Supporting Information for

The Synthesis and Properties Research of Functionalized Polyolefins

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1 Experimental Section

1.1 General methods.

Tetrahydrofuran (THF) and toluene (both from Avantor) were passed through an activated alumina column under nitrogen to remove protic impurities. All other reagent grade solvents were used without further purification. *cis*-cyclooctene (**COE**), (IMesH_2)-(IPrO)RuCl_2(CHPh) (Hoveyda-Grubbs second generation catalyst, **HGII**), dimethyl maleate were purchased from Sigma-Aldrich. The deuterated solvents CD_2Cl_2, $CDCl_3$, and 1,1,2,2-tetradhloroethane-d_2 were purchased from Cambridge Isotope Laboratories. **COE** was distilled over CaH_2 prior to use. HDPE: DMDA-8008H, produced by the China National Petroleum Corporation, PET: Item No. P875573, purchase with Shanghai Makclin Biochemical Co., Ltd.; All other chemicals were used as received. **M1**, **M2**, **M3** and **M5** were synthesized according to literature[1-4]; **M4** is commercially available.

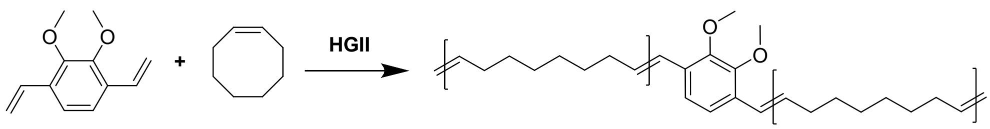
All experiments were carried out under a dry nitrogen atmosphere using standard Schlenk techniques or in a glove-box. ^{1}H NMR spectra were recorded by a Bruker Ascend Tm 400 spectrometer at ambient temperature. ^{1}H NMR chemical shifts were referenced to residual deuterated solvent peaks or the tetramethylsilane signal (0 ppm). Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) employing a series of two linear Styragel columns (HR2 and HR4) at an oven temperature of 45 ºC. A Waters 1515 pump and Waters 2414 differential refractive index detector (30 ºC) were used. The eluent was THF at a flow rate of 1.0 mL/min. A series of low polydispersity polystyrene standards was used for calibration. Molecular weight and molecular weight distribution of the hydrogenated polymer were determined by gel permeation chromatography (GPC) with a PL-220 equipped with two Agilent PLgel Olexis columns at 150 ℃ using 1, 2, 4-trichlorobenzene as a solvent, and the calibration was made using polystyrene standard. DSC measurements were performed on a TA Instruments DSC Q20. Samples (ca. 5 mg) were annealed by heating to 150 °C at 20 °C/min, cooled to 40 °C at 20 °C/min, and then analyzed while being heated to 150 °C at 20 °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℃ 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 m/min using a Universal Test Machine (UTM2502) at room temperature. At least three specimens of each copolymer were tested.

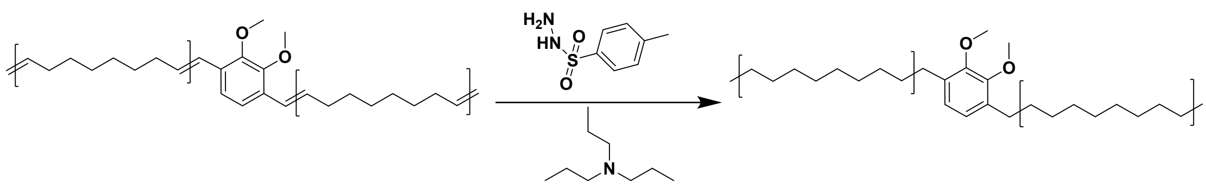
Hydrogenation of Polymer: Hydrogenation by chemical hydrogenation procedure. An example of the chemical hydrogenation procedure is described for the hydrogenation of poly(1,4-divinylbenzene-COE) (entry 5 in Table S1). A mixture of poly(1,4-divinylbenzene-COE) (1.00 g, 15.00 mmol of olefin), *p*-toluenesulfonhydrazide (2.32 g, 16 mmol), tributylamine (2.32 ml, 16 mmol) and o-xylene (40 mL) was refluxed for 8 h, and then allowed to cool to room temperature. The reaction mixture was poured into methanol and the polymer precipitated. The precipitated polymer was isolated by decantation and purified by repeating reprecipitation using dichloromethane/methanol system. The polymer was freeze dried overnight from methanol solution to afford hydrogenated **copolymer-1**. The dried hydrogenated **copolymer-1** need to repeat the above chemical hydrogenation procedure. The hydrogenation of **copolymer-1** (0.98g, 98wt%) as a white solid.

1.2 Polymerization.

Polymerization of *cis*-cyclooctene with diene/triene monomers and chemical hydrogenation.



The preparation of sample is described in detail: anhydrous dichloromethane (40 mL), **M1** (0.15 g, 0.77 mmol) and **COE** (1.70 g, 15.4 mmol) were transferred via injector into a 100 mL Schlenk flask with a constant nitrogen purge. The flask and its contents were place under vacuum and then recharged with nitrogen. The flask was immersed in an oil-bath at 40 °C immediately before transferring **HGII** catalyst (12.53 mg, 20 μmol) as a solution in 1 mL of dichloromethane. After a desired amount of time, it was evaporated to dryness under vacuum, then precipitating into 200 mL methanol. The unsaturated **copolymer-1** was isolated, washed with methanol (3×50 mL) and dried under vacuum for 12 hours at 45 °C. The polymer was characterized by ^{1}H NMR spectrum and GPC. And the unsaturated **copolymer-2, copolymer-3, copolymer-4 and copolymer-5** were synthesized by the similar method except different diene/triene monomers.



An example of the chemical hydrogenation procedure is described for the hydrogenation of polymer. A mixture of the above-mentioned unsaturated **copolymer-1** (5.66 mmol of olefin), p-toluenesulfonyl hydrazide (4.67g, 25 mmol), tripropylamine (4.01g, 28 mmol), small amount of BHT (5 mg), and o-xylene (50 mL) were refluxed for 8 h, and then allowed to cool to room temperature. The reaction mixture was poured into methanol and the polymer precipitated. The precipitated polymer was isolated by decantation and purified by repeating reprecipitation using dichloromethane /methanol system. The polymer was drained of solvent in a vacuum oven to afford hydrogenated **copolymer-1** as a solid. The polymer was characterized by high temperature ^{1}H NMR spectrum and high temperature GPC. The other hydrogenated polymers (**copolymer-2, copolymer-3, copolymer-4 and copolymer-5)** were prepared by corresponding unsaturated copolymers.

2. ^{1}H NMR and ^{1}H-^{1}H COSY NMR of the copolymers.

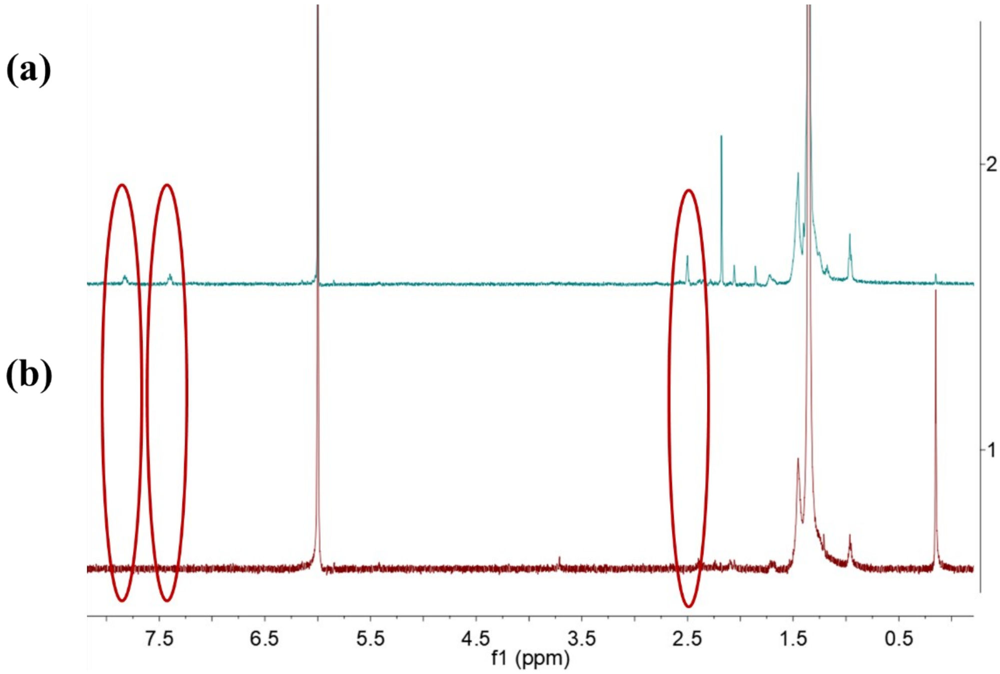


Figure S1. (a) ^{1}H NMR spectrum before degradation of **copolymer-3$^{1/20}$** ($C_2D_2Cl_4$, 120°C) **(b)** ^{1}H NMR spectrum after degradation of **copolymer-3$^{1/20}$** ($C_2D_2Cl_4$, 120°C).

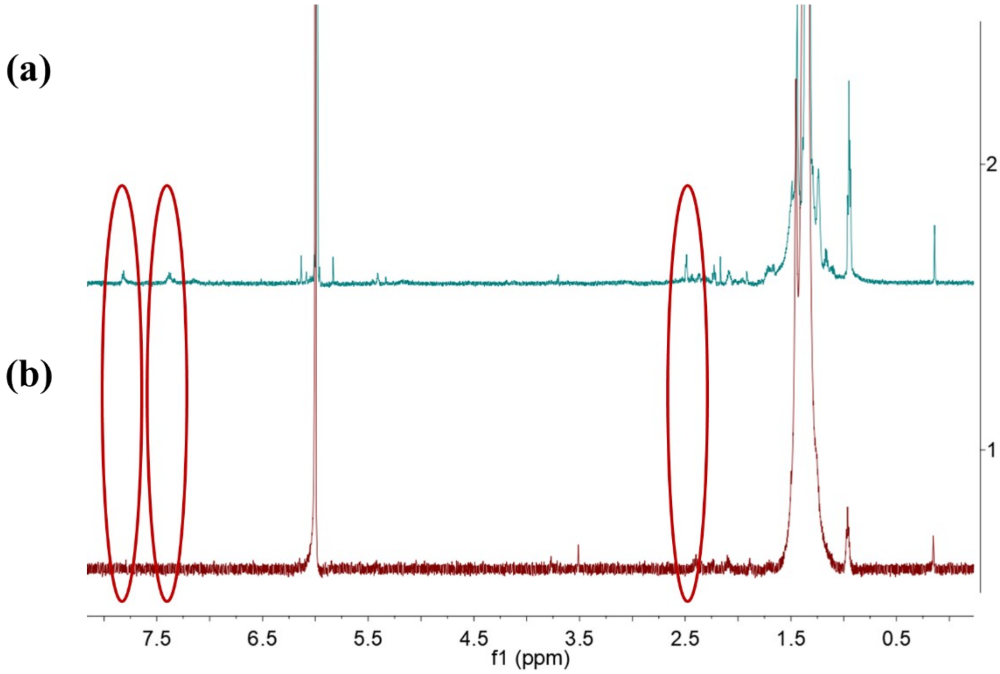


Figure S2. (a) ^{1}H NMR spectrum before degradation of **copolymer-3$^{1/100}$** ($C_2D_2Cl_4$, 120°C) **(b)** ^{1}H NMR spectrum after degradation of **copolymer-3$^{1/100}$** ($C_2D_2Cl_4$, 120°C).

