

Supporting Information

Telechelics Based on Catalytic Alternating Ring Opening Metathesis Polymerization

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Materials

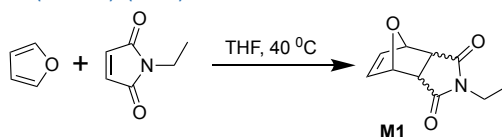
Grubbs initiators G2, α -bromoisobutryl bromide, cis-2-butene-1,4-diol, Furan, N-methylmaleimide, N-ethylmaleimide, cyclooctene and cyclooctadiene were purchased from Sigma-Aldrich and used without further purification. All other reagents and solvents were purchased from Acros organics or Sigma-Aldrich and used without further purification. Di-tert-butyl but-2-ene-1,4-diyl(Z)-dicarbamate (CTA 3) were synthesized as reported previously.¹ Deuterated solvents (CD_2Cl_2 , CDCl_3) were purchased from Cambridge Isotope Laboratories, Inc.

Characterization

All ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance DPX (360 MHz) FT NMR spectrometer. Chemical shifts were given in ppm relative to the residual solvent peak (CDCl_3 : 7.26 for ^1H ; CDCl_3 : 77.16 for ^{13}C and CD_2Cl_2 : 5.32 for ^1H ; CD_2Cl_2 : 53.88). HR MALDI FT-ICR mass spectra were measured on a Bruker FTMS 4.7T BioAPEX II in positive mode using trans-2-[3-(tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix and silver trifluoroacetate (AgTFA), sodium trifluoroacetate (NaTFA) as counter ion source. HR-MS (ESI+) mass spectra were measured on a Bruker FTMS 4.7T BioAPEX II and Thermo Scientific LTQ Orbitrap XL equipped with a static nanospray ion source. Relative molar masses and molar mass distributions were measured by size exclusion chromatography (SEC) with tetrahydrofuran and chloroform as eluent with a flow rate of 1 mL/min at room temperature. The THF and Chloroform SEC system was calibrated with polystyrene standards in a range from 10^3 to 3×10^6 Da. The THF SEC is an automated Viscotek GPCmax VE-2001 with a set of two Viscotek T6000M linear columns (300 x 8 mm, 5 μm particle size). Signal detection occurred by use of a Viscotek VE 3580 RI detector (refractive index). The Chloroform SEC is an automated PSS SECcurity System (Agilent Technologies 1260 infinity II) with a set two MZ-Gel SDplus linear columns (300 x 8 mm, 5 μm particle size). Differential scanning calorimetry (DSC) analysis were performed on Mettler-Toledo STAR system at heating and cooling rate of 10 $^\circ\text{C}/\text{min}$.

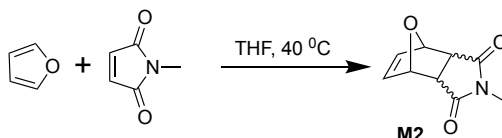
Synthesis of monomers

N-ethyloxanorbornene imide (OENI) (M1):



A mixture of N-ethylmaleimide (10g, 80 mmol, 1eq) and furan (8.16g, 120 mmol, 1.5eq) was dissolved in 5 mL of tetrahydrofuran. The solution was heated to 40 °C until complete disappearance of N-ethylmaleimide was observed. The reaction was concentrated under vacuum to give a white solid as 60:40 endo exo mixture (15.13g, 98%). The mixture was used for metathesis without any further purifications. Endo- isomer: ^1H NMR (400 MHz, CHLOROFORM-*d*) δ 6.31 - 6.40 (m, 2 H), 5.25 - 5.31 (m, 2 H), 3.41 - 3.55 (m, 2 H), 3.34 (q, $J=7.21$ Hz, 2 H), 1.00 (t, $J=7.21$ Hz, 3 H) ppm. Exo- isomer: ^1H NMR (400 MHz, CHLOROFORM-*d*) δ 6.48 (t, $J=0.92$ Hz, 2 H), 5.22 (t, $J=0.92$ Hz, 2 H), 3.41 - 3.56 (m, 2 H), 2.79 (s, 2 H), 1.12 (t, $J=7.27$ Hz, 3 H) ppm. HR-MS (ESI) calcd. For $\text{C}_{10}\text{H}_{11}\text{NO}_3\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 216.0637; Found: 216.0627.

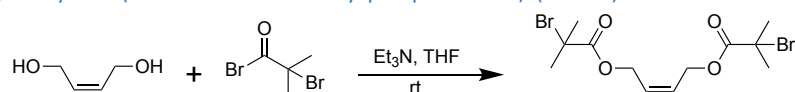
N-methyloxanorbornene imide (OENI) (M2) :



A mixture of N-methylmaleimide (10g, 90 mmol, 1eq) and furan (9.19g, 135 mmol, 1.5eq) was dissolved in 5 mL of tetrahydrofuran. The solution was heated to 40 °C until complete disappearance of N-methylmaleimide was observed. The reaction was concentrated under vacuum to give a white solid as 57:43 endo exo mixture (15.78g, 98%). The mixture was used for metathesis without any further purifications. Endo- isomer: ^1H NMR (400 MHz, CHLOROFORM-*d*) δ 6.39 (t, $J=0.86$ Hz, 2 H), 5.32 (ddd, $J=2.69, 1.71, 0.86$ Hz, 2 H), 3.52 (dd, $J=3.61, 1.65$ Hz, 2 H), 2.81 (s, 3 H) ppm. Exo- isomer: ^1H NMR (400 MHz, CHLOROFORM-*d*) δ 6.51 (t, $J=0.86$ Hz, 2 H), 5.26 (t, $J=0.86$ Hz, 2 H), 2.97 (s, 3 H), 2.85 (s, 2 H) ppm. HR-MS (ESI) calcd. For $\text{C}_9\text{H}_9\text{NO}_3\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 202.0480; Found: 202.0471.

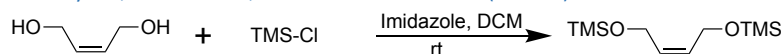
Synthesis of CTAs

(Z)-but-2-ene-1,4-diyl bis(2-bromo-2-methylpropanoate) (CTA1):



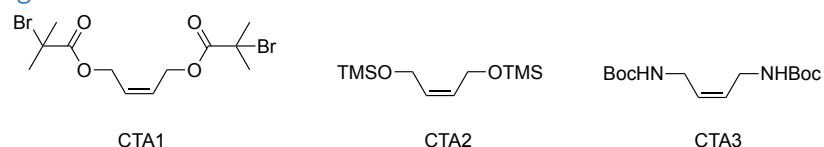
Cis-2-butene-1,4-diol (5g, 56.8 mmol, 1eq) was dissolved in 20 mL of dry tetrahydrofuran. Triethylamine (12.6g, 125 mmol, 2.2eq) was added to the solution and cooled to 0 °C. To the cooled solution α -bromoisobutyryl bromide (28.73g, 125 mmol, 2.2eq) was added dropwise and was allowed to stir for overnight at room temperature. The resulting reaction mixture was filtered and concentrated under vacuum. Finally, the mixture was chromatographed on silica (hexane:EtOAc = 70:30) to give CTA1 (21g, 96%) as colorless liquid. ^1H NMR (400 MHz, CHLOROFORM-*d*) δ 5.74 - 5.91 (m, 2 H), 4.71 - 4.93 (m, 4 H), 1.95 (s, 12 H) ppm. ^{13}C NMR (101 MHz, CHLOROFORM-*d*) δ 171.3, 127.9, 61.4, 55.4, 30.7 ppm. HR-MS (ESI) calcd. For $\text{C}_{12}\text{H}_{18}\text{Br}_2\text{O}_4\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 406.9470; Found: 406.9464.

(Z)-2,2,9,9-tetramethyl-3,8-dioxa-2,9-disiladec-5-ene (CTA2):



A mixture of cis-2-butene-1,4-diol (2g, 22.73 mmol, 1eq) and imidazole (7.7g, 113.7 mmol, 5eq) was dissolved in 30 mL of dry dichloromethane and cool to 0 °C. To the cooled solution TMS-Cl (5.4g, 50 mmol, 2.2eq) was added dropwise. The solution was allowed to warm to room temperature and stirred overnight. Afterward, the reaction mixture was concentrated in vacuum and chromatographed on silica (hexane:EtOAc = 97:3) to obtain CTA2 (5g, 95%) as colorless liquid. ¹H NMR (400 MHz, CHLOROFORM-*d*) δ 5.54 - 5.64 (m, 2 H) 4.14 - 4.28 (m, 4 H) 0.13 (s, 18 H) ppm. ¹³C NMR (101 MHz, CHLOROFORM-*d*) δ 130.22, 58.69, -0.44 ppm. HR-MS (ESI) calcd. For C₁₀H₂₄O₂Si₂Na⁺ [M+Na]⁺: 255.1213; Found: 255.1203.

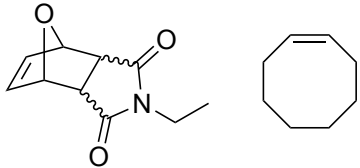
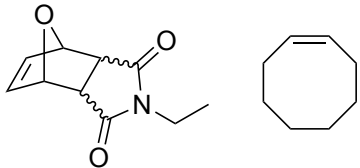
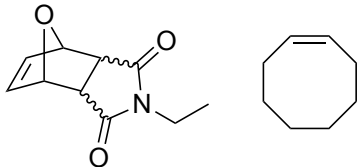
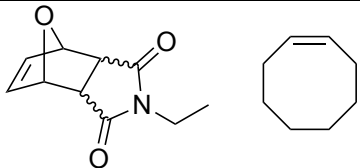
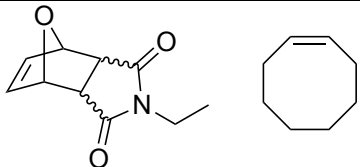
Chain transfer agents used for termination

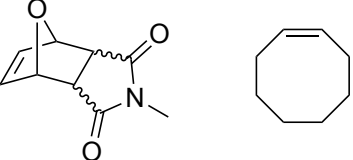
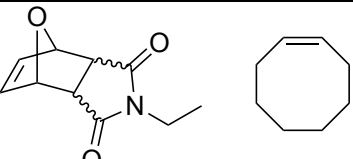
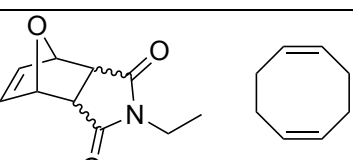
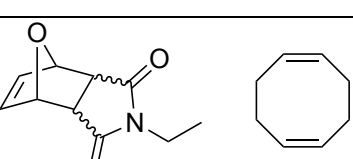
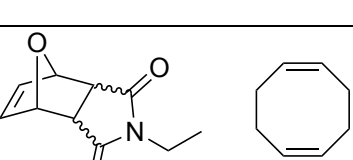
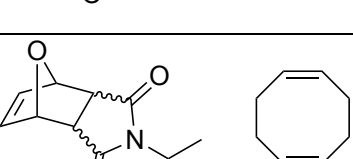


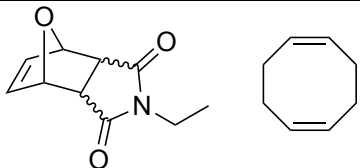
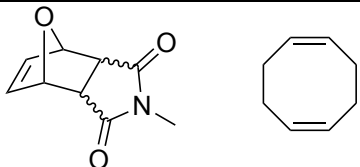
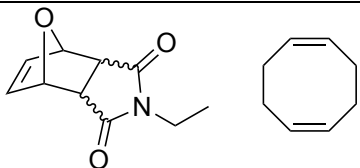
Procedure for polymer synthesis:

An equimolar mixture of monomers (M1/M2 and COE/COD) were transfer into vials equipped with a stir bar under argon atmosphere. The required amount of CTA was added to the monomer's mixture. Dry, degassed dichloromethane was added to the vial to obtain 1M monomer solution. Separately, a stock solution of catalyst G2 was prepared in dry, degassed dichloromethane and required amount (4 mg, 4.7 μmol) of catalyst solution was added to vials. The reaction mixture was heated for 36 hours at 40 °C under argon atmosphere. The reactions were quenched with excess ethyl vinyl ether and precipitated into cold methanol to obtain telechelic alternating polymers.

Table S1. Polymerization results and SEC data for different polymers

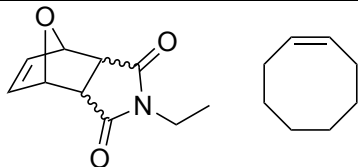
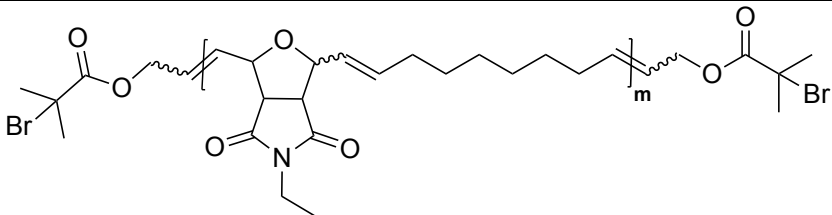
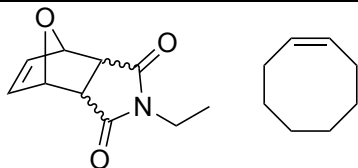
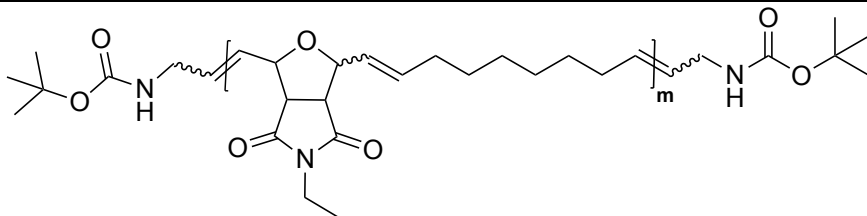
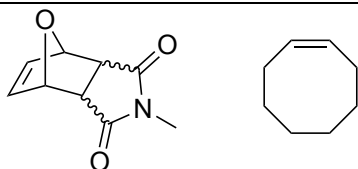
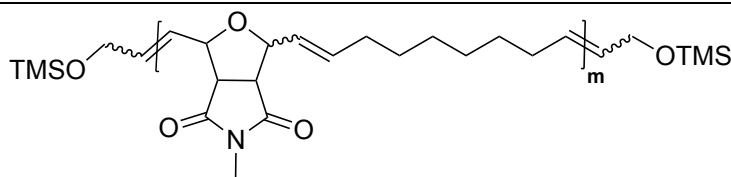
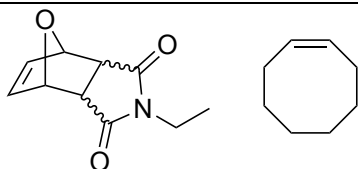
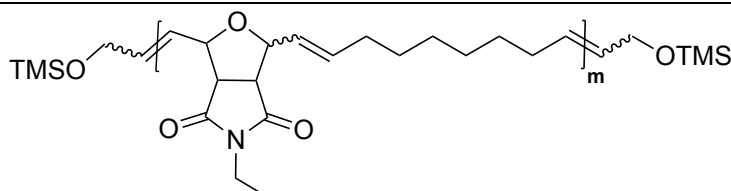
Polymer	Monomers	CTAs	Monomers/CTA/G2	Mn(theo)	Mn (cal)	PD ^[a]
P1		CTA1	500/50/1	3000	4000	1.7
P2		CTA1	1000/50/1	6000	5800	1.8
P3		CTA1	1500/50/1	9100	7700	1.8
P4		CTA1	2000/50/1	12100	10500	2
P5		CTA3	500/50/1	3000	4700	2.3

