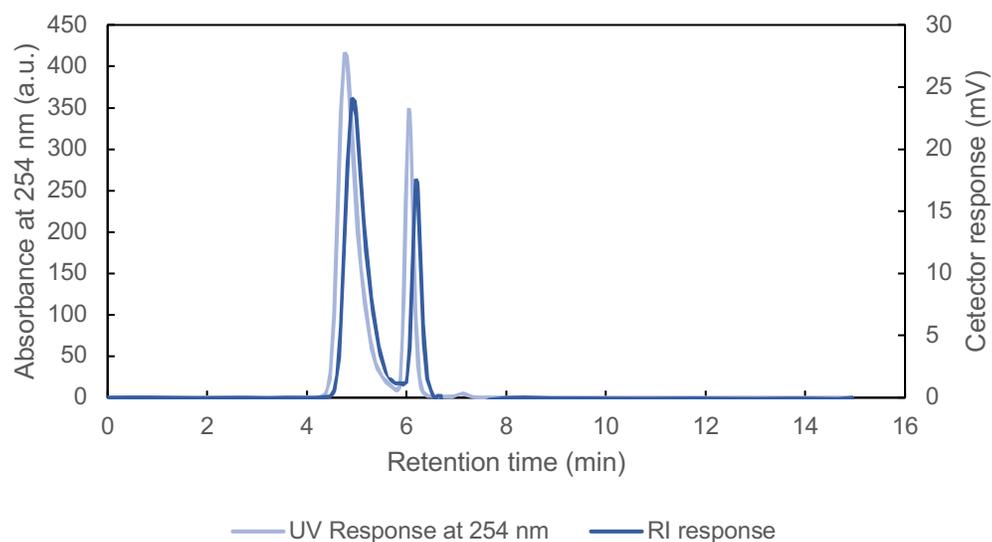
4.9 P1_{1.23} depolymerization with G1 15 min aliquot



Peak No.	Retention Time (min)	M_n^a (kg mol ⁻¹)	M_w^a (kg mol ⁻¹)	M_w/M_n^a
RI				
1	4.91	9.67	14.4	1.49
2	6.20	0.356	0.423	1.19
3	7.05	0.022	0.028	1.28
UV				
1	4.76	9.55	14.4	1.51
2	6.05	0.321	0.348	1.08
3	7.11	0.015	0.019	1.25

^a Determined by size exclusion chromatography relative to polystyrene standards at 254 nm (THF, [Sample] = 0.75 mg mL⁻¹, 40 °C, 0.35 mL min⁻¹, 10 μL injection).

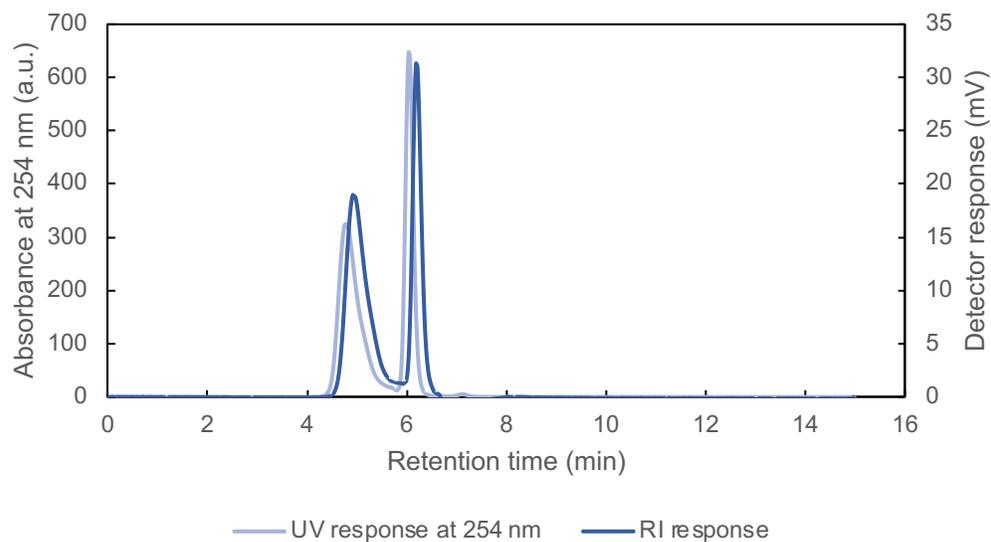
4.10 P1_{1.23} depolymerization with G1 1 h aliquot



Peak No.	Retention Time (min)	M_n^a (kg mol ⁻¹)	M_w^a (kg mol ⁻¹)	M_w/M_n^a
RI				
1	4.93	7.43	13.1	1.77
2	6.20	0.324	0.351	1.08
UV				
1	4.77	8.00	13.4	1.68
2	6.05	0.324	0.345	1.06

^a Determined by size exclusion chromatography relative to polystyrene standards at 254 nm (THF, [Sample] = 0.75 mg mL⁻¹, 40 °C, 0.35 mL min⁻¹, 10 μL injection).

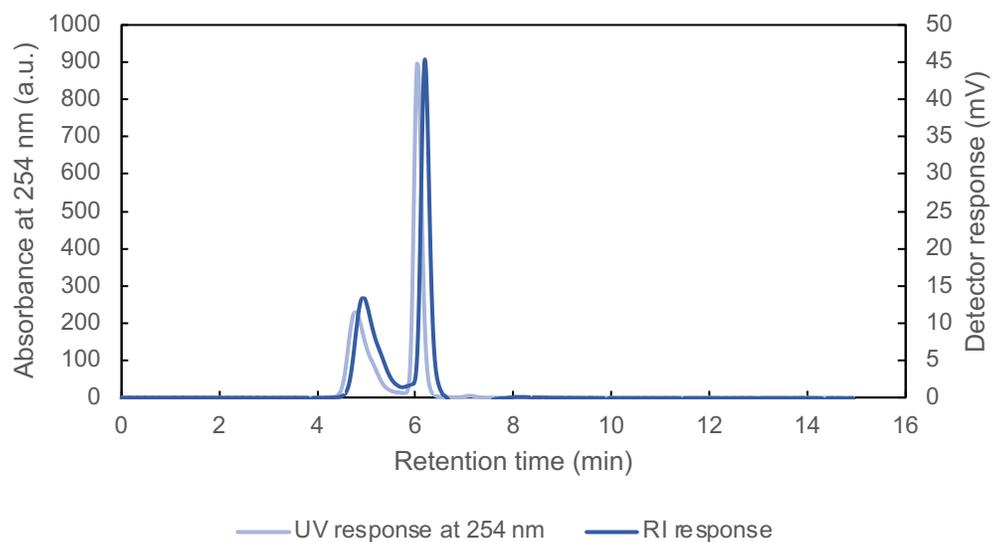
4.11 P1_{1.23} depolymerization with G1 2 h aliquot



Peak No.	Retention Time (min)	M _n ^a (kg mol ⁻¹)	M _w ^a (kg mol ⁻¹)	M _w /M _n ^a
RI				
1	4.94	6.81	12.6	1.84
2	6.20	0.316	0.344	1.09
3	7.03	23	0.030	1.31
UV				
1	4.78	7.12	12.7	1.79
2	6.05	0.320	0.344	1.07
3	7.11	0.014	0.017	1.18

^a Determined by size exclusion chromatography relative to polystyrene standards at 254 nm (THF, [Sample] = 0.75 mg mL⁻¹, 40 °C, 0.35 mL min⁻¹, 10 μL injection).

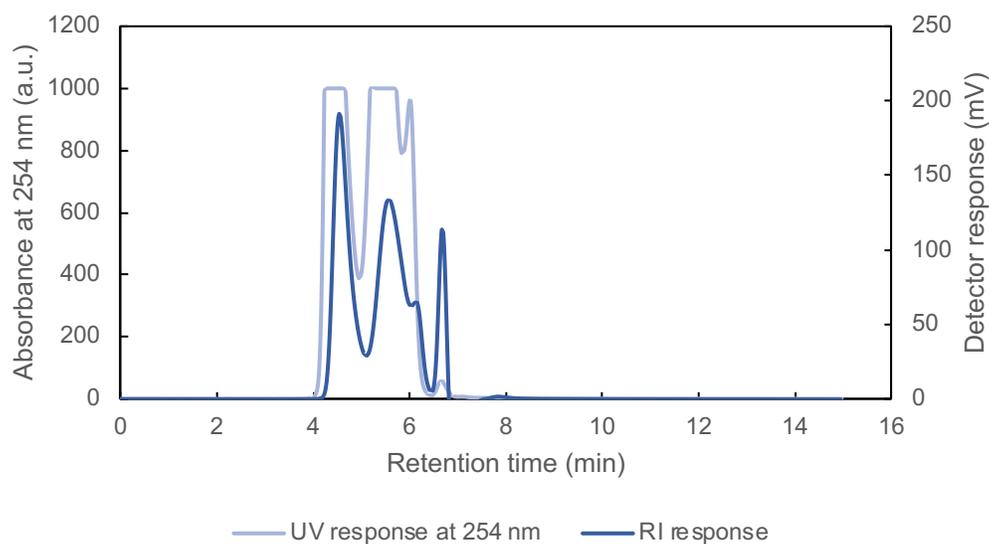
4.12 P1_{1.23} depolymerization with G1 16 h aliquot



Peak No.	Retention Time (min)	M_n^a (kg mol ⁻¹)	M_w^a (kg mol ⁻¹)	M_w/M_n^a
RI				
1	4.93	5.92	12.1	2.04
2	6.20	0.321	0.347	1.08
3	7.02	0.024	0.031	1.28
UV				
1	4.78	6.92	12.5	1.81
2	6.05	0.322	0.344	1.07
3	7.12	0.016	0.021	1.36

^a Determined by size exclusion chromatography relative to polystyrene standards at 254 nm (THF, [Sample] = 0.75 mg mL⁻¹, 40 °C, 0.35 mL min⁻¹, 10 μL injection).

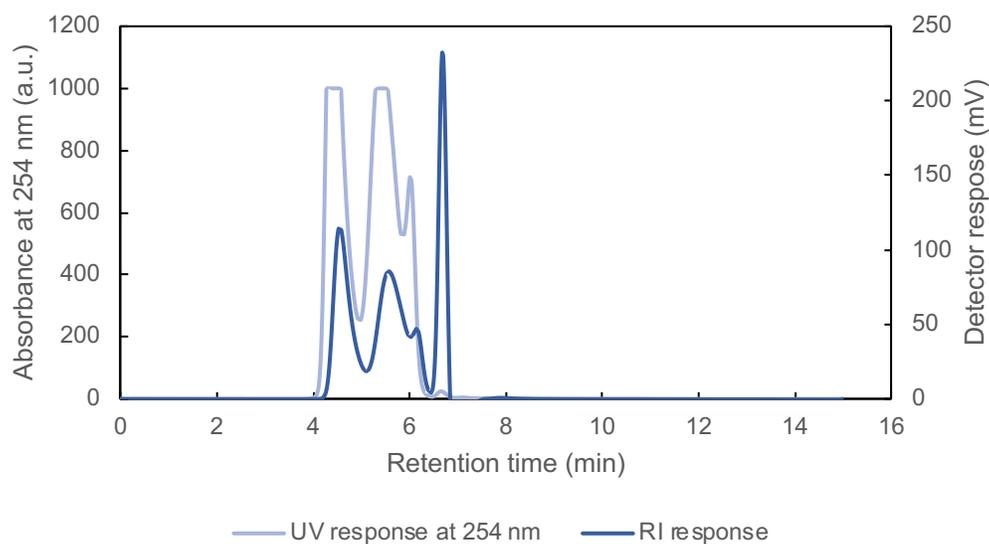
4.13 P1_{11.1} depolymerization with G1 15 min aliquot



Peak No.	Retention Time (min)	M_n^a (kg mol ⁻¹)	M_w^a (kg mol ⁻¹)	M_w/M_n^a
RI				
1	4.54	30.8	41.0	1.33
2	5.56	1.65	2505	1.52
3	6.13	0.358	0.387	1.08
4	6.68	0.085	0.089	1.04
UV				
1	4.23	26.4	38.6	1.46
2	5.18	1.70	2.68	1.58
3	6.01	0.372	0.408	1.10
4	6.66	0.015	0.046	3.13

^a Determined by size exclusion chromatography relative to polystyrene standards at 254 nm (THF, [Sample] = 1.00 mg mL⁻¹, 40 °C, 0.35 mL min⁻¹, 10 µL injection).

