Supporting information for

Ruthenium-Catalyzed Diazoacetates/Cyclooctene Metathesis Copolymerization

Minghang Ji,[a, ‡] Shengquan Zheng,[b, ‡] Chen Zou,[b,*] Min Chen[a,*]

[a] Institutes of Physical Science and Information Technology, Anhui University, Hefei, Anhui 230601, China.
[b] CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, 230026, China.

Table of Contents

1. Supplementary Table

Table S1. ROMP of COE in the presence of diazoacetates as the CTA[a]

Entry	CTA	Cat.	t(h)	T(°C)	Yield (g)[b]	Conv. (%)[c]	M_n[d]	PDI[d]
1	ethyl diazoacetate	**G2/**	1	25	1.3	0	-	-
2	ethyl diazoacetate	**HG2**	1	25	1.4	0	-	-
3	ethyl diazoacetate	**G3**	1	25	1.4	0	-	-
4	ethyl diazoacetate	**G2**	1	40	1.6	10	25900	1.99
5	ethyl diazoacetate	**HG2**	1	40	1.5	17	23200	1.77
6	ethyl diazoacetate	**G3**	1	40	1.4	15	20400	1.65

[a]Polymerization conditions: 15 mmol COE, 1 mmol ethyl diazoacetates, 0.2 mol% **HG2** Cat., 40 ml DCM, 40°C. [b]The yields and activities are the averages of at least two runs. [c]Calculated from the ratio of relative integration from repeat unit and internal olefin protons in the ^{1}H NMR spectrum. [d]Determined by size-exclusion chromatography (SEC) compared with polystyrene standard.

2. Experimental Section

2.1.   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), (IMesH2)-(Cy3P)RuCl2(CHPh) (Grubbs second generation catalyst, **G2**), (IMesH2)-(IPrO)RuCl2(CHPh) (Hoveyda-Grubbs second generation catalyst, **HG2**), (IMesH2)-(2-BrPy)2RuCl2(CHPh) (Grubbs third generation catalyst, **G3**), dimethyl maleate were purchased from Sigma-Aldrich. The deuterated solvents CDCl3, and 1,1,2,2-tetradhloroethane-d2 were purchased from Cambridge Isotope Laboratories. COE was distilled over CaH2 prior to use. HDPE: DMDA-8008H, produced by the China National Petroleum Corporation; All other chemicals were used as received.

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 °C. A Waters 1515 pump and Waters 2414 differential refractive index detector (30 °C) 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 °C 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.

Hydrogenation of Polymer: An example of the chemical hydrogenation procedure is described for the hydrogenation of the random polymers (Table 2, entries 7-8). A mixture of polymer (1.00 g, 15.00 mmol of olefin), p-toluenesulfonhydrazide (2.32 g, 16mmol), 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 polymer as a white solid was collected, washed with methanol (3×50 mL) and dried under vacuum for 12 hours at 45 °C.

Degradation of Polymer: An example of the degradation procedure is described for the degradation of the random polymers (Table 2, entries 1 and 7). A mixture of polymer (5.00 g) was subjected to methanolysis (25 mL Methanol, 2.00 g KOH and 100 mL THF) by stirring for 24 h at 80 ° C, which was evaporated to dryness under vacuum, and dispersed into 500 mL methanol. Upon isolation, an off-white solid was obtained. The polymer was washed with methanol (3× 50 mL) and dried under vacuum for 12 hours at 45 ° C.

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 m/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 prepared via evaporation of 3 to 5 % (w/w) solutions in toluene onto glass slides under ambient conditions. The solvent was evaporated on top of a glass slide for 10 minutes, and a second layer of the polymer solution was then applied to increase thickness. The water contact angles of the polymer thin 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.

Water vapor transmission rate (WVTR) was measured in a permeation cell at 25°C according to ASTM E96-95 method. The cell, made of polytetrafluoroethylene, was partially filled with water and a polymeric membrane was placed above sealing its top. The measurements were performed in a Labthink W3/010 balance with 10-5g readability and the mass loss was recorded in a computer. The reported values were at least the average of 4 measurements

Oxygen permeability was measured by a Basic 201 of Labthink equipment at 1 atm, 23 °C and 0 % relative humidity according to GB/T 1038-2000 method. The reported values were at least the average of 4 measurements.

2.2. Polymerization procedures.

Cocatalyst NaBArF (45 μmol) was placed in a 100 mL Schlenk flask with magnetic stir. Anhydrous dichloromethane (40 mL), diazoacetates or (bis)diazoacetates comonomer and COE (15 mmol) were transferred via injector into the reaction 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 Ru catalyst (30 μmol) as a solution in 1 mL of dichloromethane. After a desired amount of time, the entire solution was quenched with 0.5 mL of ethyl vinyl ether and stirred for 5 min after which was

evaporated to dryness under vacuum, then precipitating into 200 mL methanol. The polymer 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, H-H COSY, ^{13}C NMR, DOSY spectrums and GPC.
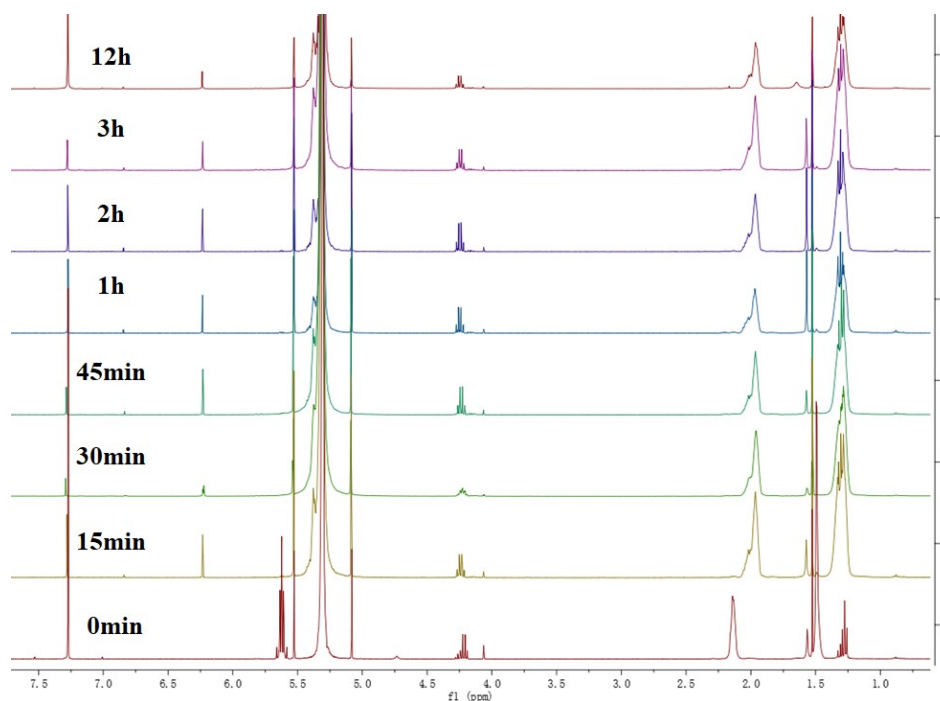
3. Characterizations of polymers.

Figure S1. ^{1}H NMR stacked plot of the ROMP reaction of COE and ethyl diazoacetate at different time catalyzed by **HG2** without NaBArF at 40°C (CDCl$_3$).
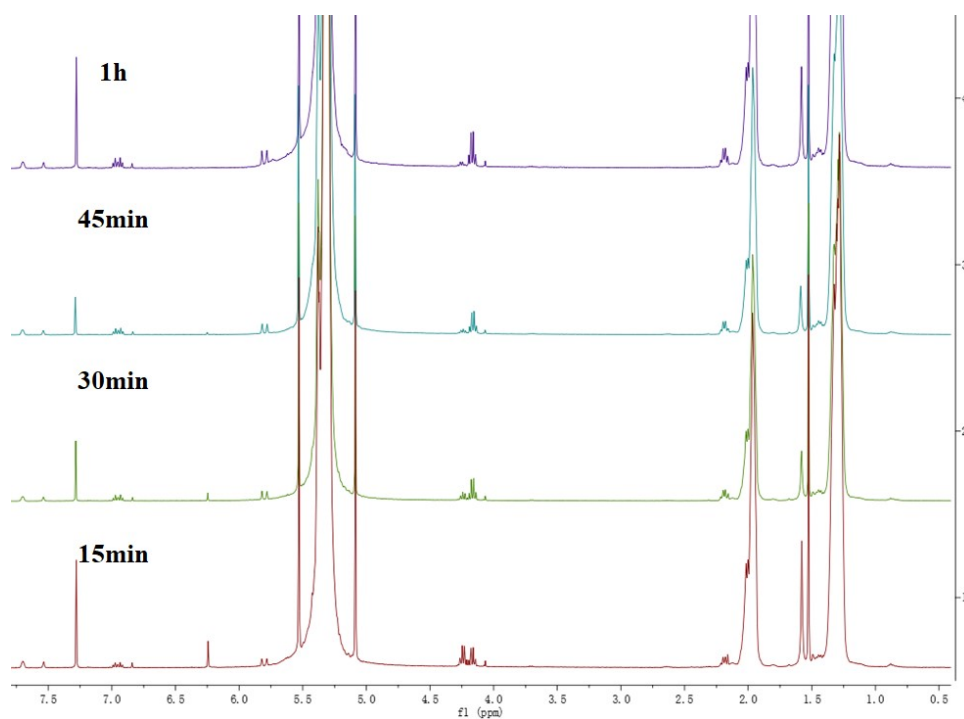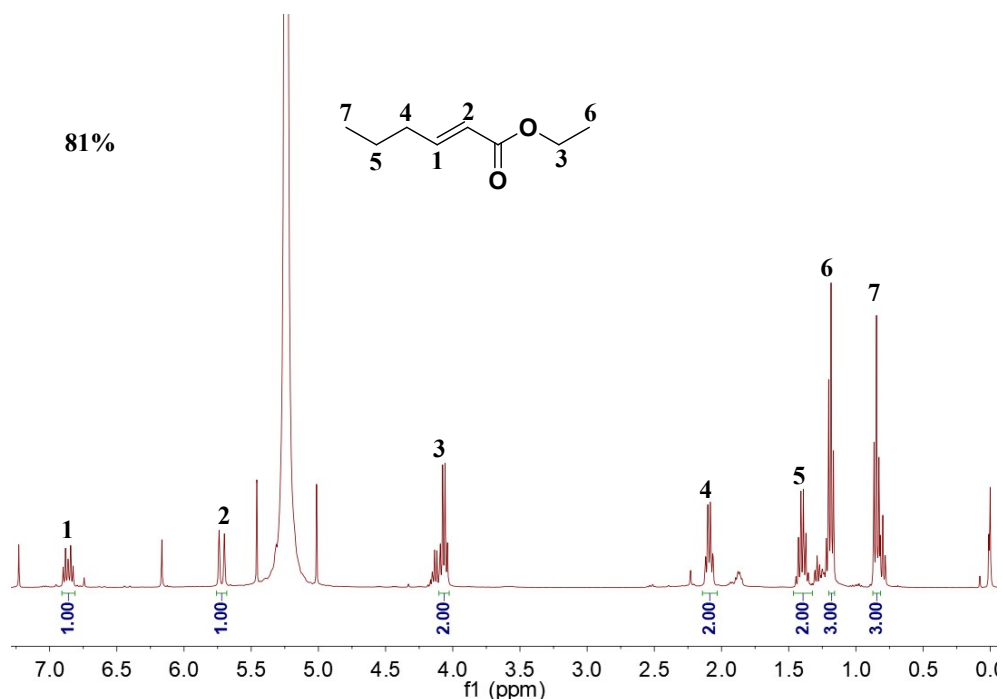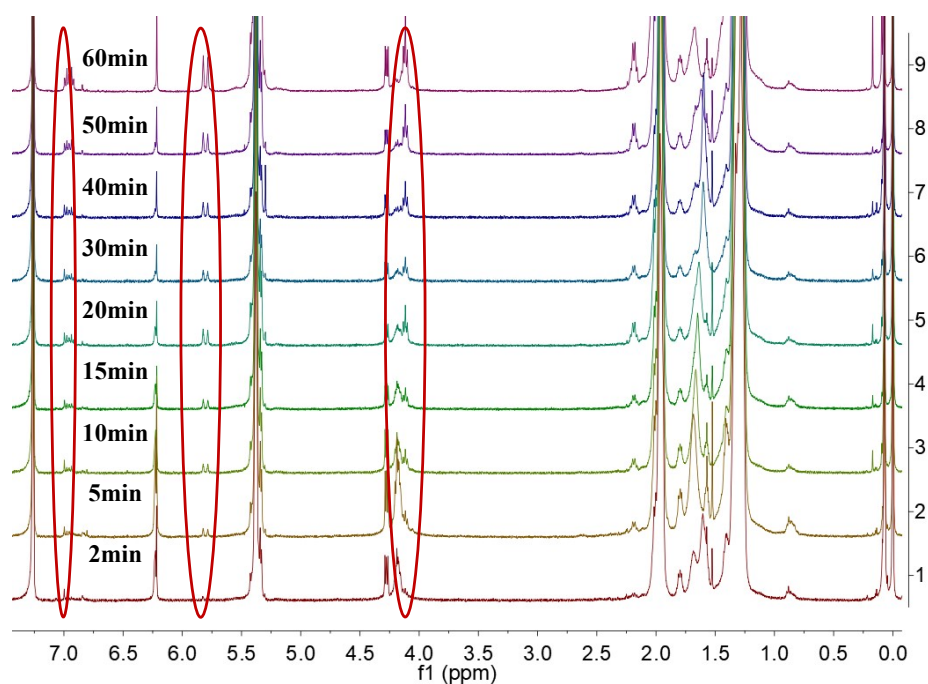

Figure S2. ^{1}H NMR stacked plot of the ROMP reaction of COE and ethyl diazoacetate at different time catalyzed by **HG2** with NaBArF at 40°C (CDCl$_3$).

Figure S3. ^{1}H NMR of the cross-metathesis model reaction of 4- octene and diethyl maleate catalyzed by **HG2** with NaBArF at 40°C (CDCl$_3$). Cocatalyst NaBArF (15 µmol, 1.5 eq.) was placed in a Schlenk flask with magnetic stir. Under dry Nitrogen atmosphere, 0.5 mmol 4-octene and 0.5 mmol diethyl maleate were dissolved in 10 mL of dichloromethane. And 10 µmol HG2 as a solution in 1 mL of dichloromethane was transferred via injector into the reaction flask. The flask was immersed in an oil-bath at 40 °C immediately for 2h.


