

*Supporting information for*

**Synthesis of Topologically Controlled Functional Polyethylenes:  
Combining C–H Activation with Copolymerization of Ethylene  
and Polar Monomers by Scandium Catalyst**

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## 1. Materials and methods

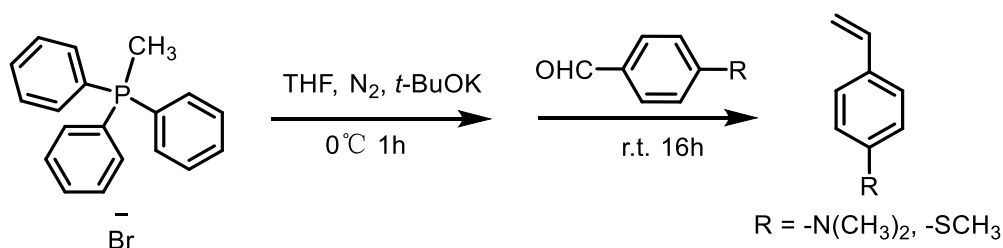
4-Vinylanisole (AR, 98%), 4-trans-propenyl-anisole (AR, 98%), P-Dimethylaminobenzaldehyde (AR, 99%), 4-Methylmercaptobenzaldehyde (RG, 98%), Potassium tert-butoxide (RG, 99%), 2,5-Norbornadiene (AR, 98%), 4-Iodoanisole (RG, 99%), 4-Bromo-N,N-Dimethylaniline (RG, >98%), (4-Iodophenyl)(Methyl)Sulfane (RG, 99%), n-Butyllithium (1.3 M n-hexane), N,N-Dimethyl-o-toluidine (AR, 99%), 1,2,3,4,5-Pentamethylcyclopenta-1,3-diene (AR, 99%), 4-Allylanisole (RG, 98%) and Dichlorobis(Triphenylphosphine)Palladium(II) (RG, 98%) were obtained from Adamas-beta. Methyltriphenylphosphonium Bromide (AR, >99.5%), N,N-Dimethylformamide (GC, >99.9%), Calcium hydride (AR, 99%), Ethyl acetate (AR, 99.5%), 2,5-Dimethoxybromobenzene (AR, 96%), Dichloromethane (AR, 99.5%) and Methanol (AR, 99.5 %) were obtained from Energy Chemical. Diisopropylamine (AR, 99%), Formic acid (AR, 98%), Sodium Chloride (AR, 99%) and Sodium Sulfate (AR, 99%) were obtained from Greagent. Anhydrous scandium chloride, Triphenylmethylium tetrakis(pentafluorophenyl)borate were obtained from Jilin University. 1,2,3,4-Tetramethyl-5-(trimethylsilyl)-1,3-cyclopentadiene (AR, 97%) was obtained from Aladdin. Toluene (HPLC, 99.9 %), n-hexane (HPLC, 99.9 %) and Tetrahydrofuran (HPLC, 99.9 %) were obtained from Yinli. The deuterated solvents Chloroform-d (99.8 atom% D) 1,1,2,2-Tetrachloroethane-d2 (99.6 atom% D) and Benzene-d6 (99.5 atom% D) were obtained from Energy Chemical.

All experiments were carried out under a dry and oxygen-free nitrogen atmosphere by using Schlenk techniques or under a nitrogen atmosphere in an MIKROUNA SUPER glovebox. The nitrogen was purified by being passed through a Dryclean column (4A molecular sieves) and a Gasclean GC-XR column. The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves (4A) catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O<sub>2</sub>/H<sub>2</sub>O Combi-Analyzer (MIKROUNA) to ensure both were always below 0.1 ppm. Solvents were purified by an MIKROUNA Solv Purer G5 Solvent Purification System and dried over fresh Na chips and molecular sieves in the glovebox (MIKROUNA). Rare-earth catalysts Cp'Sc(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-o)<sub>2</sub> (**Sc-1**: Cp' = C<sub>5</sub>Me<sub>5</sub>).

**Sc-2:** Cp' = C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>), were synthesized according to the literatures <sup>s1, s2</sup>. All polar monomers were dried over CaH<sub>2</sub> before use and vacuum transferred prior to polymerization experiment.

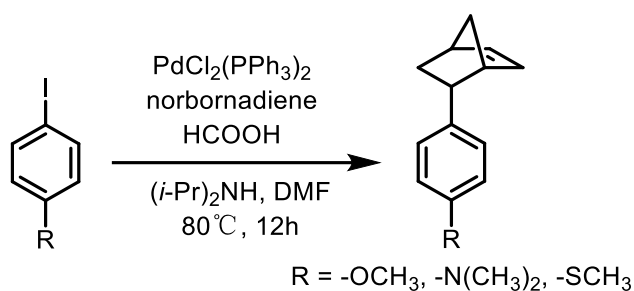
The nuclear magnetic resonance (NMR) spectra were recorded on a 400/500 MHz (Bruker, Fällanden, Switzerland) spectrometer (or JEOL JMTC-500/54/JJ NMR instrument) with Chloroform-d (CDCl<sub>3</sub> at 26.8 °C), Benzene-d<sub>6</sub> (C<sub>6</sub>D<sub>6</sub> 26.8 °C) and 1,1,2,2-Tetrachloroethane-d<sub>2</sub> (1,1,2,2-C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> at 120 °C) as solvent. The chemical shifts for <sup>1</sup>H NMR were recorded in ppm downfield from tetramethylsilane (TMS) with the solvent resonance as the internal standard (7.16 ppm for C<sub>6</sub>D<sub>6</sub>, 7.26 ppm for CDCl<sub>3</sub>, 6.0 ppm for 1,1,2,2-C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>). The chemical shifts for <sup>13</sup>C{<sup>1</sup>H} NMR were recorded in ppm downfield using the central peak of C<sub>6</sub>D<sub>6</sub> (128.06 ppm) CDCl<sub>3</sub> (77.16 ppm), 1,1,2,2-C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> (73.78 ppm) as the internal standard. The molecular weights and the molecular weight distributions of all the copolymers were determined at 150 °C by high temperature gel permeation chromatography (HT-GPC) on an HLC-8321GPC/HT apparatus (Tosoh Corporation) (or PL-GPC220 apparatus (Agilent Corporation)). 1,2-Dichlorobenzene (*o*-DCB) or 1,2,4-trichlorobenzene (TCB) was employed as an eluent at a flow rate of 1.0 mL/min. The calibration was made by using a polystyrene standard (Agilent Corporation). Differential scanning calorimetry (DSC) measurements were performed on a DSC 2500 (Mettler Toledo DSC 3) (or DSC 7000X (HITACHI)) at a rate of 10 °C/min. Any thermal history difference in the polymers was eliminated by first heating the specimen to 180 °C, cooling at 10 °C/min to -60 °C and then recording the second DSC scan.

## 2. Preparation of polar monomers.



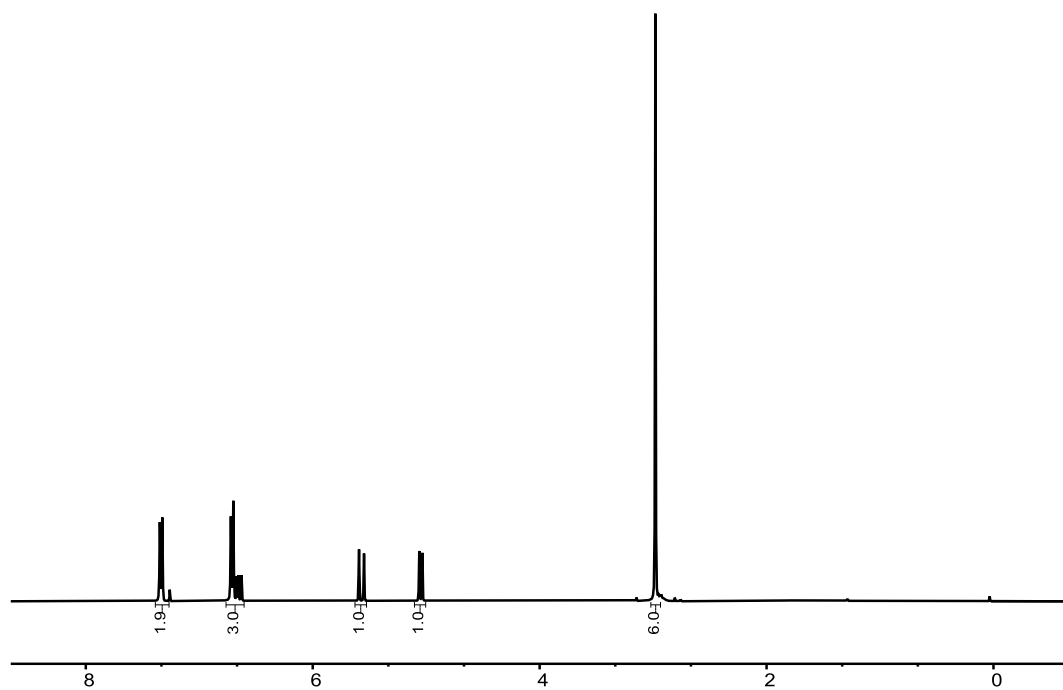
According to literature procedure<sup>s3</sup>, an oven-dried 250 mL round-bottom flask, equipped with a nitrogen atmosphere, was charged with t-BuOK (3.70 g, 33 mmol, 1.1 equiv.),

methyltriphenylphosphonium bromide (11.8 g, 33 mmol, 1.1 equiv.), and anhydrous THF (100 mL). The mixture was stirred at 0 °C for 1 hour, after which benzaldehyde (30 mmol) was added, and the reaction was allowed to proceed at room temperature for 16 hours. The reaction mixture was then quenched with saturated aqueous NaHCO<sub>3</sub>, and the resulting biphasic solution was extracted three times with ethyl acetate (AcOEt). The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using hexane/AcOEt as the eluent, yielding 4-VN or 4-VS as colorless oils.

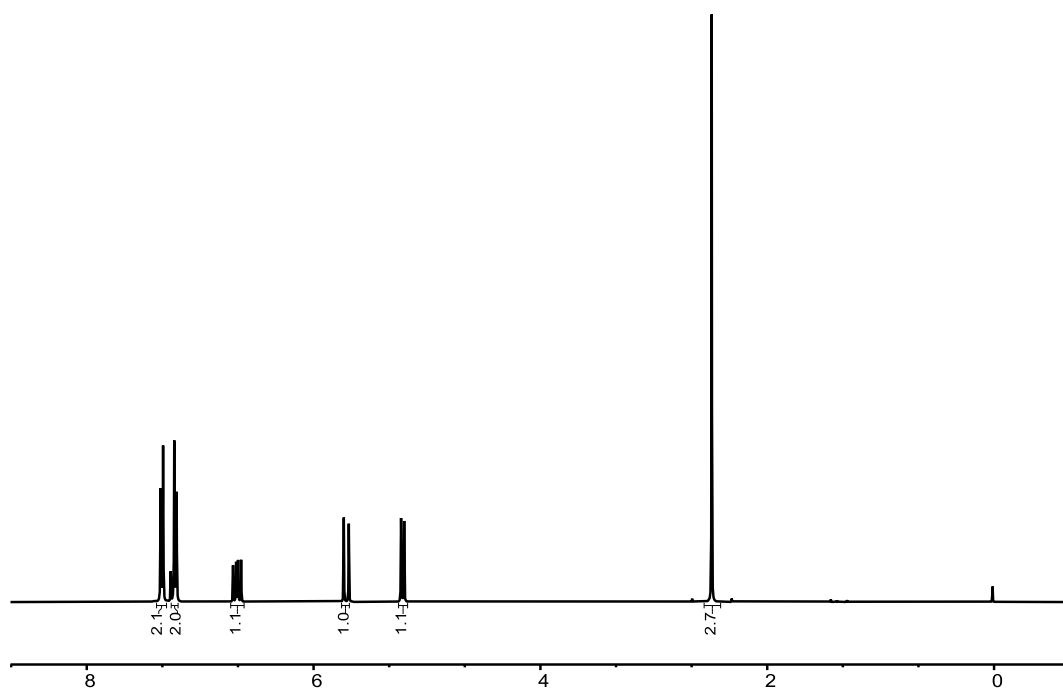


According to literature procedures<sup>s4</sup>, iodide (8.5 mmol) and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (II) (126 mg, 179 μmol) were placed in a Schlenk flask with a stir bar. The flask was evacuated and backfilled with nitrogen three times before addition of bicyclo[2.2.1]hepta-2,5-diene (4 mL, 39.3 mmol), DMF (40 mL) and diisopropylamine (10 mL). The reaction flask was then subjected to three cycles of freeze-pump-thaw, after which formic acid (2 mL, 5.30 mmol) was added dropwise, and the mixture was heated at 80 °C overnight. Upon cooling to room temperature, the mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> and washed with water and brine several times. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvent was removed under reduced pressure, after which the crude product was purified by column chromatography on silica gel using hexane/AcOEt as the eluent, yielding the product as a viscous oil.

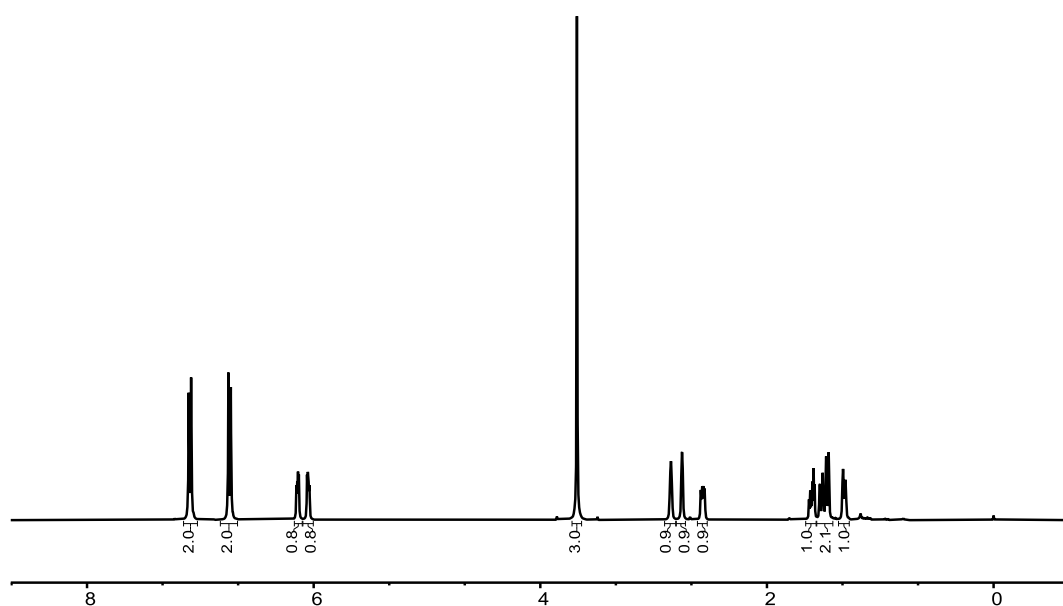
### 3. Characterization of polar monomers.



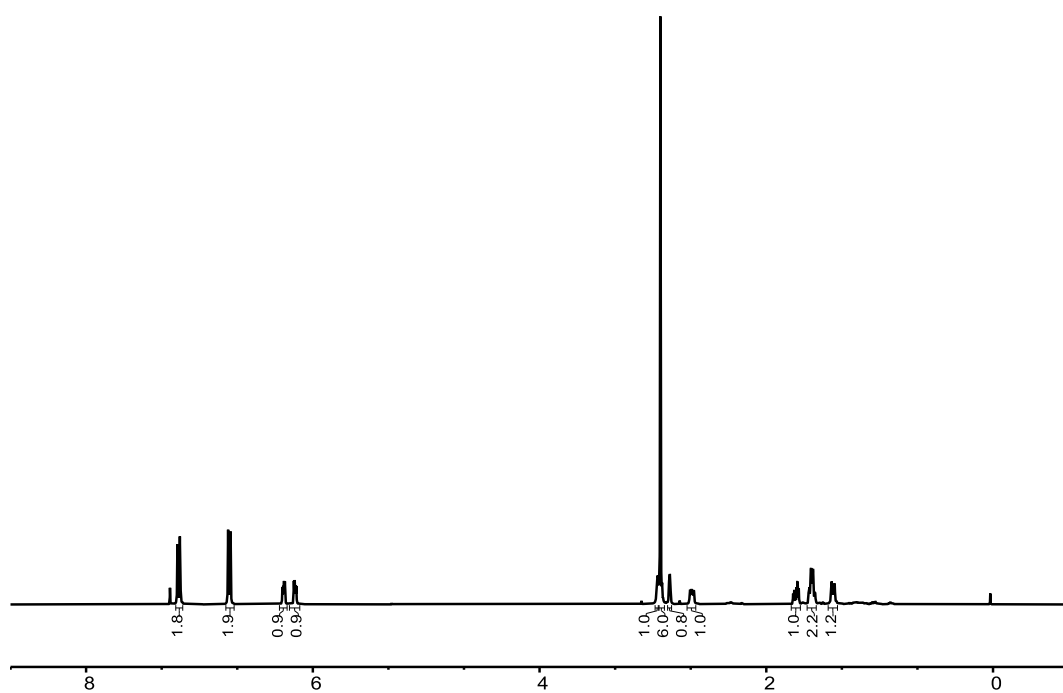
**Figure S1.** <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 26.8 °C) of *N,N*-dimethyl-4-vinylaniline (**4-VN**).



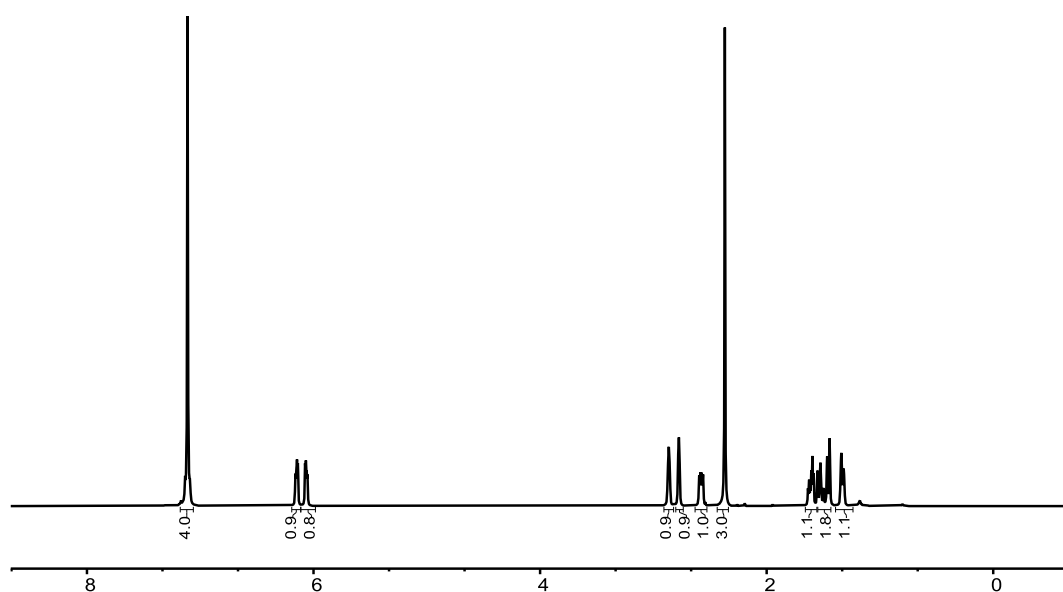
**Figure S2.** <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 26.8 °C) of methyl(4-vinylphenyl)sulfane (**4-VS**).



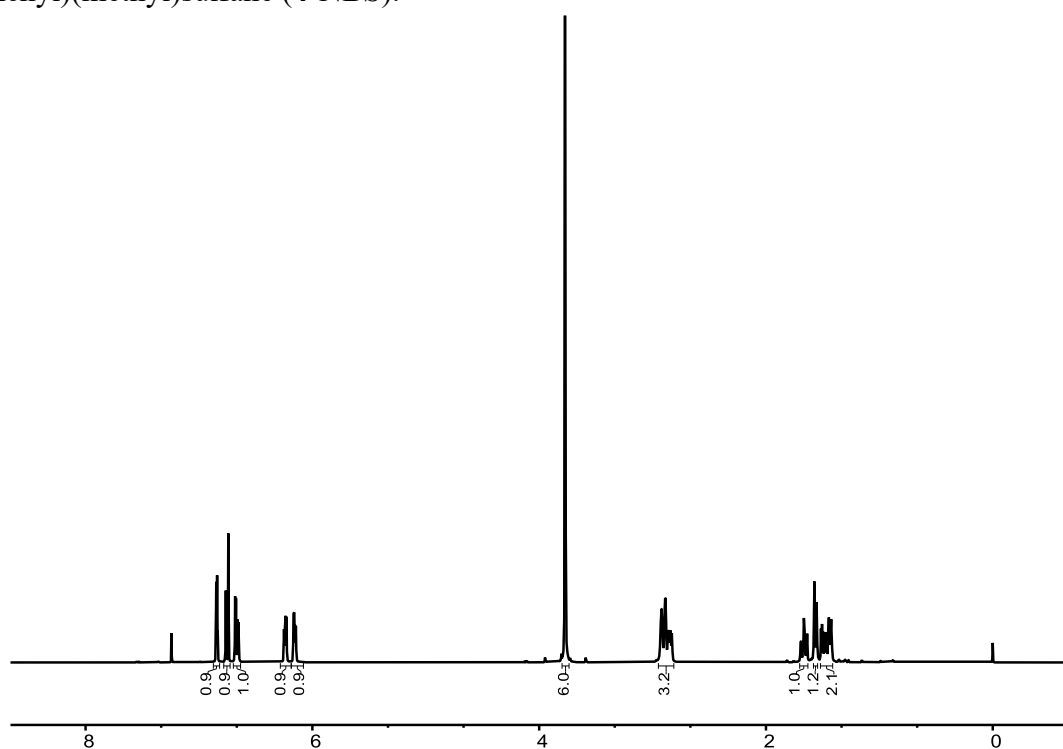
**Figure S3.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ,  $26.8\text{ }^\circ\text{C}$ ) of 5-(4-methoxyphenyl)bicyclo[2.2.1]hept-2-ene (4-NBA).



**Figure S4.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ,  $26.8\text{ }^\circ\text{C}$ ) of 4-(bicyclo[2.2.1]hept-5-en-2-yl)-*N,N*-dimethylaniline (4-NBN).



**Figure S5.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ,  $26.8\text{ }^\circ\text{C}$ ) of (4-(bicyclo[2.2.1]hept-5-en-2-yl)phenyl)(methyl)sulfane (**4-NBS**).

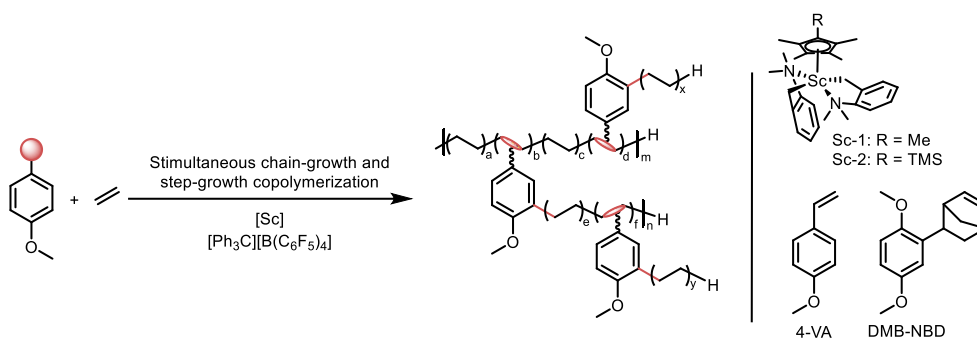


**Figure S6.**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ,  $26.8\text{ }^\circ\text{C}$ ) of 5-(2,5-dimethoxyphenyl)bicyclo[2.2.1]hept-2-ene (**DMB-NBD**).

#### 4. General Polymerization Procedures.

In a THF-free glovebox, a toluene solution (48 mL) of polar monomer was charged into a three-necked flask with a magnetic stir bar. The flask was taken outside, set in an oil bath (25 °C or 70 °C), and connected to a well-purged Schlenk ethylene line and a paraffin oil-sealed stopper by use of a three-way cock. Ethylene (1 atm) was introduced into the system and was saturated in the solution by stirring for 2 min. A toluene solution (2 mL) of  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  (18.5 mg, 0.02 mmol) and  $\text{Cp}'\text{Sc}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_2$  (**Sc-1**-8.9 mg, **Sc-2**-10.2 mg, 0.02 mmol) as then added through a syringe under vigorous stirring. When the polymerization was achieved at the indicated time, MeOH (150 mL) was added at the end of the reaction. The polymer product was collected by filtration, washed with methanol, and then dried in vacuum at 60 °C to a constant weight. The resulting polymer was soluble in deuterated 1,1,2,2-tetrachloroethane under heating. The content of polar monomers in the copolymer was calculated by  $^1\text{H}$  NMR analysis.

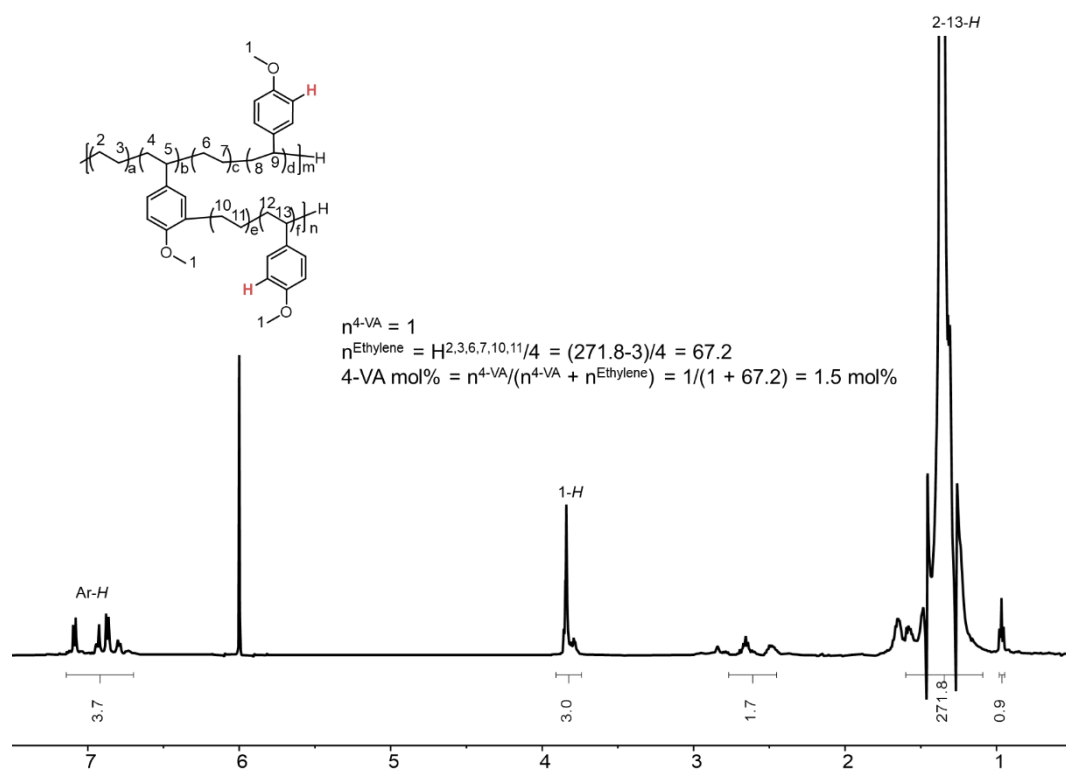
**Table S1.** copolymerization of anisole derivatives with ethylene by half-sandwich rare-earth catalysts<sup>[a]</sup>.



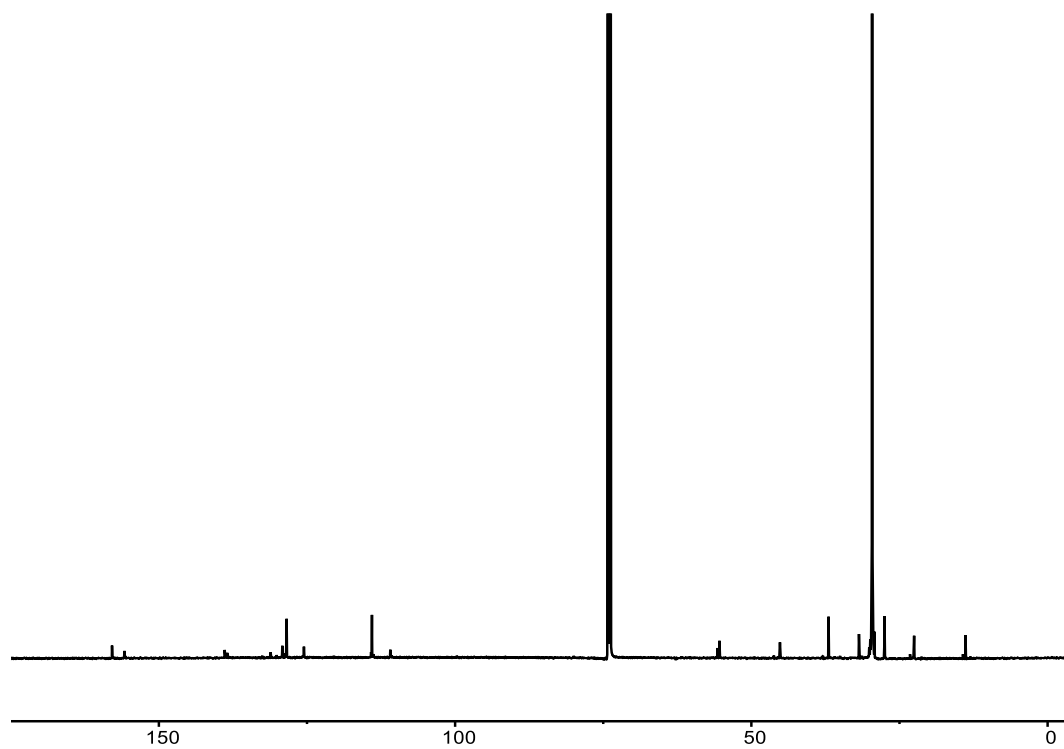
Entry	M	Ln	[M]:[Ln]	Time (h)	Yield (g) <sup>[b]</sup>	Conversion (%) <sup>[c]</sup>	Activity			Incorp. ([O].mol%) <sup>[e]</sup>	mol % of C-H activation <sup>[e]</sup>	$T_m$ <sup>[f]</sup>
							(kg·Ln <sup>-1</sup> ·mol <sup>-1</sup> ·h <sup>-1</sup> )	$M_n$ (× kg/mol) <sup>[d]</sup>	$M_w/M_n$ <sup>[d]</sup>			
1	-	Sc-1	-	10 min	0.63	-	190	76	2.93	-	-	135
2	4-VA	Sc-1	100:1	5	3.69	100	36.9	52.6	4.3	1.6	100	126/131
3	4-VA	Sc-1	500:1	15	1.02	56	3.4	3.6	1.8	37	70	n.o
4	4-VA	Sc-1	500:1	27	7.10	100	13.1	63.8	2.6	4.7	100	124/129
5	4-VA	Sc-2	100:1	0.7	0.65	92	46.4	13.1	2.2	11.3	70	86/107
6	4-VA	Sc-2	100:1	1.1	1.09	100	49.5	17.7	2.5	6.4	90	104/131
7	4-VA	Sc-2	500:1	1	0.66	32	33	5.0	3.8	28.8	40	n.o
8	4-VA	Sc-2	500:1	7	2.80	100	20	167.6	1.3	16.5	70	110
9	DMB-NBD	Sc-1	100:1	2	1.47	89	36.8	19.2	2.0	4.5	50	110
10	DMB-NBD	Sc-1	100:1	3	3.7	100	61.7	33.1	2.6	1.7	100	128

[a] Conditions: [Ln] (0.02 mmol), [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (0.02 mmol), ethylene (1 atm), 50 mL toluene, Temperature (70 °C). [b] Yield of final polymer. [c] Conversion of polar monomers. [d] Determined by GPC in *o*-DCB at 150 °C against polystyrene standard. [e] Determined by <sup>1</sup>H NMR analysis. [f] Determined by differential scanning calorimetry.

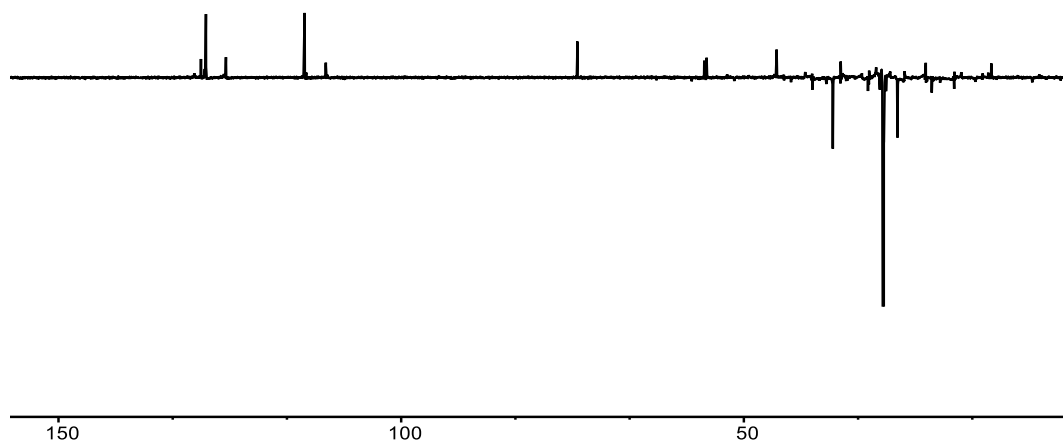
## 5. Characterization of copolymers



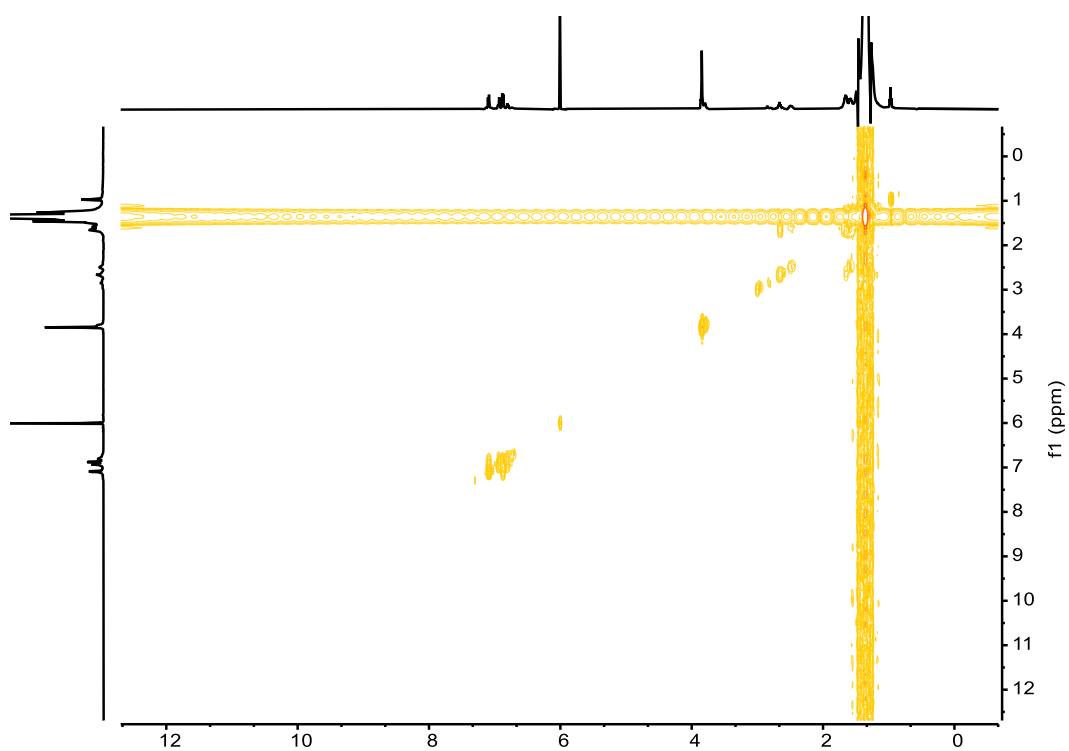
**Figure S7.**  $^1\text{H}$  NMR spectrum of the polymer from Table 1, Entry 1 (1,1,2,2-Tetrachloroethane- $d_2$ ).