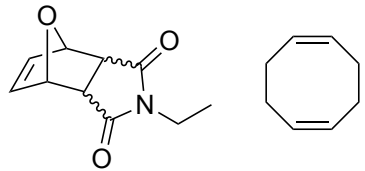
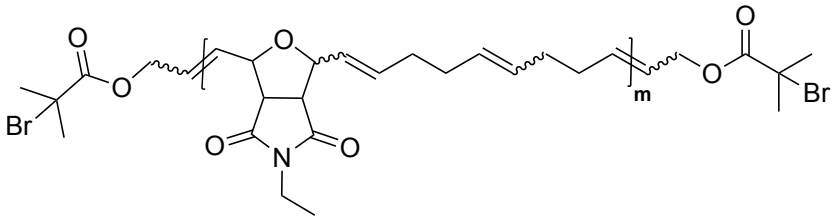
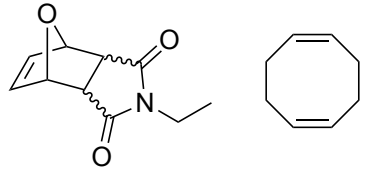
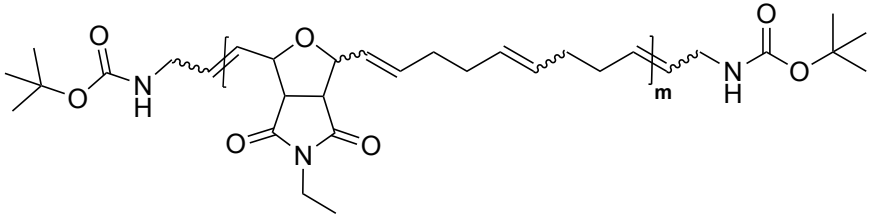
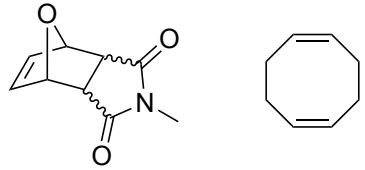
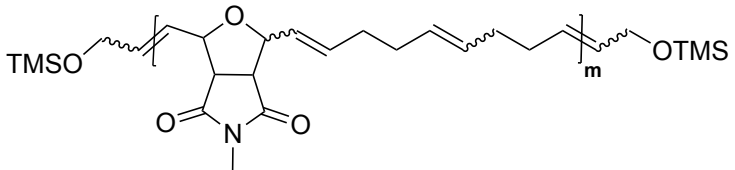
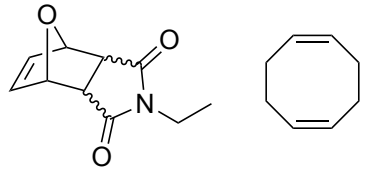
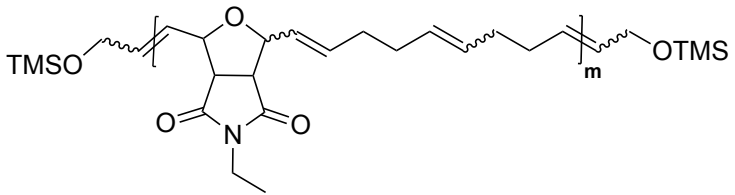
P6		CTA2	1000/25/1	11600	14900	1.7
P7		CTA2	2000/25/1	24300	23000	1.9
P8		CTA1	500/50/1	3000	4300	1.7
P9		CTA1	1000/50/1	6000	7200	2
P10		CTA1	1500/50/1	9000	10400	2
P11		CTA1	2000/50/1	12000	14700	2

P12		CTA3	500/50/1	3000	4600	2.2
P13		CTA2	1000/25/1	11500	11800	1.9
P14		CTA2	2000/25/1	24000	26650	1.8

[a] P1-4, P8-11 were measured by THF SEC and P5-7, P12-14 were measured by CHCl₃ SEC.

Table S2. Summary of polymers

Polymer	Monomers	CTA	Polymer structure
P1-4		CTA1	
P5		CTA3	
P6		CTA2	
P7		CTA2	

P8-11		CTA1	
P12		CTA3	
P13		CTA2	
P14		CTA2	

NMR Spectra of substrates

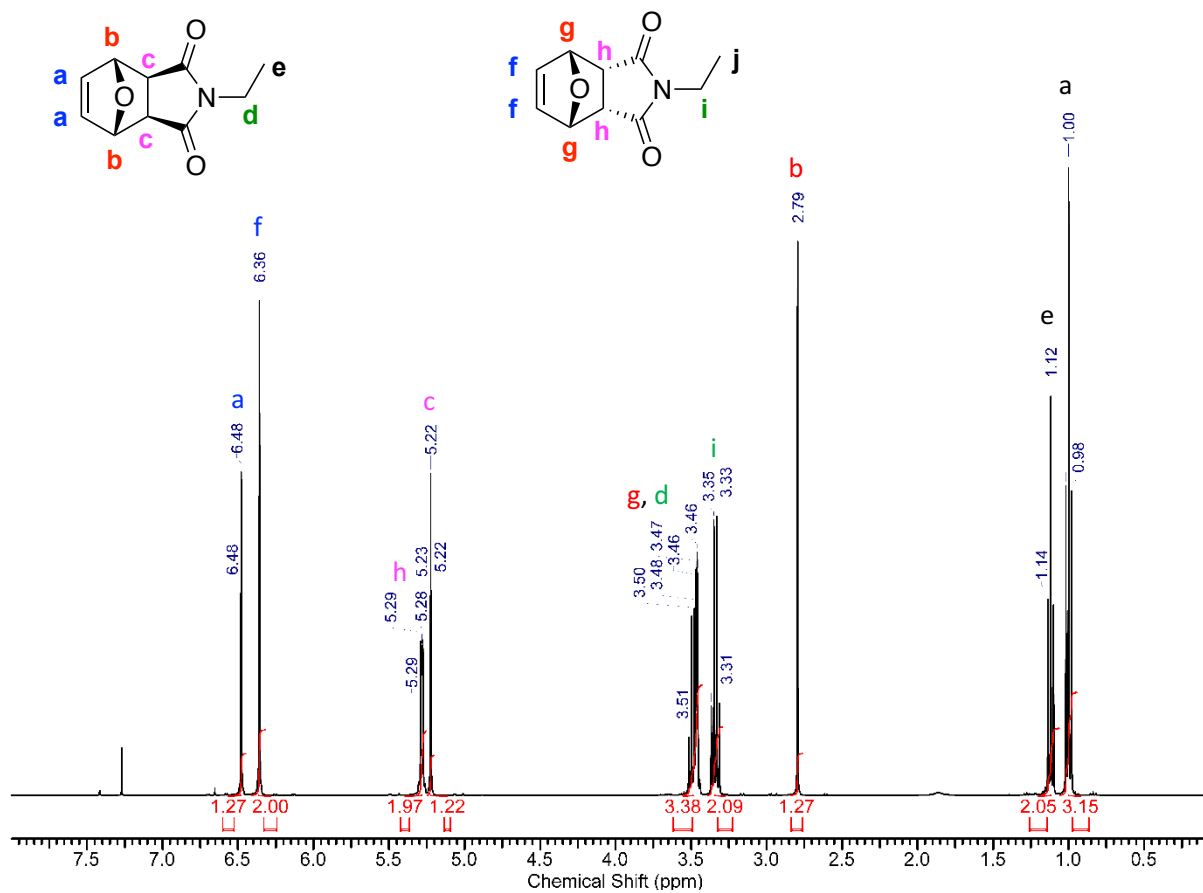


Figure S1: ¹H NMR (chloroform-d, 400 MHz) spectrum of compound **M1**.

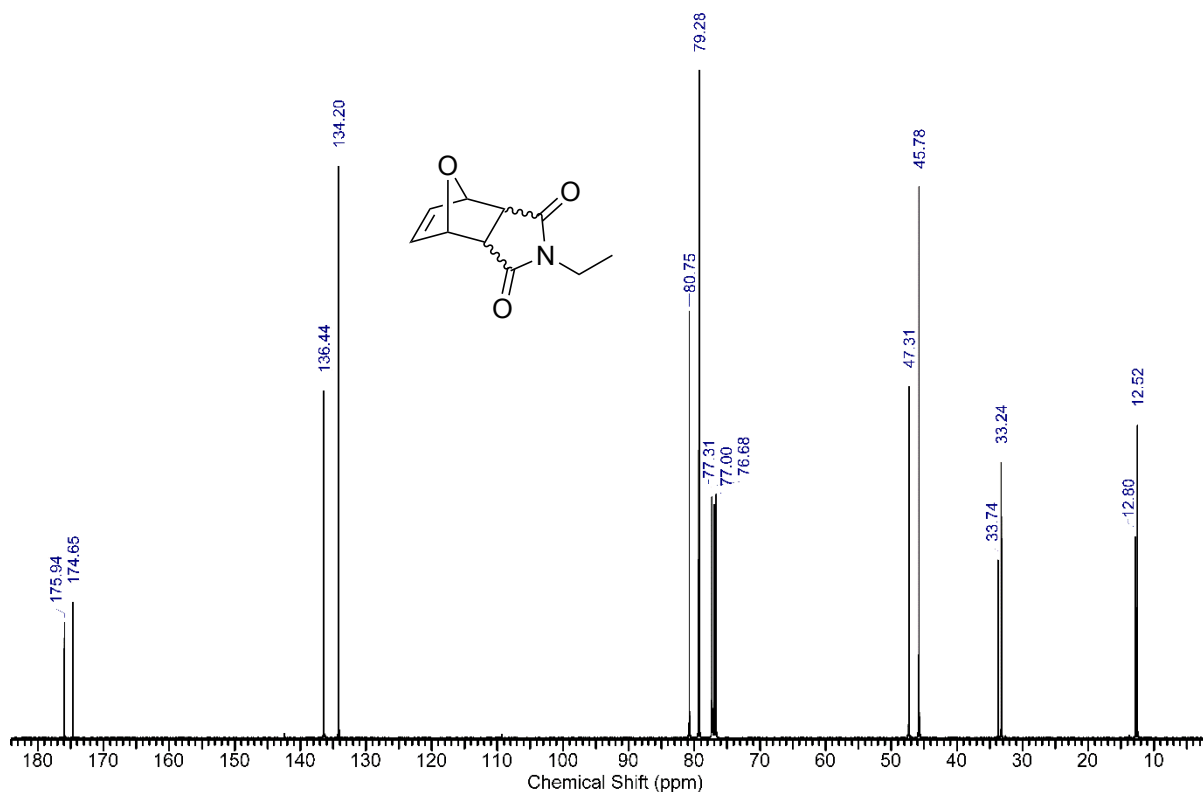
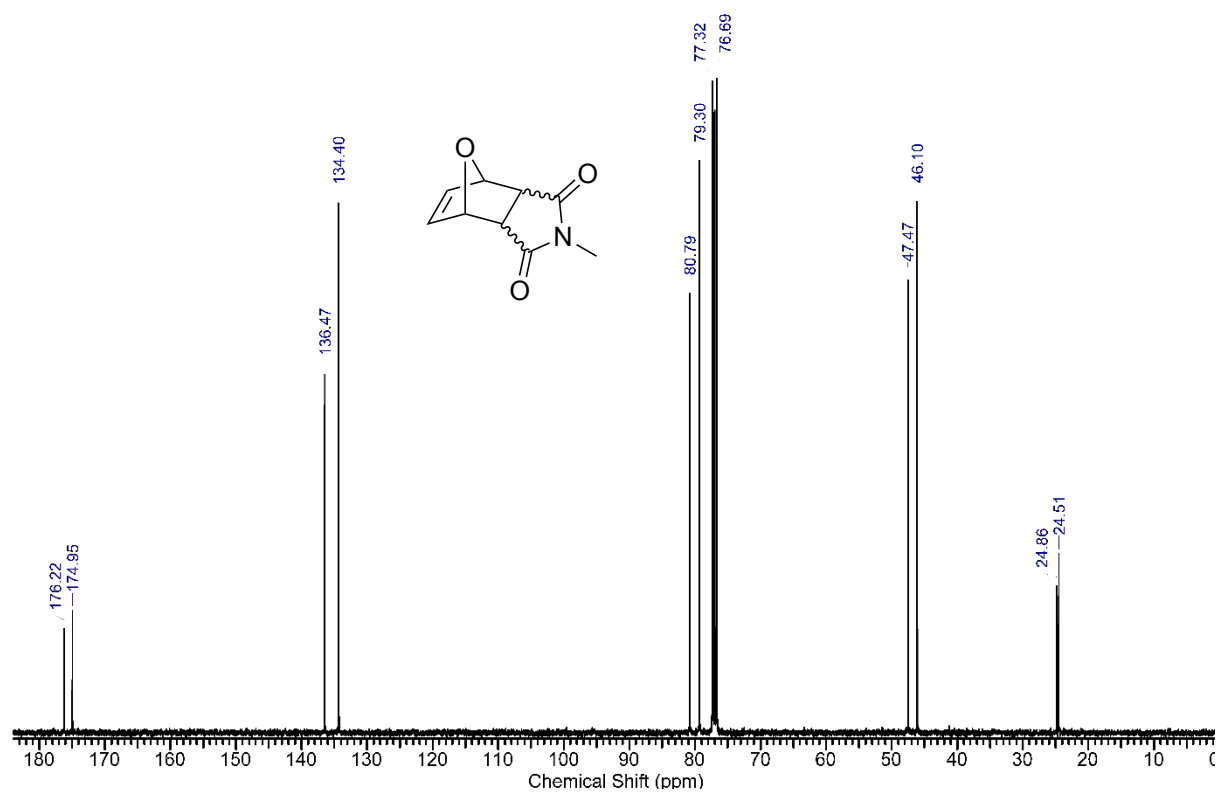
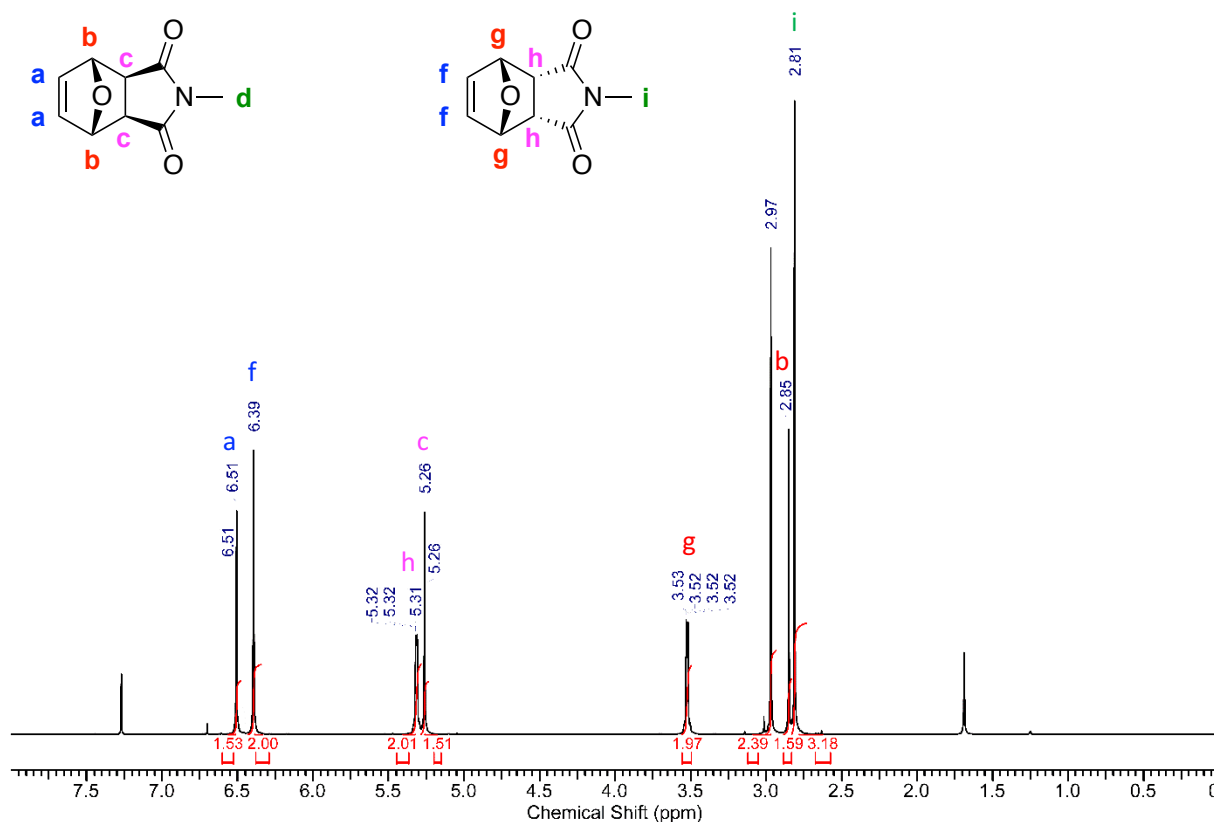


Figure S2: ¹³C NMR (chloroform-d, 100 MHz) spectrum of compound **M1**.