Figure S4. ^{1}H NMR stacked plot of the ROMP reaction of COE and C6-(bis)diazoacetates at different time catalyzed by **HG2** with NaBArF at 40°C (CDCl$_3$).
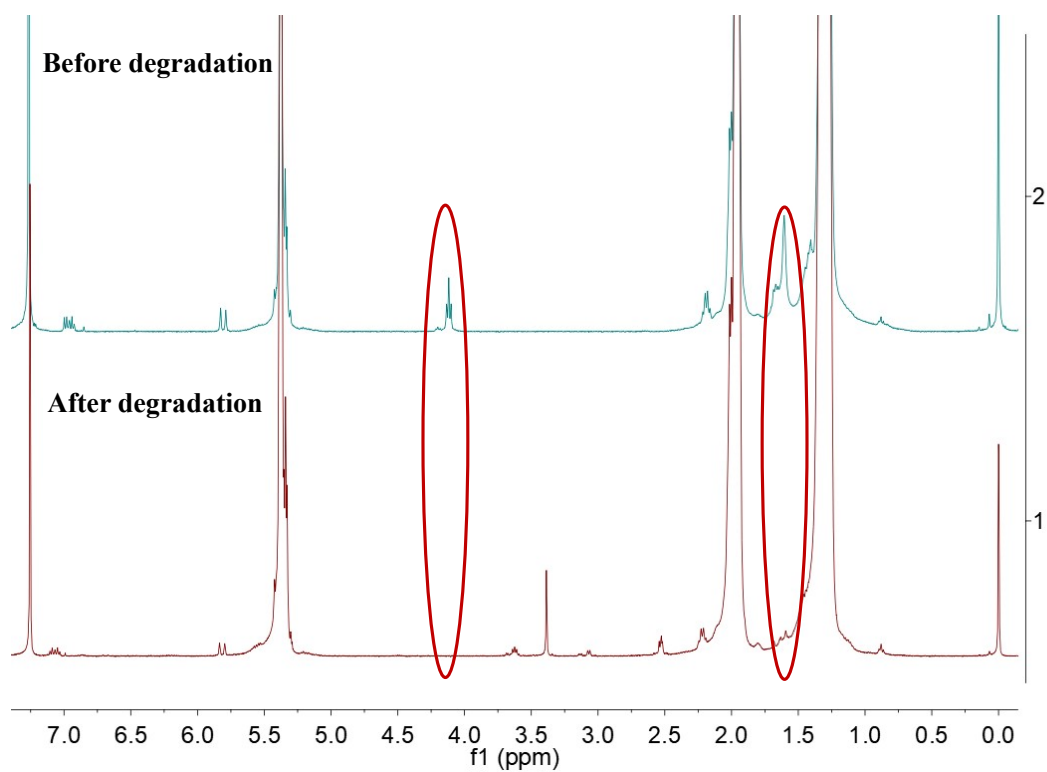
Figure S5. Comparisons of ^{1}H NMR spectra: samples before (Table 2, entry 1) and after degradation (CDCl$_3$).
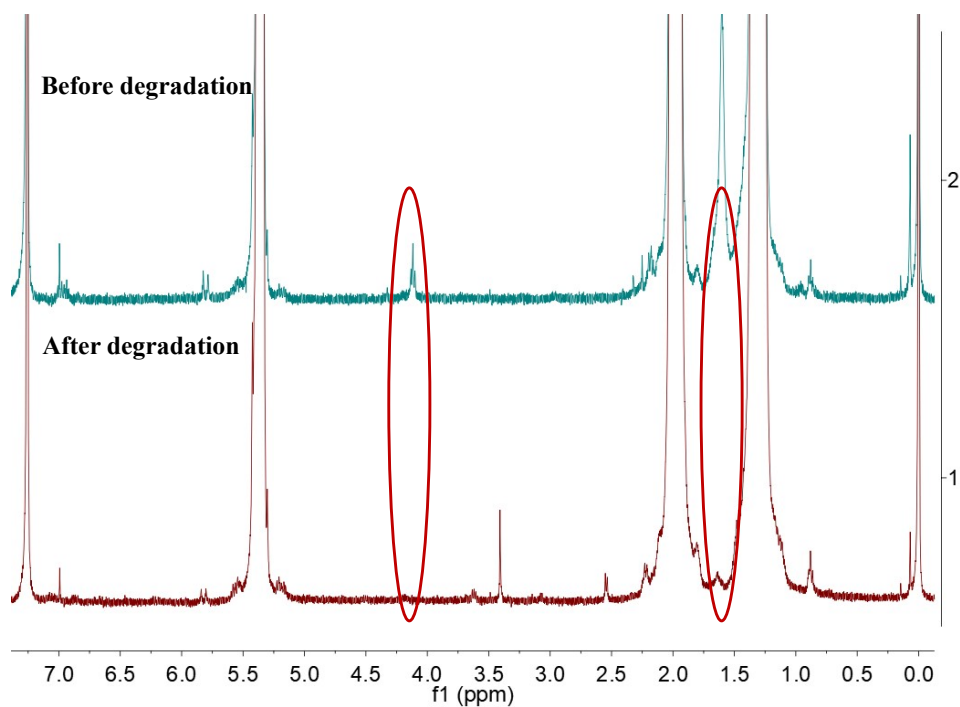
Figure S6. Comparisons of ^{1}H NMR spectra: samples before (Table 2, entry 7) and after degradation (CDCl$_3$).
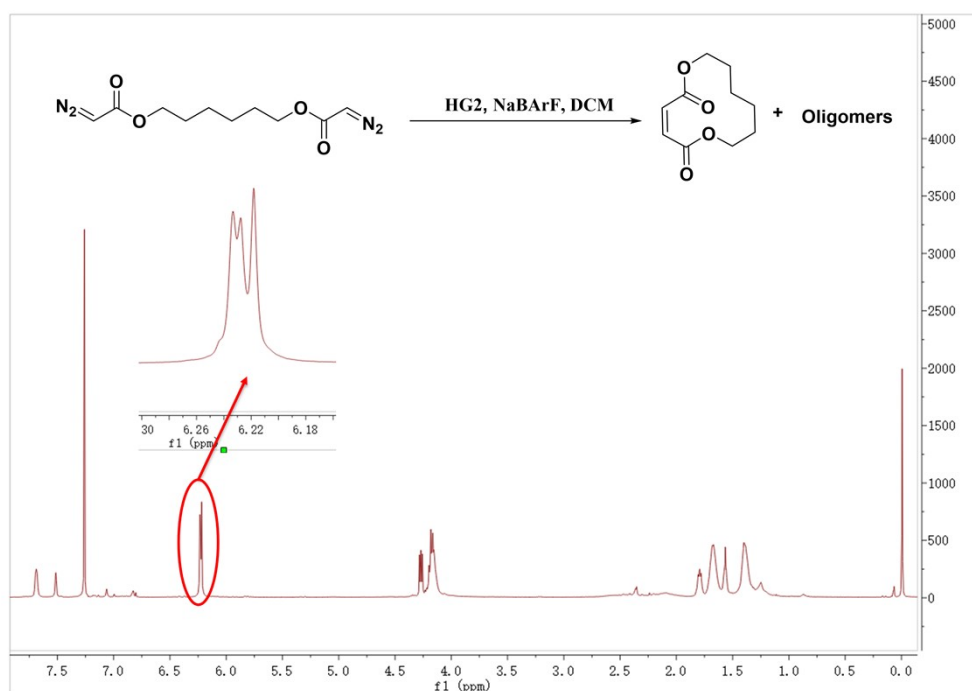
Figure S7. ^{1}H NMR spectrum of C6-(bis)diazoacetates catalyzed by **HG2** with NaBArF at 40°C (CDCl$_3$). Cocatalyst NaBArF (15 μmol, 1.5 eq.) was placed in a 10 mL Schlenk flask with magnetic stir. Under dry Nitrogen atmosphere, 0.5 mmol C6-(bis)diazoacetates was dissolved in 10 mL of dichloromethane. And 10 μmol HG2 as a solution in 1 mL of dichloromethane was transferred via injector into the reaction flask. The flask was immersed in an oil-bath at 40 °C immediately for 0.5 h.
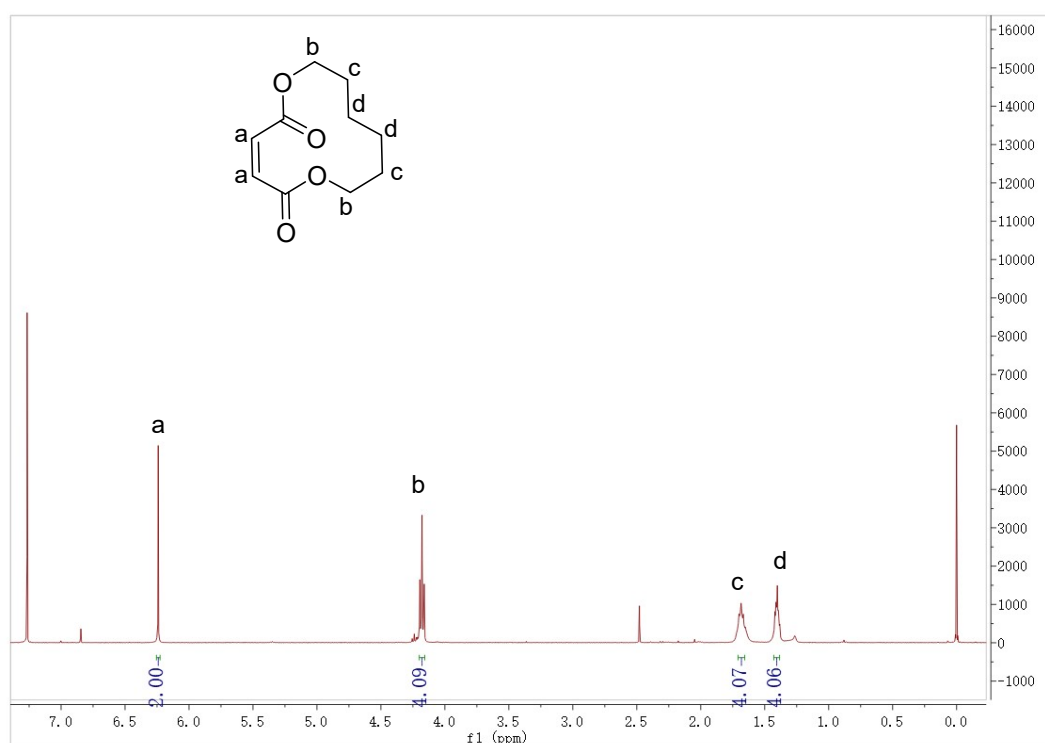
Figure S8. ^{1}H NMR spectrum of isolated cyclic intermediate (CDCl$_3$).
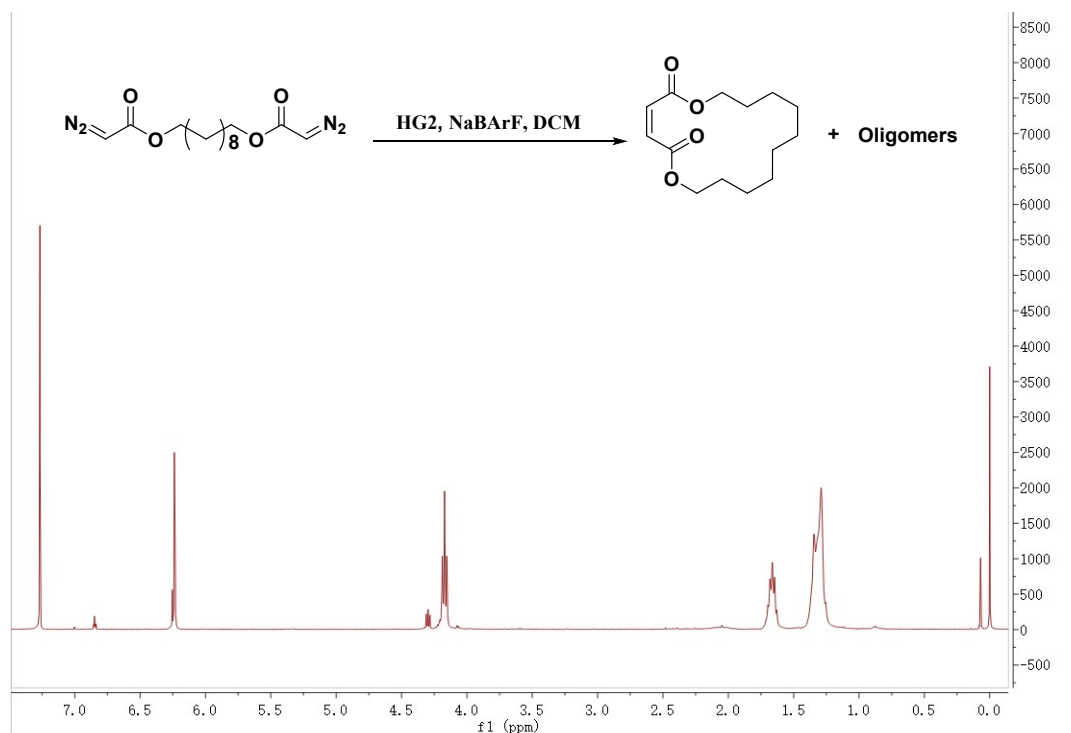
Figure S9. ^{1}H NMR spectrum of C10-(bis)diazoacetates catalyzed by **HG2** with NaBArF at 40°C (CDCl$_3$, the procedure was similar to Figure S7).
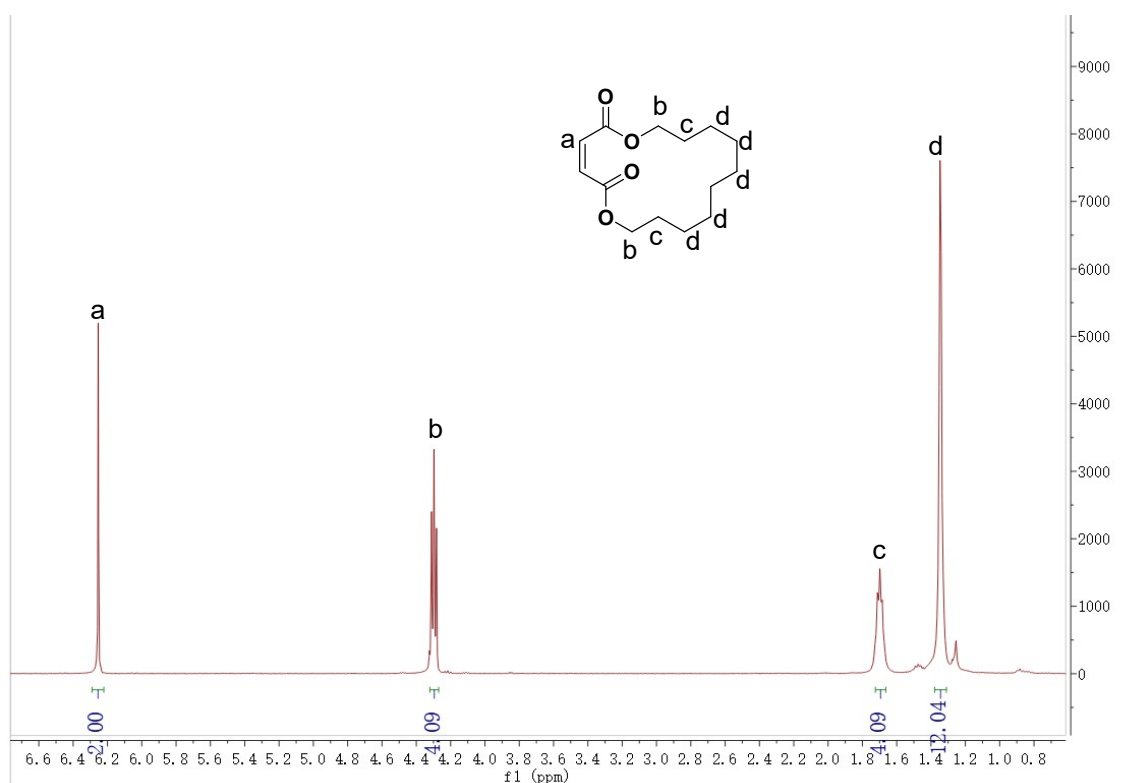
Figure S10. ^{1}H NMR spectrum of isolated cyclic intermediate (CDCl$_3$).
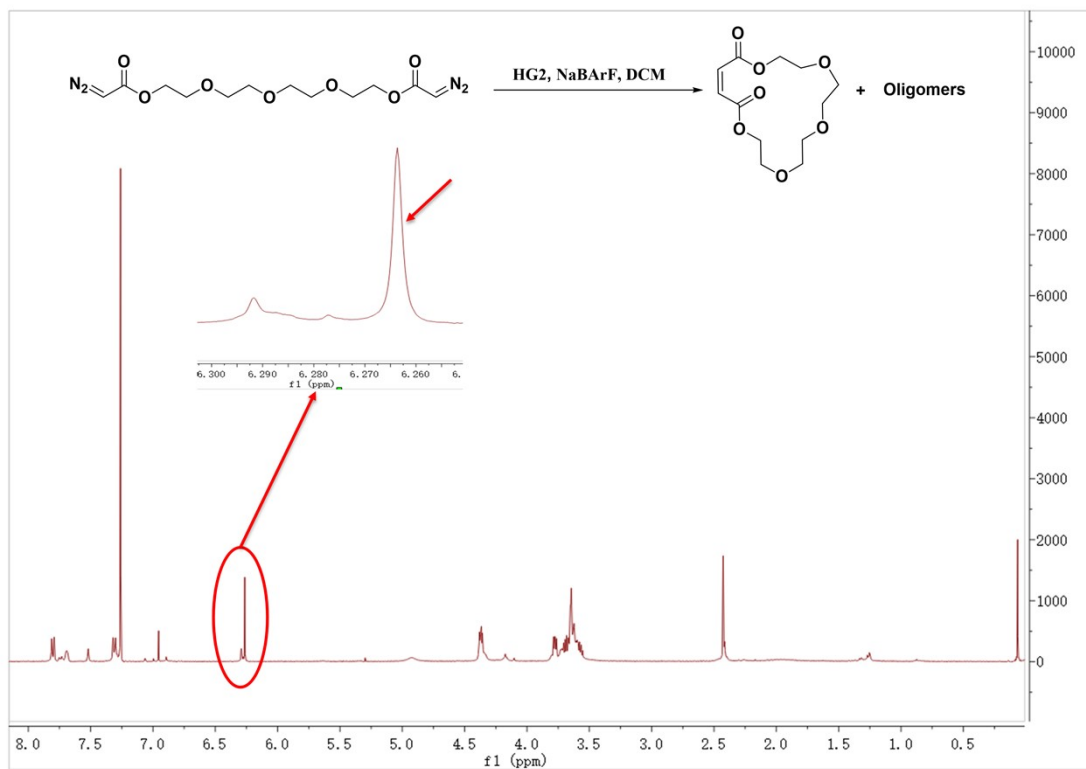
Figure S11. ^{1}H NMR spectrum of polyethylene glycol-(bis)diazoacetates catalyzed by **HG2** with NaBArF at 40°C (CDCl$_3$, the procedure was similar to Figure S7) .
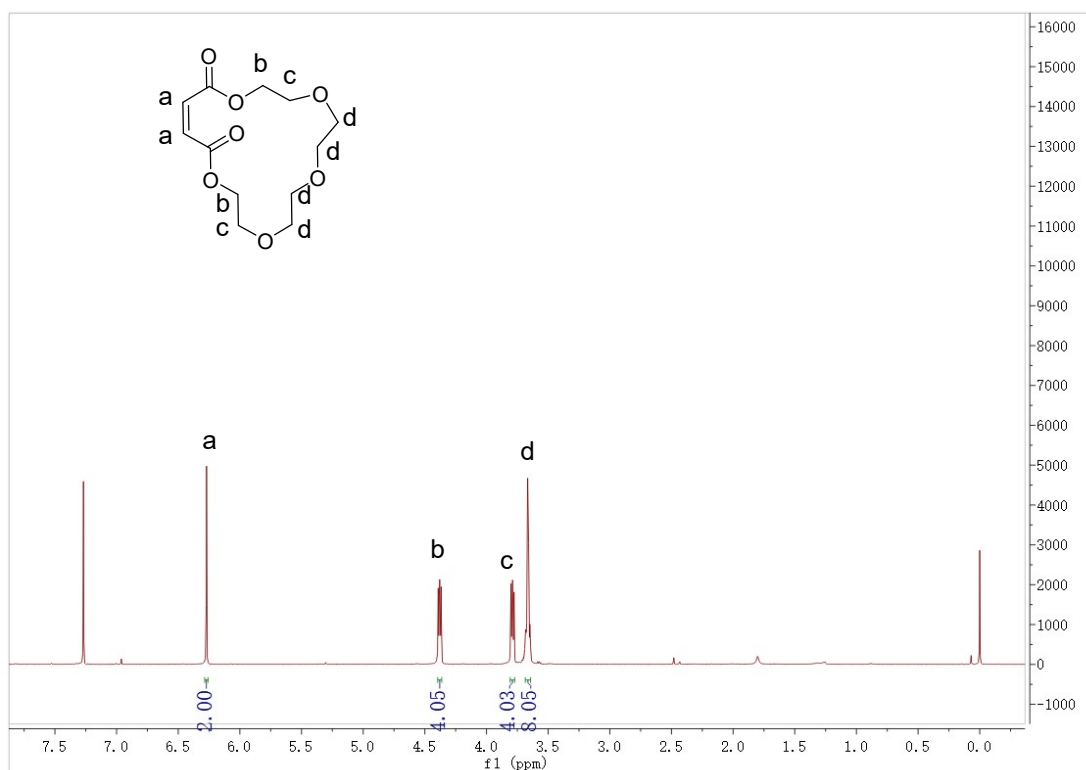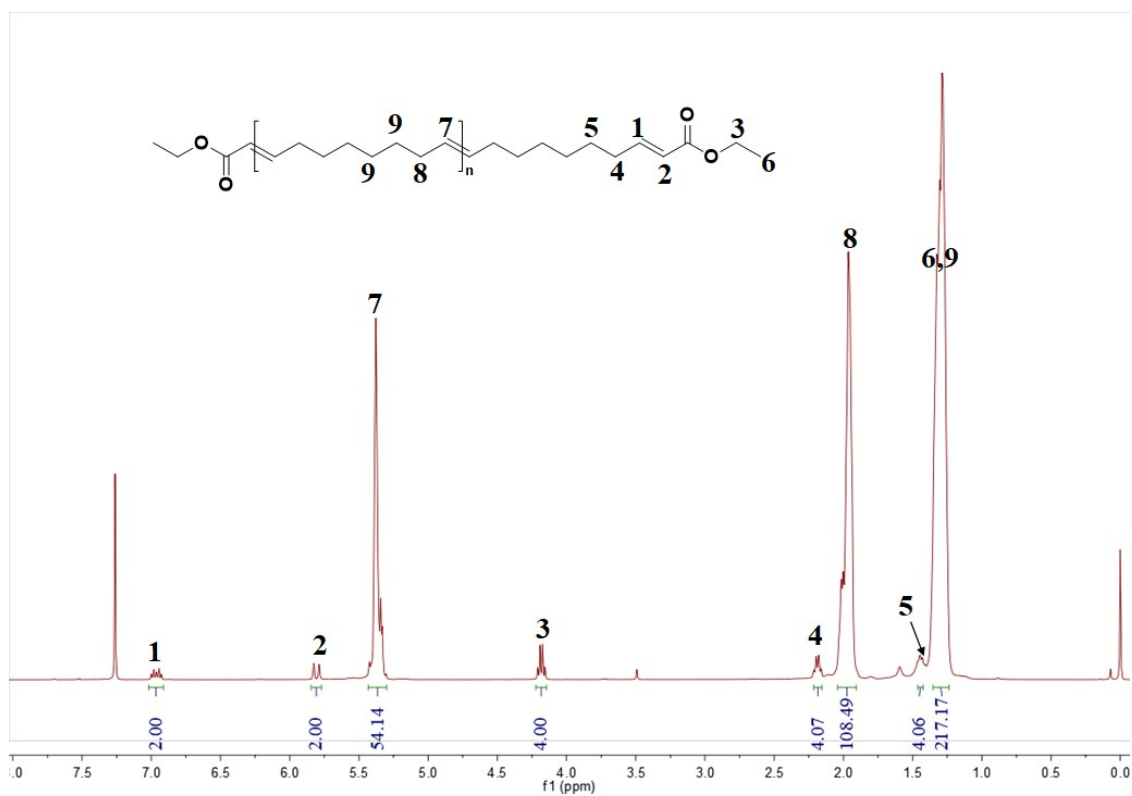

Figure S12. ^{1}H NMR spectrum of isolated cyclic intermediate (CDCl$_3$).