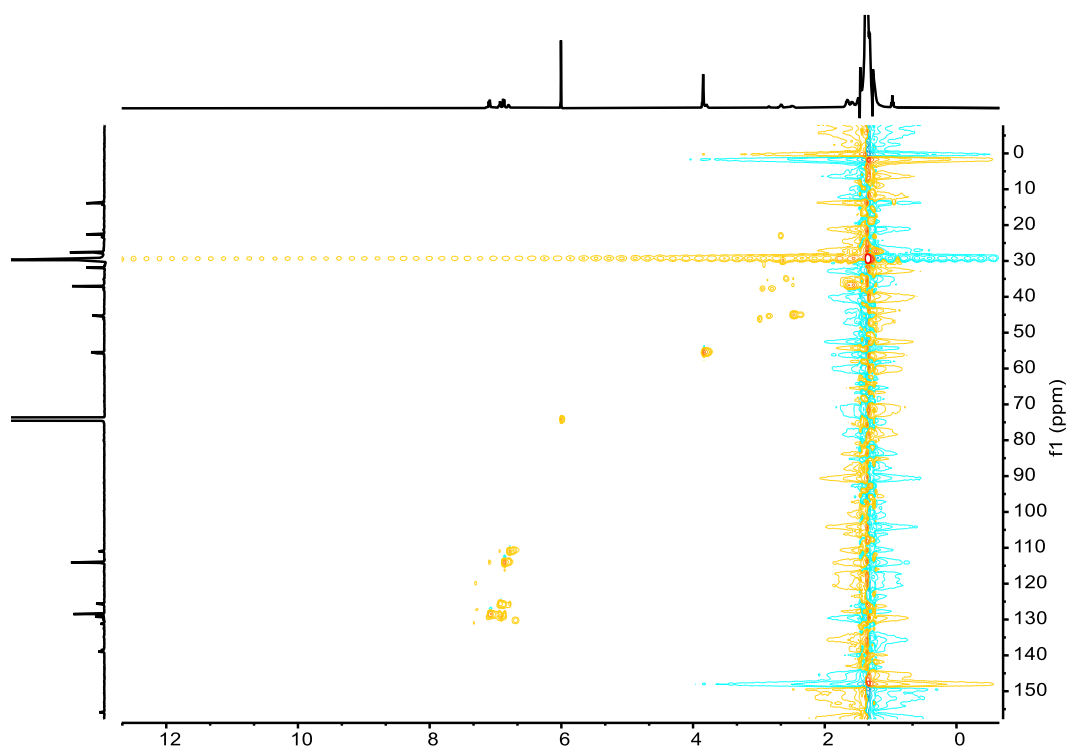
**Figure S8.**  $^{13}\text{C}$  NMR spectrum of the polymer from Table 1, Entry 1 (1,1,2,2- $\text{C}_2\text{D}_2\text{Cl}_4$ ).



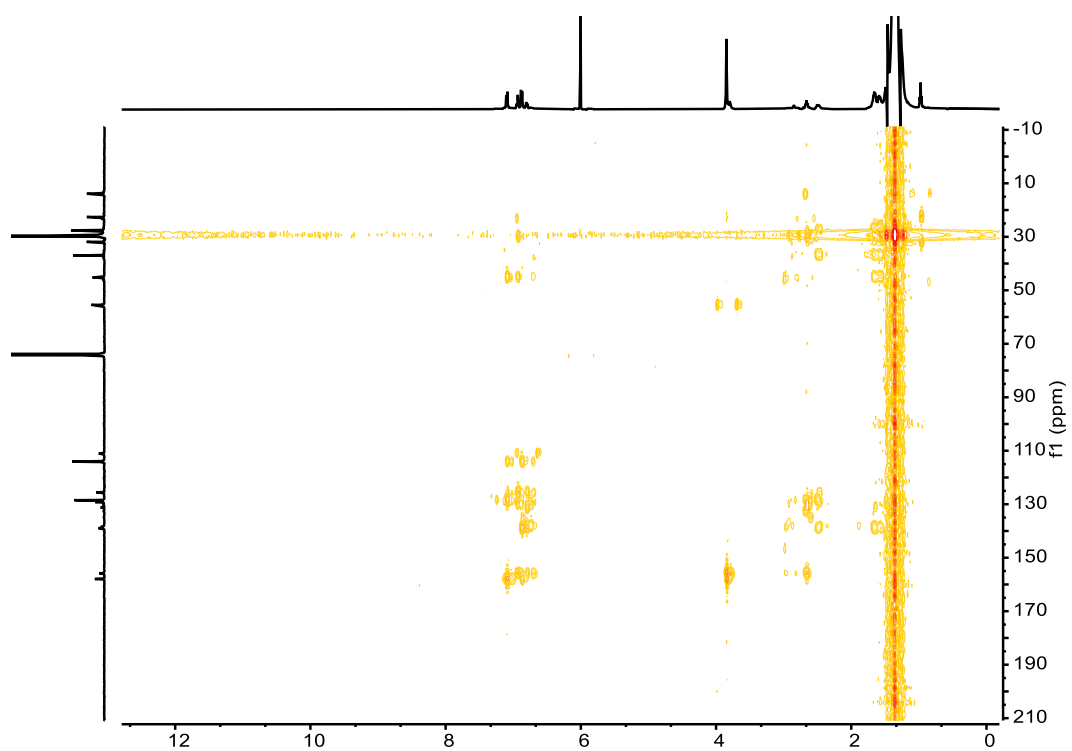
**Figure S9.** DEPT  $^{13}\text{C}$  NMR spectrum of the polymer from Table 1, Entry 1 (1,1,2,2- $\text{C}_2\text{D}_2\text{Cl}_4$ ).



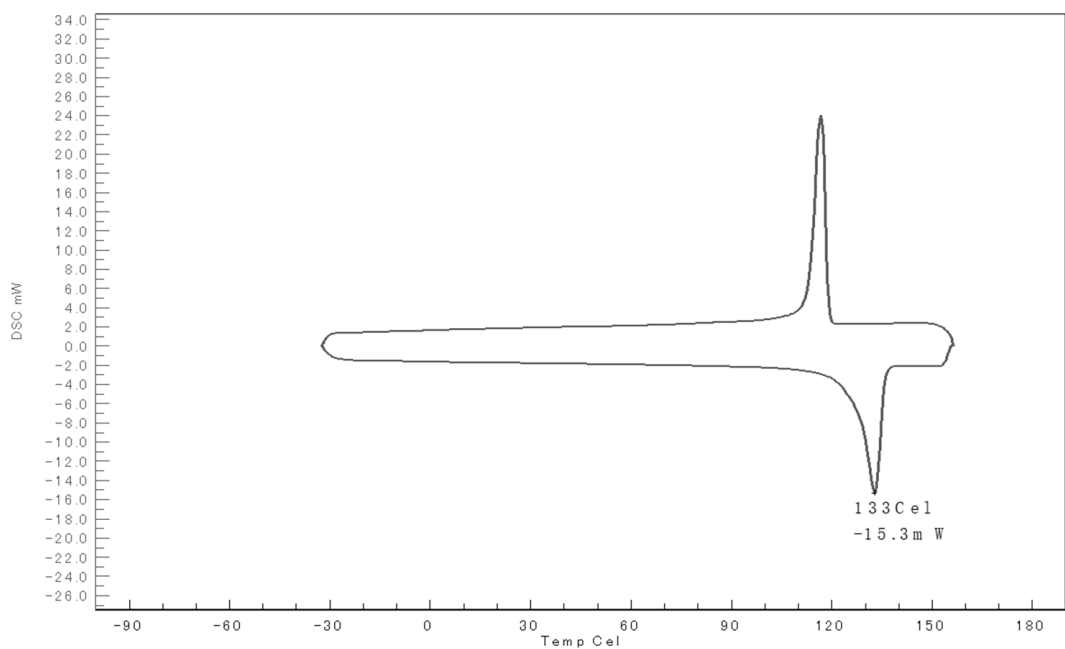
**Figure S10.**  $\text{H,H-COSY}$  spectrum of the polymer from Table 1, Entry 1 (1,1,2,2- $\text{C}_2\text{D}_2\text{Cl}_4$ ).



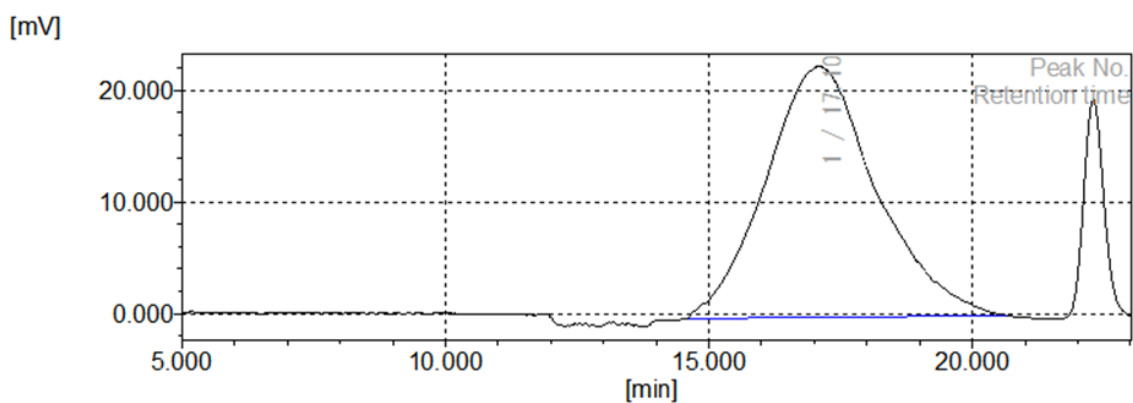
**Figure S11.** HSQC spectrum of the polymer from Table 1, Entry 1 (1,1,2,2- $C_2D_2Cl_4$ )



**Figure S12.** HMBC spectrum of the polymer from Table 1, Entry 1 (1,1,2,2- $C_2D_2Cl_4$ )



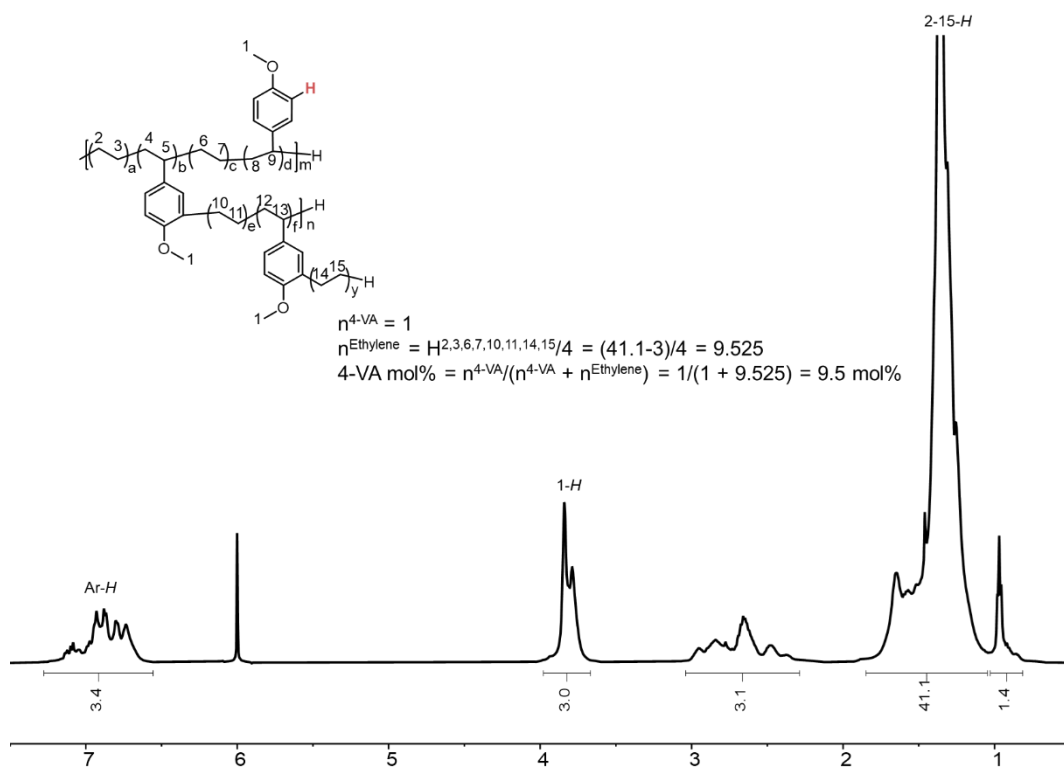
**Figure S13.** DSC curve of the polymer from Table 1, Entry 1.



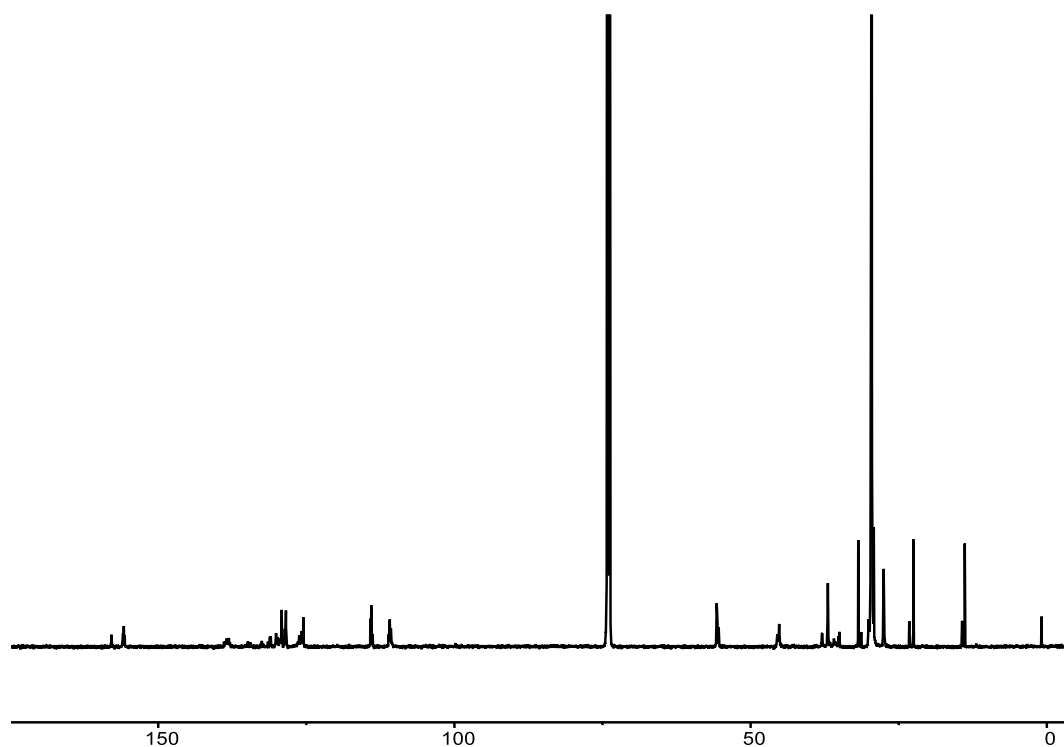
**Molecular mass calculation result (RI)**

Total	[min]	[mV]	[mol]	Mn	57,265
Peak start	14.618	-0.455	964,047	Mw	147,299
Peak top	17.103	22.134	112,299	Mz	268,352
Peak end	20.662	-0.175	2,672	Mz+1	392,589
				Mv	147,299
Height [mV]			22.474	Mp	123,741
Area [mV*s]			3269.804	Mz/Mw	1.822
Height% [%]			100.000	Mw/Mn	2.572
[eta]			147299.08048	Mz+1/Mw	2.665

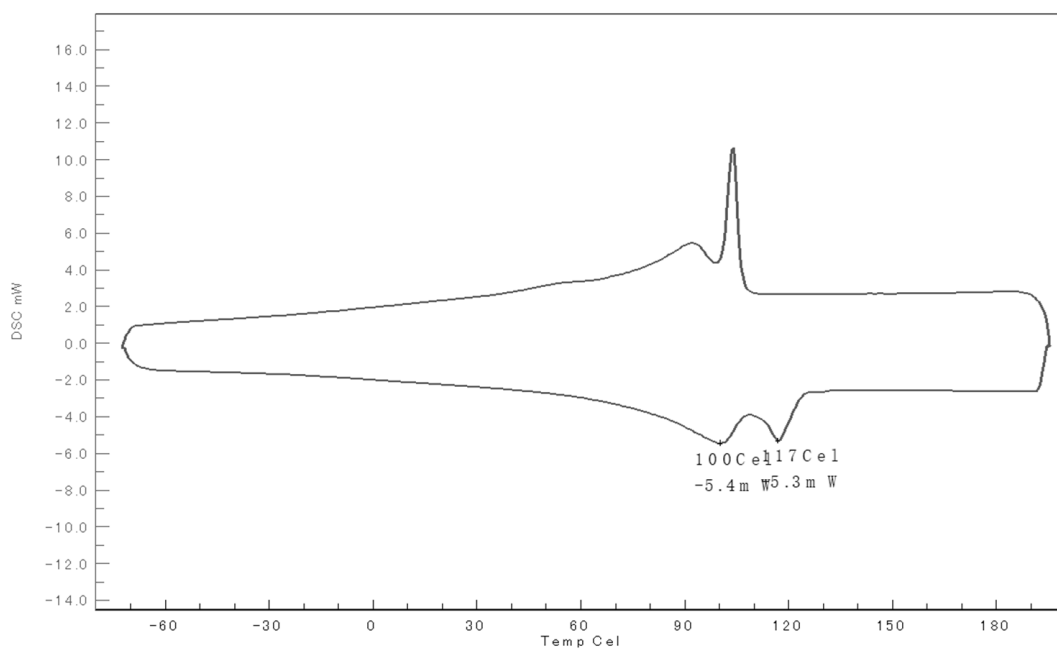
**Figure S14.** GPC trace of the polymer from Table 1, Entry 1.



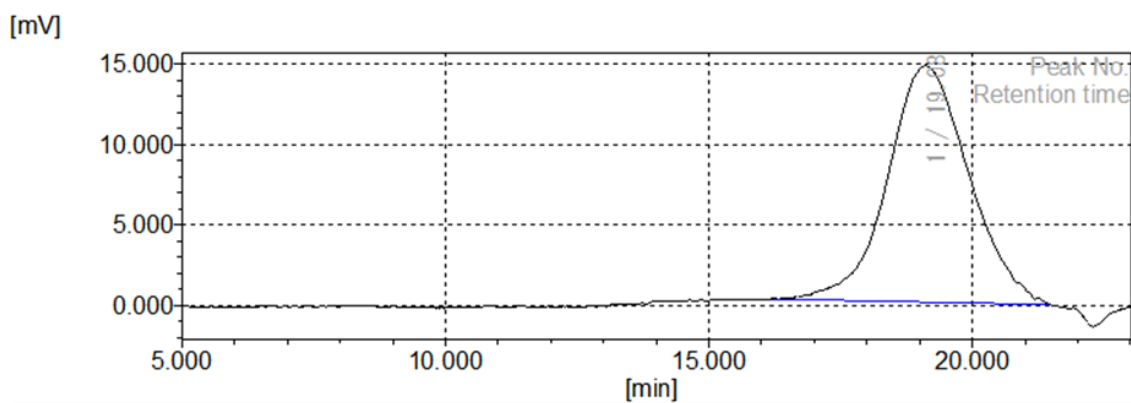
**Figure S15.**  $^1\text{H}$  NMR spectrum of the polymer from Table 1, Entry 2 (1,1,2,2-Tetrachloroethane- $d_2$ ).



**Figure S16.**  $^{13}\text{C}$  NMR spectrum of the polymer from Table 1, Entry 2 (1,1,2,2-Tetrachloroethane- $d_2$ ).



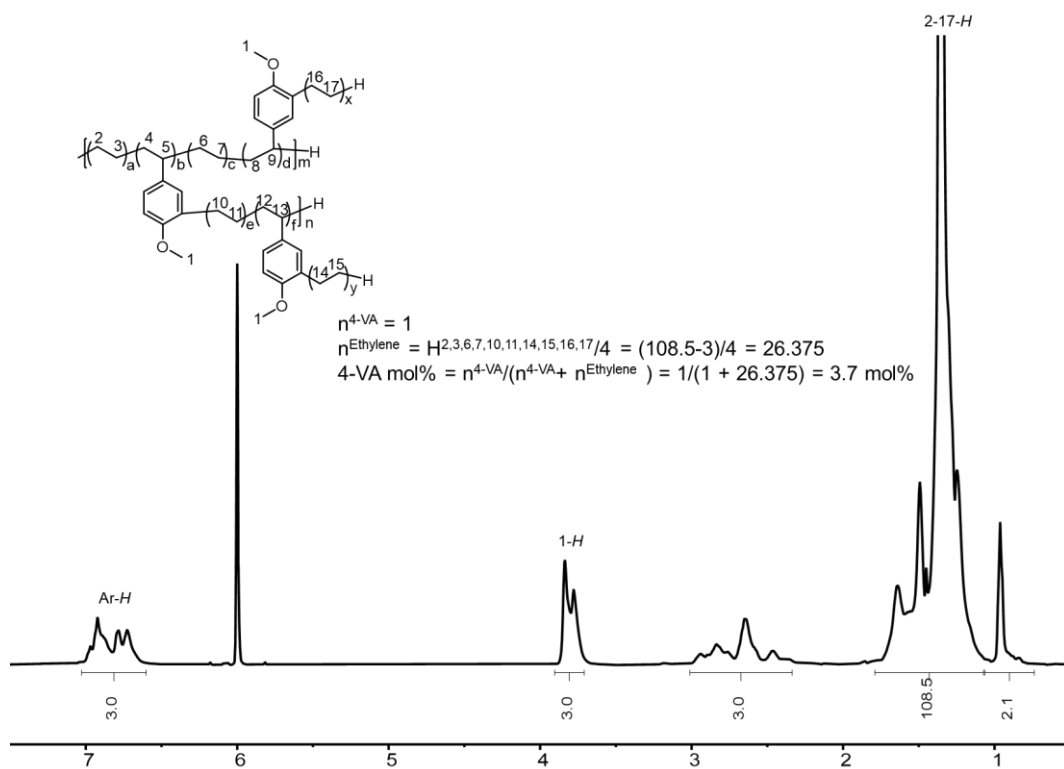
**Figure S17.** DSC curve of the polymer from Table 1, Entry 2.



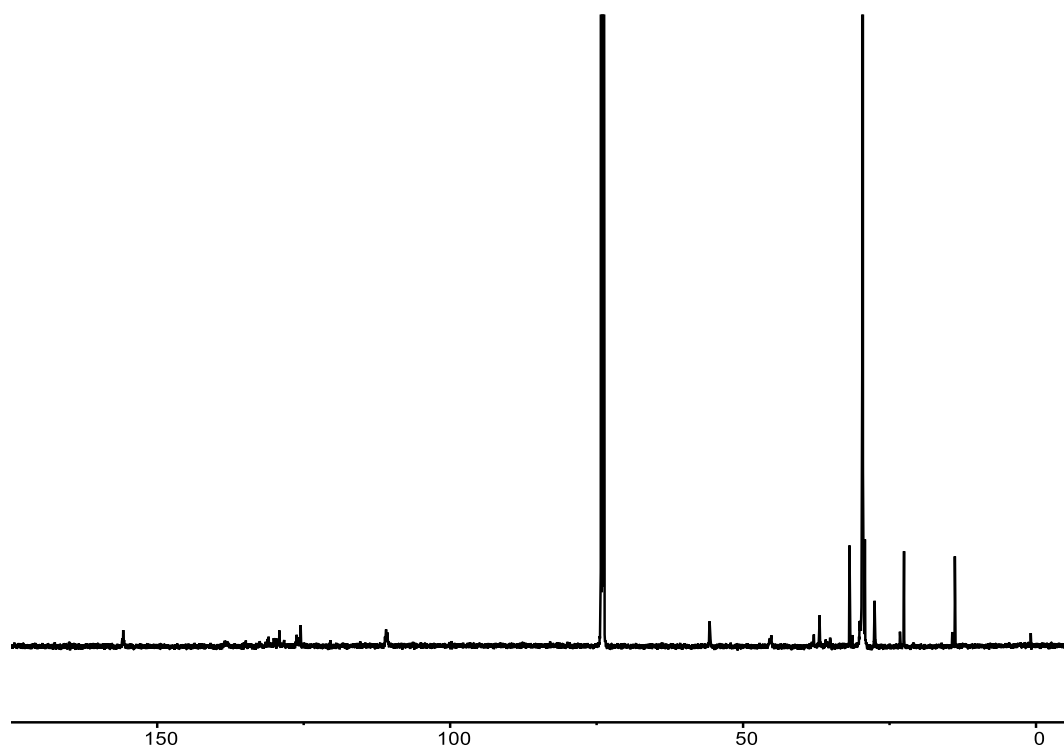
**Molecular mass calculation result (RI)**

Total					
	[min]	[mV]	[mol]		
Peak start	16.162	0.399	269,242	Mn	10,584
Peak top	19.082	14.904	16,092	Mw	19,581
Peak end	21.478	0.045	744	Mz	37,432
				Mz+1	71,253
				Mv	19,581
Height [mV]			14.699	Mp	15,539
Area [mV*s]			1580.225	Mz/Mw	1.912
Height% [%]			100.000	Mw/Mn	1.850
[eta]			19581.34009	Mz+1/Mw	3.639

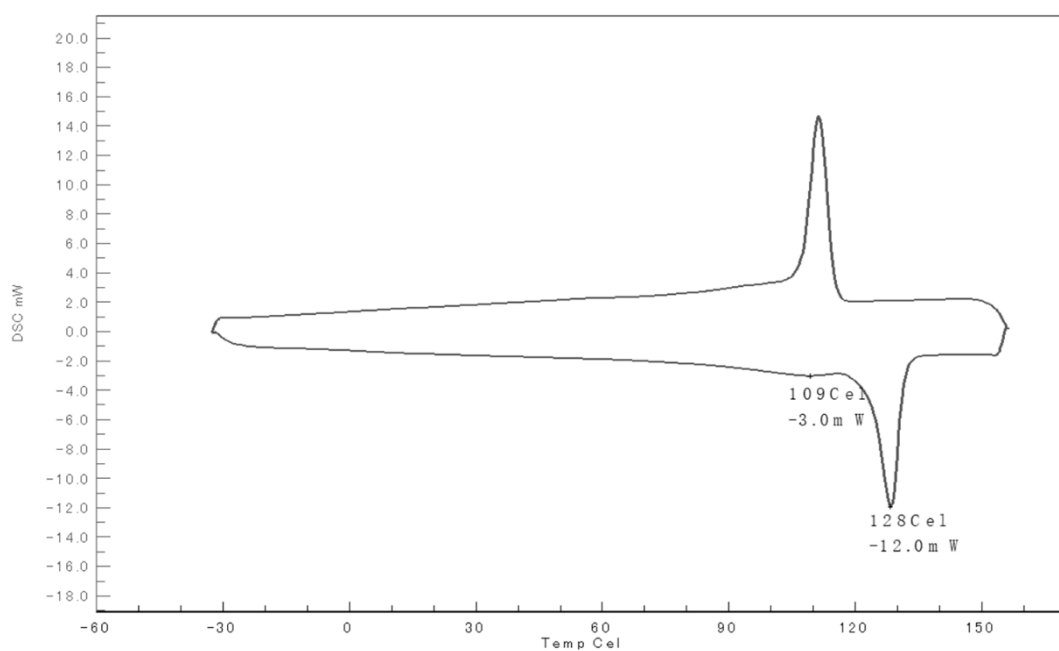
**Figure S18.** GPC trace of the polymer from Table 1, Entry 2.



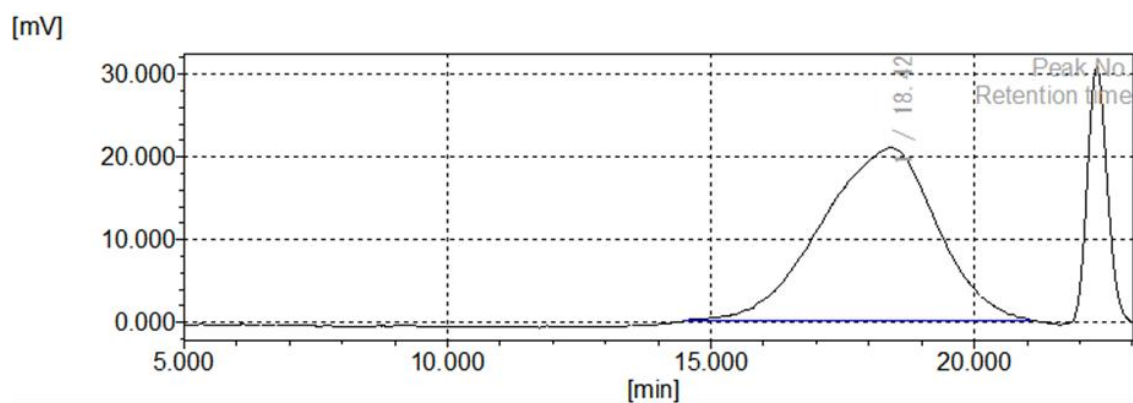
**Figure S19.**  $^1\text{H}$  NMR spectrum of the polymer from Table 1, Entry 3 (1,1,2,2-Tetrachloroethane- $d_2$ ).



**Figure S20.**  $^{13}\text{C}$  NMR spectrum of the polymer from Table 1, Entry 3 (1,1,2,2-Tetrachloroethane- $d_2$ ).



**Figure S21.** DSC curve of the polymer from Table 1, Entry 3.

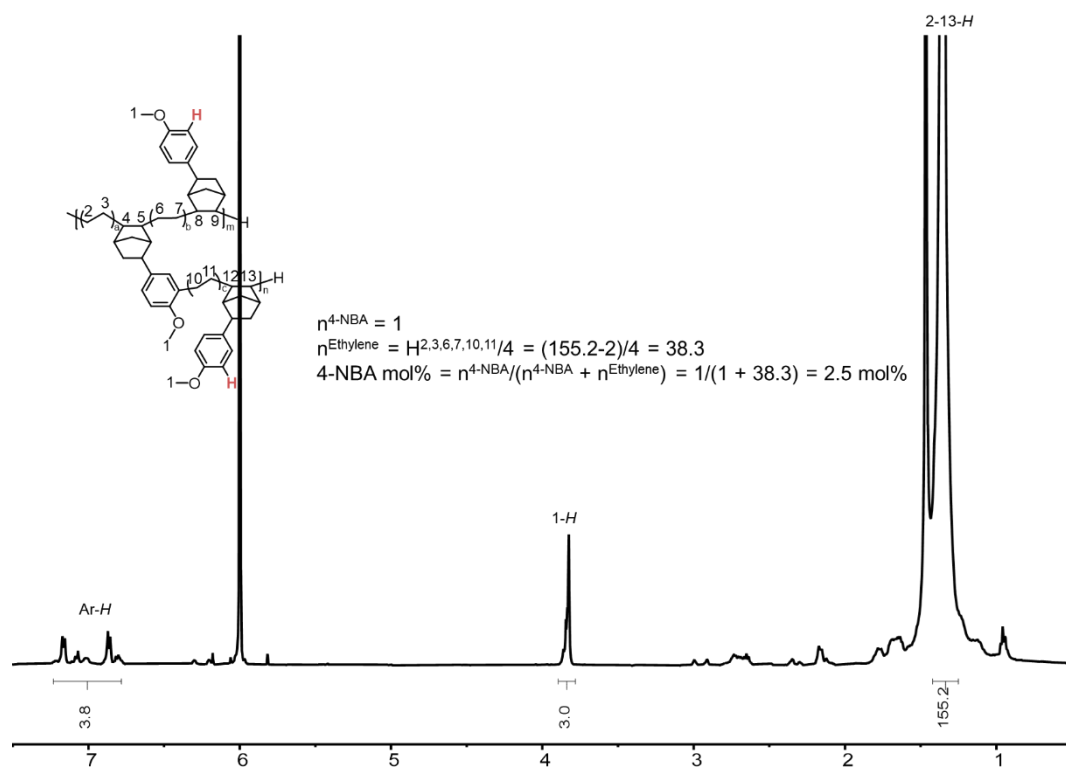


**Molecular mass calculation result (RI)**

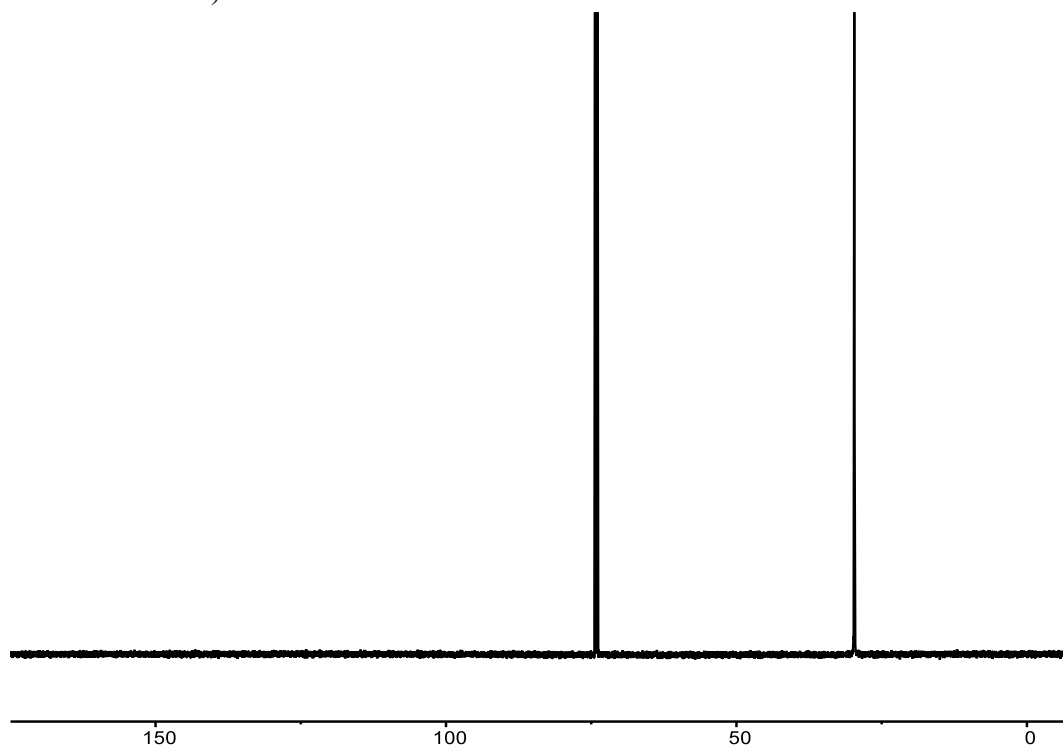
Total

	[min]	[mV]	[mol]	Mn	25,159
Peak start	14.485	0.167	1,109,363	Mw	68,650
Peak top	18.427	21.117	31,121	Mz	176,869
Peak end	21.103	0.223	1,535	Mz+1	356,521
				Mv	68,650
Height [mV]			20.917	Mp	31,069
Area [mV*s]			3192.564	Mz/Mw	2.576
Height% [%]			100.000	Mw/Mn	2.729
[eta]			68649.73877	Mz+1/Mw	5.193

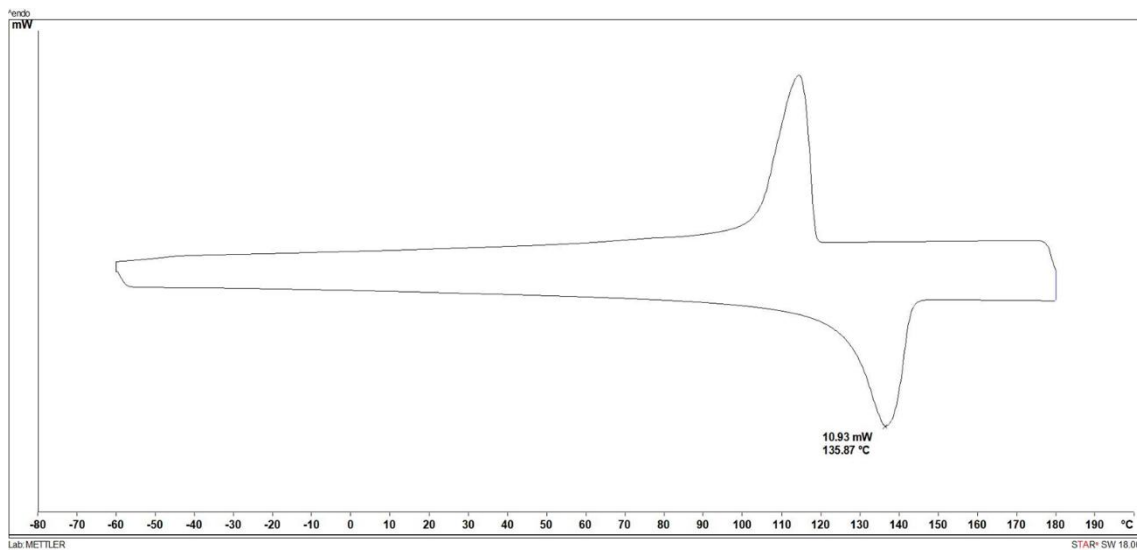
**Figure S22.** GPC trace of the polymer from Table 1, Entry 3.