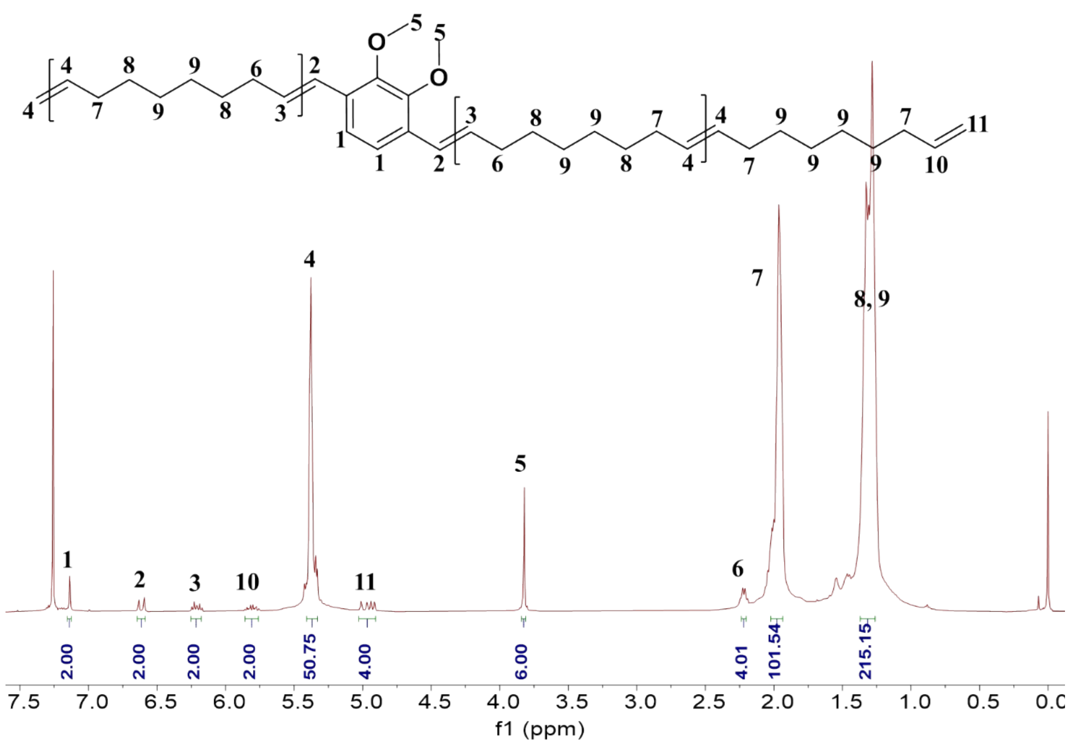


Figure S3. ^{1}H NMR spectrum of the **copolymer-1$^{1/20}$** ($CDCl_3$).

$$Incorporation(\%) = \frac{I(H\text{-}1)/2}{I(H\text{-}1)/2 + I(H\text{-}4)/2} \times 100\% = \frac{2.00/2}{2.00/2 + 50.75/2} \times 100\% = 3.8\%$$

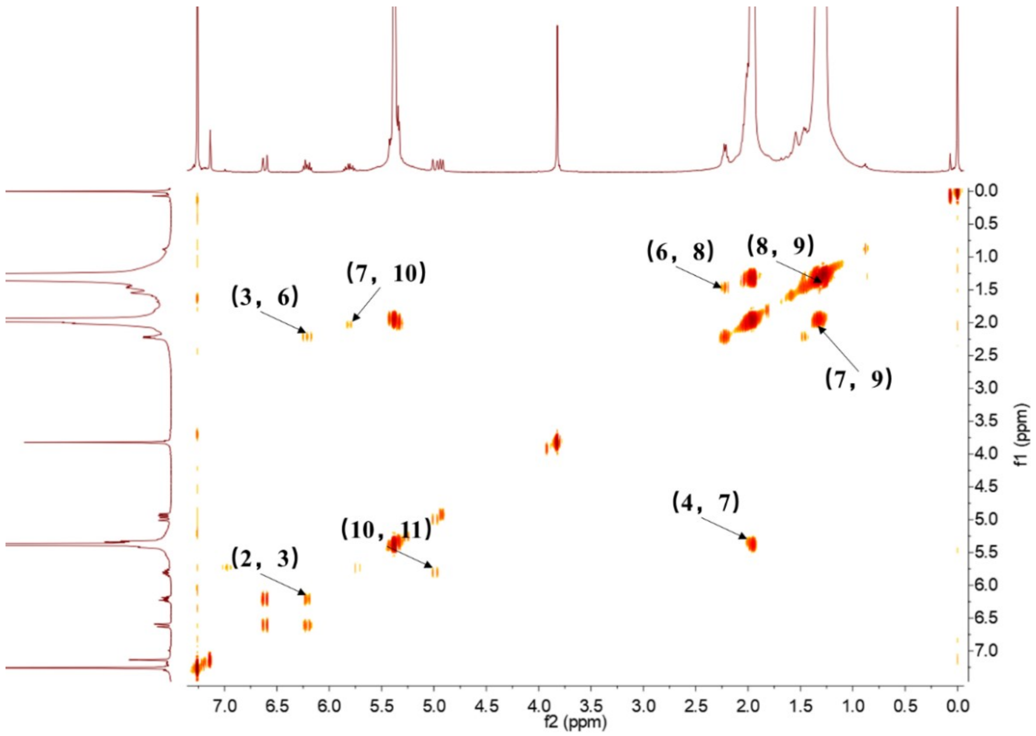


Figure S4. ^{1}H COSY NMR spectrum of the **copolymer-1$^{1/20}$** ($CDCl_3$).

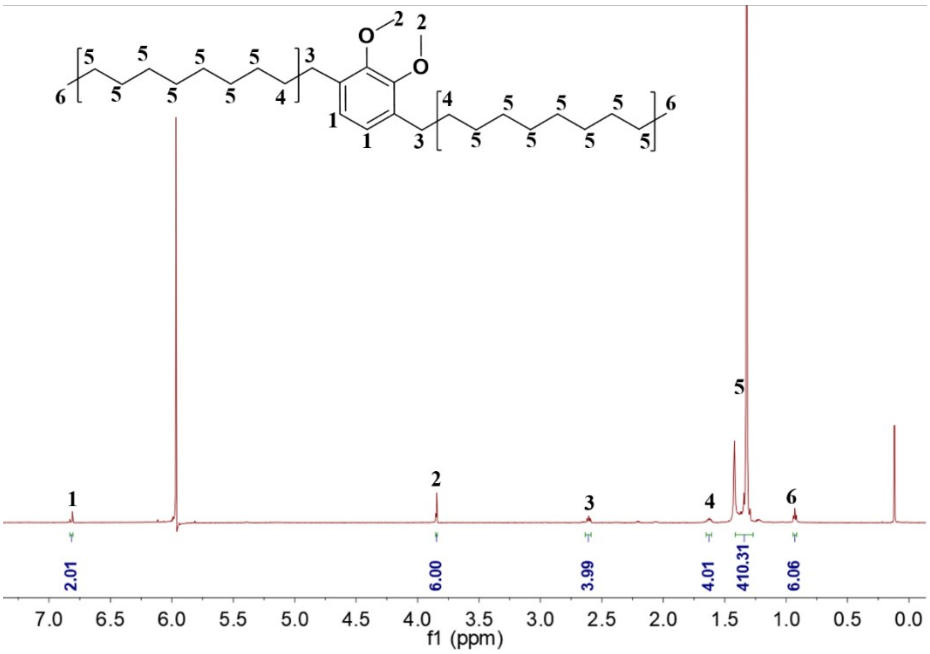


Figure S5. ^{1}H NMR spectrum of the **copolymer-1$^{1/20}$** ($C_2D_2Cl_4$, 120°C).

$$Incorporation(\%) = \frac{I(H\text{-}1)/2}{I(H\text{-}1)/2 + I(H\text{-}4 + H\text{-}5 + H\text{-}6)/4} \times 100\% = \frac{2.01/2}{2.01/2 + (4.01 + 410.3\ldots} \times 100\% = 0.9\%$$

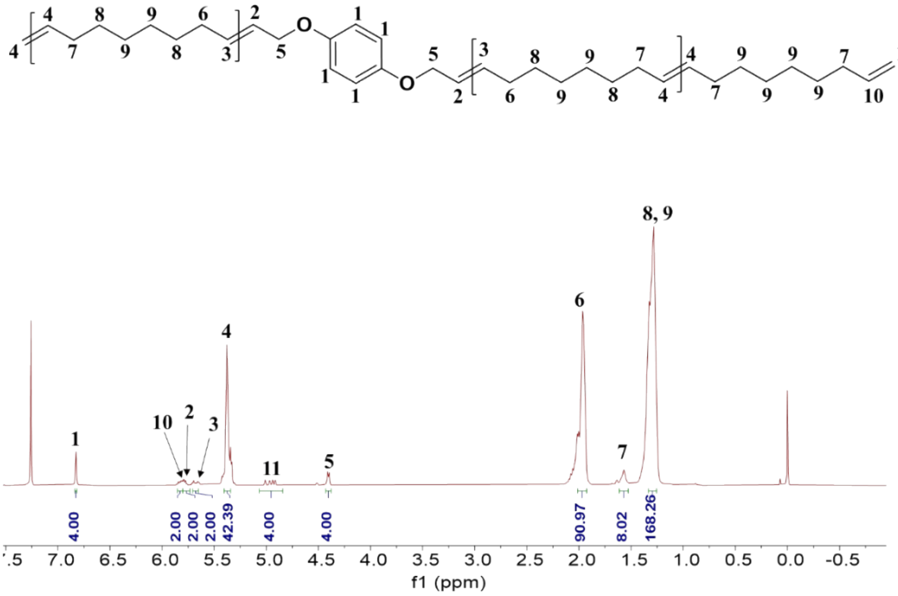


Figure S6. ^{1}H NMR spectrum of the **copolymer-2$^{1/20}$** ($CDCl_3$).

$$Incorporation(\%) = \frac{I(H\text{-}1)/4}{I(H\text{-}1)/4 + I(H\text{-}4)/2} \times 100\% = \frac{4.00/4}{4.00/4 + 42.39/2} \times 100\% = 4.5\%$$

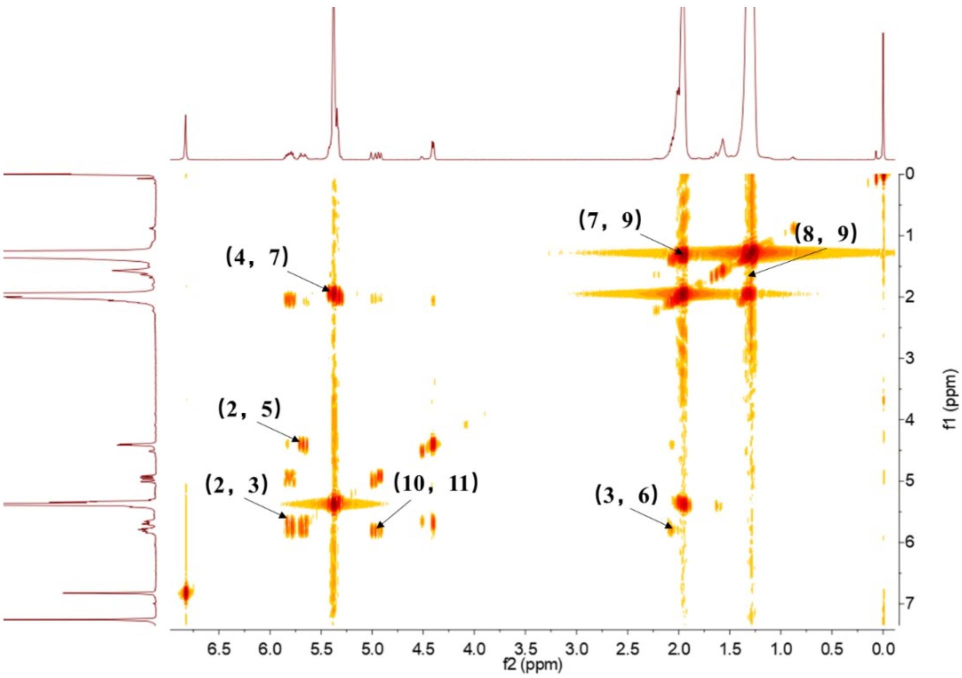


Figure S7. ^{1}H COSY NMR spectrum of the **copolymer-2$^{1/20}$** ($CDCl_3$).