Figure S13. ^{1}H NMR spectrum of the polymer from Table 1, entry 2 (CDCl$_3$).
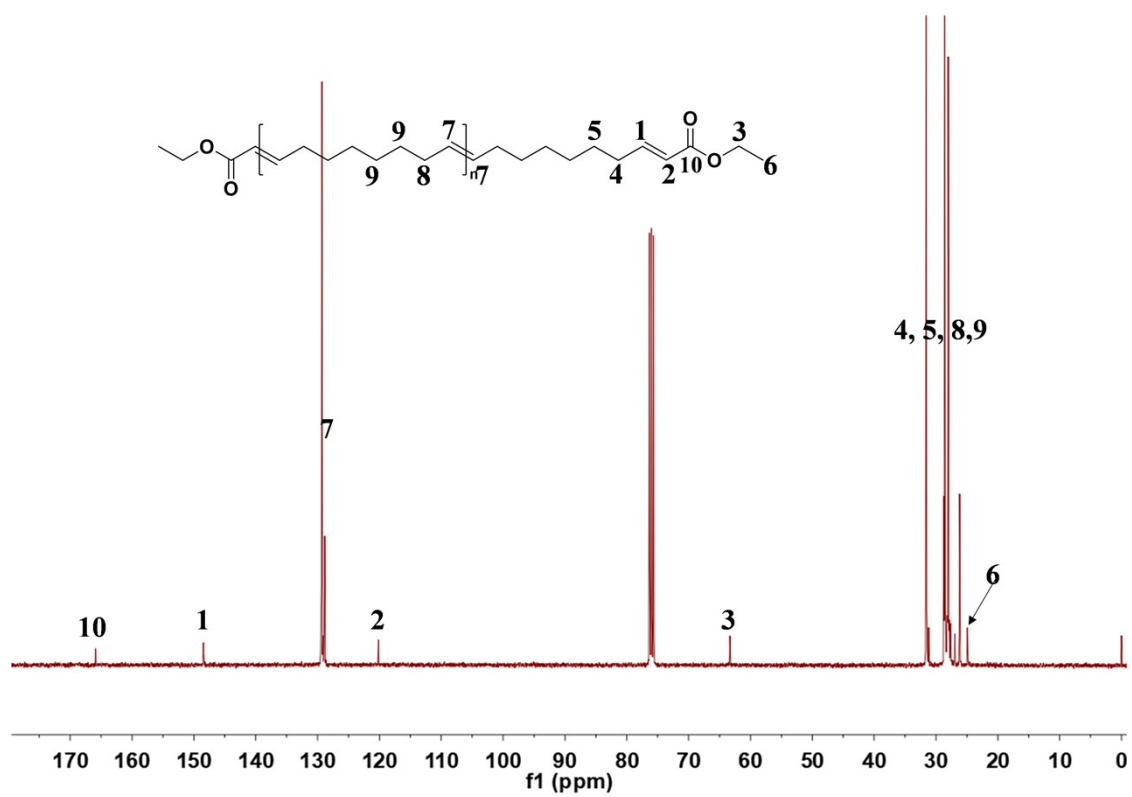
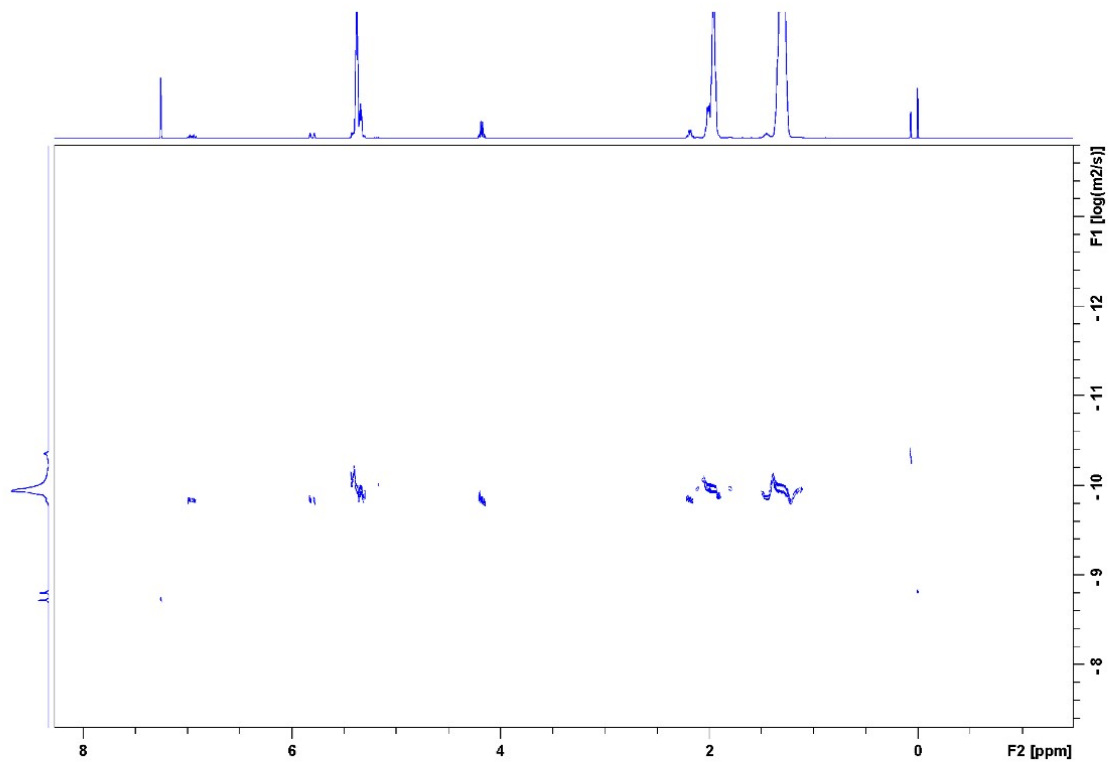**Figure S14.** ^{13}C NMR spectrum of the polymer from Table 1, entry 4 (CDCl$_3$).

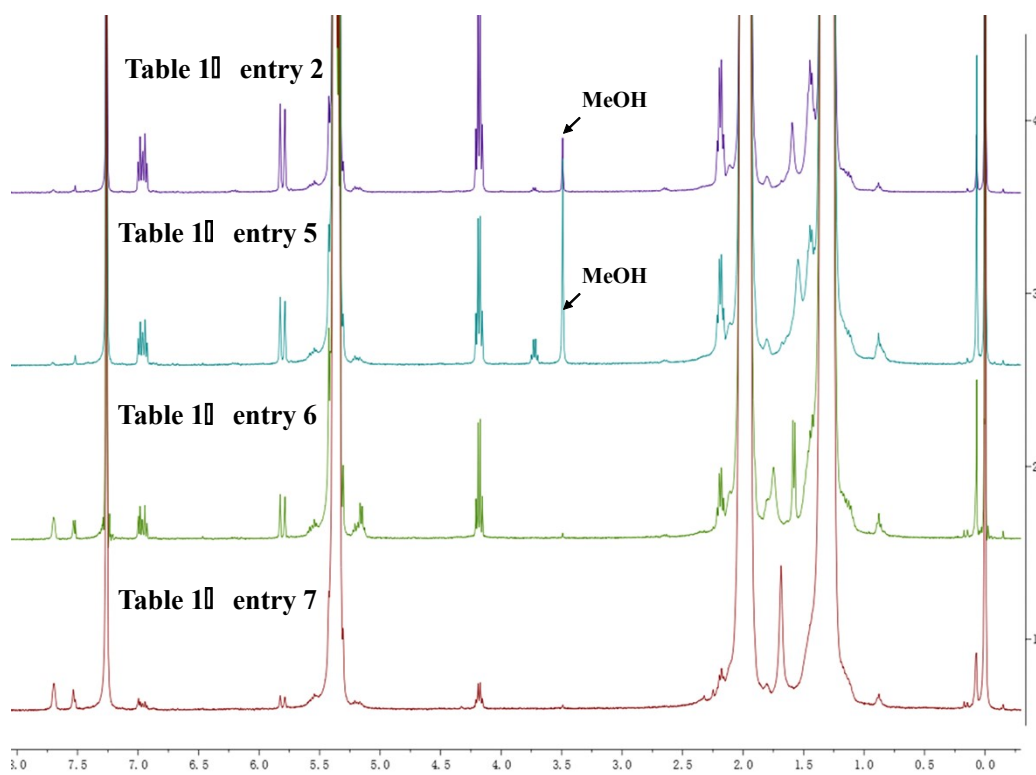**Figure S15.** 2D DOSY NMR spectrum of the polymer from Table 1, entry 4 (CDCl$_3$).

Figure S16. ^{1}H NMR stacked plot of the polymers from Table 1, entries 2, 5, 6, 7 (CDCl$_3$).
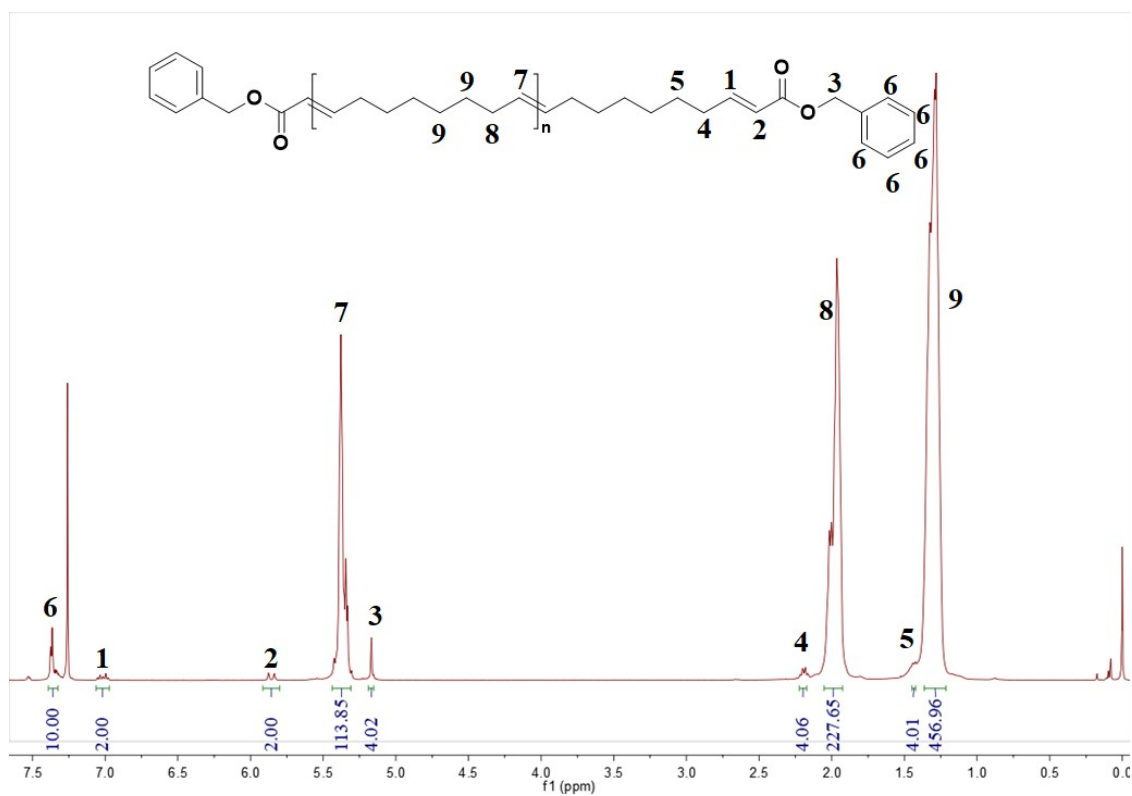
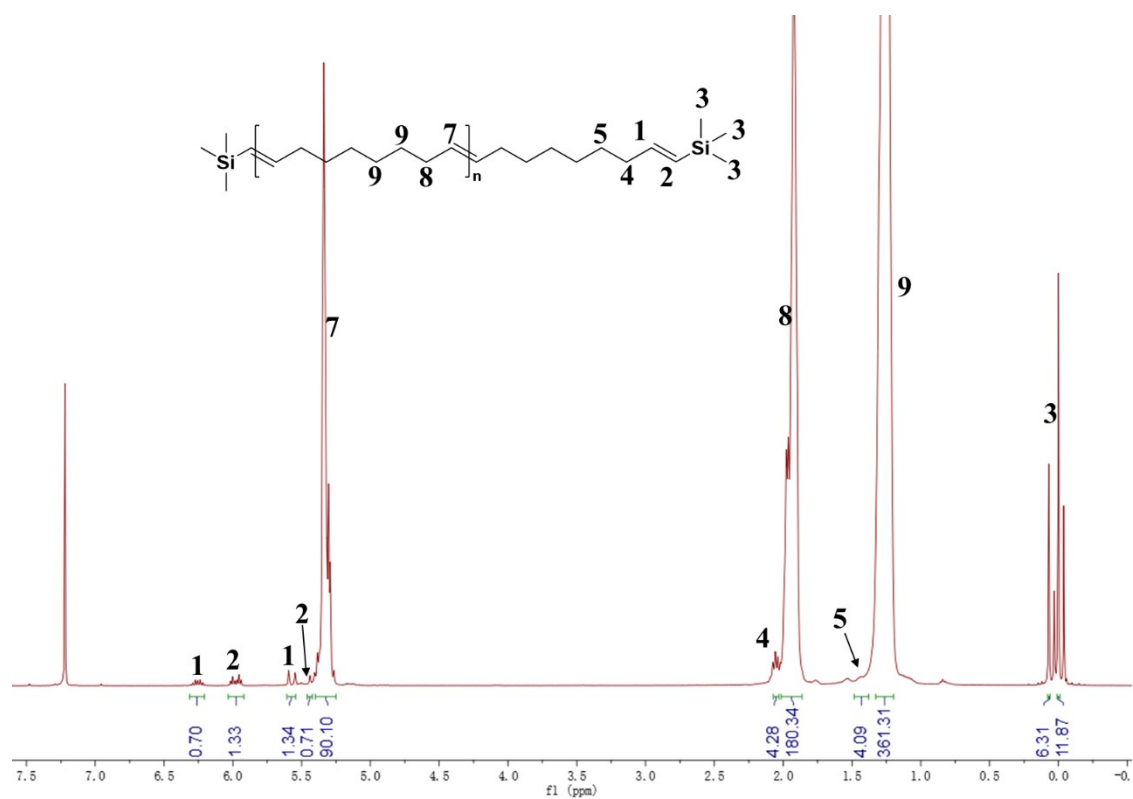**Figure S17.** ^{1}H NMR spectrum of the polymer from Table 1, entry 8 (CDCl$_3$).

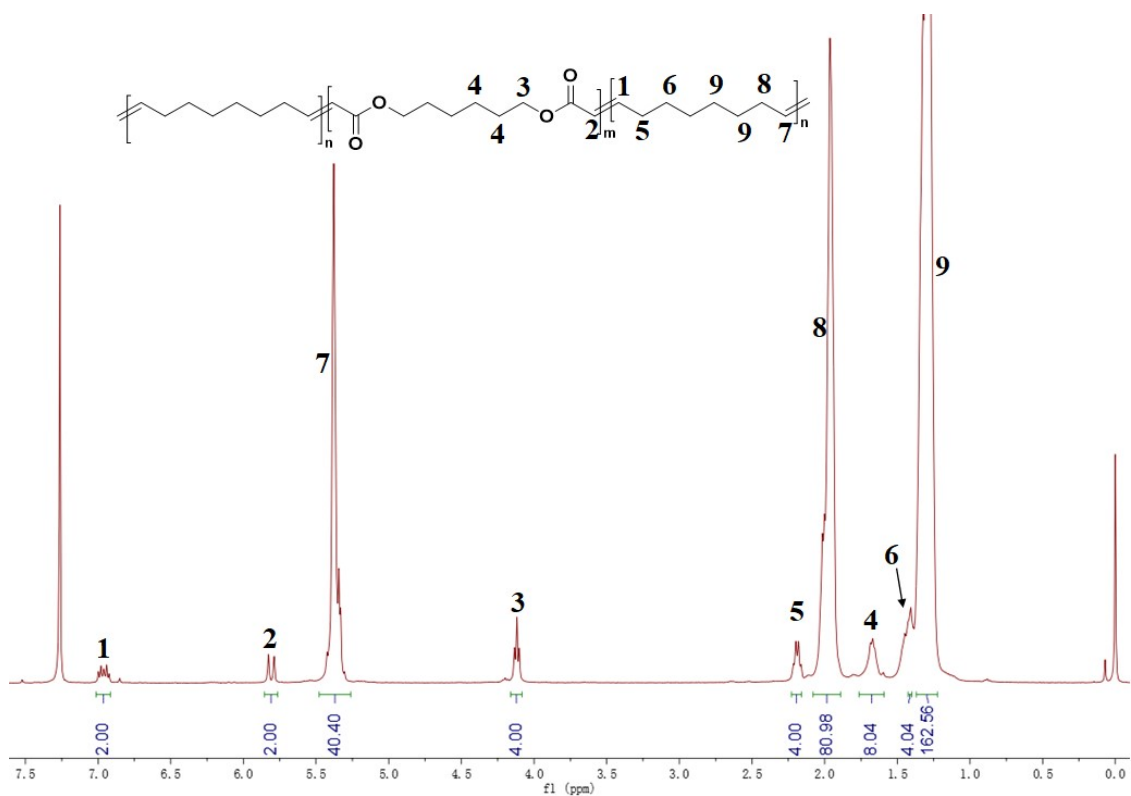**Figure S18.** ^{1}H NMR spectrum of the polymer from Table 1, entry 9 (CDCl$_3$).