**Figure S23.**  $^1\text{H}$  NMR spectrum of the polymer from Table 1, Entry 4 (1,1,2,2-Tetrachloroethane- $d_2$ ).



**Figure S24.**  $^{13}\text{C}$  NMR spectrum of the polymer from Table 1, Entry 4 (1,1,2,2-Tetrachloroethane- $d_2$ ).



**Figure S25.** DSC curve of the polymer from Table 1, Entry 4.

**MW Averages**

Mp: 799552

Mn: 271199

Mv: 780140

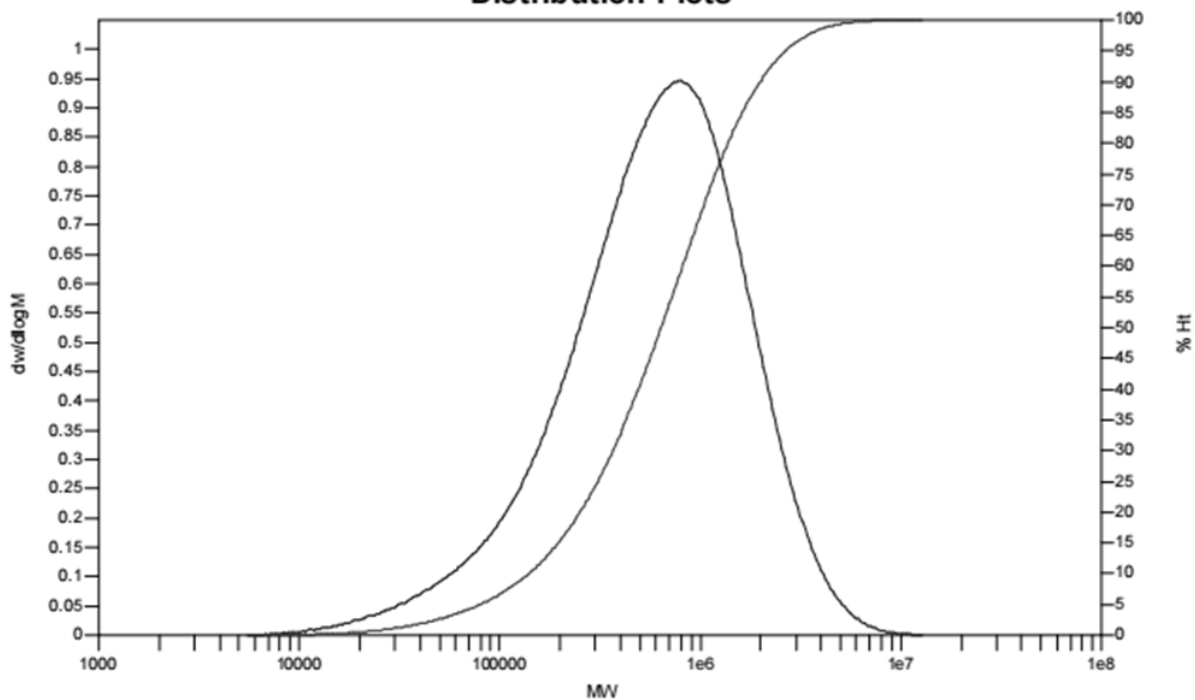
Mw: 884173

Mz: 1796531

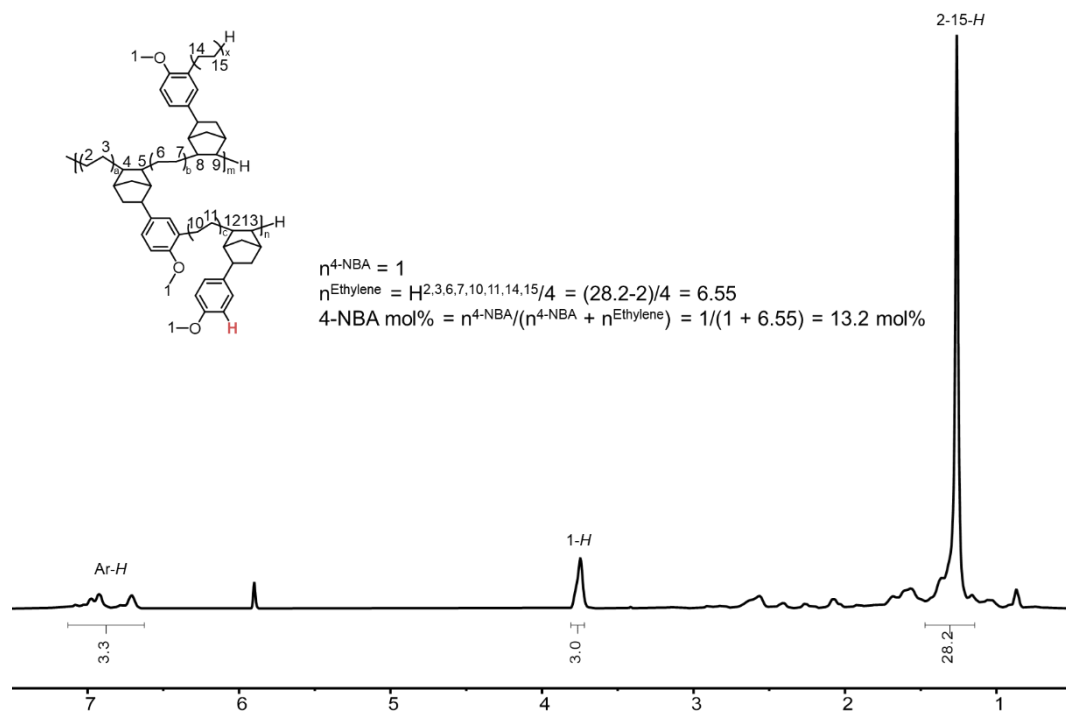
Mz+1: 3003113

PD: 3.2602

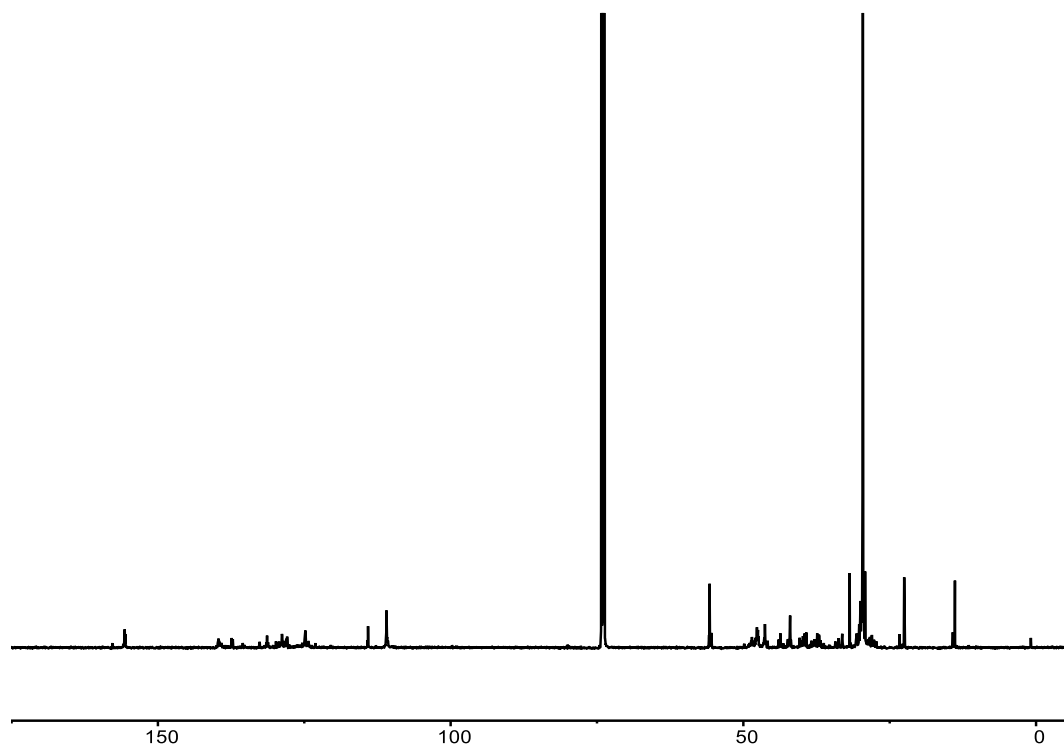
**Distribution Plots**



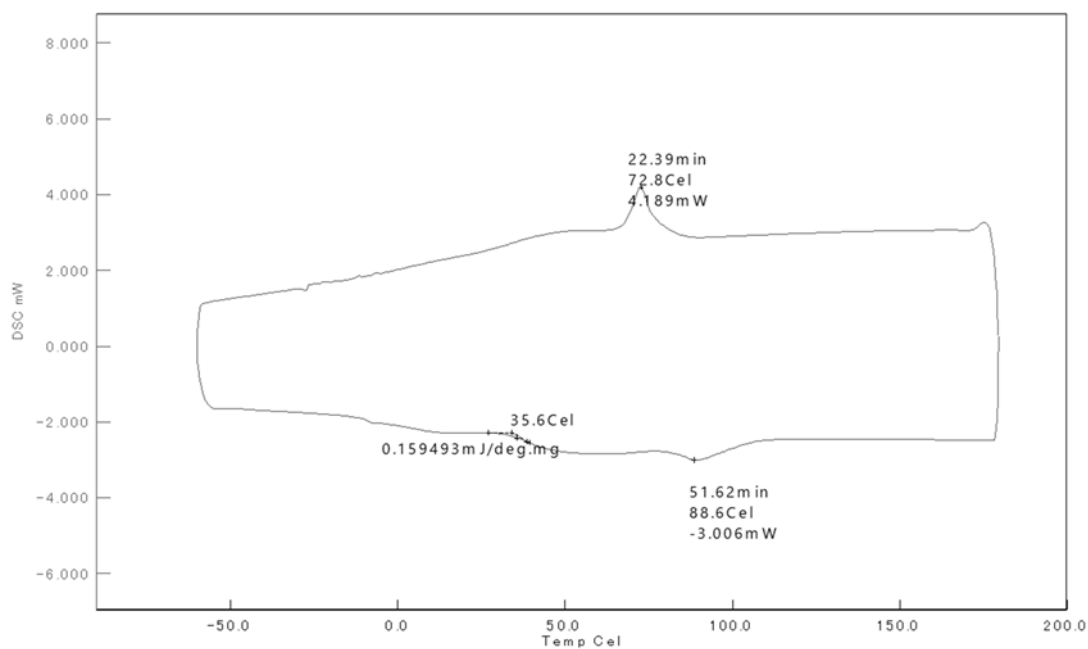
**Figure S26.** GPC trace of the polymer from Table 1, Entry 4.



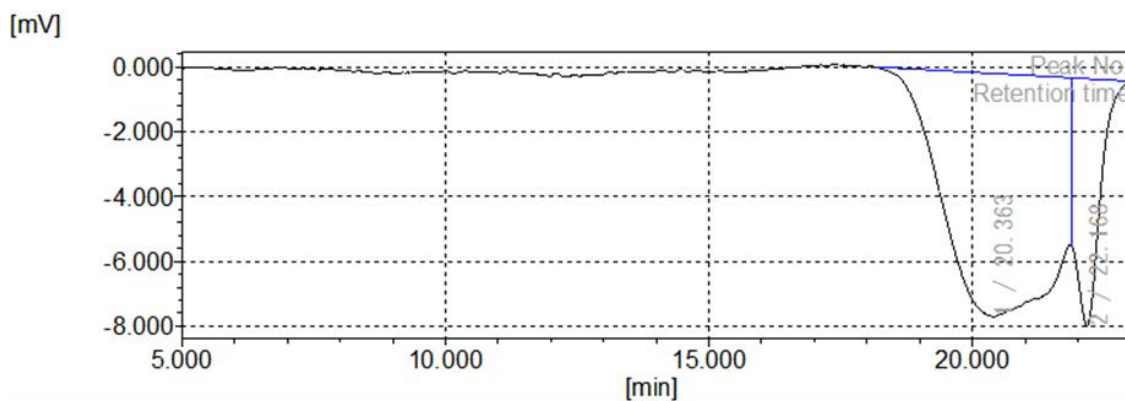
**Figure S27.**  $^1\text{H}$  NMR spectrum of the polymer from Table 1, Entry 5 (1,1,2,2-Tetrachloroethane- $d_2$ ).



**Figure S28.**  $^{13}\text{C}$  NMR spectrum of the polymer from Table 1, Entry 5 (1,1,2,2-Tetrachloroethane- $d_2$ ).



**Figure S29.** DSC curve of the polymer from Table 1, Entry 5.

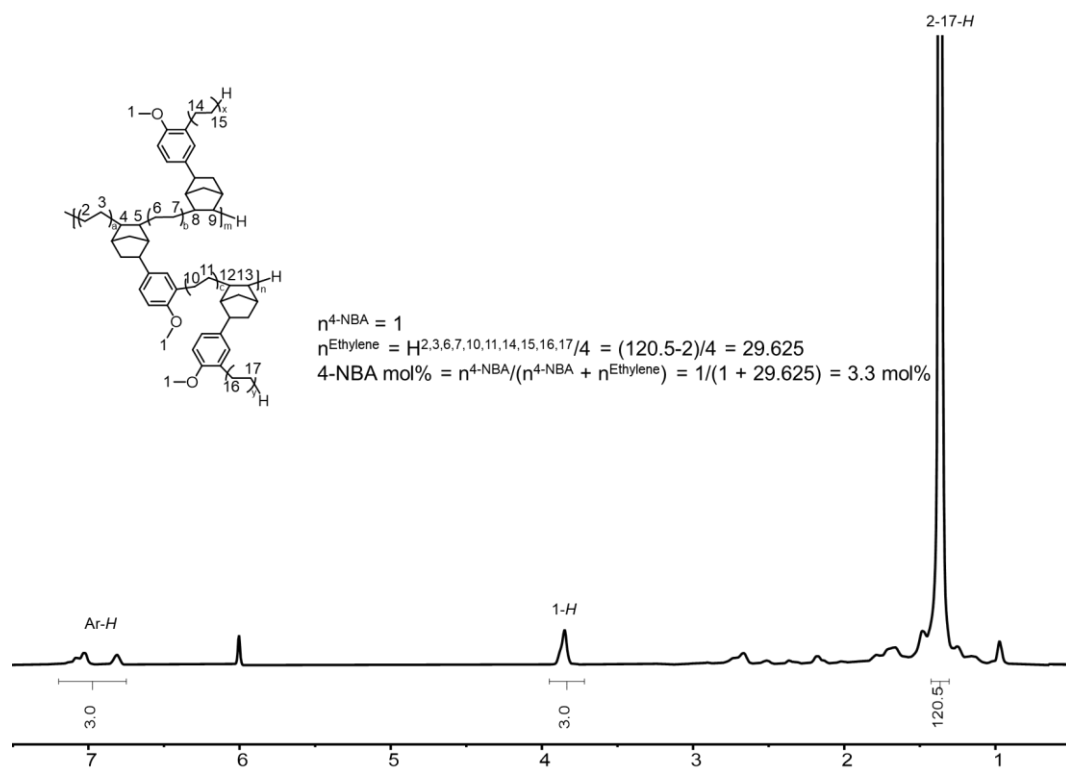


**Molecular mass calculation result (RI)**

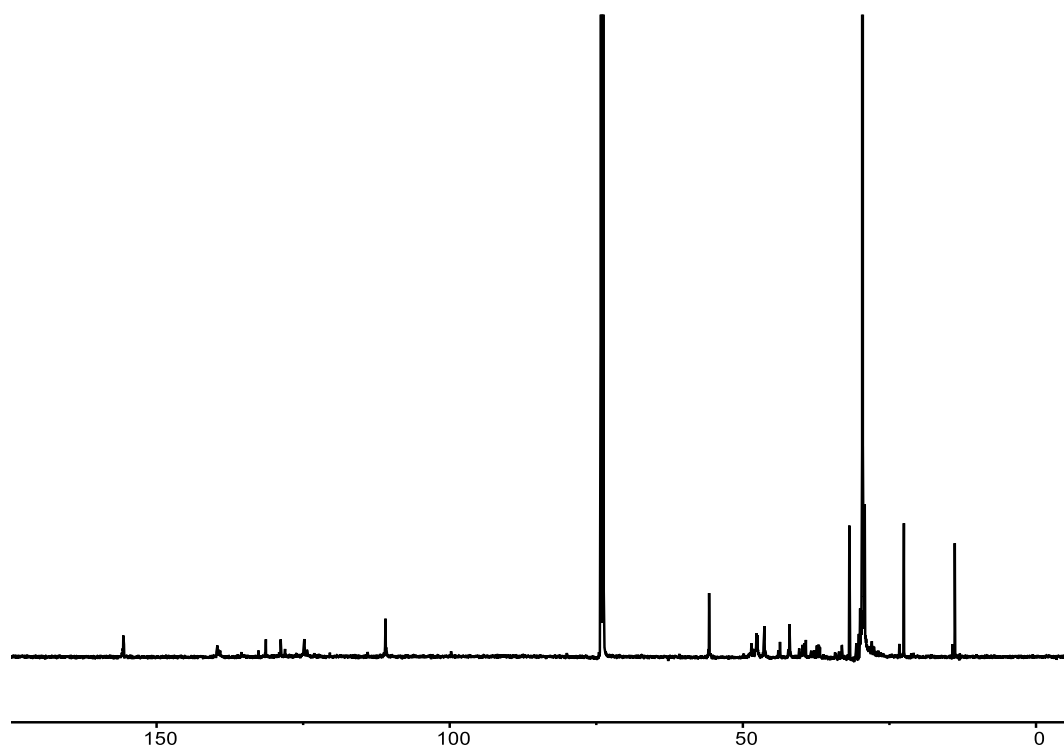
Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	18.150	0.013	32,284	Mn	1,027
Peak top	20.363	-7.703	3,156	Mw	3,571
Peak end	21.872	-5.505	138	Mz	7,047
				Mz+1	10,236
				Mv	3,571
Height [mV]			7.513	Mp	4,413
Area [mV*s]			1061.149	Mz/Mw	1.974
Height% [%]			49.622	Mw/Mn	3.476
[eta]			3570.61295	Mz+1/Mw	2.867

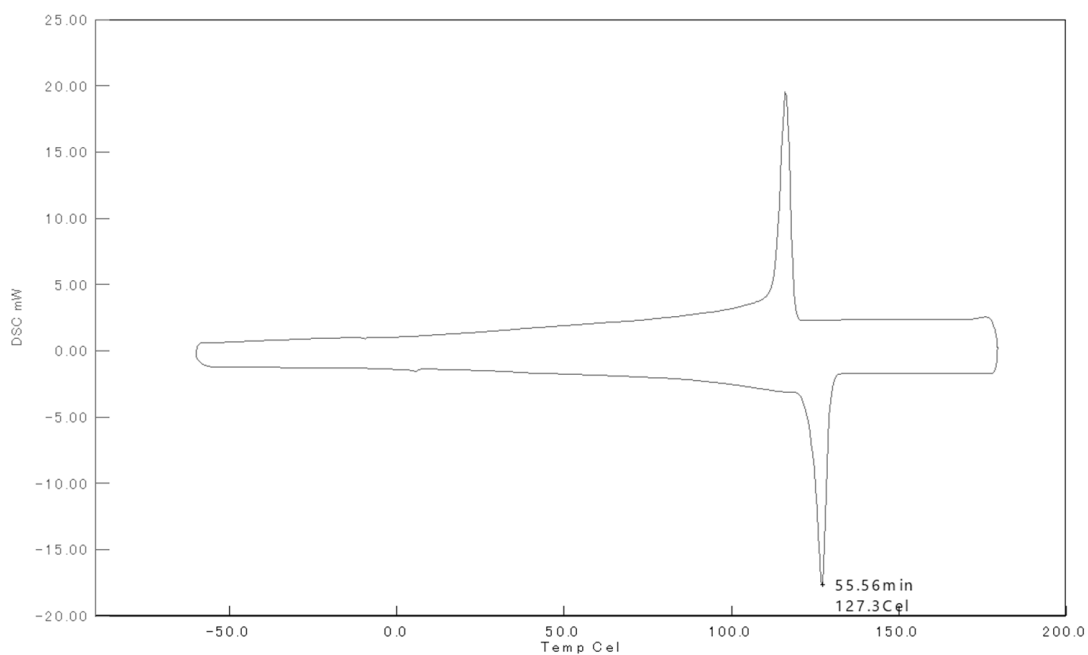
**Figure S30.** GPC trace of the polymer from Table 1, Entry 5.



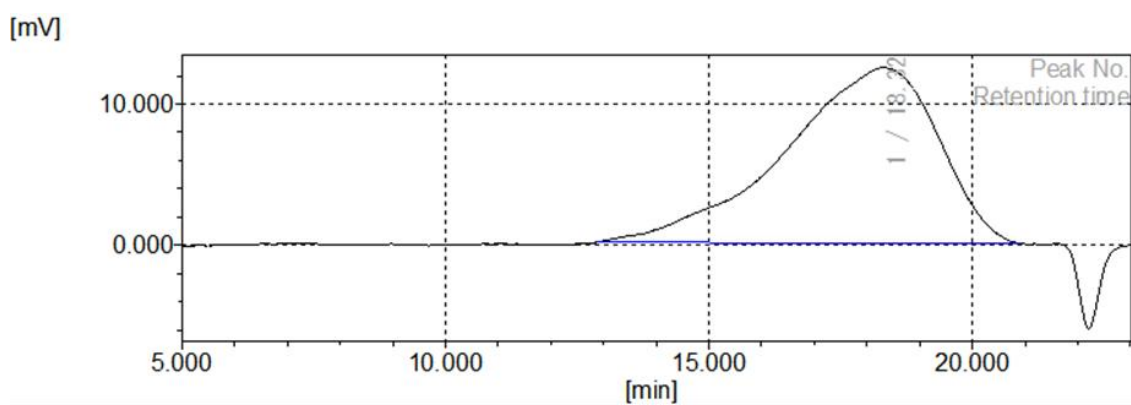
**Figure S31.**  $^1\text{H}$  NMR spectrum of the polymer from Table 1, Entry 6 (1,1,2,2-Tetrachloroethane- $d_2$ ).



**Figure S32.**  $^{13}\text{C}$  NMR spectrum of the polymer from Table 1, Entry 6 (1,1,2,2-Tetrachloroethane- $d_2$ ).



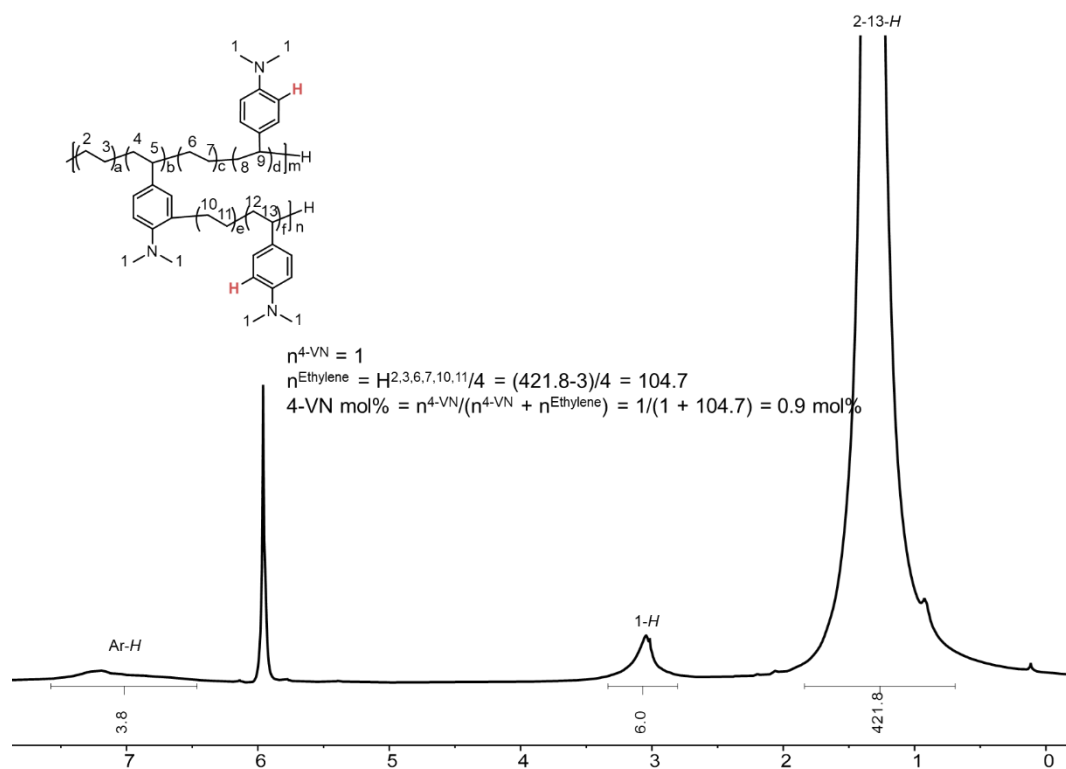
**Figure S33.** DSC curve of the polymer from Table 1, Entry 6.



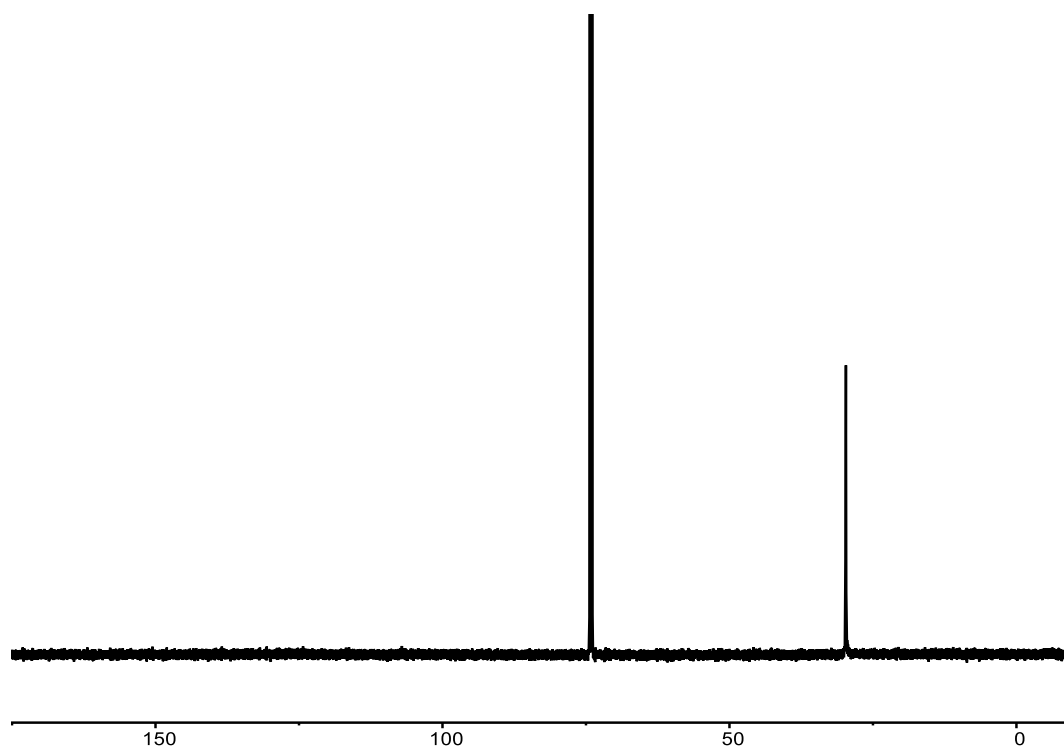
**Molecular mass calculation result (RI)**

Total		[min]	[mV]	[mol]		
Peak start	12.880	0.216	8,604,028	Mn	23,833	
Peak top	18.322	12.583	27,090	Mw	135,830	
Peak end	20.905	0.114	1,463	Mz	918,722	
				Mz+1	2,739,614	
				Mv	135,830	
Height [mV]			12.436	Mp	28,511	
Area [mV*s]			2516.226	Mz/Mw	6.764	
Height% [%]			100.000	Mw/Mn	5.699	
[eta]			135830.22712	Mz+1/Mw	20.169	

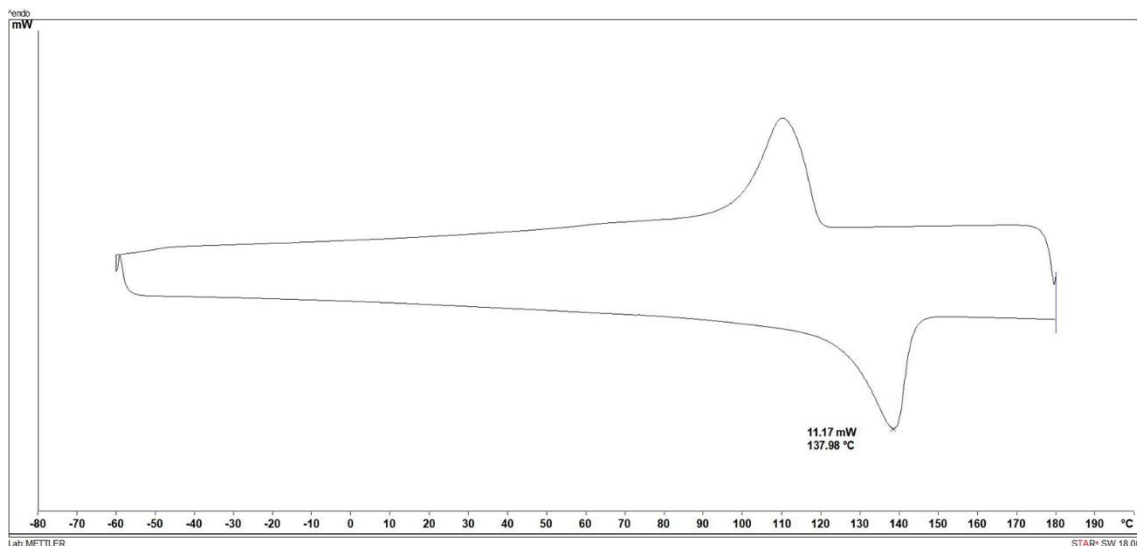
**Figure S34.** GPC trace of the polymer from Table 1, Entry 6.



**Figure S35.**  $^1\text{H}$  NMR spectrum of the polymer from Table 1, Entry 7 (1,1,2,2-Tetrachloroethane- $d_2$ ).



**Figure S36.**  $^{13}\text{C}$  NMR spectrum of the polymer from Table 1, Entry 7 (1,1,2,2-Tetrachloroethane- $d_2$ ).



**Figure S37.** DSC curve of the polymer from Table 1, Entry 7.

**MW Averages**

Mp: 960106

Mn: 466286

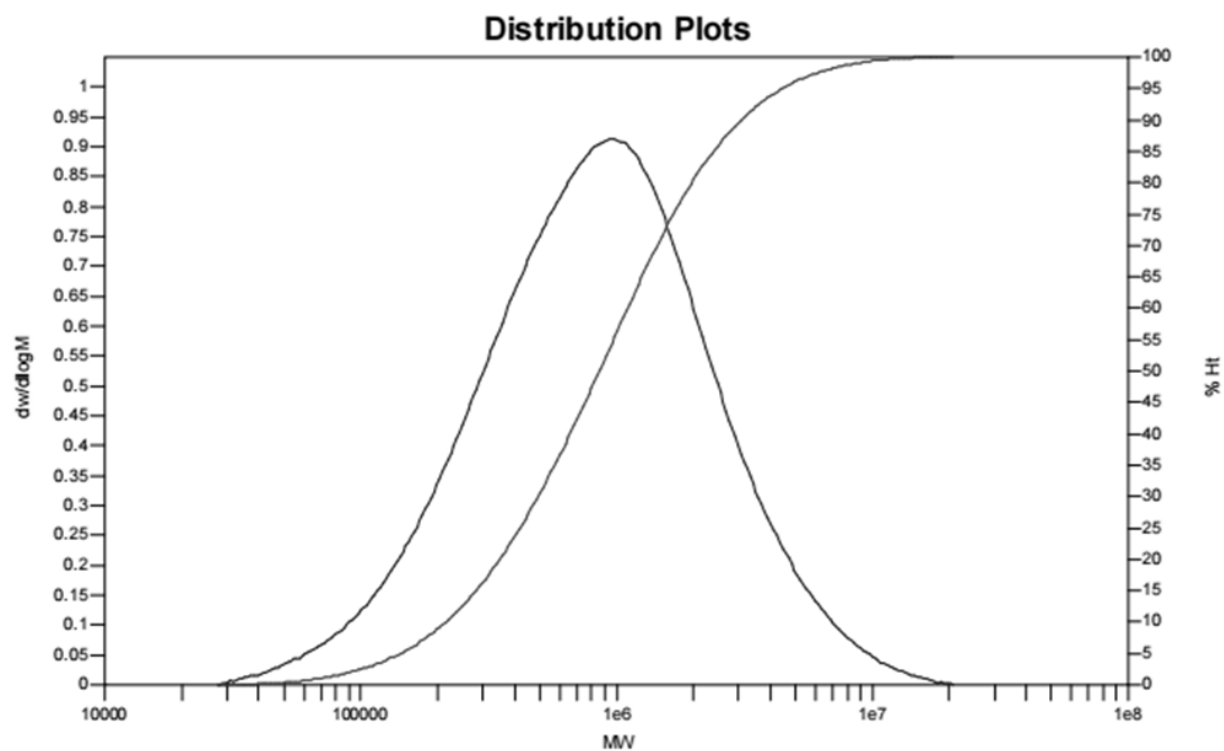
Mv: 1160664

Mw: 1346492

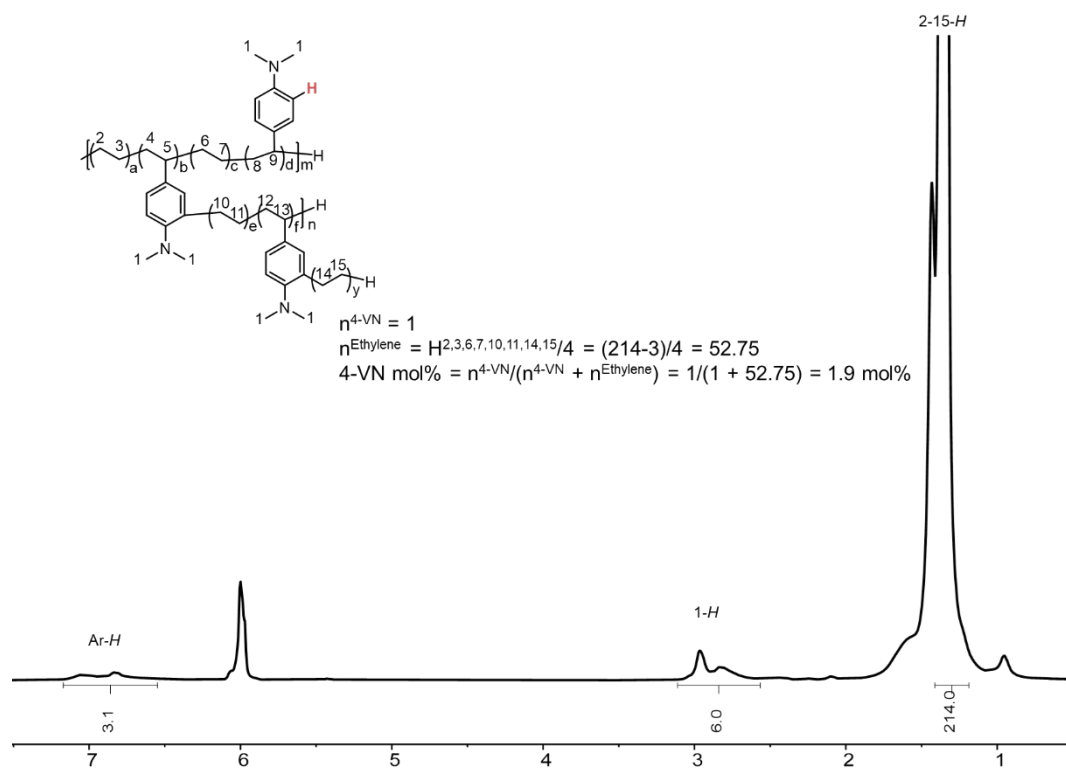
Mz: 3327095

Mz+1: 6364862

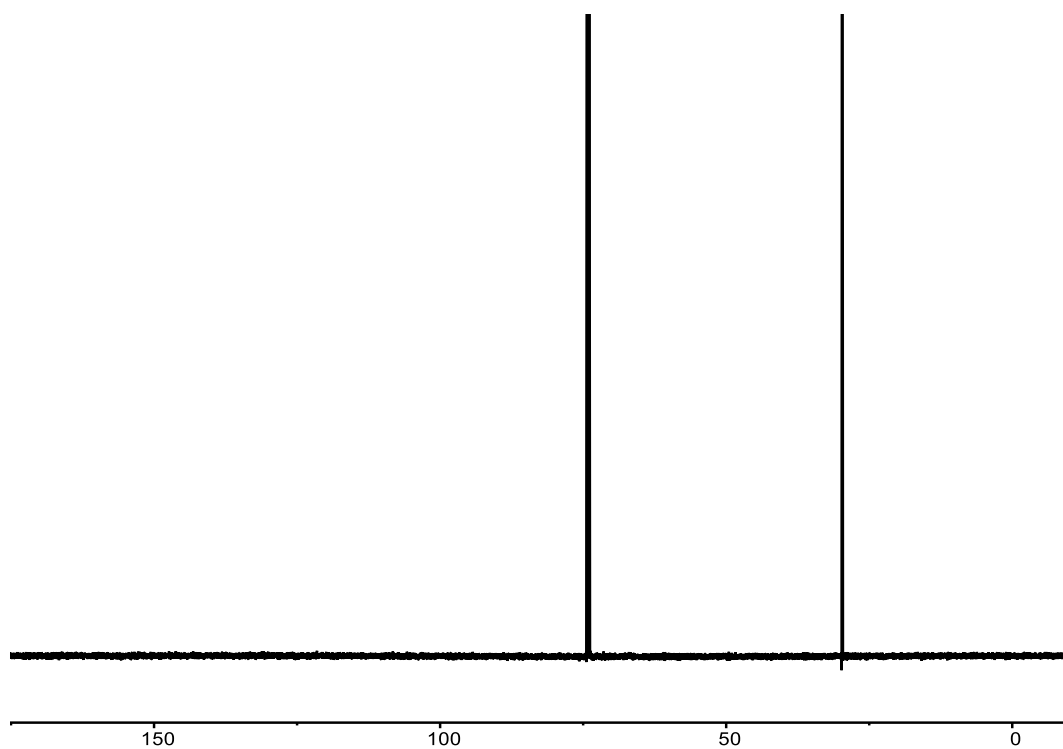
PD: 2.8877



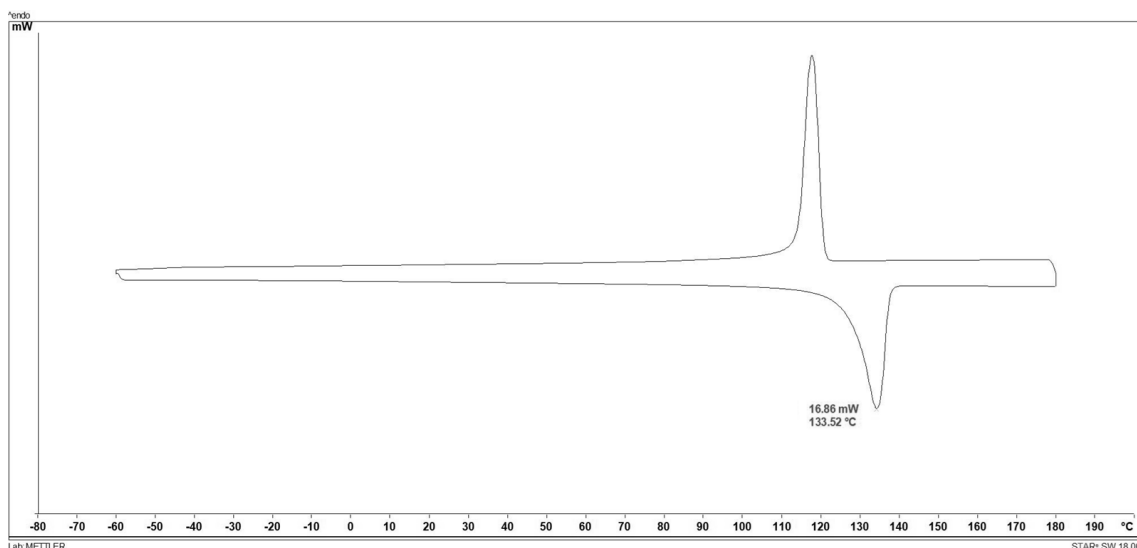
**Figure S38.** GPC trace of the polymer from Table 1, Entry 7.



