Palladium-catalyzed Copolymerization to Synthesize Sulfur-containing Polyethylene Materials

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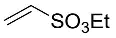
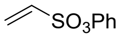
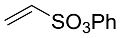
1. Table and Figure

Table S1. Polymerization data taken from literatures for the comparisons

Ent.	Cat.	Comonomer	c (M)	p (atm)	T (°C)	Act. (10^4)	X_M (%)	M_n
1[a]	**Pd1**		1.1	5	95	0.33	8.1	2000
2[a]	**Pd1**		1	5	95	0.26	7.2	4550
3[b]	**Pd1**		0.3	5	95	4.7	2.5	6400
4[b]	**Pd1**		0.3	5	95	0.77	5.0	2900
5[b]	**Pd1**		1	5	95	0.08	10.2	2800

[a] Data taken from ref. 1. [b] Data taken from ref. 2.

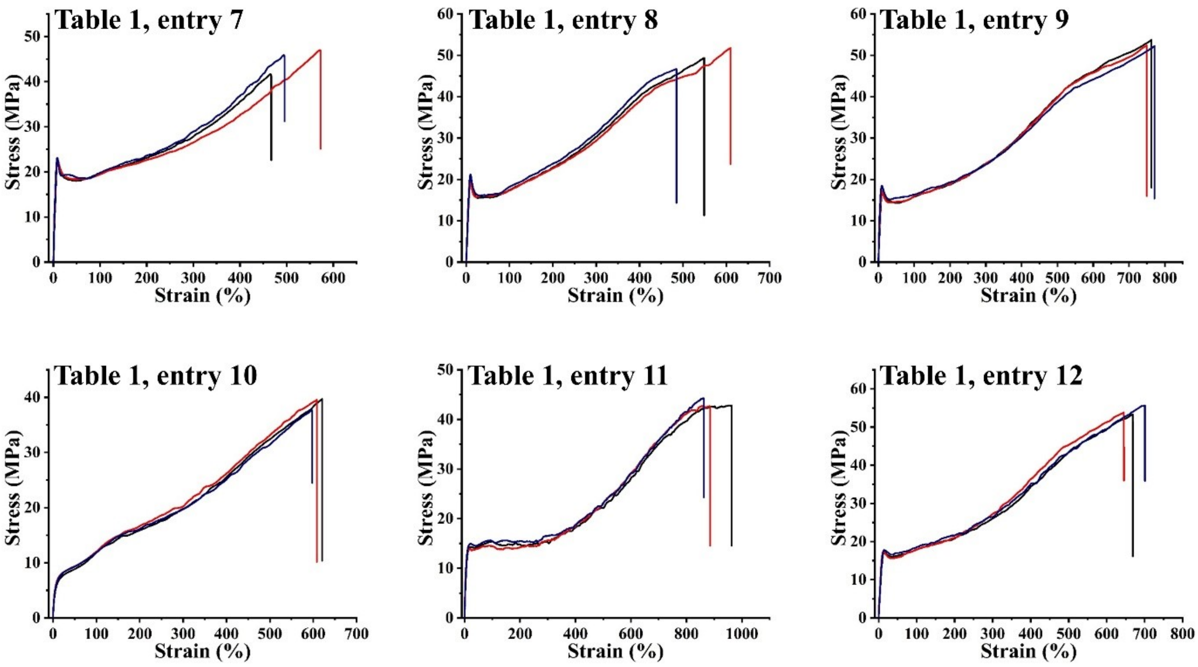


Figure S1. Stress-strain curves of the copolymer from Table 1, entries 7-12.

2. Experimental Section

2.1 General methods

All manipulations of air- and water-sensitive compounds were carried out using standard Schlenk, high-vacuum, and glovebox techniques. Deuterated solvents used for NMR were dried and distilled prior to use. ^1H, ^{13}C NMR spectra were recorded by a Bruker Ascend Tm 400 spectrometer at ambient temperature unless otherwise stated. The chemical shifts of the ^1H and ^{13}C NMR spectra were referenced to the residual solvent; Coupling constants are in Hz. NMR analyses of polymers were performed in 1,1,2,2-tetrachloroethane-d_2 at 120 °C. Samples were preheated for at least 30 min before acquiring data. The chemical shifts of the ^{1}H NMR spectra are referenced to the residual proton resonance of chloroform-*d* (δ: 7.26) and 1,1,2,2-tetrachloroethane-d_2 (δ: 6.00). The chemical shifts of the ^{13}C NMR spectra are referenced to the carbon resonance of chloroform-*d* (δ: 77.16) and 1,1,2,2-tetrachloroethane-d_2 (δ: 74.47). For copolymers with high incorporation ratios (Table 1, entries 1-4), extra CD_3SOCD_3 was used to disrupt the strong dipole-dipole interactions between sulfur-containing groups in copolymers, thereby enabling the acquisition of clear ^{1}H NMR spectra.

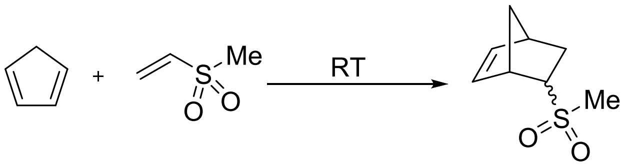
Molecular weight and molecular weight distribution of the polymer were determined by gel permeation chromatography (GPC) with a PL-220 equipped with two Agilent PLgel Olexis columns at 150 °C using 1,2,4-trichlorobenzene as a solvent, and the calibration was made using polystyrene standard and are corrected for linear polyethylene by universal calibration using the Mark–Houwink parameters of Rudin: $K = 1.75 \times 10^{-2}$ cm^3/g and $R = 0.67$ for polystyrene and $K = 5.90 \times 10^{-2}$ cm^3/g and $R = 0.69$ for polyethylene.

DSC measurements were performed on a TA Instruments DSC Q20. Samples (ca. 5 mg) were annealed by heating to 150 °C at 10 °C /min, cooled to 0 °C at 10 °C /min, and then analyzed while being heated to 150 °C at 10 °C /min.

A standard test method, ASTM 638, was followed to measure the tensile properties of the polyethylene samples. Polymers were melt-pressed at 30 to 35°C above their melting point to obtain the dog-bone-shaped tensile-test specimens. The test specimens showed 25-mm gauge length, 2-mm width, and thickness of 0.4 mm. Stress/strain experiments were performed at 10 mm/min using a Universal Test Machine (UTM2502) at room temperature. At least three specimens of each copolymer were tested.

The water contact angles on polymer films were measured with a Contact Angle Meter SL200B (Solon Tech. Co., Ltd.) using the dynamic sessile drop method. Samples for water contact angle measurements were melt-pressed polymer films. The water contact angles of the polymer films were measured using a contact angle goniometer at 25 °C with an accuracy of ±3°. The reported values are the average of at least six measurements made at different positions of the film.

2.2 Synthesis of comonomers



Synthesis of $NBSO_2Me$: Freshly cracked cyclopentadiene (21.81 g, 330 mmol, 1.1 eq) was added drop-wise with stirring to methyl vinyl sulfone (31.84 g, 300 mmol, 1.0 eq) in THF (300 mL). The reaction mixture was stirred at room temperature until TLC indicated the complete consumption of methyl vinyl sulfone. After column chromatography, **$NBSO_2Me$** was obtained as a clear liquid. Yield: 49.1 g (95%, *endo*: *exo* = 8: 2).

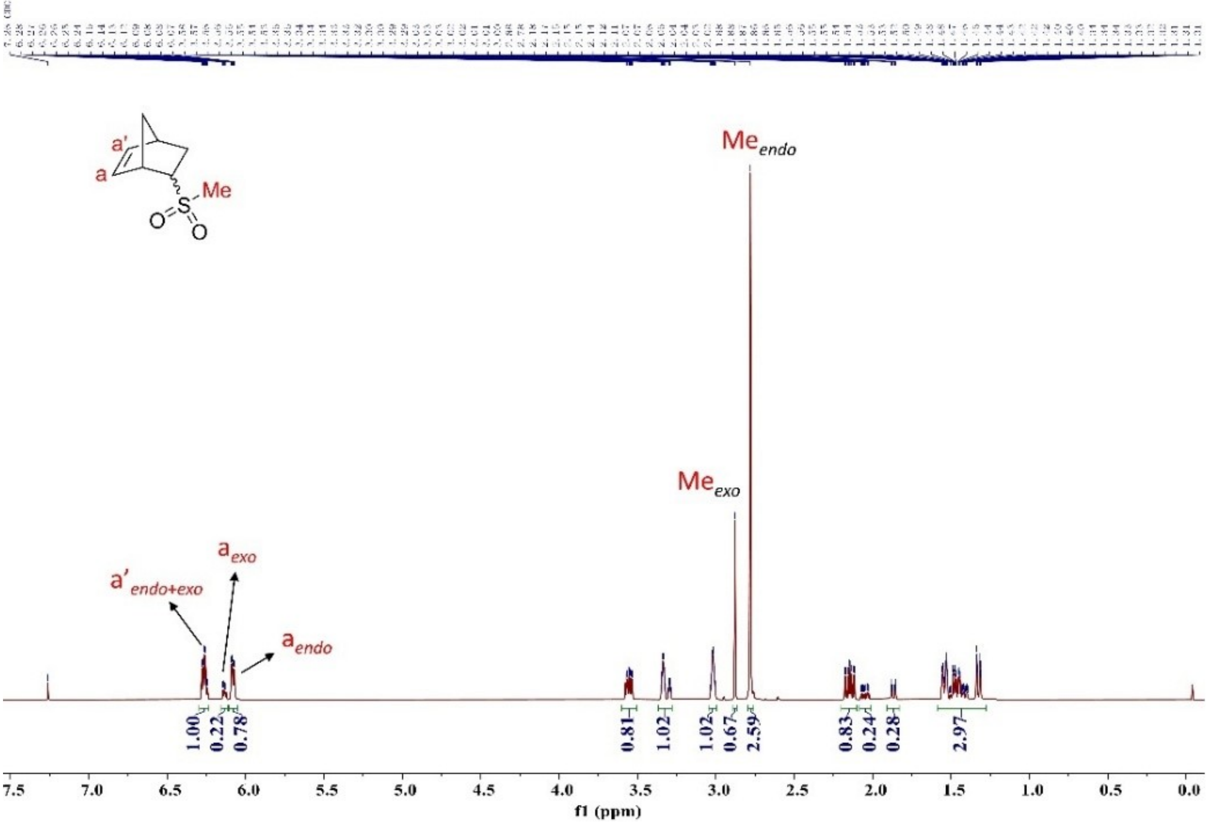


Figure S2. ^{1}H NMR spectrum of **NBSO$_2$Me**. (400 MHz, CDCl$_3$).

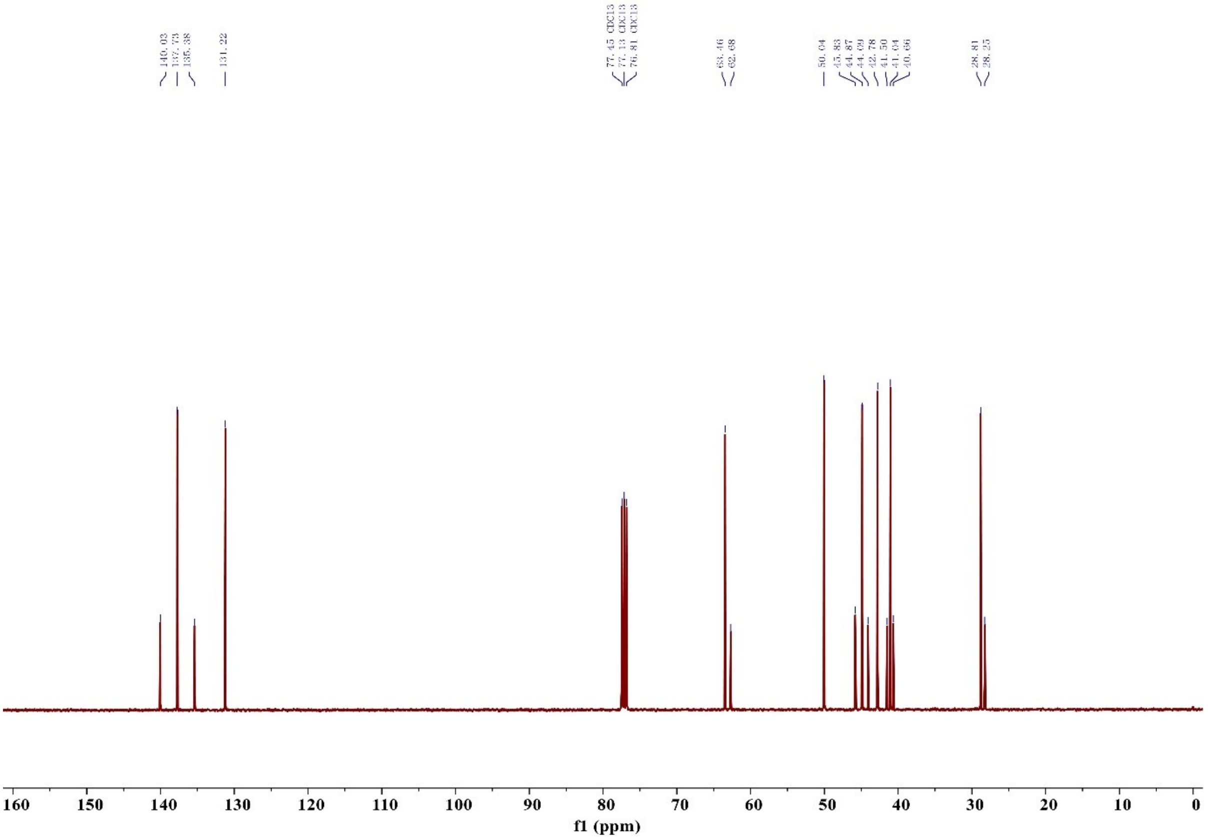
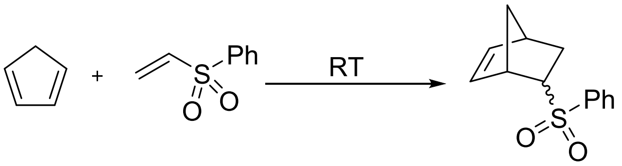


Figure S3. ^{13}C NMR spectrum of **NBSO$_2$Me**. (101 MHz, CDCl$_3$).



Synthesis of NBSO$_2$Ph: Freshly cracked cyclopentadiene (21.81 g, 330 mmol, 1.1 eq) was added drop-wise with stirring to phenyl vinyl sulfone (50.46 g, 300 mmol, 1.0 eq) in THF (300 mL). The reaction mixture was stirred at room temperature until TLC indicated the complete consumption of phenyl vinyl sulfone. After column chromatography, **NBSO$_2$Ph** was obtained as a white solid. Yield: 66.1 g (95%, *endo*: *exo* = 7: 3).

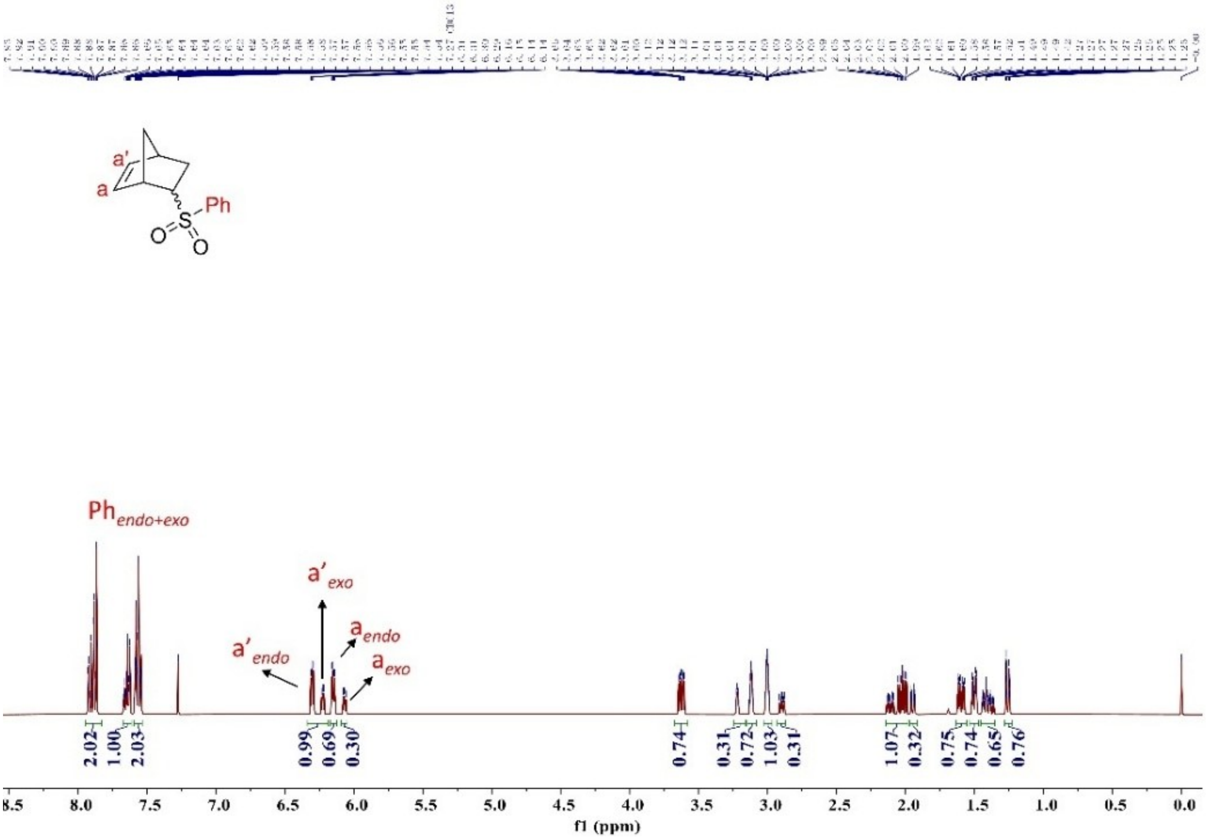


Figure S4. ^{1}H NMR spectrum of **NBSO$_2$Ph**. (400 MHz, CDCl$_3$).