Figure S19. ^{1}H NMR spectrum of the polymer from Table 2, entry 1 (CDCl$_3$).
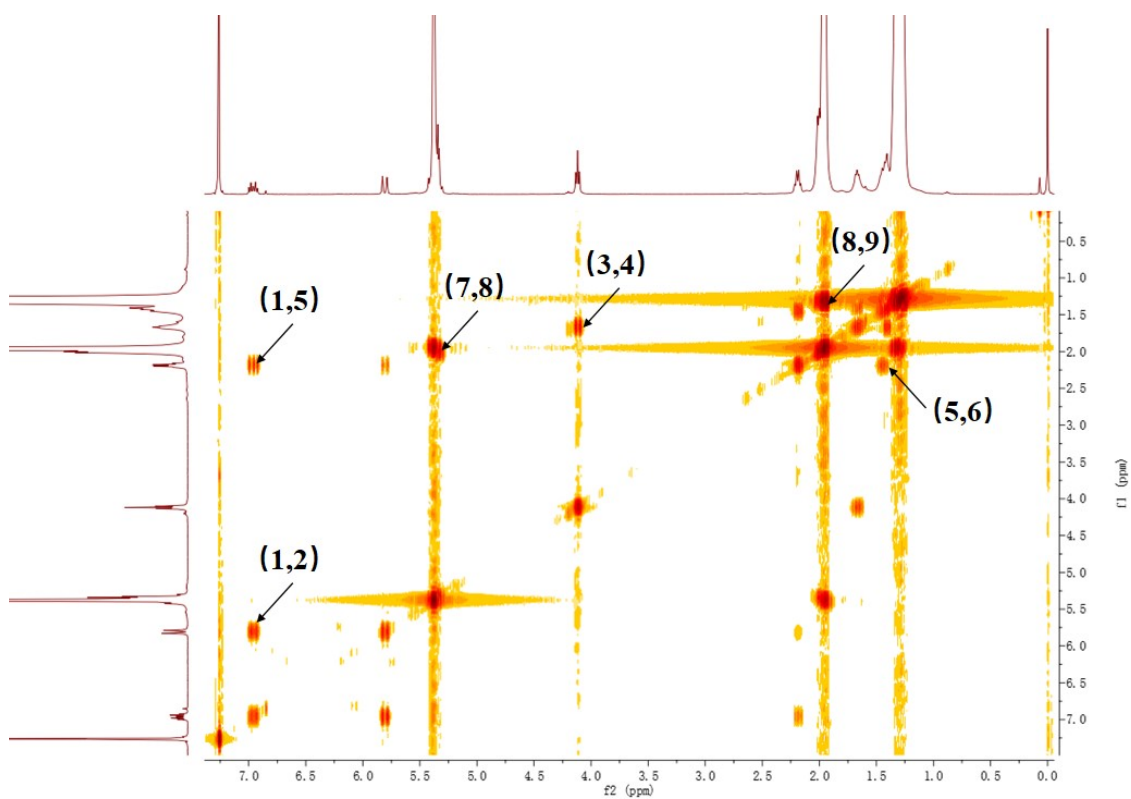

Figure S20. H-H COSY NMR spectrum of the polymer from Table 2, entry 1 (CDCl$_3$).
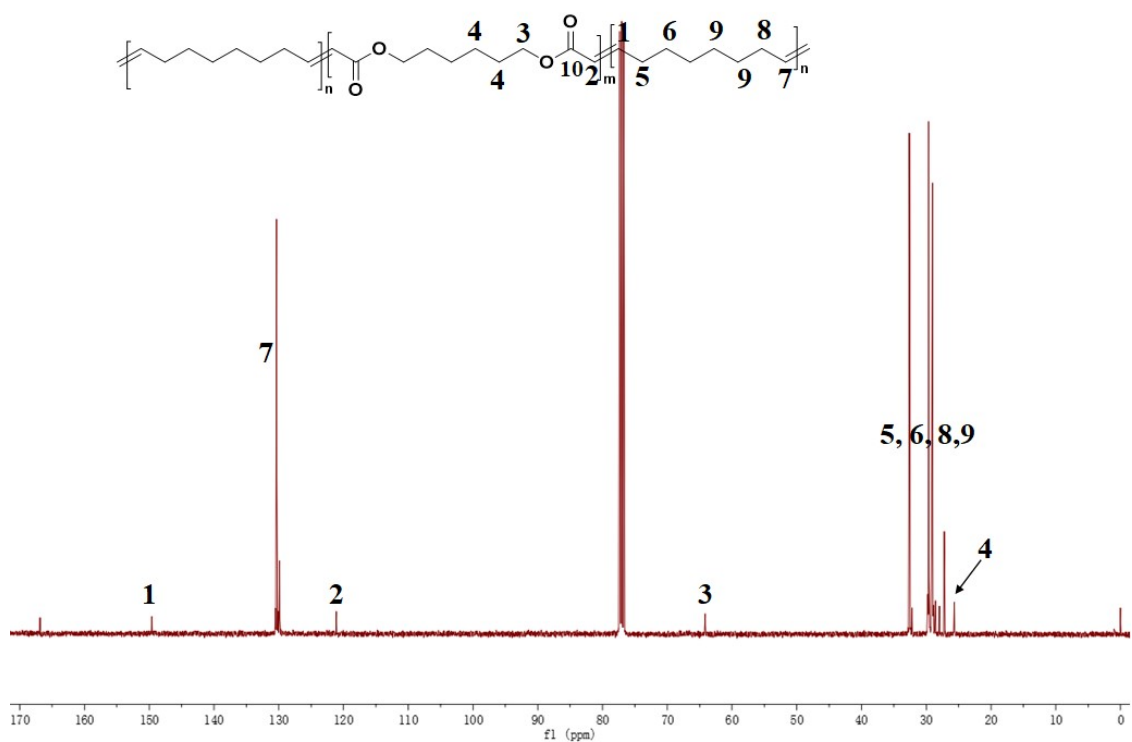
Figure S21. ^{13}C NMR spectrum of the polymer from Table 2, entry 1 (CDCl$_3$).

Figure S22. ^{1}H NMR spectrum of the polymer from Table 2, entry 2 (CDCl$_3$).

Figure S23. H-H COSY NMR spectrum of the polymer from Table 2, entry 2 (CDCl₃).

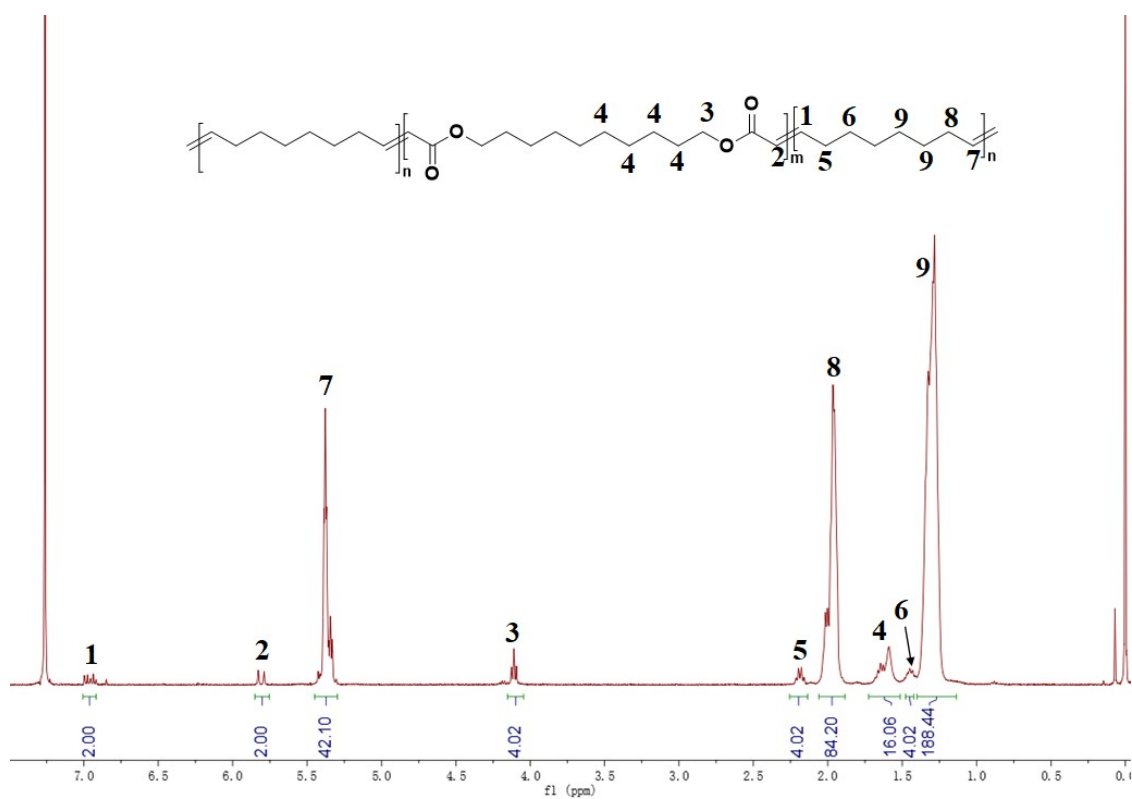**Figure S24.** ^{13}C NMR spectrum of the polymer from Table 2, entry 2 (CDCl₃).

Figure S25. ^1H NMR spectrum of the polymer from Table 2, entry 3 (CDCl$_3$).

Figure S26. H-H COSY NMR spectrum of the polymer from Table 2, entry 3 (CDCl$_3$).

Figure S27. ^{13}C NMR spectrum of the polymer from Table 2, entry 3 (CDCl$_3$).
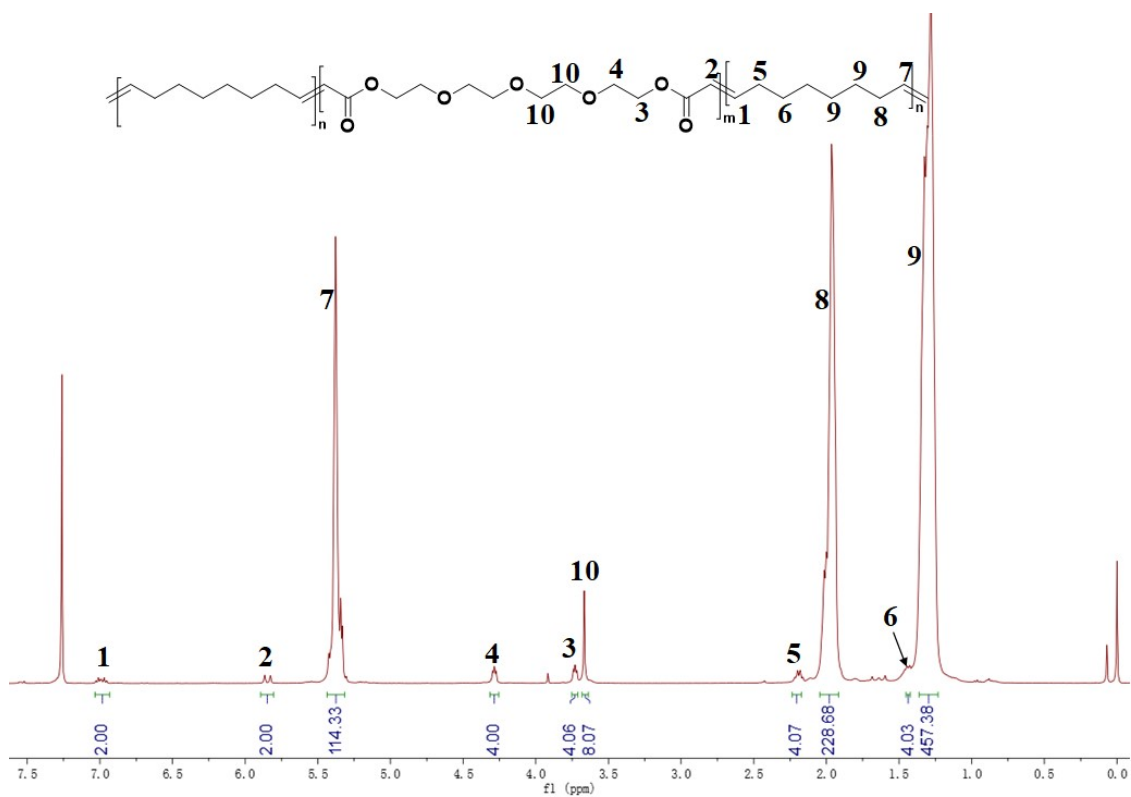
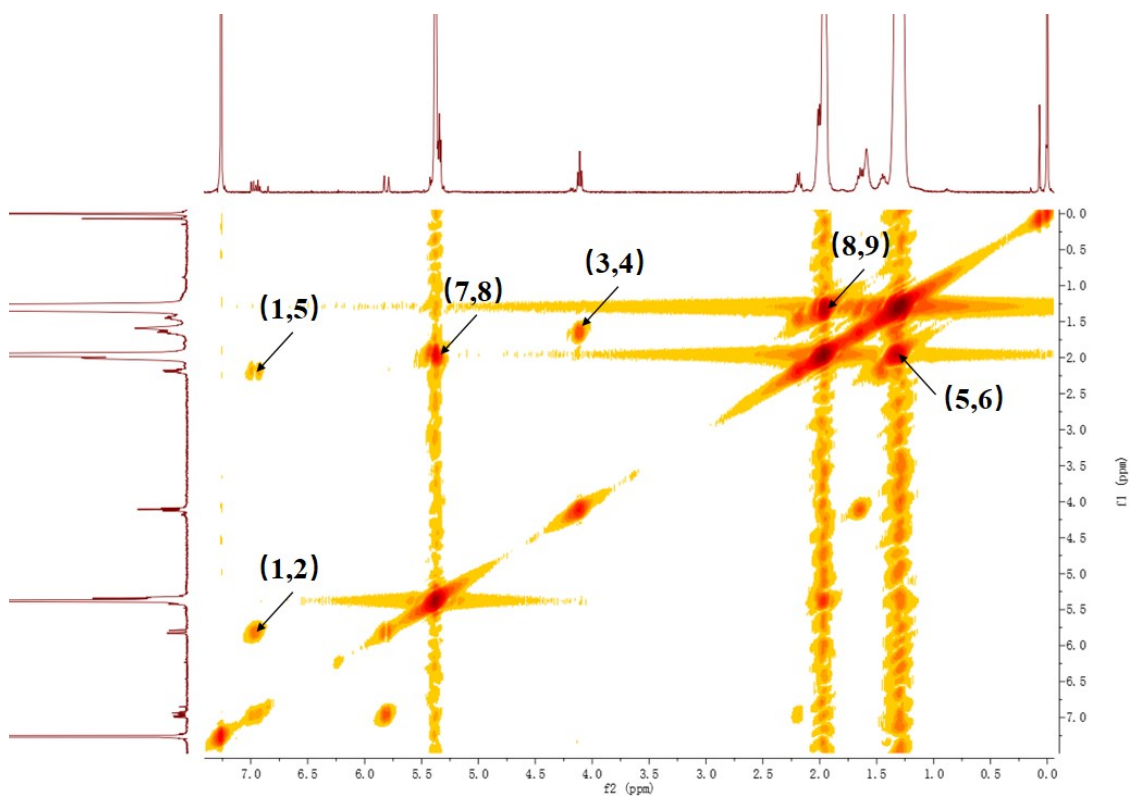**Figure S28.** ^{1}H NMR spectrum of the polymer from Table 2, entry 4 (CDCl$_3$).