**Figure S39.**  $^1\text{H}$  NMR spectrum of the polymer from Table 1, Entry 8 (1,1,2,2-Tetrachloroethane- $d_2$ ).



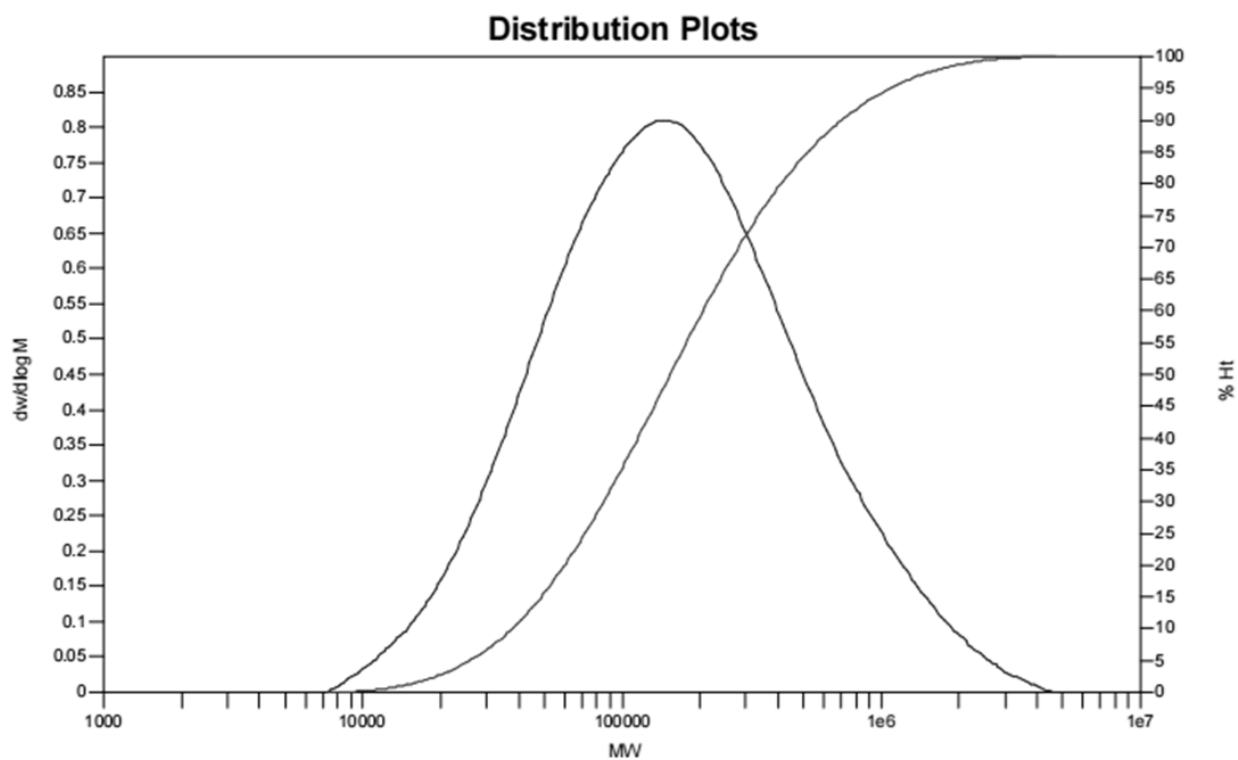
**Figure S40.**  $^{13}\text{C}$  NMR spectrum of the polymer from Table 1, Entry 8 (1,1,2,2-Tetrachloroethane- $d_2$ ).



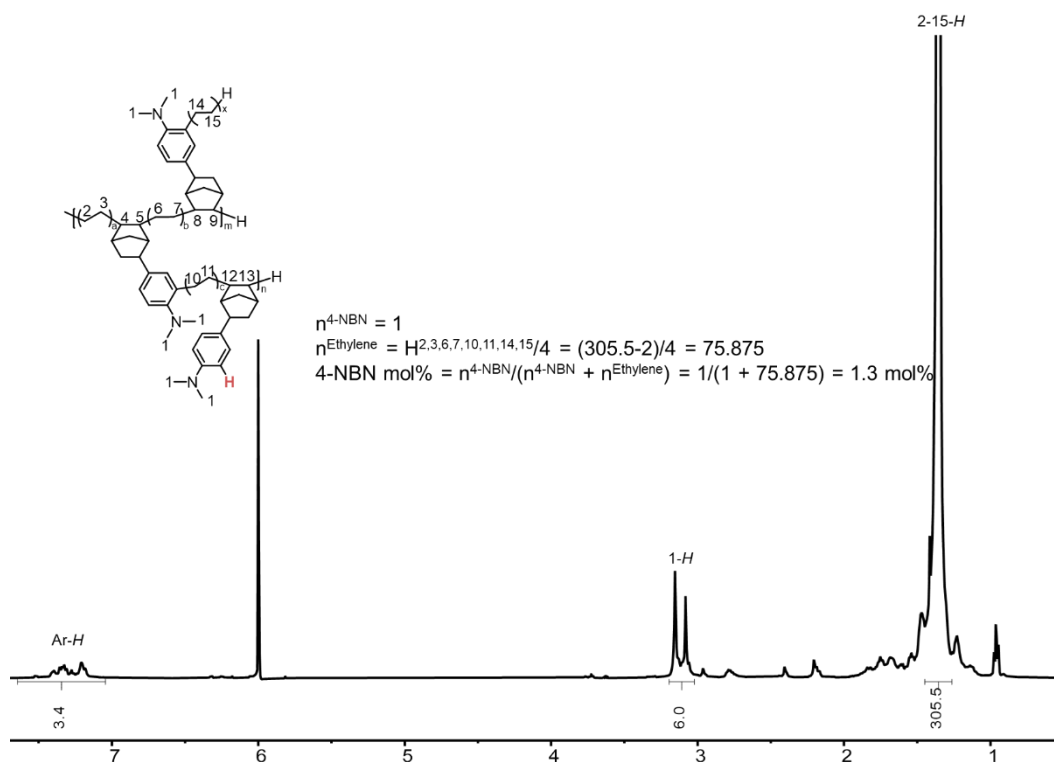
**Figure S41.** DSC curve of the polymer from Table 1, Entry 8.

**MW Averages**

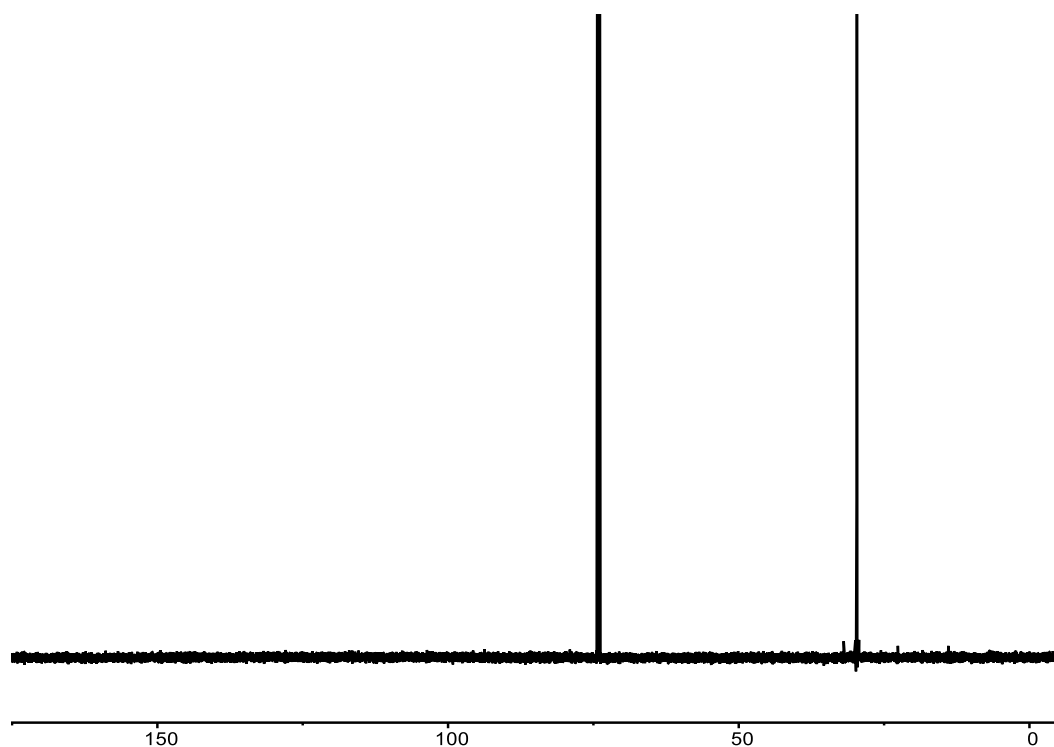
Mp: 150003	Mn: 85590	Mv: 237385	Mw: 285966
Mz: 850312	Mz+1: 1627128	PD: 3.3411	



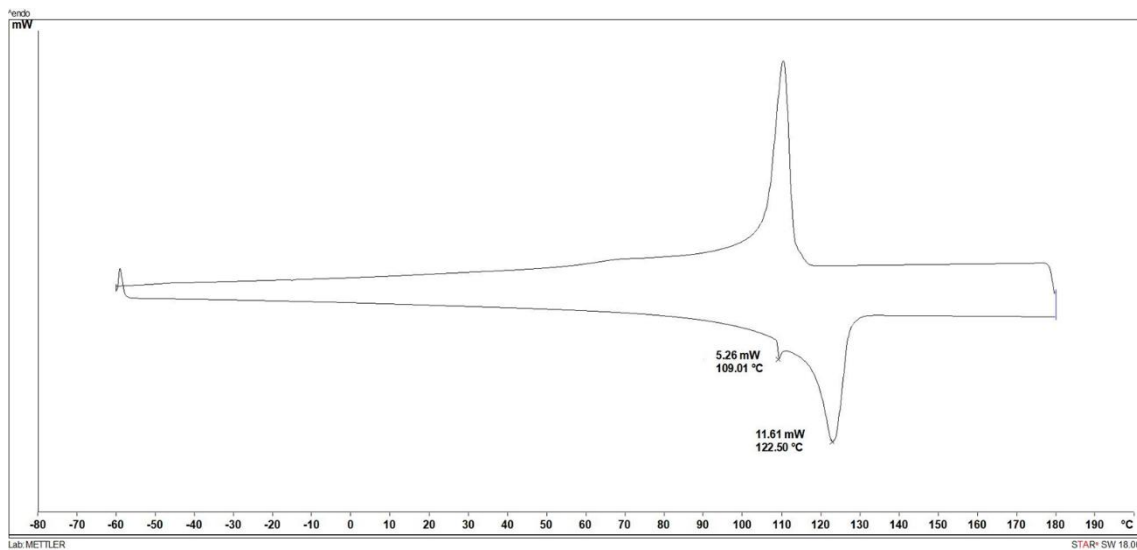
**Figure S42.** GPC trace of the polymer from Table 1, Entry 8.



**Figure S43.**  $^1\text{H}$  NMR spectrum of the polymer from Table 1, Entry 9 (1,1,2,2-Tetrachloroethane- $d_2$ ).



**Figure S44.**  $^{13}\text{C}$  NMR spectrum of the polymer from Table 1, Entry 9 (1,1,2,2-Tetrachloroethane- $d_2$ ).



**Figure S45.** DSC curve of the polymer from Table 1, Entry 9.

**MW Averages**

Mp: 49731

Mn: 16256

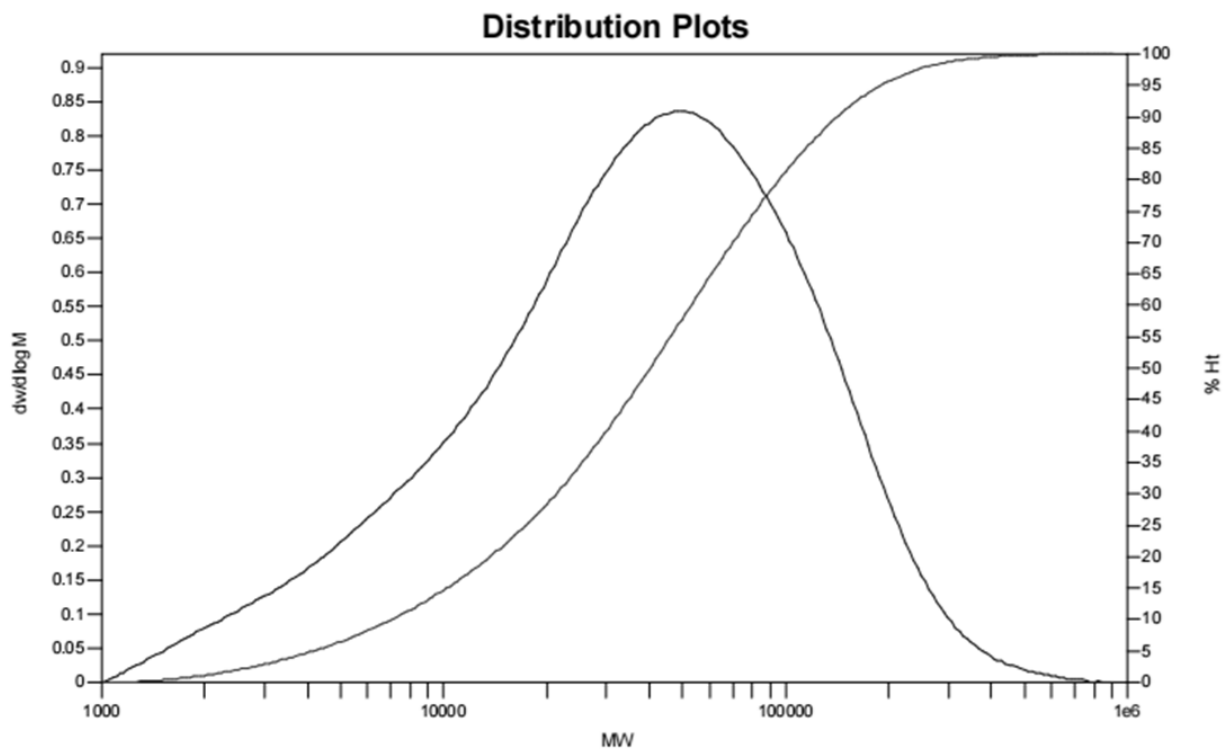
Mv: 51318

Mw: 59414

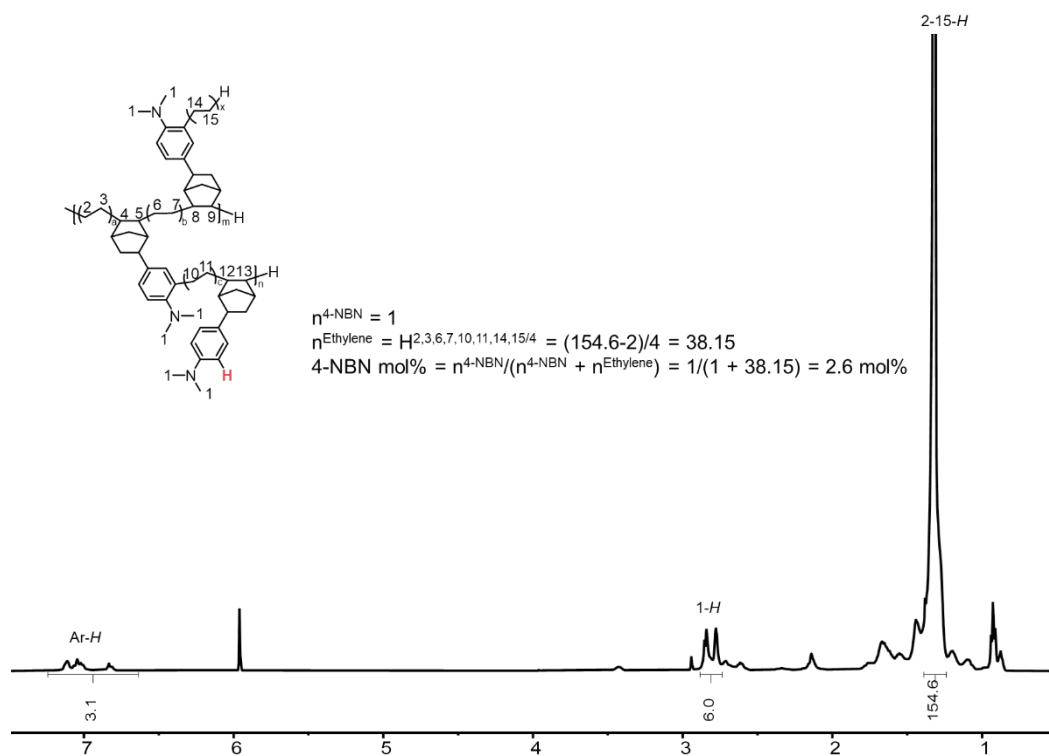
Mz: 132148

Mz+1: 225477

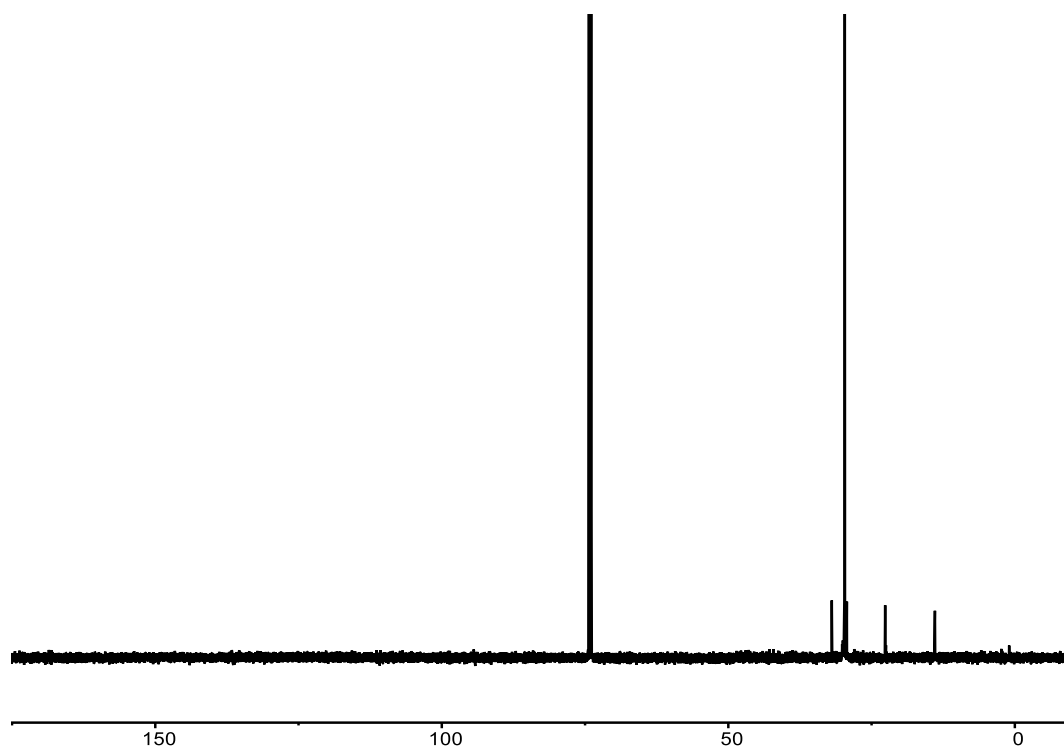
PD: 3.6549



**Figure S46.** GPC trace of the polymer from Table 1, Entry 9.



**Figure S47.**  $^1\text{H}$  NMR spectrum of the polymer from Table 1, Entry 10 (1,1,2,2-Tetrachloroethane- $d_2$ ).



**Figure S48.**  $^{13}\text{C}$  NMR spectrum of the polymer from Table 1, Entry 10 (1,1,2,2-Tetrachloroethane- $d_2$ ).

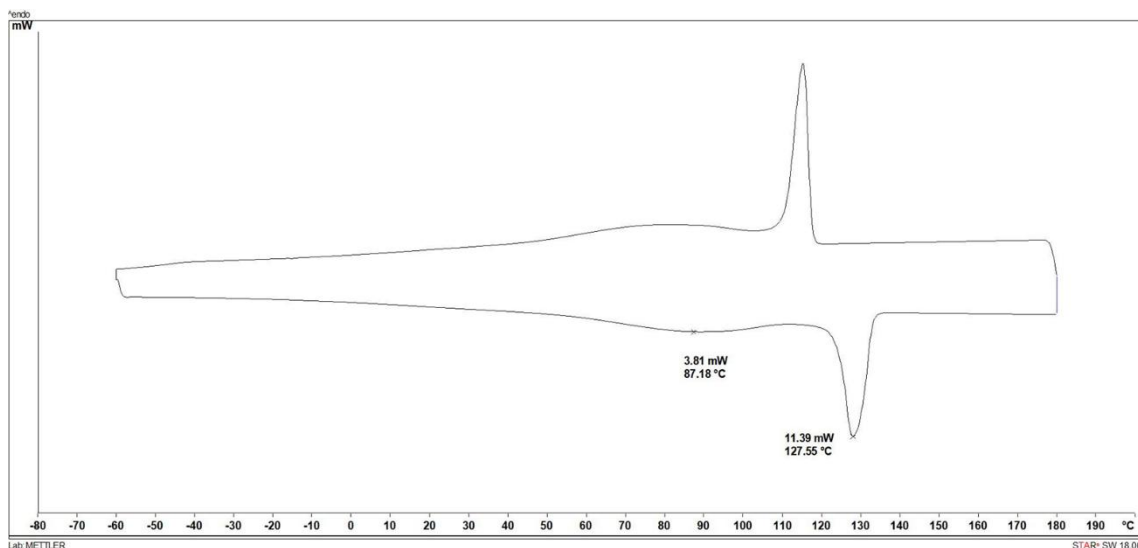


Figure S49. DSC curve of the polymer from Table 1, Entry 10.

**MW Averages**

Mp: 11005

Mn: 5415

Mv: 10324

Mw: 11290

Mz: 18470

Mz+1: 25174

PD: 2.0849

**Distribution Plots**

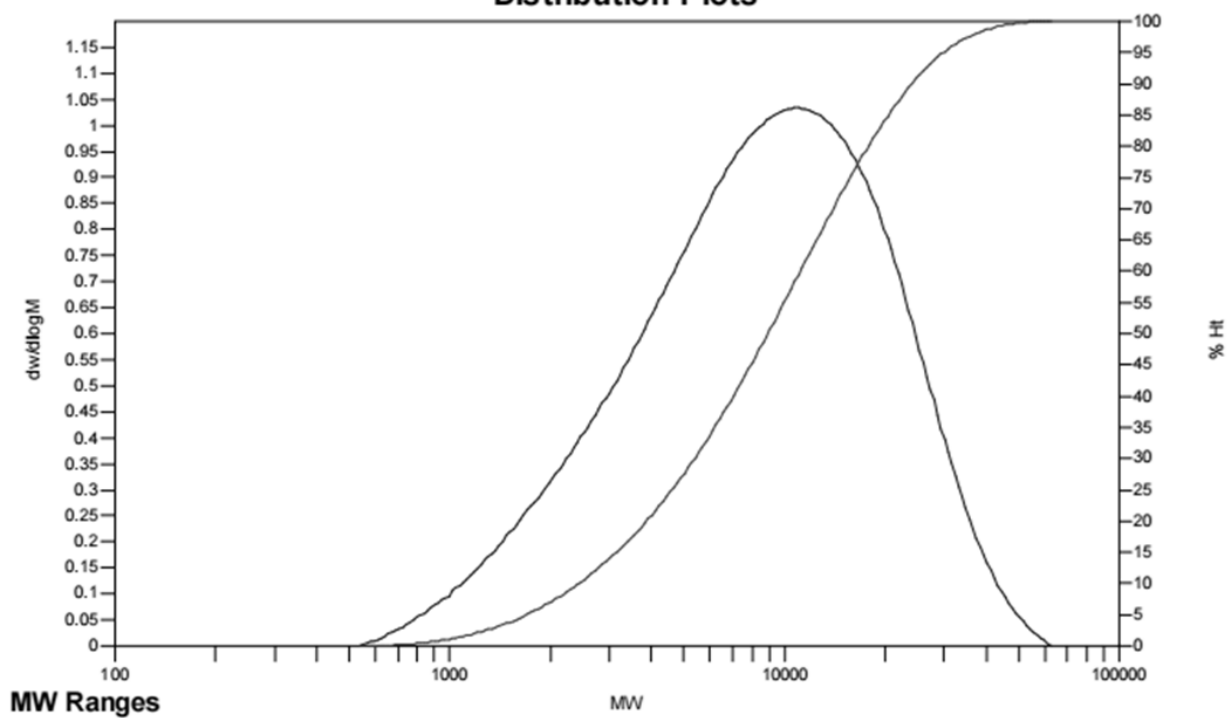
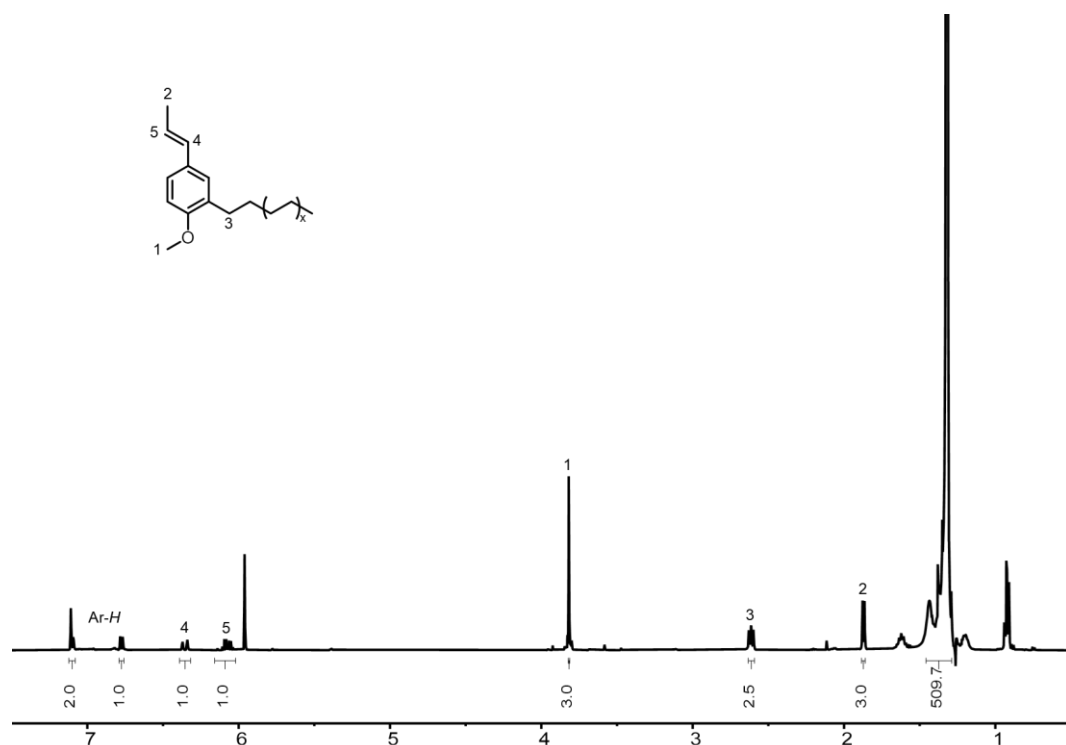
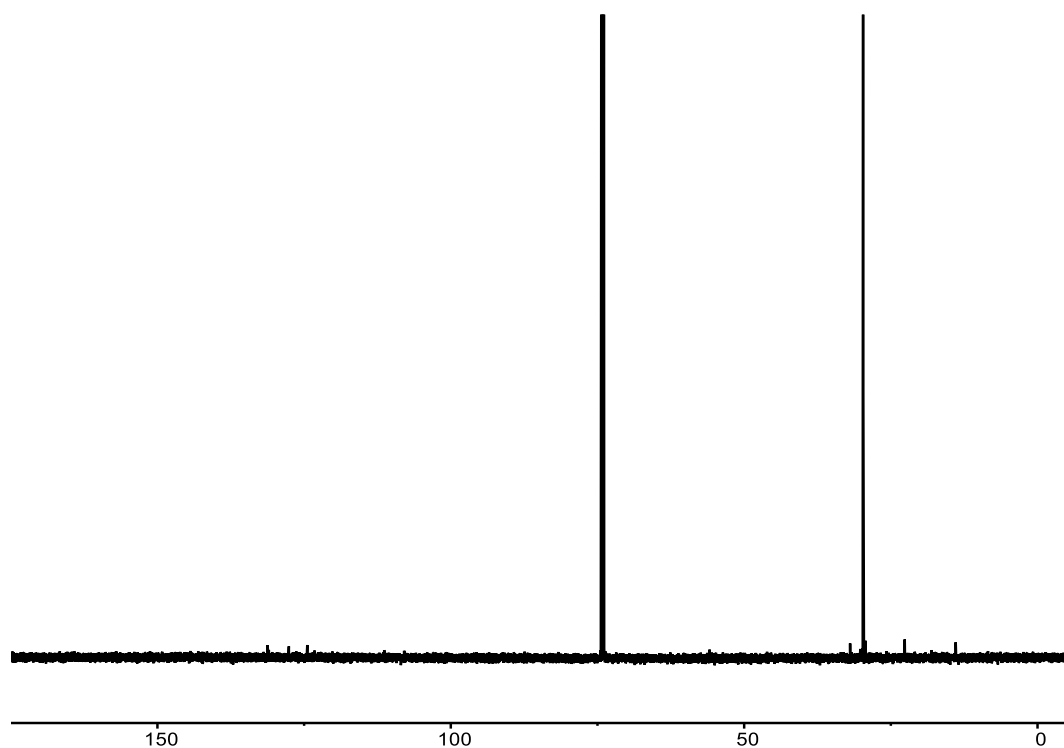


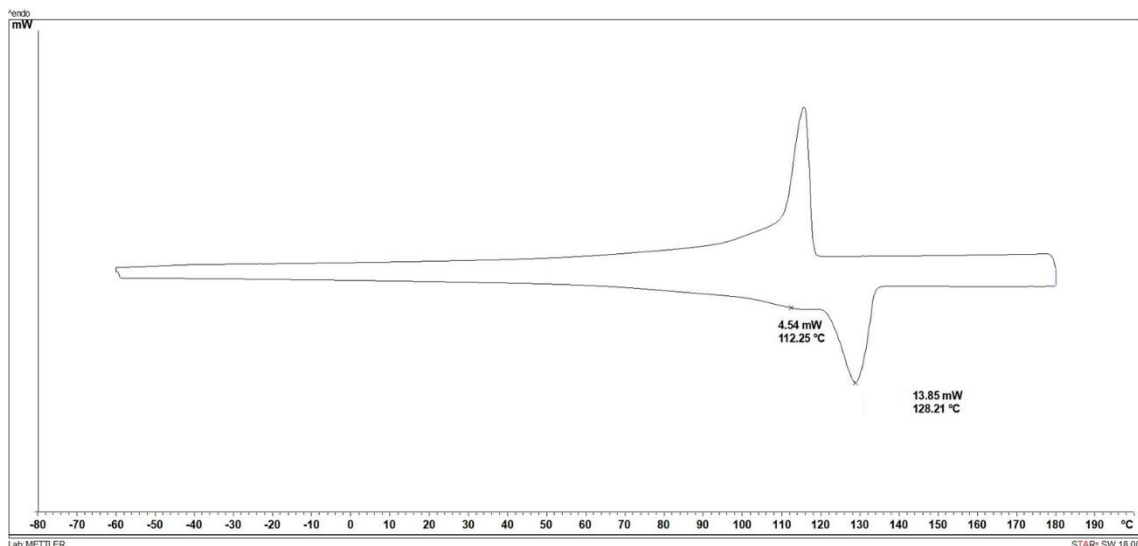
Figure S50. GPC trace of the polymer from Table 1, Entry 10.



**Figure S51.**  $^1\text{H}$  NMR spectrum of the polymer from Table 1, Entry 11 (1,1,2,2-Tetrachloroethane- $d_2$ ).



**Figure S52.**  $^{13}\text{C}$  NMR spectrum of the polymer from Table 1, Entry 11 (1,1,2,2-Tetrachloroethane- $d_2$ ).