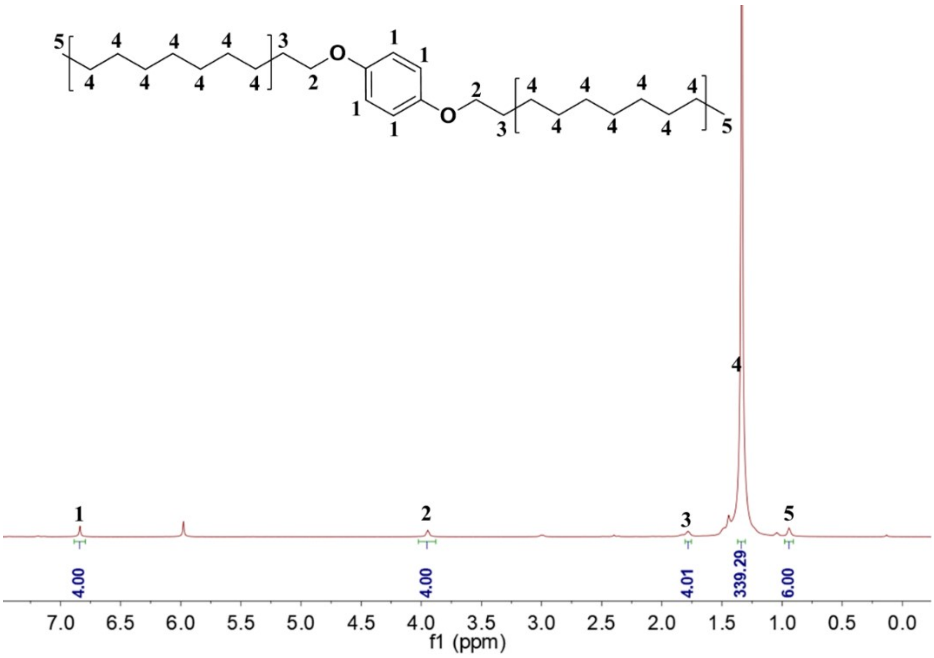


Figure S8. ^{1}H NMR spectrum of the **copolymer-2$^{1/20}$** ($C_2D_2Cl_4$, 120°C).

$$Incorporation(\%) = \frac{I(H\text{-}1)/4}{\frac{I(H\text{-}1)}{4} + I(H\text{-}4 + H\text{-}5)/4} \times 100\% = \frac{4.00/4}{4.00/4 + (339.29 + 6)/4} \times 100\% = 1.0\%$$

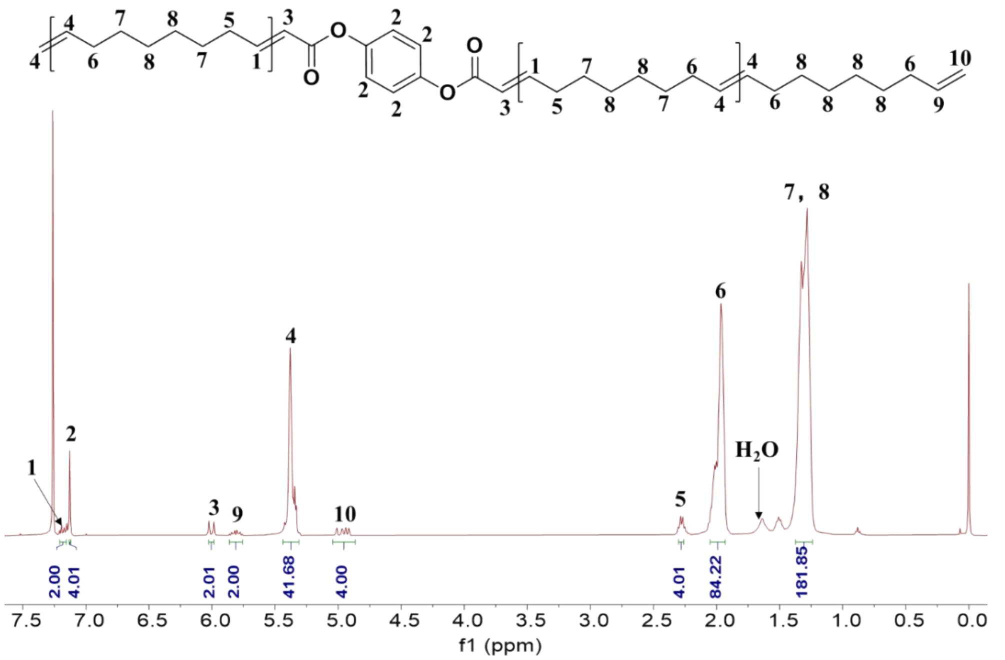


Figure S9. ^{1}H NMR spectrum of the **copolymer-3$^{1/20}$** ($CDCl_3$).

$$Incorporation(\%) = \frac{I(H\text{-}2)/4}{I(H\text{-}2)/4 + I(H\text{-}4)/2} \times 100\% = \frac{4.01/4}{4.01/4 + 41.68/2} \times 100\% = 4.6\%$$

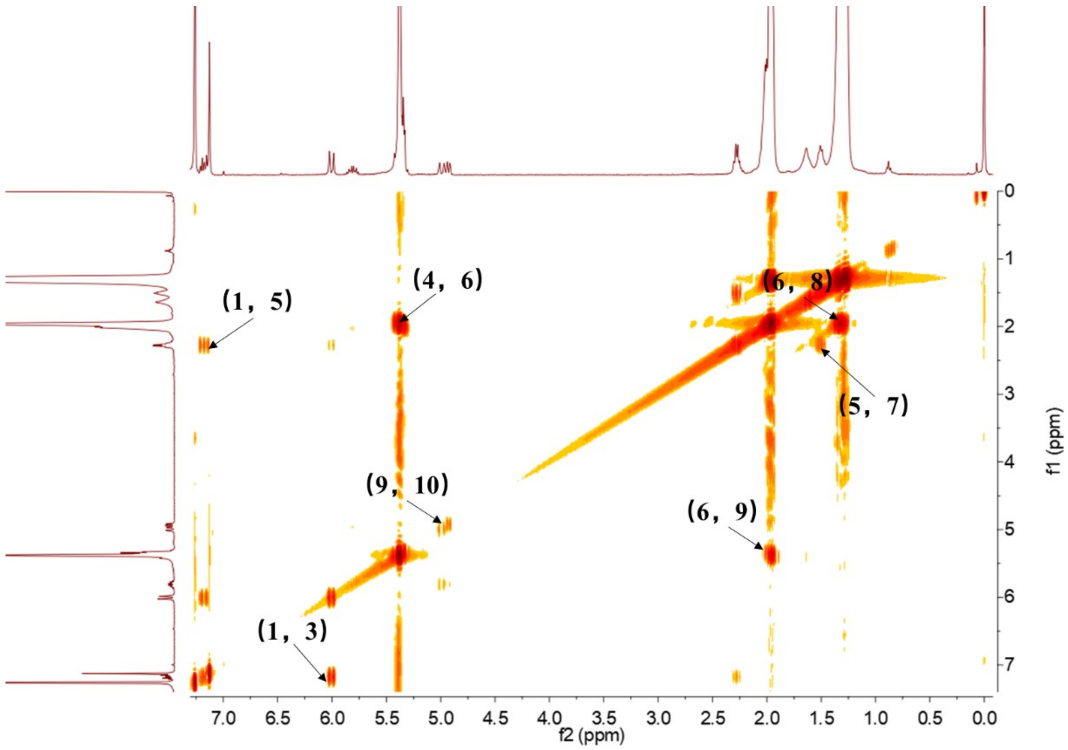


Figure S10. ^{1}H COSY NMR spectrum of the **copolymer-3$^{1/20}$** ($CDCl_3$).

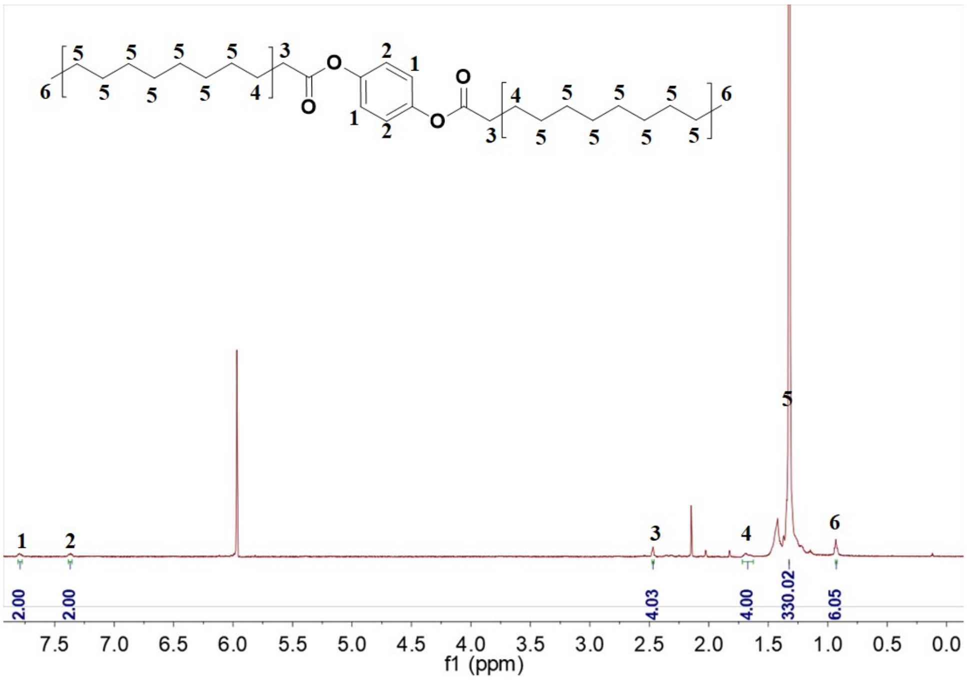


Figure S11. ^{1}H NMR spectrum of the **copolymer-3$^{1/20}$** ($C_2D_2Cl_4$, 120°C).

$$Incorporation(\%) = \frac{I(H\text{-}1)/4}{I(H\text{-}1)/2 + I(H\text{-}4 + H\text{-}5 + H\text{-}6)/4} \times 100\% = \frac{2.00/2}{2.00/2 + (4.00 + 330.02} \times 100\% = 1.2\%$$