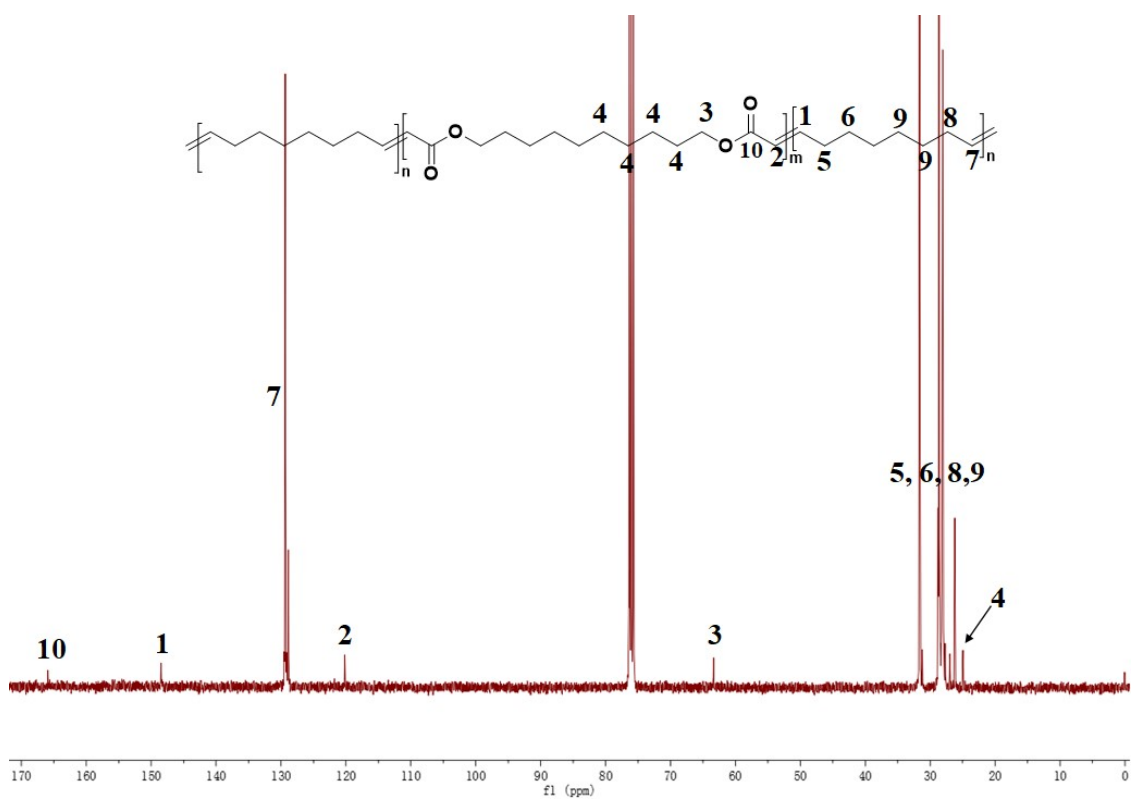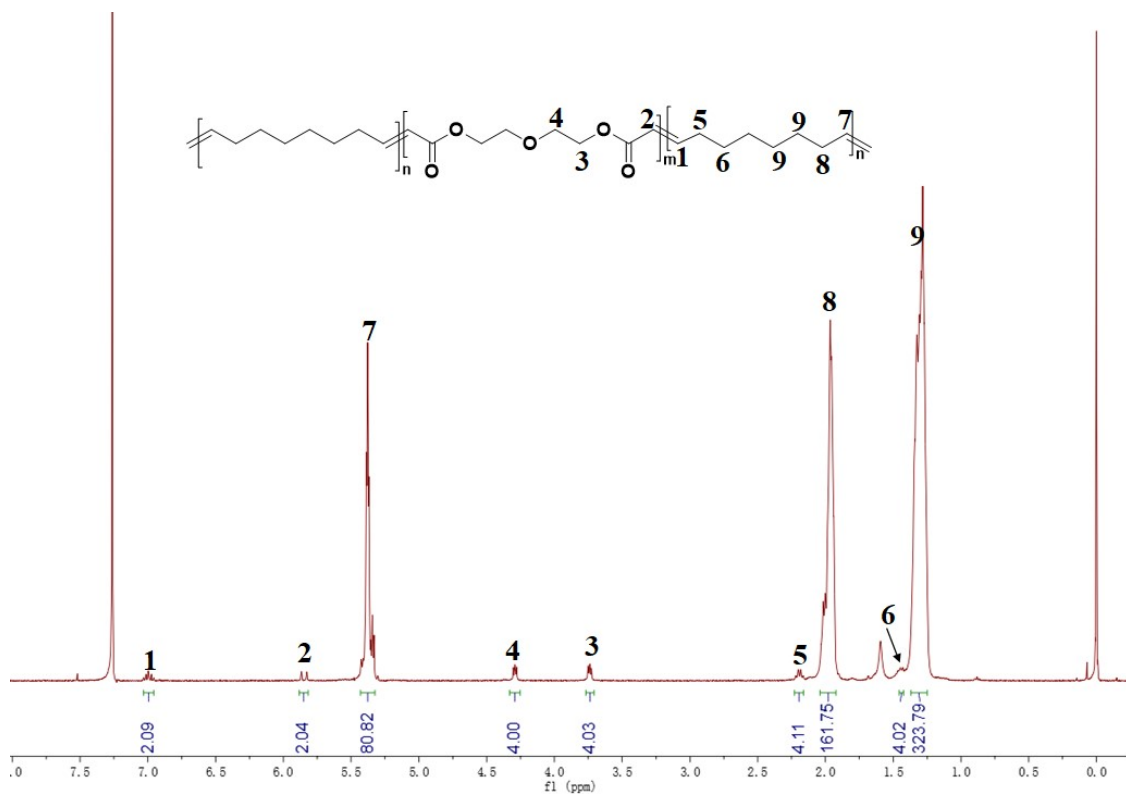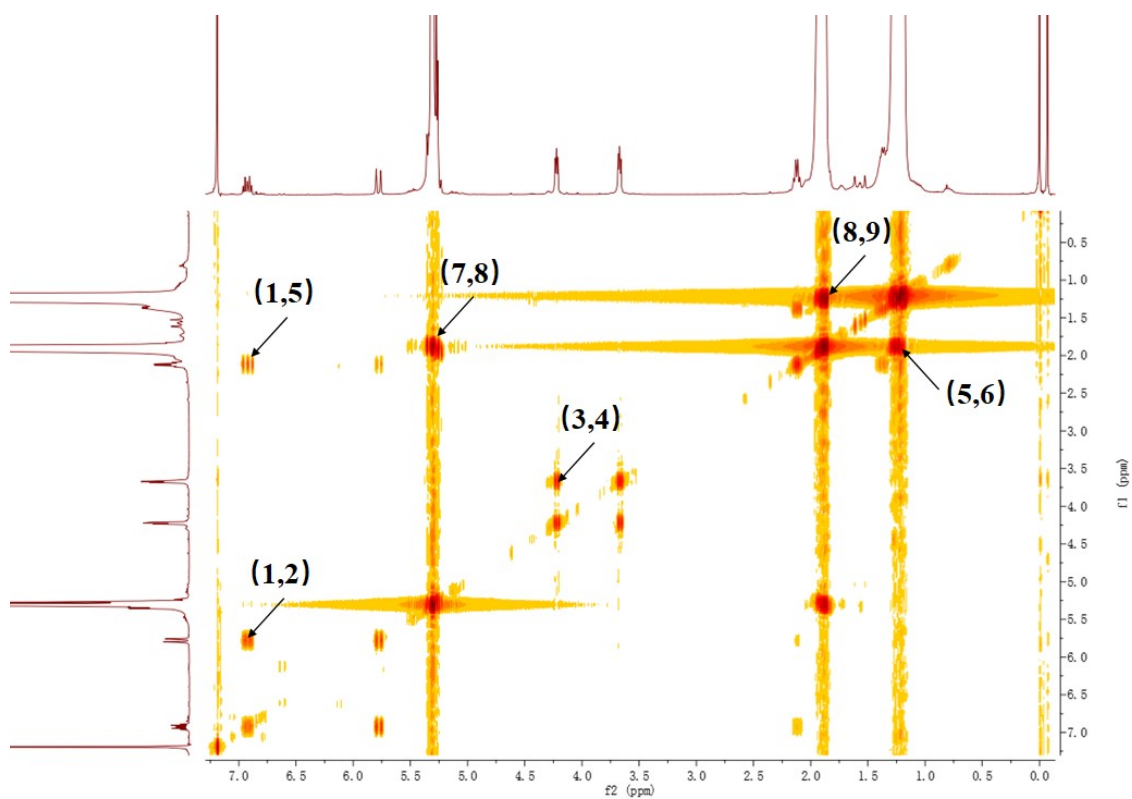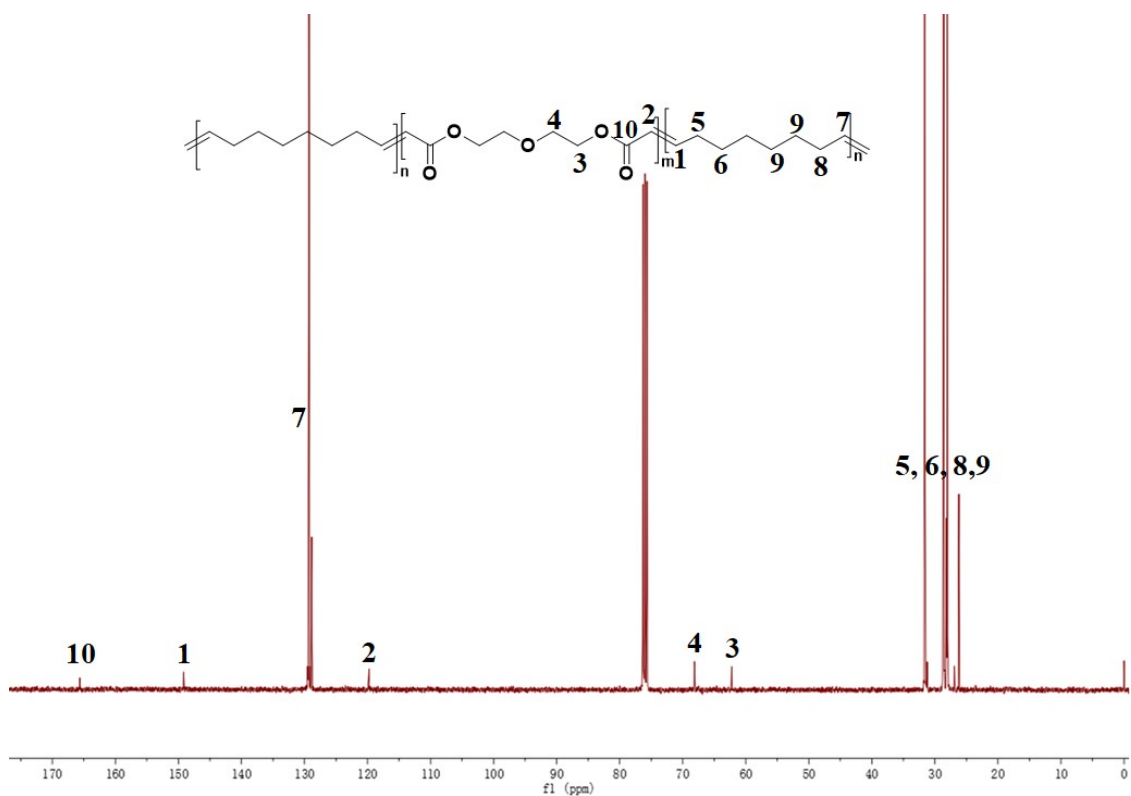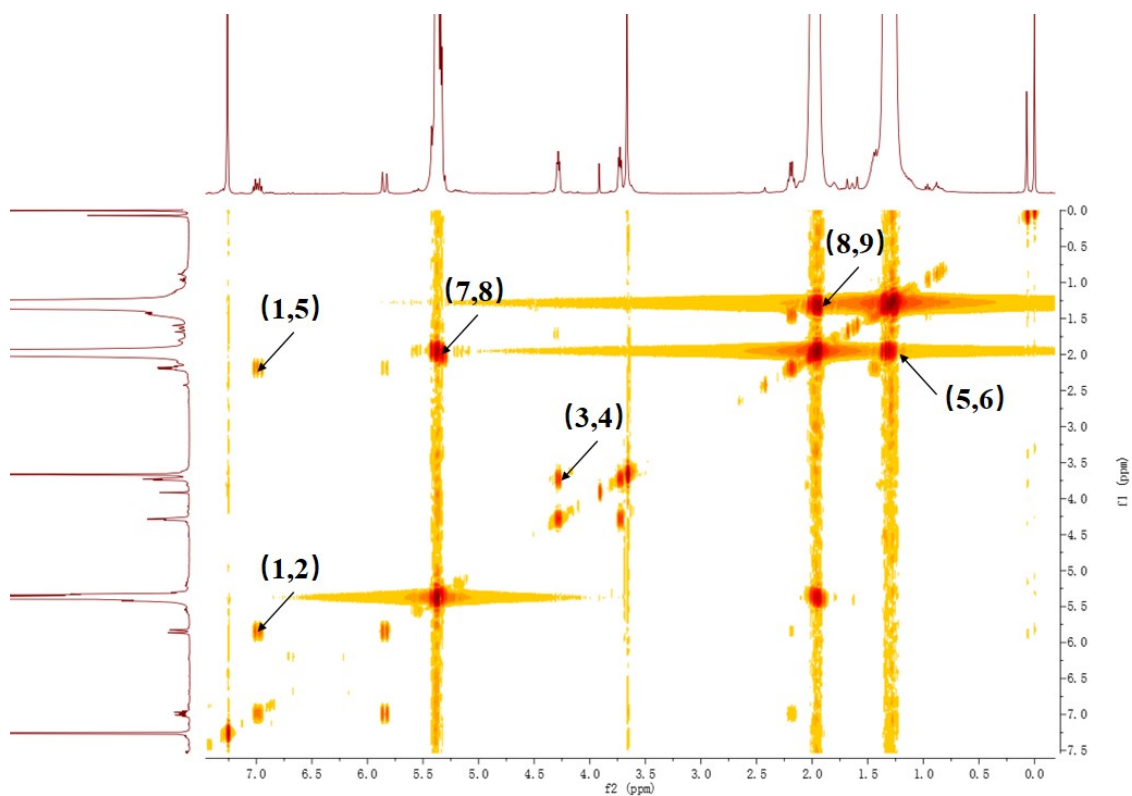**Figure S29.** H-H COSY NMR spectrum of the polymer from Table 2, entry 4 (CDCl$_3$).
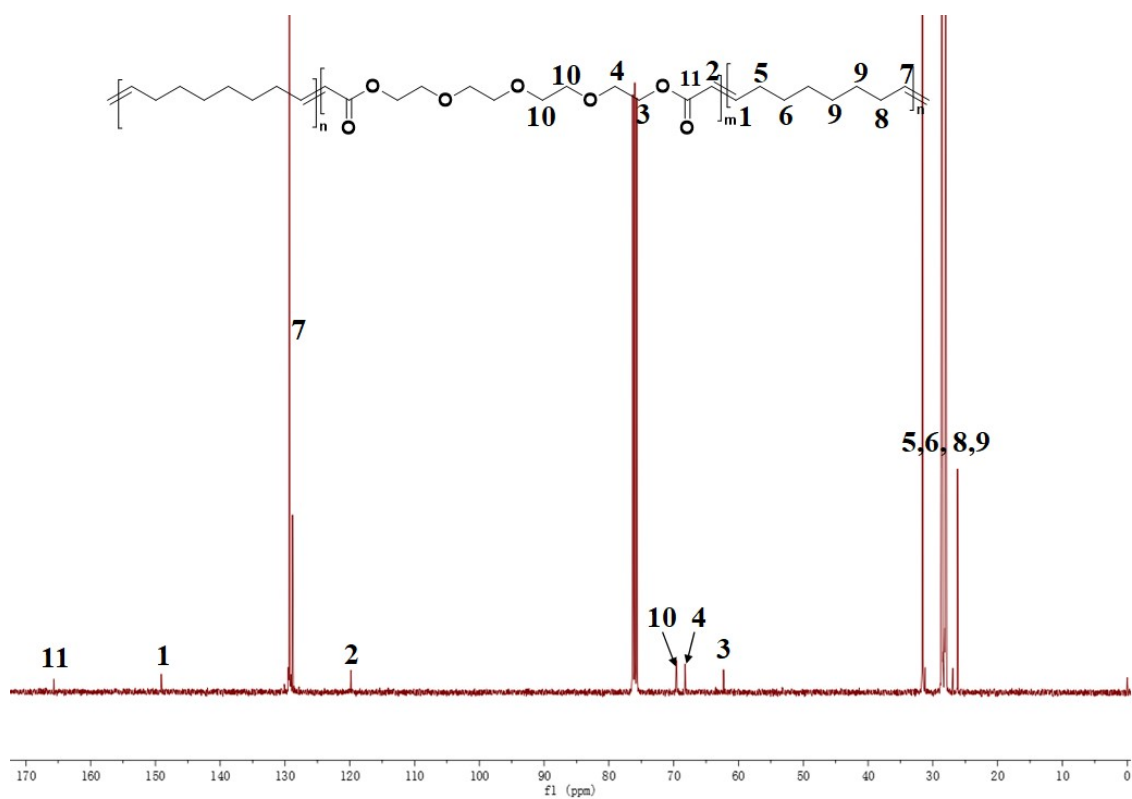
Figure S30. ^{13}C NMR spectrum of the polymer from Table 2, entry 4 (CDCl$_3$).
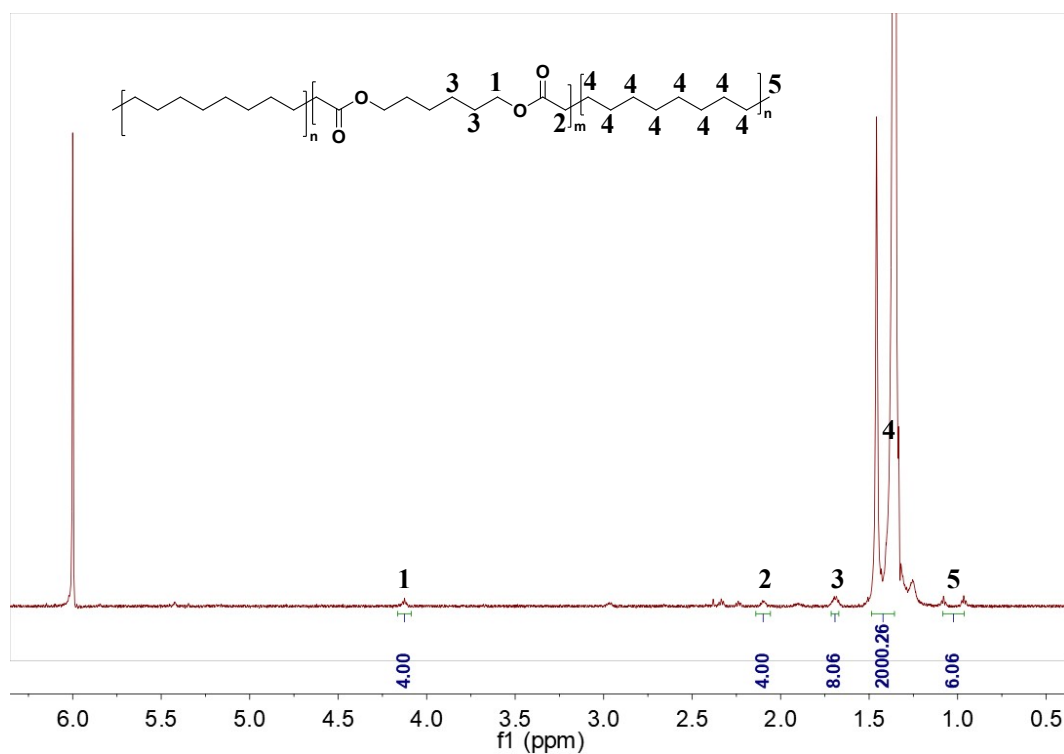
Figure S31. ^1H NMR spectrum of **Polymer-1**($C_2D_2Cl_4$, 120°C).