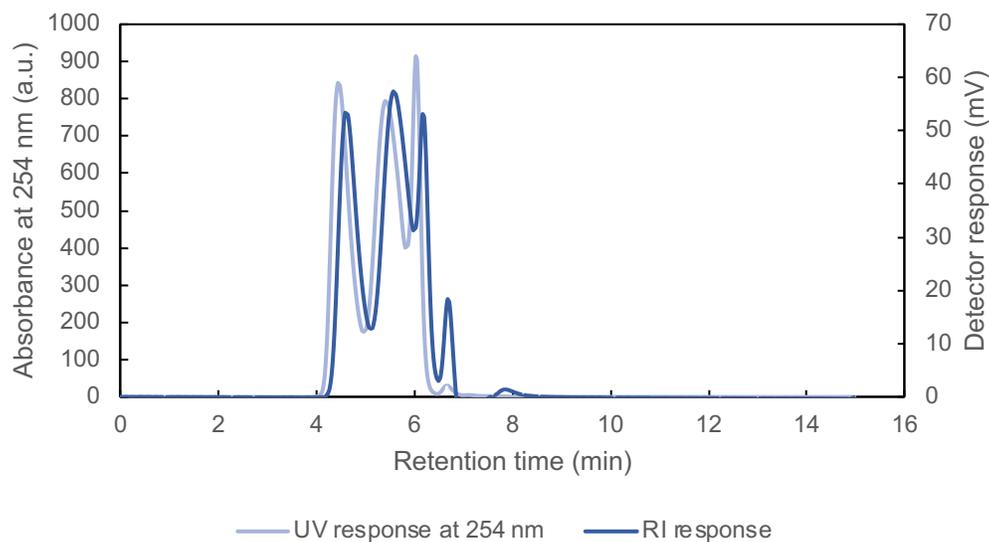
4.14 P1_{11.1} depolymerization with G1 30 min aliquot



Peak No.	Retention Time (min)	M_n^a (kg mol ⁻¹)	M_w^a (kg mol ⁻¹)	M_w/M_n^a
RI				
1	4.55	30.6	40.5	1.32
2	5.57	1.69	2.55	1.51
3	6.15	0.367	0.398	1.08
4	6.68	0.042	0.075	1.77
UV				
1	4.27	28.3	39.2	1.38
2	5.29	1.71	2.56	1.50
3	6.02	0.361	0.394	1.09
4	6.66	0.010	0.042	4.07

^a Determined by size exclusion chromatography relative to polystyrene standards at 254 nm (THF, [Sample] = 1.00 mg mL⁻¹, 40 °C, 0.35 mL min⁻¹, 10 μL injection).

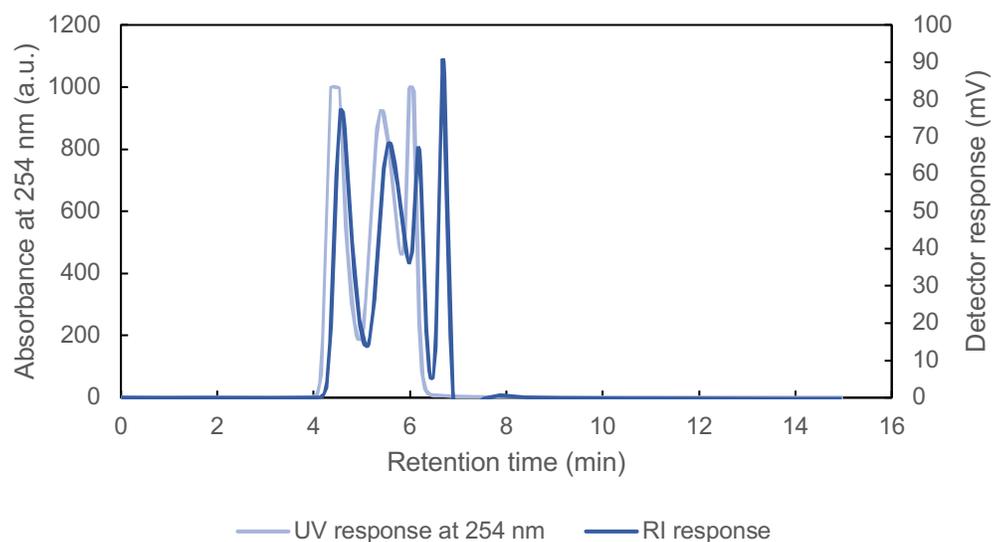
4.15 P1_{11.1} depolymerization with G1 1 h aliquot



Peak No.	Retention Time (min)	M_n^a (kg mol ⁻¹)	M_w^a (kg mol ⁻¹)	M_w/M_n^a
RI				
1	4.61	26.9	35.8	1.33
2	5.57	1.71	2.53	1.48
3	6.18	0.354	0.389	1.10
4	6.69	0.083	0.087	1.05
UV				
1	4.45	27.1	36.0	1.33
2	5.42	1756	2.54	1.45
3	6.03	0.355	0.388	1.09
4	6.66	0.050	0.055	1.11

^a Determined by size exclusion chromatography relative to polystyrene standards at 254 nm (THF, [Sample] = 1.00 mg mL⁻¹, 40 °C, 0.35 mL min⁻¹, 10 µL injection).

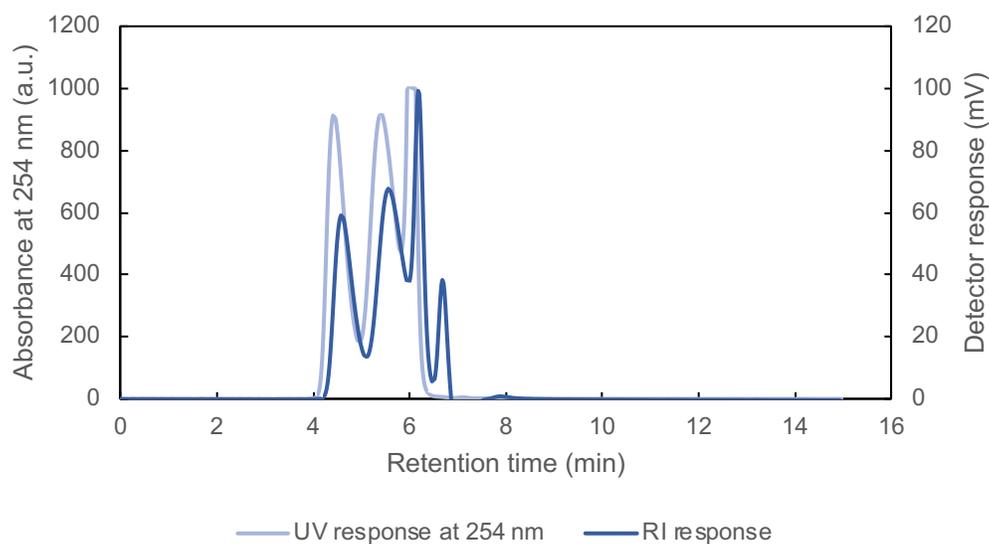
4.16 P1_{11.1} depolymerization with G1 2 h aliquot



Peak No.	Retention Time (min)	M_n^a (kg mol ⁻¹)	M_w^a (kg mol ⁻¹)	M_w/M_n^a
RI				
1	4.58	29.3	38.4	1.31
2	5.56	1.73	2.55	1.48
3	6.18	0.356	0.389	1.09
4	6.69	0.079	0.084	1.06
UV				
1	4.34	29.2	38.5	1.32
2	5.41	1.77	2.58	1.45
3	5.99	0.351	0.386	1.10

^a Determined by size exclusion chromatography relative to polystyrene standards at 254 nm (THF, [Sample] = 1.00 mg mL⁻¹, 40 °C, 0.35 mL min⁻¹, 10 μL injection).

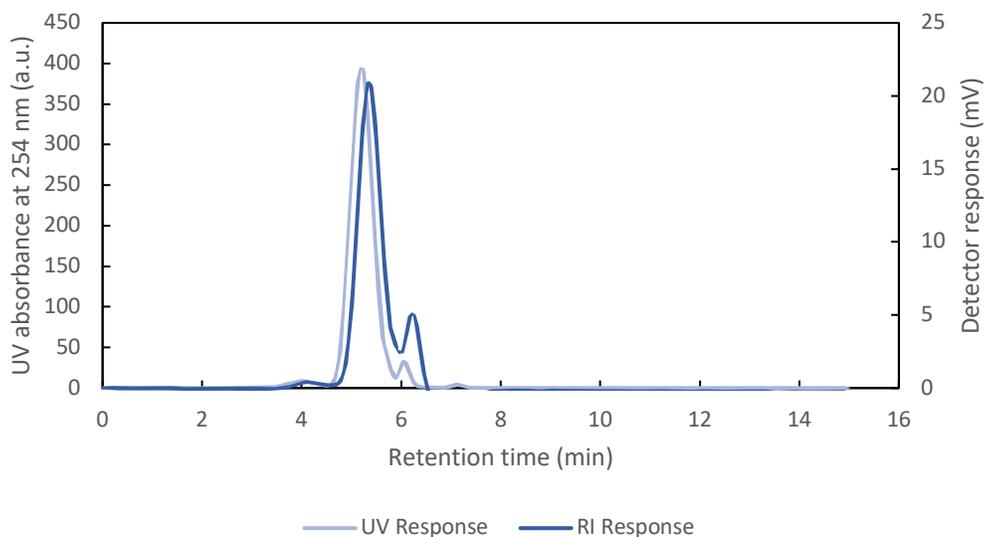
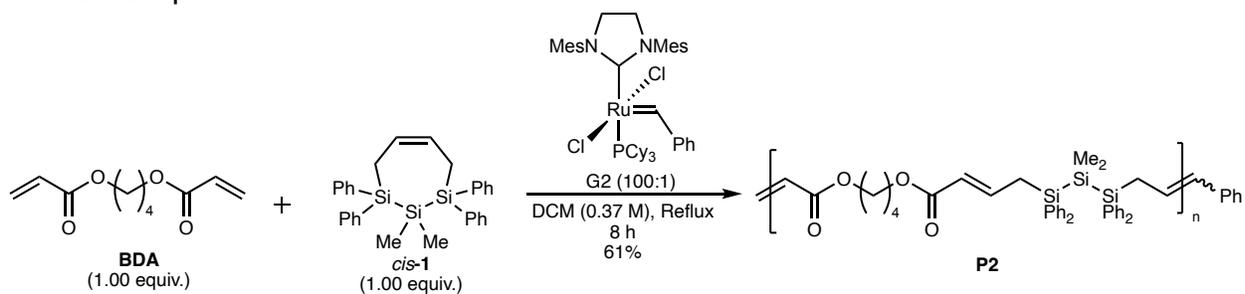
4.17 P1_{11.1} depolymerization with G1 16 h aliquot



Peak No.	Retention Time (min)	M _n ^a (kg mol ⁻¹)	M _w ^a (kg mol ⁻¹)	M _w /M _n ^a
RI				
1	4.59	27.6	37.2	1.35
2	5.56	1.77	2.56	1.45
3	6.19	0.348	0.383	1.10
4	6.68	0.082	0.086	1.05
5	7.43	0.07	0.010	1.31
UV				
1	4.43	28.2	37.5	1.33
2	5.40	1.82	2.61	1.43
3	5.95	0.334	0.384	1.15

^a Determined by size exclusion chromatography relative to polystyrene standards at 254 nm (THF, [Sample] = 1.00 mg mL⁻¹, 40 °C, 0.35 mL min⁻¹, 10 μL injection).