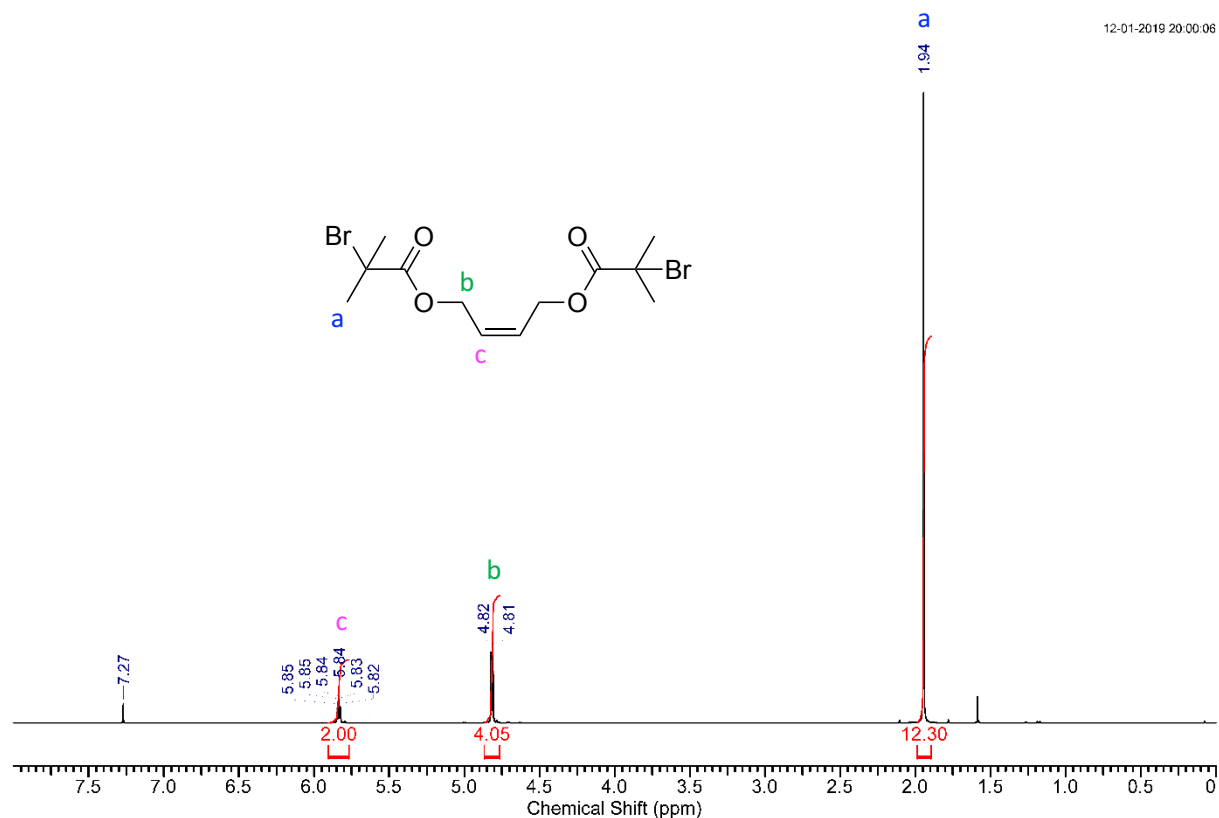


Figure S5: ¹H NMR (chloroform-d, 400 MHz) spectrum of compound **CTA1**.

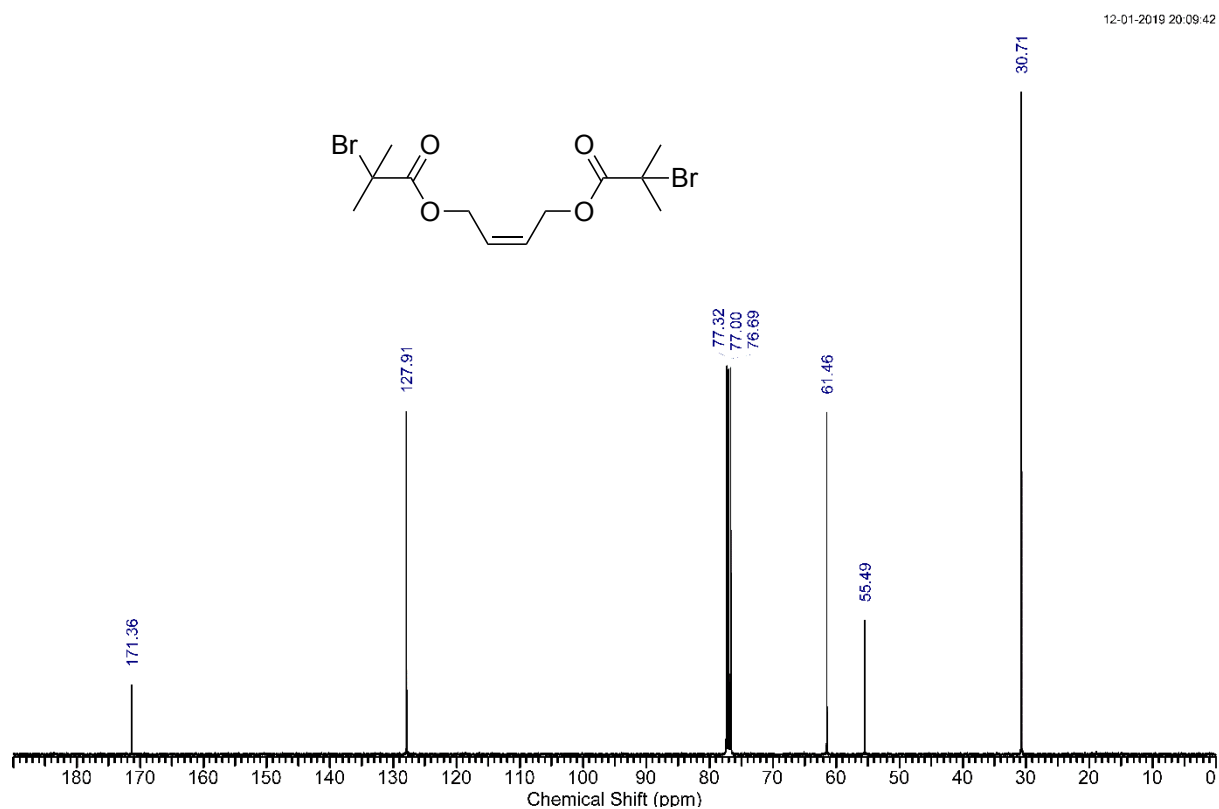


Figure S6: ¹³C NMR (chloroform-d, 100 MHz) spectrum of compound **CTA1**.

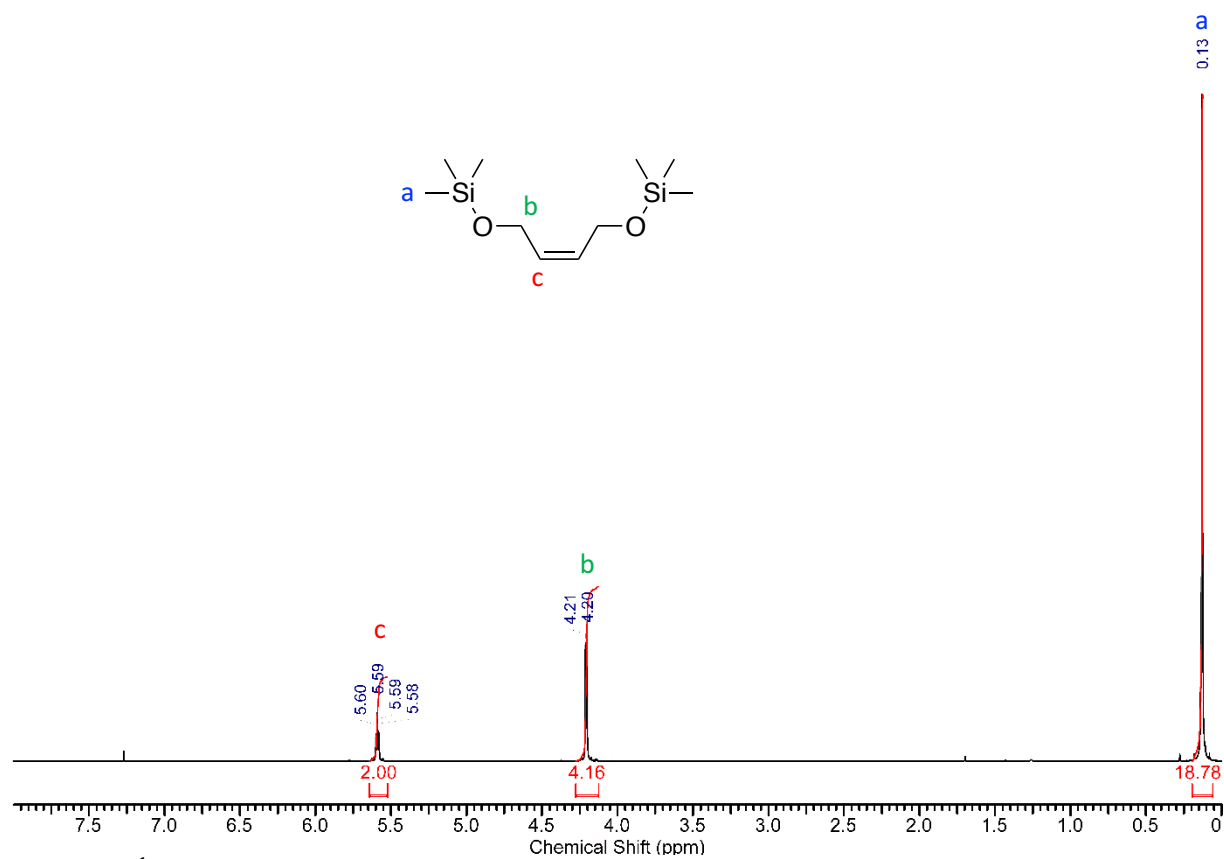


Figure S7: ¹H NMR (chloroform-d, 400 MHz) spectrum of compound **CTA2**.

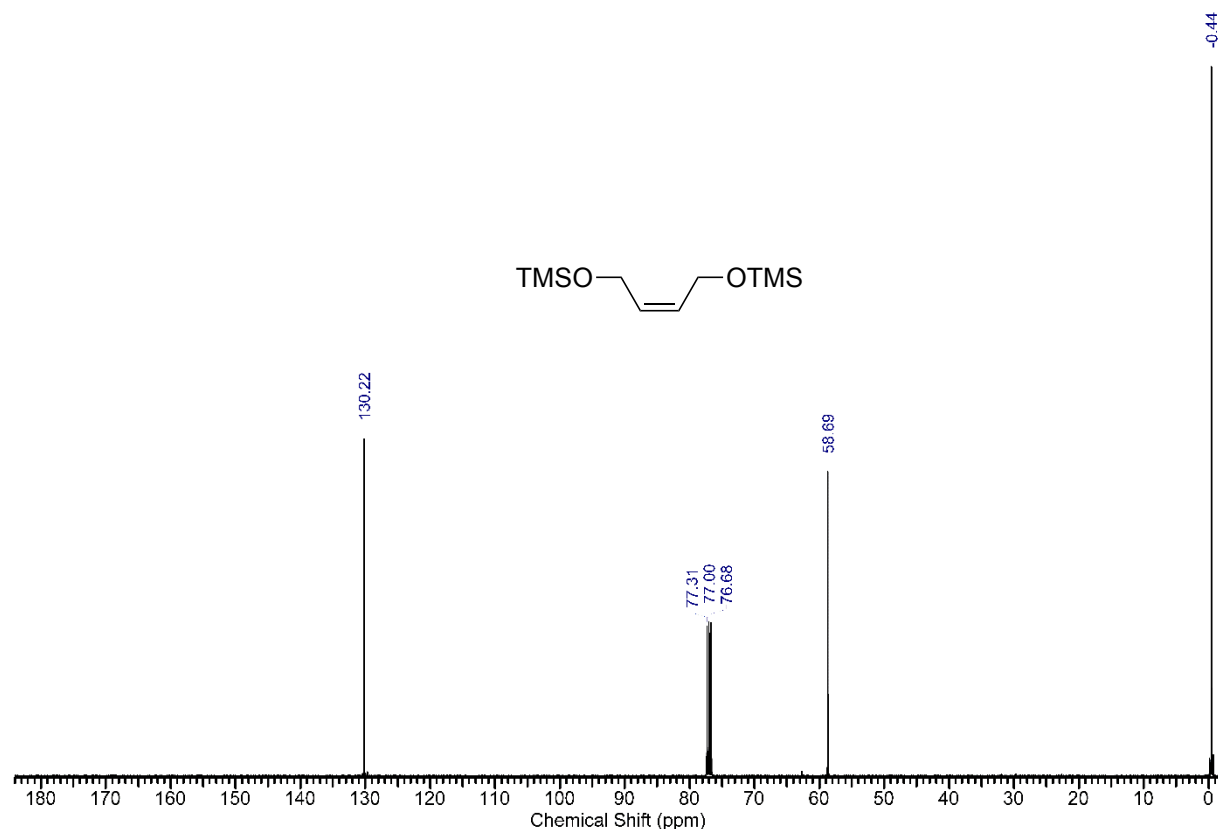


Figure S8: ¹³C NMR (chloroform-d, 100 MHz) spectrum of compound **CTA2**.

SEC of polymers

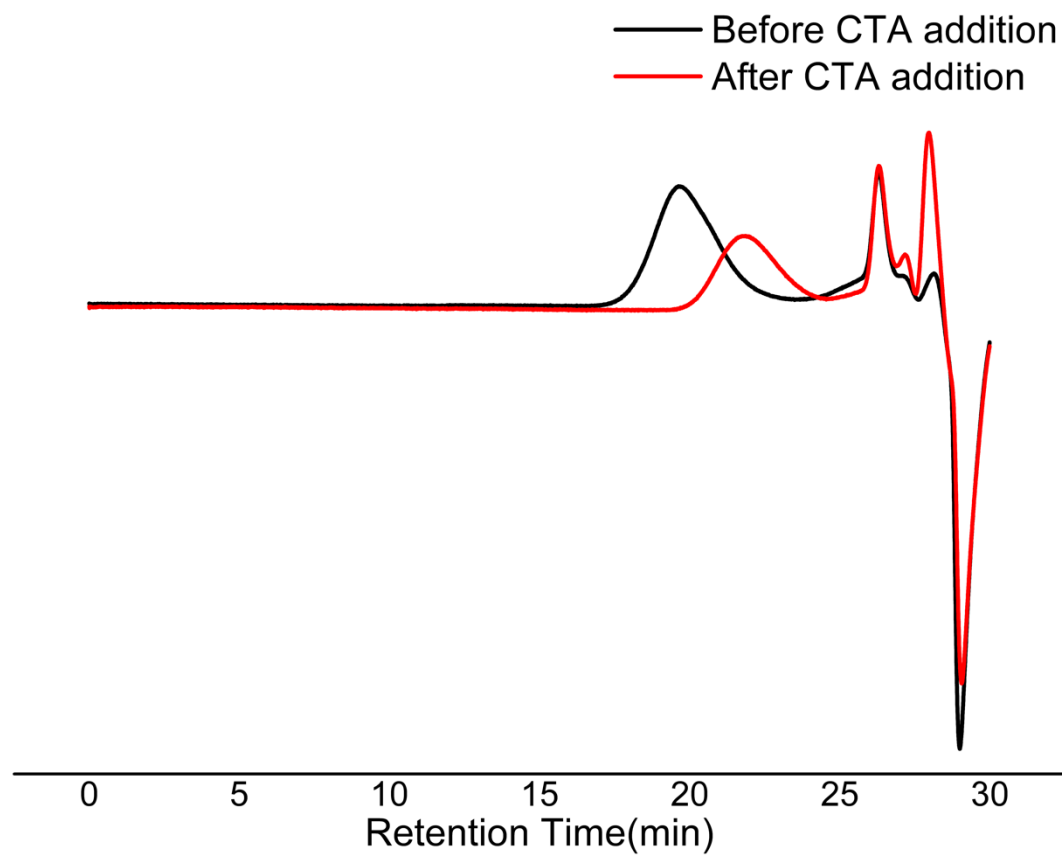


Figure S9: SEC (THF) trace of the copolymer (monomer **M1** and **COE**) before and **after** addition of **CTA1**.