4.GPC and DSC Spectrums of Polymers.
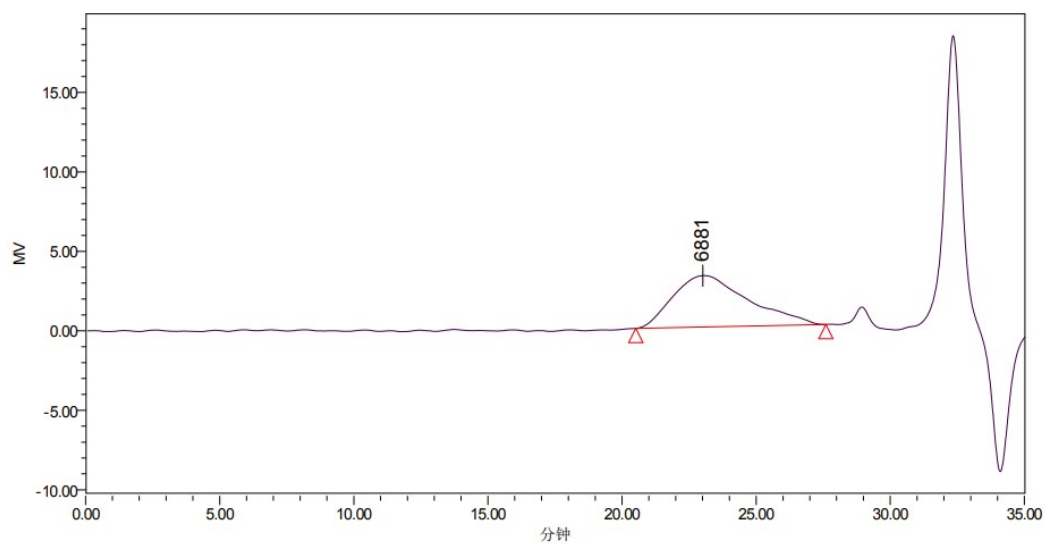
GPC Results

Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1	23.017	23.017	23.017	5726	7807	6881	10665	14000	1.366166	1.793337

Figure S32. GPC trace of the polymer from Table 1, entry 1.
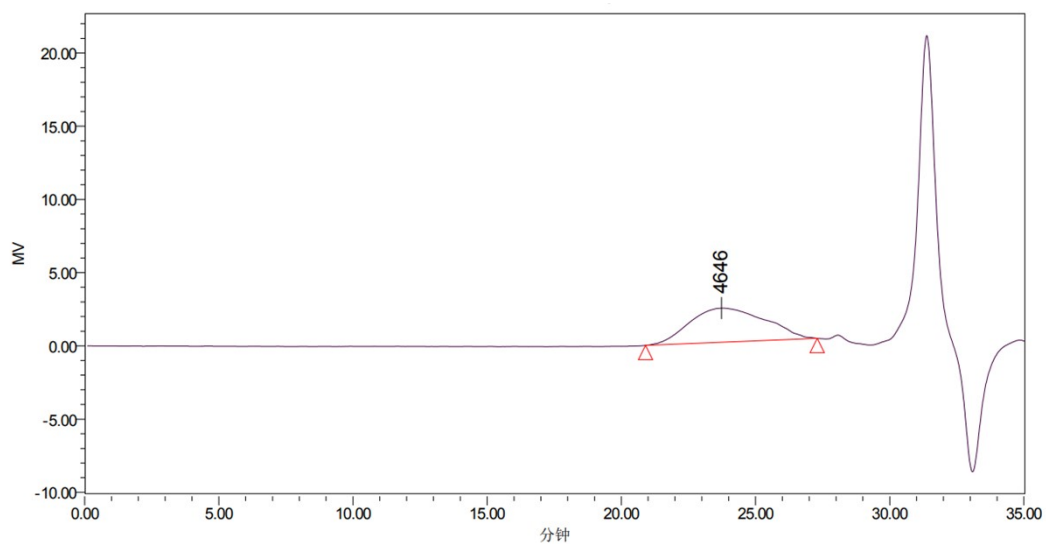
GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		23.733	23.733	23.733	4639	5867	4646	7567	9643	1.289755	1.643586

Figure S33. GPC trace of the polymer from Table 1, entry 2.

GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		23.053	23.053	23.053	5560	7463	6746	10167	13590	1.362293	1.821041

Figure S34. GPC trace of the polymer from Table 1, entry 3.

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		23.603	23.603	23.603	4812	6205	4995	8195	10730	1.320728	1.729331

Figure S35. GPC trace of the polymer from Table 1, entry 4.

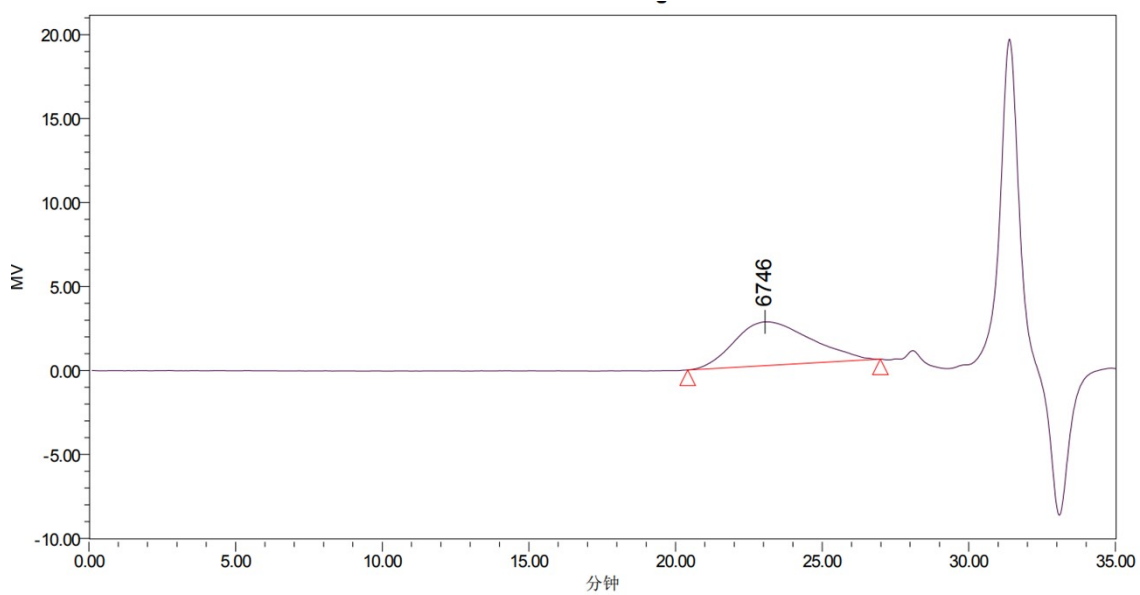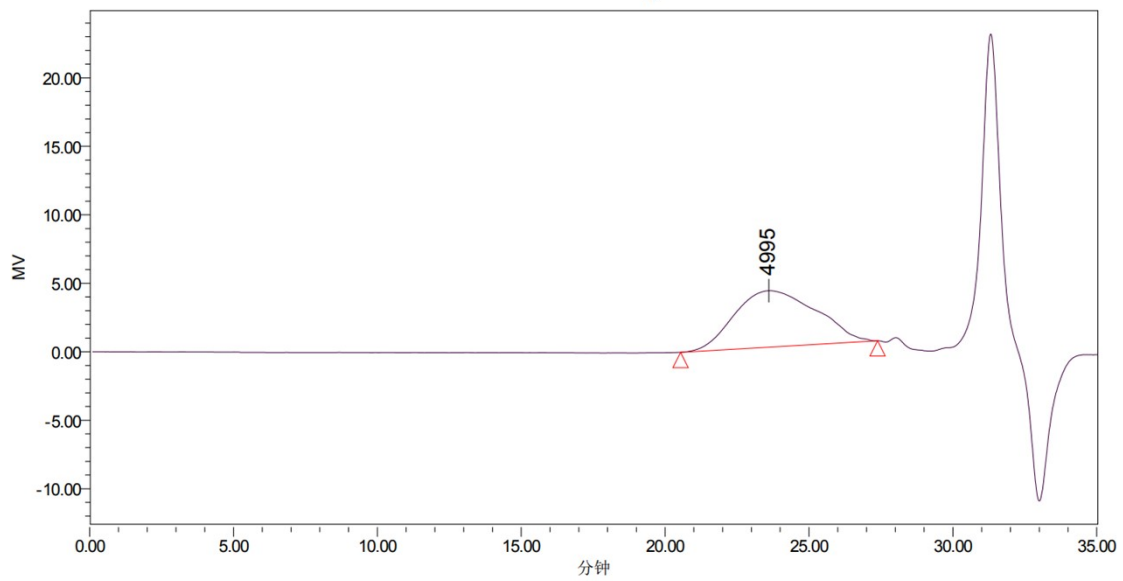|	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		21.800	21.800	21.800	7603	11879	9848	17468	22942	1.470456	1.931280

Figure S36. GPC trace of the polymer from Table 1, entry 5.

GPC Results

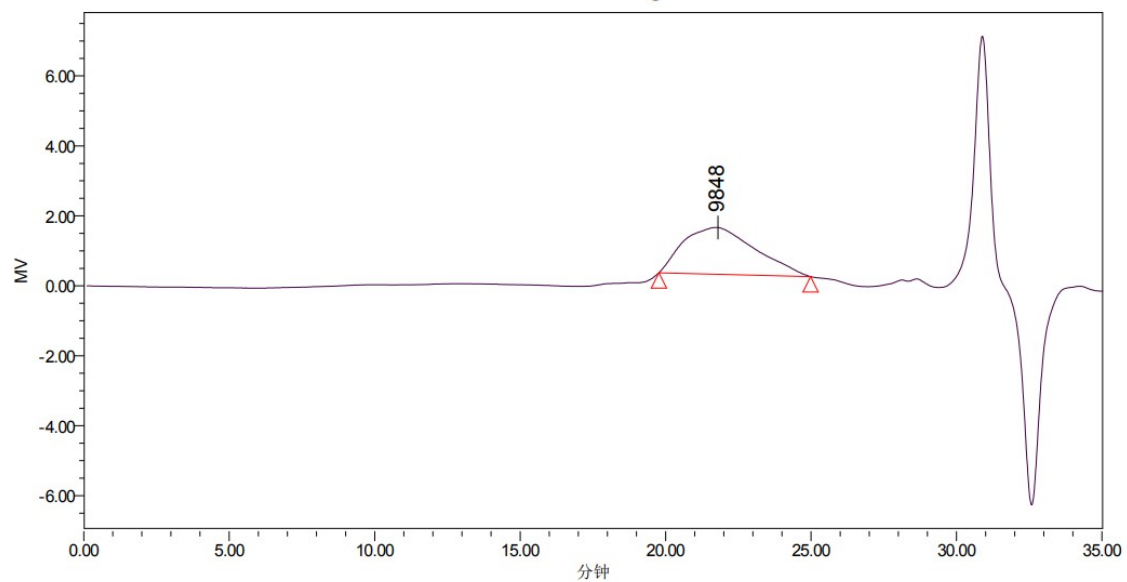|	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		21.636	21.636	21.636	10271	15637	15876	22780	30845	1.456850	1.972602

Figure S37. GPC trace of the polymer from Table 1, entry 6.

GPC Results

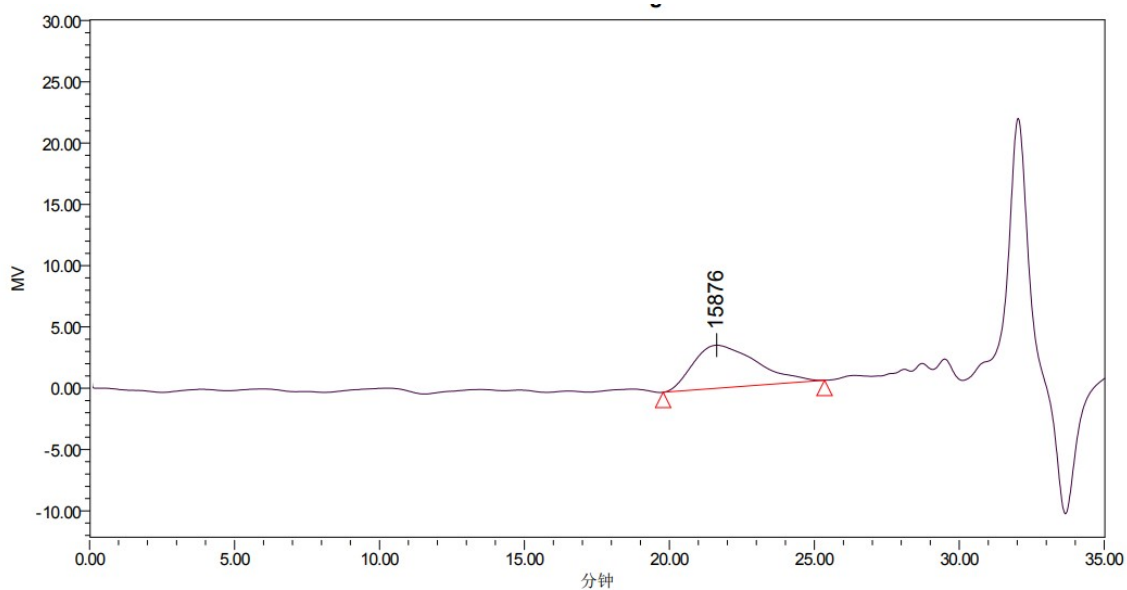|	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		20.969	20.969	20.969	15834	27134	26581	45568	69427	1.679345	2.558657

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

GPC Results

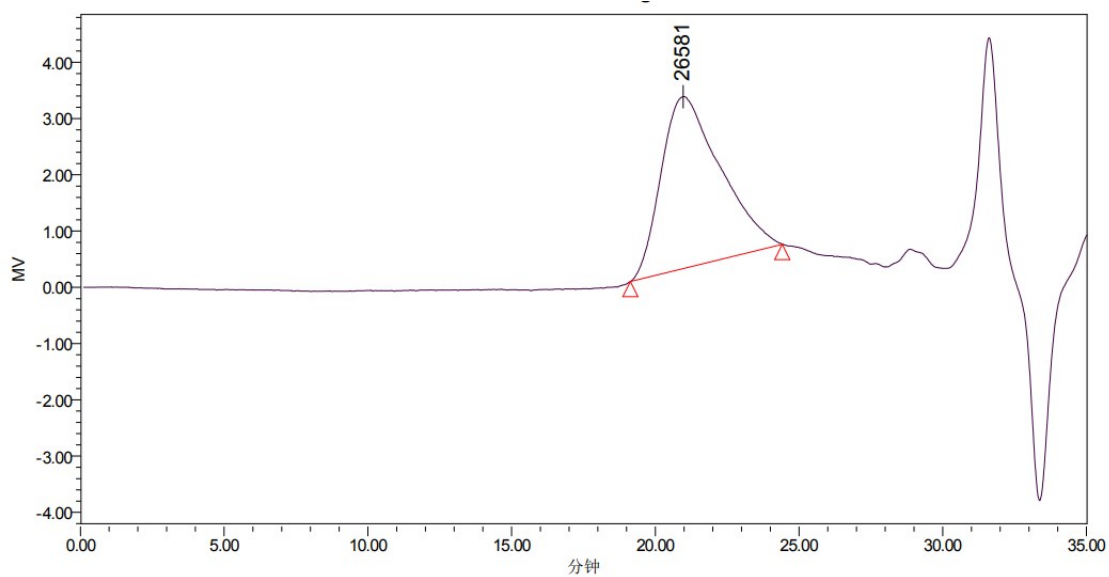|	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		22.050	22.050	22.050	6522	10151	8376	16039	23374	1.580080	2.302694

Figure S39. GPC trace of the polymer from Table 1, entry 8.

GPC Results

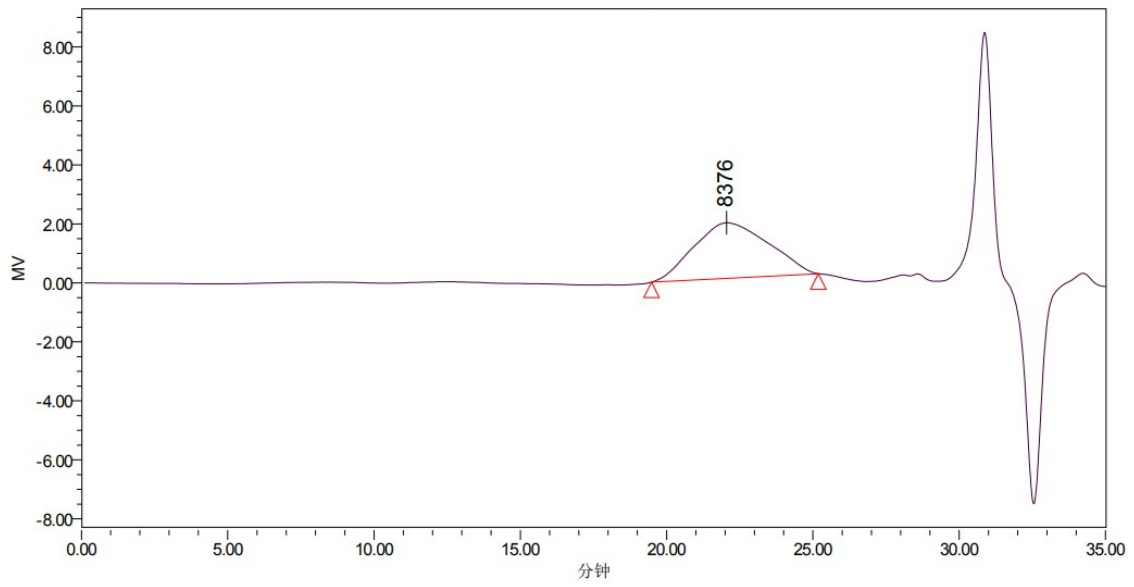|	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		20.592	20.592	20.592	12753	38021	37462	88256	154633	2.321272	4.067092

Figure S40. GPC trace of the polymer from Table 1, entry 9.