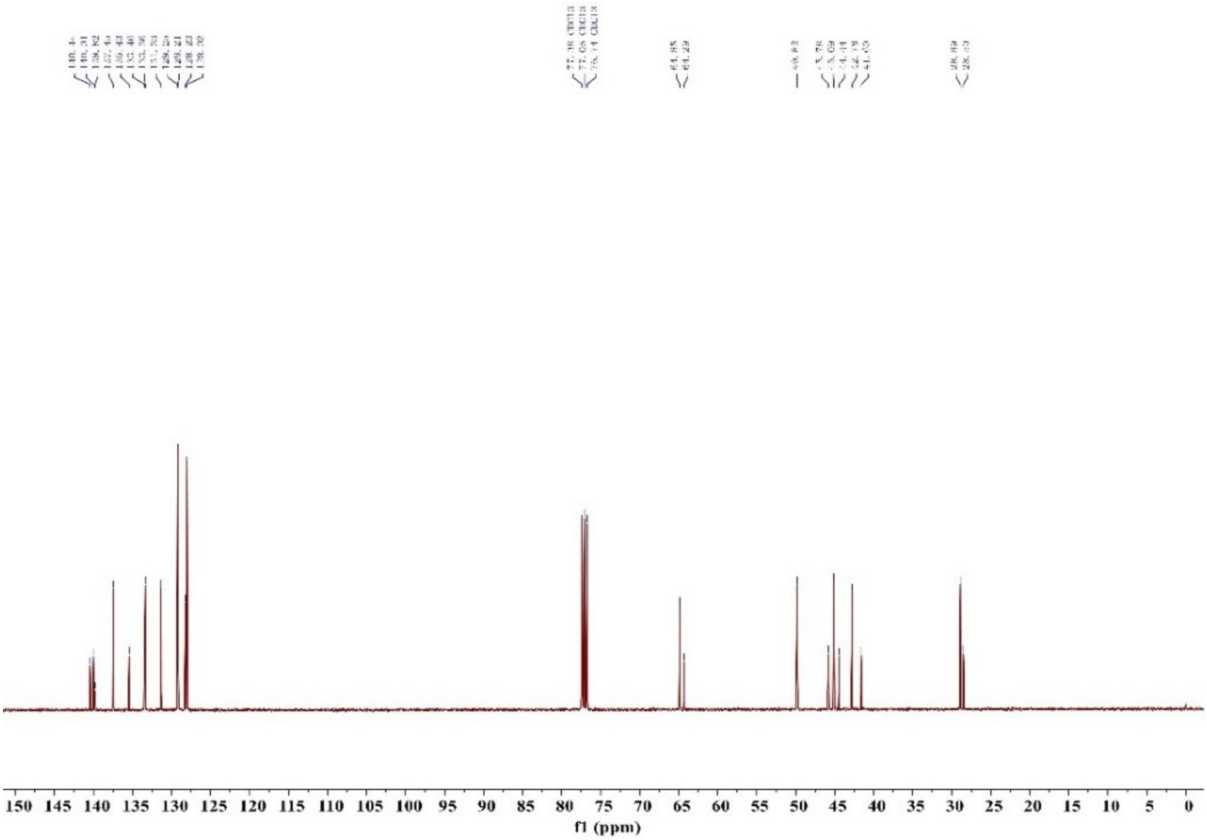
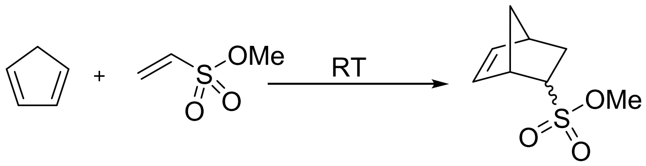


Figure S5. ^{13}C NMR spectrum of **$NBSO_2Ph$**. (101 MHz, $CDCl_3$).



Synthesis of $NBSO_3Me$: Freshly cracked cyclopentadiene (21.81 g, 330 mmol, 1.1 eq) was added drop-wise with stirring to methyl ethenesulfonate (36.64 g, 300 mmol, 1.0 eq) in THF (300 mL). The reaction mixture was stirred at room temperature until TLC indicated the complete consumption of methyl ethenesulfonate. After column chromatography, **$NBSO_3Me$** was obtained as a clear liquid. Yield: 52.5 g (93%, *endo*: *exo* = 8: 2).

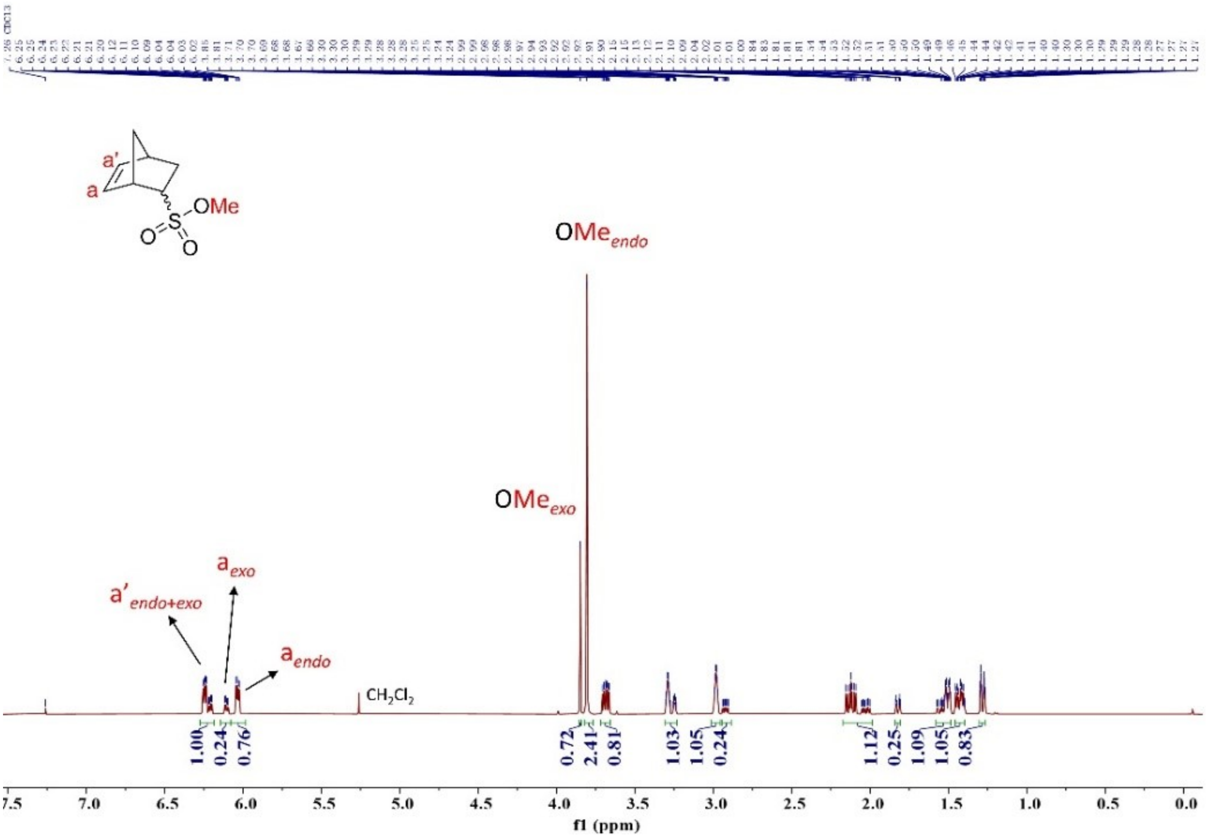


Figure S6. ^{1}H NMR spectrum of **NBSO$_3$Me**. (400 MHz, CDCl$_3$).

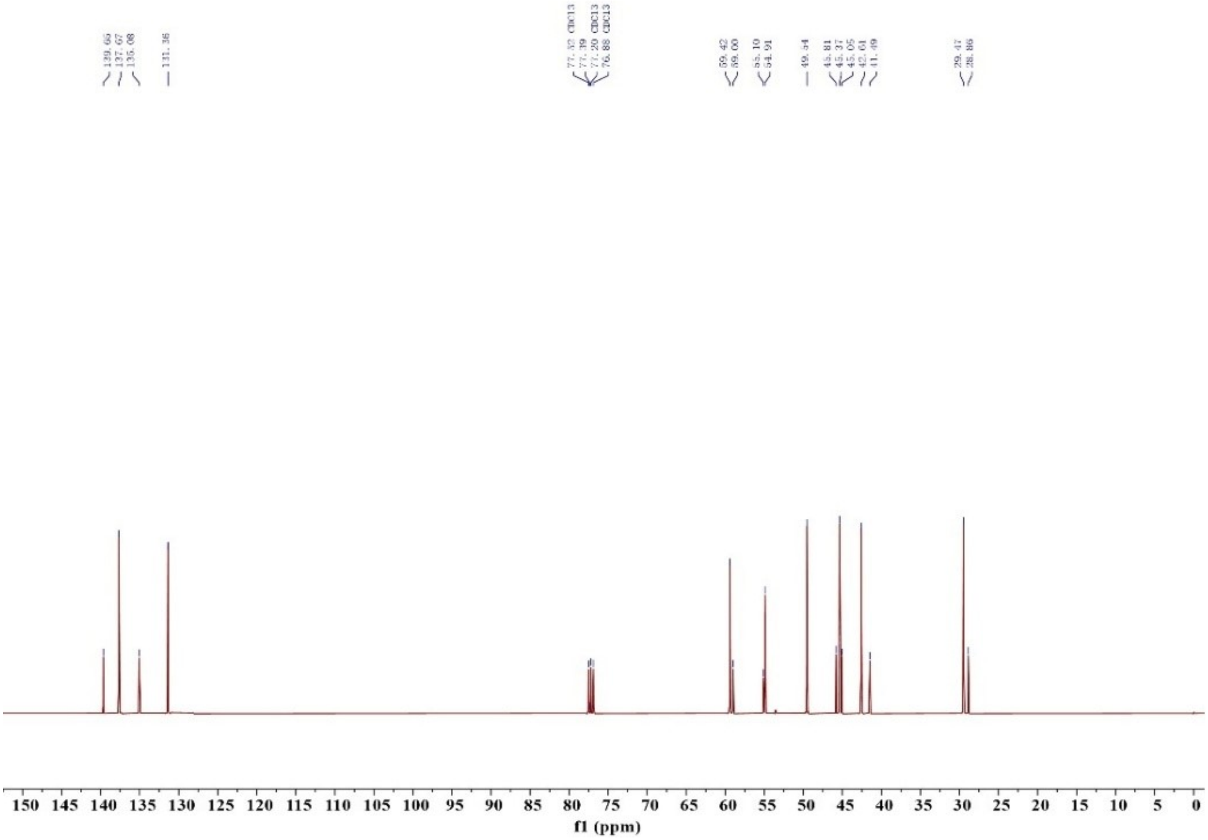
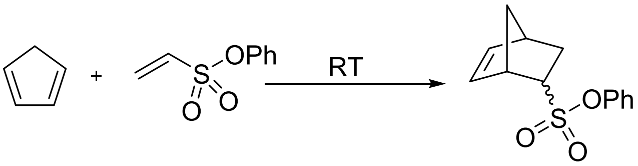


Figure S7. ^{13}C NMR spectrum of **NBSO$_3$Me**. (101 MHz, CDCl$_3$).



Synthesis of NBSO$_3$Ph: Freshly cracked cyclopentadiene (21.81 g, 330 mmol, 1.1 eq) was added drop-wise with stirring to phenyl ethenesulfonate (55.26 g, 300 mmol, 1.0 eq) in THF (300 mL). The reaction mixture was stirred at room temperature until TLC indicated the complete consumption of phenyl ethenesulfonate. After column chromatography, **NBSO$_3$Ph** was obtained as a white solid. Yield: 72.1 g (96%, *endo*: *exo* = 8: 2).

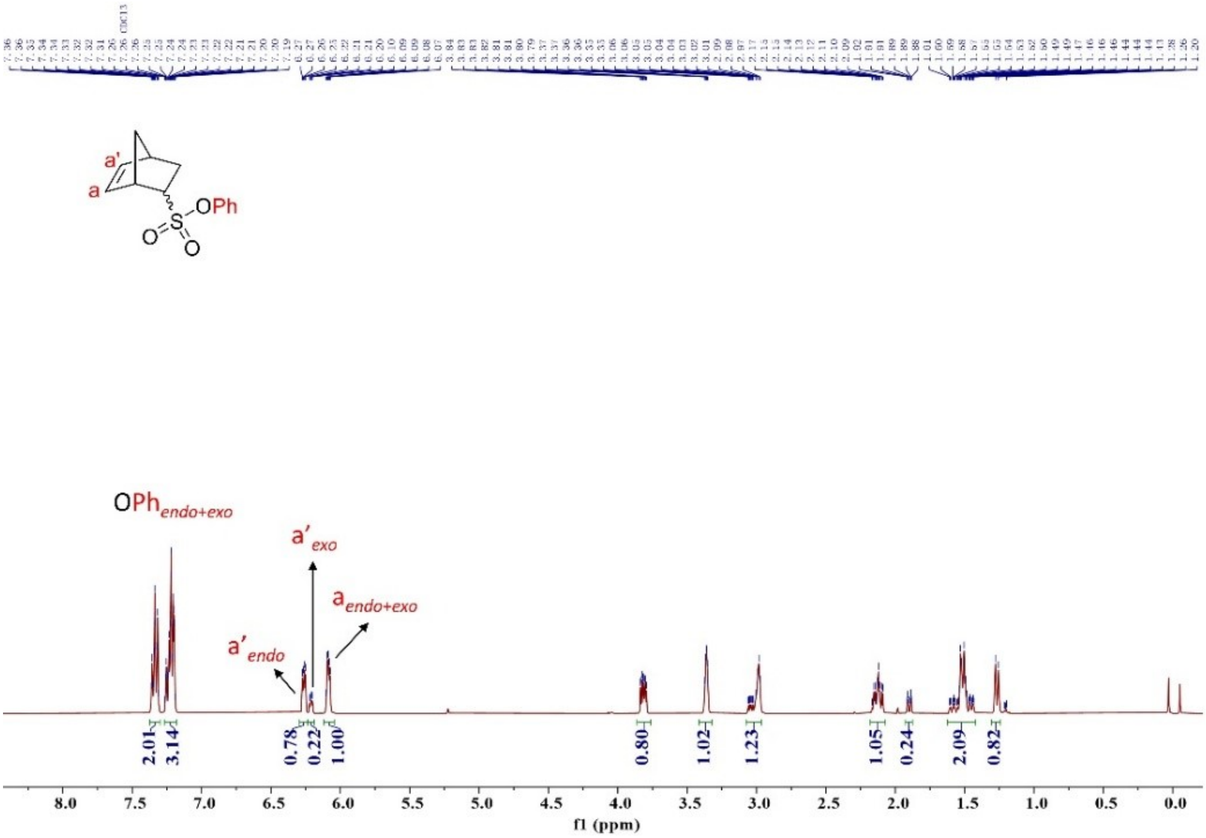


Figure S8. ^{1}H NMR spectrum of **NBSO$_3$Ph**. (400 MHz, CDCl$_3$).