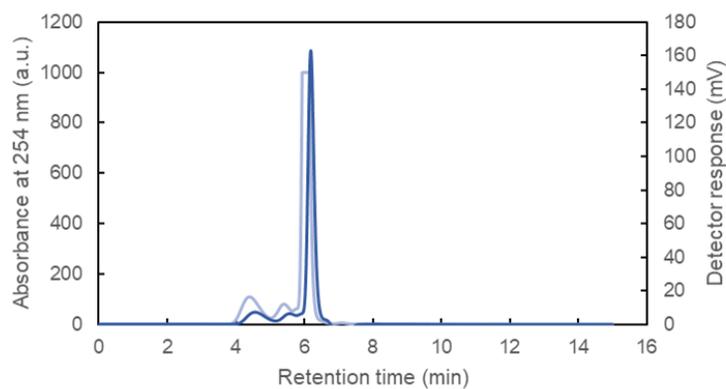
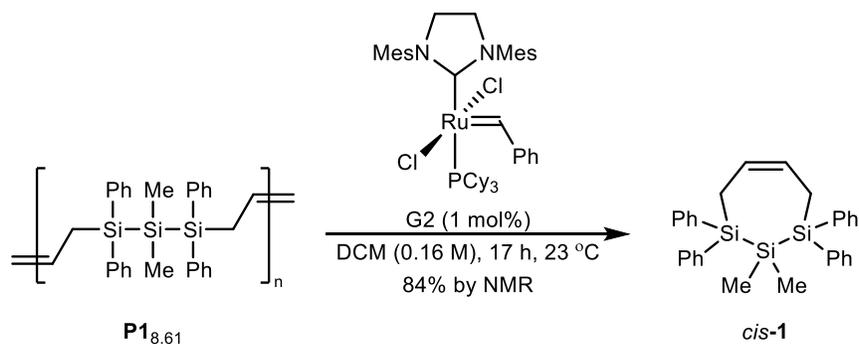
4.18 GPC Spectra of **P2**



Peak No.	Retention Time (min)	M_n^a (kg mol ⁻¹)	M_w^a (kg mol ⁻¹)	M_w/M_n^a
RI				
1	4.21	101.0	227.0	2.26
2	5.35	3.05	4.94	1.62
3	6.21	0.297	0.340	1.15
UV				
1	3.99	107.0	201.0	1.87
2	5.75	3.310	5.02	1.52
3	7.12	0.079	0.289	3.68

^a Determined by size exclusion chromatography relative to polystyrene standards at 254 nm (THF, [**P2**] = 0.65 mg mL⁻¹, 40 °C, 0.35 mL min⁻¹, 10 μL injection).

4.19 P1_{8.61} depolymerization with G2 GPC spectra



— UV response — RI Response

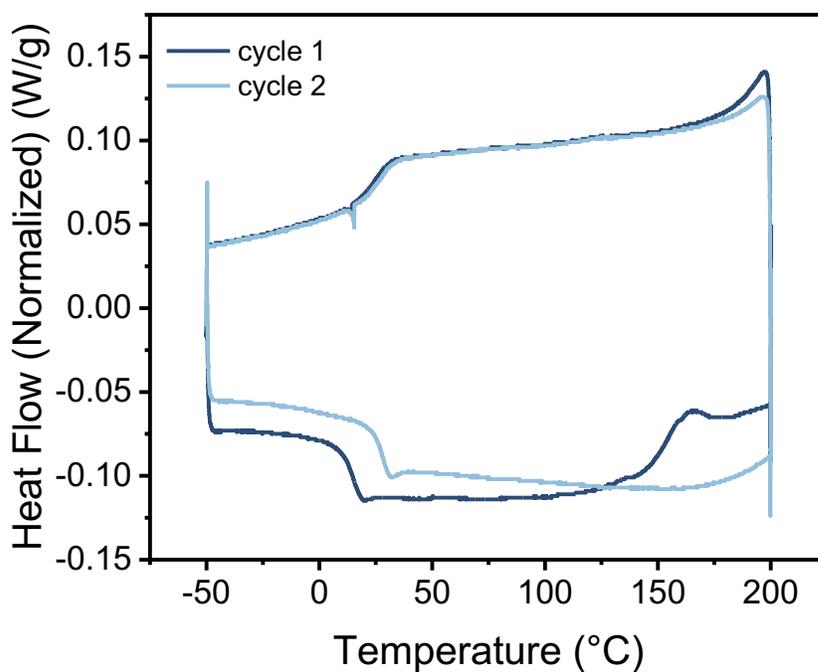
Peak No.	Retention Time (min)	M _n ^a (kg mol ⁻¹)	M _w ^a (kg mol ⁻¹)	M _w /M _n ^a
RI				
1	4.56	37.5	56.5	1.51
2	5.58	2.58	3.41	1.32
3	6.19	0.388	0.430	1.11
UV				
1	4.40	36.8	55.7	1.52
2	5.41	2.53	3.24	1.28
3	5.94	0.374	0.420	1.12

^a Determined by size exclusion chromatography relative to polystyrene standards at 254 nm (THF, [Sample] = 1.00 mg mL⁻¹, 40 °C, 0.35 mL min⁻¹, 10 μL injection).

5. Thermal Characterization

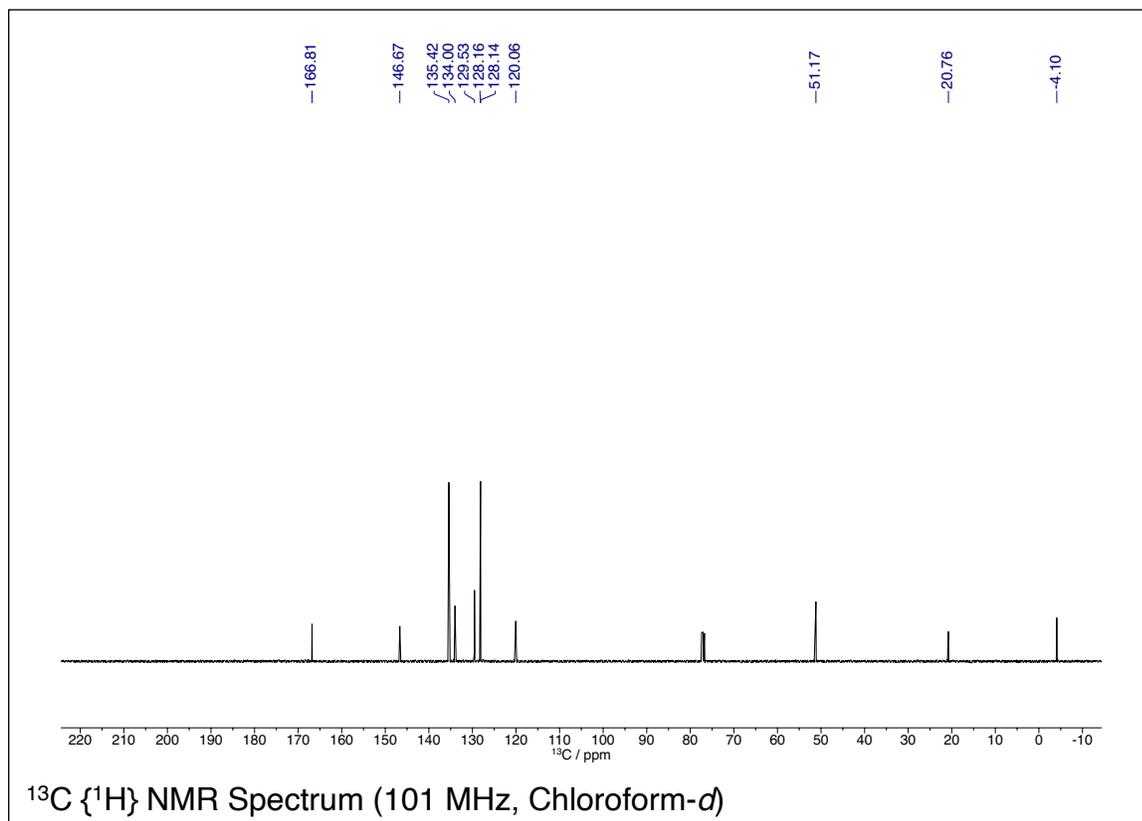
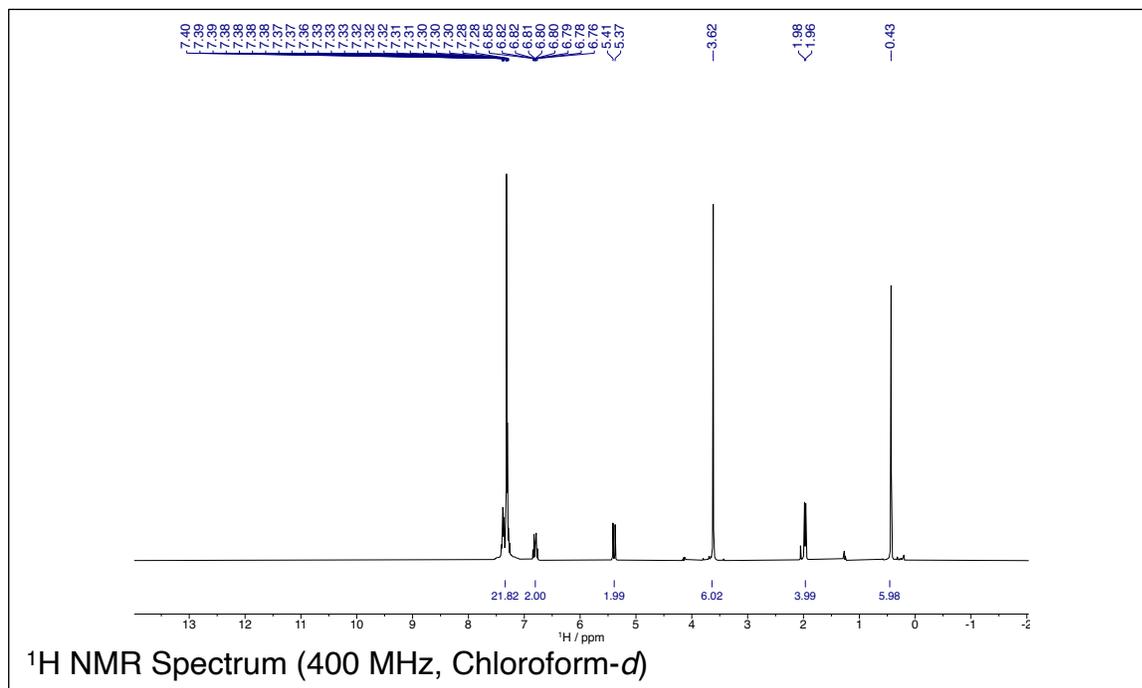
5.1 Differential Scanning Calorimetry (DSC)