**Figure S53.** DSC curve of the polymer from Table 1, Entry 11.

**MW Averages**

Mp: 4551

Mn: 3028

Mv: 4520

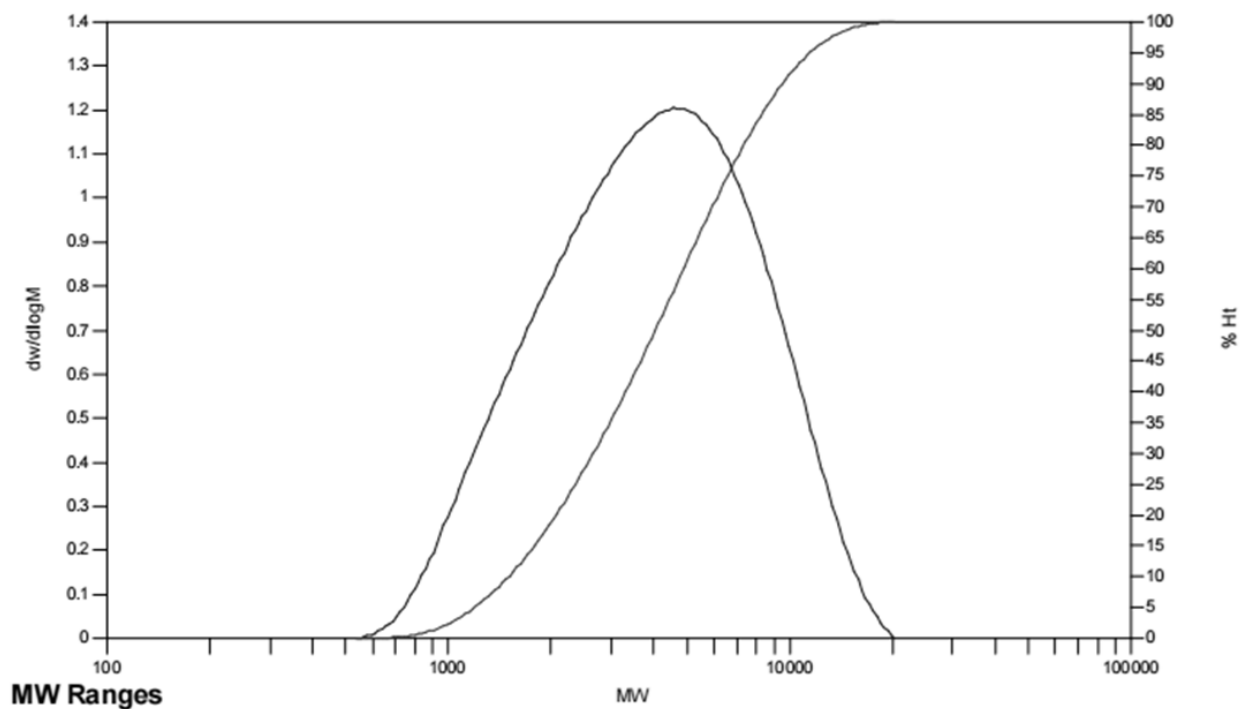
Mw: 4817

Mz: 6979

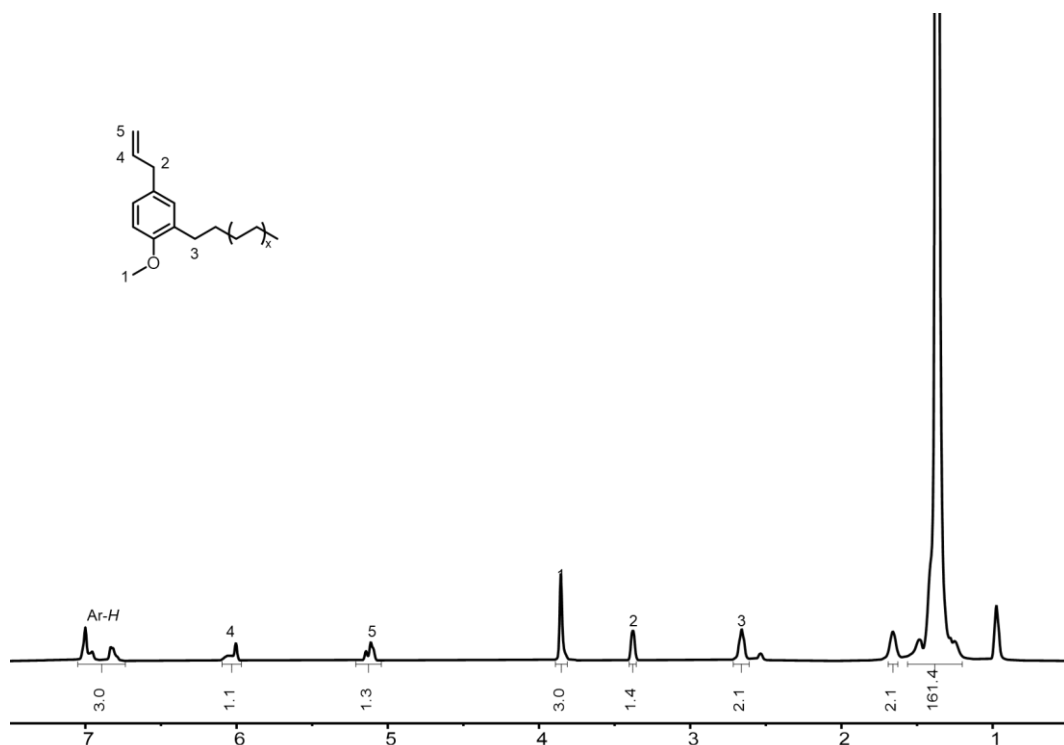
Mz+1: 9001

PD: 1.5908

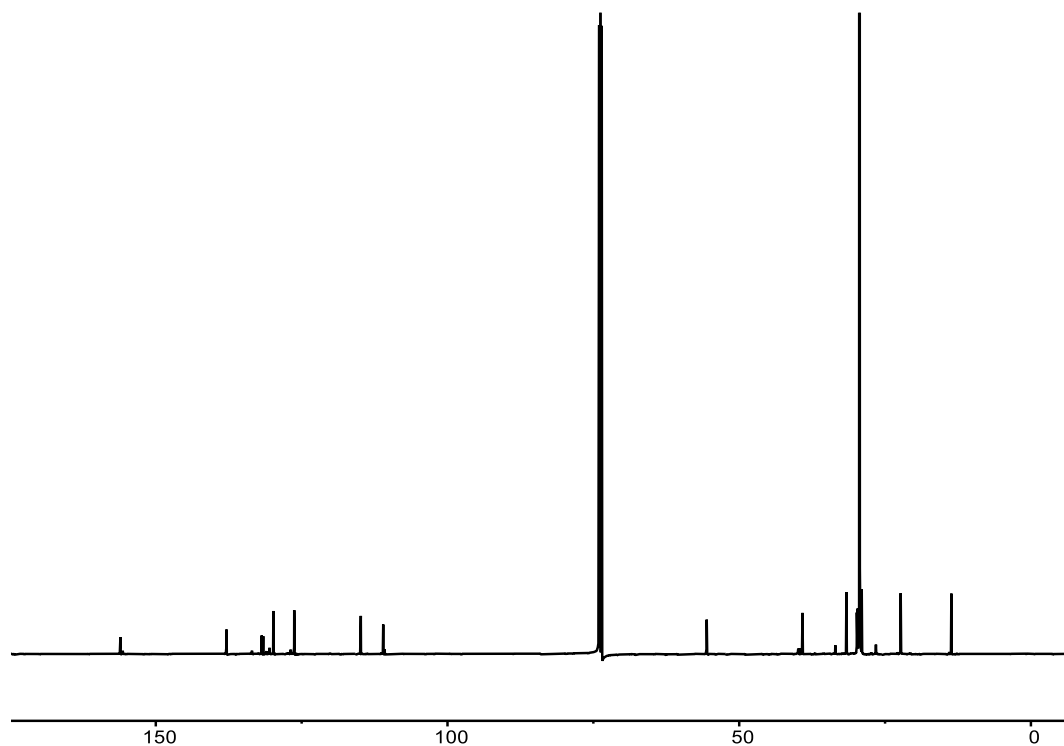
**Distribution Plots**



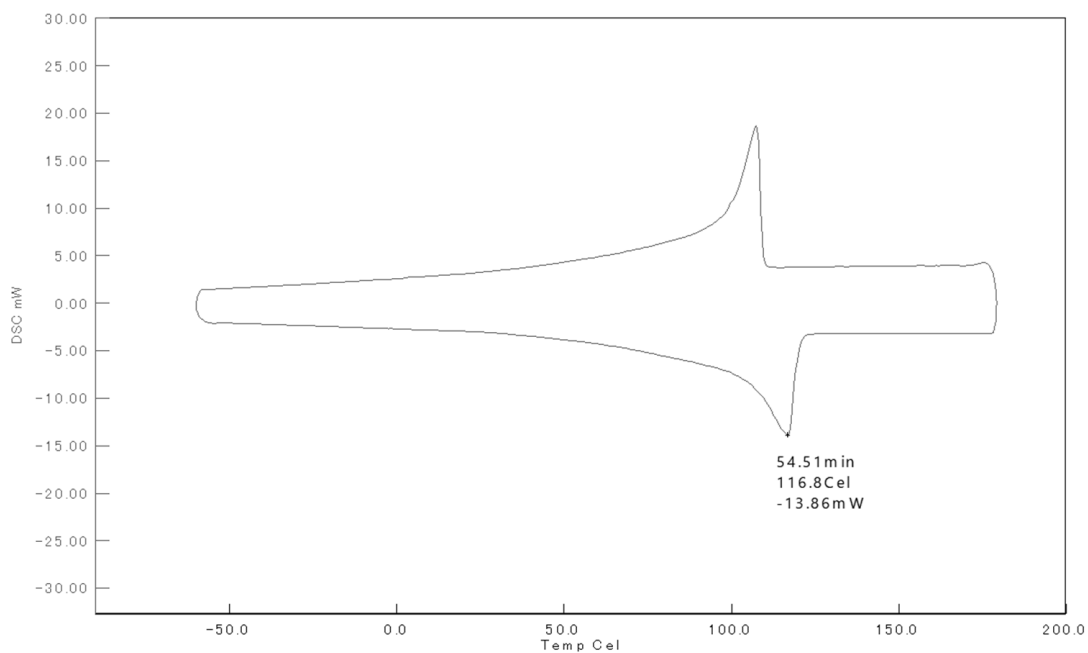
**Figure S54.** GPC trace of the polymer from Table 1, Entry 11.



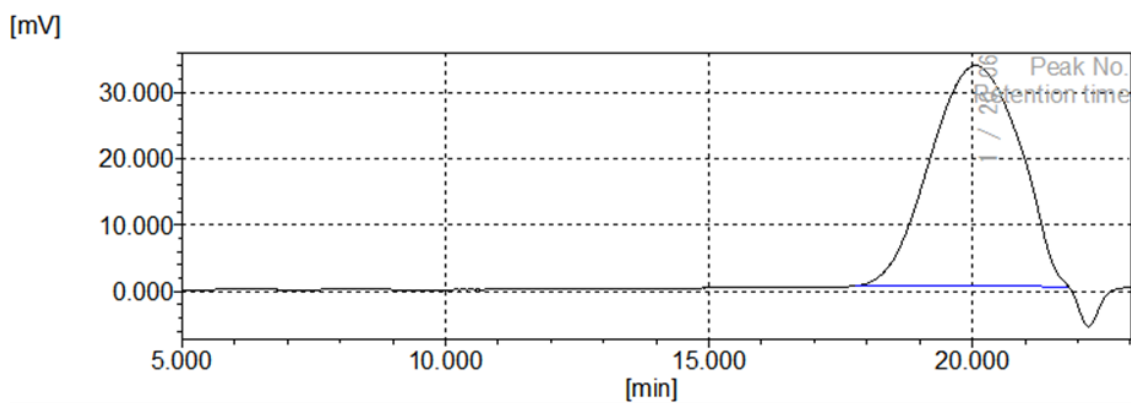
**Figure S55.** <sup>1</sup>H NMR spectrum of the polymer from Table 1, Entry 12 (1,1,2,2-Tetrachloroethane-d<sub>2</sub>).



**Figure S56.** <sup>13</sup>C NMR spectrum of the polymer from Table 1, Entry 12 (1,1,2,2-Tetrachloroethane-d<sub>2</sub>).



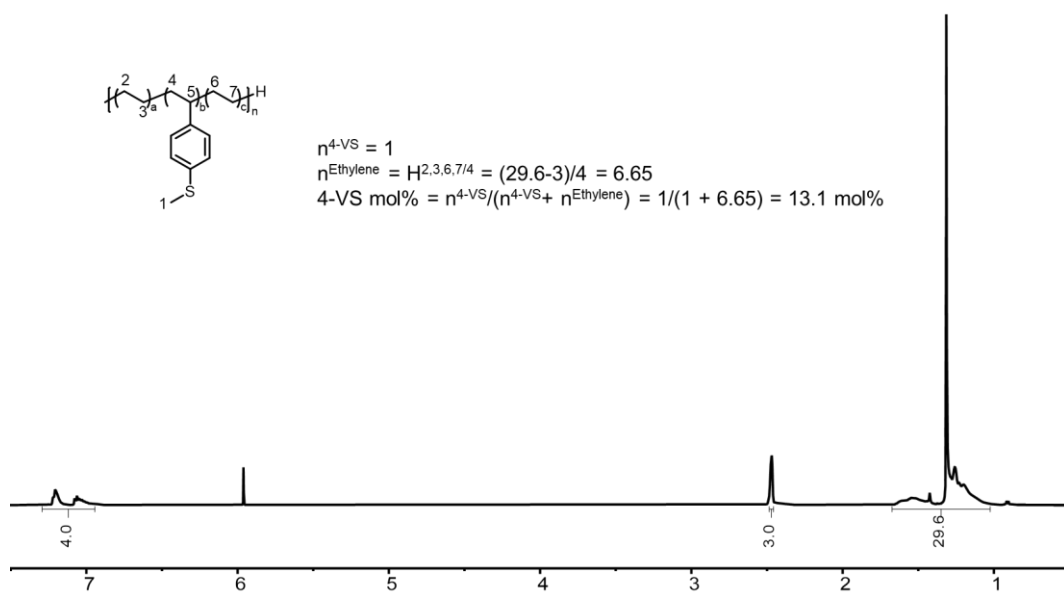
**Figure S57.** DSC curve of the polymer from Table 1, Entry 12.



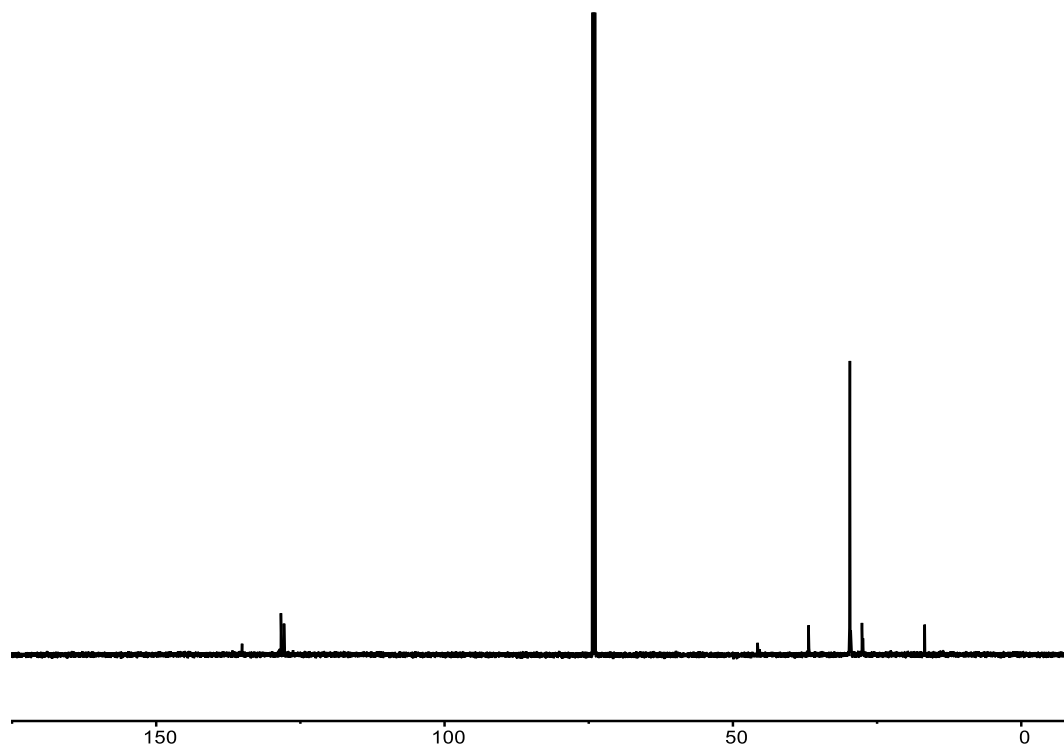
**Molecular mass calculation result (RI)**

Total	[min]	[mV]	[mol]	Mn	
Peak start	17.778	0.827	47,087	Mw	5,941
Peak top	20.063	34.026	4,487	Mz	10,217
Peak end	21.823	0.732	164	Mz+1	14,981
				Mv	5,941
Height [mV]			33.253	Mp	5,282
Area [mV*s]			3925.983	Mz/Mw	1.720
Height% [%]			100.000	Mw/Mn	2.131
[eta]			5940.75079	Mz+1/Mw	2.522

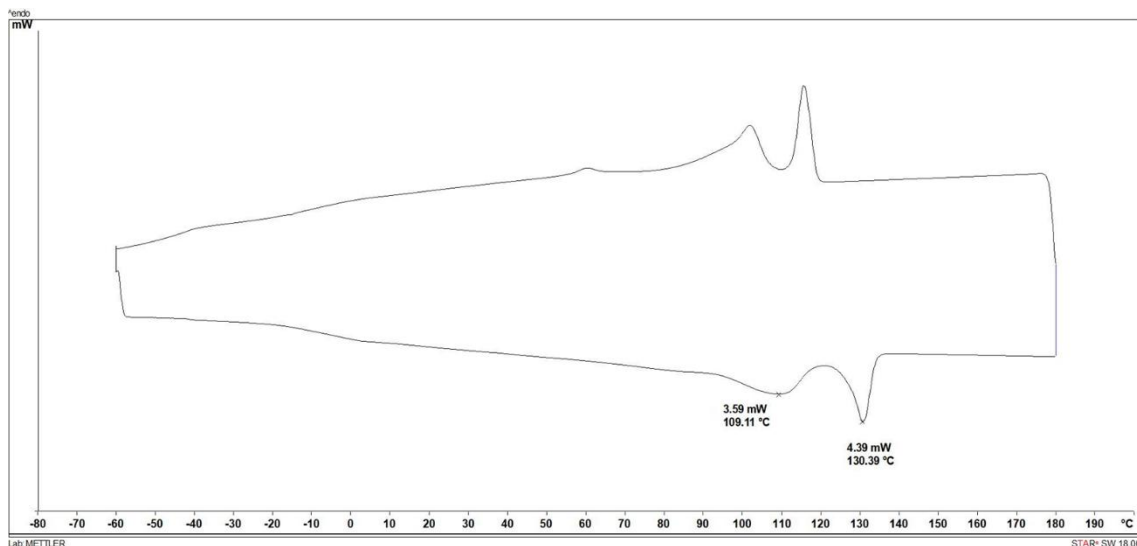
**Figure S58.** GPC trace of the polymer from Table 1, Entry 12.



**Figure S59.**  $^1\text{H}$  NMR spectrum of the polymer from Table 2, Entry 1 (1,1,2,2-Tetrachloroethane- $d_2$ ).



**Figure S60.**  $^{13}\text{C}$  NMR spectrum of the polymer from Table 2, Entry 1 (1,1,2,2-Tetrachloroethane- $d_2$ ).

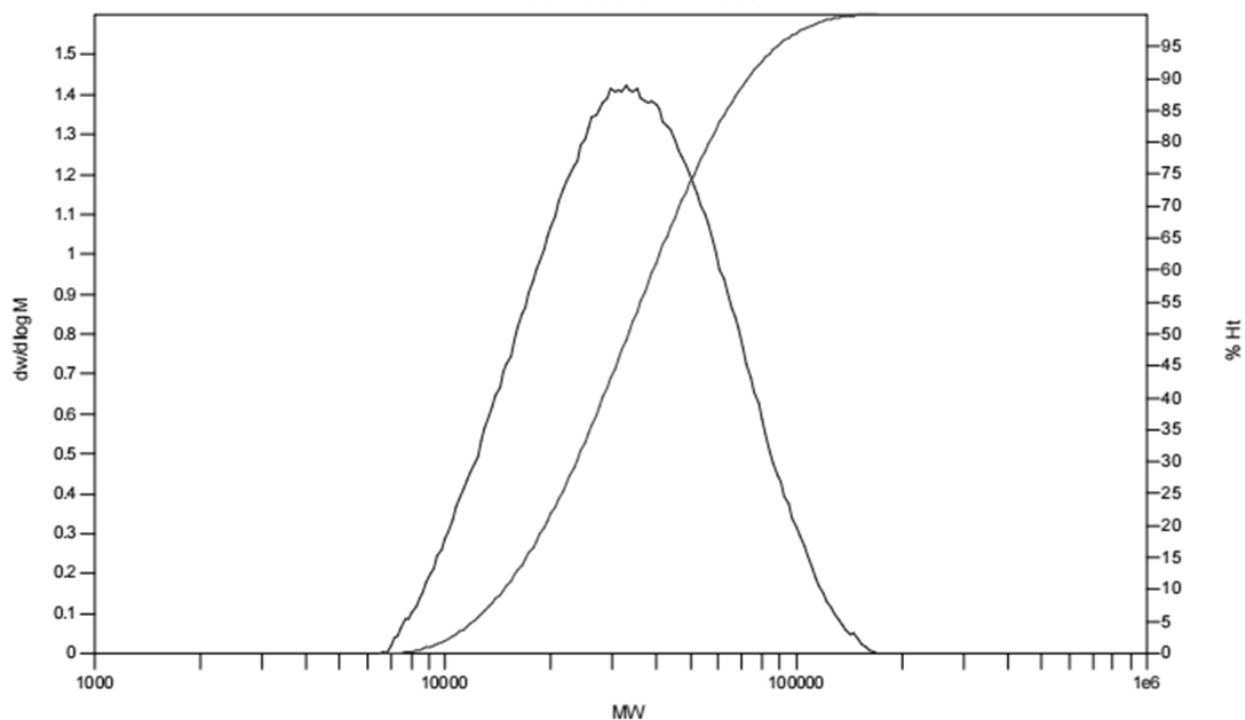


**Figure S61.** DSC curve of the polymer from Table 2, Entry 1.

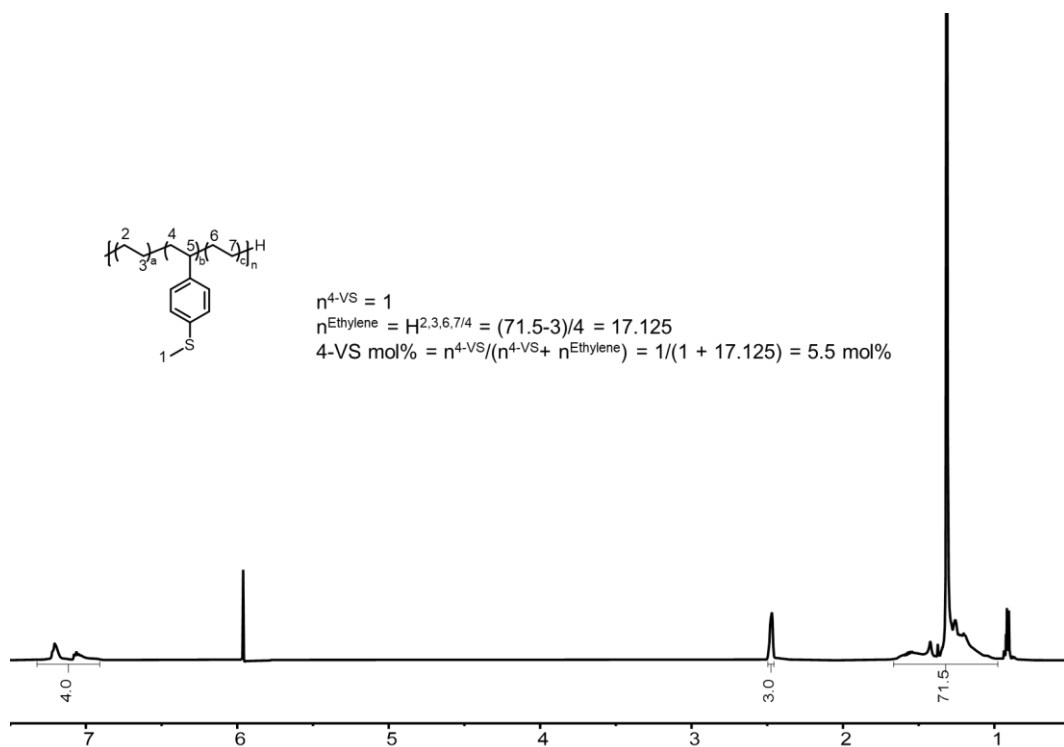
**MW Averages**

Mp: 32682	Mn: 27019	Mv: 36641	Mw: 38601
Mz: 53325	Mz+1: 68875	PD: 1.4287	

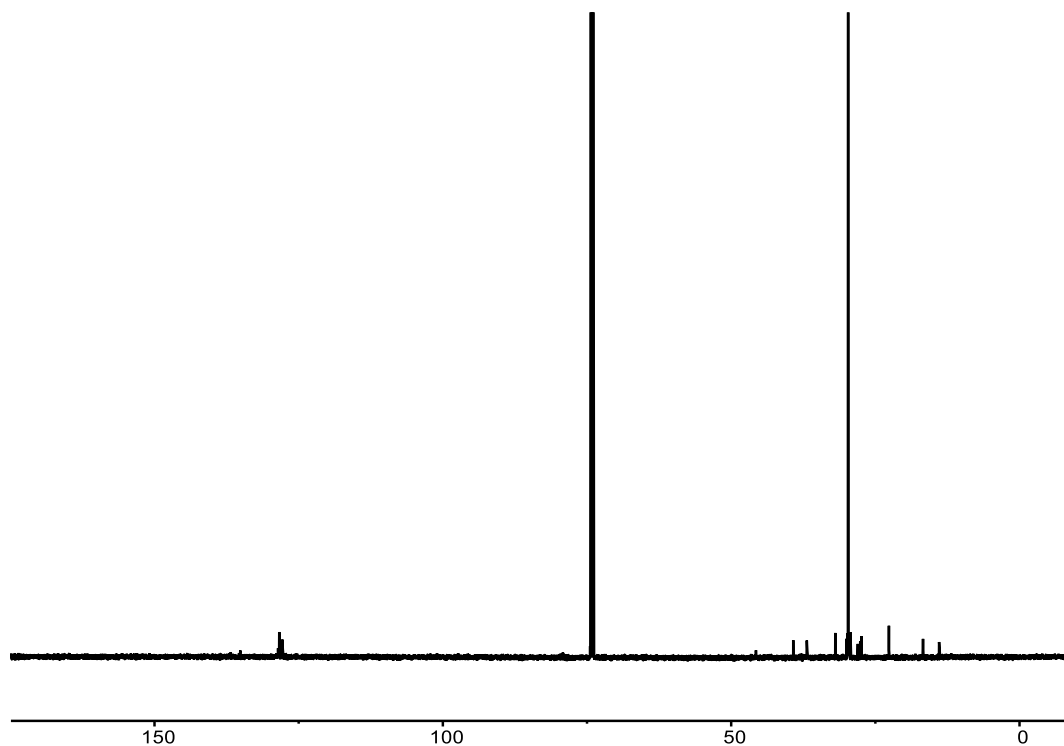
**Distribution Plots**



**Figure S62.** GPC trace of the polymer from Table 2, Entry 1.



**Figure S63.**  $^1\text{H}$  NMR spectrum of the polymer from Table 2, Entry 2 (1,1,2,2-Tetrachloroethane- $d_2$ ).



**Figure S64.**  $^{13}\text{C}$  NMR spectrum of the polymer from Table 2, Entry 2 (1,1,2,2-Tetrachloroethane- $d_2$ ).

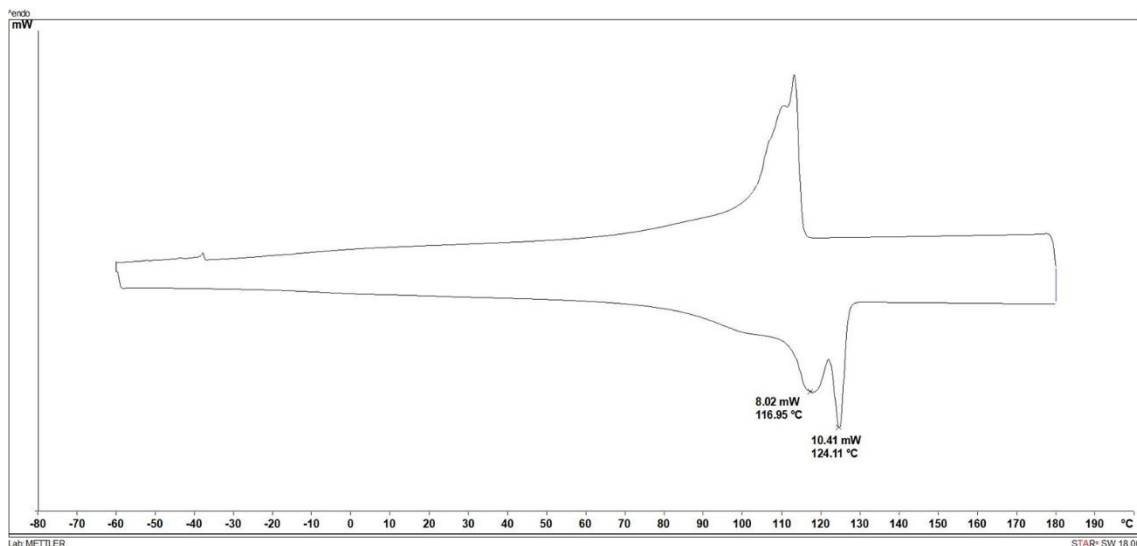


Figure S65. DSC curve of the polymer from Table 2, Entry 2.

**MW Averages**

Mp: 6056	Mn: 3760	Mv: 5866	Mw: 6286
Mz: 9612	Mz+1: 13857	PD: 1.6718	

**Distribution Plots**

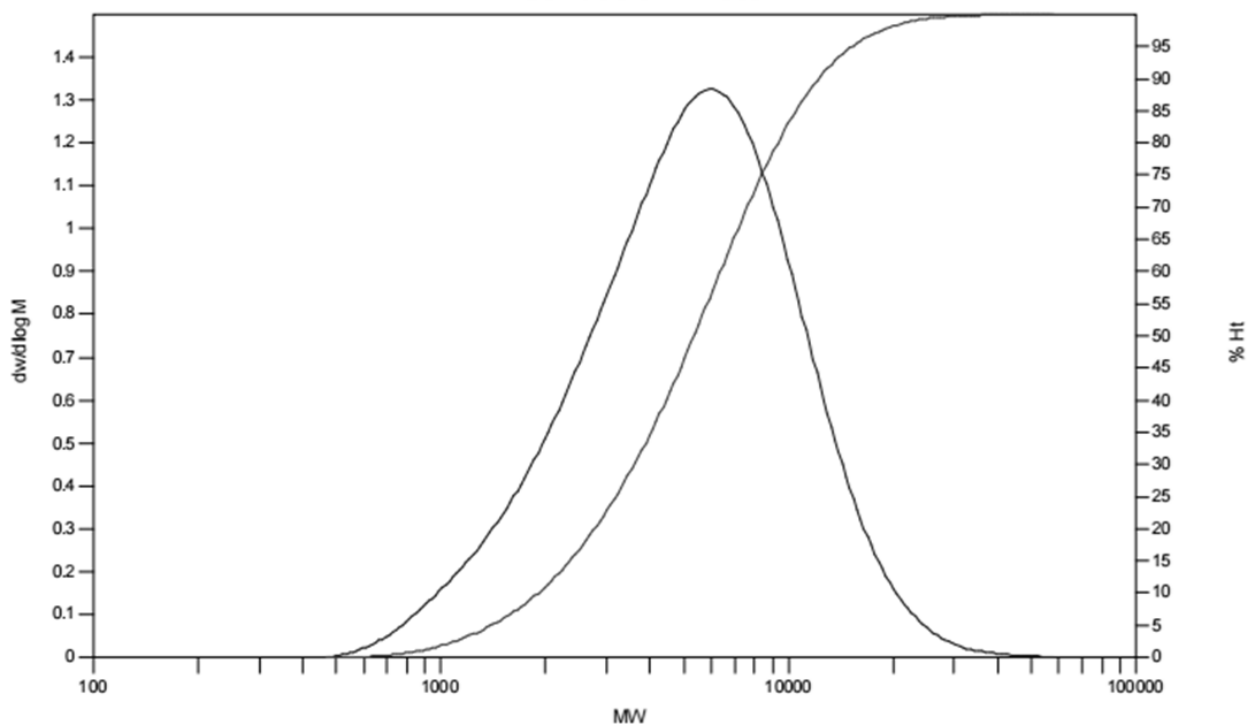
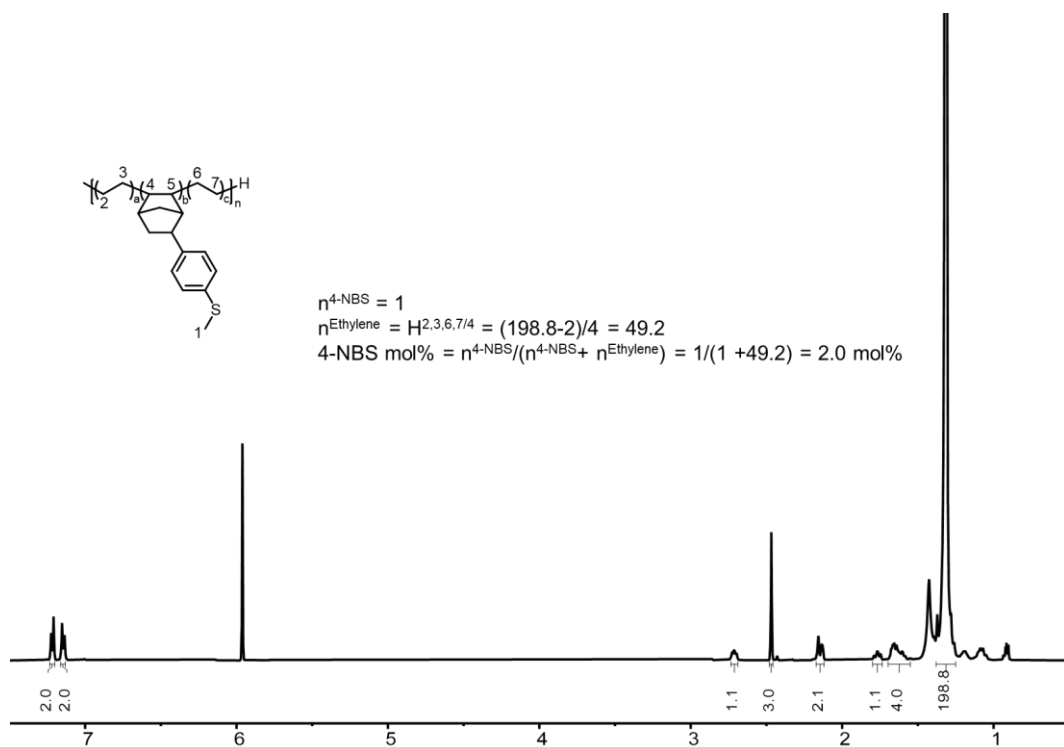
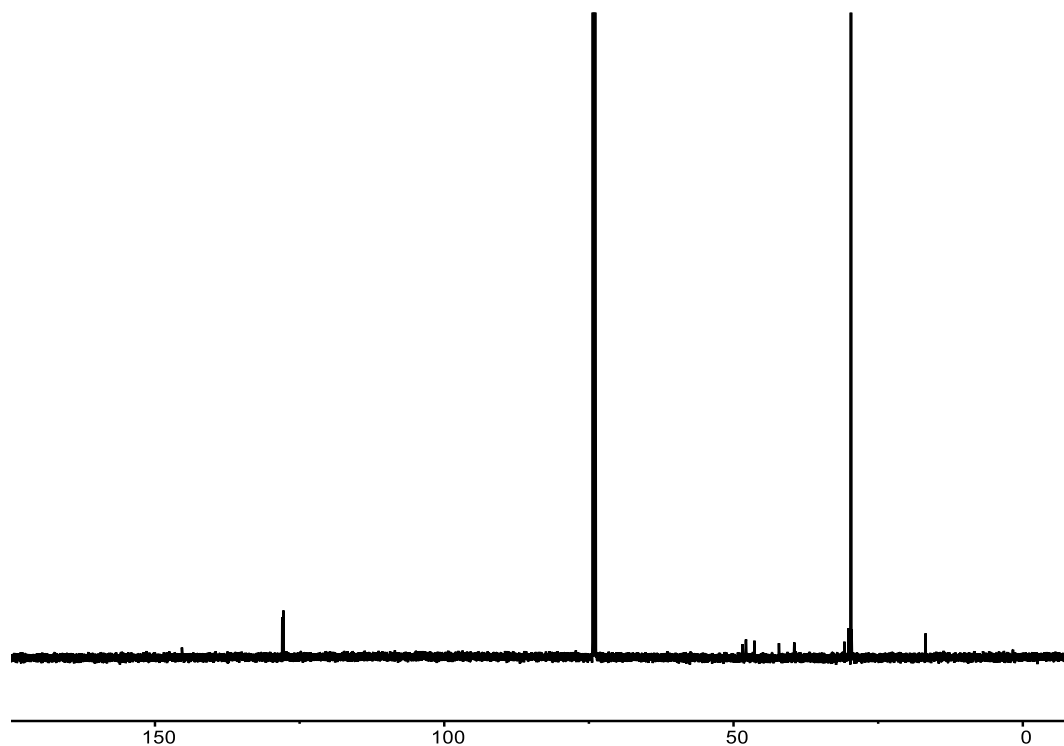


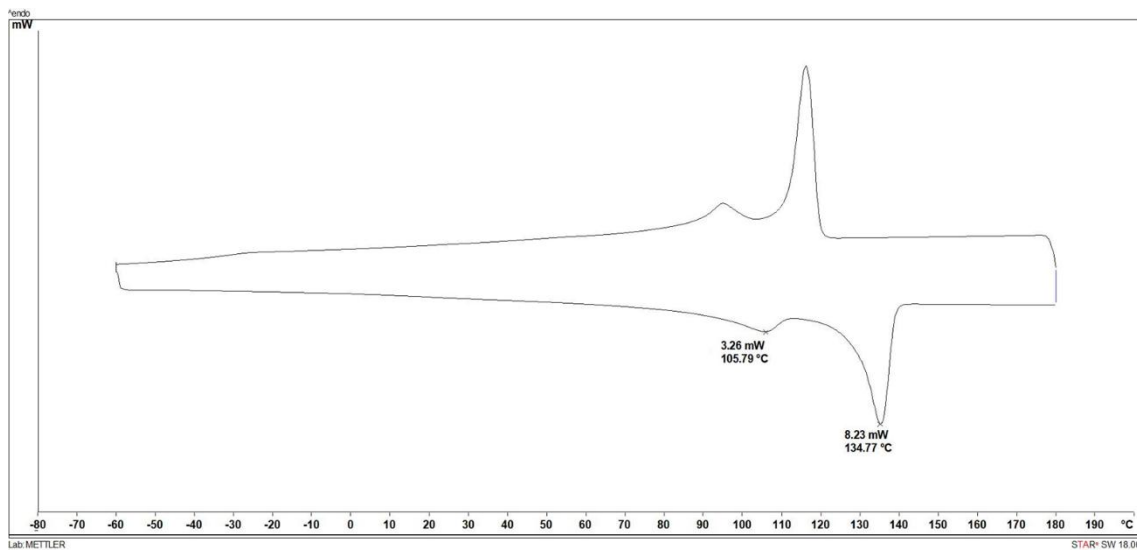
Figure S66. GPC trace of the polymer from Table 2, Entry 2.