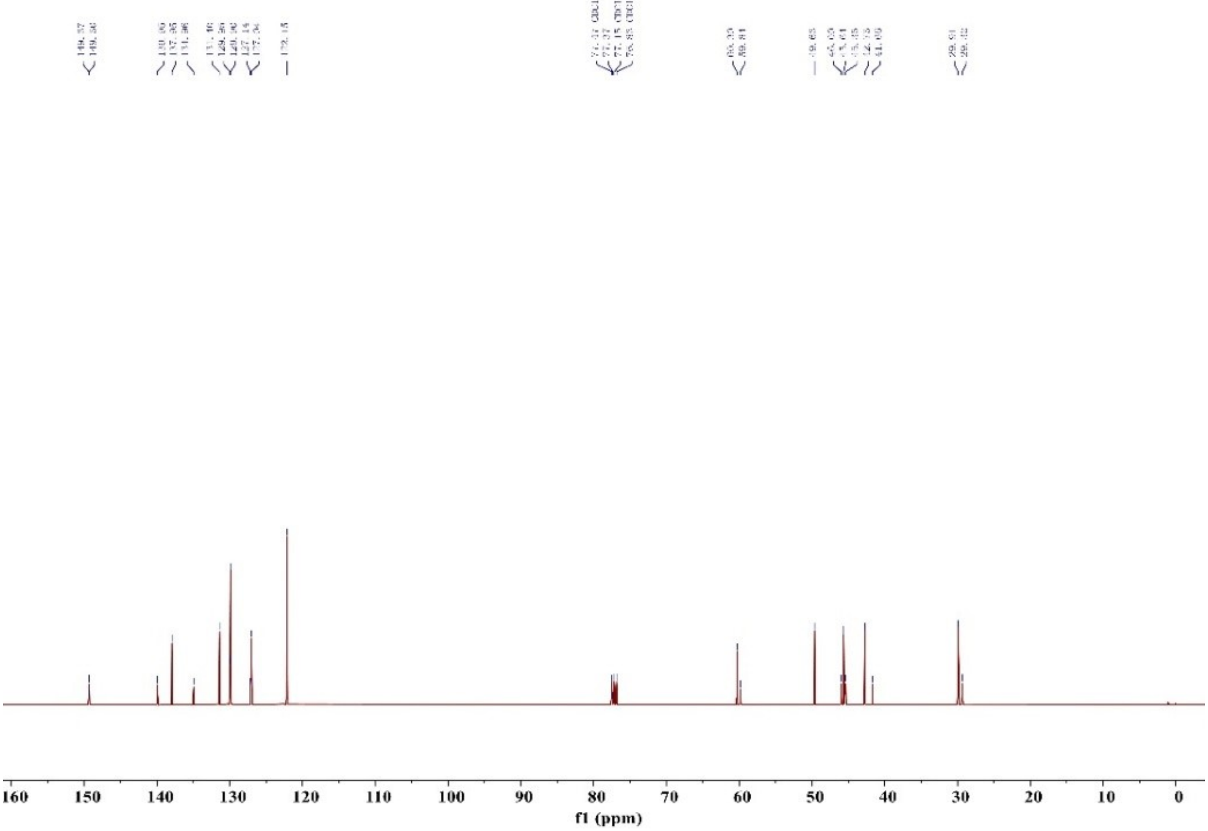
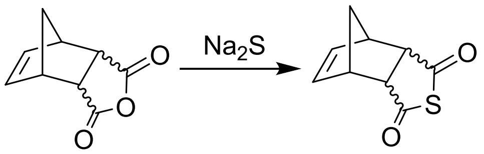


Figure S9. ^{13}C NMR spectrum of **NBSO$_3$Ph**. (101 MHz, CDCl$_3$).



Synthesis of CS-*endo*: The mixture, containing *endo-cis*-5-norbornene-2,3-dicarboxylic anhydride (32.83 g, 200 mmol) in THF (400 mL), was treated with sodium sulfide (7.8 g, 100 mmol) in 150 mL of water. The resulting mixture was stirred for 12h, poured into 500 mL of ethyl ether and separated. The aqueous phase was extracted with ethyl ether (2 x 250 mL). The combined ether extract was washed with water, saturated sodium bicarbonate and brine (2 x 250 mL), dried (magnesium sulfate), and evaporated under reduced pressure to afford the crude product. After column chromatography, **CS-*endo*** was obtained as a white solid. Yield: 20.2 g (56%). The NMR data is consistent with that found in the literature.[3]

Synthesis of CS-*exo*: A similar procedure to **CS-*endo*** except using *exo-cis*-5-norbornene-2,3-dicarboxylic anhydride. After column chromatography, **CS-*exo*** was obtained as a white solid. Yield: 16.2 g (45%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.32 (t, J = 2.0 Hz, 2H), 3.34 (p, J = 1.7 Hz, 2H), 3.15 (d, J = 1.5 Hz, 2H), 1.79 (dt, J = 9.7, 1.6 Hz, 1H), 1.63 (dt, J = 9.8, 1.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 201.43, 138.92, 61.18, 48.08, 43.63.

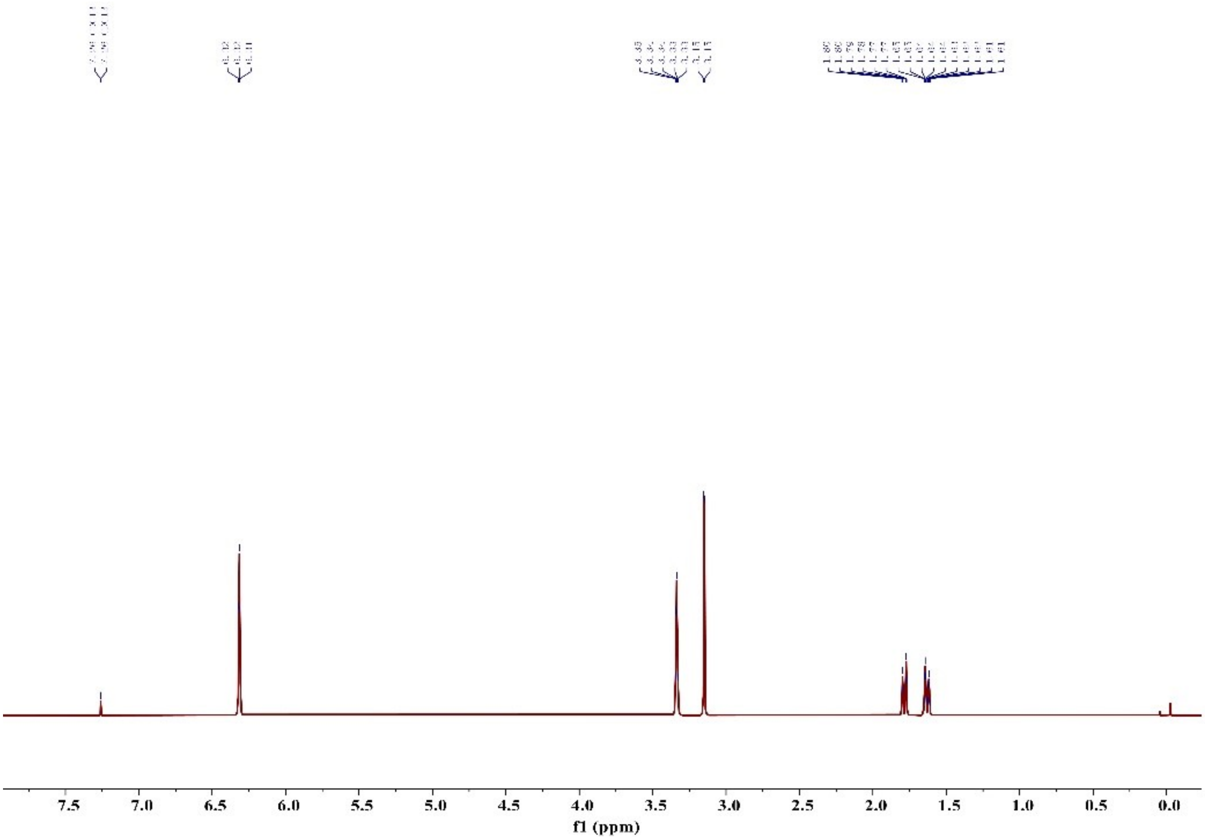


Figure S10. ^{1}H NMR spectrum of **CS-*exo***. (400 MHz, $CDCl_3$).

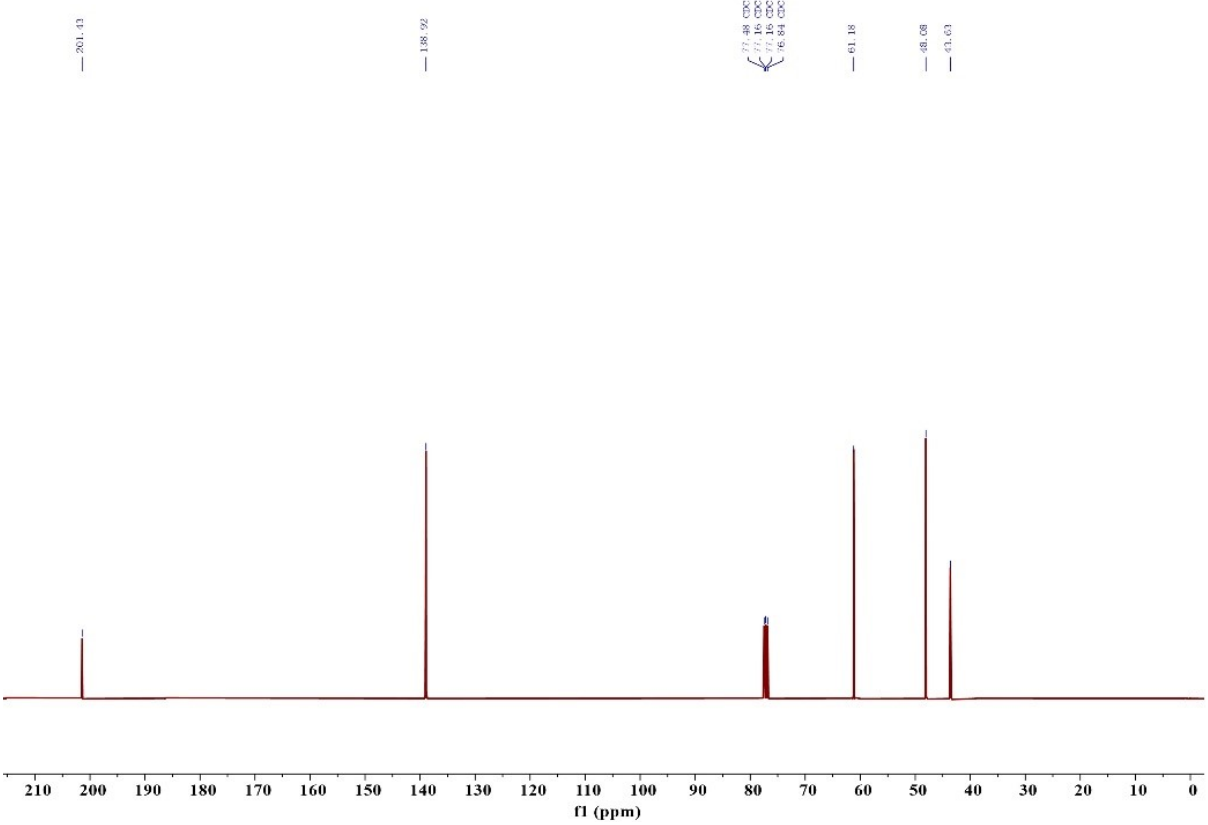


Figure S11. ^{13}C NMR spectrum of **CS-*exo***. (101 MHz, $CDCl_3$).

2.3 Procedure for copolymerization.

In a typical experiment, a 350 mL glass thick-walled pressure vessel was charged with toluene, a desired amount of comonomer and a magnetic stir bar in the glovebox (A stainless steel Parr autoclave equipped with mechanical stirring was used for the runs at ethylene pressure of 8 atm). The pressure vessel was connected to a high-pressure line and the solution was degassed. The vessel was warmed to the desire temperature using an oil bath and allowed to equilibrate for 5 min. The palladium catalyst in CH_2Cl_2 (1 mL) was injected into the polymerization system via syringe. With rapid stirring, the reactor was pressurized, maintained at a desired ethylene pressure, and stirred continuously for the desired period of time. Then the pressure vessel was vented; the polymerization was quenched via the addition of methanol (20 mL) and the polymer was precipitated using excess methanol. After filtration, the copolymer was obtained and dried at 50 °C for 24 h under vacuum. The polar monomer incorporation (mol %) was calculated from NMR analysis.

2.4 Synthesis of P-SO_3H

Polymer samples (500 mg) were suspended in 15 mL of ethanol in a round bottom flask. 5 mL of a 25 wt% sodium methoxide in methanol solution was added to the mixture and the reaction was allowed to reflux for 72 h under argon. After the reaction was cooled, 5 mL of 12 M hydrochloric acid was added dropwise while stirring. The mixture was allowed to reflux for 24 h under argon. After the reactions were cooled and concentrated, the flasks were flooded with a cold 2 m hydrochloric acid solution. Polymers were filtered, washed twice more with the acid solution, and the sulfonic acid polymer was collected and dried under vacuum.

3. Characterization of copolymers

3.1 NMR spectra of copolymers.

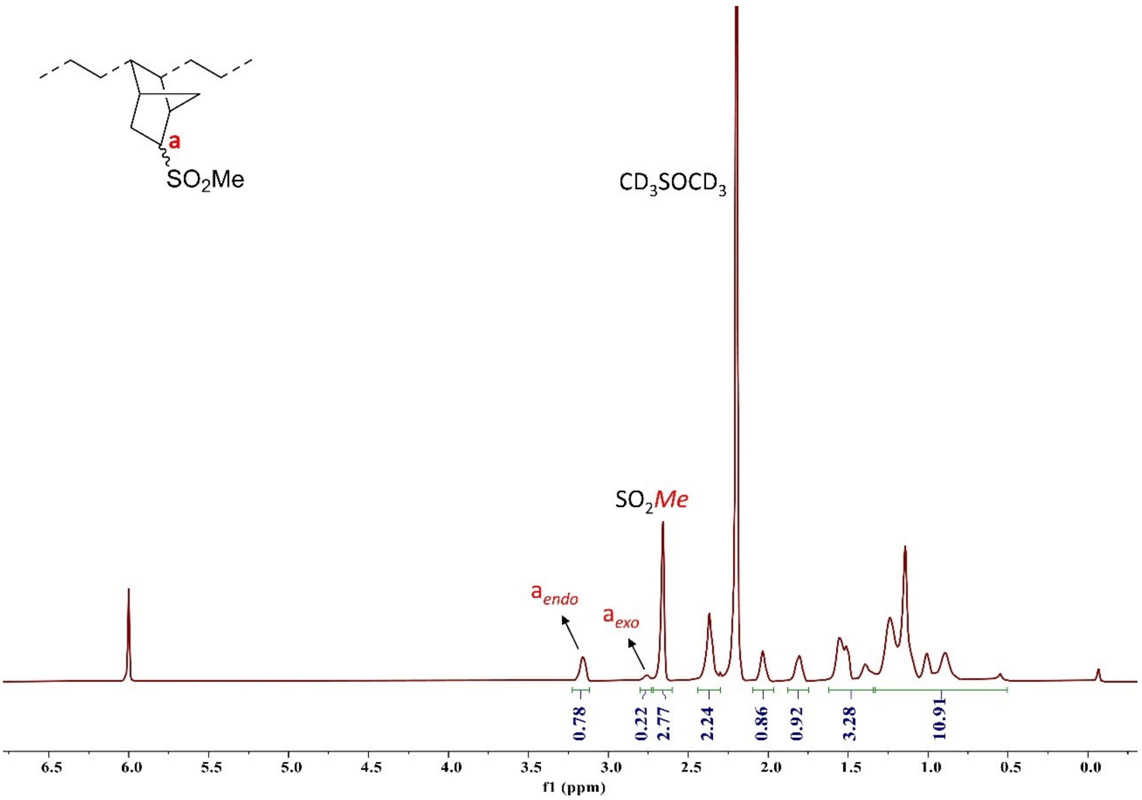


Figure S12. ^{1}H NMR spectrum of the copolymer from Table 1, entry 1. ($C_2D_2Cl_4/CD_3SOCD_3$ = 4 v/v, 120 °C).