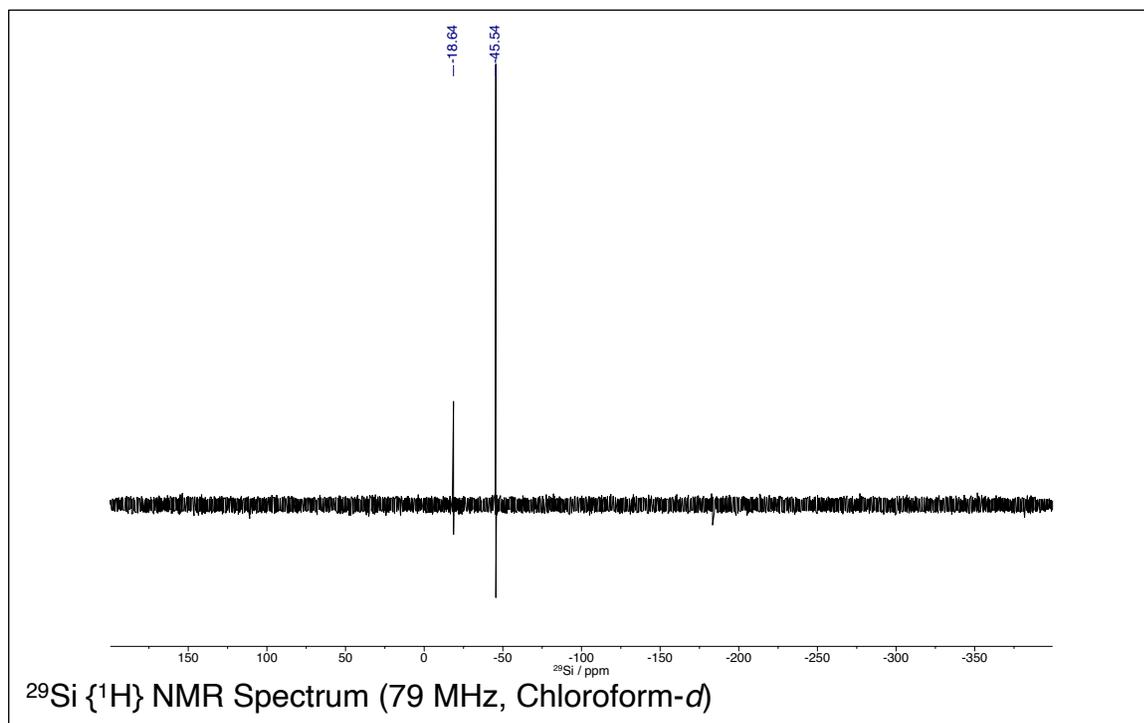
Differential scanning calorimetry (DSC) was conducted using a TA Instrument DSC 2500. A **P2** sample of ~10 mg was sealed in Tzero Aluminum pans. The DSC experiment was carried out under N₂ flow (50 mL/min) following the procedure below: -50 °C (5 min), heat from -50 °C to 200 °C (5 °C/min), isothermal 200 °C (5 min), cool from 200 °C to -50 °C (5 °C/min) for two consecutive cycles. The glass transition temperature (T_g) was determined from the second cooling cycle as 22.7 °C. A cold crystallization peak was observed in the first heating cycle at ~165 °C.



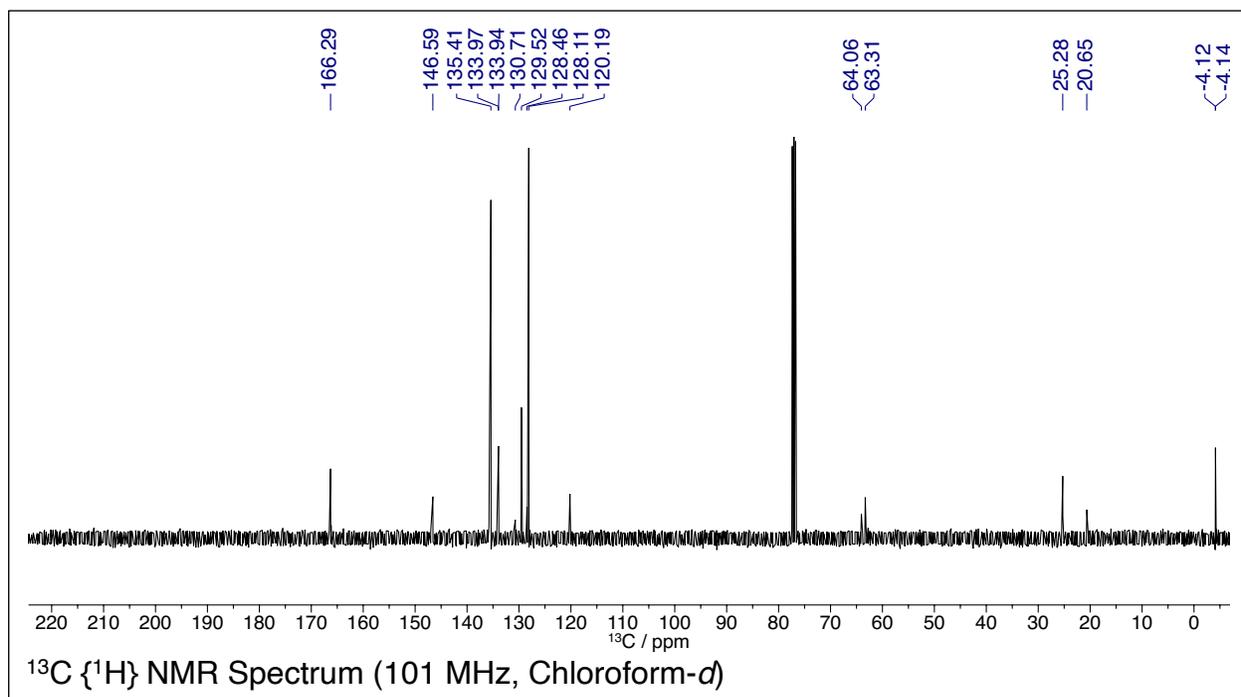
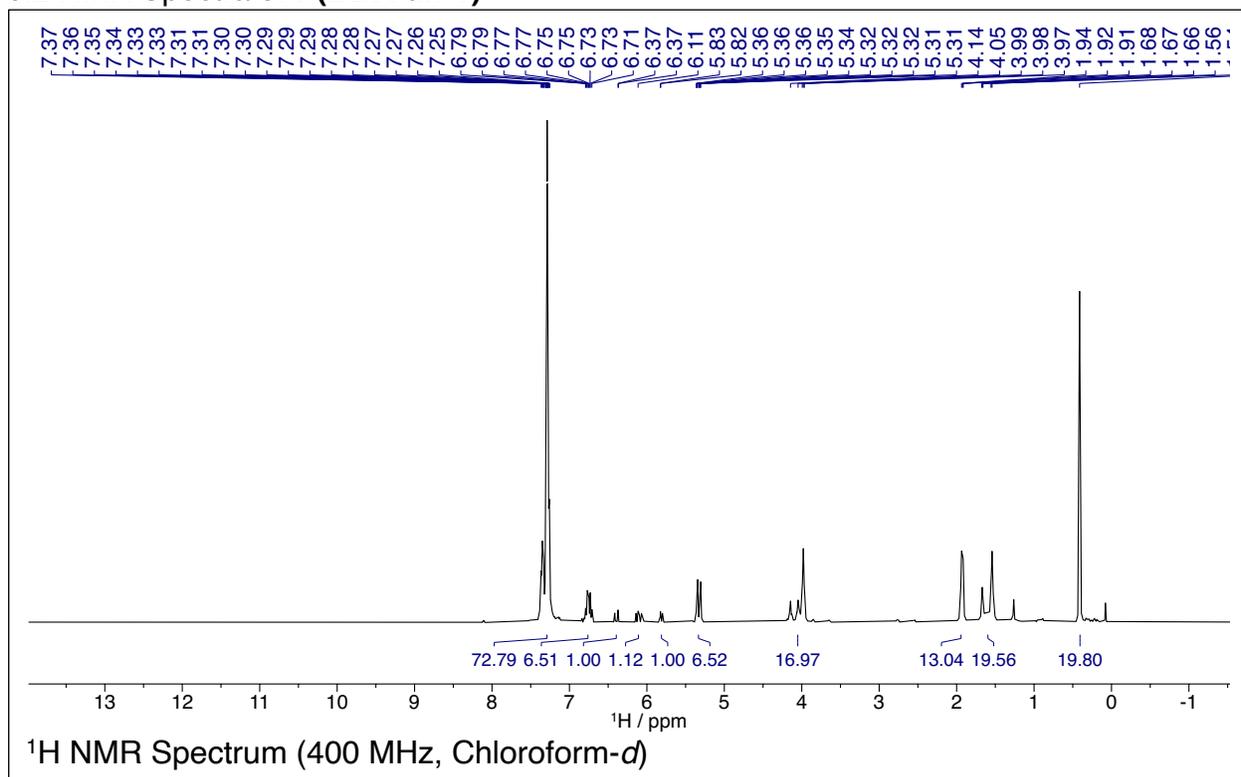
6. NMR Spectra