NMR of polymers

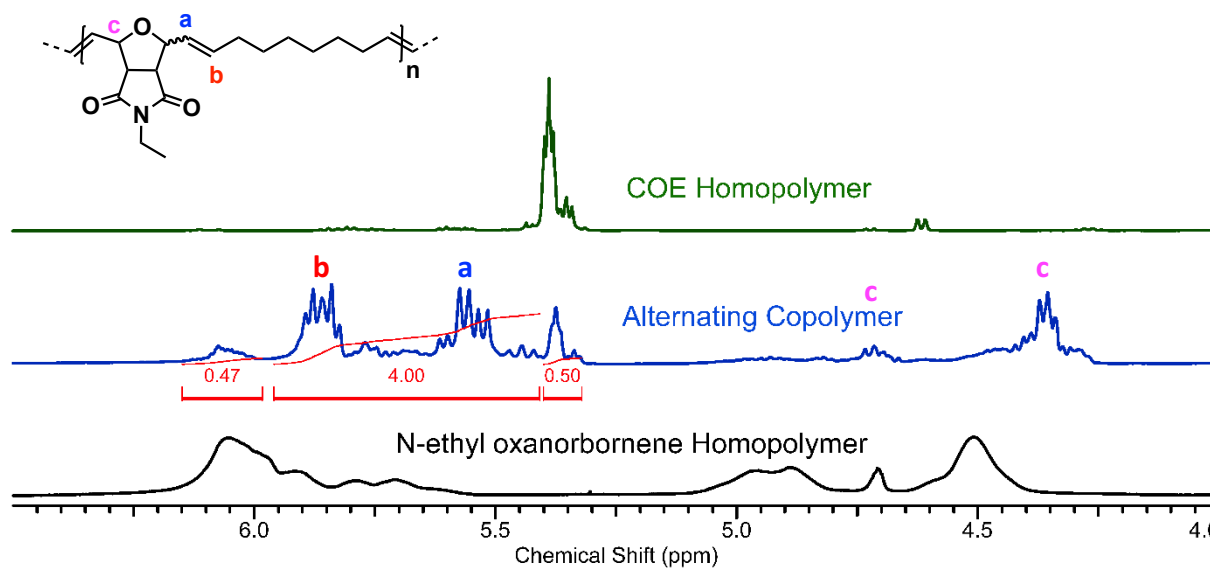


Figure S10: ^1H NMR (chloroform- d , 400 MHz) of alternating copolymer synthesis with **M1** and **COE**. Calculated by assigning the alternating backbone as 4H and quantify the remaining homopolymer signal.

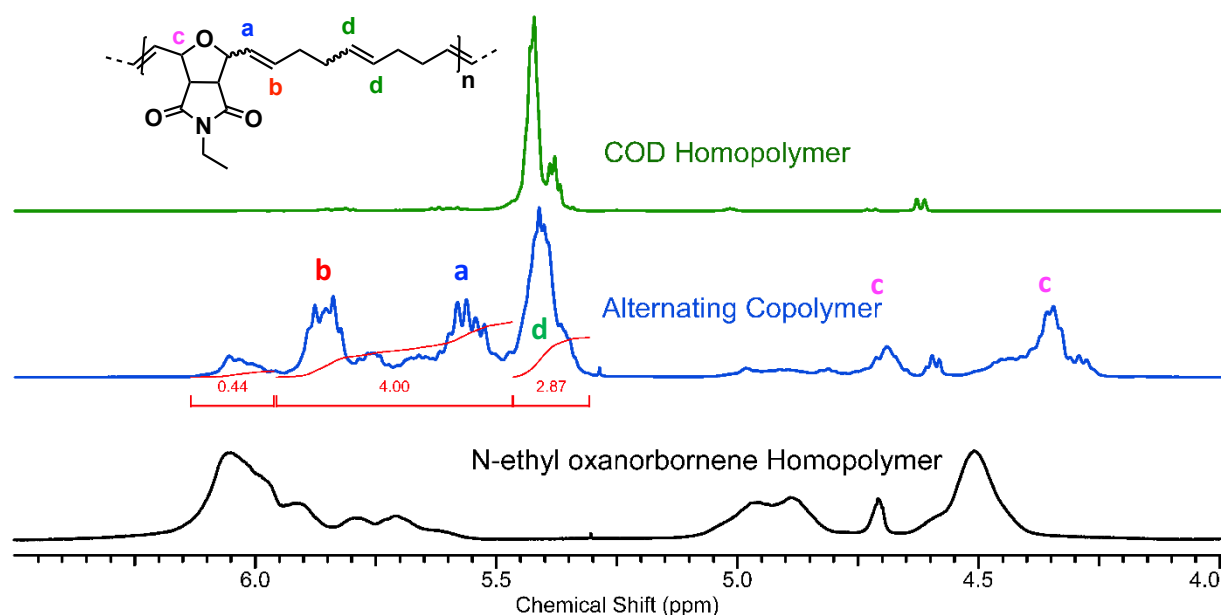


Figure S11: ^1H NMR (chloroform- d , 400 MHz) of alternating copolymer synthesis with **M1** and **COD**. Calculated by assigning the alternating backbone as 4H and quantify the remaining homopolymer signal.

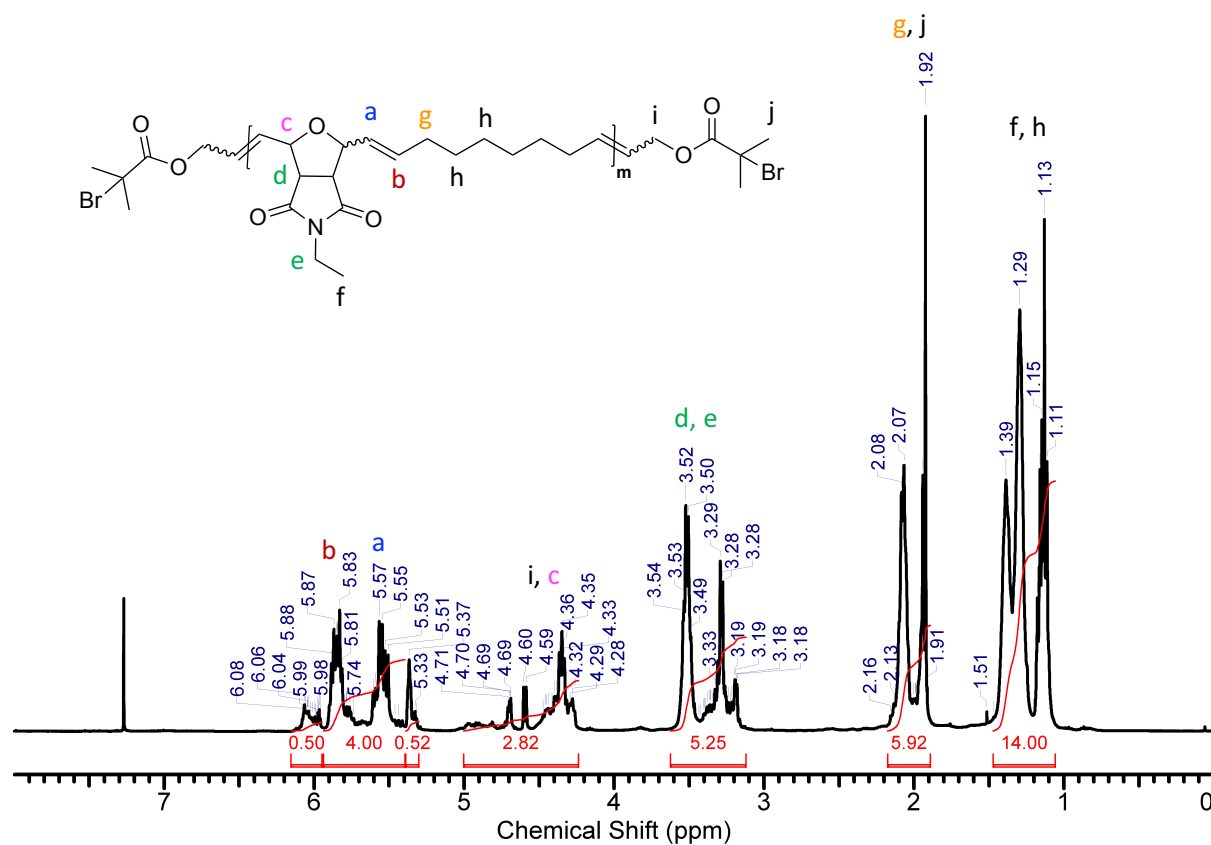


Figure S12: ¹H NMR (chloroform-d, 400 MHz) spectrum of compound P1.

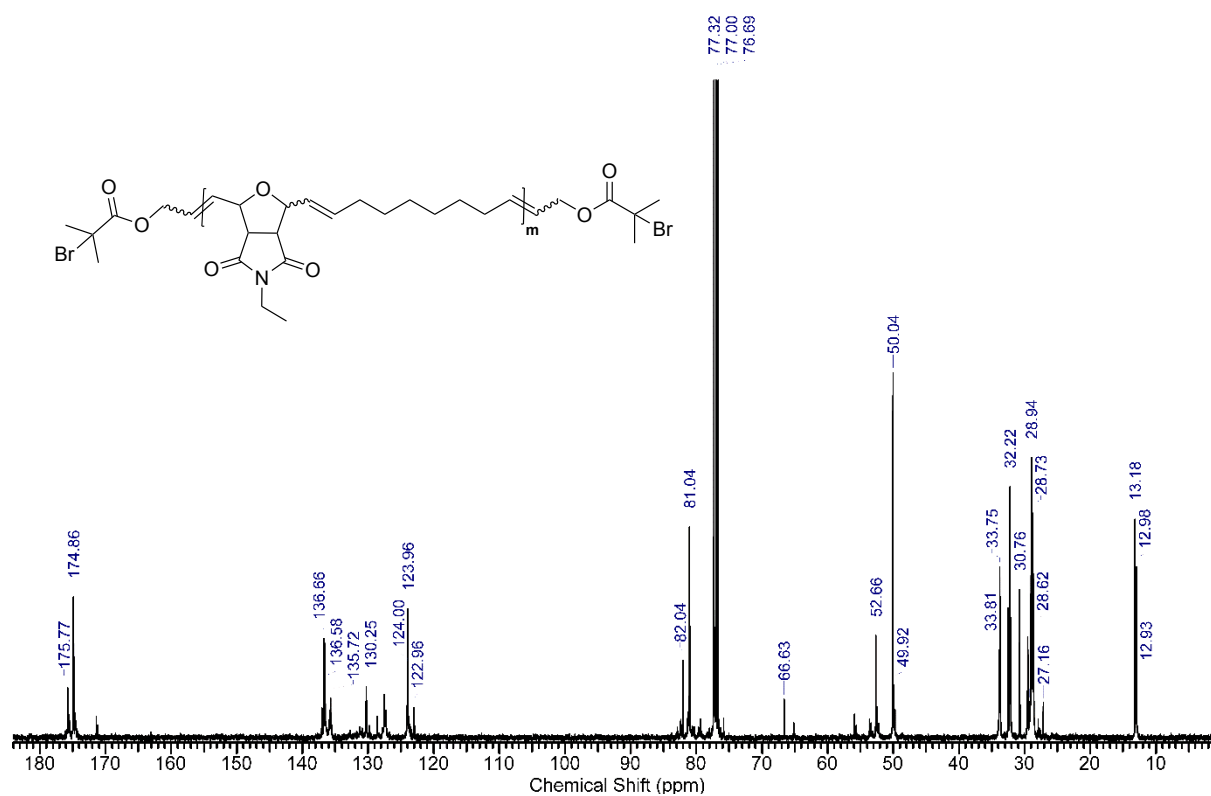
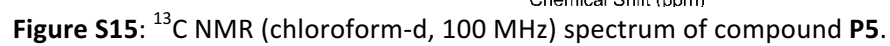
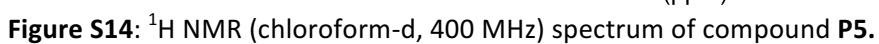


Figure S13: ¹³C NMR (chloroform-d, 100 MHz) spectrum of compound P1.



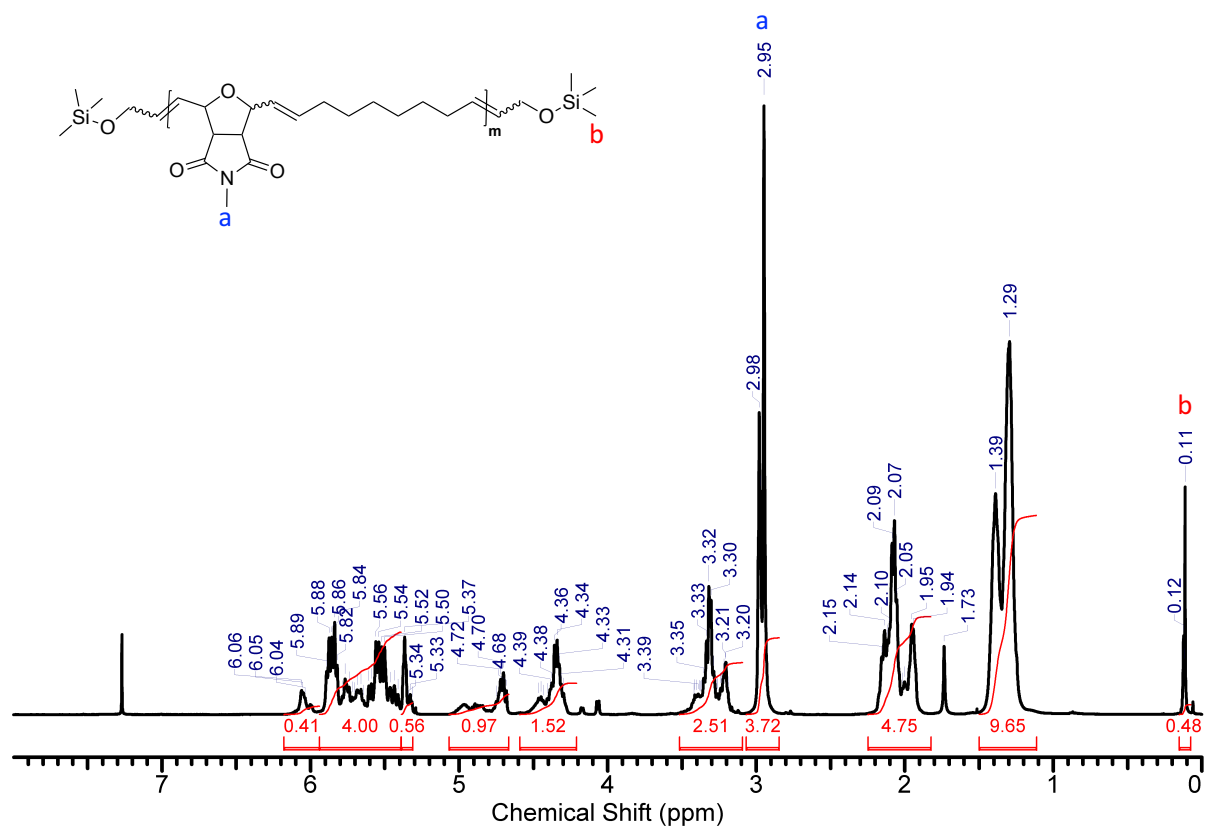


Figure S16: ^1H NMR (chloroform- d , 400 MHz) spectrum of compound **P6**.