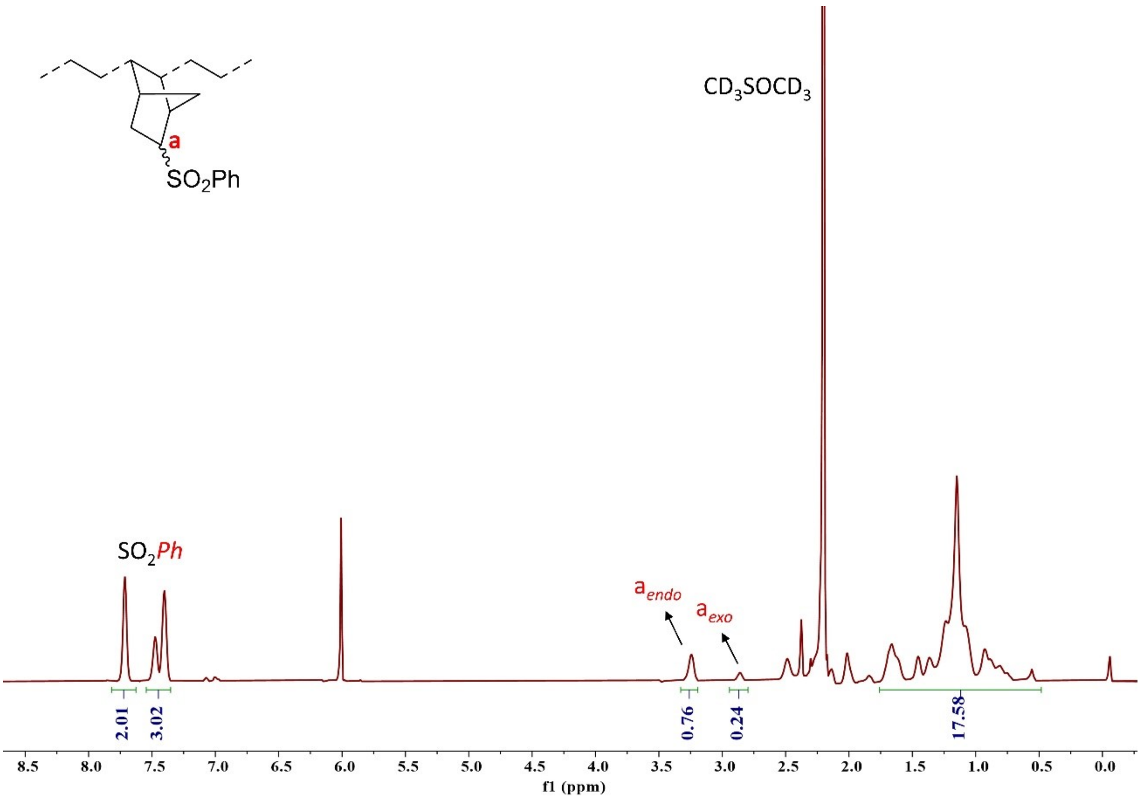


Figure S13. ^{1}H NMR spectrum of the copolymer from Table 1, entry 2. ($C_2D_2Cl_4/CD_3SOCD_3$ = 4 v/v, 120 °C).

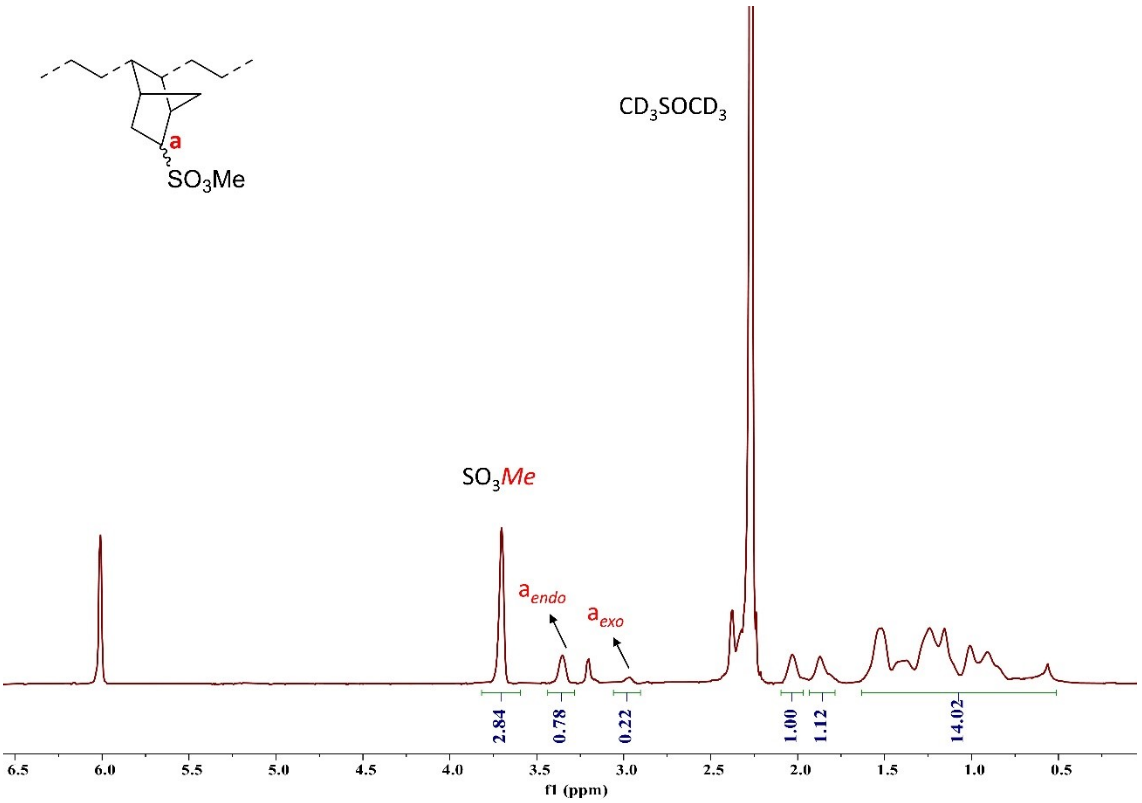


Figure S14. ^{1}H NMR spectrum of the copolymer from Table 1, entry 3. ($C_2D_2Cl_4/CD_3SOCD_3$ = 4 v/v, 120 °C).

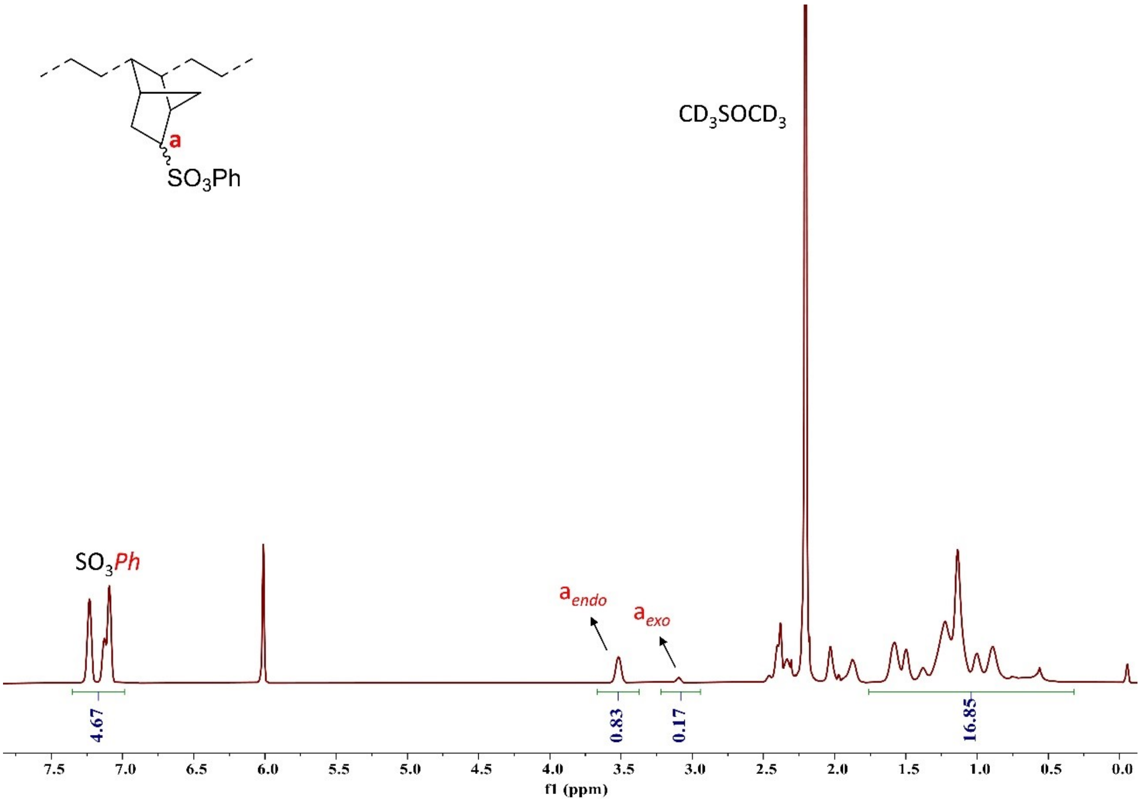


Figure S15. ^{1}H NMR spectrum of the copolymer from Table 1, entry 4. ($C_2D_2Cl_4/CD_3SOCD_3$ = 4 v/v, 120 °C).

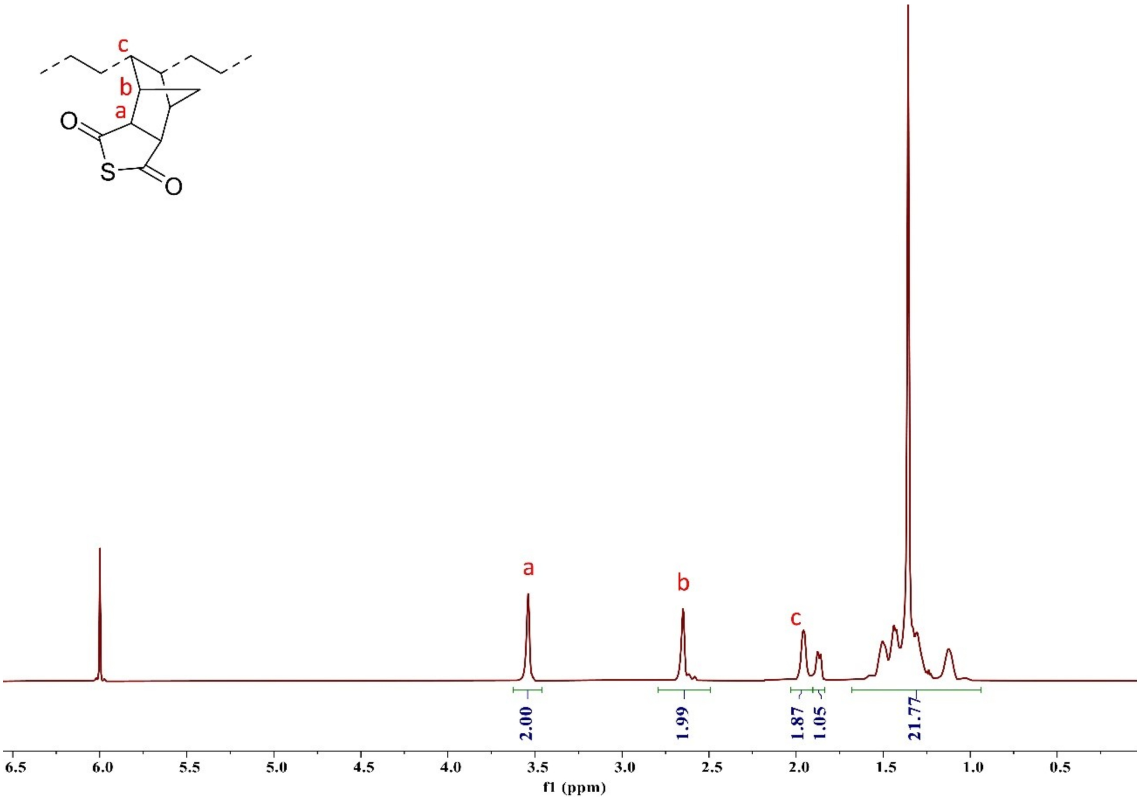


Figure S16. ^{1}H NMR spectrum of the copolymer from Table 1, entry 5. ($C_2D_2Cl_4$, 120 °C).

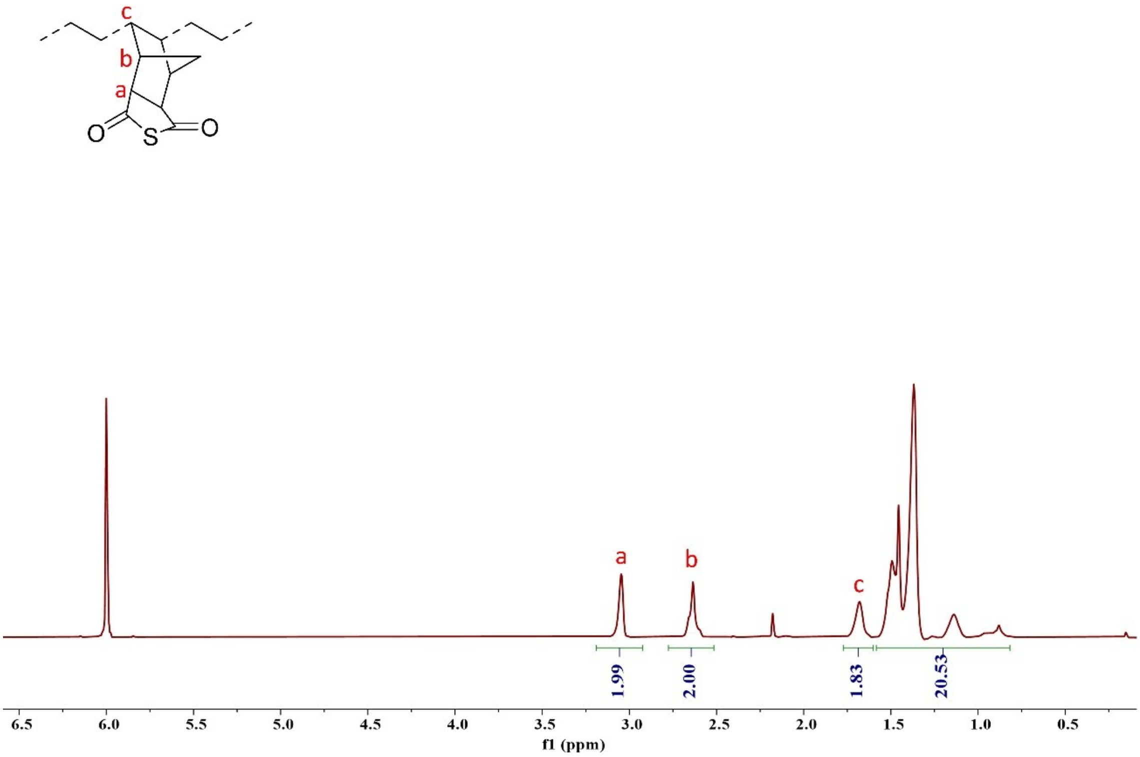


Figure S17. ^{1}H NMR spectrum of the copolymer from Table 1, entry 6. ($C_2D_2Cl_4$, 120 °C).

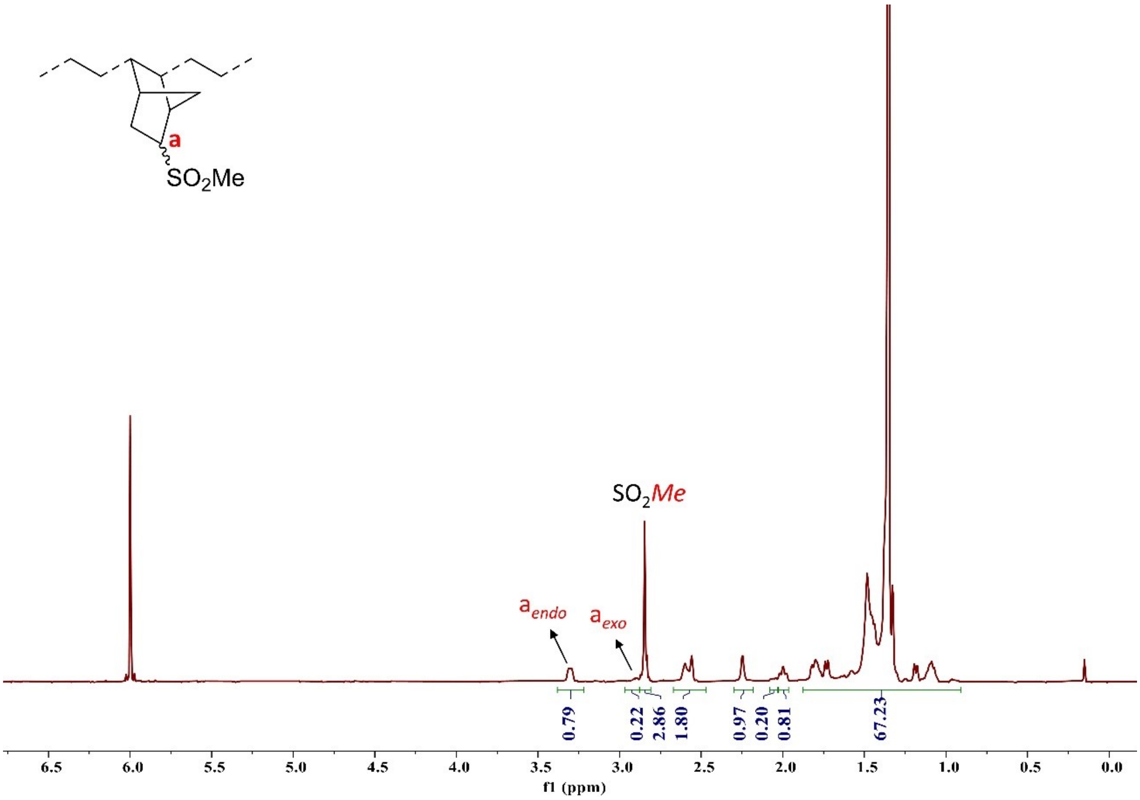


Figure S18. ^{1}H NMR spectrum of the copolymer from Table 1, entry 7. ($C_2D_2Cl_4$, 120 ^{o}C).