GPC Results

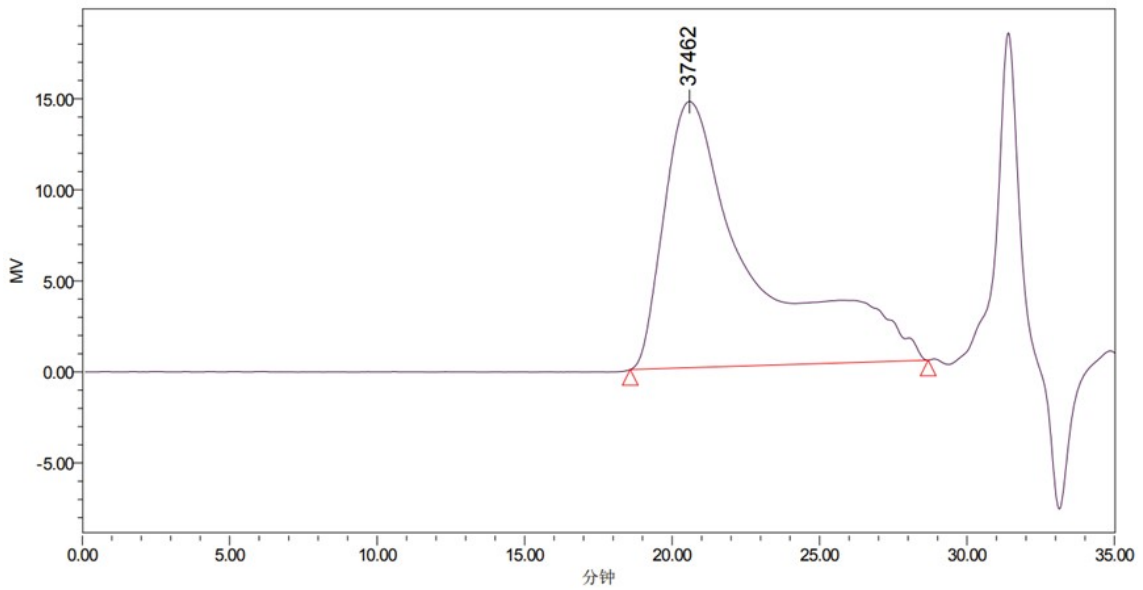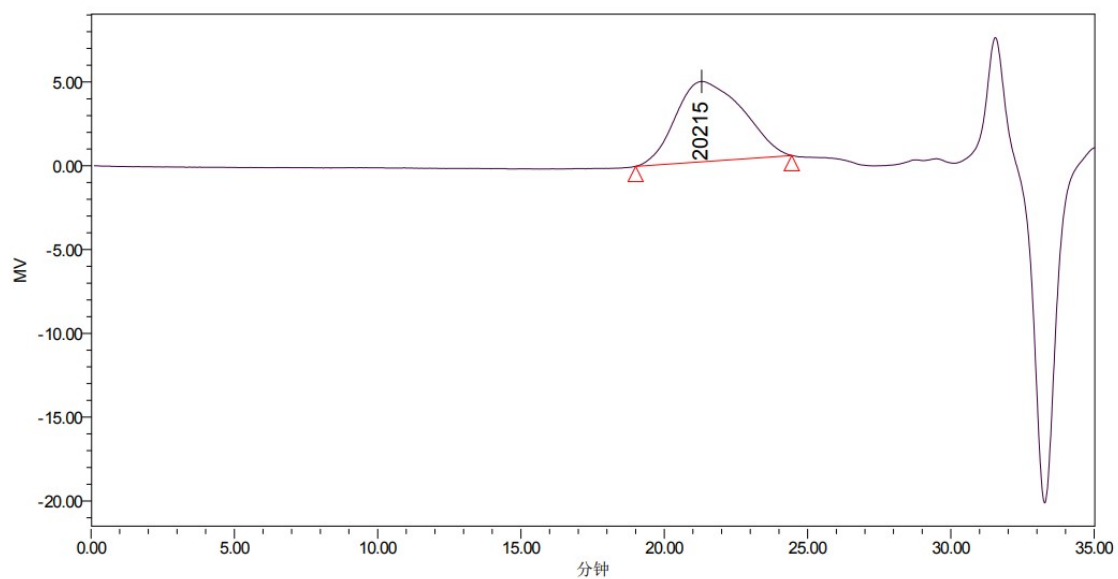|	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		21.307	21.307	21.307	13419	23003	20215	43524	77433	1.892085	3.366195

Figure S41. GPC trace of the polymer from Table 2, entry 1.

GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		23.733	23.733	23.733	4639	5867	4646	7769	10112	1.324351	1.723586

Figure S42. GPC trace of the sample (Table 2, entry 1) after degradation.

GPC Results

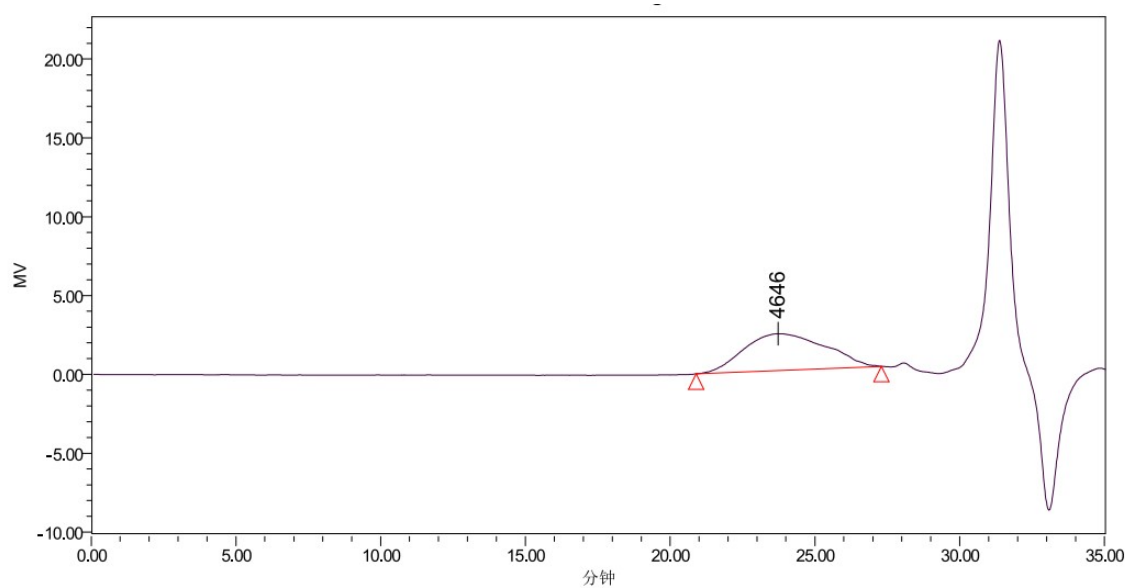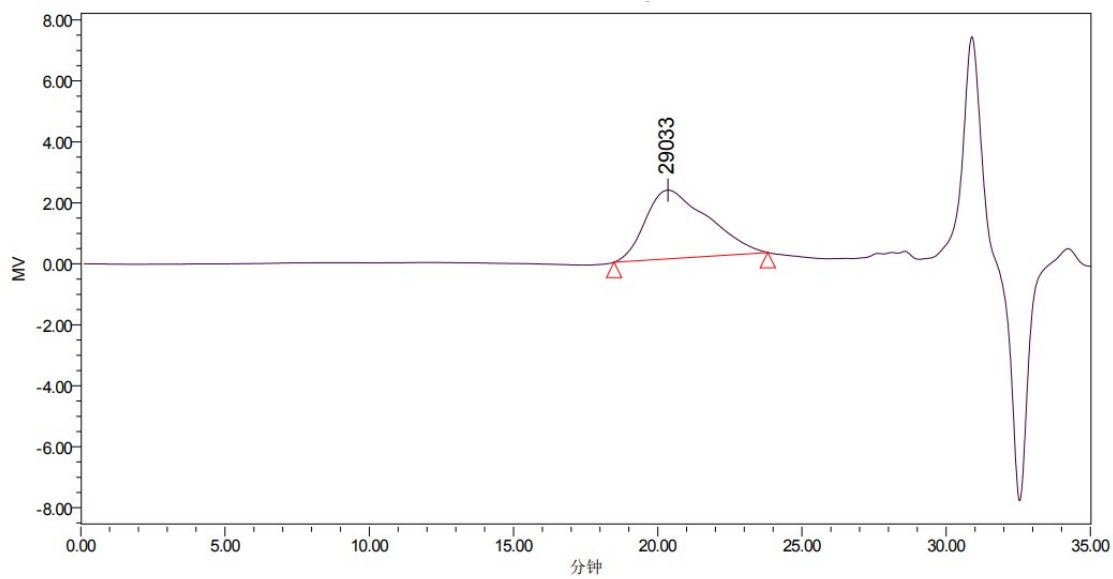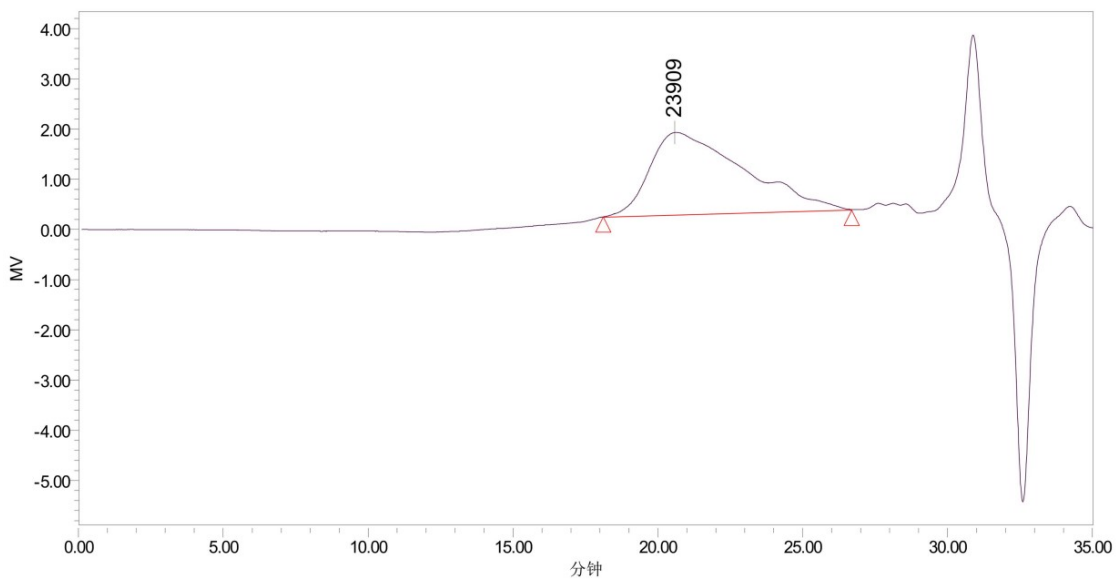|	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		20.353	20.353	20.353	15623	28573	29033	49247	74693	1.723521	2.614083

Figure S43. GPC trace of the polymer from Table 2, entry 2.

GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		20.583	20.583	20.583	11611	20785	23909	42078	69084	2.024381	3.323776

Figure S44. GPC trace of the polymer from Table 2, entry 3.

GPC Results

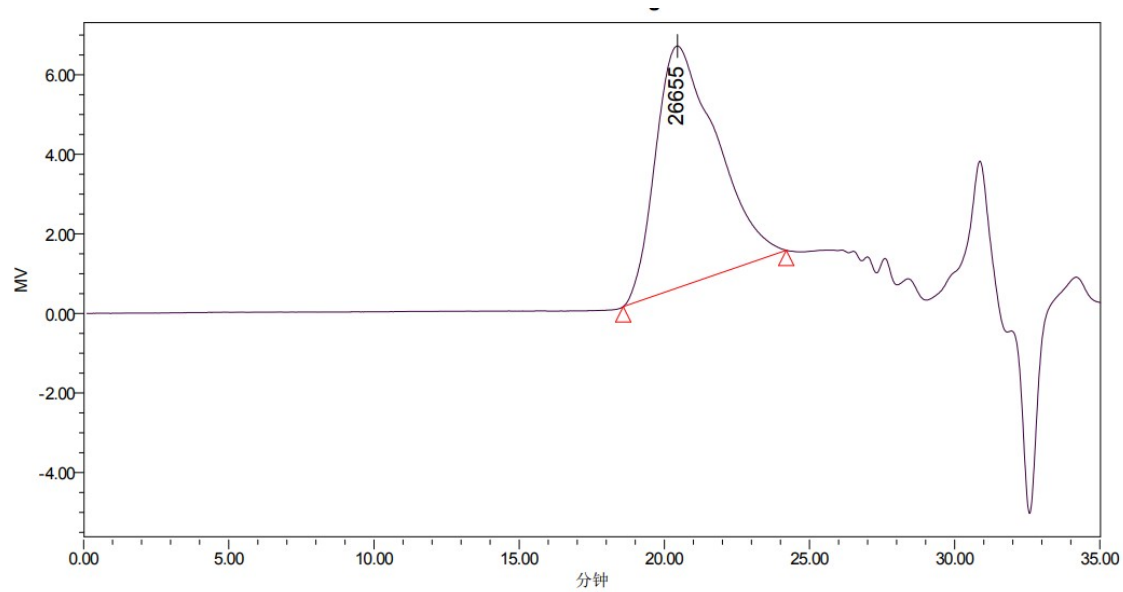|	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		20.453	20.453	20.453	14423	25631	26655	42172	61935	1.645369	2.416422

Figure S45. GPC trace of the polymer from Table 2, entry 4.

GPC Results

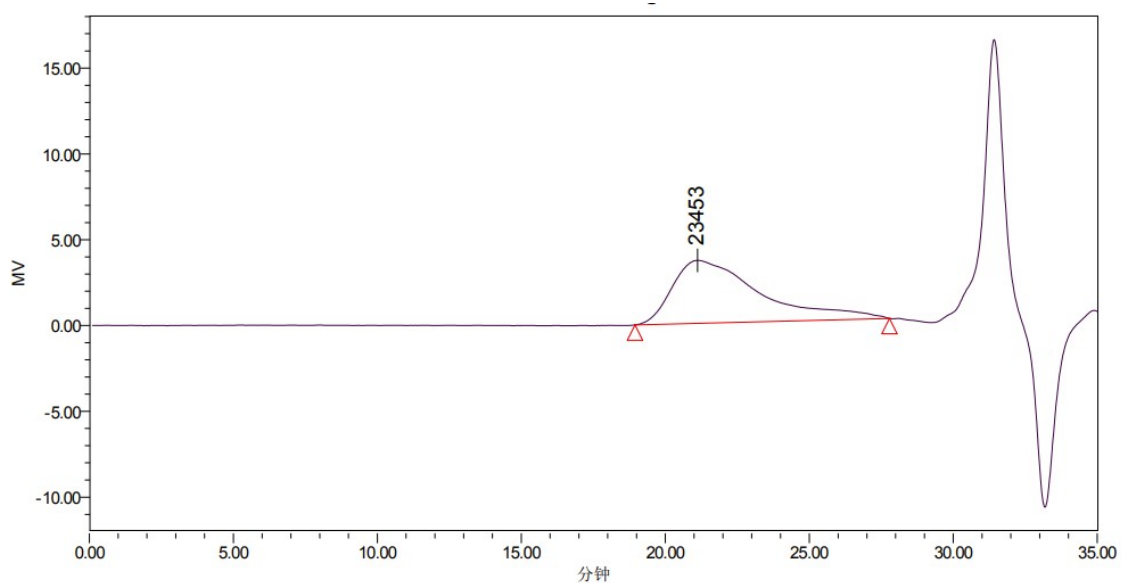|	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		21.119	21.119	21.119	10486	22354	23453	46337	82180	2.072907	3.676349

Figure S46. GPC trace of the polymer from Table 2, entry 5.

GPC Results

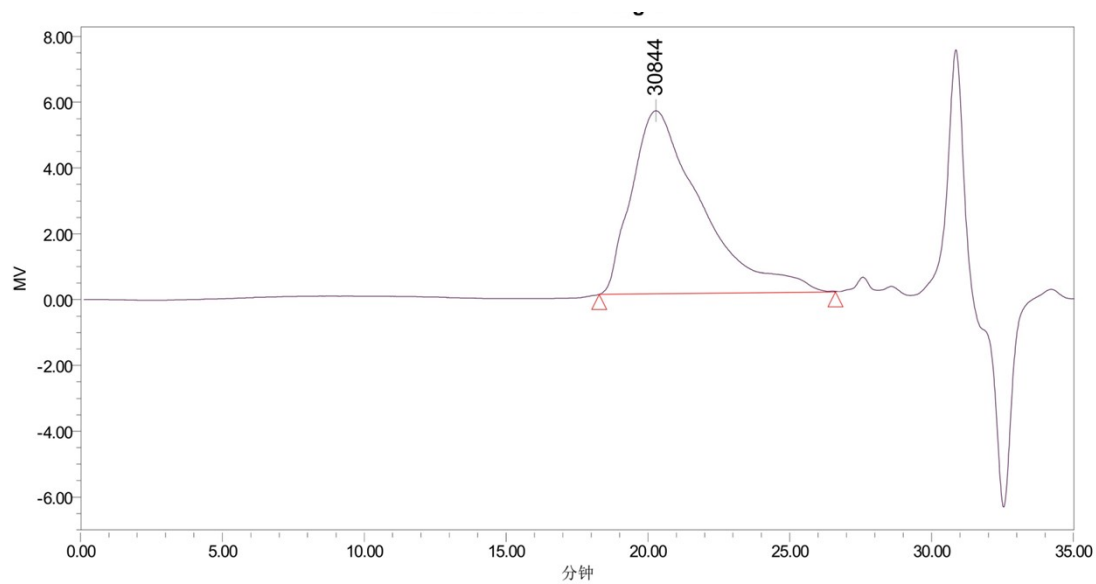|	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		20.283	20.283	20.283	15477	30182	30844	58205	88388	1.928436	2.928501

Figure S47. GPC trace of the polymer from Table 2, entry 6.