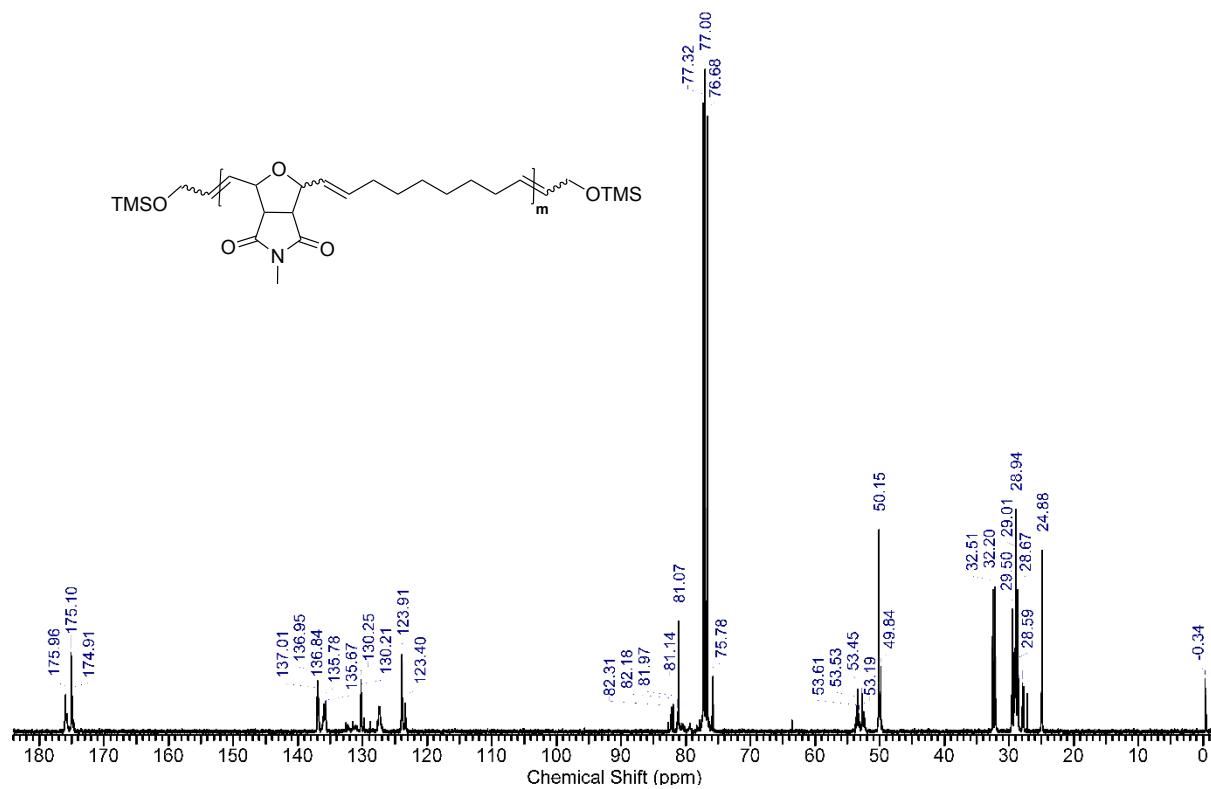


Figure S17: ^{13}C NMR (chloroform- d , 100 MHz) spectrum of compound **P6**.

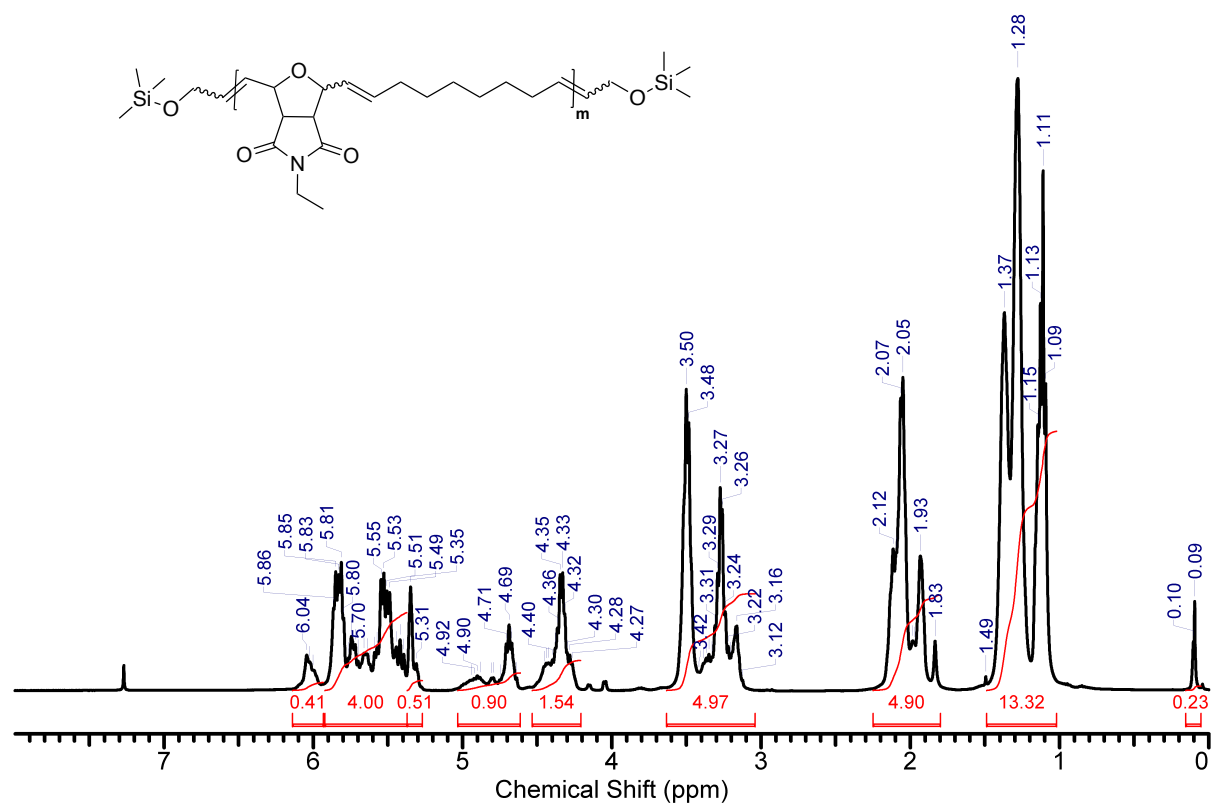


Figure S18: ^1H NMR (chloroform- d , 400 MHz) spectrum of compound P7.

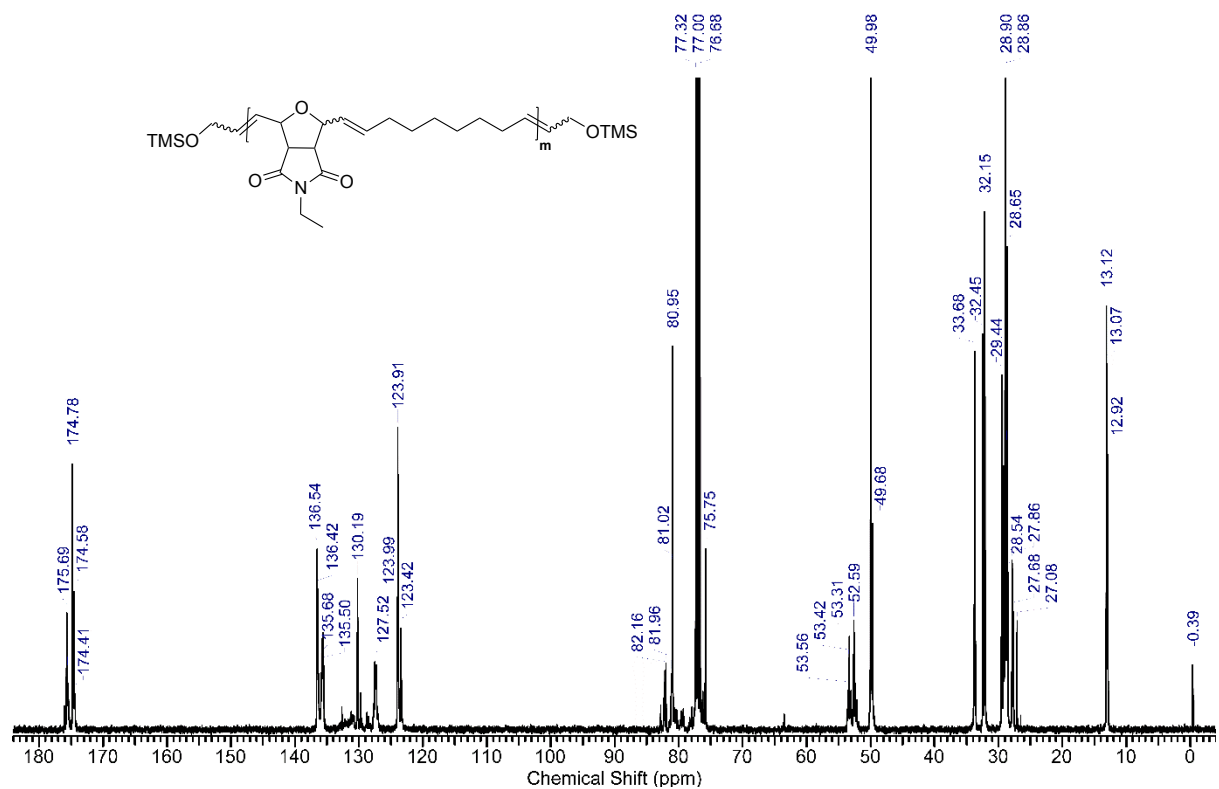


Figure S19: ^{13}C NMR (chloroform- d , 100 MHz) spectrum of compound P7.

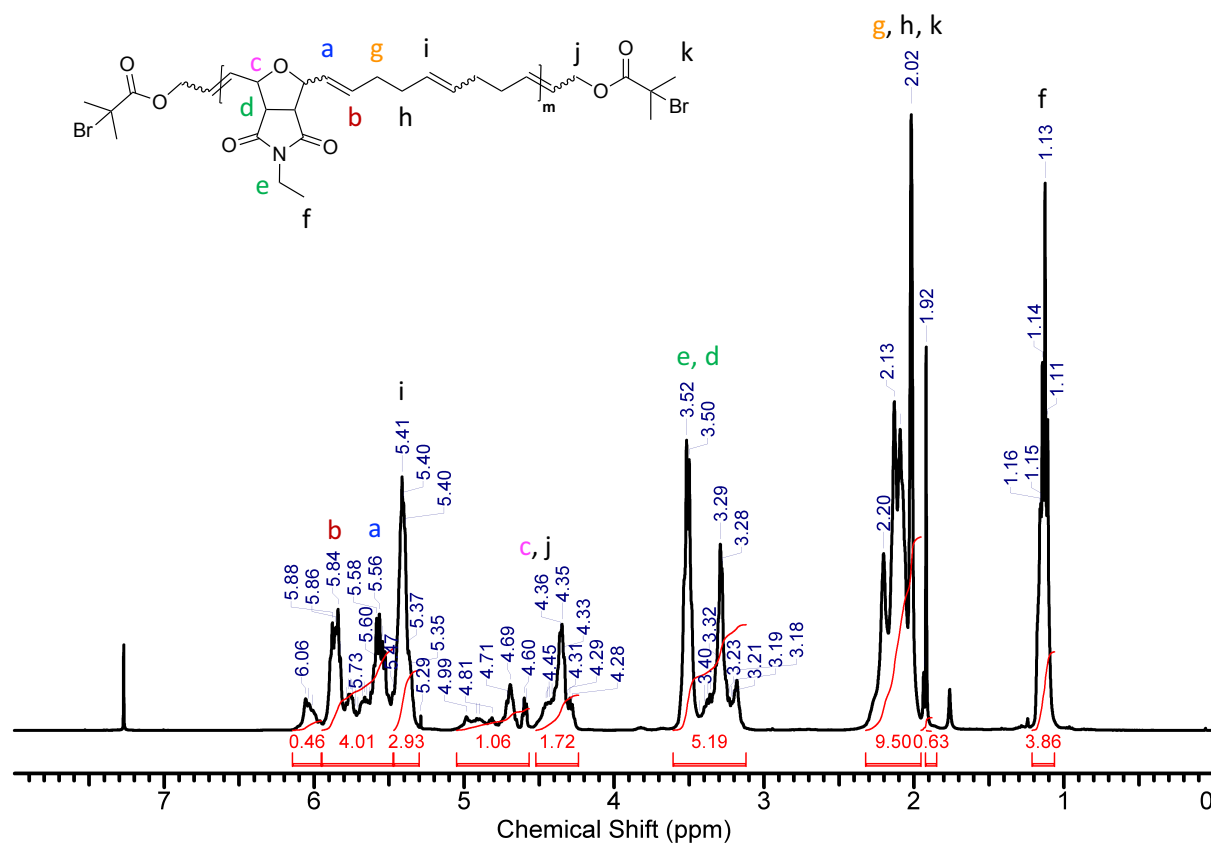


Figure S20: ^1H NMR (chloroform- d , 400 MHz) spectrum of compound P9.

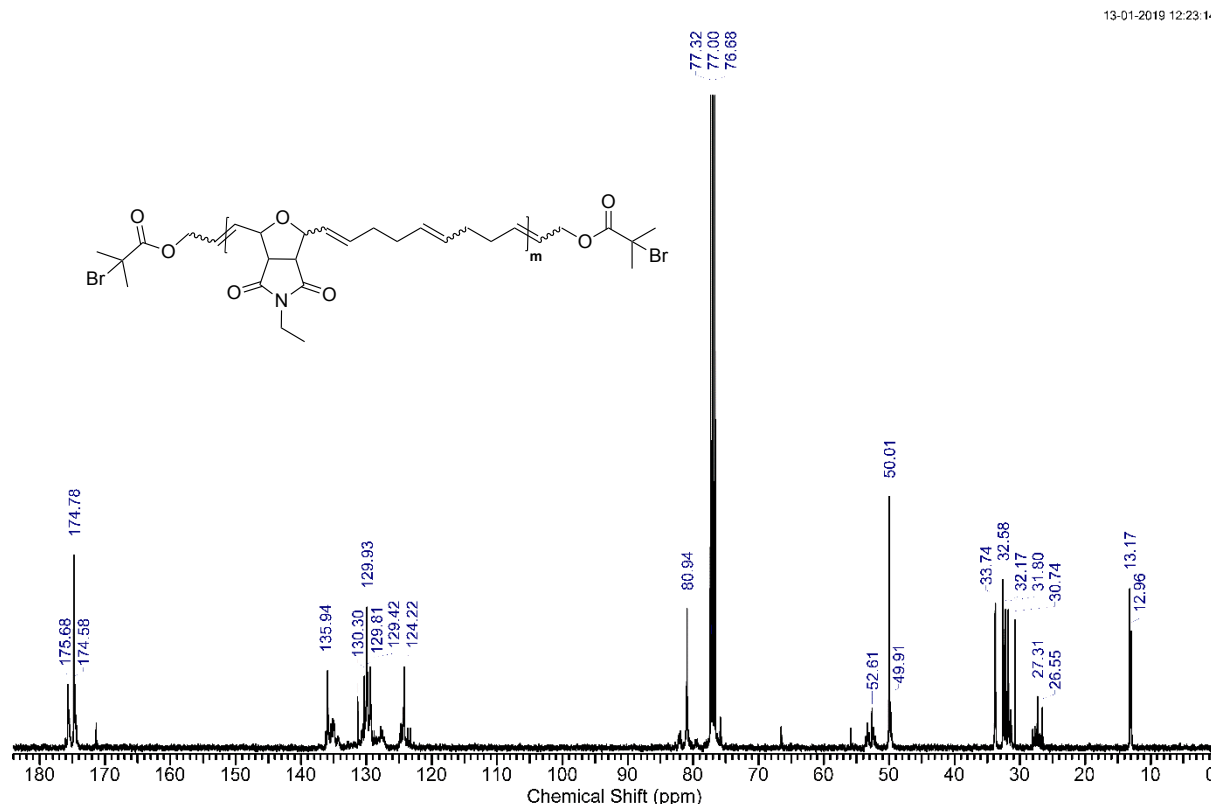


Figure S21: ^{13}C NMR (chloroform- d , 100 MHz) spectrum of compound P9.