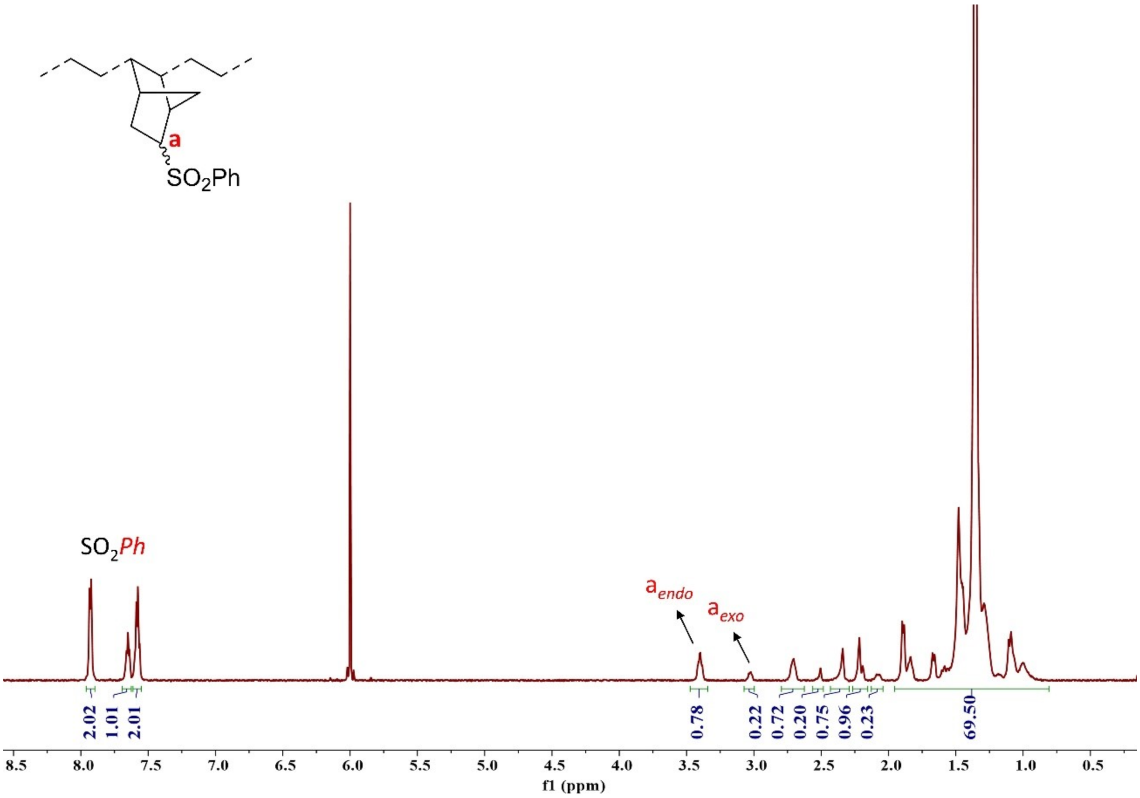


Figure S19. ^{1}H NMR spectrum of the copolymer from Table 1, entry 8. ($C_2D_2Cl_4$, 120 ^{o}C).

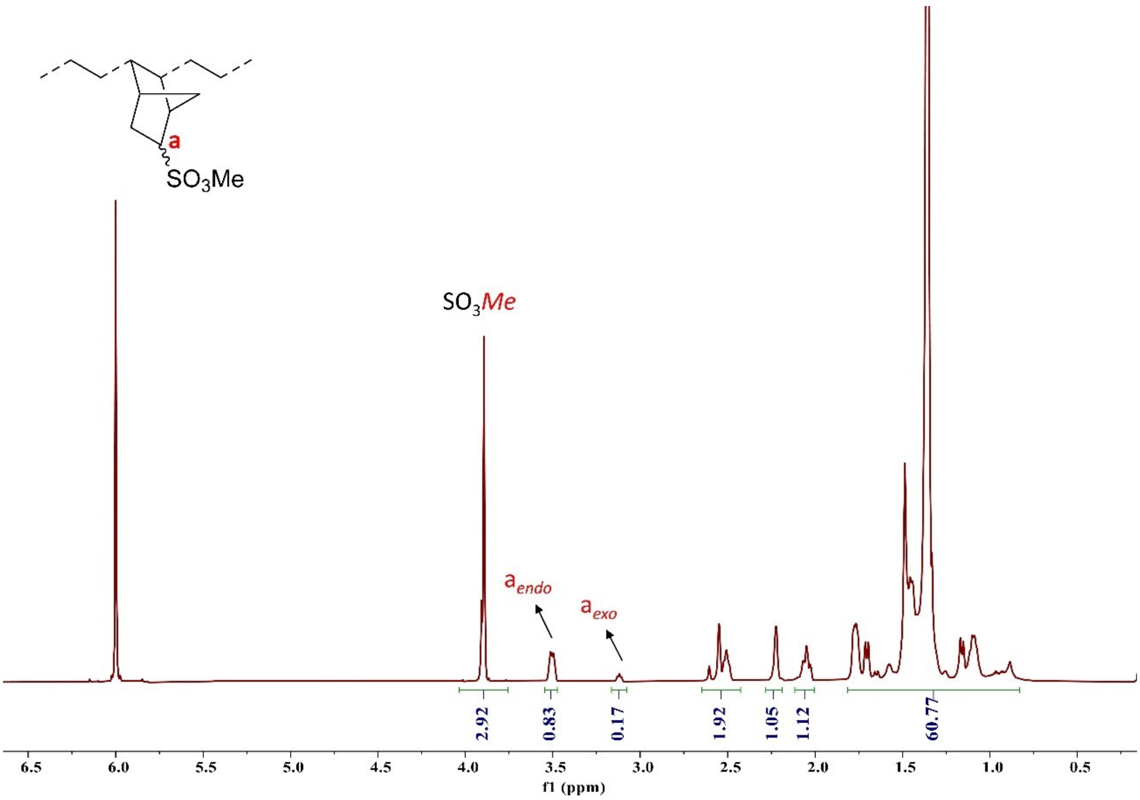


Figure S20. ^{1}H NMR spectrum of the copolymer from Table 1, entry 9. ($C_2D_2Cl_4$, 120 ^{o}C).

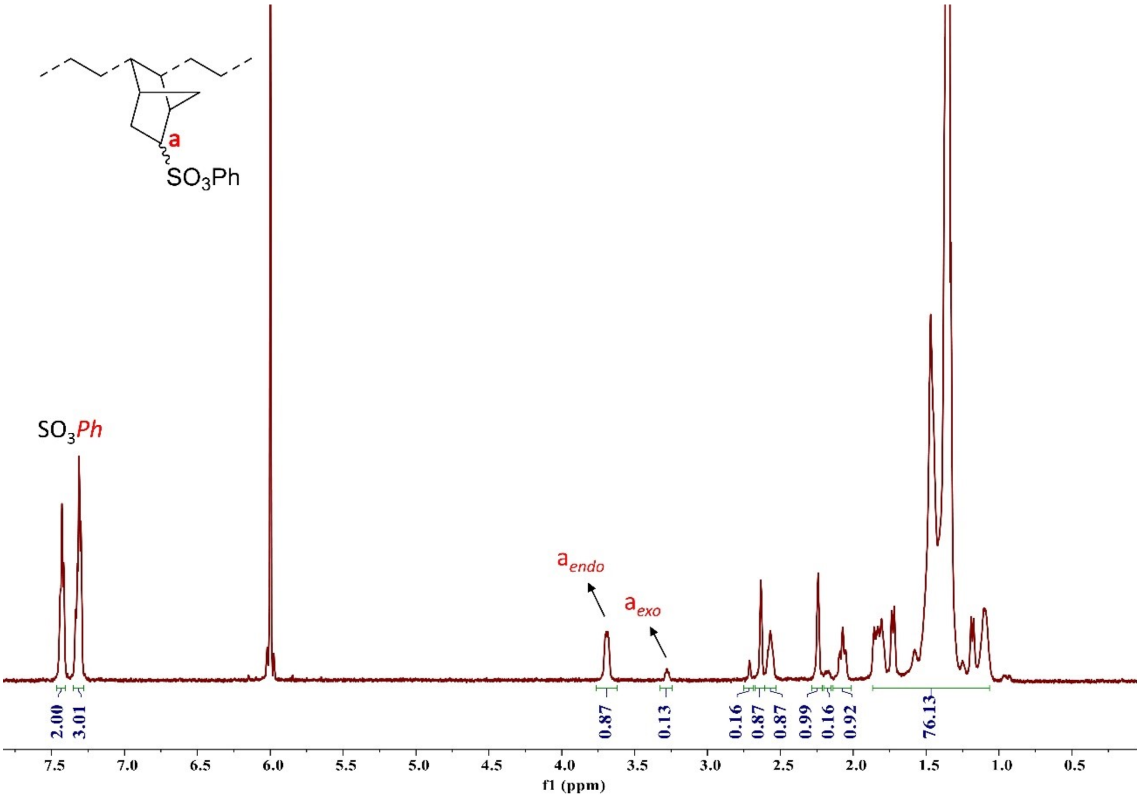


Figure S21. ^{1}H NMR spectrum of the copolymer from Table 1, entry 10. ($C_2D_2Cl_4$, 120 ^{o}C).

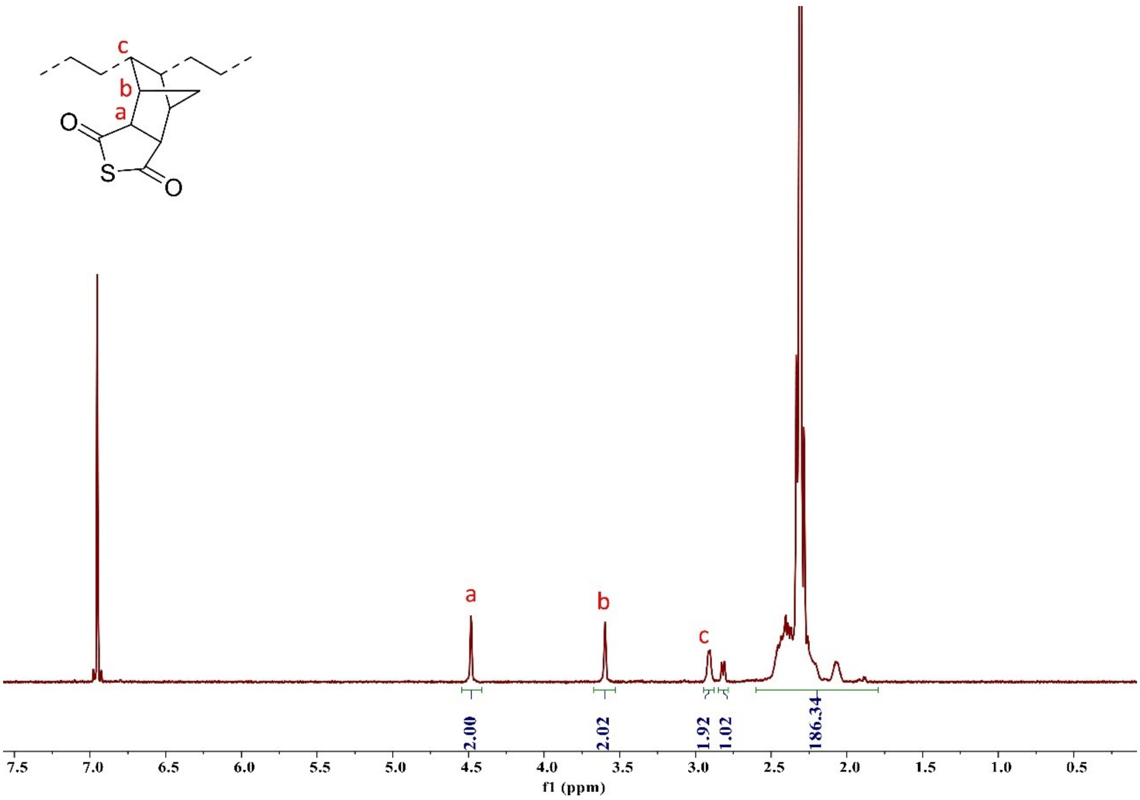


Figure S22. ^{1}H NMR spectrum of the copolymer from Table 1, entry 11. ($C_2D_2Cl_4$, 120 ^{o}C).

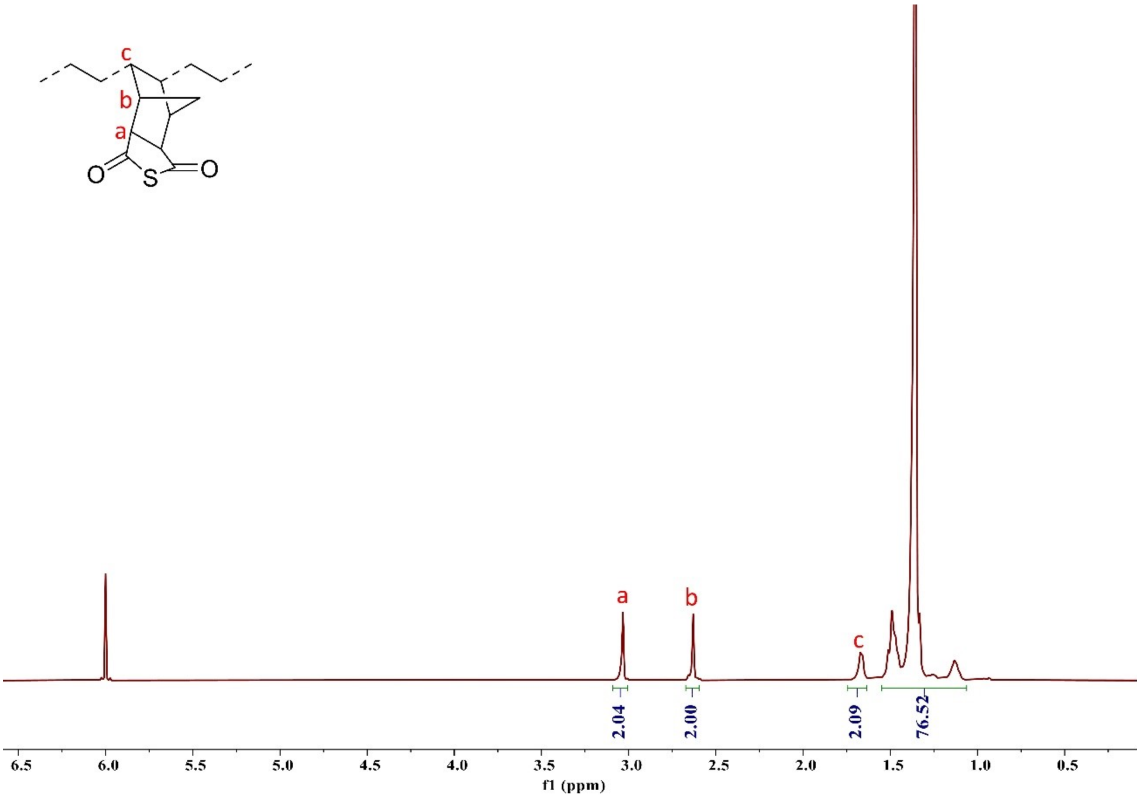


Figure S23. ^{1}H NMR spectrum of the copolymer from Table 1, entry 12. ($C_2D_2Cl_4$, 120 ^{o}C).