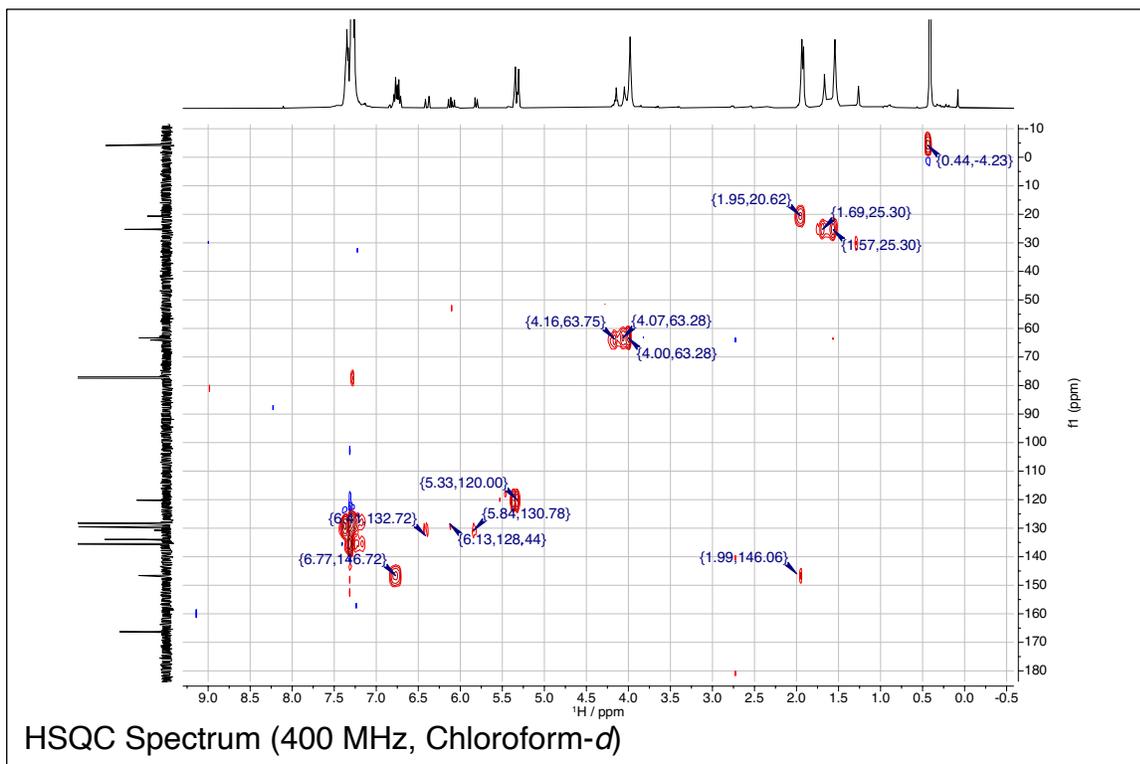
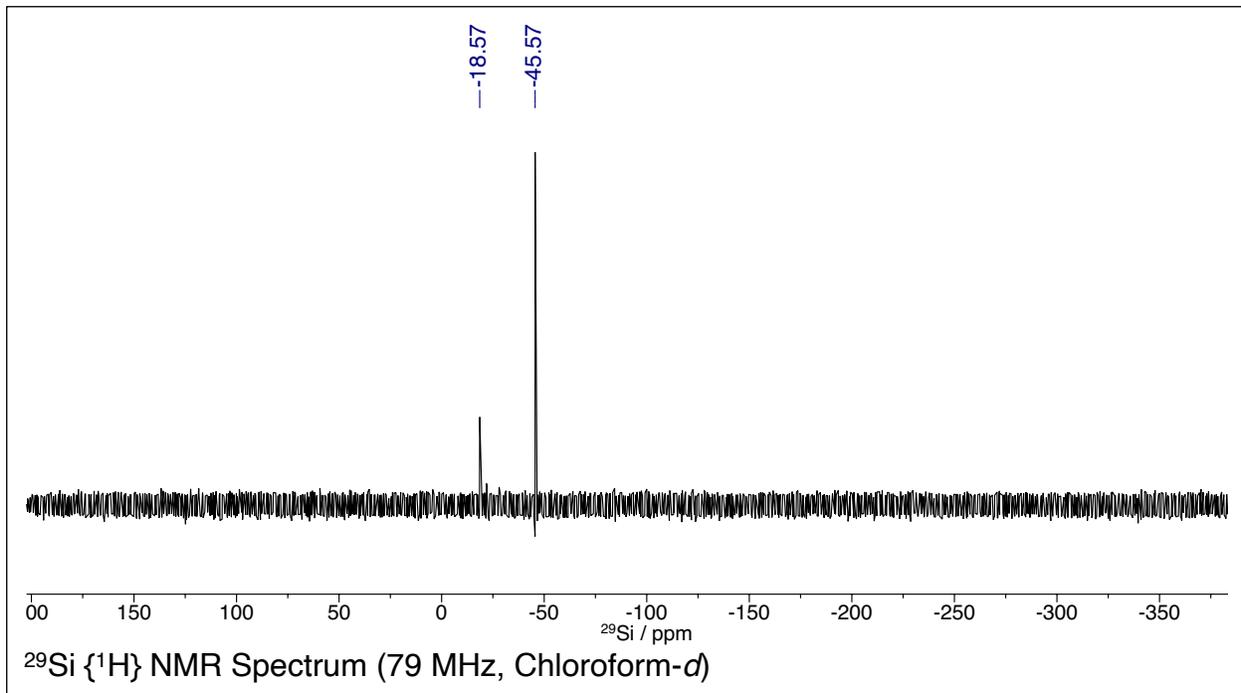
6.1 NMR Spectra of DiMA-1

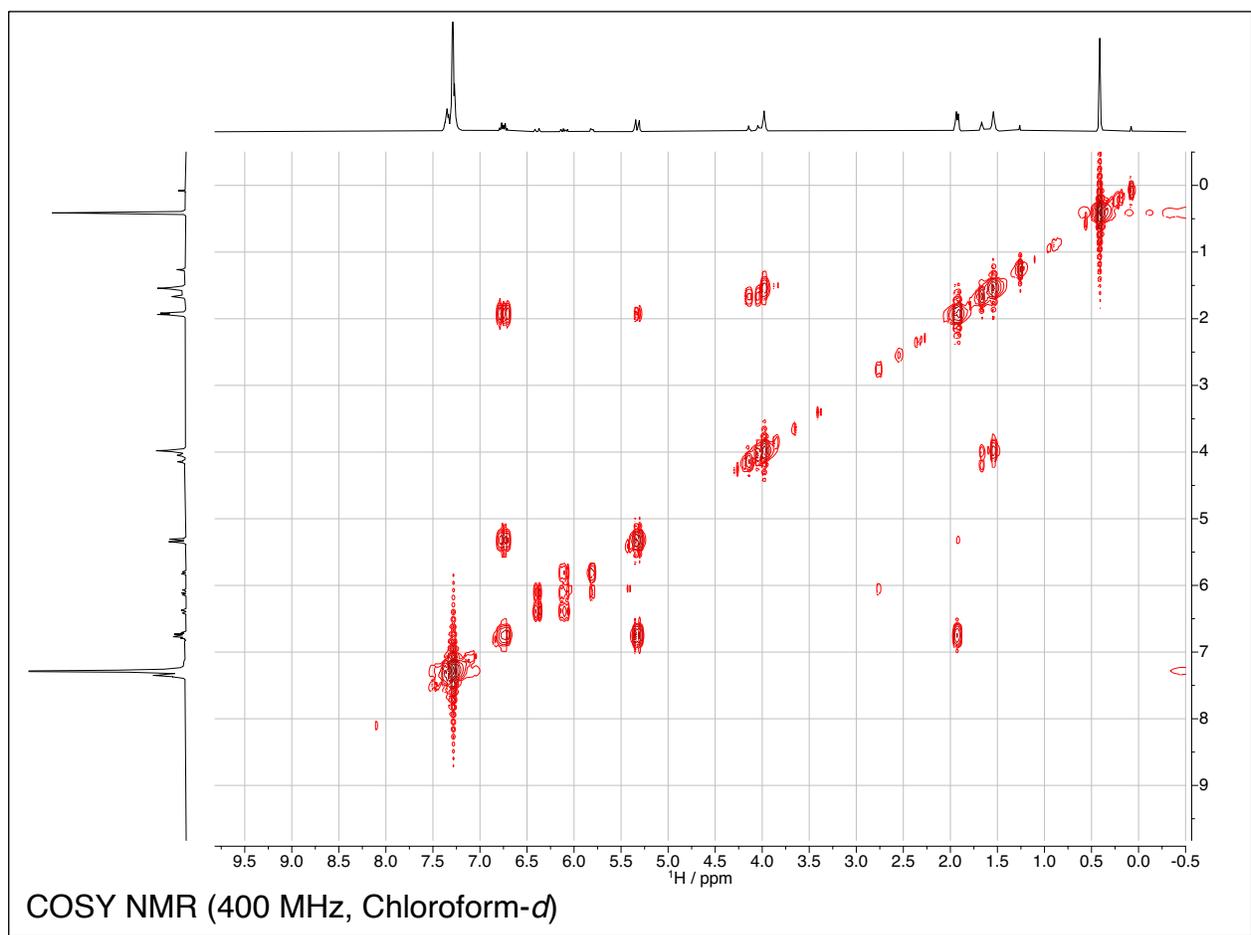




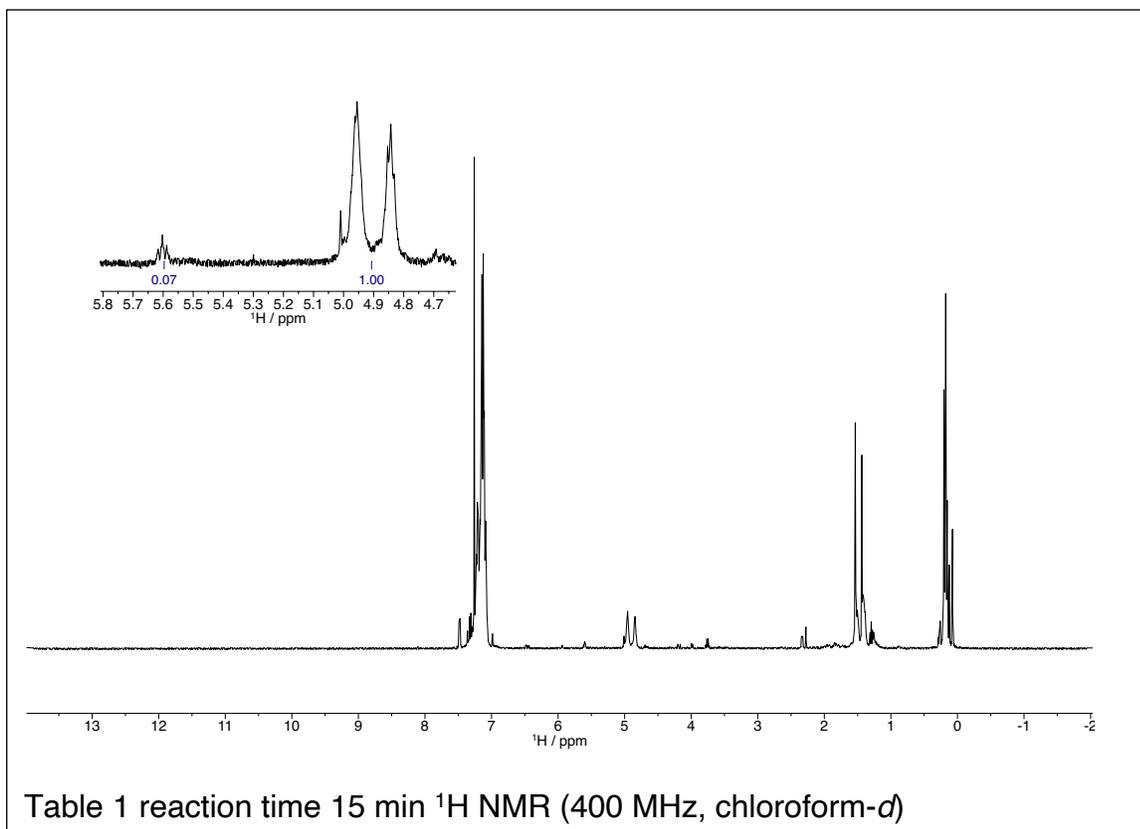
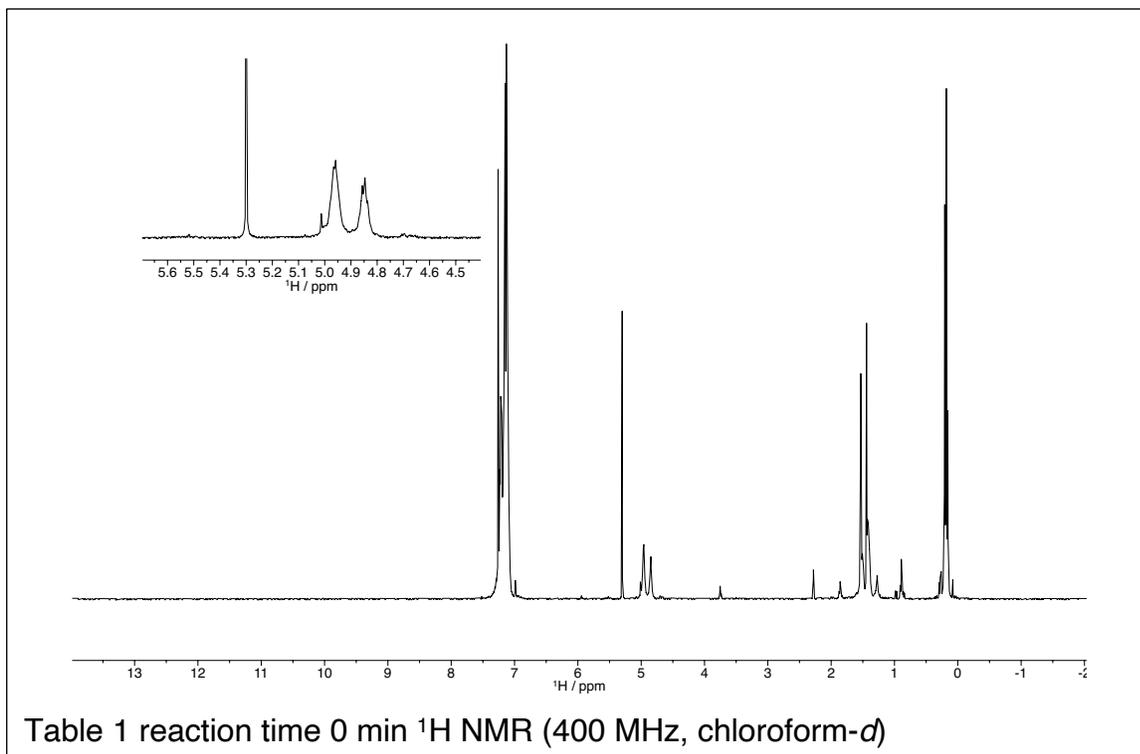
6.2 NMR Spectra of P(BDA-alt-1)