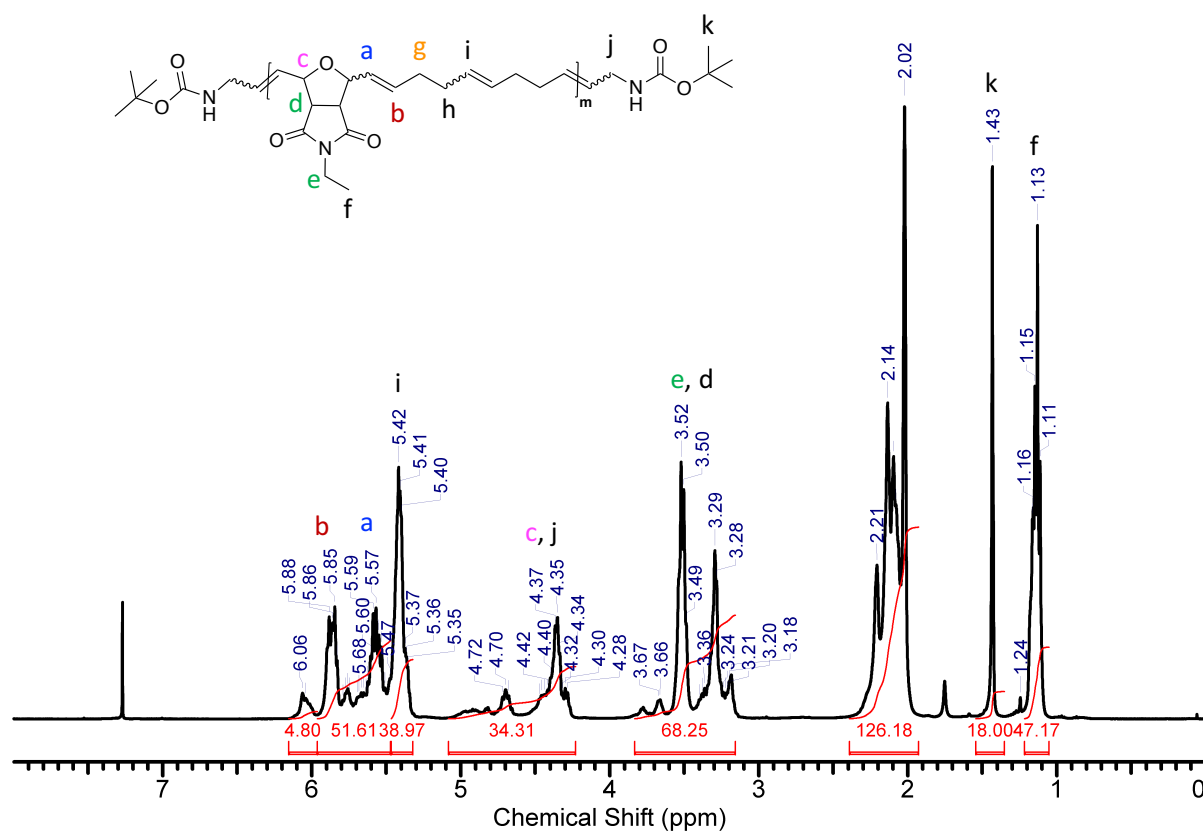


Figure S22: ^1H NMR (chloroform- d , 400 MHz) spectrum of compound **P12**.

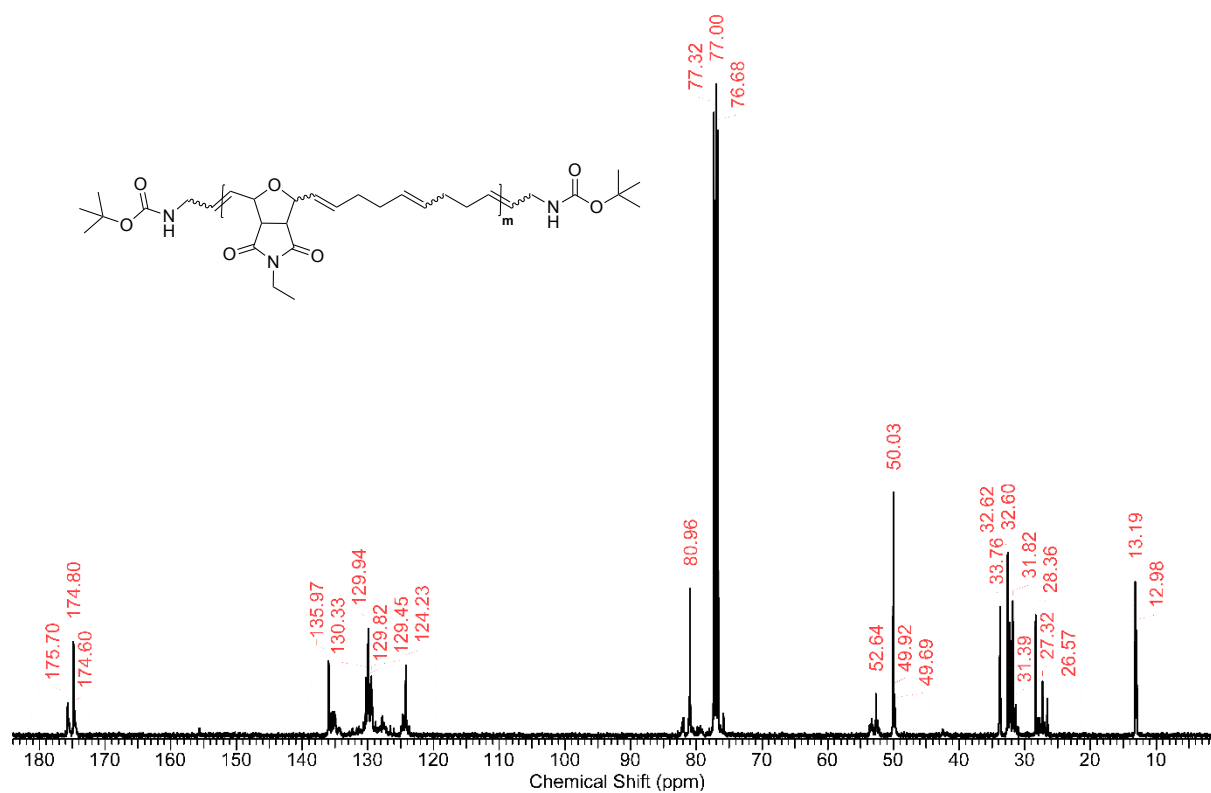


Figure S23: ^{13}C NMR (chloroform- d , 100 MHz) spectrum of compound **P12**.

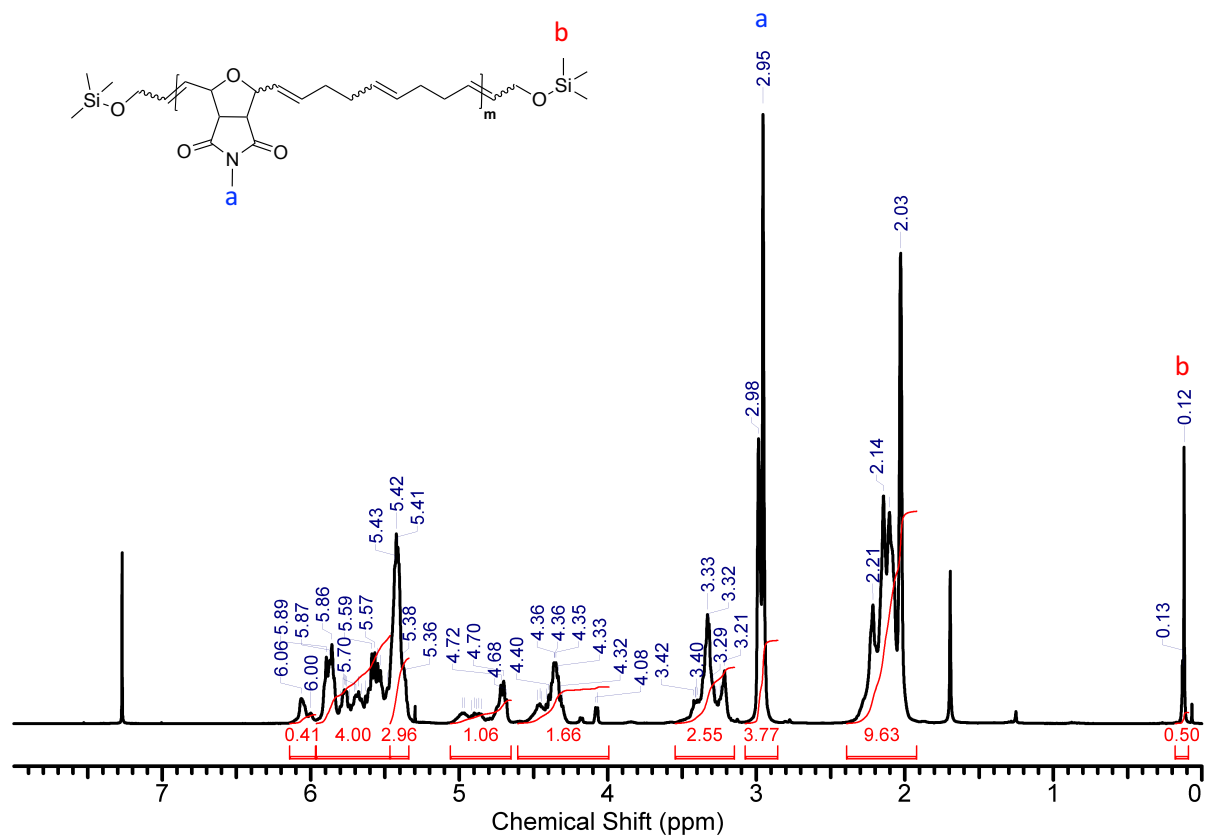


Figure S24: ^1H NMR (chloroform- d , 400 MHz) spectrum of compound **P 13**.

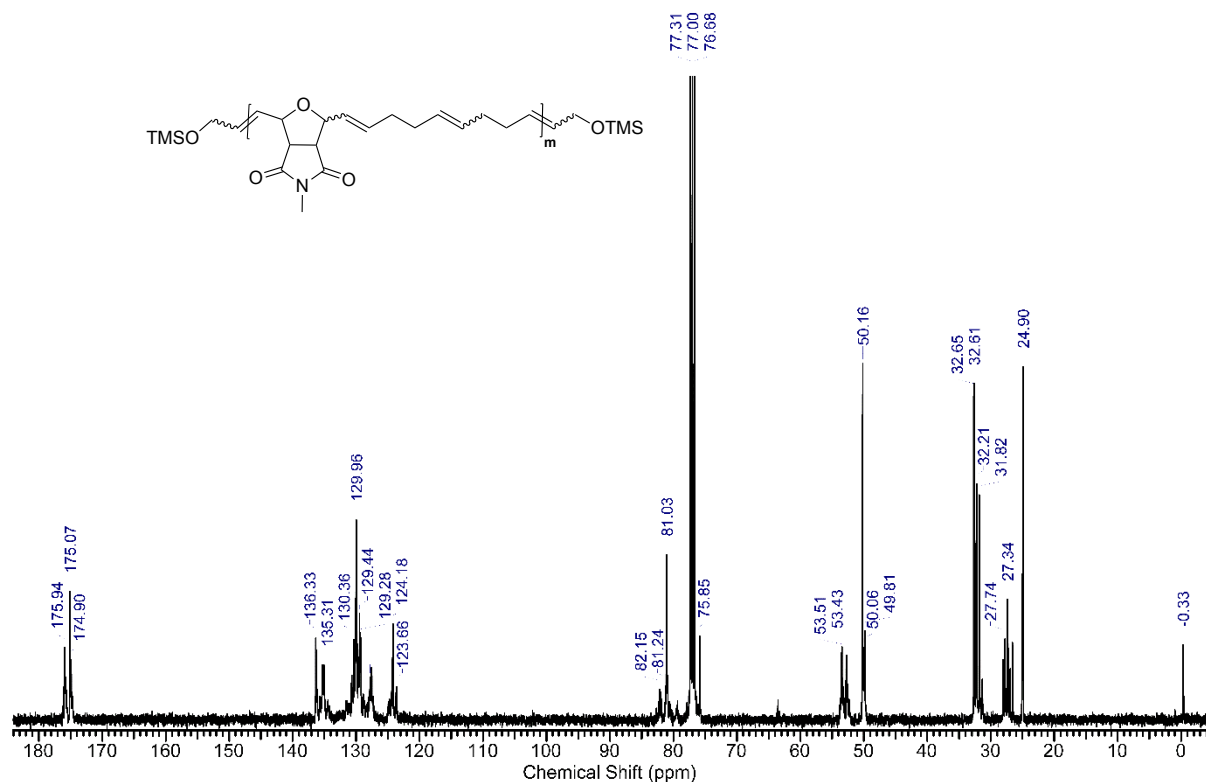


Figure S25: ^{13}C NMR (chloroform- d , 100 MHz) spectrum of compound **P13**.

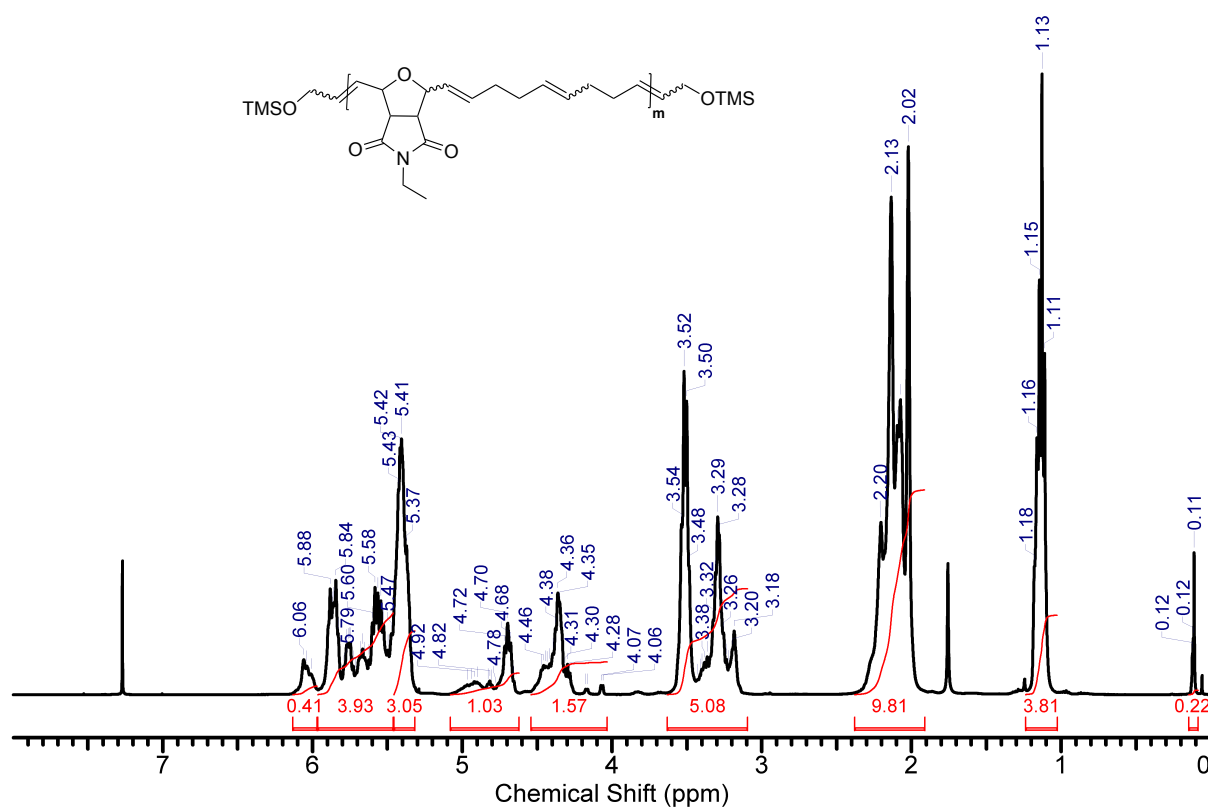


Figure S26: ¹H NMR (chloroform-d, 400 MHz) spectrum of compound **P14**.

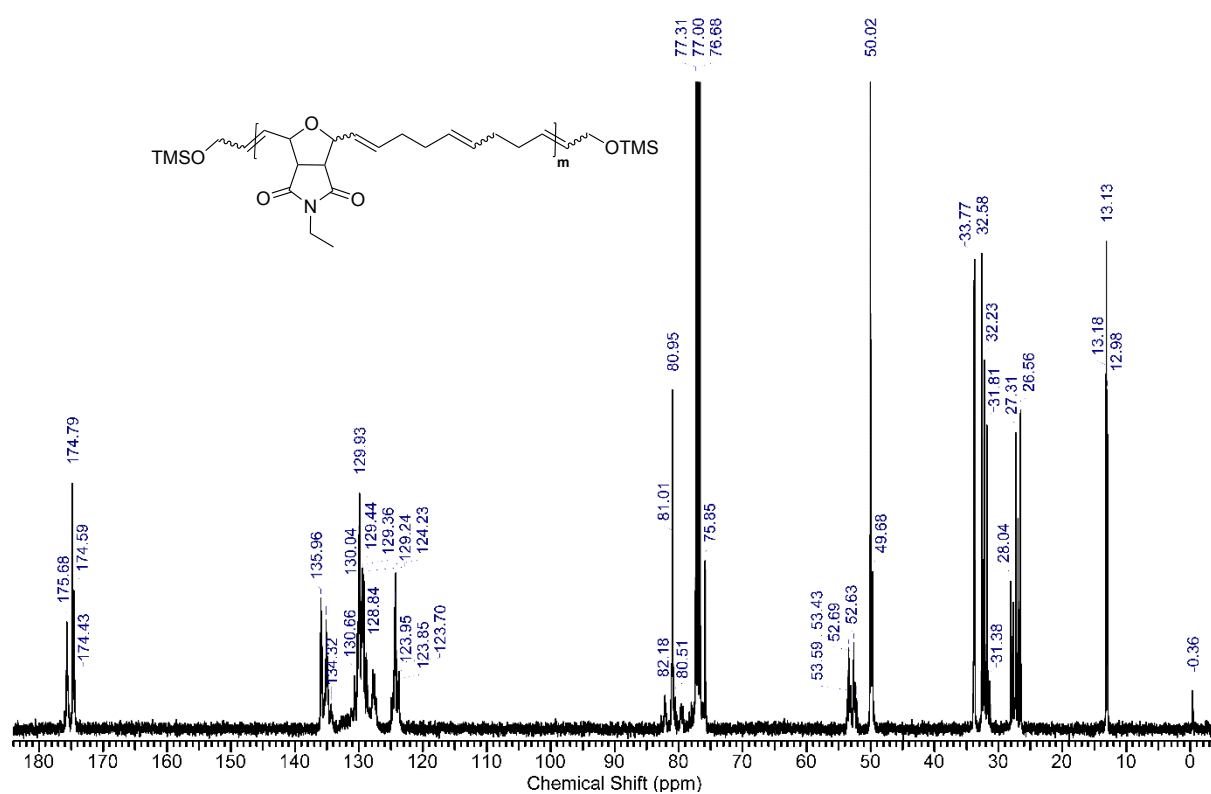


Figure S27: ¹³C NMR (chloroform-d, 100 MHz) spectrum of compound **P14**.