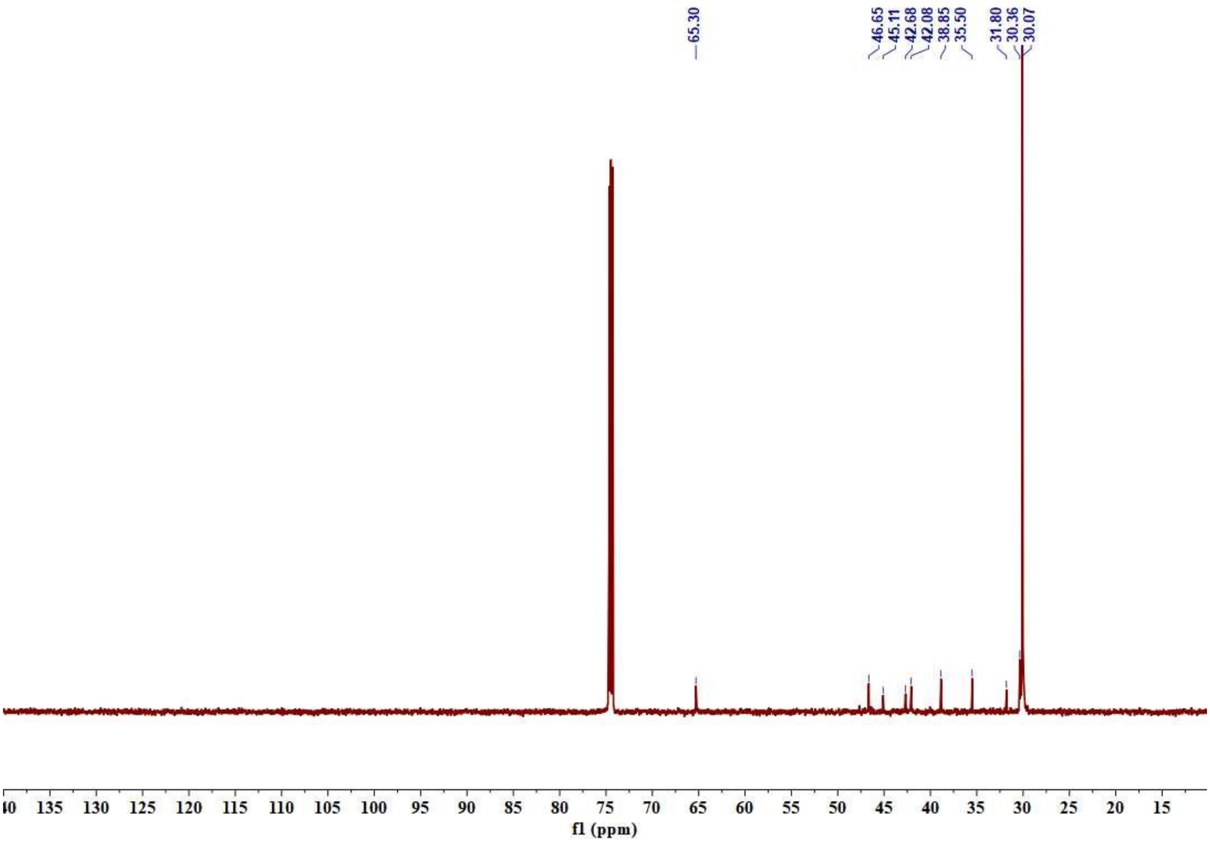


Figure S24. ^{13}C NMR spectrum of the copolymer from Table 1, entry 7. ($C_2D_2Cl_4$, 120 ^{o}C).

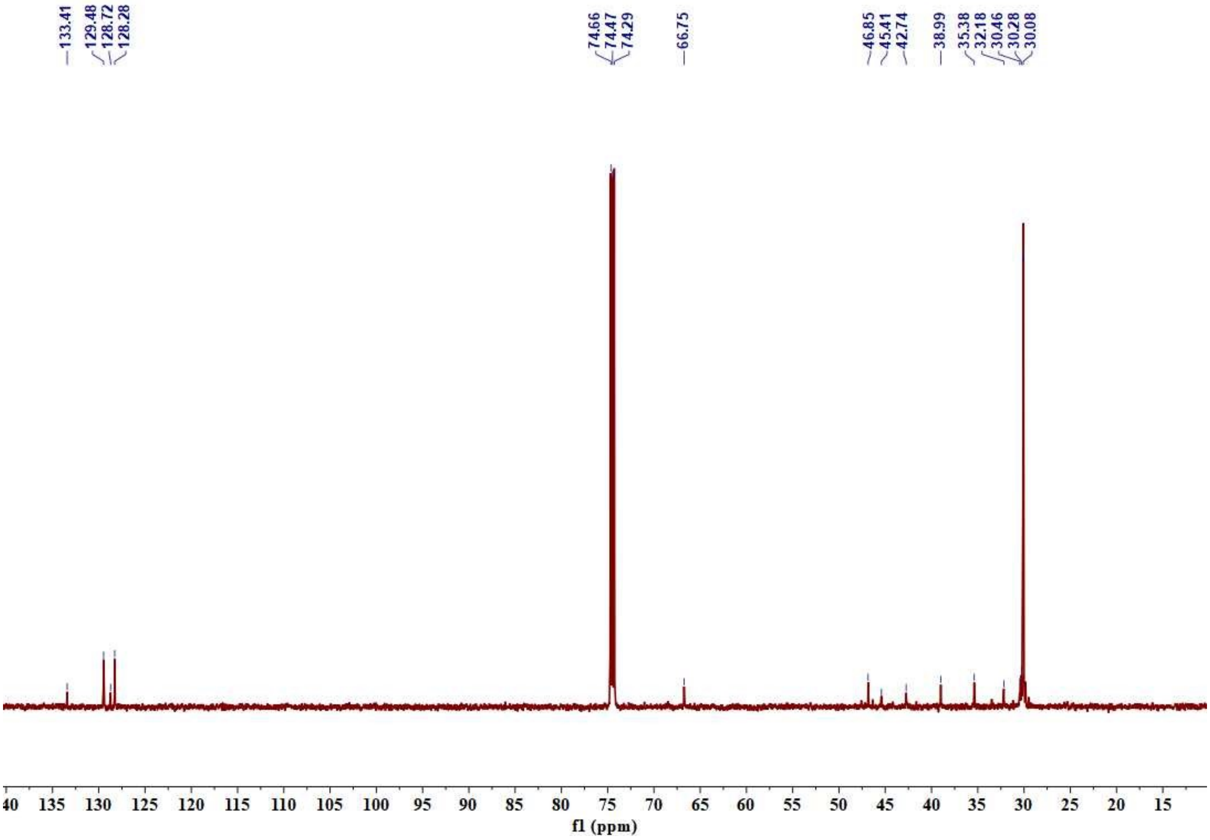


Figure S25. ^{13}C NMR spectrum of the copolymer from Table 1, entry 8. ($C_2D_2Cl_4$, 120 ^{o}C).

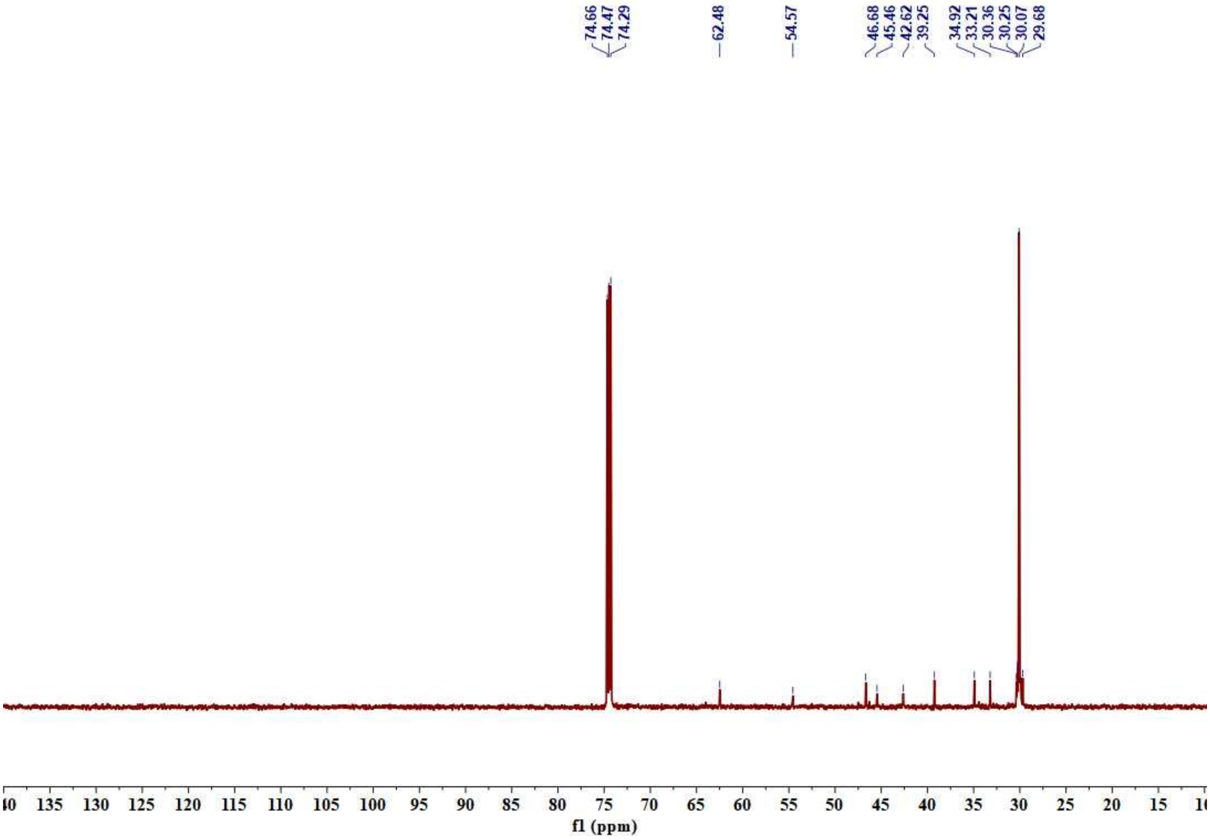


Figure S26. ^{13}C NMR spectrum of the copolymer from Table 1, entry 9. ($C_2D_2Cl_4$, 120 ^{o}C).

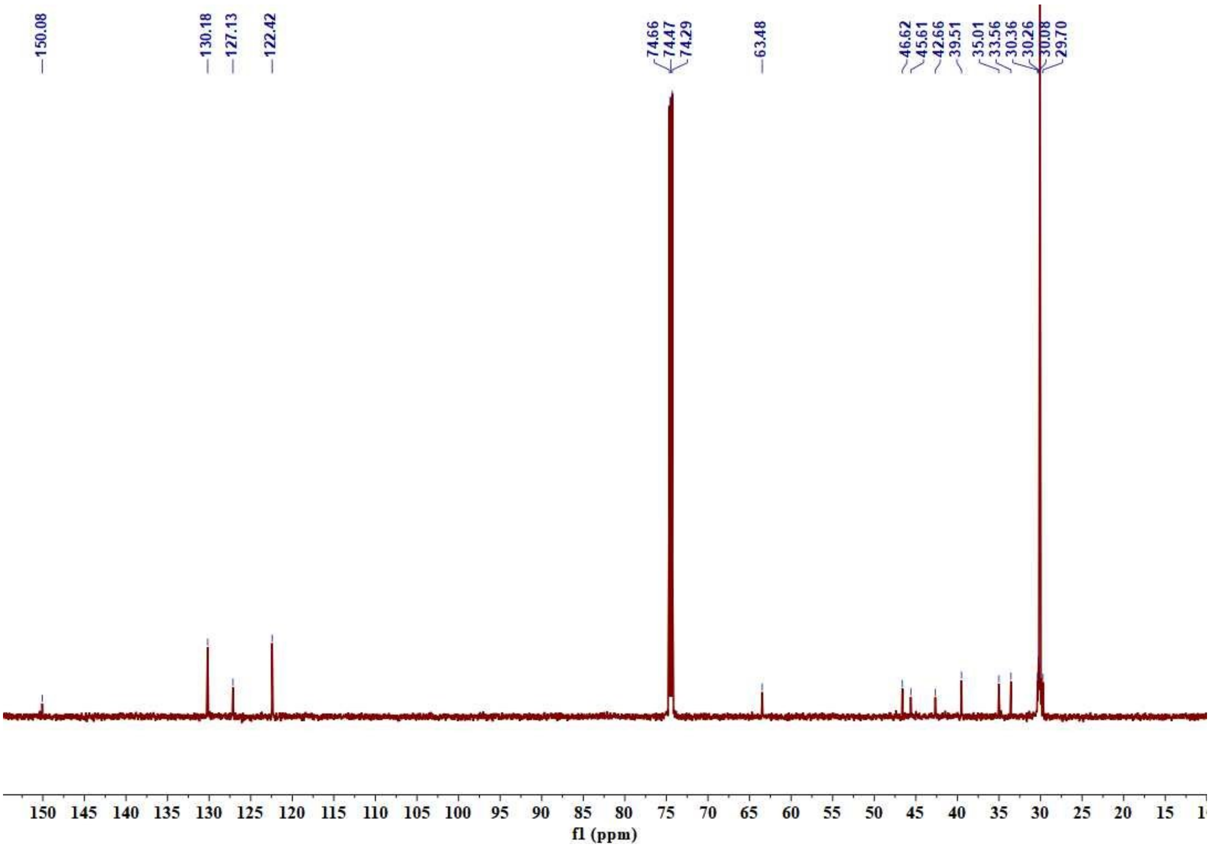


Figure S27. ^{13}C NMR spectrum of the copolymer from Table 1, entry 10. ($C_2D_2Cl_4$, 120 ^{o}C).

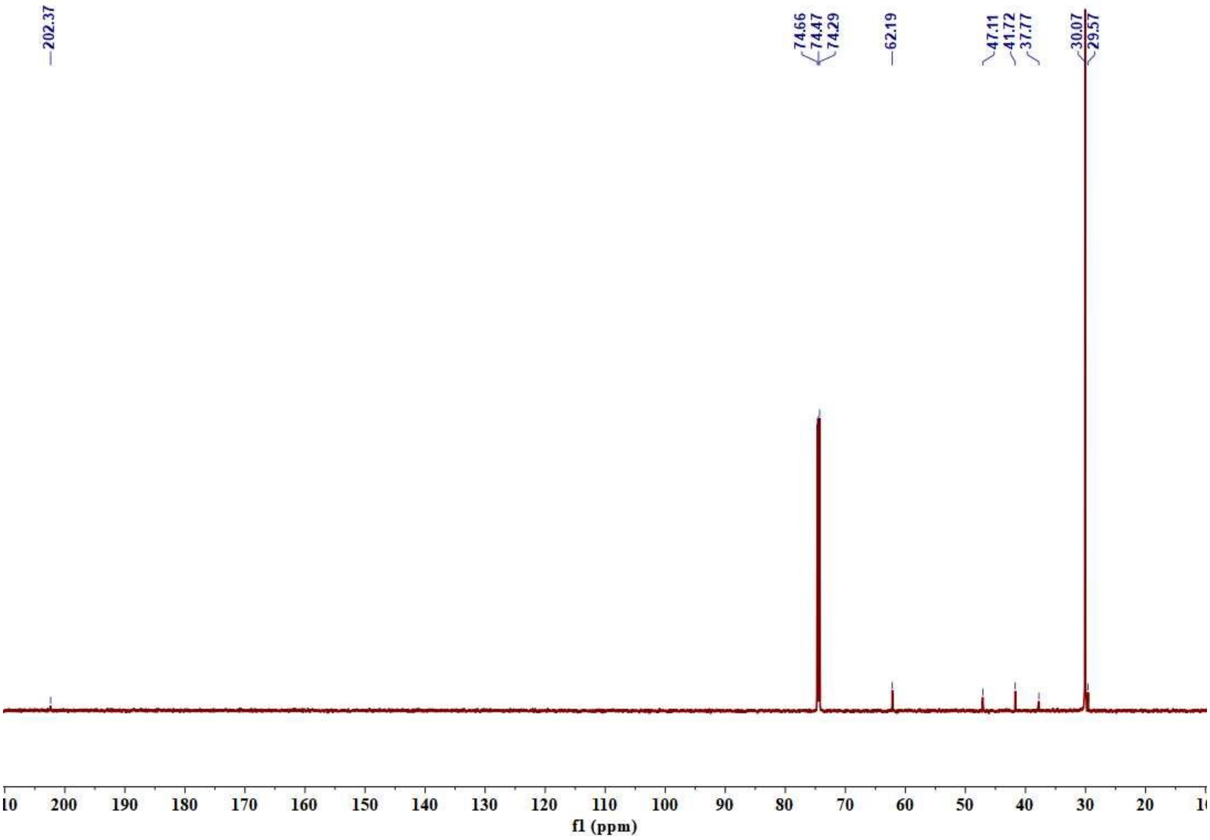


Figure S28. ^{13}C NMR spectrum of the copolymer from Table 1, entry 11. ($C_2D_2Cl_4$, 120 °C).