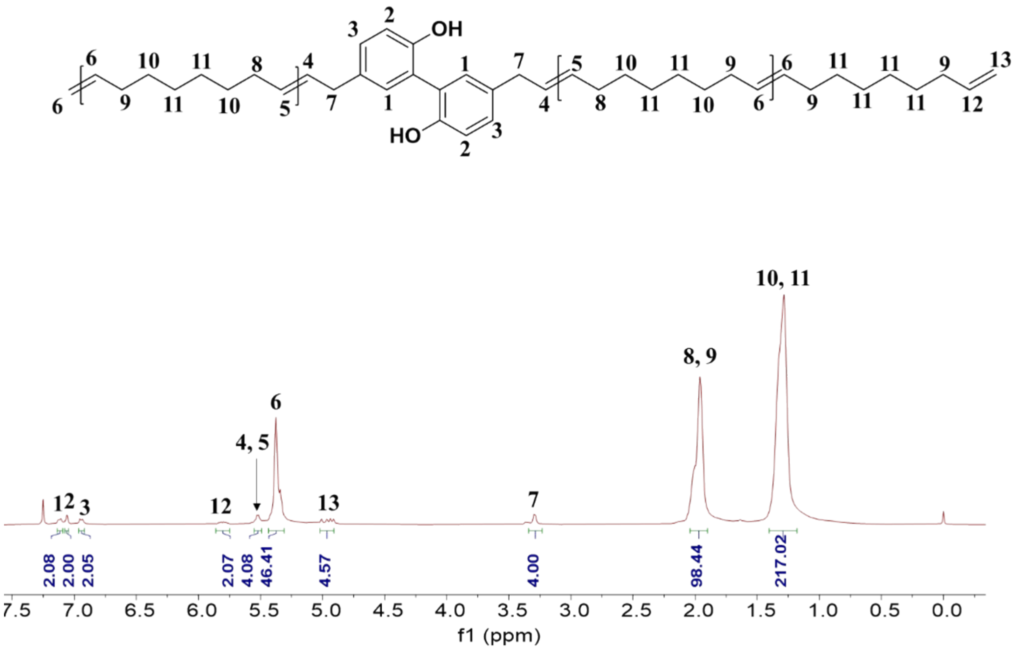


Figure S12. ^{1}H NMR spectrum of the **copolymer-4$^{1/20}$** ($CDCl_3$).

$$Incorporation(\%) = \frac{I(H\text{-}1)/2}{I(H\text{-}1)/2 + I(H\text{-}6)/2} \times 100\% = \frac{2.08/3}{2.08/2 + 46.41/2} \times 100\% = 4.3\%$$

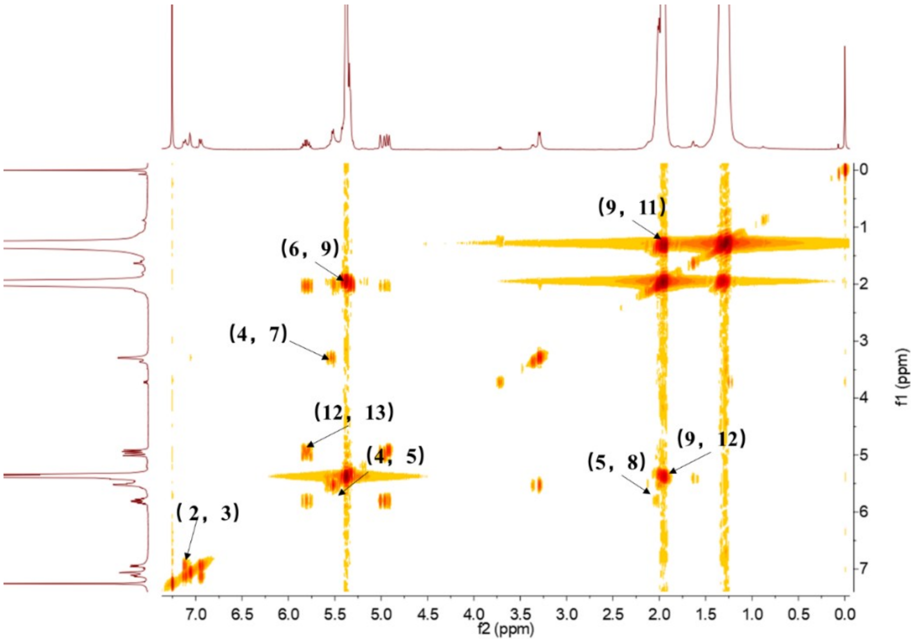


Figure S13. ^{1}H COSY NMR spectrum of the **copolymer-4$^{1/20}$** ($CDCl_3$).

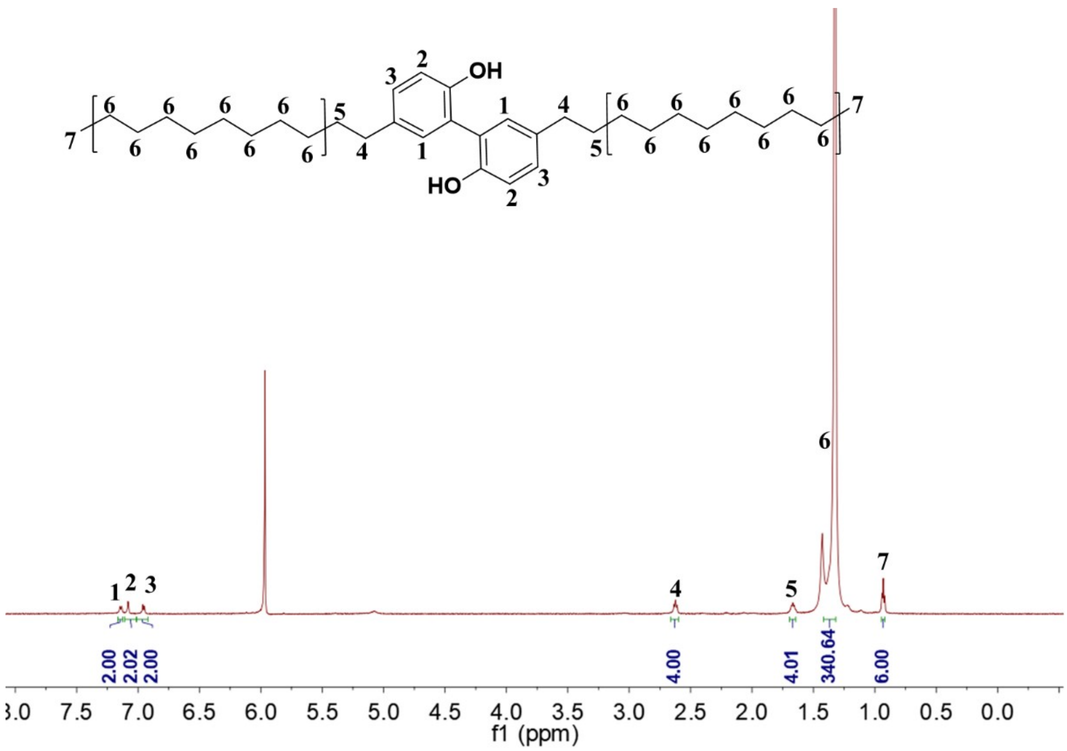


Figure S14. ^{1}H NMR spectrum of the **copolymer-4$^{1/20}$** ($C_2D_2Cl_4$, 120°C)

$$Incorporation(\%) = \frac{I(H\text{-}1)/2}{I(H\text{-}1)/2 + I(H\text{-}6 + H\text{-}7)/4} \times 100\% = \frac{2.00/2}{2.00/2 + (340.64 + 6)/4} \times 100\% = 1.1\%$$

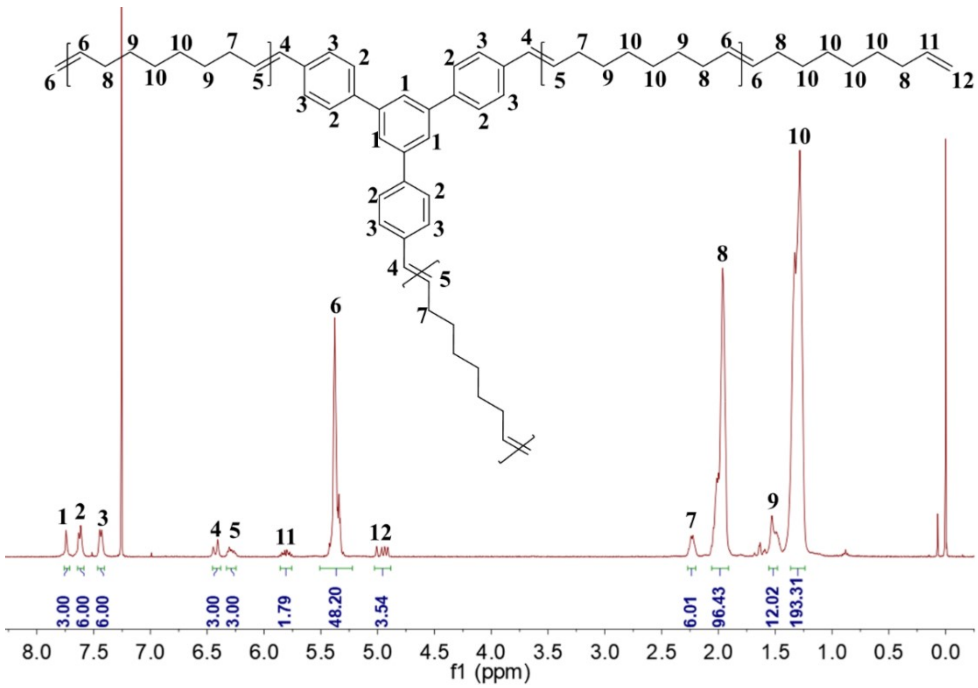


Figure S15. ¹H NMR spectrum of the **copolymer-$5^{1/20}$** ($CDCl_3$).

$$Incorporation(\%) = \frac{I(H\text{-}1)/3}{I(H\text{-}1)/3 + I(H\text{-}6)/2} \times 100\% = \frac{3.00/3}{3.00/3 + 48.20/2} \times 100\% = 4.0\%$$

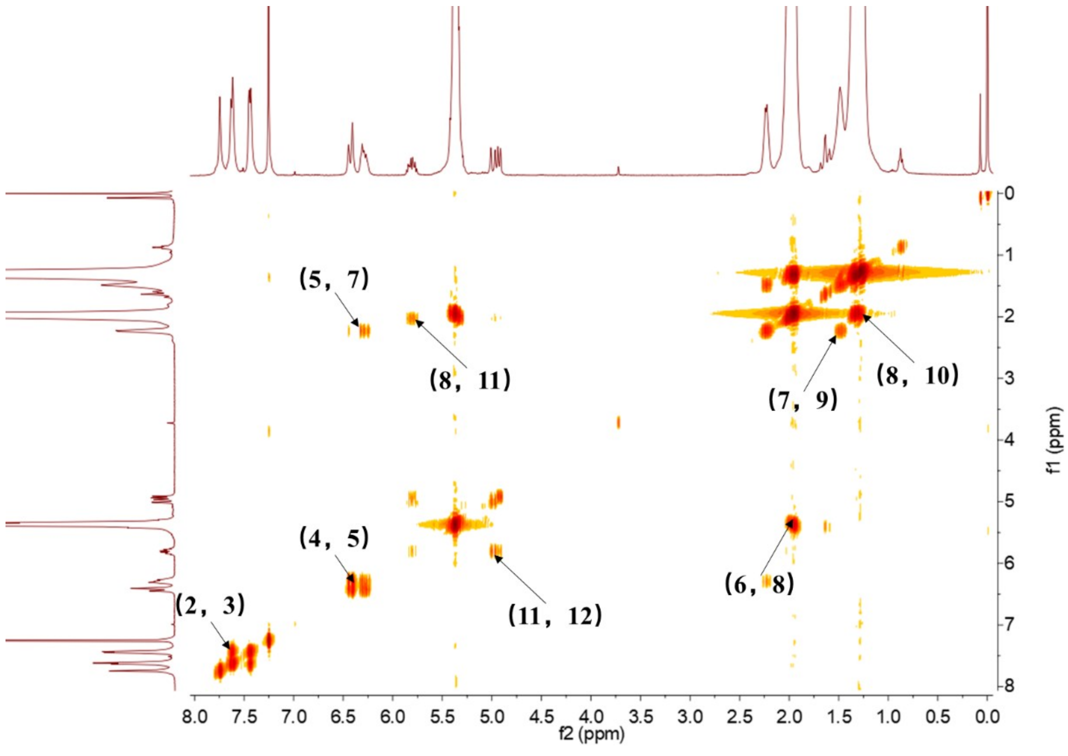


Figure S16. ¹H COSY NMR spectrum of the **copolymer-$5^{1/20}$** ($CDCl_3$).