MALDI-ToF mass spectrometric data of polymers

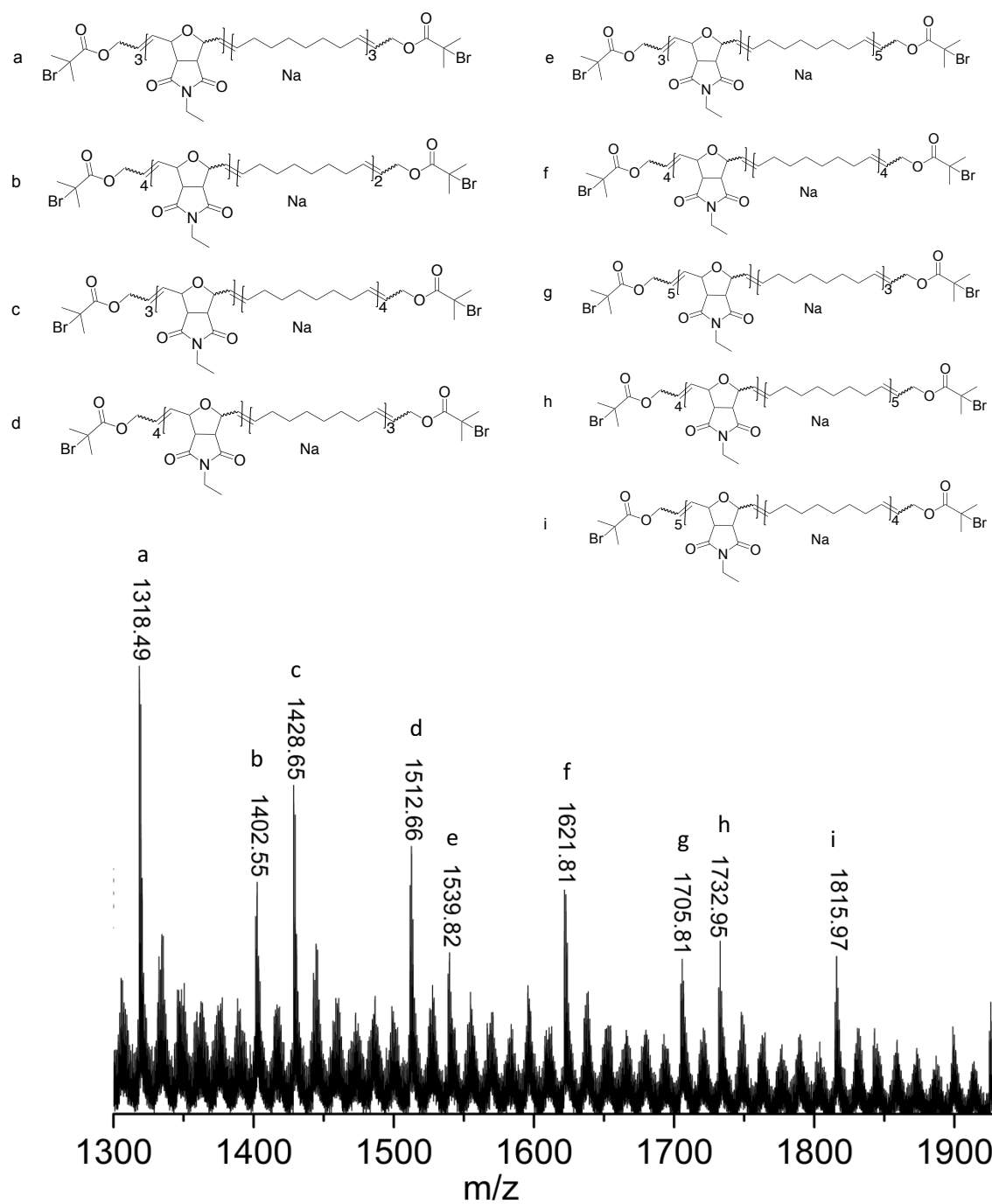


Figure S28: MALDI-ToF mass spectra (DCTB, NaTFA) of **P1**.

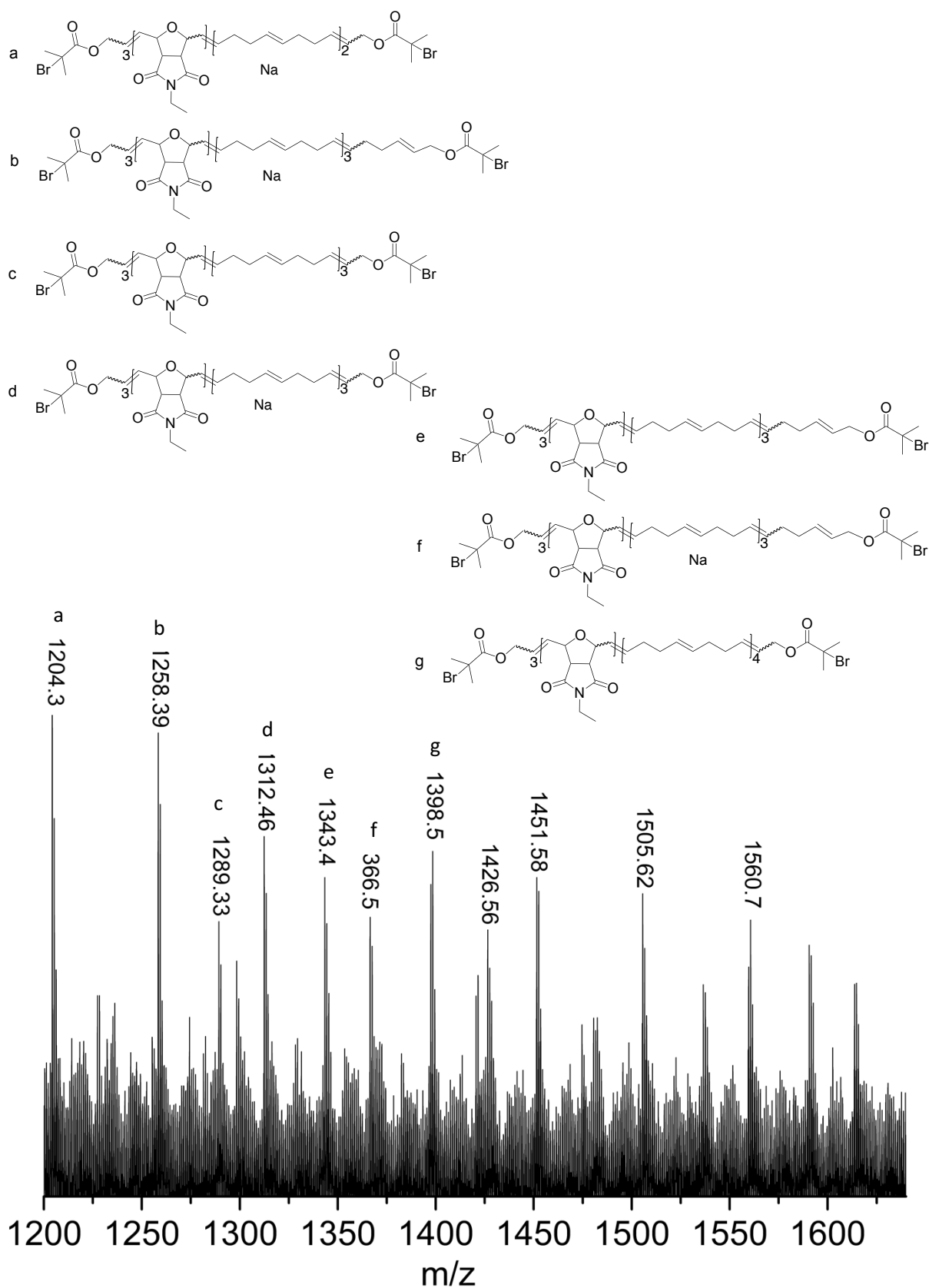


Figure S29: MALDI-ToF mass spectra (DCTB, NaTFA) of **P8**.

Table S3. Polymerization results and SEC data for different polymers at higher temperature.^[a]

Polymer	M1: CTA: G2	M _n (theo)	M _n (cal)	Đ ^[b]
P1H	500:50:1	3000	6000	1.7
P2H	1000:50:1	6000	10000	1.8
P3H	1500:50:1	9100	15600	2
P4H	2000:50:1	12100	20000	1.8

[a] All the reactions were carried out with **G2** (2 mg, 0.0024 mmol) at 60 °C for 36 hours. For entry **P1H-P4H**, the reactions were carried out with **CTA1** (45 mg, 0.12 mmol), monomer **M1** and cyclooctene (**COE**). [b] Measured by CHCl₃ SEC.

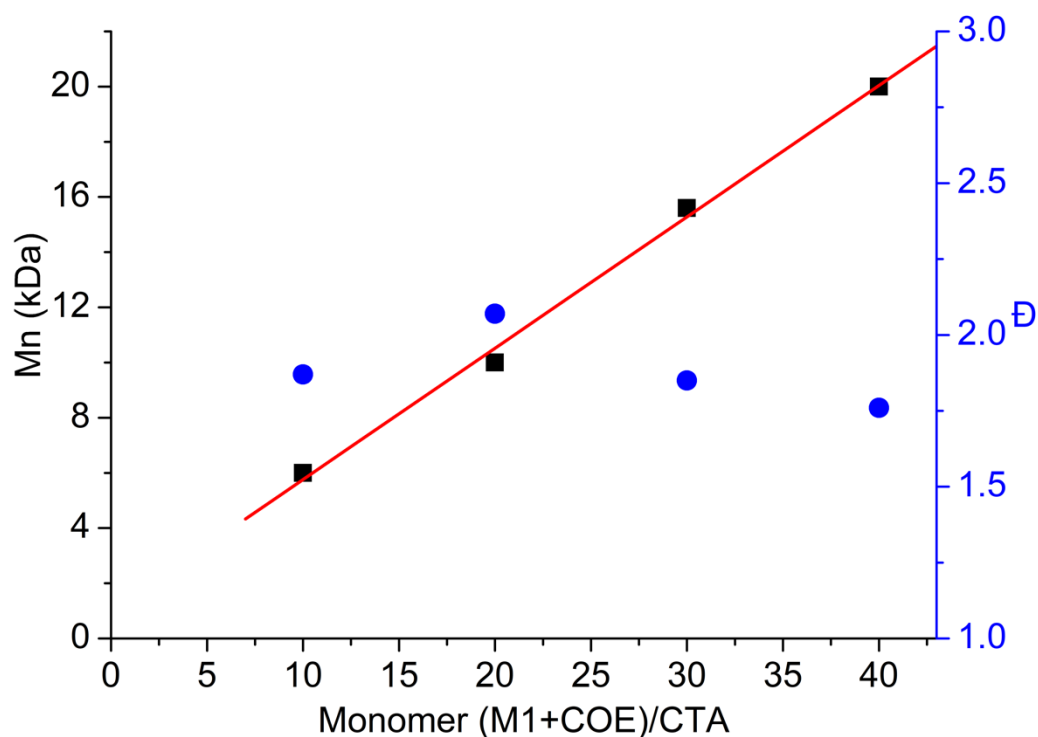


Figure S30: Dependence of observed molar mass (SEC, see Table SI1) vs. monomer (**M1+COE**) to **CTA1** ratio at 60 °C in 1,2-dichloroethane.

Table S4. Equilibration Kinetic and SEC data for M1, COD copolymerization.^[a]

Entry	M1: CTA1: G2	M _n (theo)	M _n (cal)	Time(hours)	Đ ^[b]
1	2000: 50: 1	12000	18500	2	1.9
2	2000: 50: 1	12000	14800	7	2.3
3	2000: 50: 1	12000	14300	17	2.3

[a] The reaction was carried out with **G2** (2 mg, 0.0024 mmol, 1eq), **CTA1** (45 mg, 0.12 mmol, 50eq), monomer **M1** (910 mg, 4.7 mmol, 2000eq) and cyclooctadiene(**COD**) (507 mg, 4.7 mmol, 2000eq) at 40 °C in DCM. [b] Measured by CHCl₃ SEC.

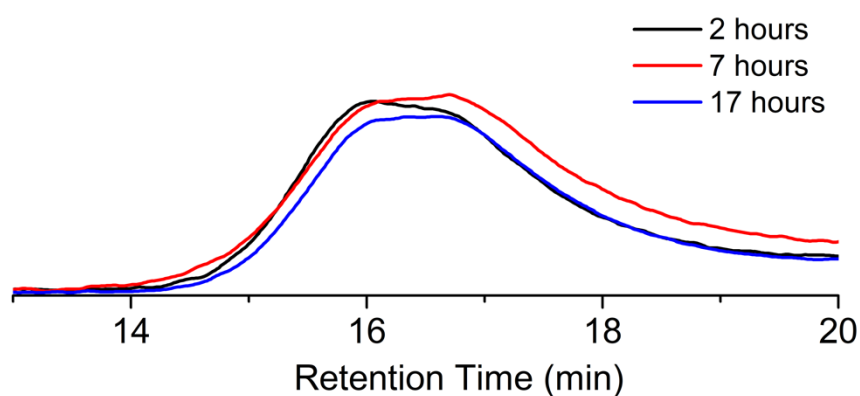


Figure S31: SEC (CHCl₃) trace of the copolymerization of the monomer **M1** and **COD** at different time intervals.

DSC of polymers

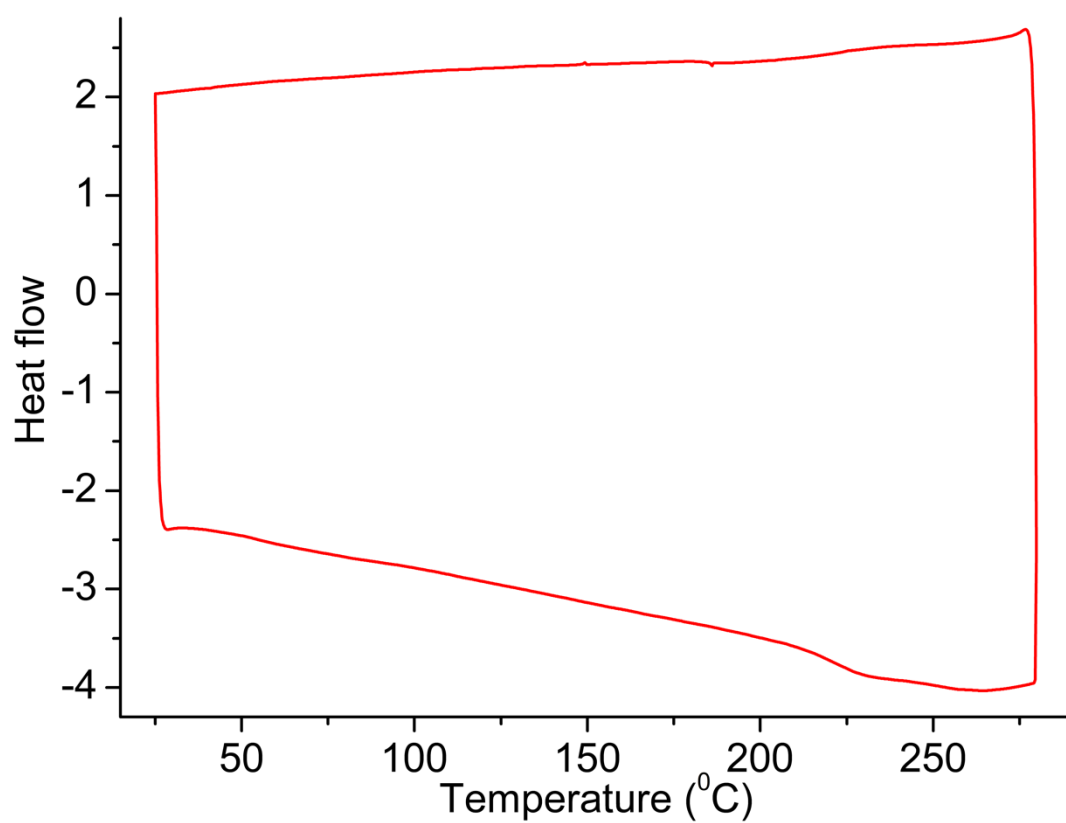


Figure S32: DSC data of homopolymer of **M1** (second cycle from 0 °C to 300 °C).