**Figure S67.**  $^1\text{H}$  NMR spectrum of the polymer from Table 2, Entry 3 (1,1,2,2-Tetrachloroethane- $d_2$ ).



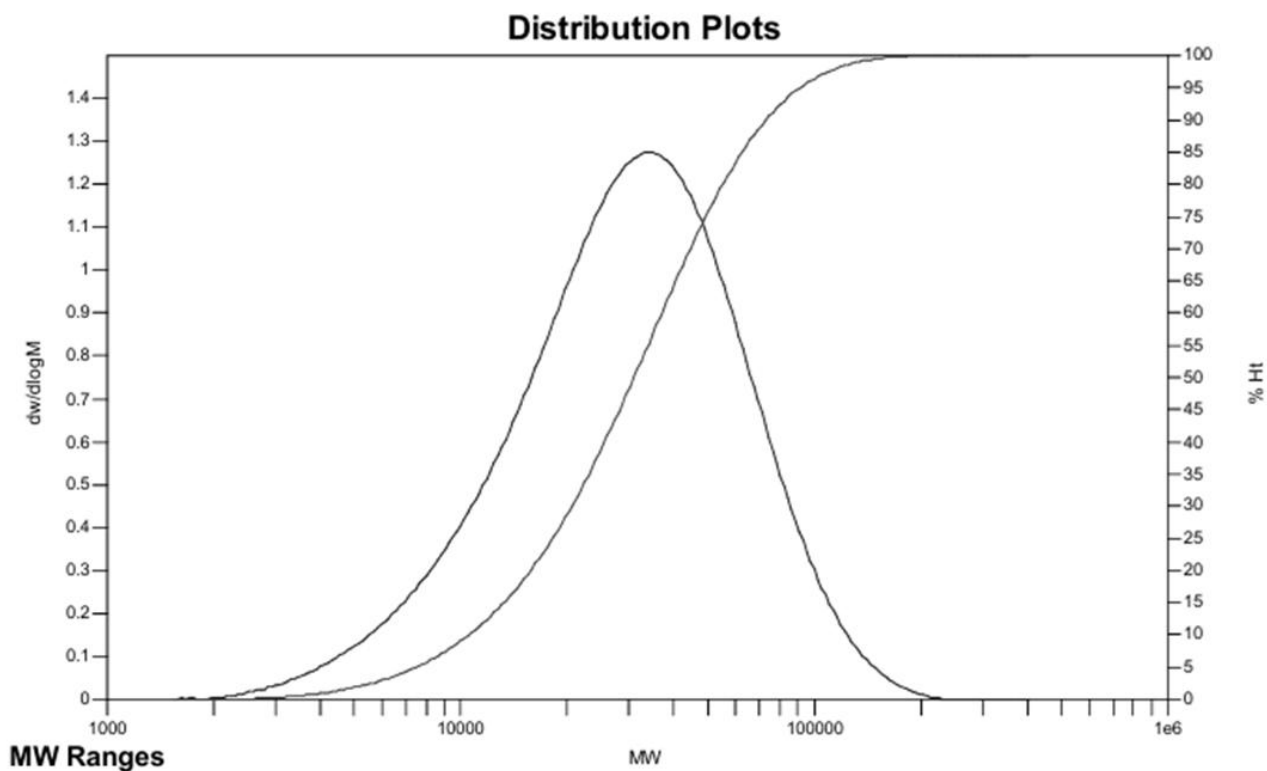
**Figure S68.**  $^{13}\text{C}$  NMR spectrum of the polymer from Table 2, Entry 3 (1,1,2,2-Tetrachloroethane- $d_2$ ).



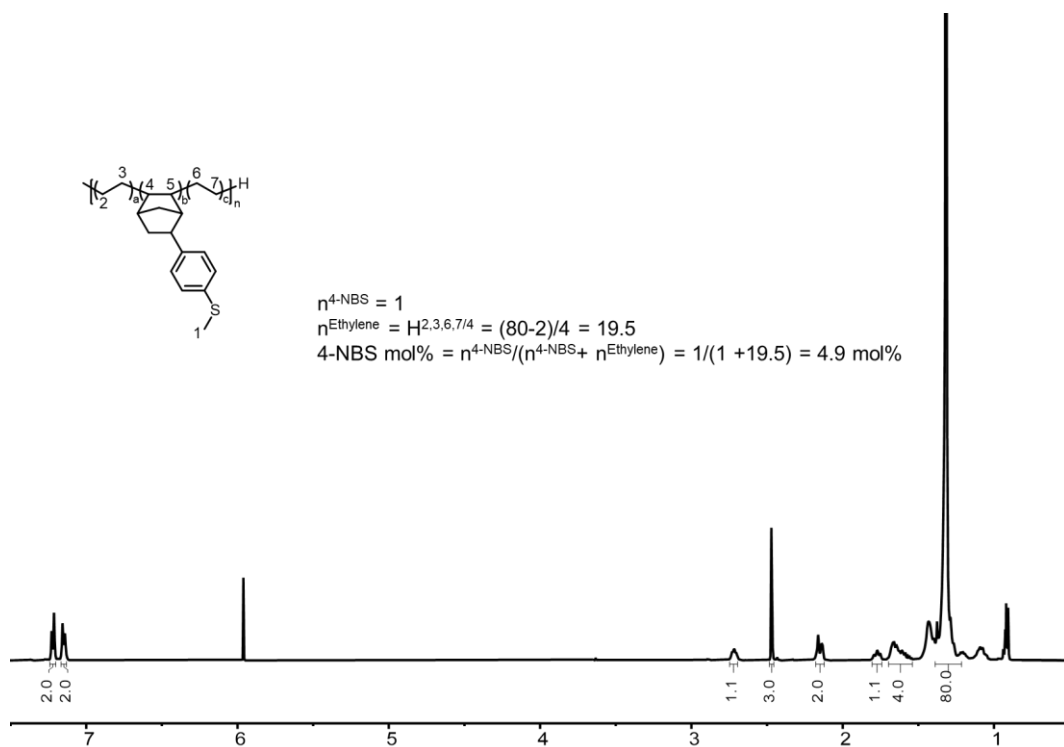
**Figure S69.** DSC curve of the polymer from Table 2, Entry 3.

**MW Averages**

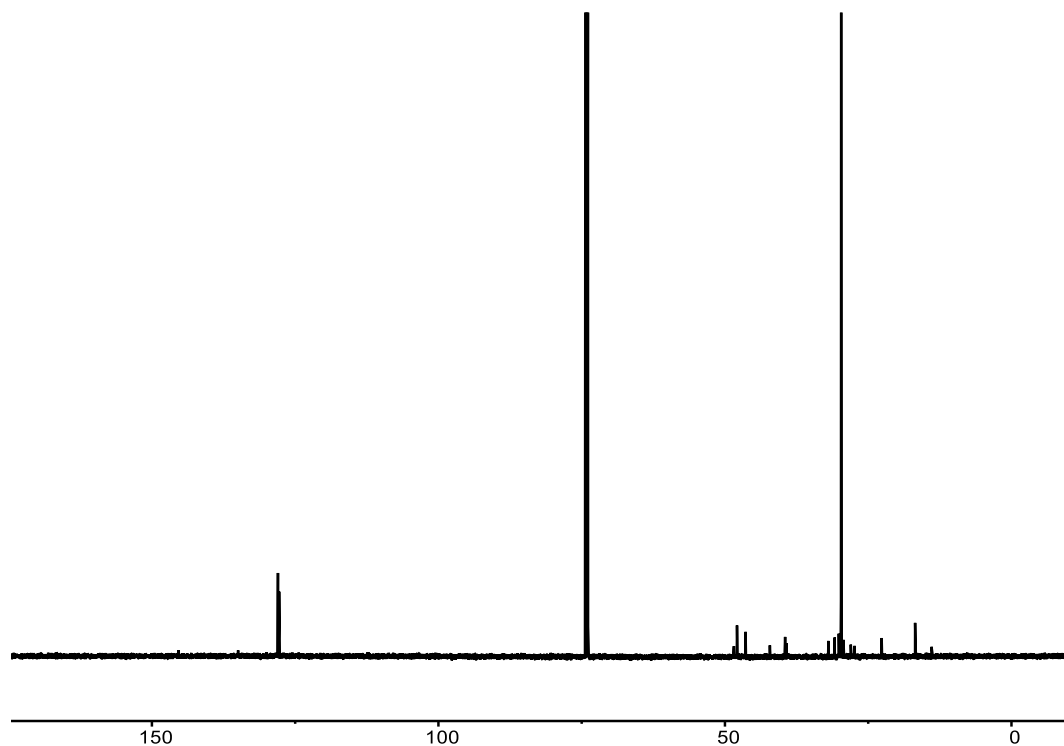
Mp: 34003	Mn: 21110	Mv: 34568	Mw: 37132
Mz: 56695	Mz+1: 78165	PD: 1.7590	



**Figure S70.** GPC trace of the polymer from Table 2, Entry 3.



**Figure S71.**  $^1\text{H}$  NMR spectrum of the polymer from Table 2, Entry 4 (1,1,2,2-Tetrachloroethane- $d_2$ ).



**Figure S72.**  $^{13}\text{C}$  NMR spectrum of the polymer from Table 2, Entry 4 (1,1,2,2-Tetrachloroethane- $d_2$ ).

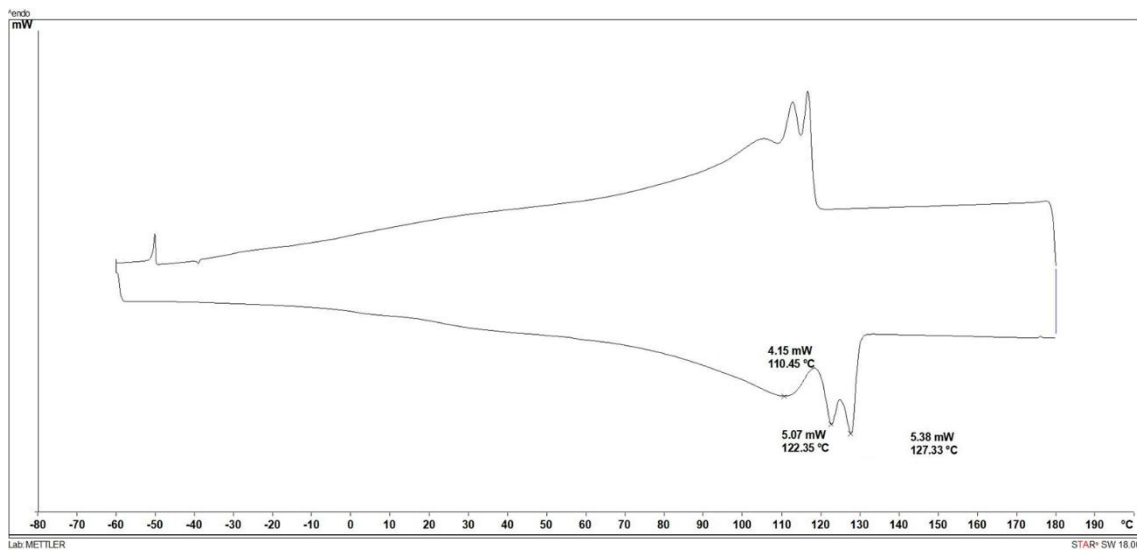


Figure S73. DSC curve of the polymer from Table 2, Entry 4.

**MW Averages**

Mp: 7855	Mn: 4929	Mv: 10464	Mw: 12444
Mz: 44250	Mz+1: 112276	PD: 2.5247	

**Distribution Plots**

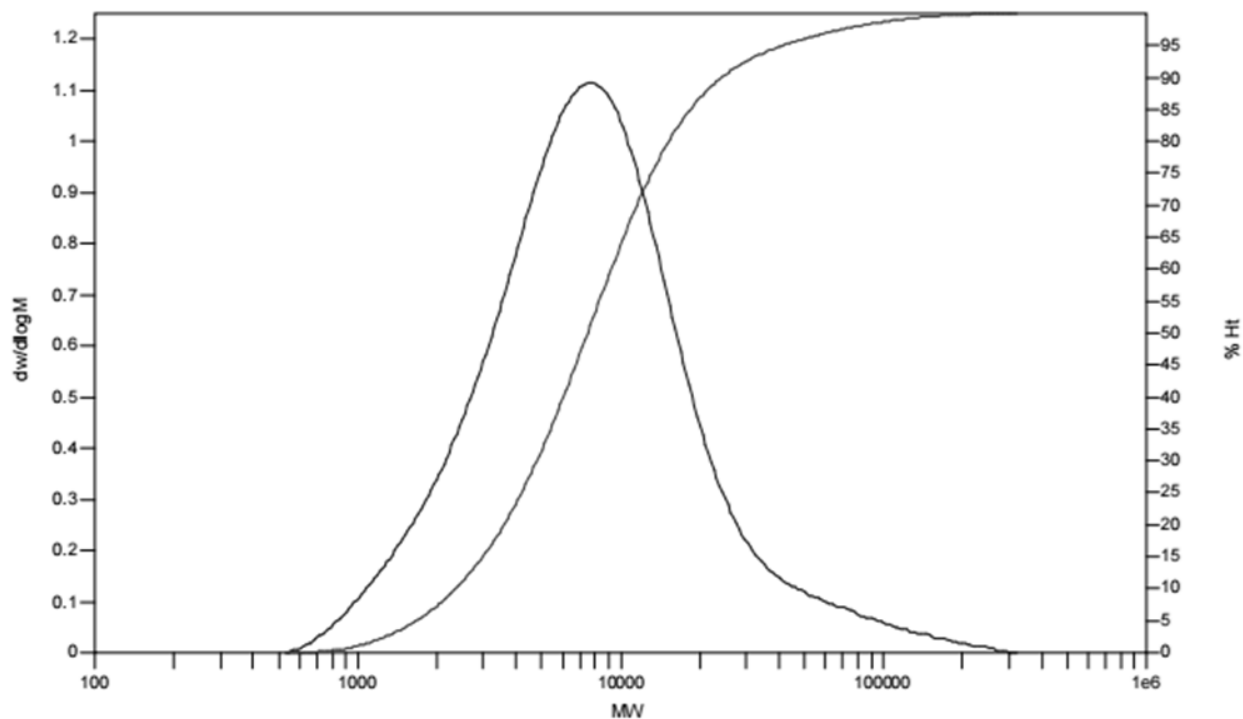
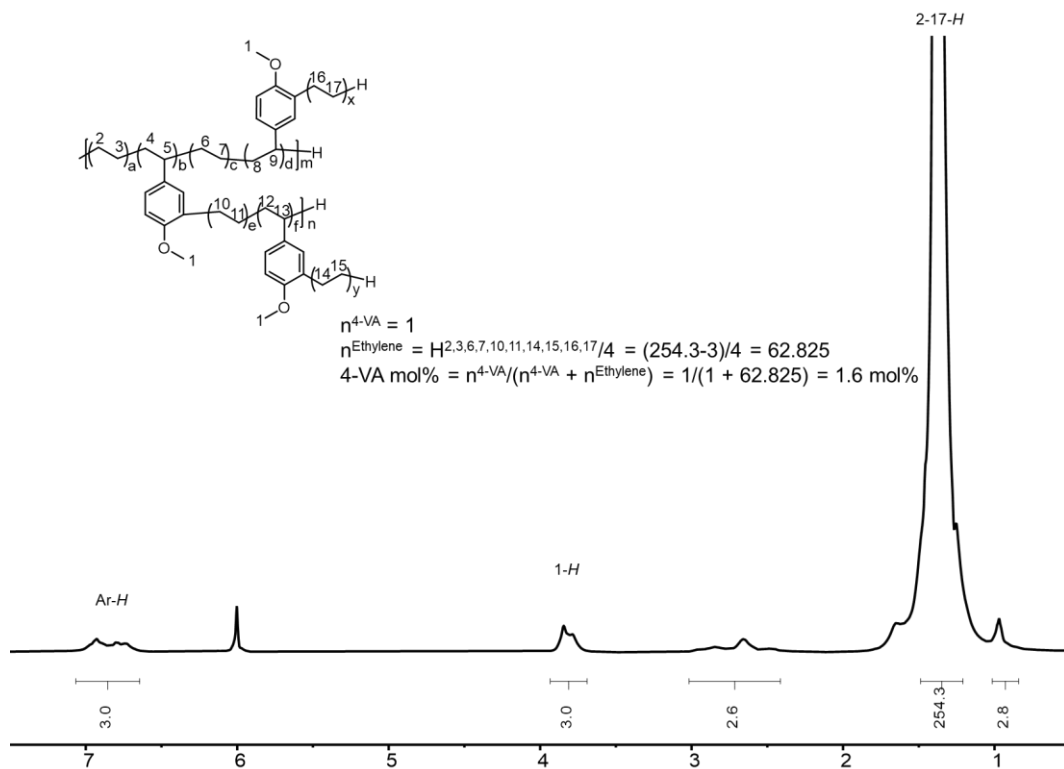
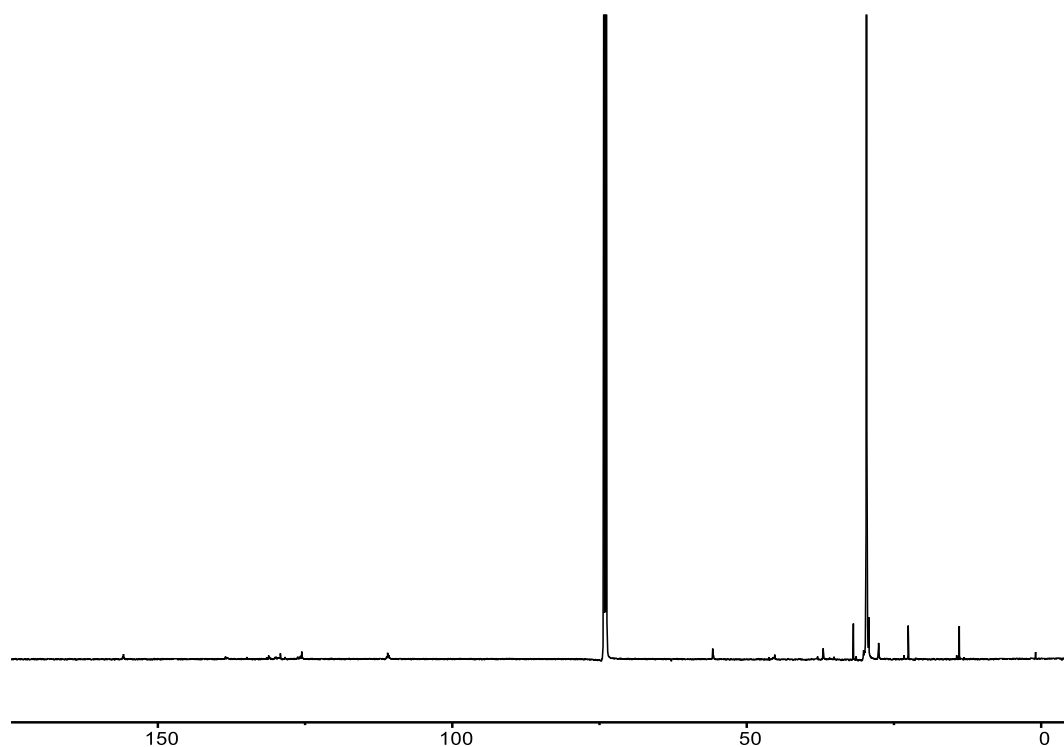


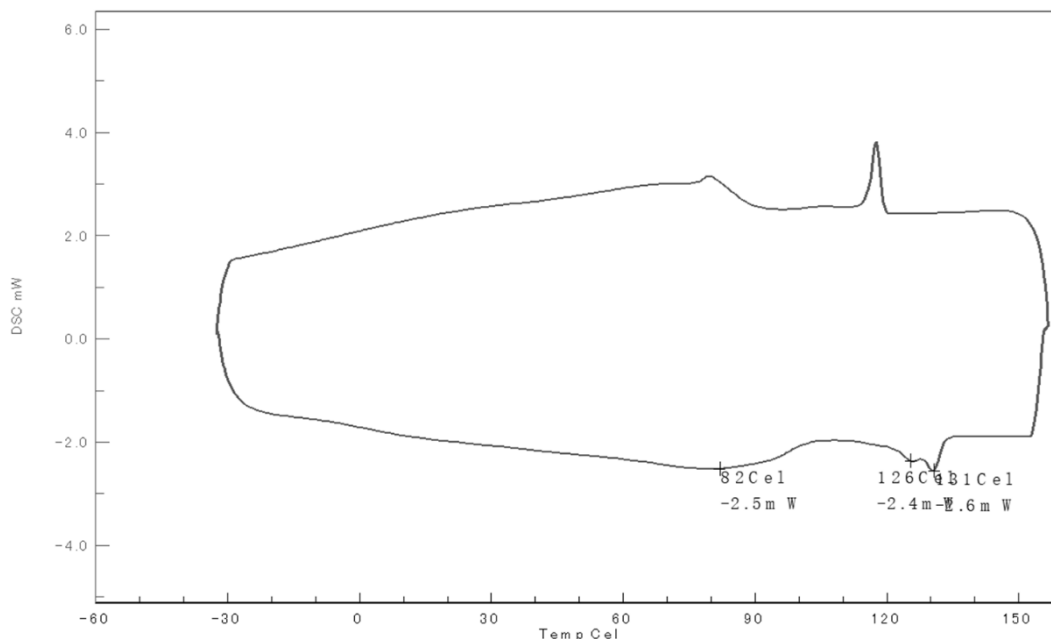
Figure S74. GPC trace of the polymer from Table 2, Entry 4.



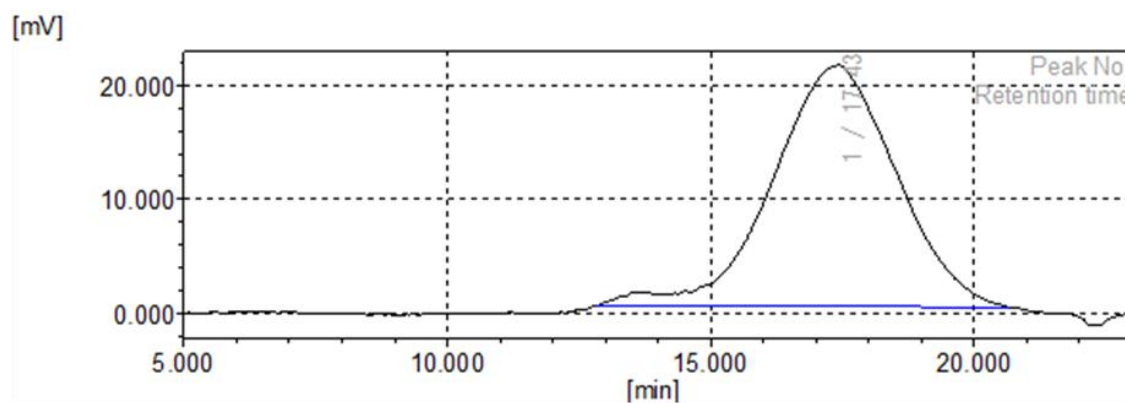
**Figure S75.**  $^1\text{H}$  NMR spectrum of the polymer from Table S1, Entry 2 (1,1,2,2-Tetrachloroethane- $d_2$ ).



**Figure S76.**  $^{13}\text{C}$  NMR spectrum of the polymer from Table S1, Entry 2 (1,1,2,2-Tetrachloroethane- $d_2$ ).



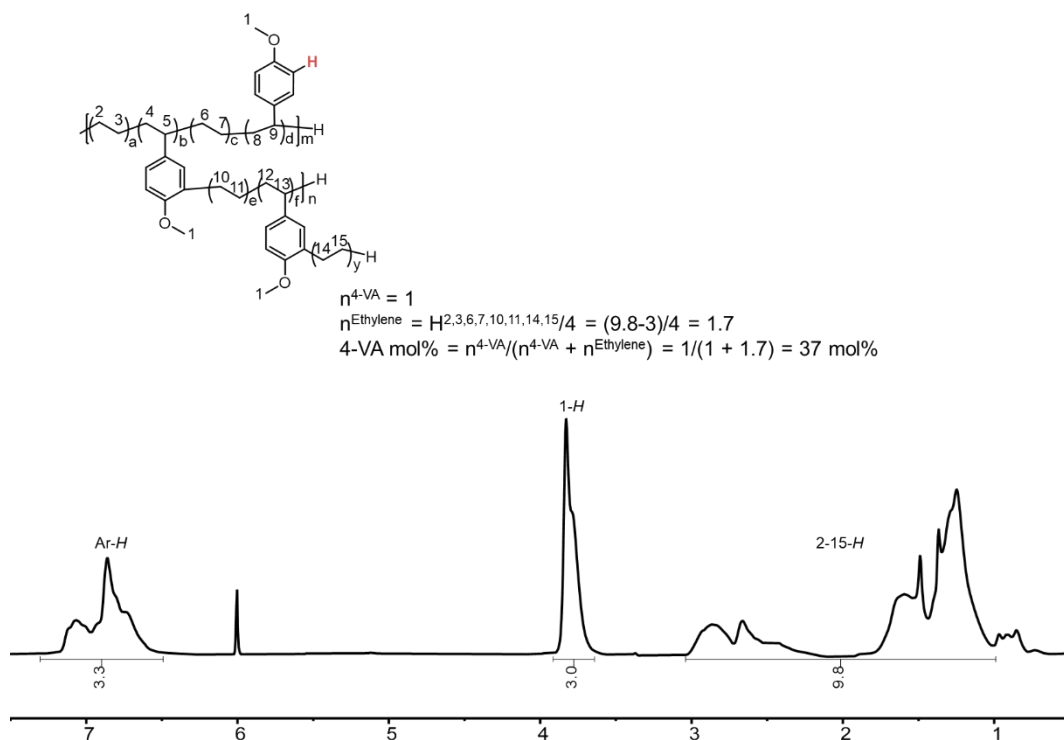
**Figure S77.** DSC curve of the polymer from Table S1, Entry 2.



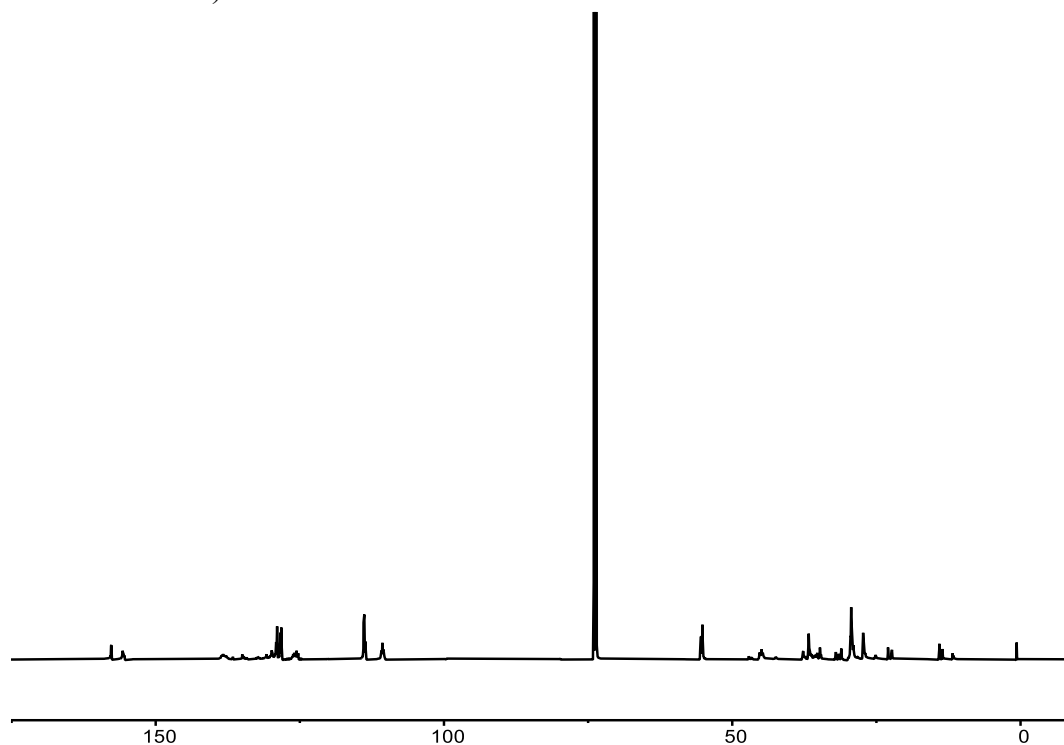
**Molecular mass calculation result (RI)**

Total		[min]	[mV]	[mol]	Mn	52,582
Peak start	12.832	0.770	28,522,217	Mw	227,172	
Peak top	17.432	21.734	85,278	Mz	2,969,094	
Peak end	20.662	0.620	3,113	Mz+1	10,286,397	
				Mv	227,172	
Height [mV]			21.052	Mp	100,644	
Area [mV*s]			3435.874	Mz/Mw	13.070	
Height% [%]			100.000	Mw/Mn	4.320	
[eta]			227171.84575	Mz+1/Mw	45.280	

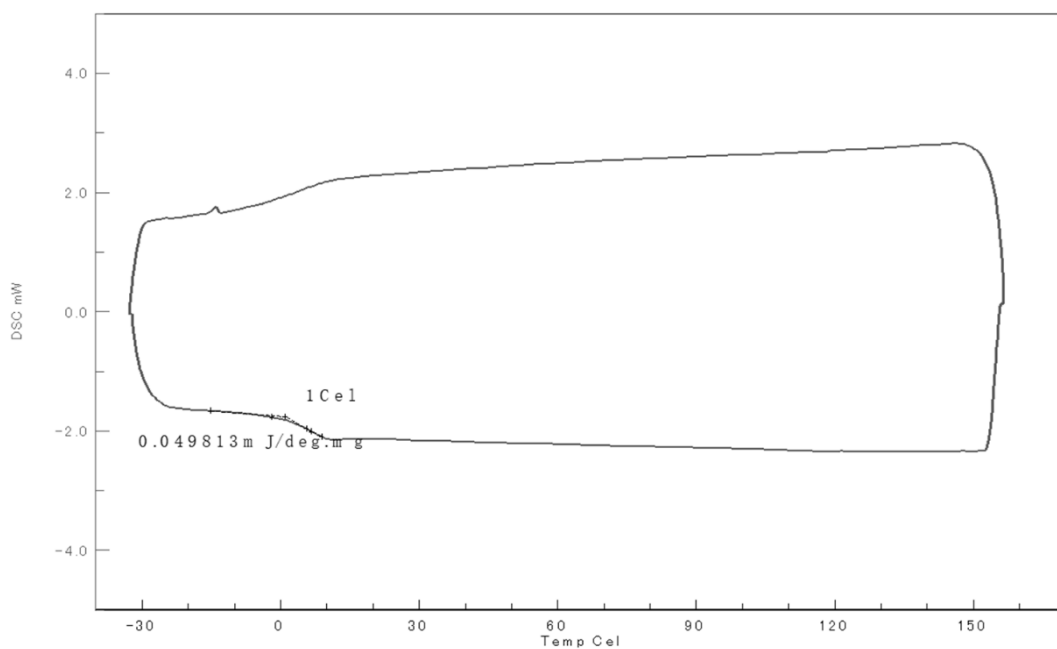
**Figure S78.** GPC trace of the polymer from Table S1, Entry 2.



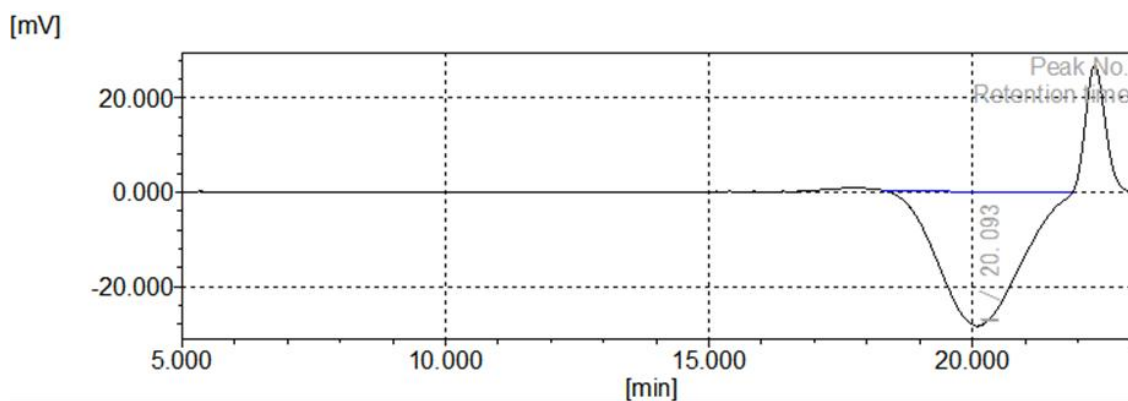
**Figure S79.**  $^1\text{H}$  NMR spectrum of the polymer from Table S1, Entry 3 (1,1,2,2-Tetrachloroethane- $d_2$ ).



**Figure S80.**  $^{13}\text{C}$  NMR spectrum of the polymer from Table S1, Entry 3 (1,1,2,2-Tetrachloroethane- $d_2$ ).



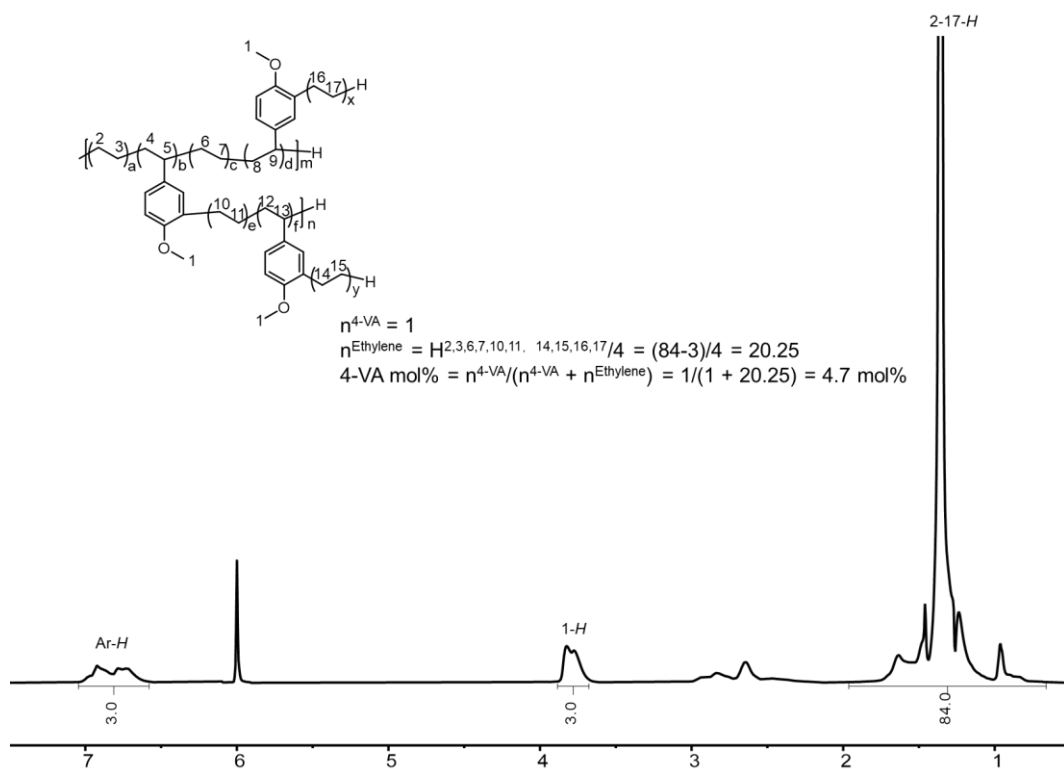
**Figure S81.** DSC curve of the polymer from Table S1, Entry 3.