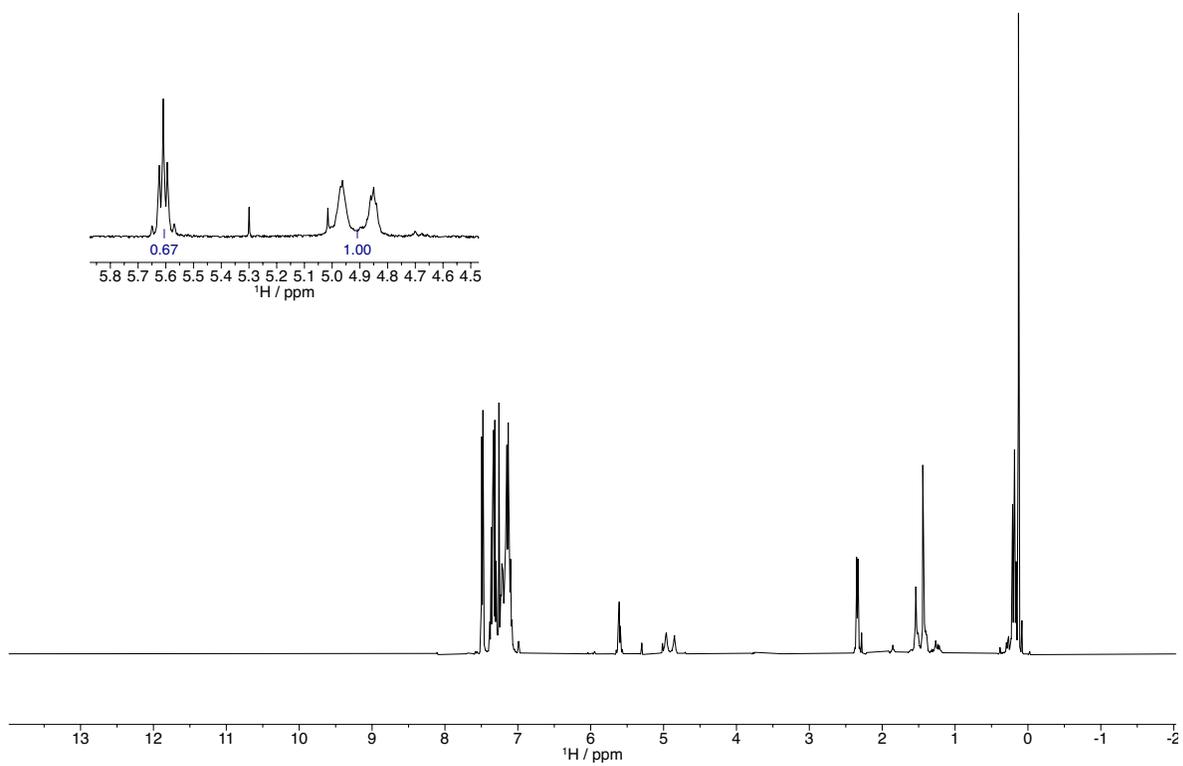
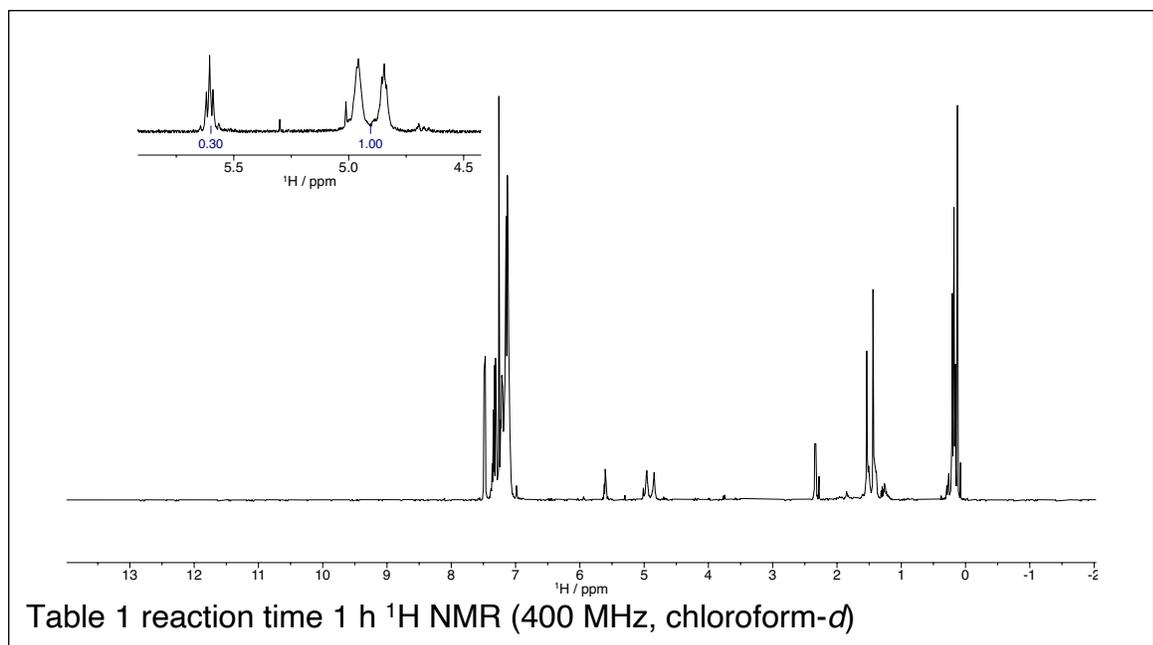