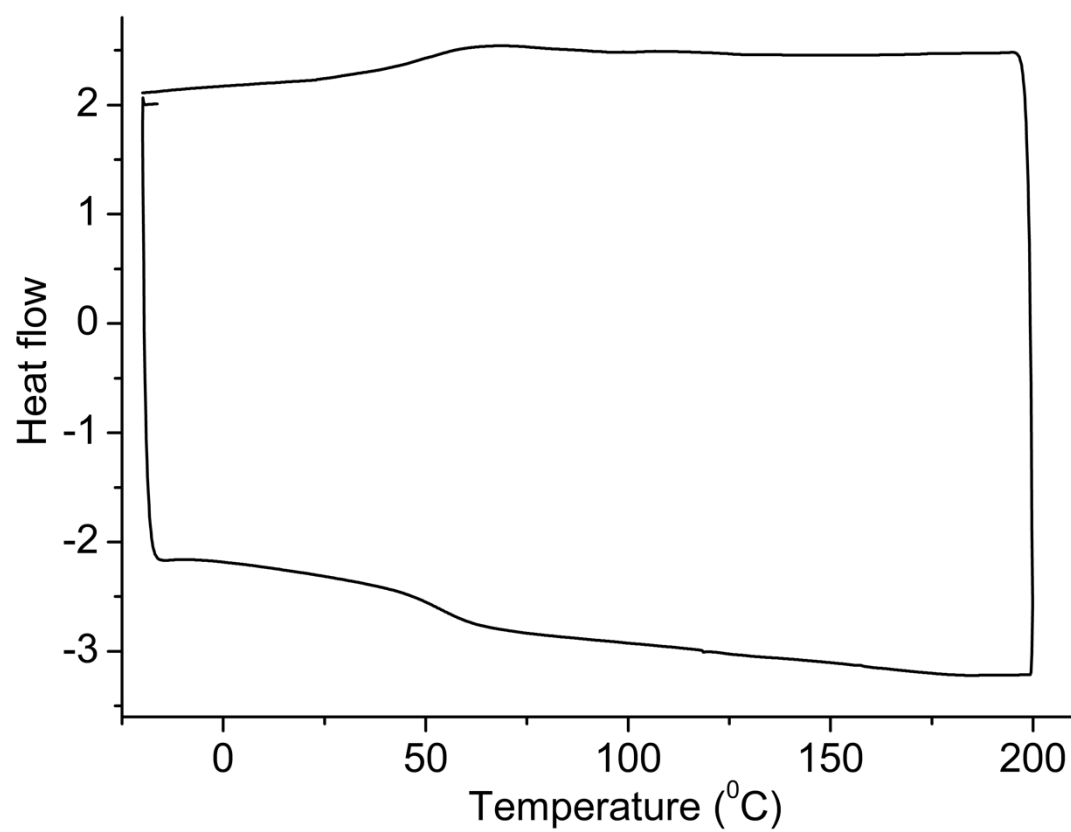


Figure S33: DSC data of **P10** (second cycle from -20 °C to 200 °C).

High-resolution mass spectrometric data

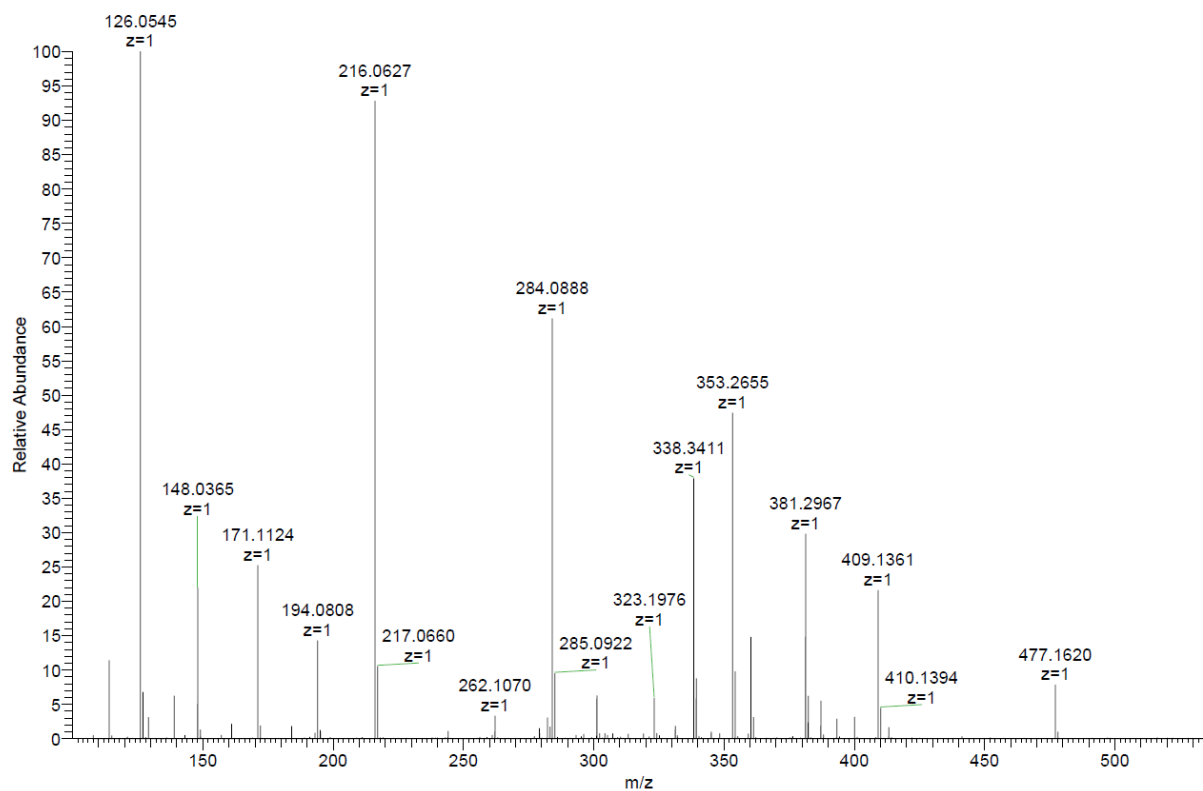


Figure S34: HR-MS of M1.

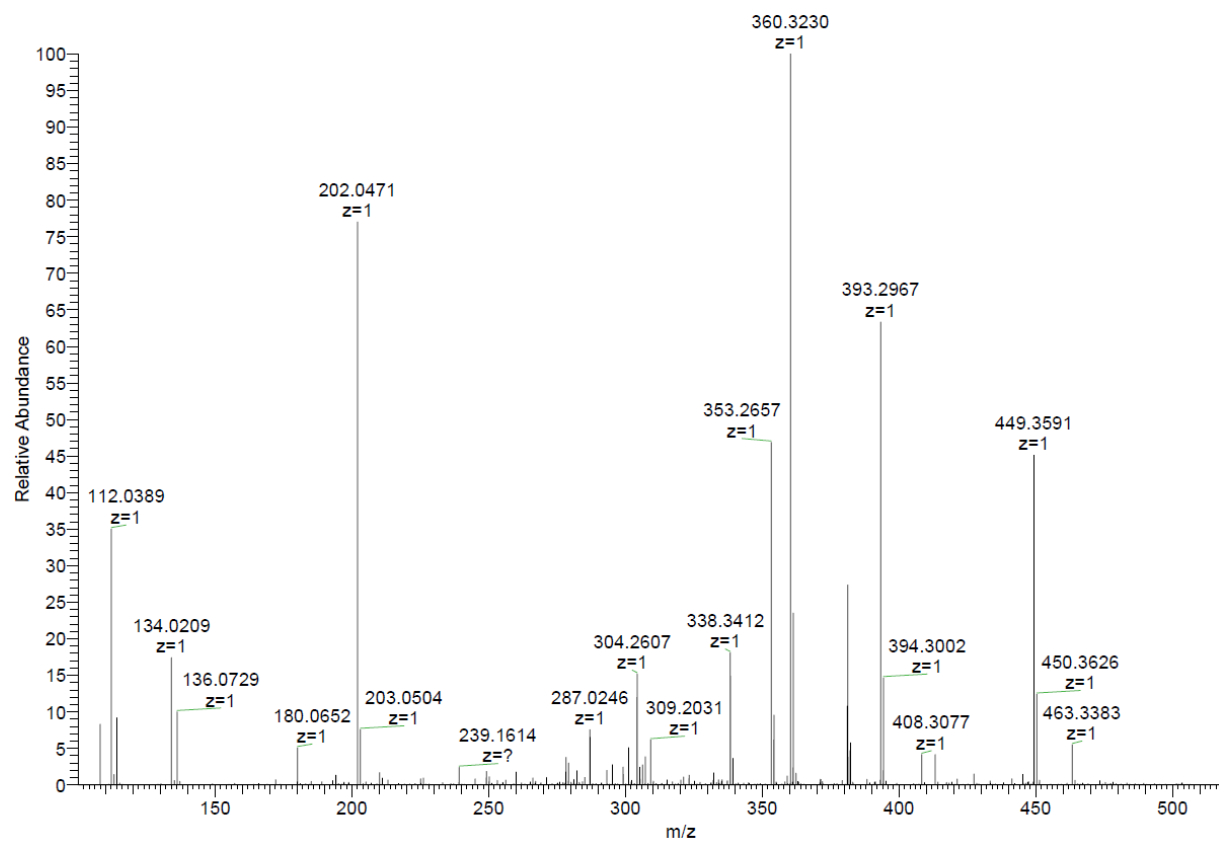


Figure S35: HR-MS of M2.

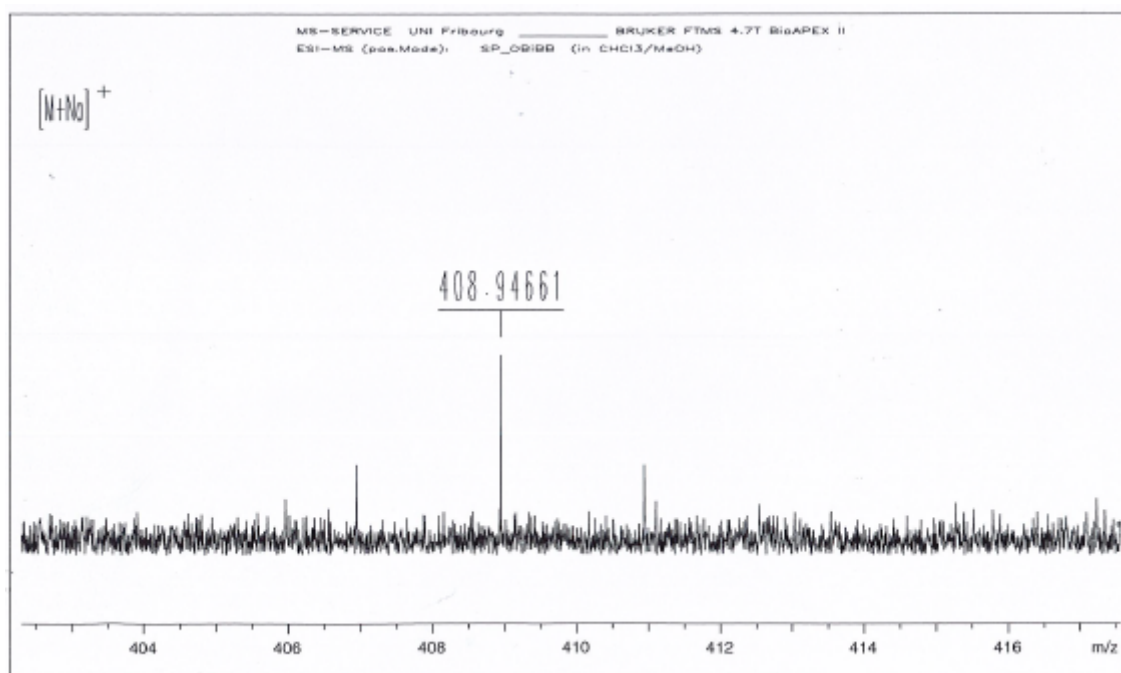


Figure S36: HR-MS of CTA1.

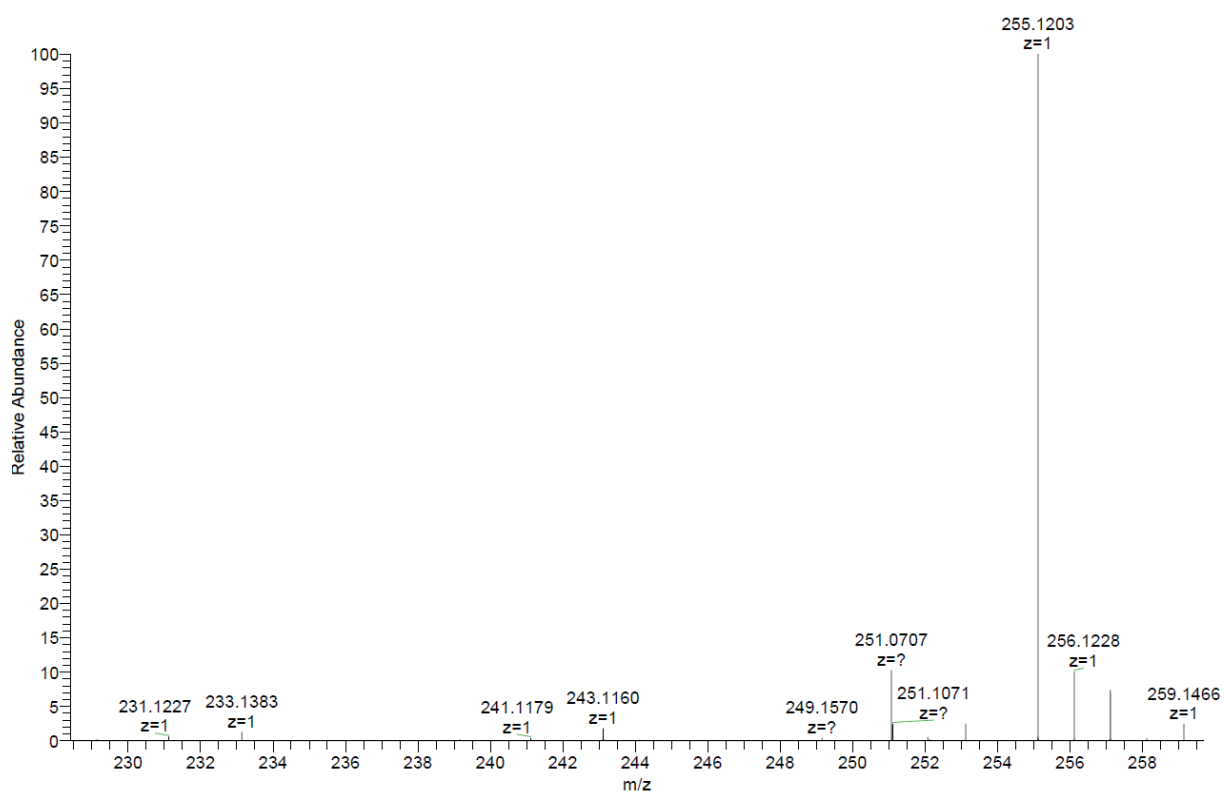


Figure S37: HR-MS of CTA2.