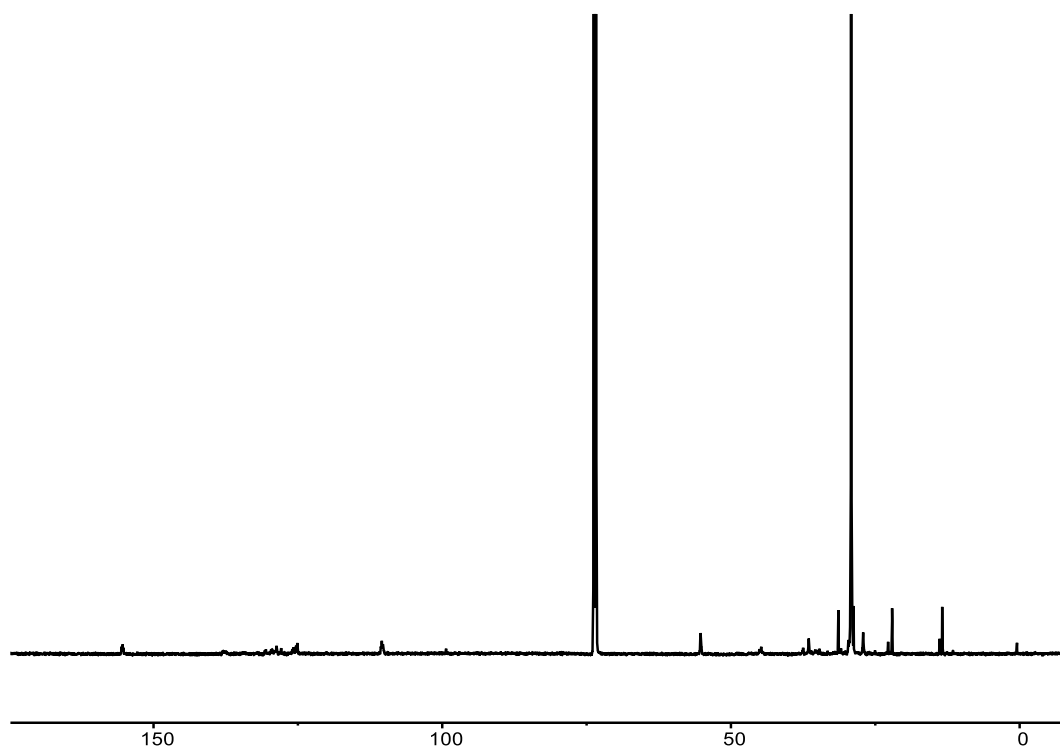
**Molecular mass calculation result (RI)**

Total				Mn	3,566
	[min]	[mV]	[mol]	Mw	6,544
Peak start	18.323	0.356	34,558	Mz	9,774
Peak top	20.093	-28.410	5,759	Mz+1	12,985
Peak end	21.897	-0.117	250	Mv	6,544
Height [mV]			28.532	Mp	6,406
Area [mV*s]			2905.533	Mz/Mw	1.494
Height% [%]			100.000	Mw/Mn	1.835
[eta]			6544.13021	Mz+1/Mw	1.984

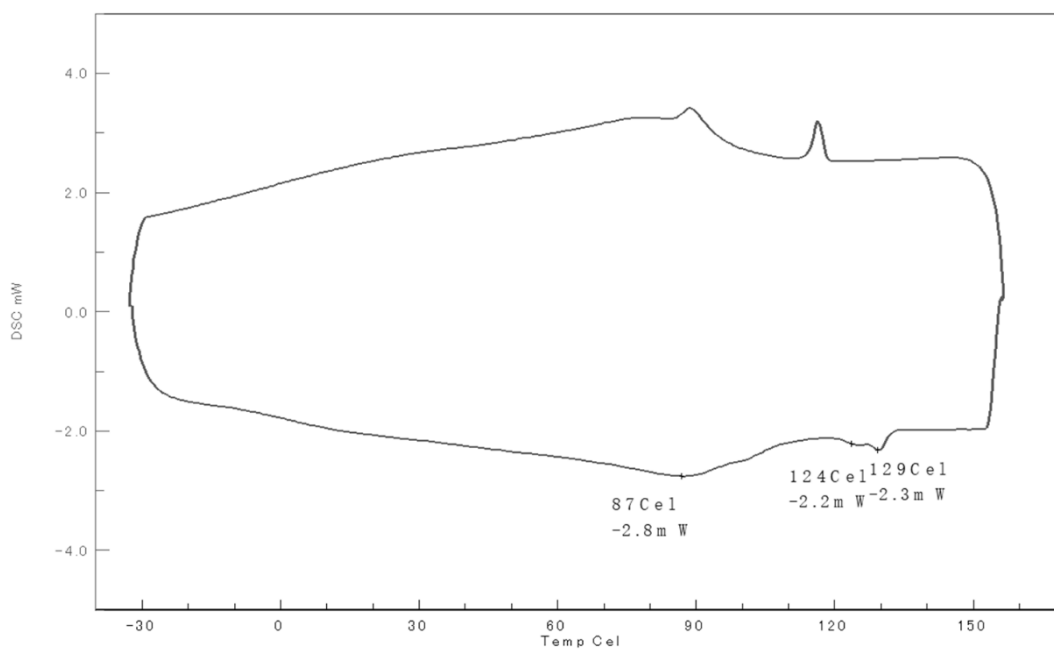
**Figure S82.** GPC trace of the polymer from Table S1, Entry 3.



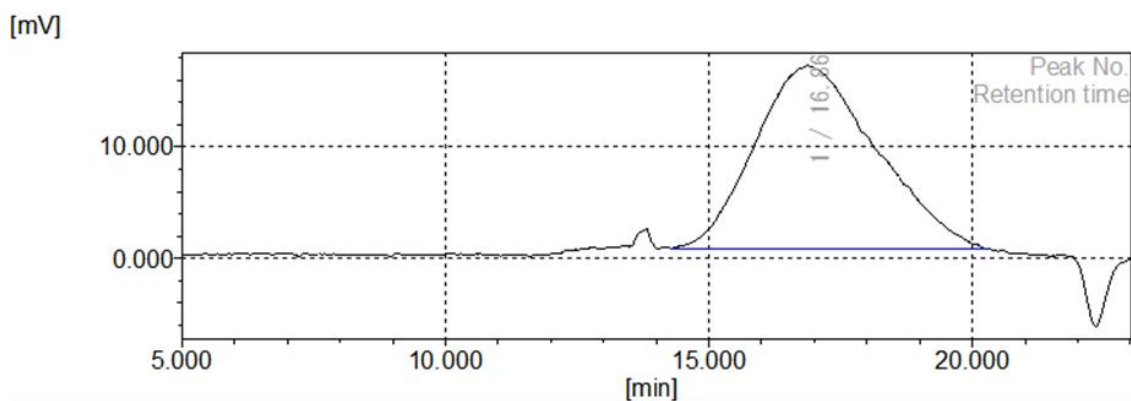
**Figure S83.**  $^1\text{H}$  NMR spectrum of the polymer from Table S1, Entry 4 (1,1,2,2-Tetrachloroethane- $d_2$ ).



**Figure S84.**  $^{13}\text{C}$  NMR spectrum of the polymer from Table S1, Entry 4 (1,1,2,2-Tetrachloroethane- $d_2$ ).



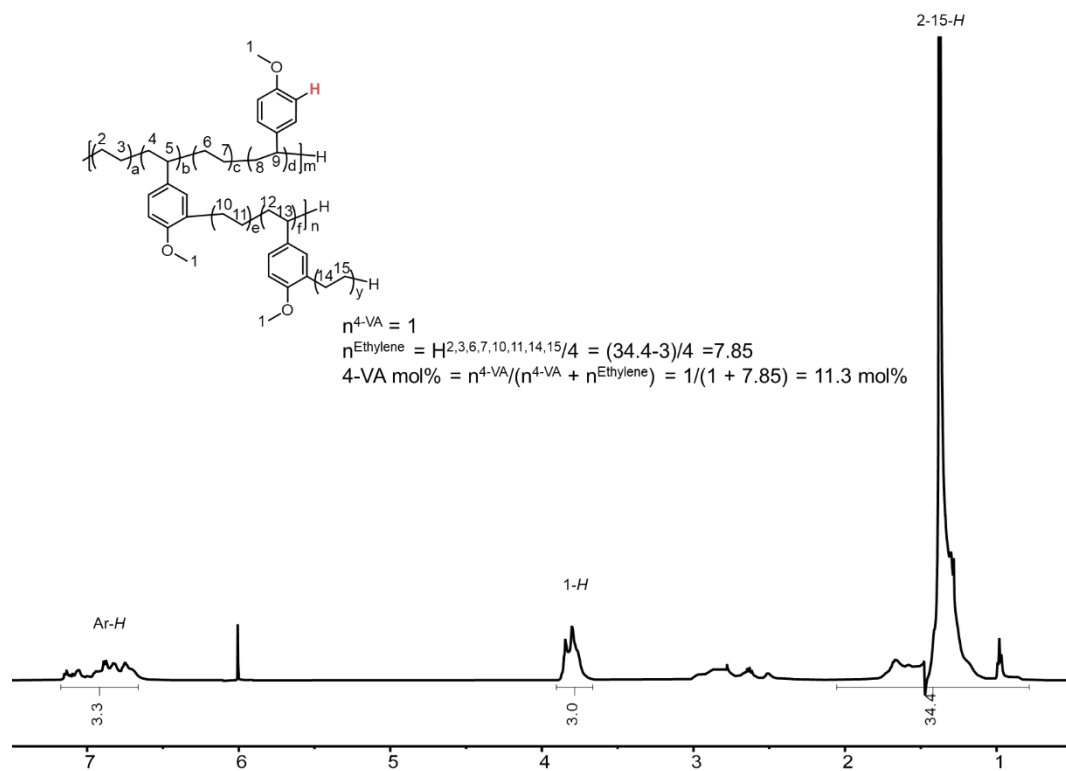
**Figure S85.** DSC curve of the polymer from Table S1, Entry 4.



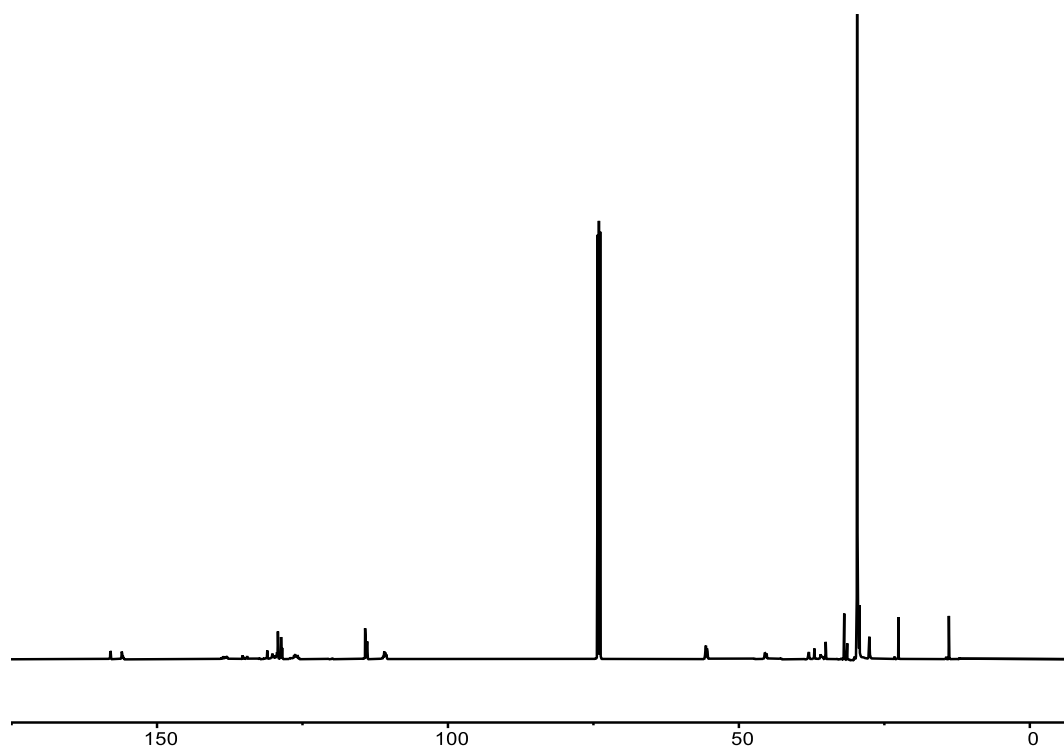
**Molecular mass calculation result (RI)**

Total	[min]	[mV]	[mol]	Mn	63,806
Peak start	14.265	0.923	1,386,075	Mw	164,982
Peak top	16.868	17.272	144,552	Mz	300,769
Peak end	20.287	0.894	4,655	Mz+1	438,544
				Mv	164,982
Height [mV]			16.362	Mp	153,204
Area [mV*s]			2602.765	Mz/Mw	1.823
Height% [%]			100.000	Mw/Mn	2.586
[eta]			164982.28566	Mz+1/Mw	2.658

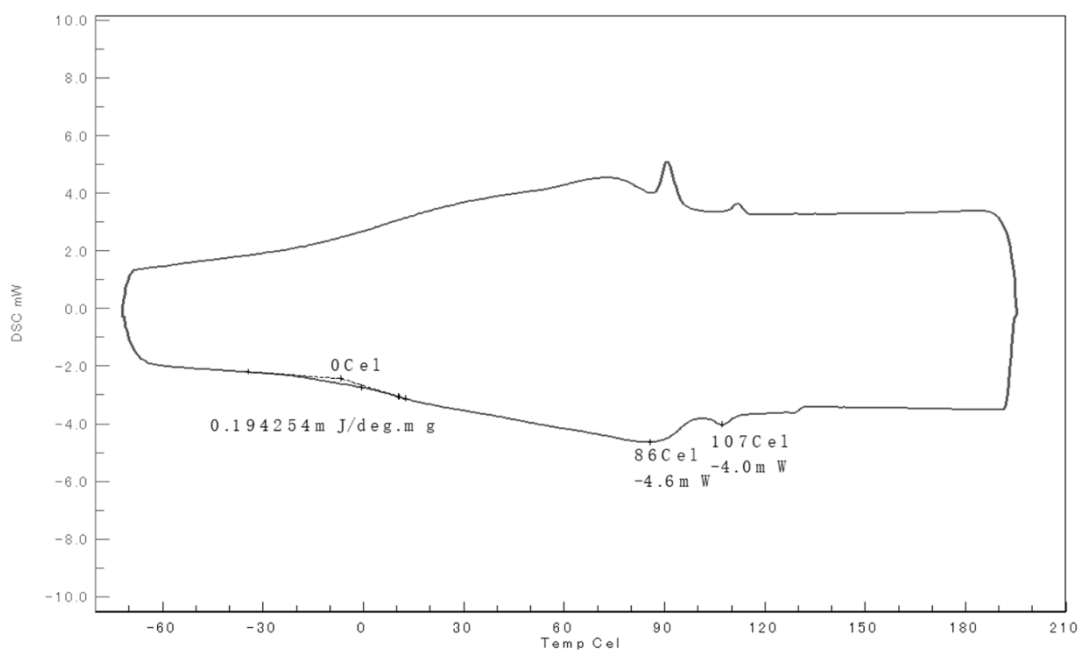
**Figure S86.** GPC trace of the polymer from Table S1, Entry 4.



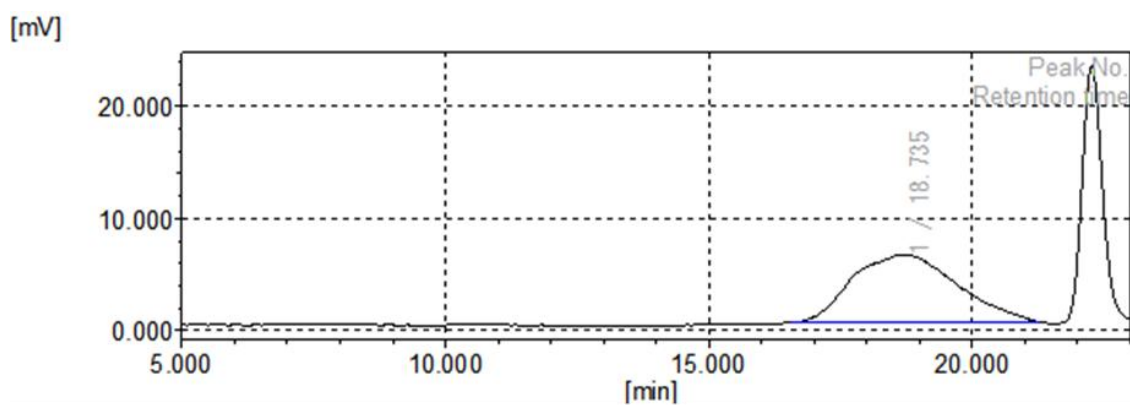
**Figure S87.**  $^1\text{H}$  NMR spectrum of the polymer from Table S1, Entry 5 (1,1,2,2-Tetrachloroethane- $d_2$ ).



**Figure S88.**  $^{13}\text{C}$  NMR spectrum of the polymer from Table S1, Entry 5 (1,1,2,2-Tetrachloroethane- $d_2$ ).



**Figure S89.** DSC curve of the polymer from Table S1, Entry 5.

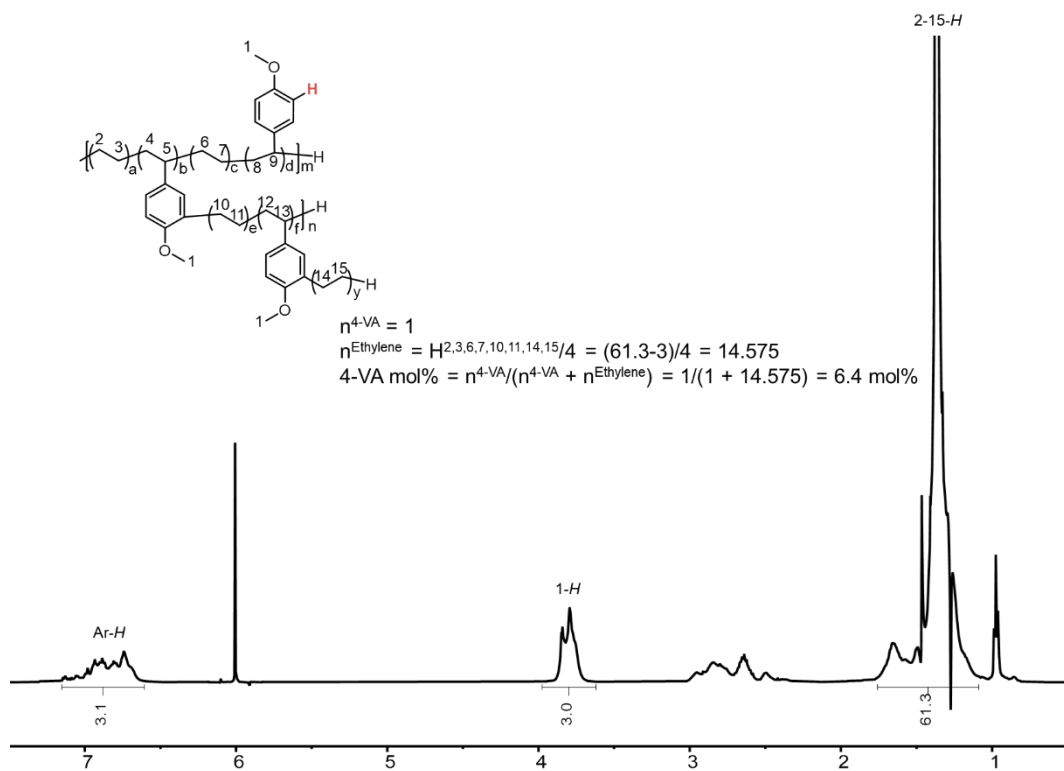


**Molecular mass calculation result (RI)**

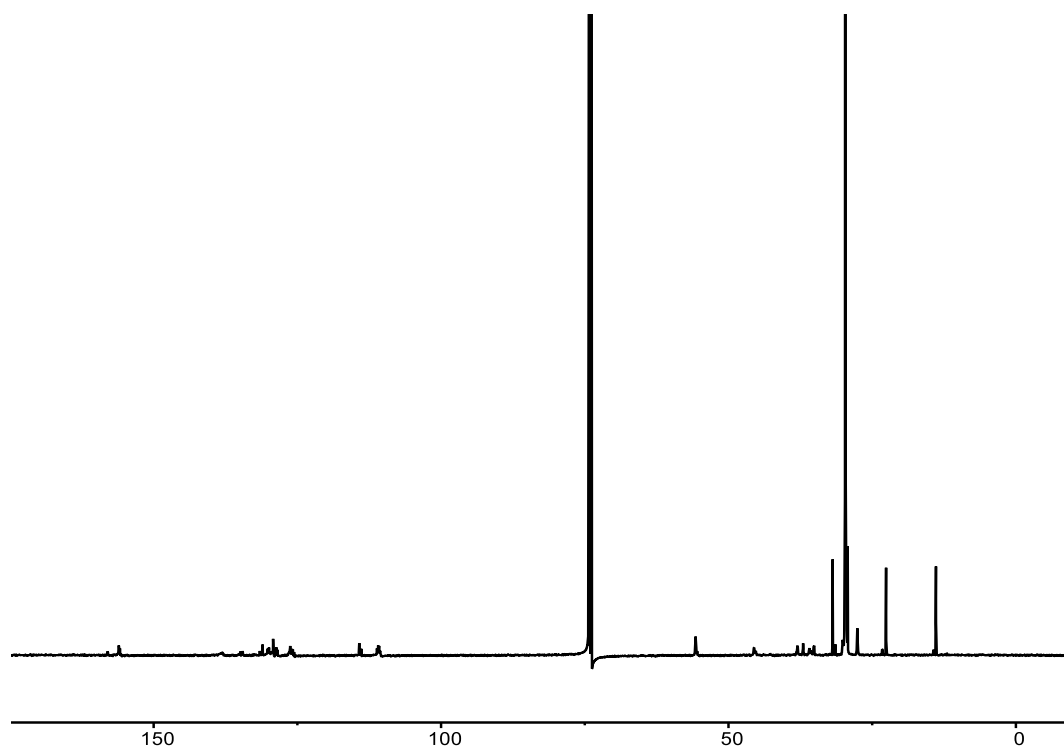
Total

	[min]	[mV]	[mol]	Mn	13,111
Peak start	16.558	0.687	187,776	Mw	29,029
Peak top	18.735	6.784	21,512	Mz	50,016
Peak end	21.302	0.752	947	Mz+1	70,388
				Mv	29,029
Height [mV]			6.067	Mp	21,512
Area [mV*s]			840.962	Mz/Mw	1.723
Height% [%]			100.000	Mw/Mn	2.214
[eta]			29028.86053	Mz+1/Mw	2.425

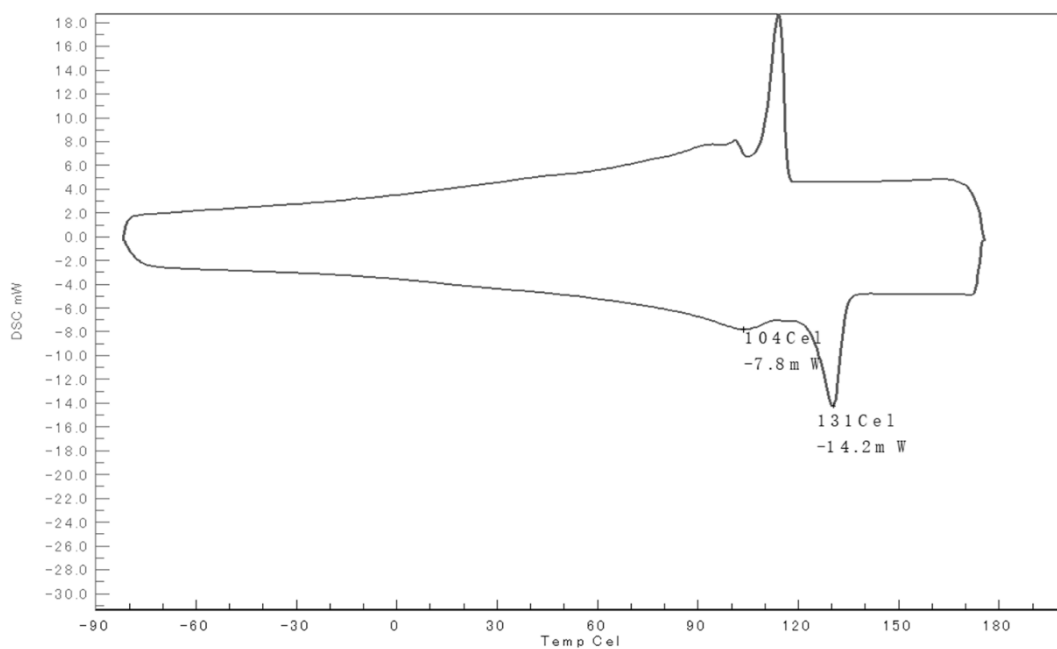
**Figure S90.** GPC trace of the polymer from Table S1, Entry 5.



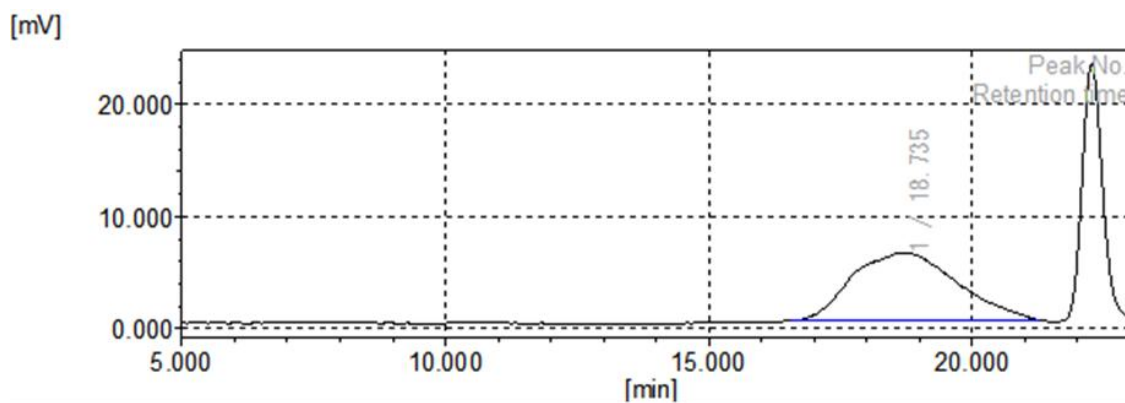
**Figure S91.**  $^1\text{H}$  NMR spectrum of the polymer from Table S1, Entry 6 (1,1,2,2-Tetrachloroethane- $d_2$ ).



**Figure S92.**  $^{13}\text{C}$  NMR spectrum of the polymer from Table S1, Entry 6 (1,1,2,2-Tetrachloroethane- $d_2$ ).



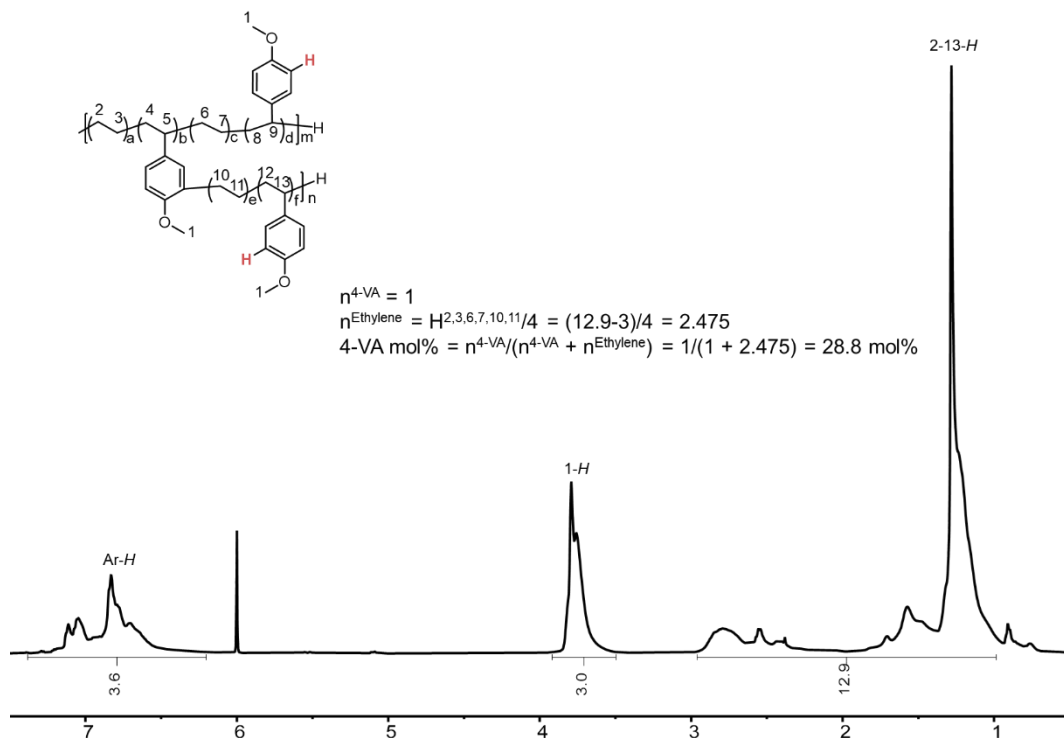
**Figure S93.** DSC curve of the polymer from Table S1, Entry 6.



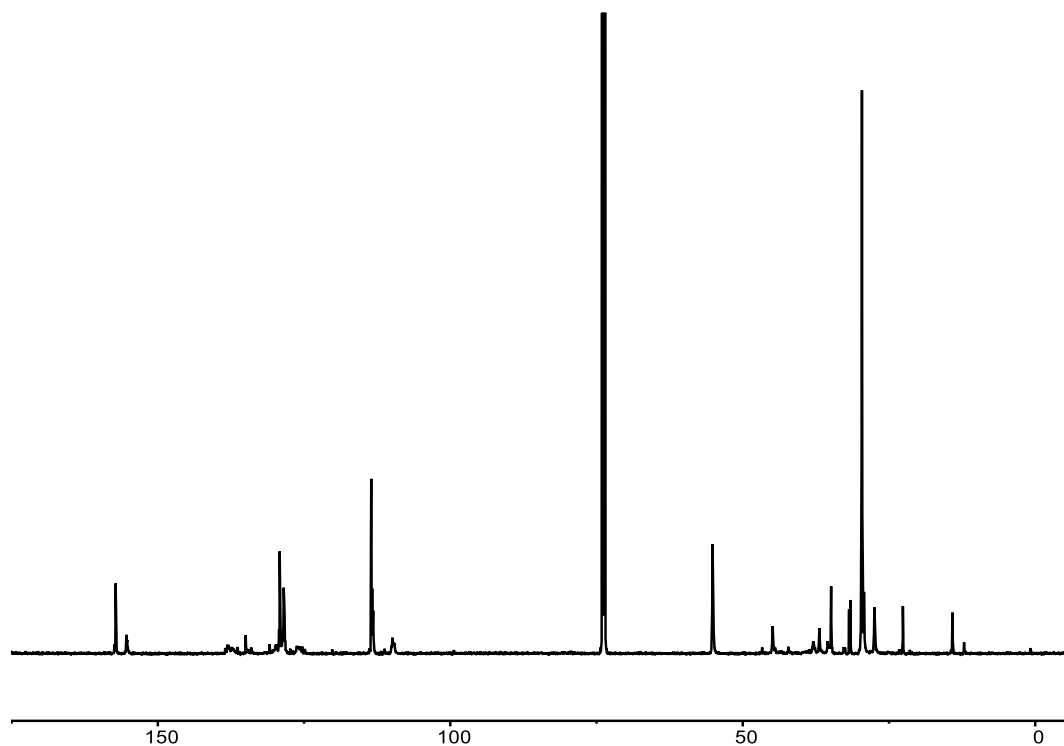
**Molecular mass calculation result (RI)**

Total					
	[min]	[mV]	[mol]		
Peak start	15.698	1.728	391,551	Mn	17,747
Peak top	18.742	11.195	21,368	Mw	43,783
Peak end	20.993	2.580	1,633	Mz	92,156
				Mz+1	144,634
				Mv	43,783
Height [mV]			8.977	Mp	21,368
Area [mV*s]			1322.287	Mz/Mw	2.105
Height% [%]			100.000	Mw/Mn	2.467
[eta]			43782.98036	Mz+1/Mw	3.303

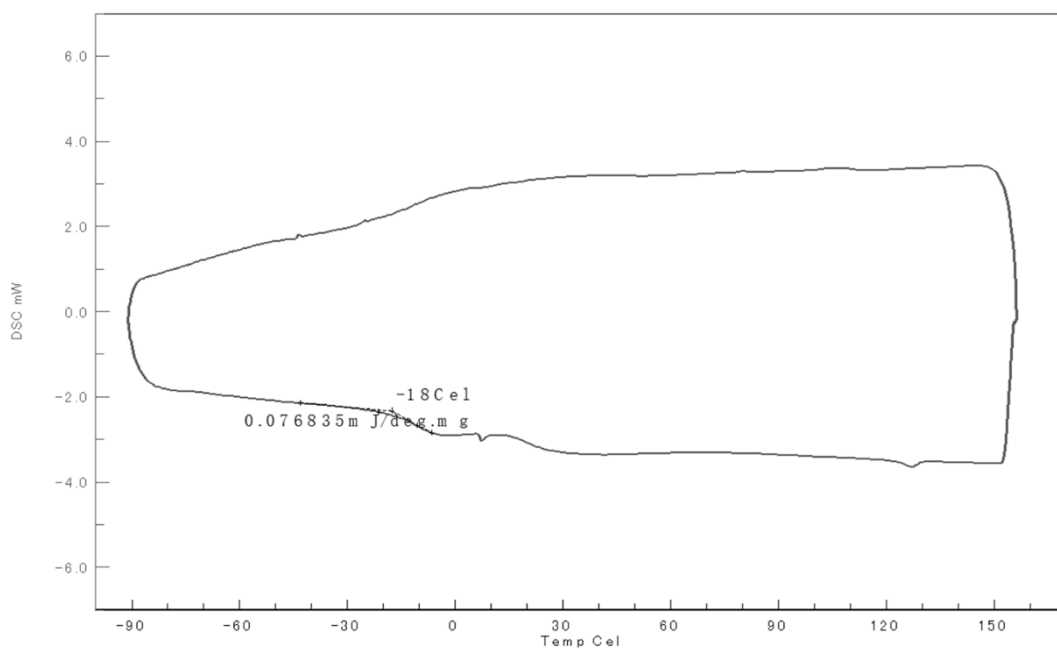
**Figure S94.** GPC trace of the polymer from Table S1, Entry 6.



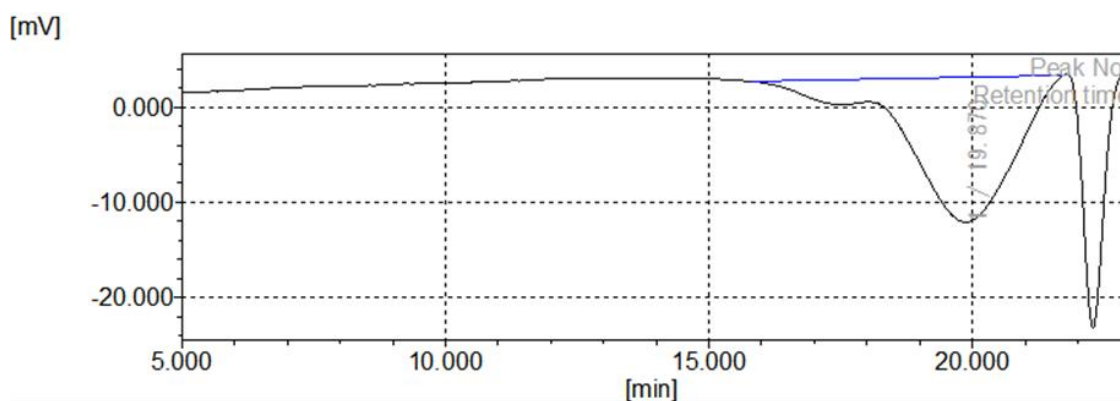
**Figure S95.**  $^1\text{H}$  NMR spectrum of the polymer from Table S1, Entry 7 (1,1,2,2-Tetrachloroethane- $d_2$ ).