6.3 Depolymerization NMRs from Table 5.2.1





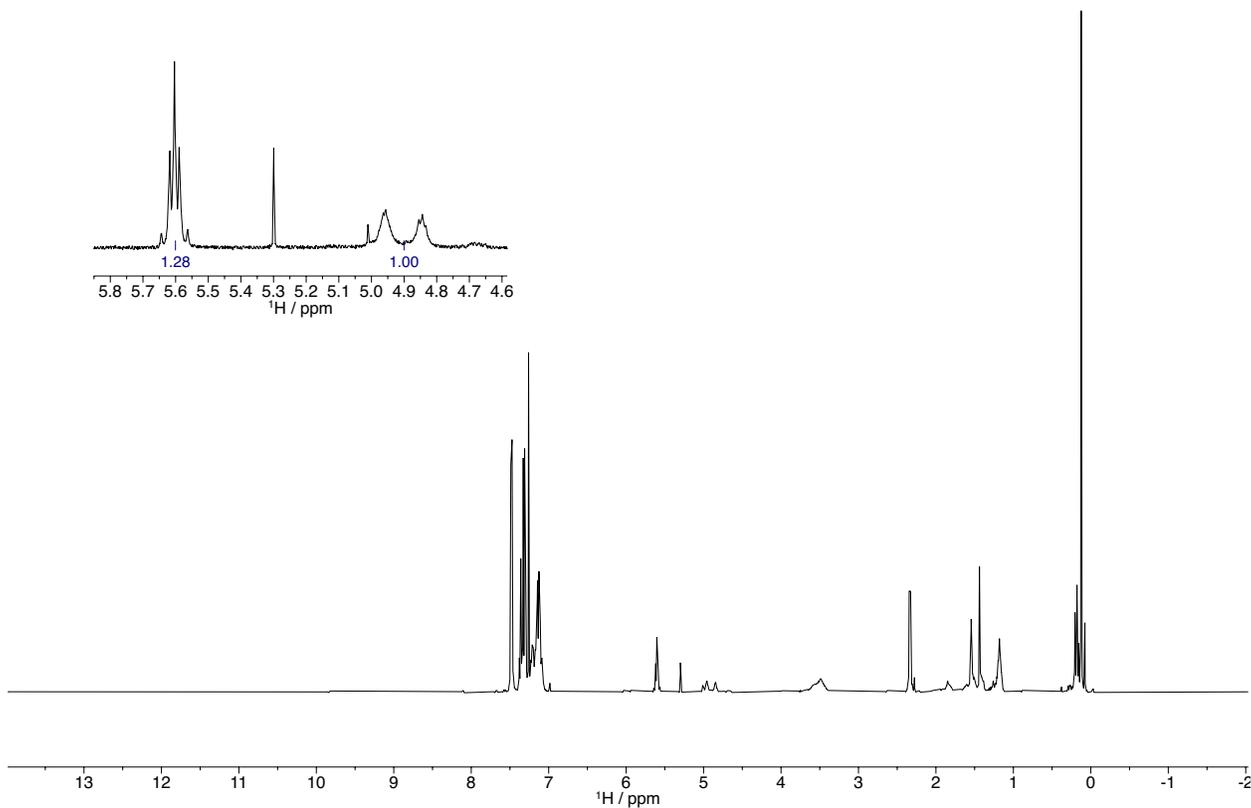
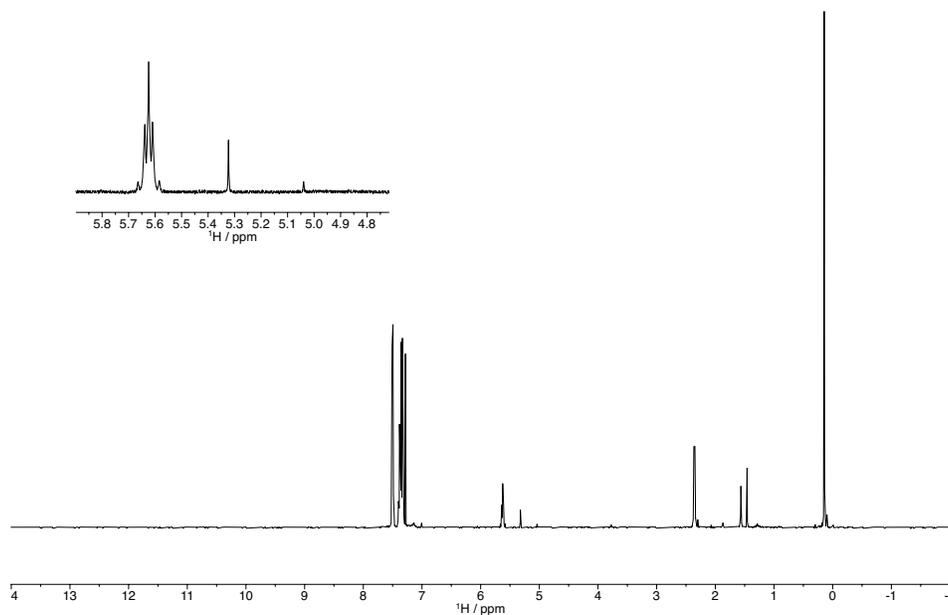
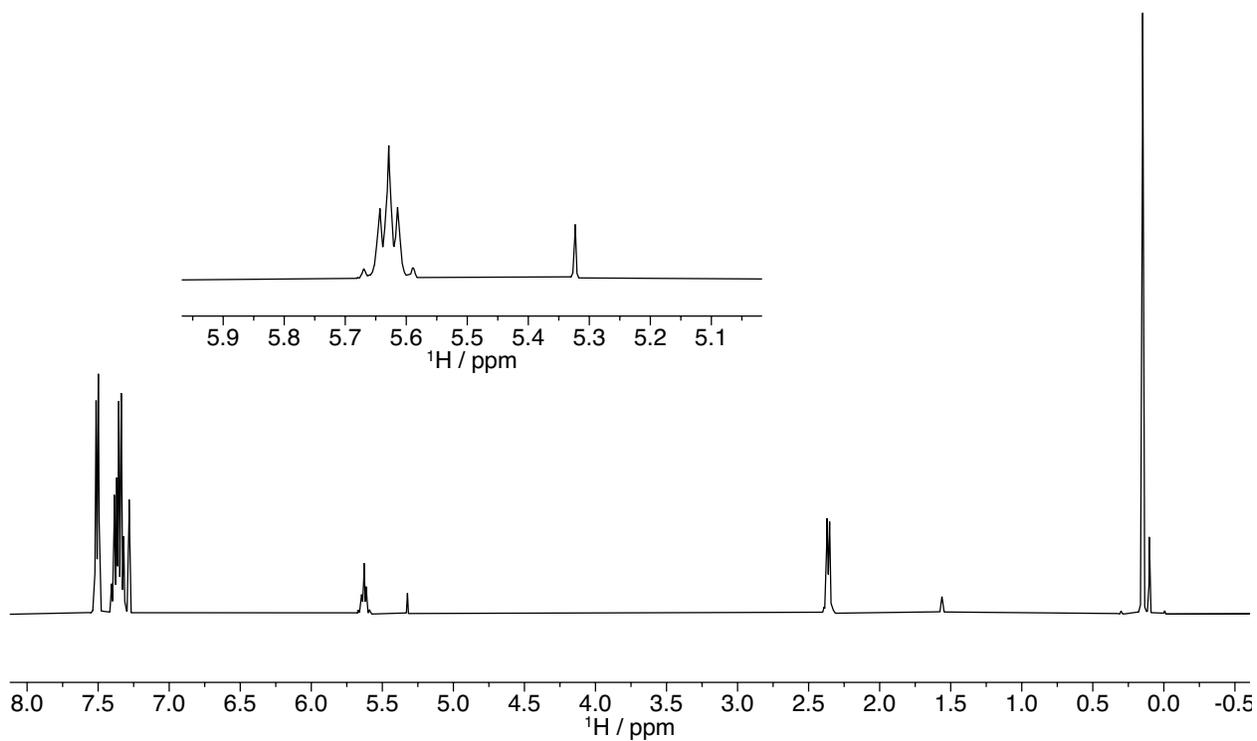


Table 1 reaction time 16 h ^1H NMR (400 MHz, chloroform- d) from entry 1 Table 2

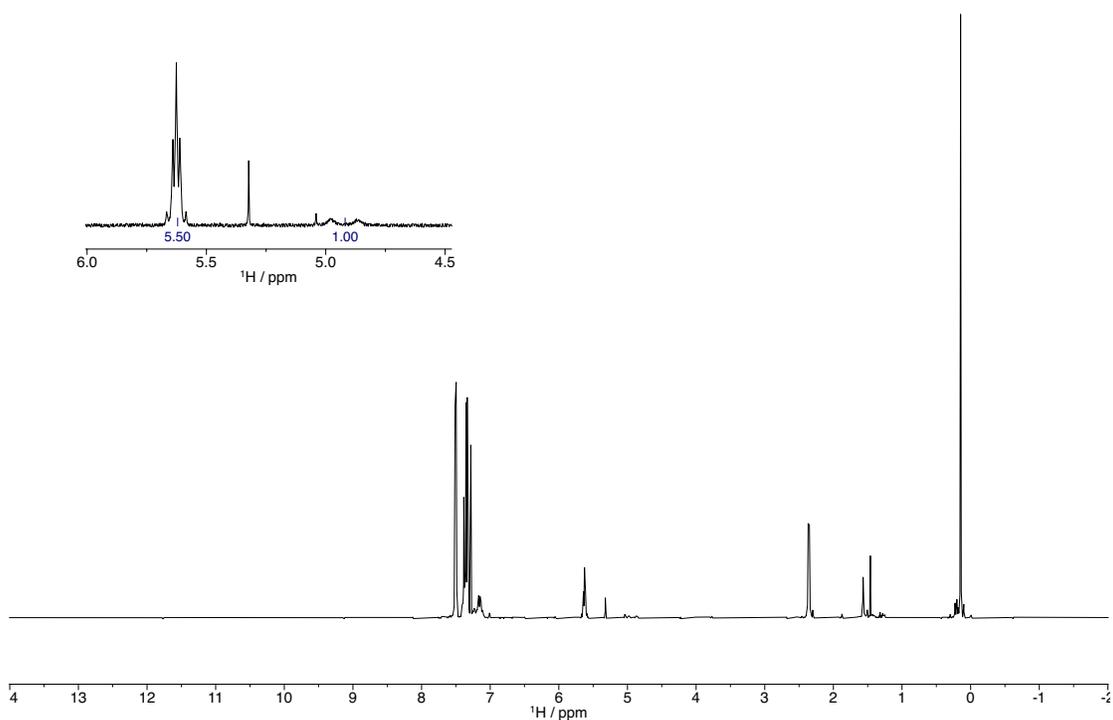
6.4 Depolymerization NMRs from Figure 2



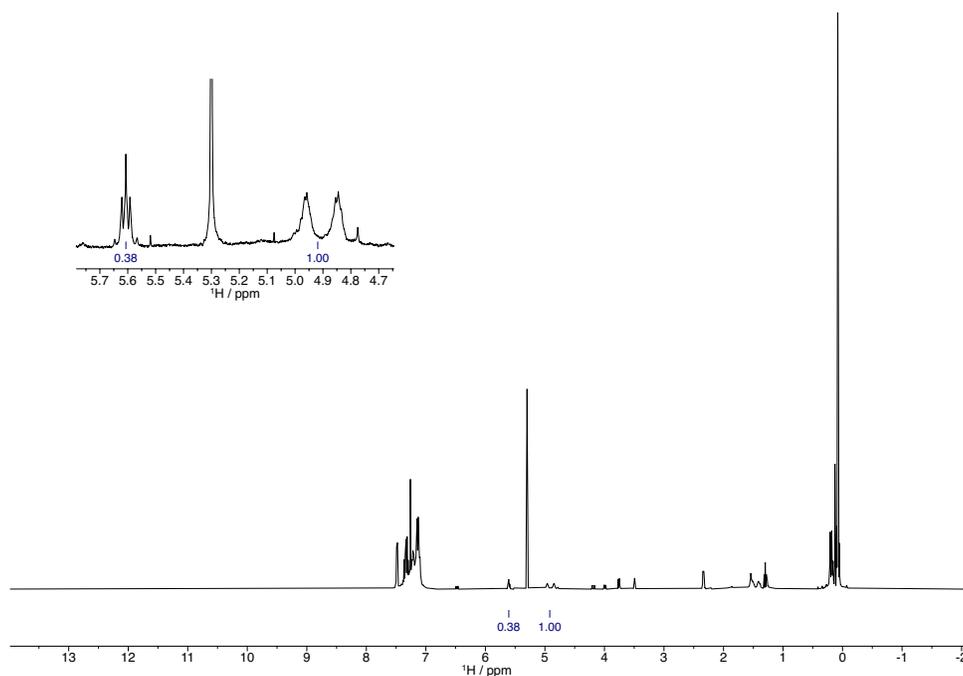
^1H NMR (400 MHz, $\text{chloroform-}d$) of **P1**_{1.23} depolymerization by G2 (1 mol%) from entry 2 Table 2



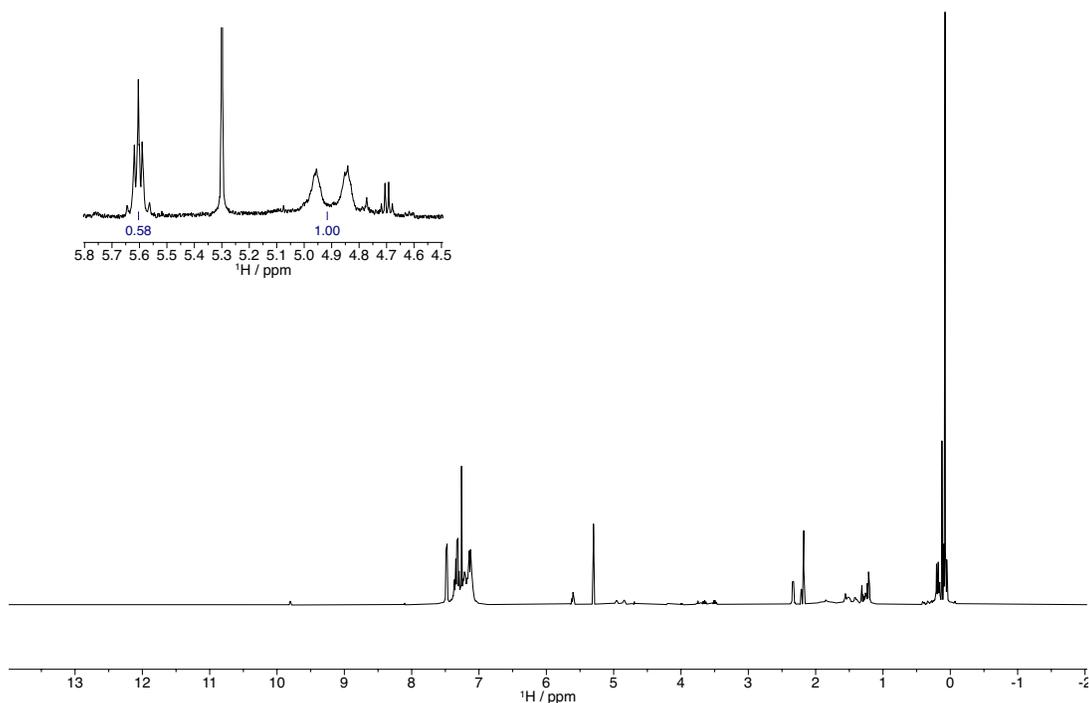
^1H NMR (400 MHz, $\text{chloroform-}d$) of **P1**_{2.13} depolymerization by G2 (1 mol%) from entry 3, Table 2