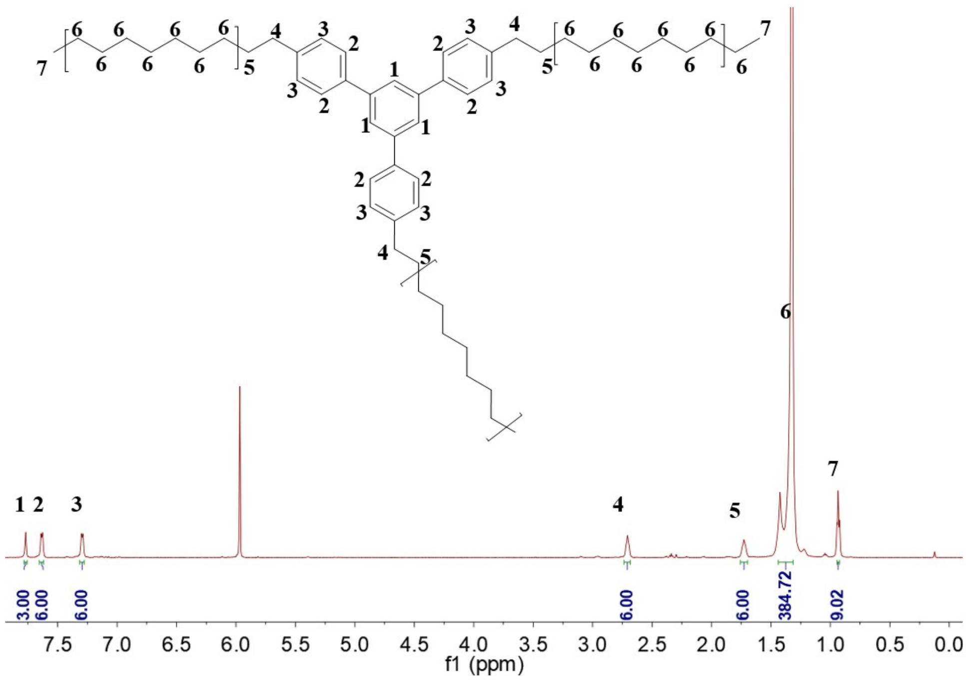
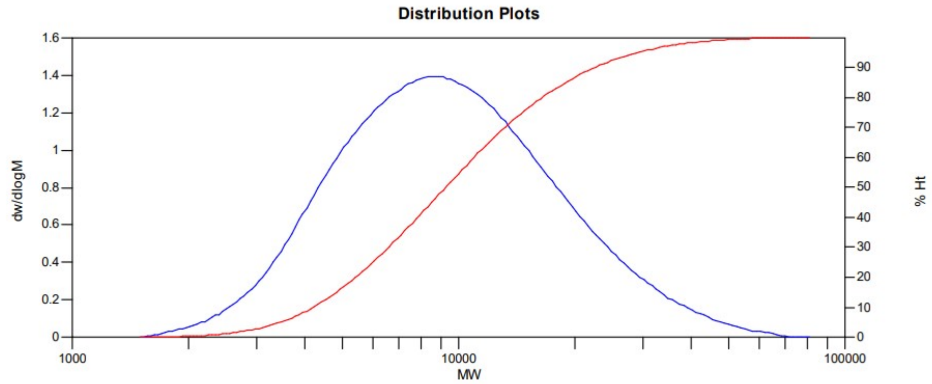


Figure S17. ^{1}H NMR spectrum of the **copolymer-5$^{1/20}$** ($C_2D_2Cl_4$, 120°C).

$$Incorporation(\%) = \frac{I(H\text{-}1)/3}{I(H\text{-}1)/3 + I(H\text{-}6 + H\text{-}7)/4} \times 100\% = \frac{3.00/3}{3.00/3 + (384.72 + 9.02)/4} \times 100\% = 1.0\%$$

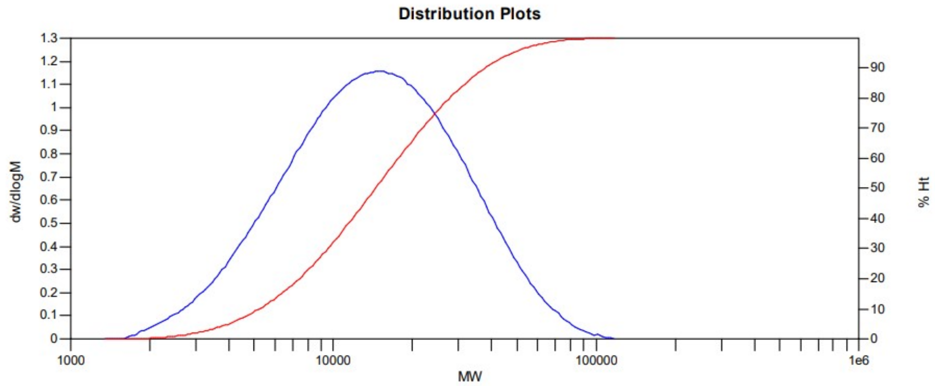
3. GPC and DSC Spectrum of the Copolymers.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	8909	7593	11409	17472	25403	10672	1.50257

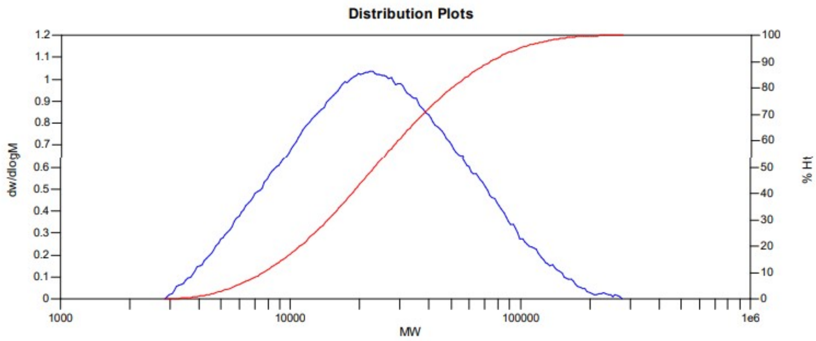
Figure S18. GPC trace of the **copolymer-1$^{1/5}$** from Table 1, Entry 1.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	15187	10376	18092	29040	41214	16680	1.74364

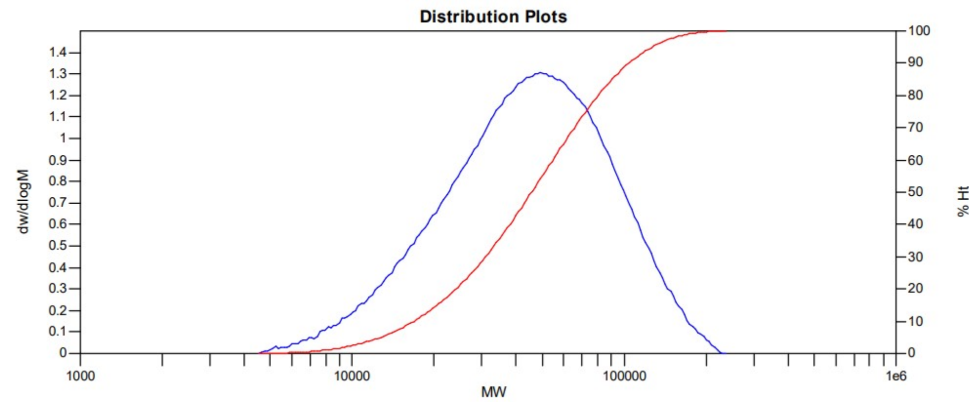
Figure S19. GPC trace of the **copolymer-1**$^{1/20}$ from Table 1, Entry 2.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	21988	16495	33253	62986	99229	29922	2.01594

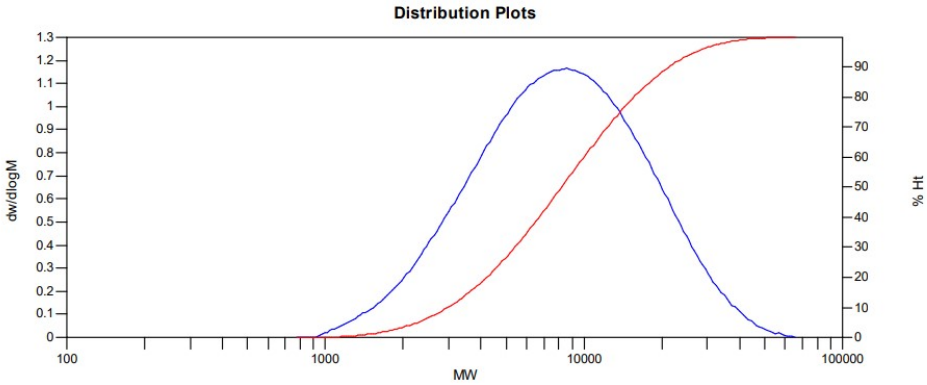
Figure S20. GPC trace of the **copolymer-1**$^{1/100}$ from Table 1, Entry 3.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	49354	33337	53700	77235	100069	50352	1.61082

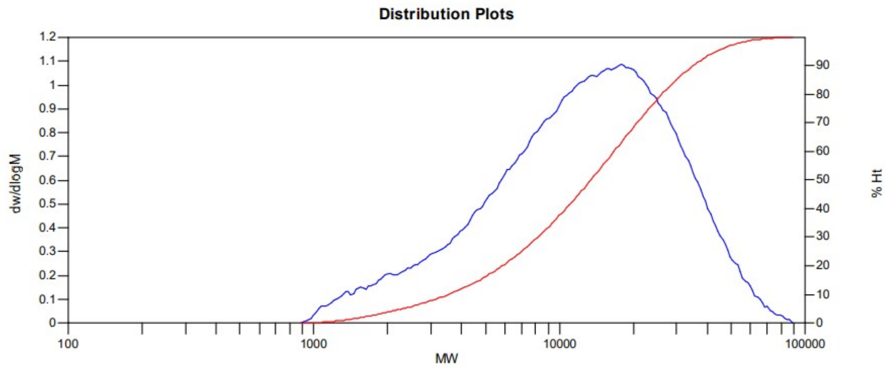
Figure S21. GPC trace of the **copolymer-1**$^{1/200}$ from Table 1, Entry 4.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	8596	5895	10215	16317	23093	9451	1.73282