GPC Results

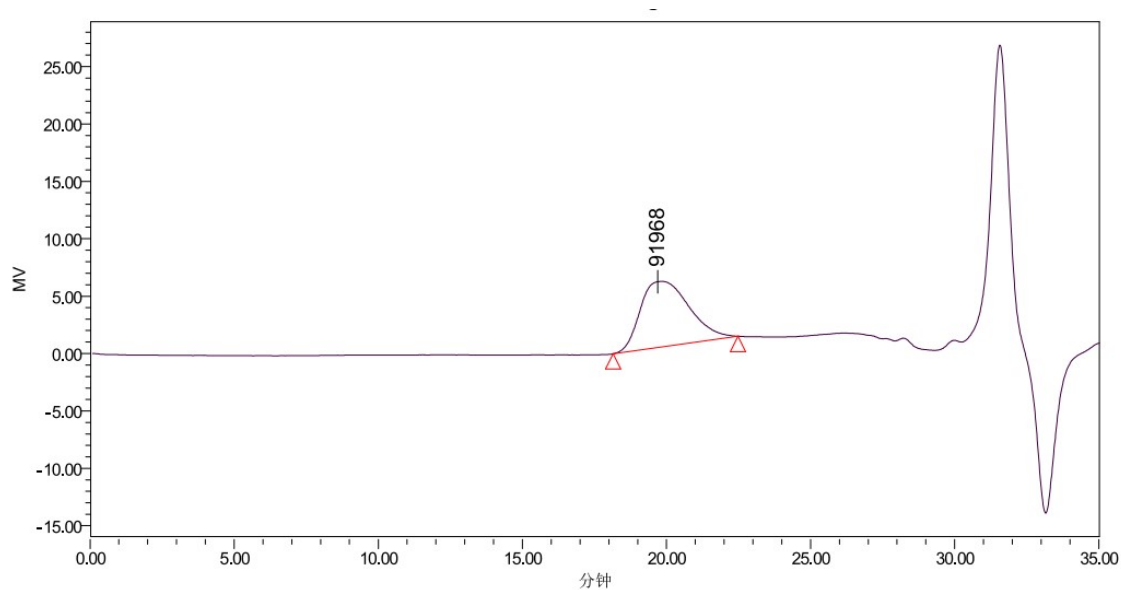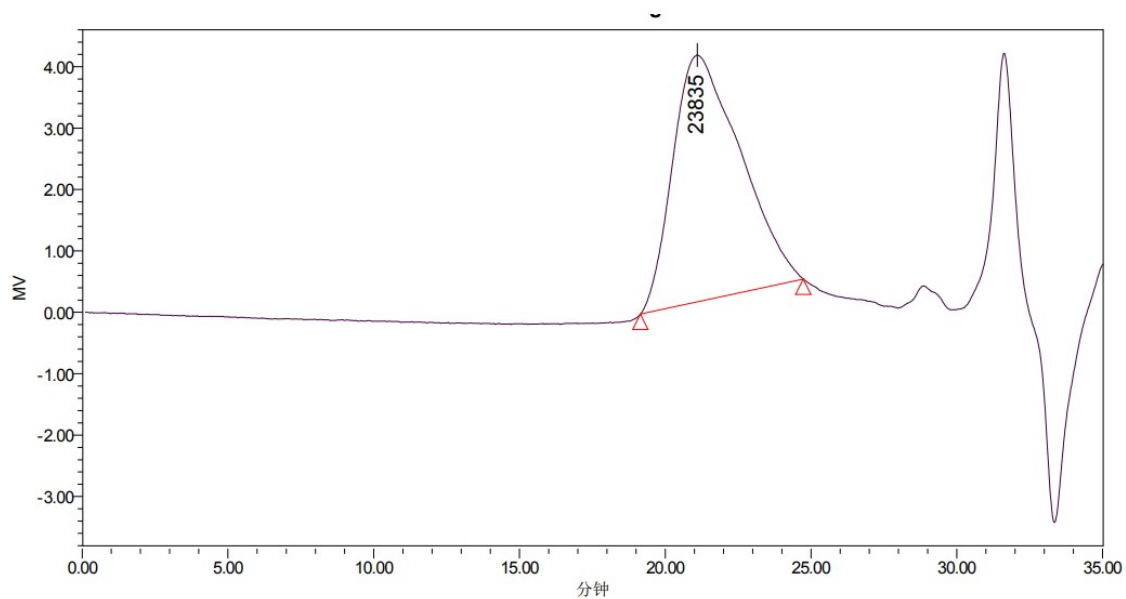|	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		19.700	19.700	19.700	53745	97014	91968	160750	253302	1.805064

Figure S48. GPC trace of the polymer from Table 2, entry 7.

GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		21.100	21.100	21.100	13584	24523	23835	44104	70386	1.798487	2.870210

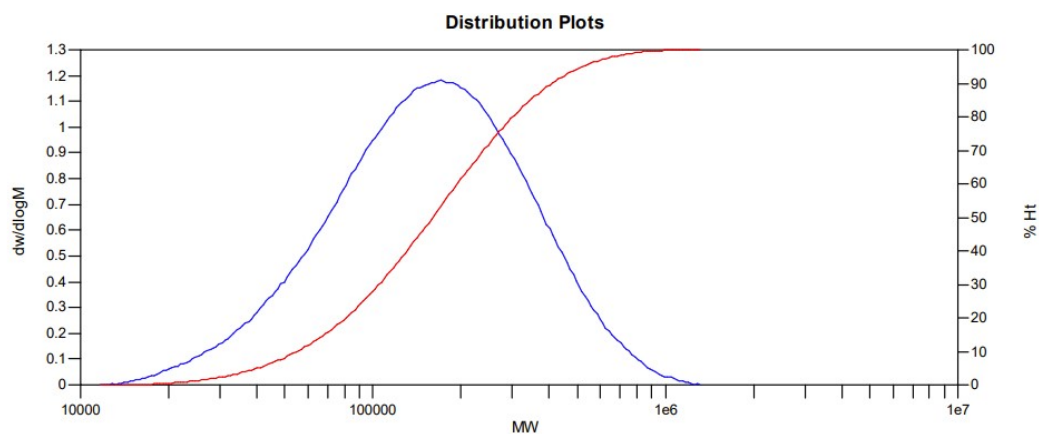**Figure S49.** GPC trace of the sample (Table 2, entry 7) after degradation.
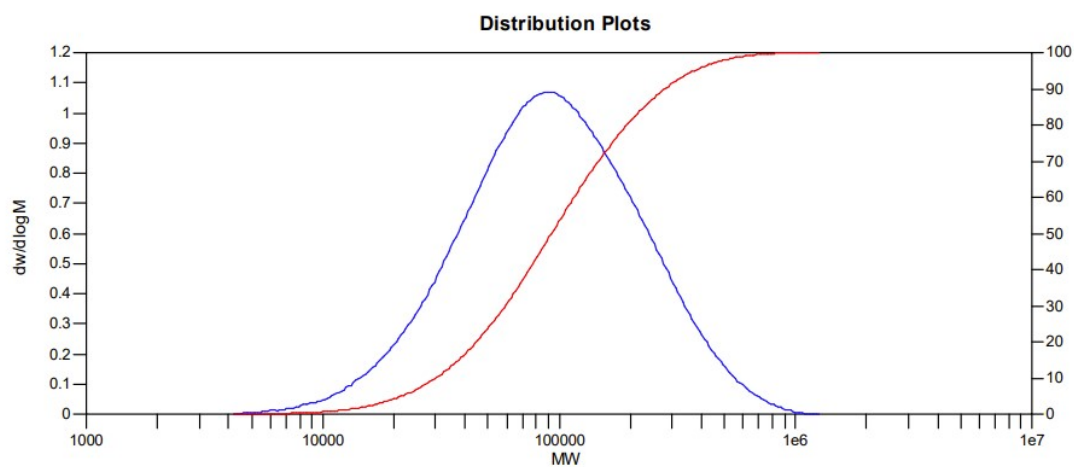
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	88697	62317	129542	239195	373456	117001	2.07876

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.25	13.15	15.33	-10.8203	0	1002.96	100

Figure S50. GPC trace of the **Polymer-1**.

Distribution Plots

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	170048	112130	201211	321795	456027	185980	1.79444

Processed Peaks

| Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.22	12.68	14.60	-5.72121	0	479.642	100

Figure S51. GPC trace of the **Polymer-2**
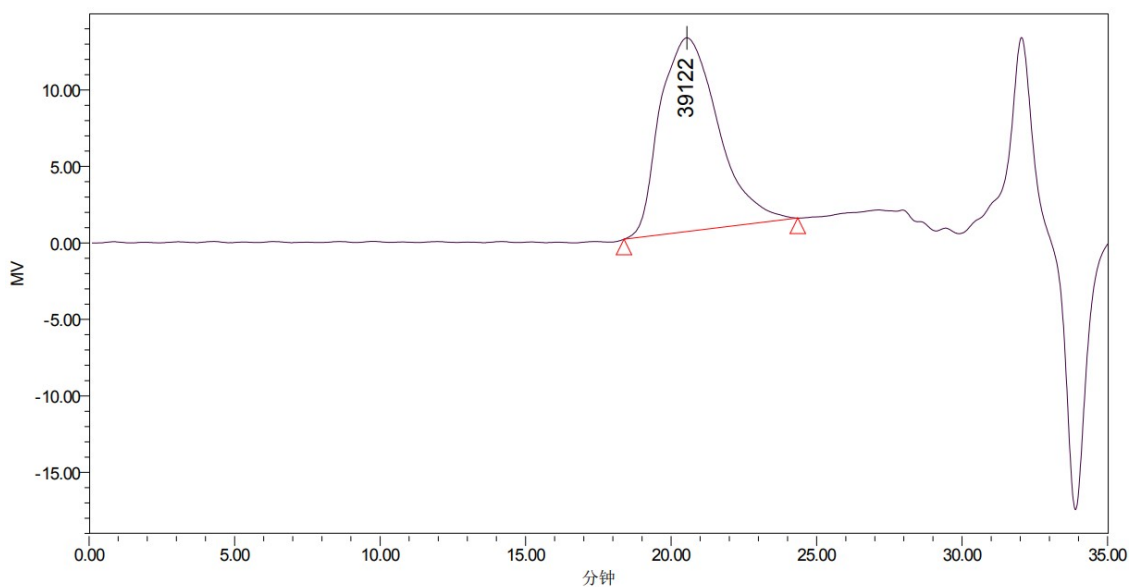
GPC Results

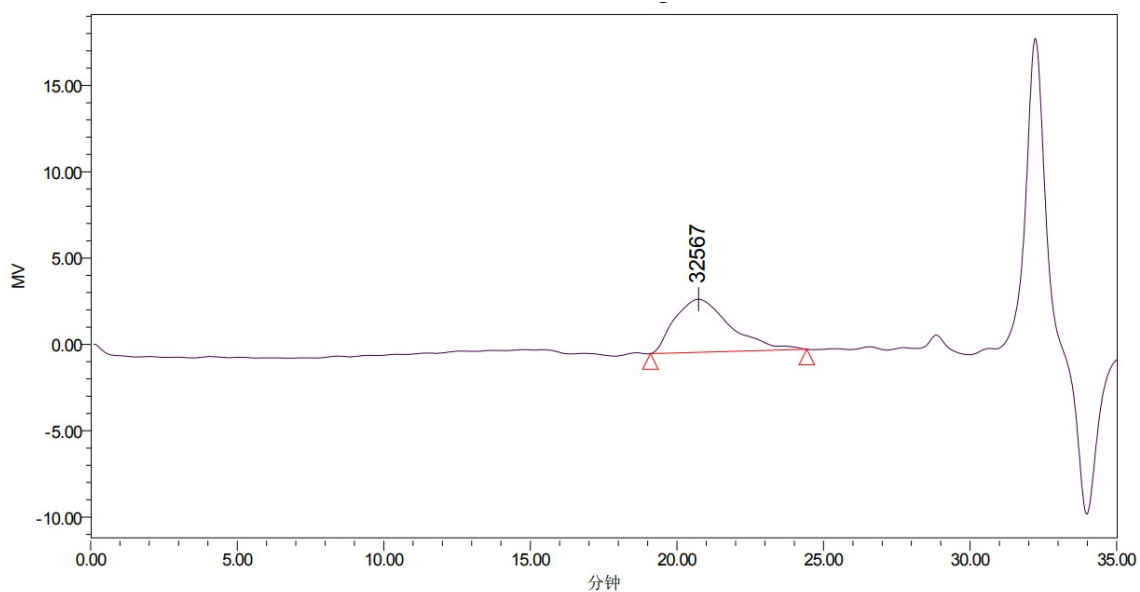|	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		20.547	20.547	20.547	25900	52586	39122	104450	180083	1.986263	3.424524

Figure S52. GPC trace of the polymer from Table S1, entry 4.
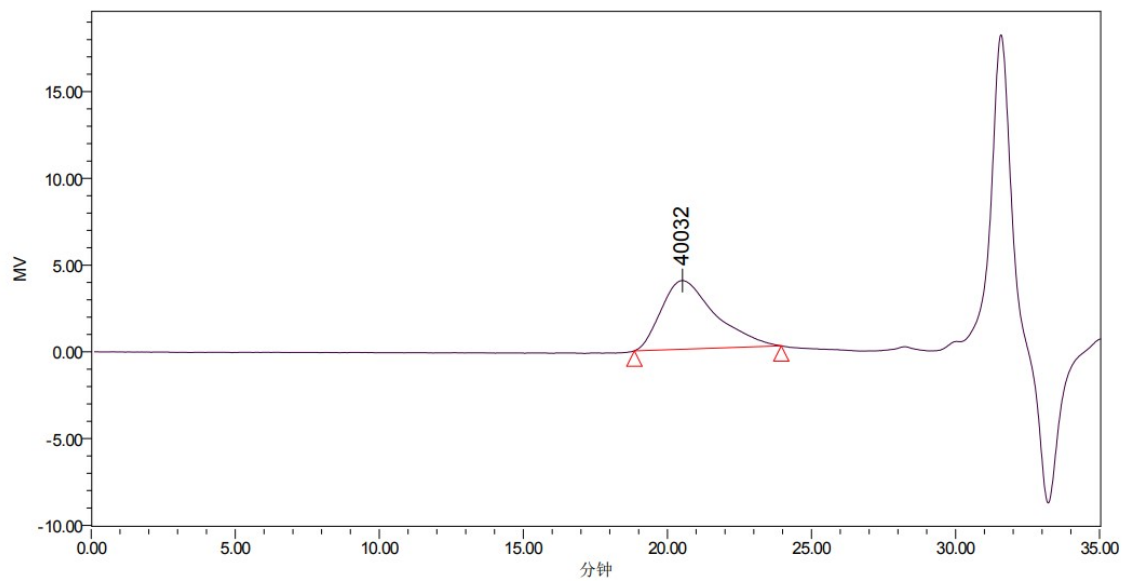
S31

GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		20.524	20.524	20.524	23270	43379	40032	77096	119451	1.777272	2.753649

Figure S53. GPC trace of the polymer from Table S1, entry 5.

GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		20.740	20.740	20.740	20396	37166	32567	61409	87483	1.652292	2.353844

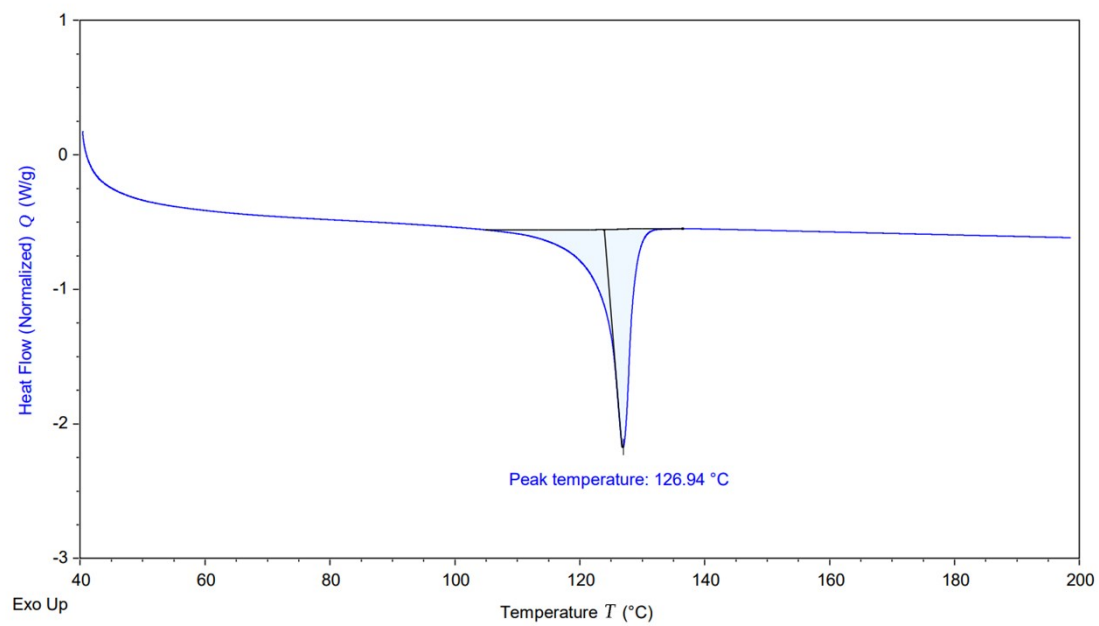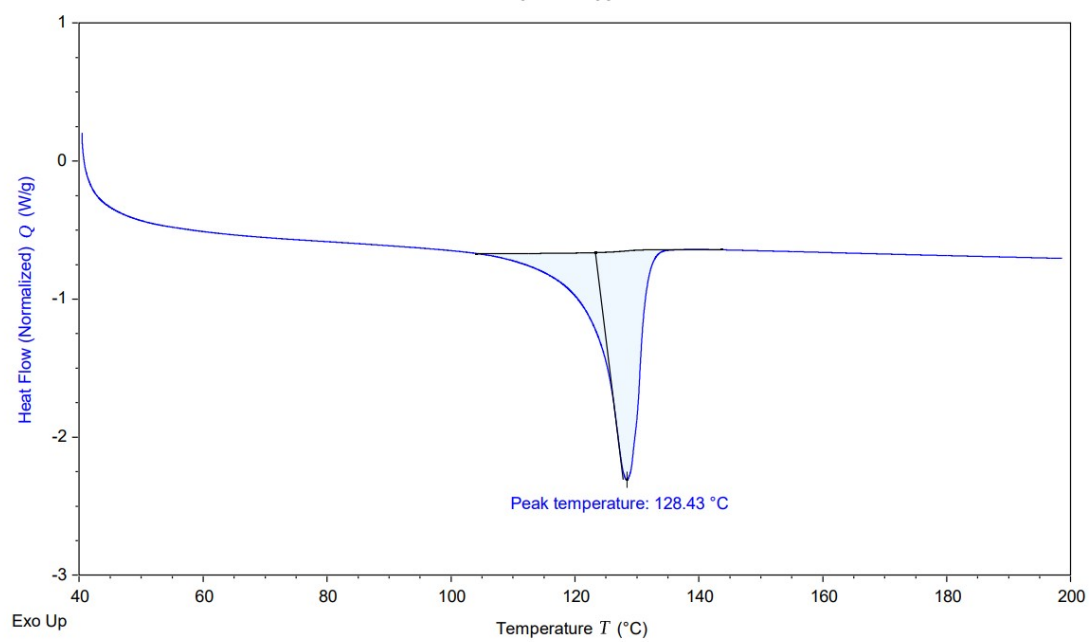**Figure S54.** GPC trace of the polymer from Table S1, entry 6.

Figure S55. DSC data of **Polymer-1**.

Figure S56. DSC data of **Polymer-2**.