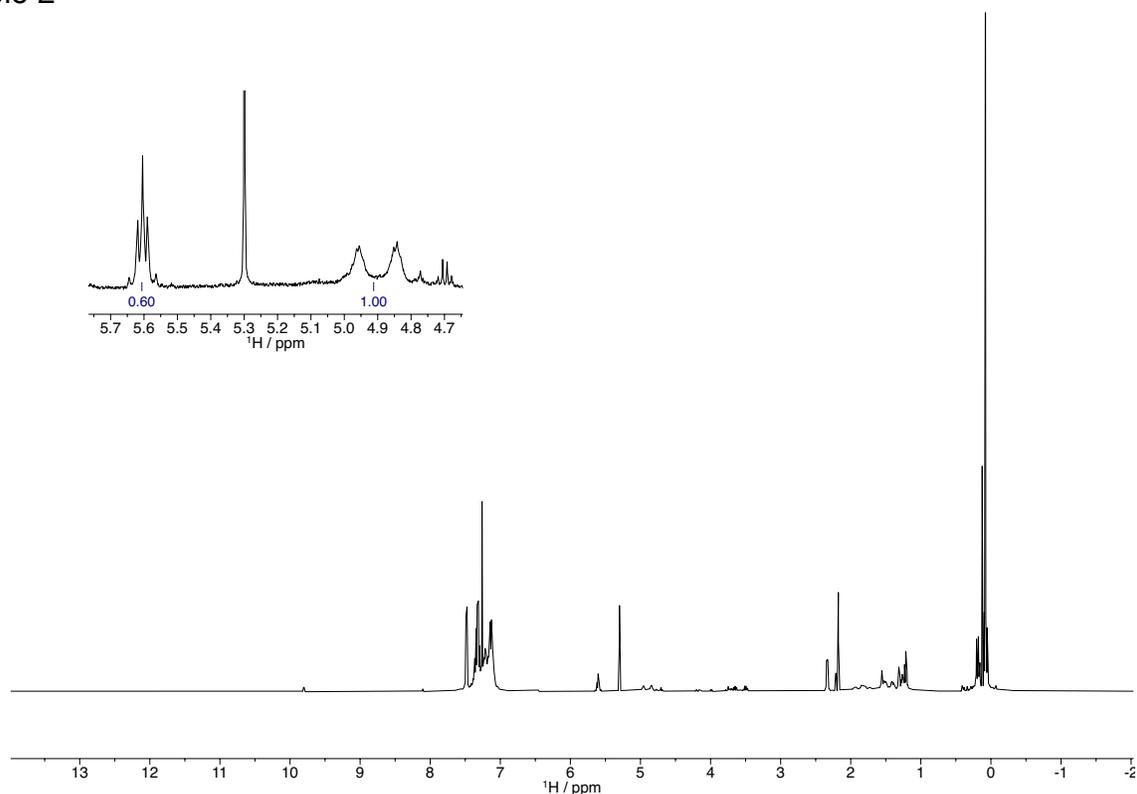
¹H NMR (400 MHz, chloroform-*d*) of **P1**_{1.23} depolymerization by G3 (1 mol%) from entry 4, Table 2



¹H NMR (400 MHz, chloroform-*d*) of **P1**_{11.1} depolymerization by G1 (1 mol%), entry 5, Table 2

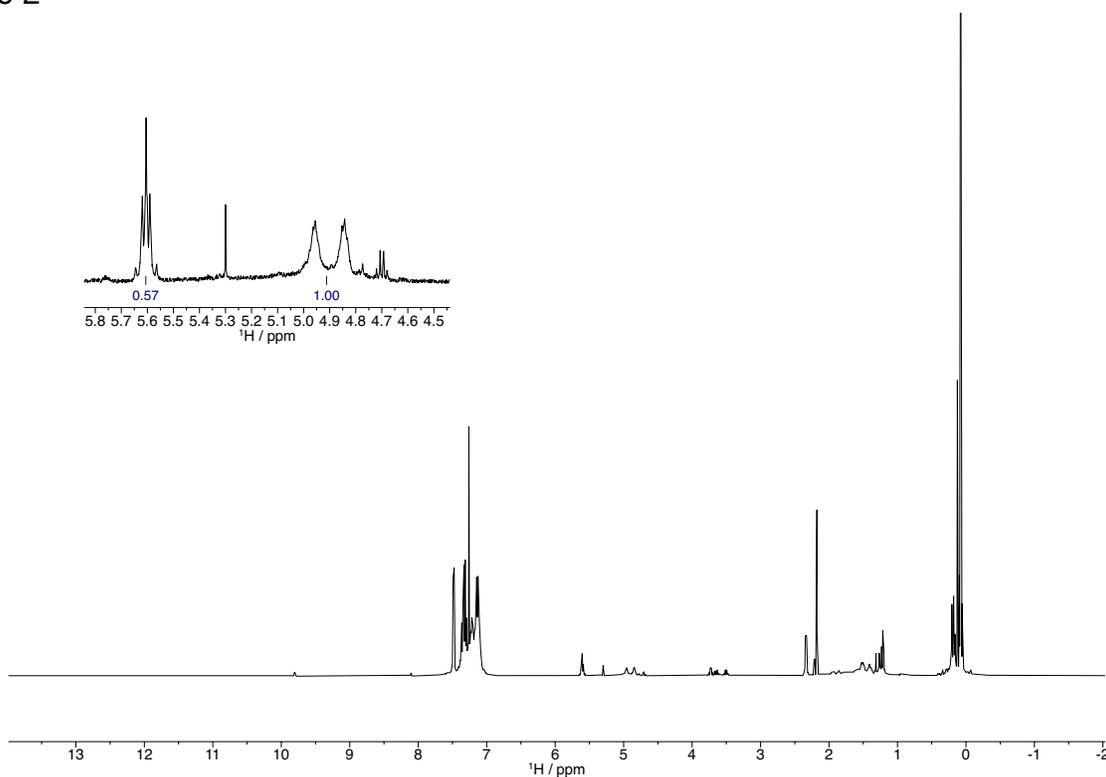


^1H NMR (400 MHz, chloroform-*d*) of **P1**_{11.1} depolymerization by G1 (3 mol%), entry 6 Table 2

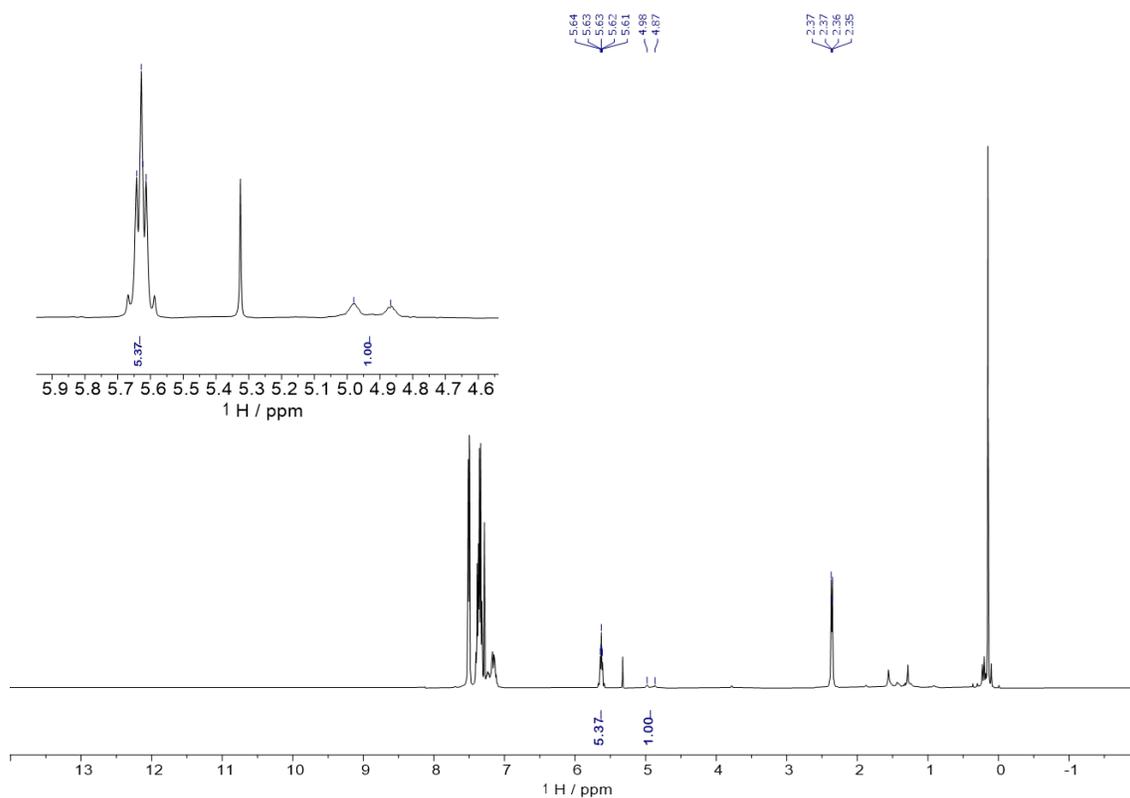


^1H NMR (400 MHz, chloroform-*d*) of **P1**_{11.1} depolymerization by G1 (5 mol%), entry 7,

Table 2



^1H NMR (400 MHz, chloroform-*d*) of $\text{P1}_{11.1}$ depolymerization by G1 (1 mol%) at 50 °C, entry 8 Table 2.



^1H NMR (400 MHz, chloroform-*d*) of **P18.61** depolymerization by G2 (1 mol%) at 23 °C, entry 9 Table 2

7. References

- [25] H. Wakefield, I. Kevlishvili, K. E. Wentz, Y. Yao, T. B. Kouznetsova, S. J. Melvin, E. G. Ambrosius, A. Herzog-Arbeitman, M. A. Siegler, J. A. Johnson, S. L. Craig, H. J. Kulik, R. S. Klausen, *J. Am. Chem. Soc.* **2023**, *145*, 10187–10196.
- [48] J. A. Love, J. P. Morgan, T. M. Trnka, R. H. Grubbs, *Angew. Chemie Int. Ed.* **2002**, *41*, 4035–4037.