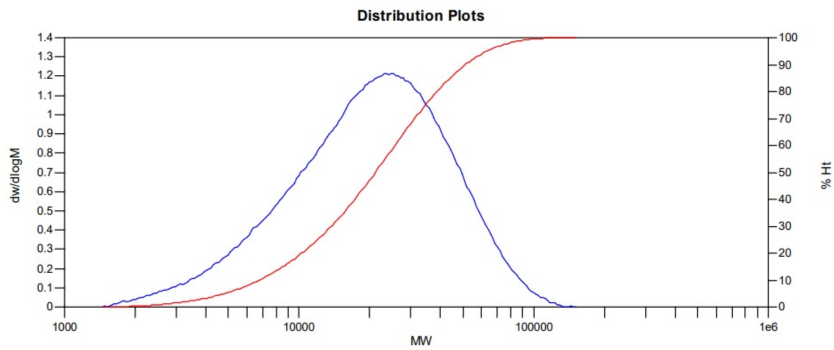
Figure S22. GPC trace of the **copolymer-2$^{1/5}$** from Table 1, Entry 5.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	17838	7869	16655	26863	36321	15258	2.11653

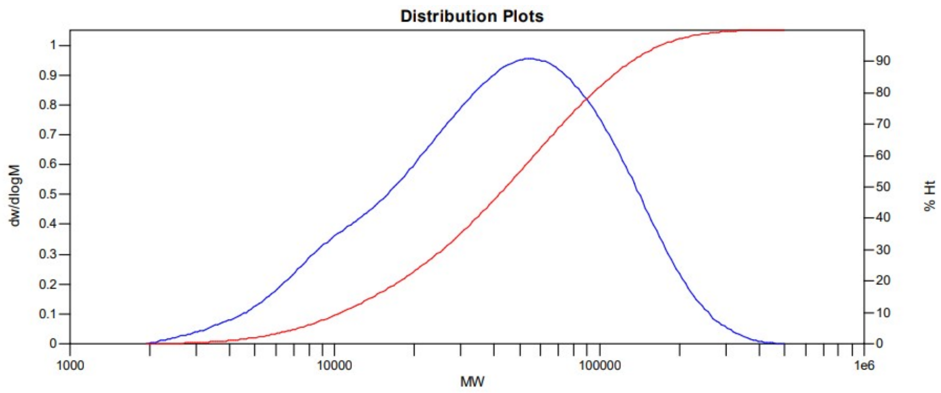
Figure S23. GPC trace of the **copolymer-2$^{1/20}$** from Table 1, Entry 6.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	24698	13996	25505	39022	52495	23678	1.82231

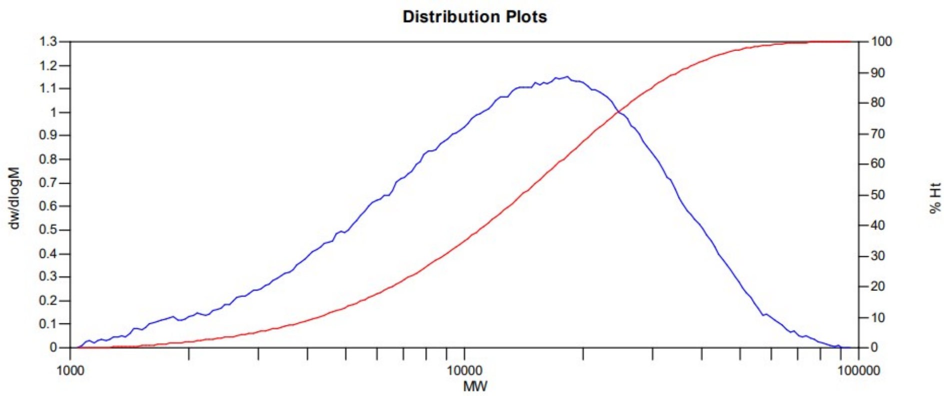
Figure S24. GPC trace of the **copolymer-2$^{1/100}$** from Table 1, Entry 7.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	54994	23923	58811	107040	156246	52517	2.45835

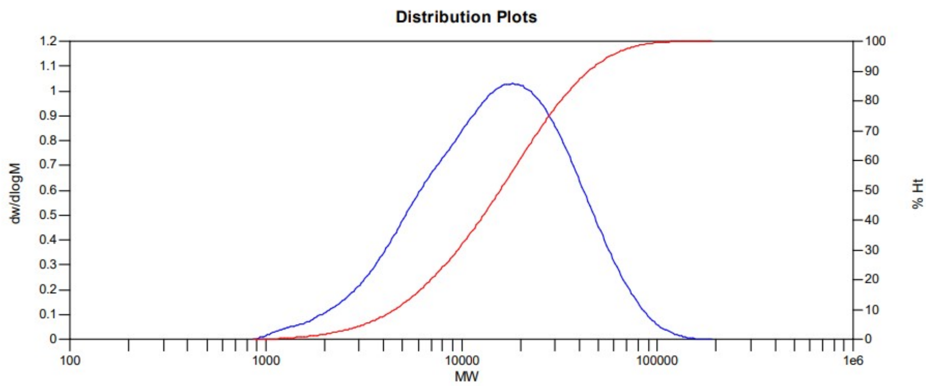
Figure S25. GPC trace of the **copolymer-2$^{1/200}$** from Table 1, Entry 8.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	18257	8976	17046	26423	35375	15764	1.89906

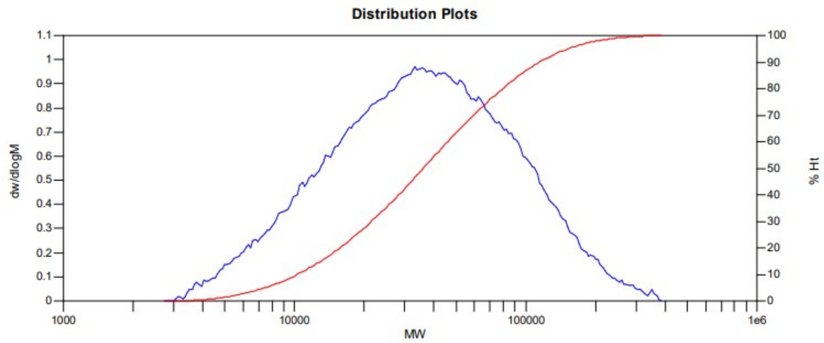
Figure S26. GPC trace of the **copolymer-3$^{1/5}$** from Table 1, Entry 9.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	18255	9499	20480	36029	53270	18560	2.15602

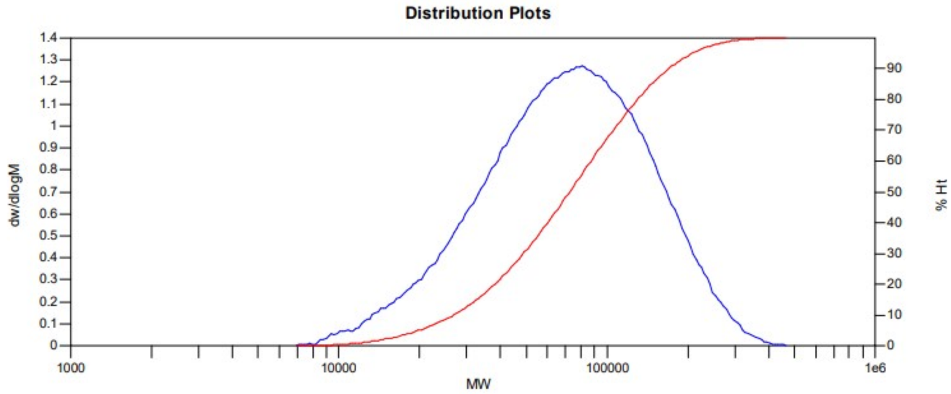
Figure S27. GPC trace of the **copolymer-3$^{1/20}$** from Table 1, Entry 10.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	33166	23068	51571	98599	152234	45942	2.23561

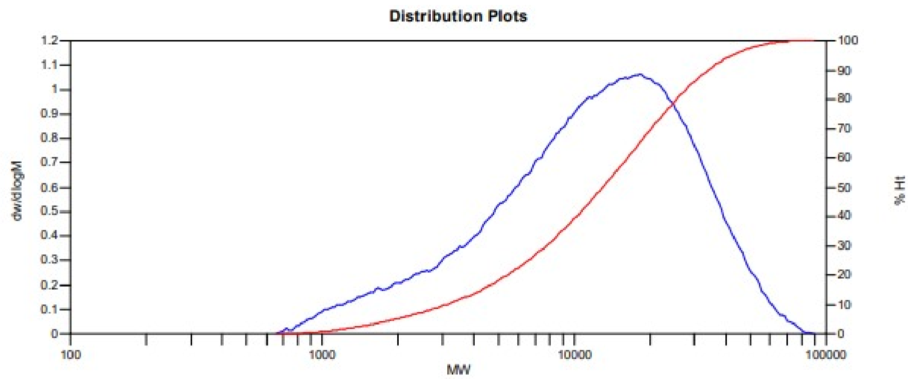
Figure S28. GPC trace of the **copolymer-3$^{1/100}$** from Table 1, Entry 11.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	80645	52925	86678	127406	168803	81015	1.63775

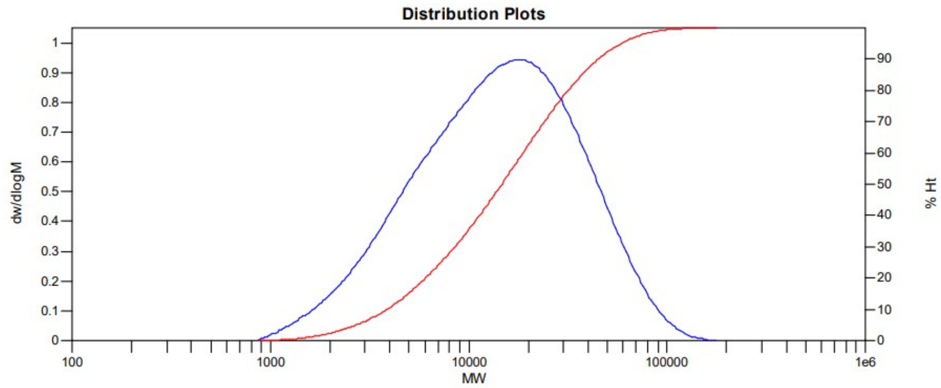
Figure S29. GPC trace of the **copolymer-3$^{1/200}$** from Table 1, Entry 12.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	18257	7079	16114	26210	35217	14710	2.27631

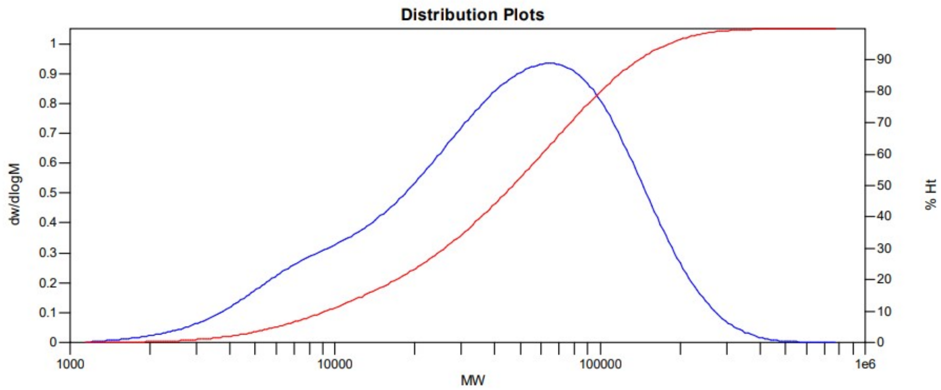
Figure S30. GPC trace of the **copolymer-4$^{1/5}$** from Table 1, Entry 13.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	18255	8482	19867	36901	55014	17790	2.34225