**Figure S96.**  $^{13}\text{C}$  NMR spectrum of the polymer from Table S1, Entry 7 (1,1,2,2-Tetrachloroethane- $d_2$ ).



**Figure S97.** DSC curve of the polymer from Table S1, Entry 7.

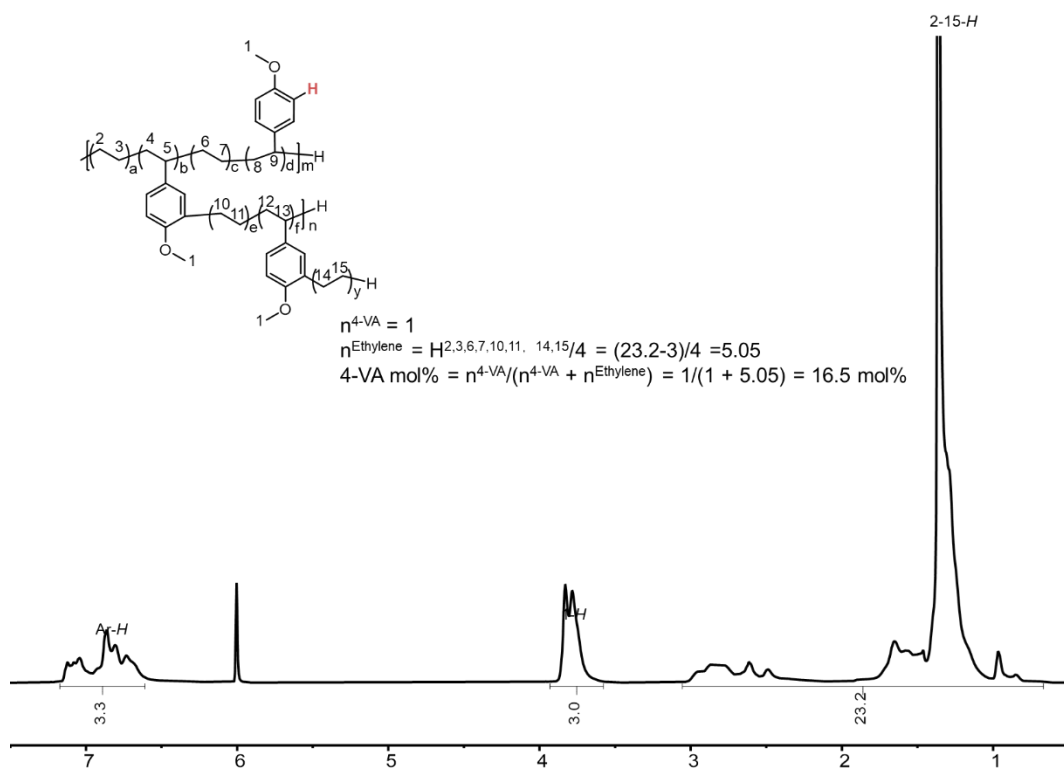


**Molecular mass calculation result (RI)**

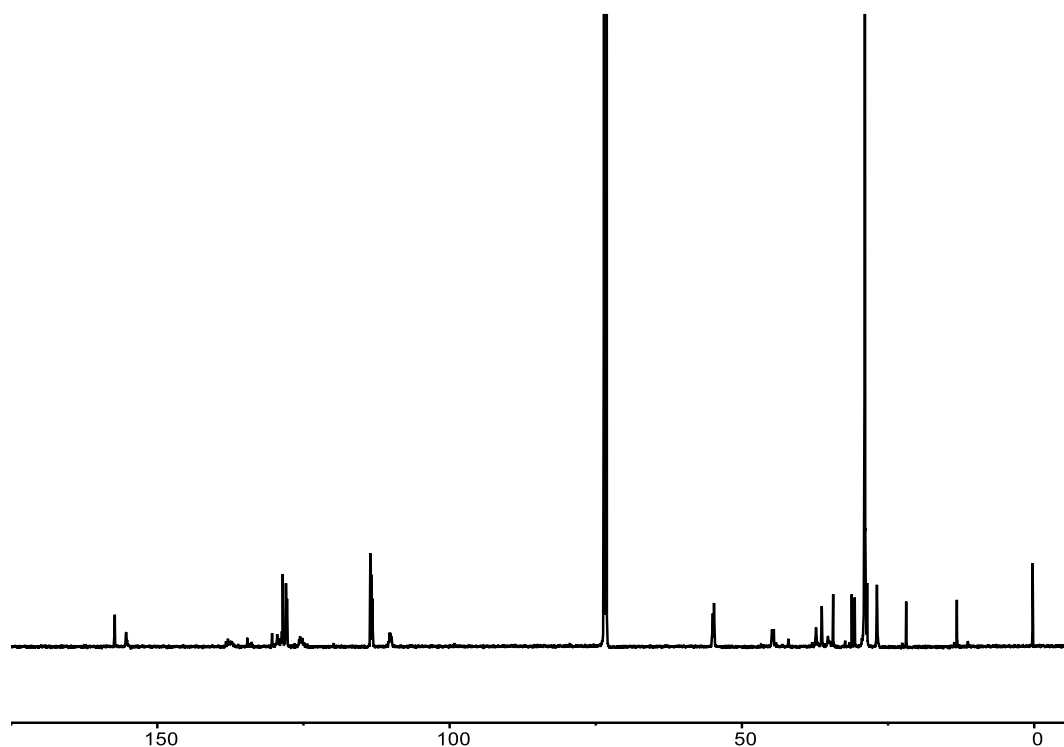
Total

	[min]	[mV]	[mol]	Mn	4.981
Peak start	15.808	2.672	357,961	Mw	19,007
Peak top	19.870	-12.091	6,818	Mz	80,959
Peak end	21.720	3.312	377	Mz+1	150,994
				Mv	19,007
Height [mV]			15.203	Mp	7,560
Area [mV*s]			2064.623	Mz/Mw	4.259
Height% [%]			100.000	Mw/Mn	3.816
[eta]			19006.81265	Mz+1/Mw	7.944

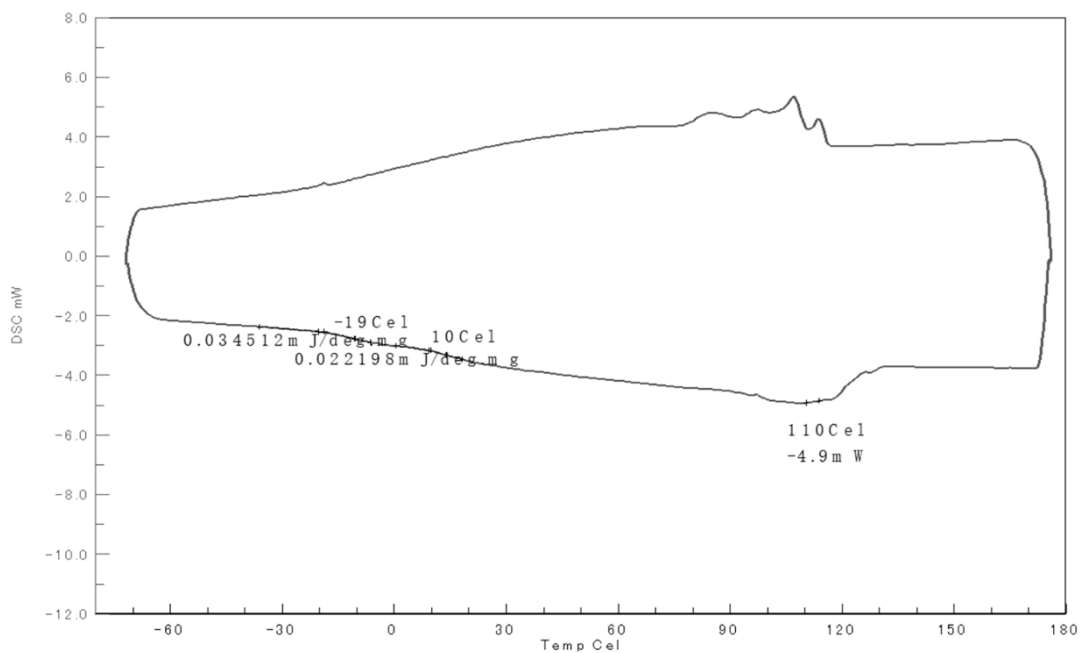
**Figure S98.** GPC trace of the polymer from Table S1, Entry 7.



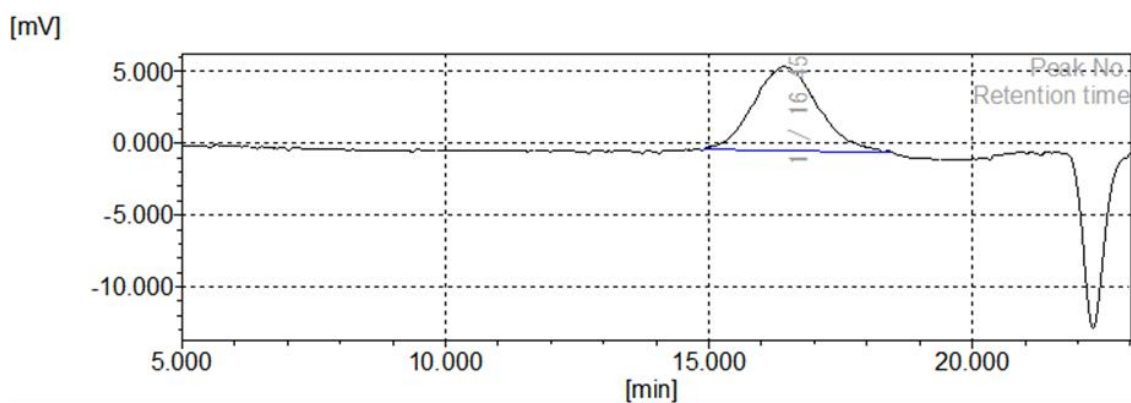
**Figure S99.**  $^1\text{H}$  NMR spectrum of the polymer from Table S1, Entry 8 (1,1,2,2-Tetrachloroethane- $d_2$ ).



**Figure S100.**  $^{13}\text{C}$  NMR spectrum of the polymer from Table S1, Entry 8 (1,1,2,2-Tetrachloroethane- $d_2$ ).



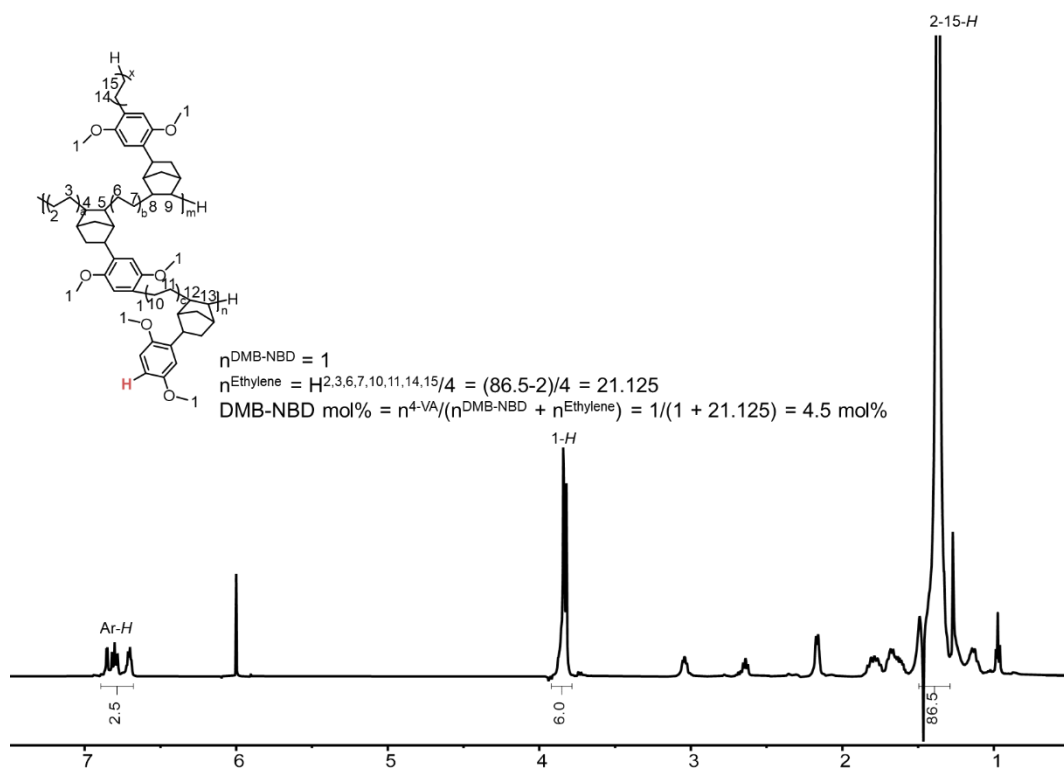
**Figure S101.** DSC curve of the polymer from Table S1, Entry 8.



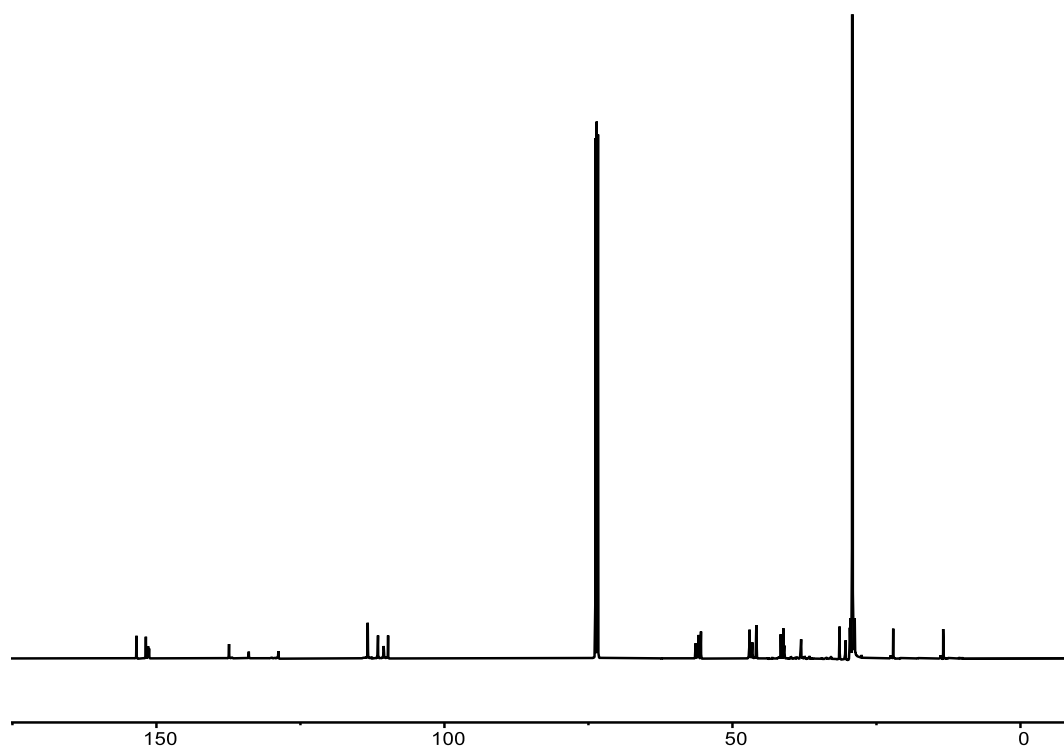
**Molecular mass calculation result (RI)**

Total					
	[min]	[mV]	[mol]		
Peak start	14.905	-0.414	747,947	Mn	167,574
Peak top	16.455	5.324	206,101	Mw	221,377
Peak end	18.478	-0.657	27,898	Mz	275,858
				Mz+1	329,965
				Mv	221,377
Height [mV]			5.843	Mp	218,373
Area [mV*s]			495.774	Mz/Mw	1.246
Height% [%]			100.000	Mw/Mn	1.321
[eta]			221377.11964	Mz+1/Mw	1.491

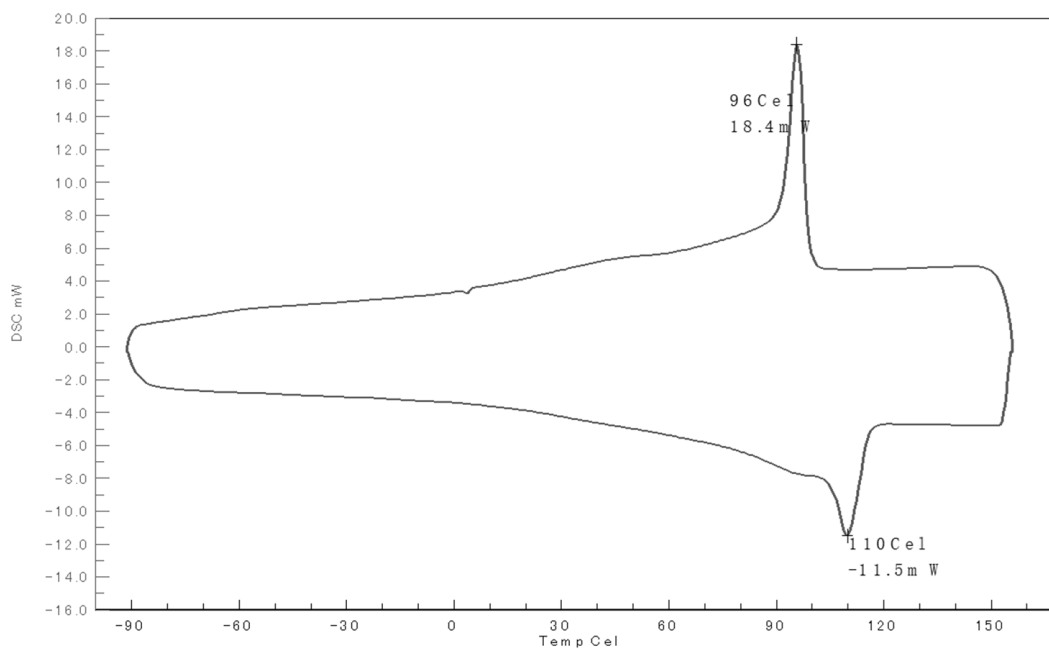
**Figure S102.** GPC trace of the polymer from Table S1, Entry 8.



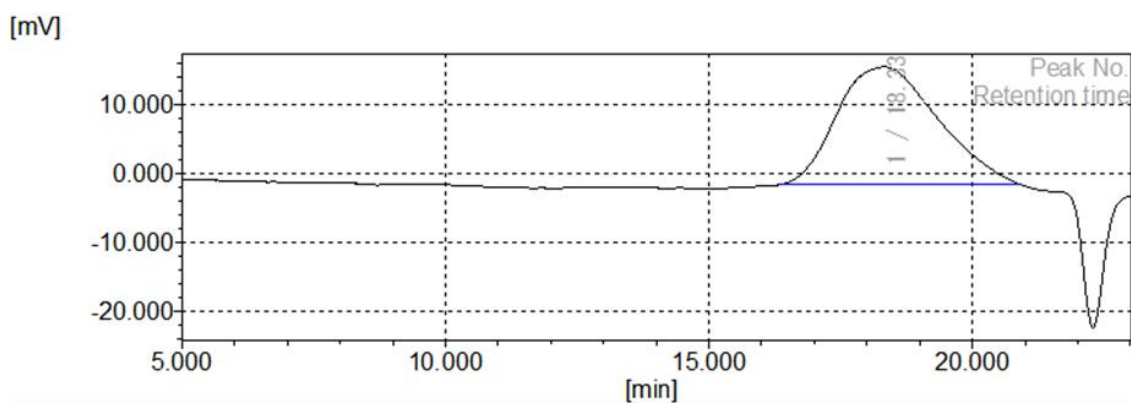
**Figure S103.** <sup>1</sup>H NMR spectrum of the polymer from Table S1, Entry 9 (1,1,2,2-Tetrachloroethane-d<sub>2</sub>).



**Figure S104.** <sup>13</sup>C NMR spectrum of the polymer from Table S1, Entry 9 (1,1,2,2-Tetrachloroethane-d<sub>2</sub>).



**Figure S105.** DSC curve of the polymer from Table S1, Entry 9.

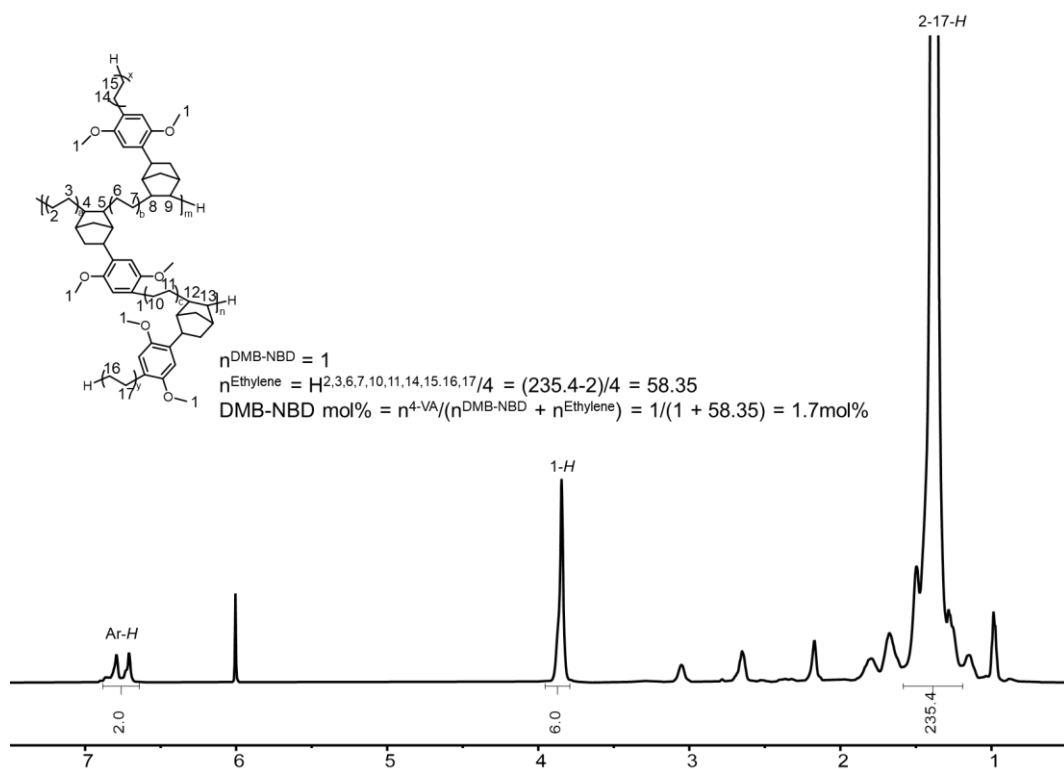


**Molecular mass calculation result (RI)**

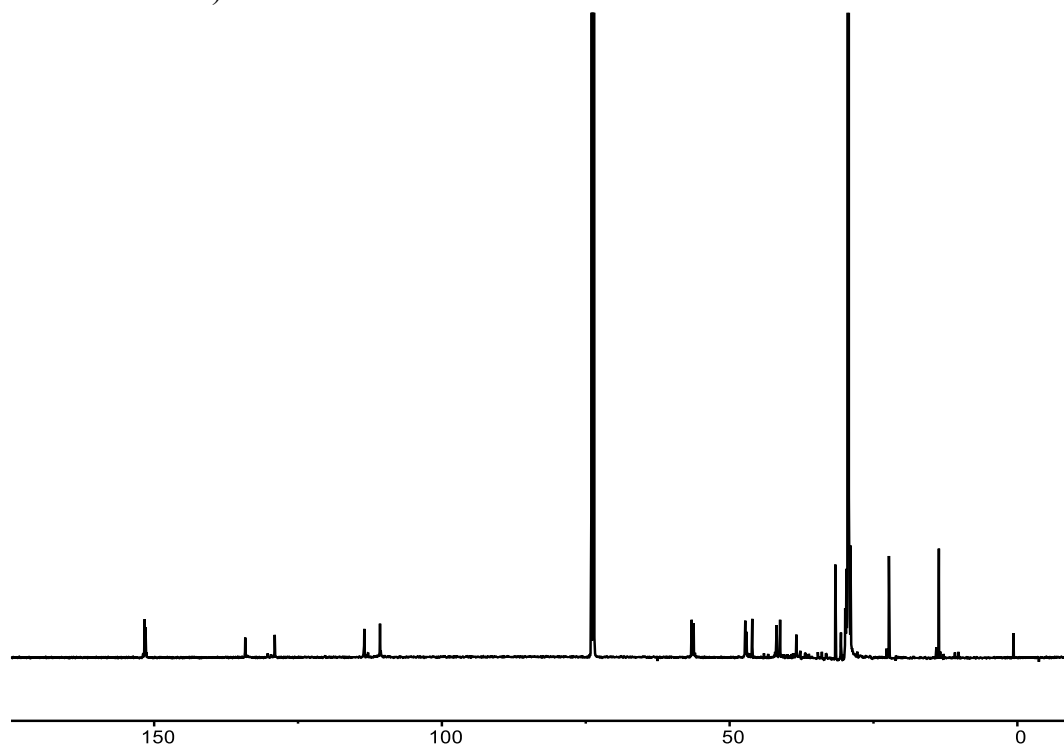
Total

	[min]	[mV]	[mol]	Mn	19,176
Peak start	16.317	-1.656	232,937	Mw	38,946
Peak top	18.338	15.554	32,175	Mz	64,516
Peak end	20.905	-1.561	1,878	Mz+1	89,490
				Mv	38,946
Height [mV]			17.168	Mp	32,176
Area [mV*s]			2278.908	Mz/Mw	1.657
Height% [%]			100.000	Mw/Mn	2.031
[eta]			38946.21754	Mz+1/Mw	2.298

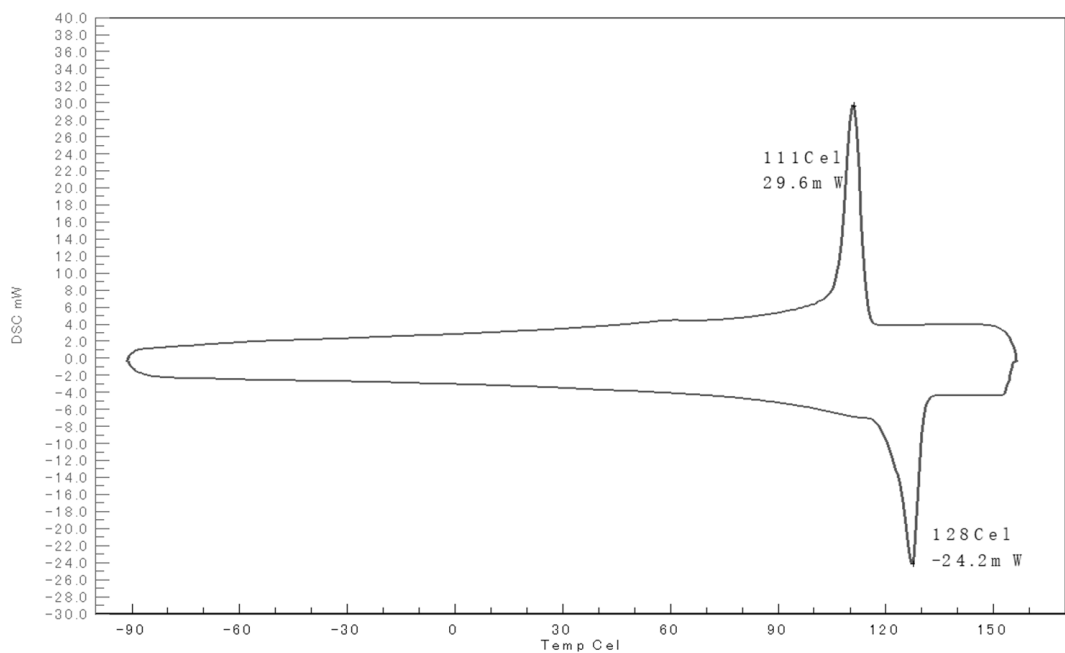
**Figure S106.** GPC trace of the polymer from Table S1, Entry 9.



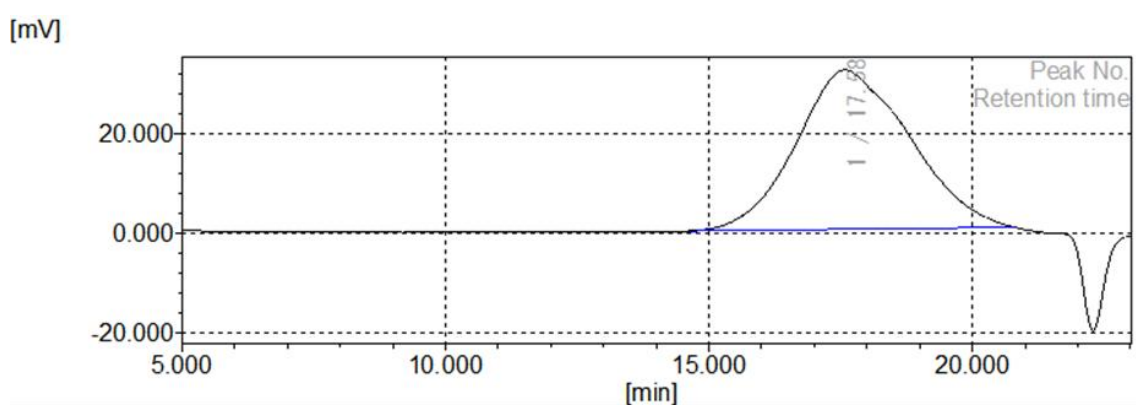
**Figure S107.**  $^1\text{H}$  NMR spectrum of the polymer from Table S1, Entry 10 (1,1,2,2-Tetrachloroethane- $d_2$ ).



**Figure S108.**  $^{13}\text{C}$  NMR spectrum of the polymer from Table S1, Entry 10 (1,1,2,2-Tetrachloroethane- $d_2$ ).



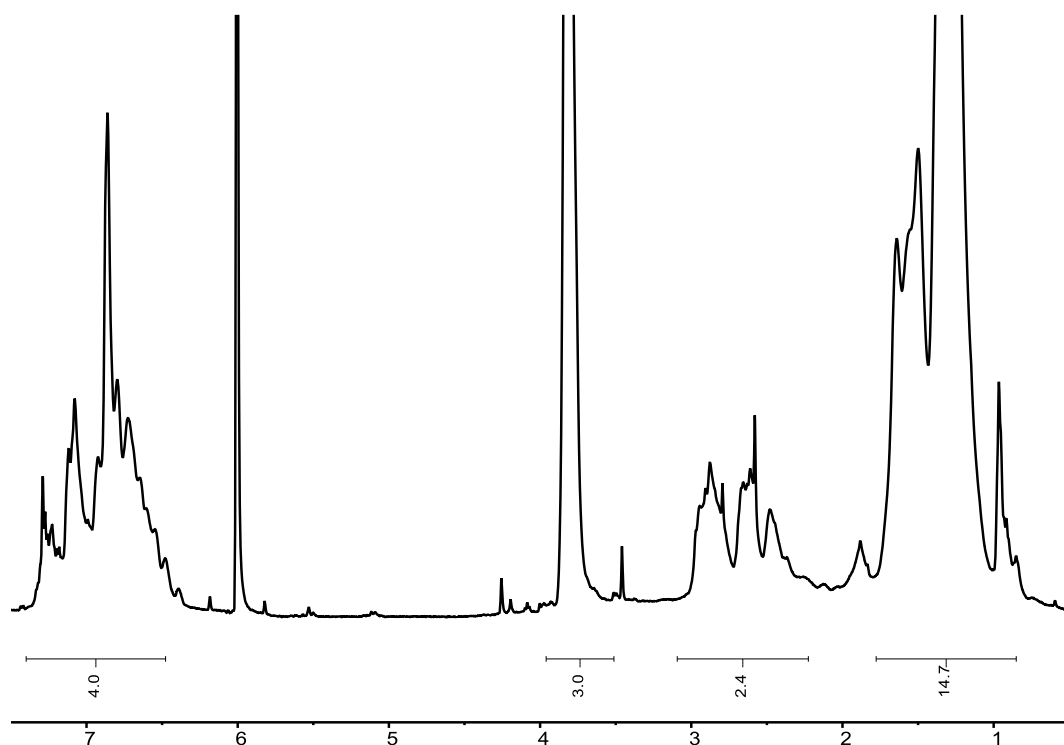
**Figure S109.** DSC curve of the polymer from Table S1, Entry 10.



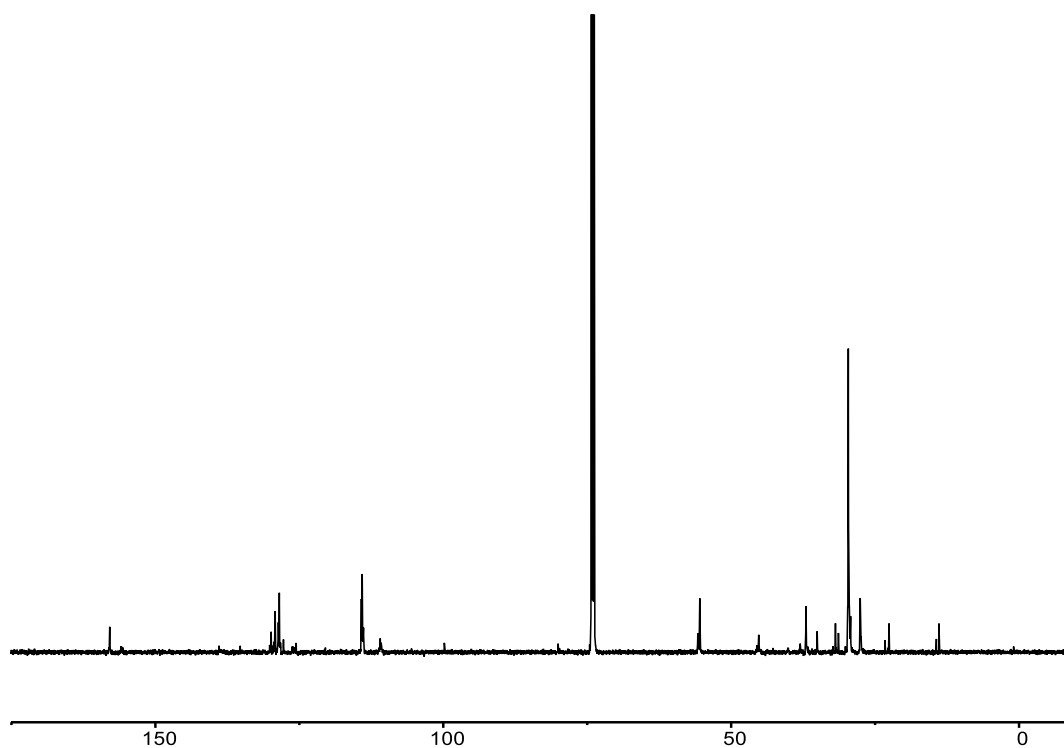
**Molecular mass calculation result (RI)**

Total	[min]	[mV]	[mol]	Mn	33,124
Peak start	14.640	0.484	945,001	Mw	86,171
Peak top	17.585	32.875	69,483	Mz	175,353
Peak end	20.793	1.229	2,220	Mz+1	282,042
				Mv	86,171
Height [mV]			32.034	Mp	71,627
Area [mV*s]			4793.469	Mz/Mw	2.035
Height% [%]			100.000	Mw/Mn	2.601
[eta]			86170.50781	Mz+1/Mw	3.273

**Figure S110.** GPC trace of the polymer from Table S1, Entry 10.



**Figure S111.** <sup>1</sup>H NMR spectrum of the oligomers of 4-VA and ethylene after reacting at 70°C for 10 minutes (1,1,2,2-Tetrachloroethane-d<sub>2</sub>).



**Figure S112.** <sup>13</sup>C NMR spectrum of the oligomers of 4-VA and ethylene after reacting at 70°C for 10 minutes (1,1,2,2-Tetrachloroethane-d<sub>2</sub>).

## References

- [1] Li, X.; Nishiura, M.; Mori, K.; Mashiko, T., Hou, Z. *Chem. Commun.* **2007**, 4137-4139.
- [2] Nishiura, M.; Baldamus, J.; Shima, T.; Mori, K., Hou, Z. *Chem. Eur. J.* **2011**, 17, 5033-5044.
- [3] Jiang, Y., Yorimitsu, H., *JACS Au* **2022**, 11, 2514-2521.
- [4] Cox, J., Kang, H., Igarashi, T., Swager, T., *ACS Macro Lett.* **2012**, 1, 334-337.