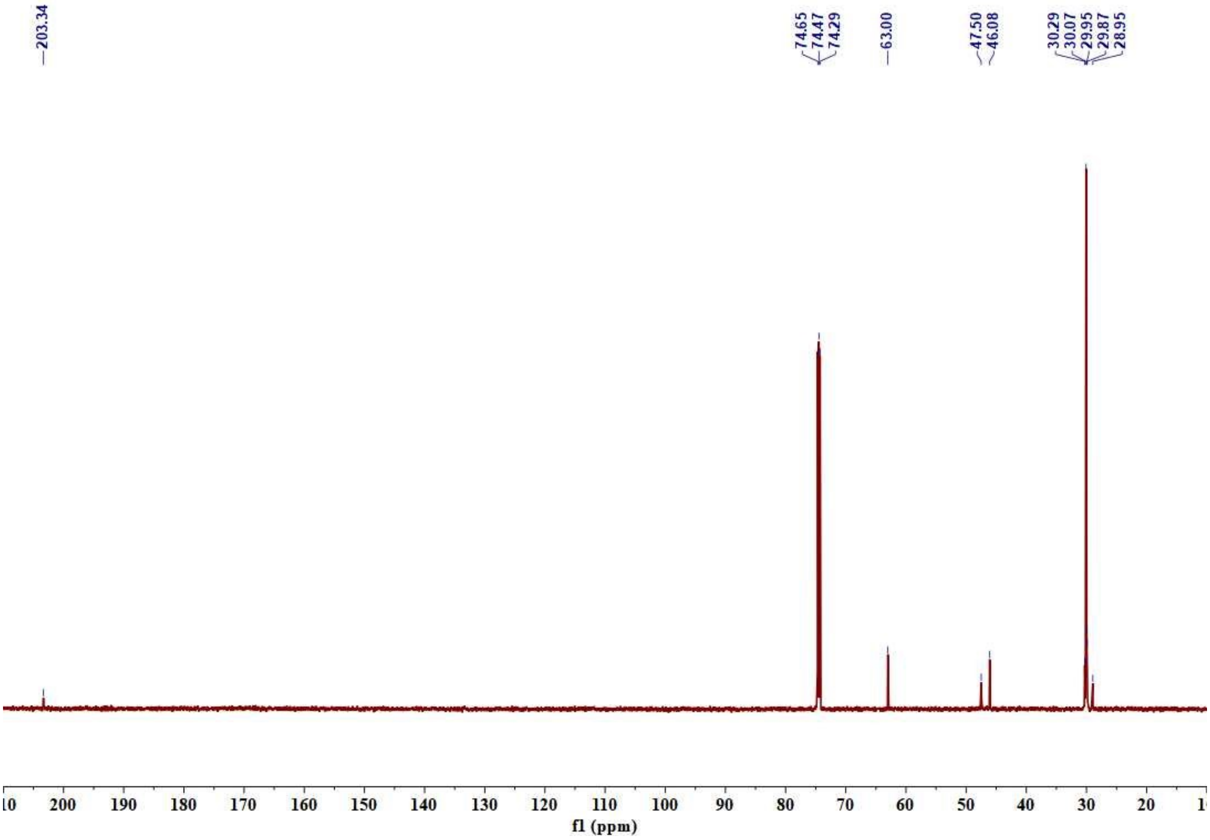
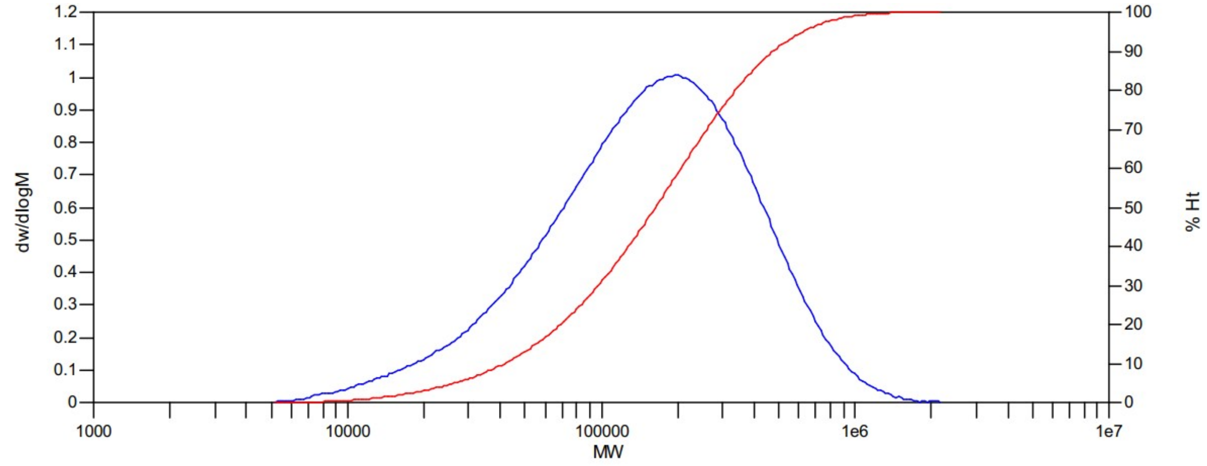


Figure S29. ^{13}C NMR spectrum of the copolymer from Table 1, entry 12. ($C_2D_2Cl_4$, 120 °C).

3.2 GPC of copolymers.



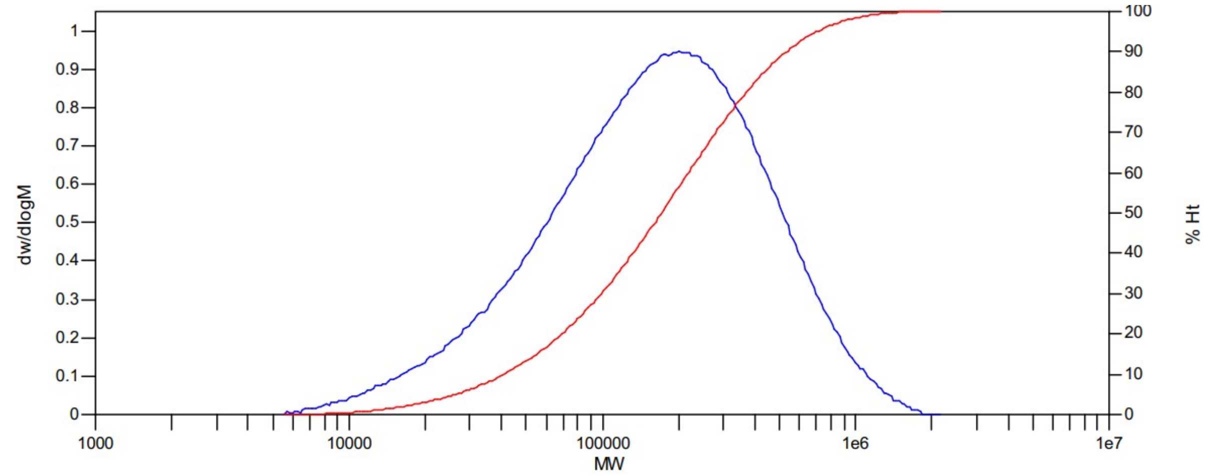
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	195806	89411	219771	403262	619636	197530	2.45799

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.37	13.07	15.63	-7.70726	0	747.823	100

Figure S30. GPC of the copolymer from table1, entry 1.



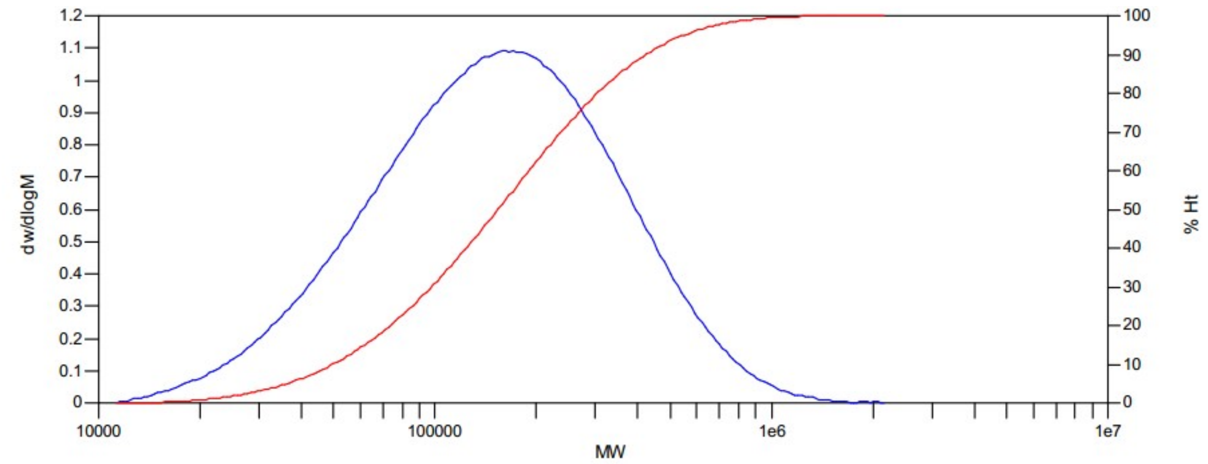
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	200474	90817	238427	453845	688565	212416	2.62536

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.37	13.05	15.58	-4.52815	0	468.318	100

Figure S31. GPC of the copolymer from table1, entry 3.



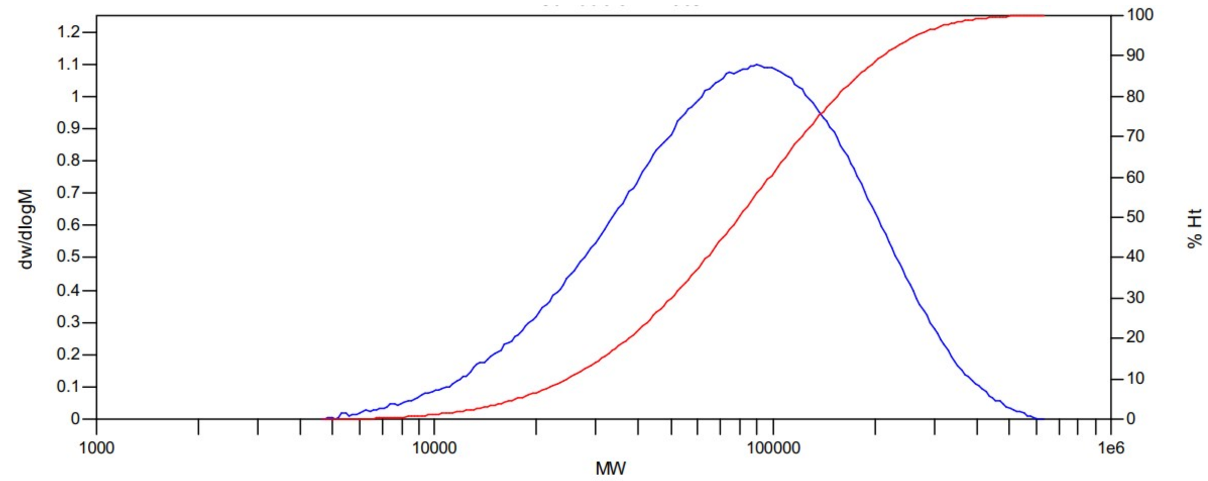
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	169991	104358	202742	353365	548143	184998	1.94275

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.37	13.17	15.08	9.61475	0	861.7	100

Figure S32. GPC of the copolymer from table1, entry 4.



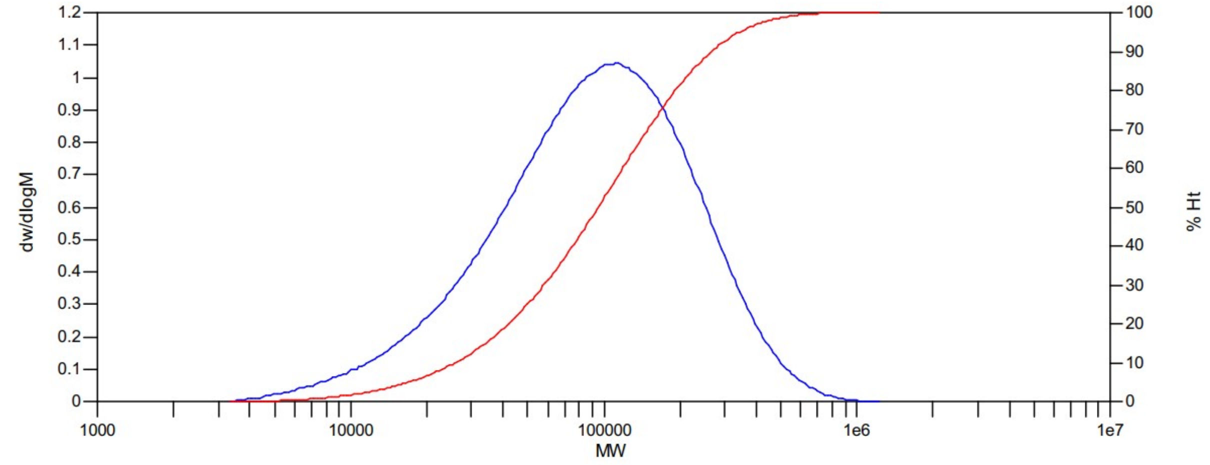
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	89976	51717	100961	164841	230831	92700	1.95218

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.23	13.62	15.72	4.33204	0	385.371	100

Figure S33. GPC of the copolymer from table1, entry 5.



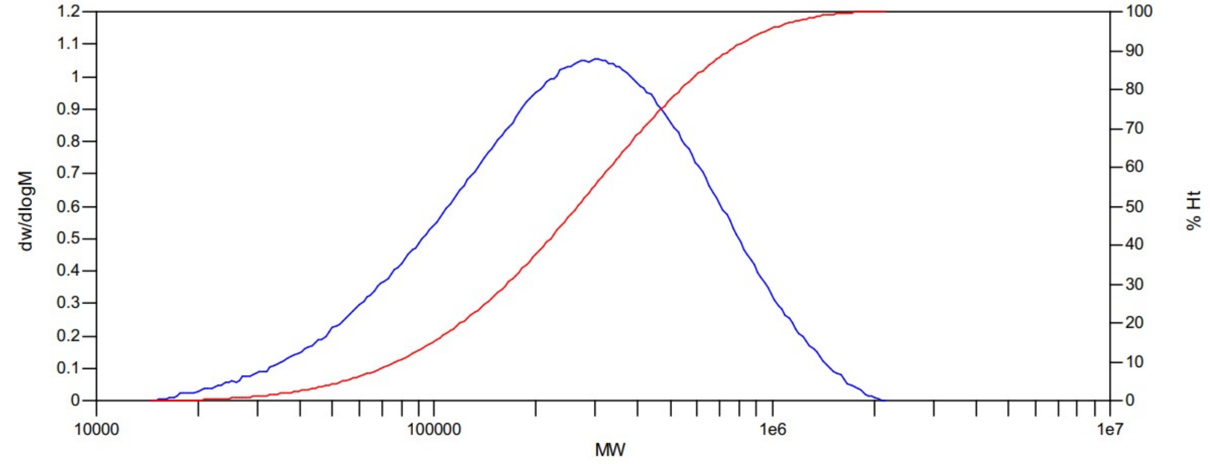
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	113884	55033	124898	218939	324472	113190	2.26951

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.77	13.45	15.95	9.48617	0	888.808	100

Figure S34. GPC of the copolymer from table1, entry 6.