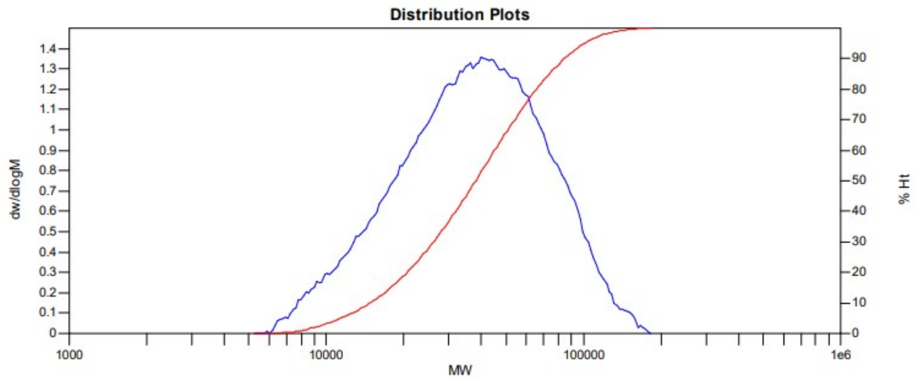
Figure S31. GPC trace of the **copolymer-4$^{1/20}$** from Table 1, Entry 14.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	66754	21547	61750	115258	170383	54691	2.86583

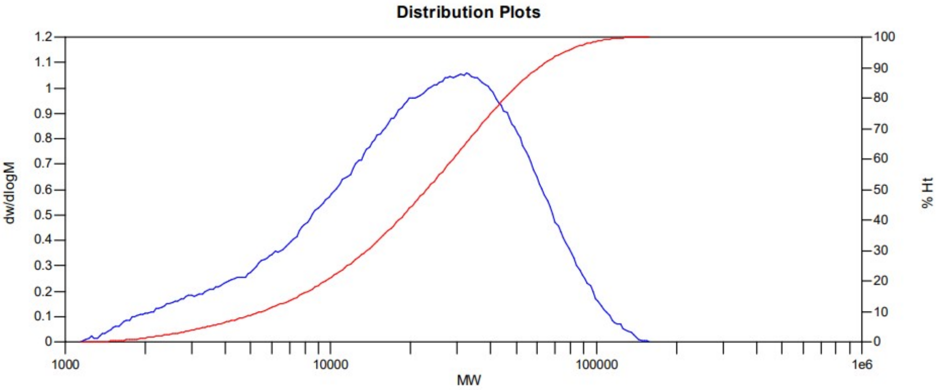
Figure S32. GPC trace of the **copolymer-4$^{1/100}$** from Table 1, Entry 15.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	39988	29013	44187	61882	79079	41661	1.52301

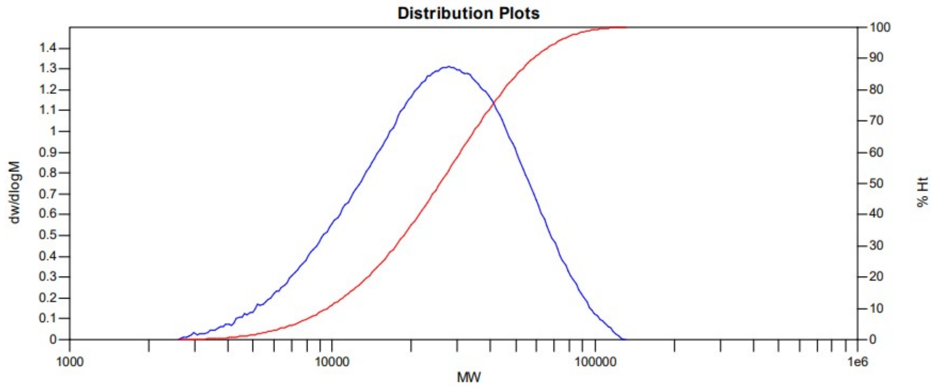
Figure S33. GPC trace of the **copolymer-4$^{1/200}$** from Table 1, Entry 16.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	32399	12455	28625	46762	62959	26021	2.29827

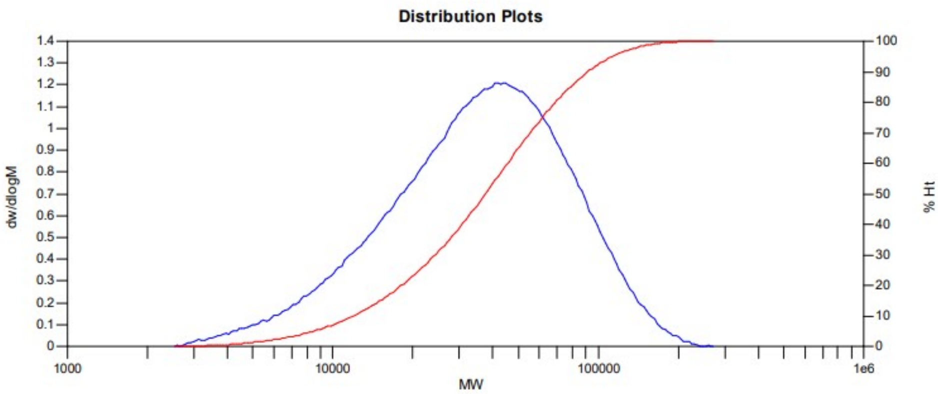
Figure S34. GPC trace of the **copolymer-5$^{1/5}$** from Table 1, Entry 17.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	27742	18811	30135	43186	55841	28335	1.60199

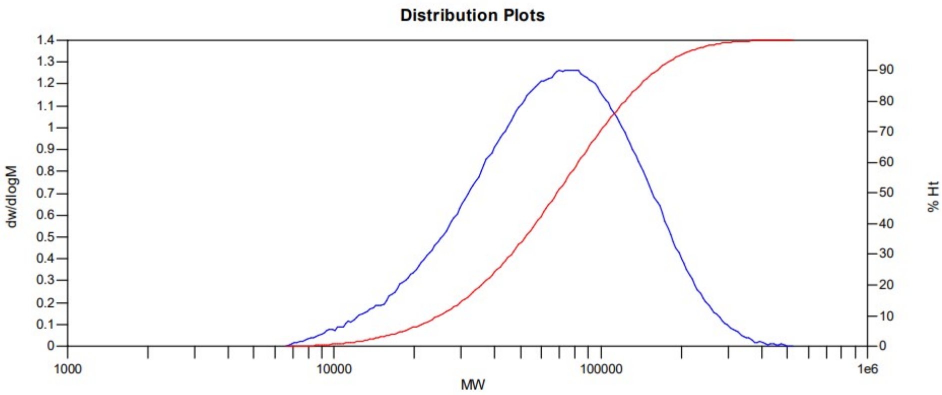
Figure S35. GPC trace of the **copolymer-5$^{1/20}$** from Table 1, Entry 18.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	43909	24747	45416	69776	94085	42021	1.83521

Figure S36. GPC trace of the **copolymer-5$^{1/100}$** from Table 1, Entry 19.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	70089	49288	82222	123022	167064	76663	1.6682

Figure S37. GPC trace of the **copolymer-5$^{1/200}$** from Table 1, Entry 20.

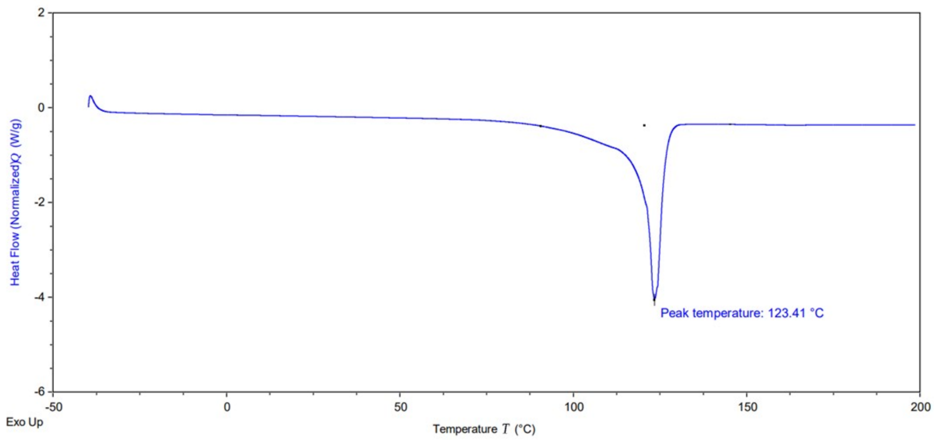


Figure S38. DSC trace of the **copolymer-1$^{1/20}$** from Table 1, Entry 2.

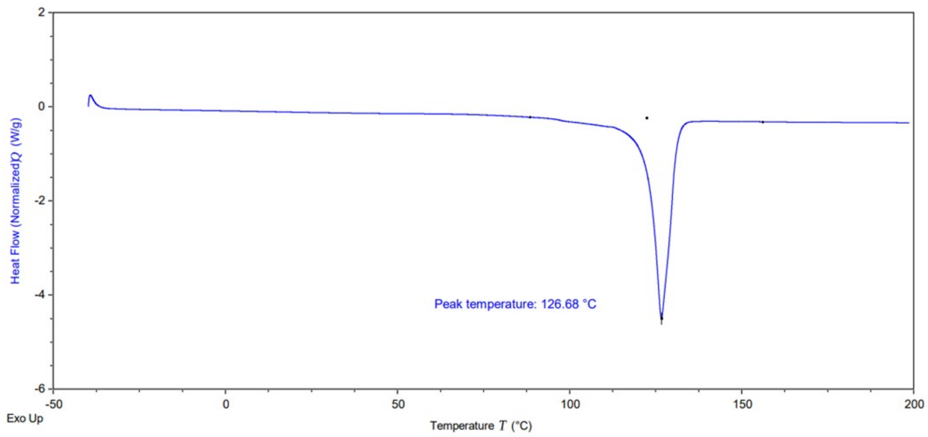


Figure S39. DSC trace of the **copolymer-1$^{1/100}$** from Table 1, Entry 3.

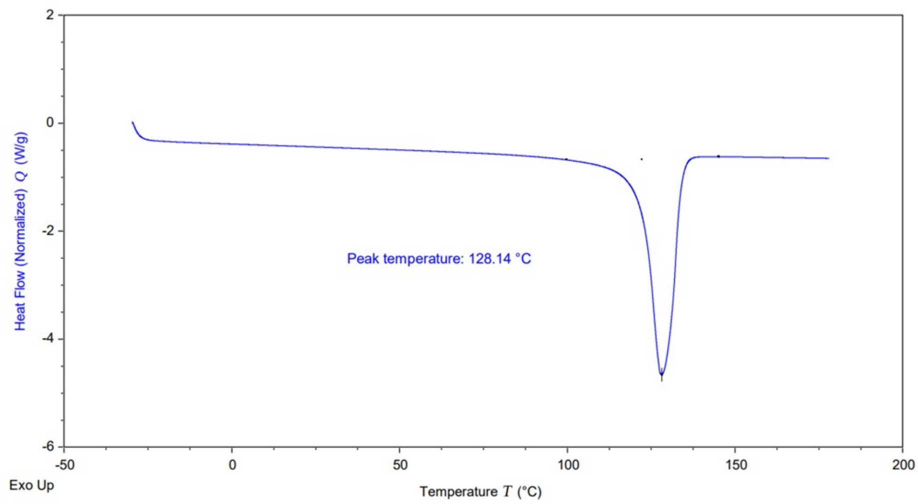


Figure S40. DSC trace of the **copolymer-1$^{1/200}$** from Table 1, Entry 4.