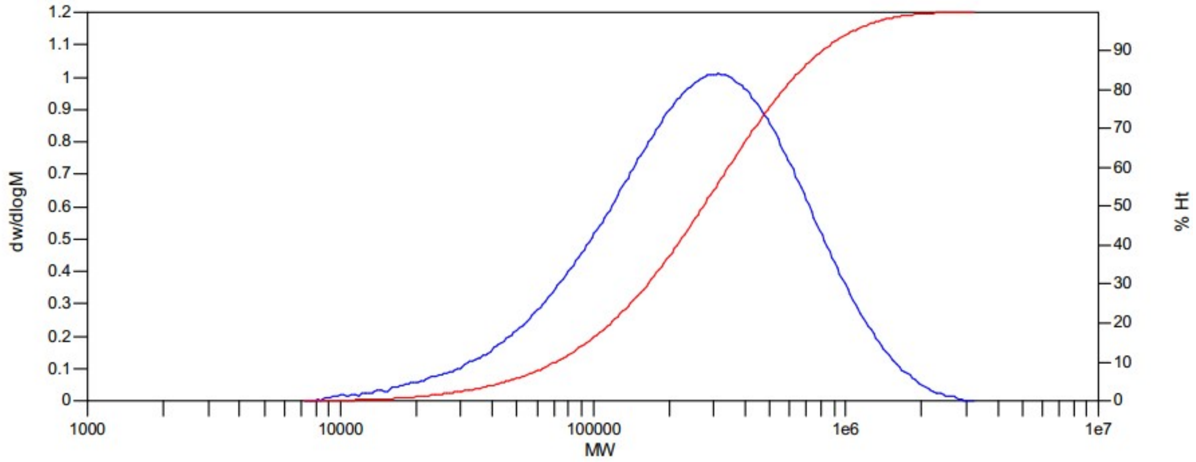
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	299243	166031	347869	591783	839501	316755	2.09521

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.37	12.77	14.92	-3.8043	0	352.9	100

Figure S35. GPC of the copolymer from table1, entry 8.



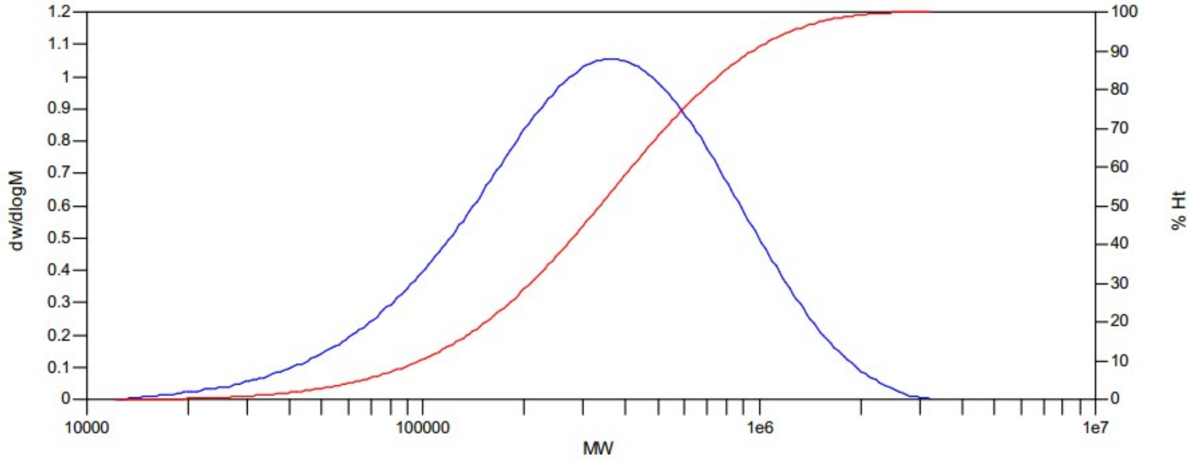
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	313682	149577	369729	679037	1029349	332231	2.47183

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.08	12.73	15.40	-6.36598	0	615.551	100

Figure S36. GPC of the copolymer from table1, entry 10.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	352904	204347	445849	780411	1147823	404541	2.18182

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.08	12.65	15.03	-10.2184	0	946.446	100

Figure S37. GPC of the copolymer from table1, entry 12.

3.3 DSC of copolymers.

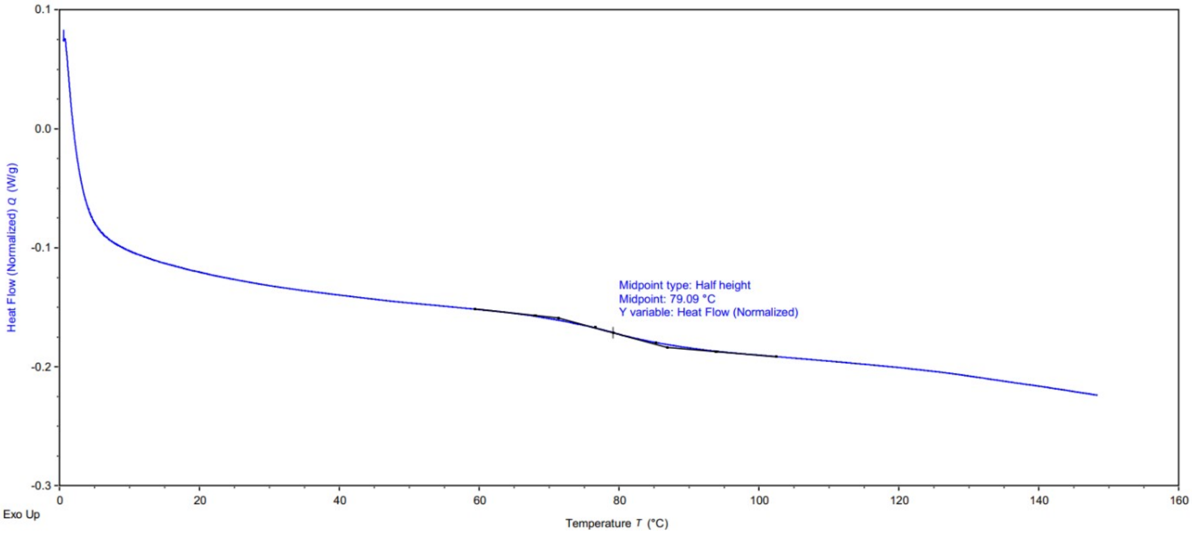


Figure S38. DSC of the copolymer from Table 1, entry 3.

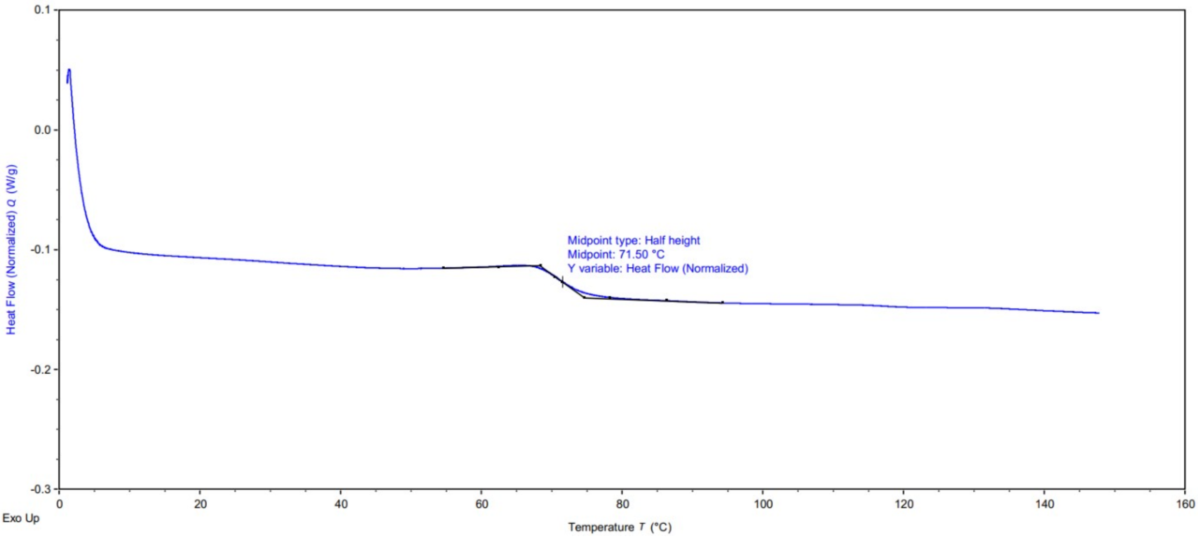


Figure S39. DSC of the copolymer from Table 1, entry 4.

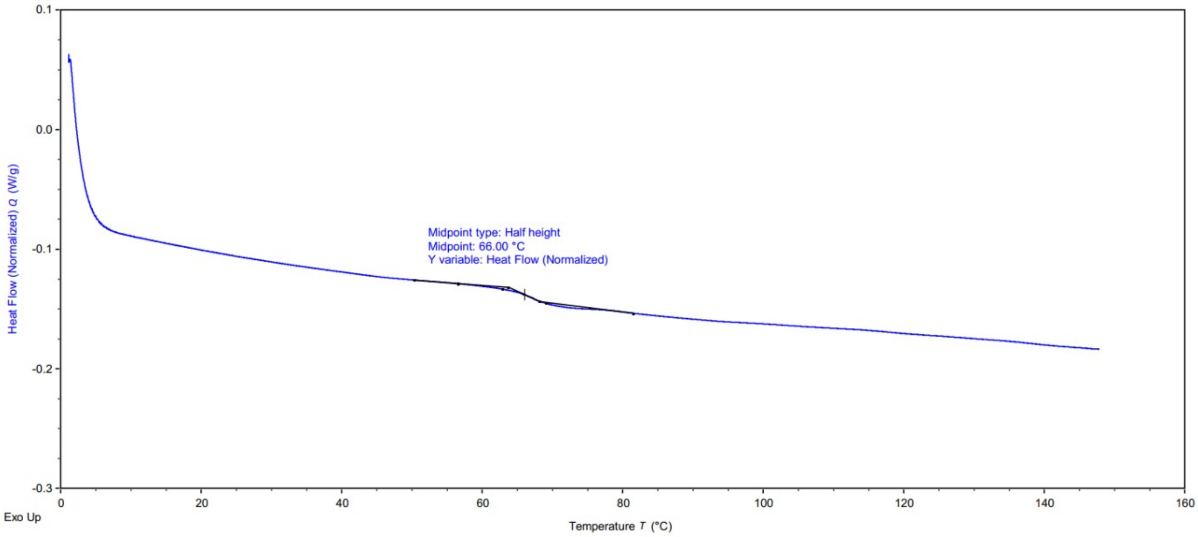


Figure S40. DSC of the copolymer from Table 1, entry 6.

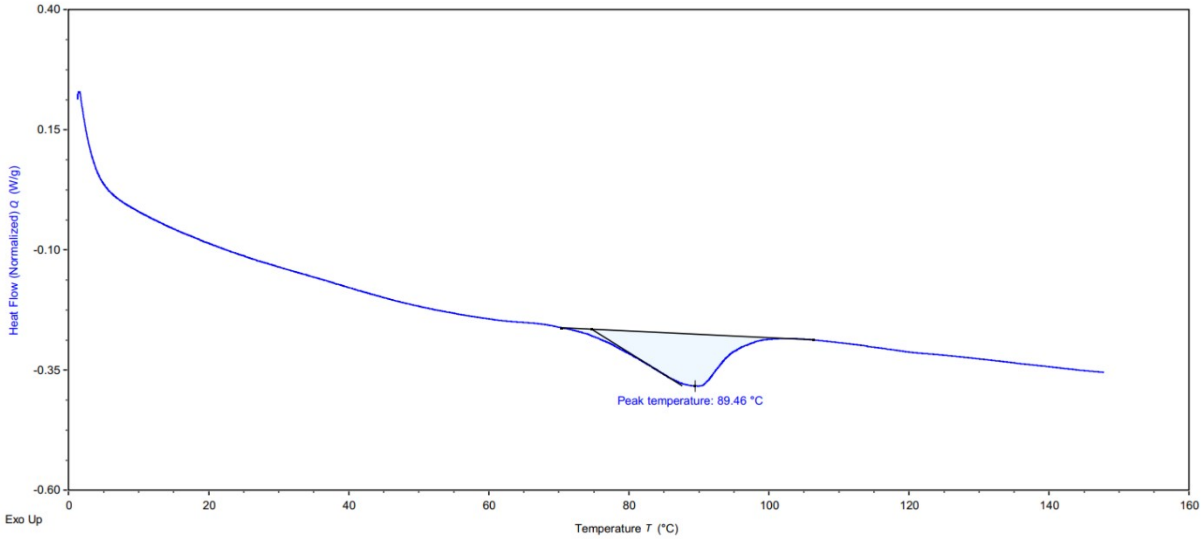


Figure S41. DSC of the copolymer from Table 1, entry 7.

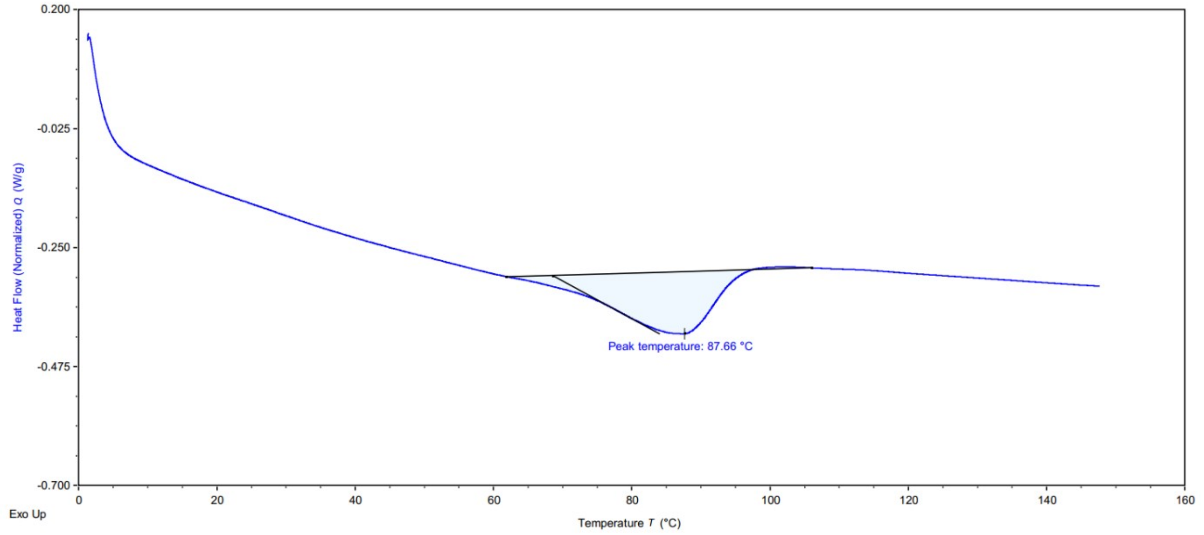


Figure S42. DSC of the copolymer from Table 1, entry 9.

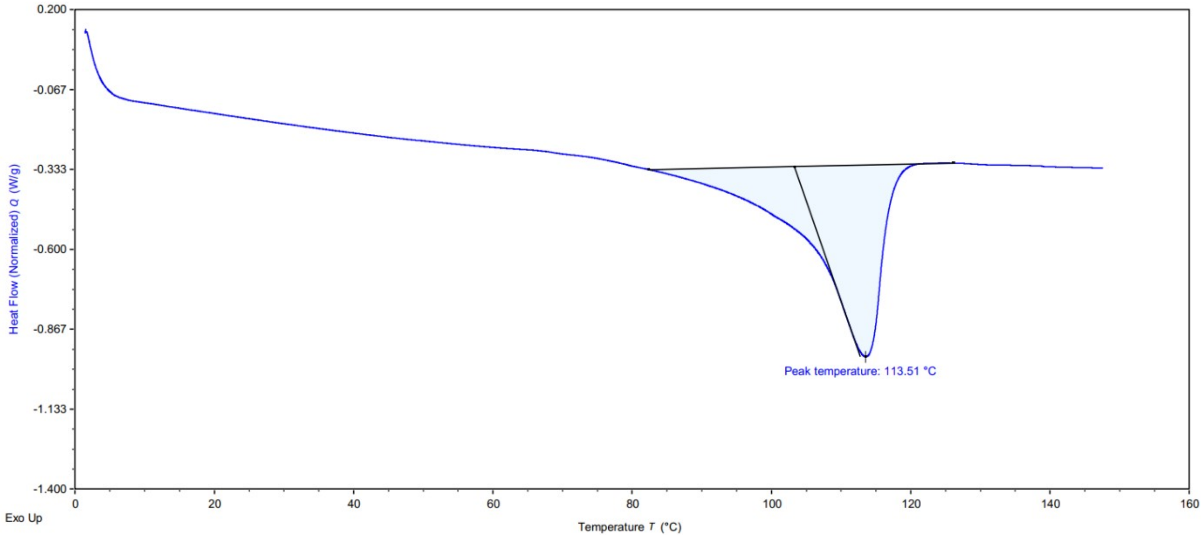


Figure S43. DSC of the copolymer from Table 1, entry 11.

4. References

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[2] T. Rünzi, *PhD Thesis*, Konstanz, 2014.

[3] M.J. Kates and J.H. Schauble, *J. Heterocycl. Chern.,*1995, **32**, 971.