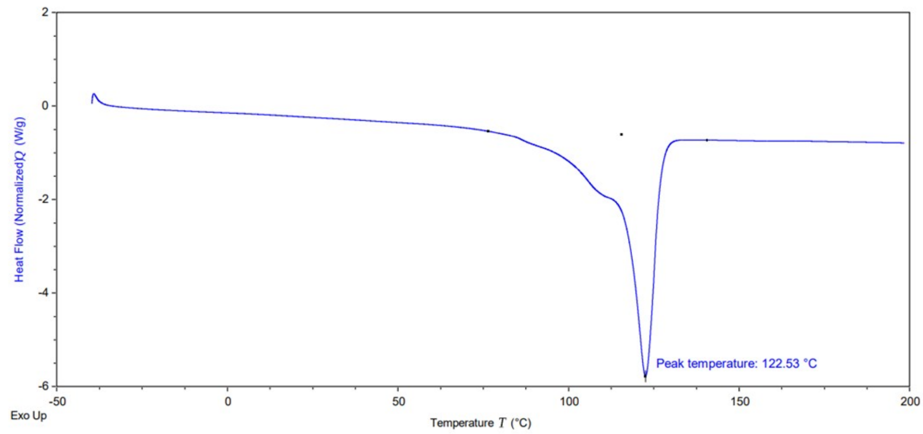


Figure S41. DSC trace of the **copolymer-2$^{1/20}$** from Table 1, Entry 6.

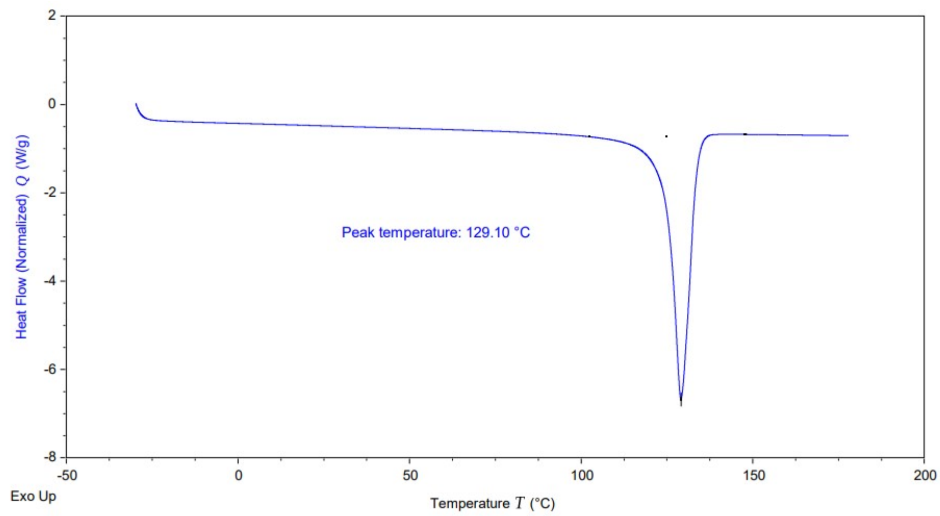


Figure S42. DSC trace of the **copolymer-2$^{1/200}$** from Table 1, Entry 8.

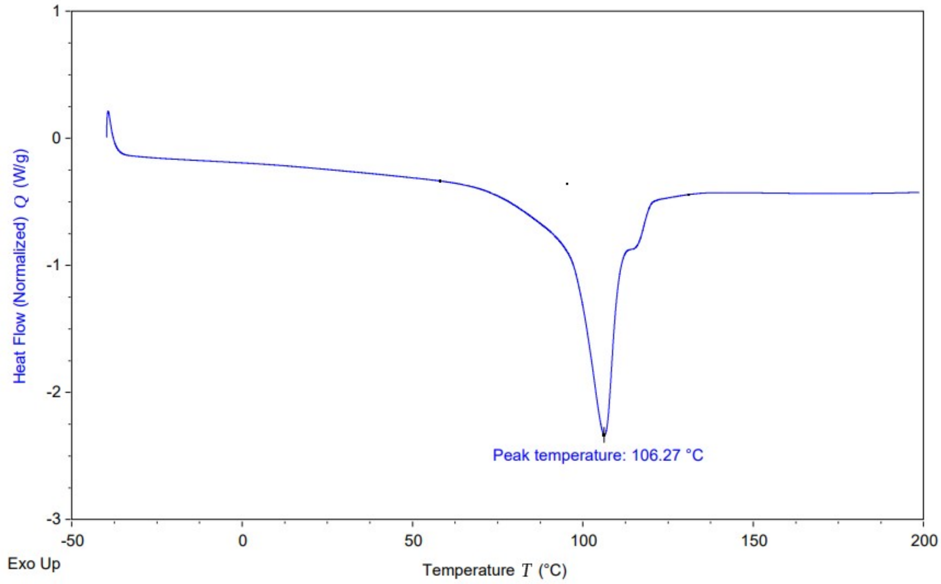


Figure S43. DSC trace of the **copolymer-3$^{1/5}$** from Table 1, Entry 9.

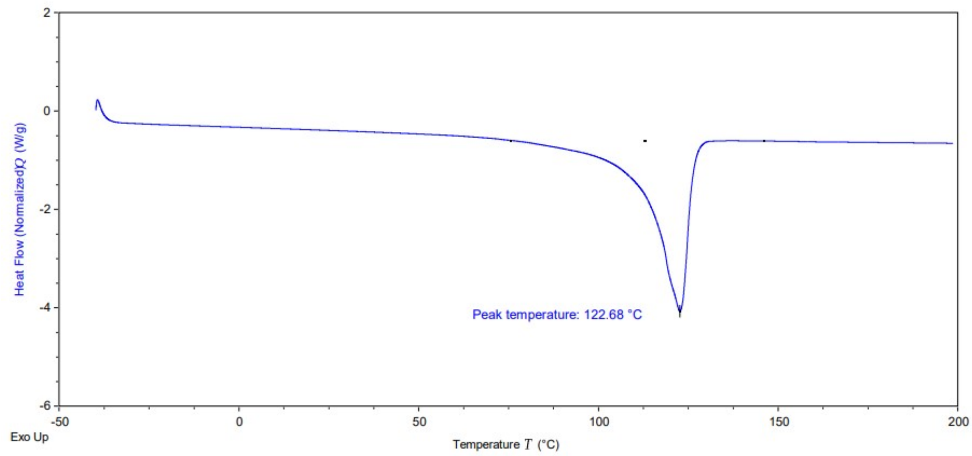


Figure S44. DSC trace of the **copolymer-3$^{1/20}$** from Table 1, Entry 10.

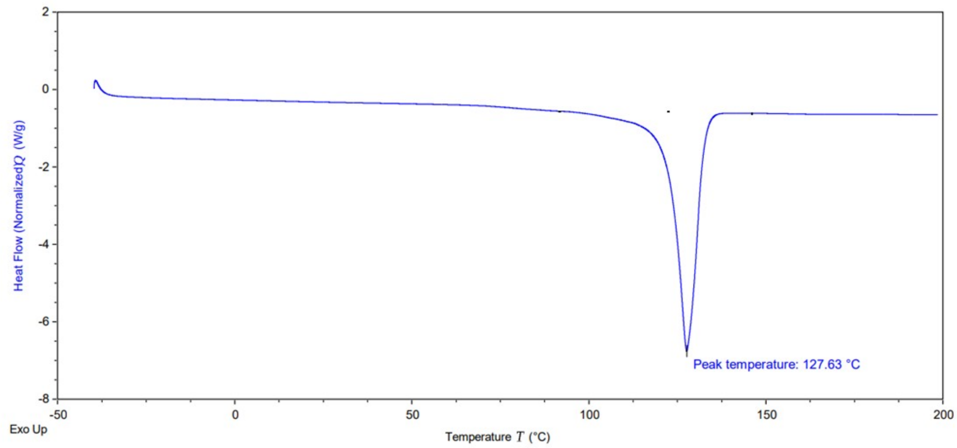


Figure S45. DSC trace of the **copolymer-3$^{1/100}$** from Table 1, Entry 11.

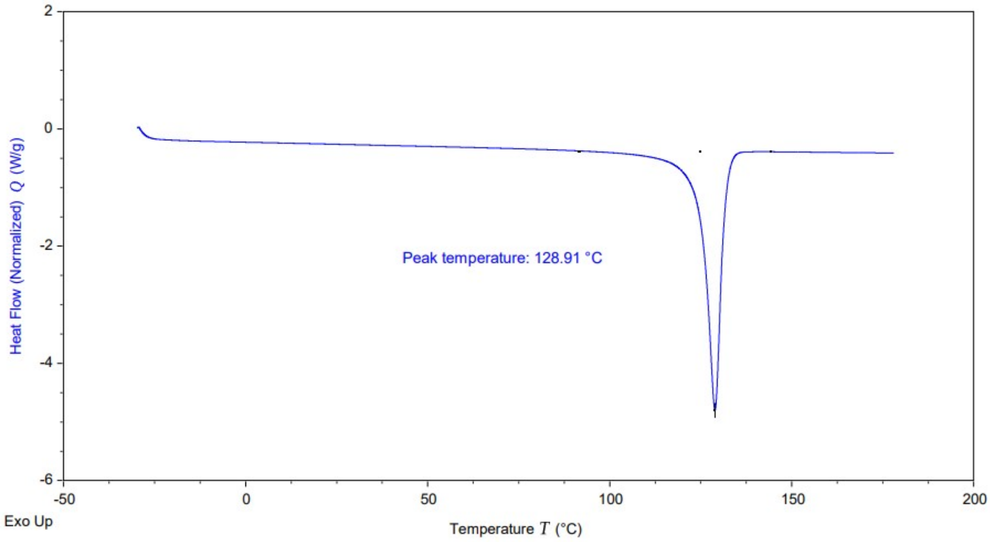


Figure S46. DSC trace of the **copolymer-3**$^{\mathbf{1/200}}$ from Table 1, Entry 12.

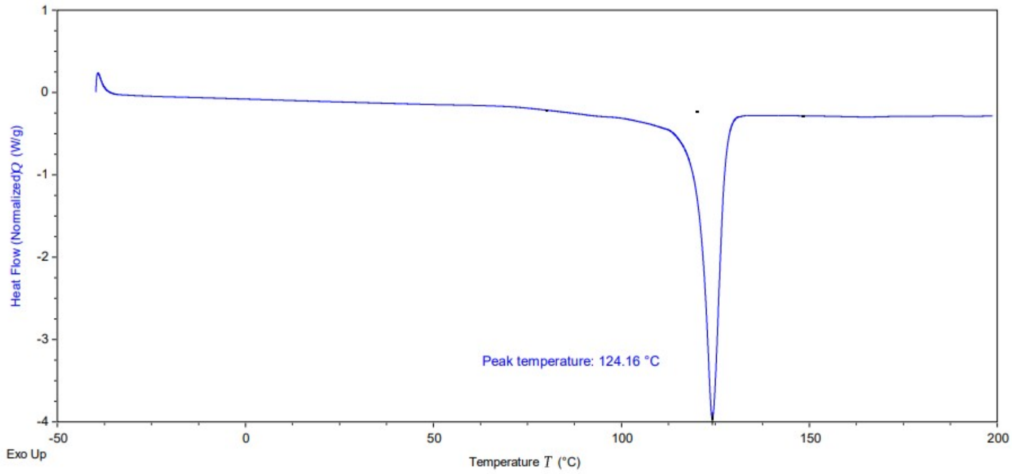


Figure S47. DSC trace of the **copolymer-5**$^{\mathbf{1/100}}$ from Table 1, Entry 19.

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