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General information

All reactions were carried out in an argon filled glove box or using standard Schlenk techniques under nitrogen. All copolymerizations were performed in a 300-mL stainless steel autoclave. Ethylene (>99.9%) was purchased from Air Liquide (Shanghai) Compressed Gas Co., Ltd. and used as received. Anhydrous toluene was purchased from Adamas and distilled over sodium. Anhydrous DMF was purchased from Adamas and used as received. *N,N*-Diisopropylethylamine was purchased from Energy Chemical and distilled over calcium hydride. Sodium and calcium hydride were purchased from Sinopharm Chemical Reagent Co., Ltd. 1,3-Bis(diphenylphosphino)propane (dppp) was purchased from Bidepharm and stored in an argon filled glovebox. Benzenesulfonic acid was purchased from Energy Chemical and stored in an argon filled glovebox. PdMeCl(cod) and [Ru(Bpy)₃]Cl₂ were purchased from Innochem and stored in an argon filled glovebox. Triethanolamine (TEOA), 2-bromoanisole, dimethoxybenzene, chlorodiisopropylphosphine, chlorodicyclohexylphosphane, trichlorophosphane, DL-menthol, 2,6-lutidine were purchased from Tansoole and used as received. 1,3-Dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]-imidazole (BIH),^[1] RuCl₂(CO)₂(Bpy),^[2] [Ru(CO)₂(Bpy)₂](PF₆)₂,^[3] **[Pd]-1**,^[4] **[Pd]-2**,^[5] **[Pd]-3**,^[4] **[Pd]-4**,^[4] **[Pd]-5**,^[4] and **[Pd]-6**^[6] was prepared according to literature procedures. NMR spectra were recorded on a Quantum-I Plus (¹H: 400 MHz, ¹³C: 101 MHz) NMR spectrometer at ambient temperature unless otherwise noted. Chemical shift values for protons are referenced to the residual proton resonance of 1,1,2,2-tetrachloroethane-*d*₂ (C₂D₂Cl₄, δ: 6.00). Chemical shift values for carbons are referenced to the carbon resonances of 1,1,2,2-tetrachloroethane (C₂D₂Cl₄, δ: 74.0 ppm). ¹H NMR analyses of polymers were performed on ca. 5 wt % solutions of the polymers in C₂D₂Cl₄ at 120 °C using a relaxation time of 5.0 s. ¹³C{¹H} NMR analyses of polymers were performed on ca. 15 weight% solutions of the polymers and ca. 0.05 M Cr(acac)₃ as a relaxation agent in 1,1,2,2-tetrachloroethane unlocked at 120 °C. The gas mixture in the headspace was analyzed by a Shimadzu GC-2014C gas chromatograph. The gas analysis of the ¹³C labeling experiment was analyzed by an Agilent 7890B-5977B gas chromatographic mass spectrometer (GC-MS). Size exclusion chromatography (SEC) analyses were carried out with an EcoSEC (HLC-8321GPC/HT) and Agilent (PLgel MIXED-B) equipped with refractive index (RI) detector by eluting the columns with 1,2-dichlorobenzene at 1.0 mL/min at 145 °C. Molecular weights were determined using narrow polystyrene standards. Differential scanning calorimetry (DSC) measurements of polymers were performed on a DSC 2500 analyzer at a heating and cooling rate of 10 °C/min. Thermo-gravimetric analyses of the resulted polymers were measured on TGA8000, and the sample was heated at a rate of 10 °C/min. ATR-IR spectra of polymers were measured on a Thermo Fisher Nicolet 6700.

Experimental procedures

A representative procedure for photocatalytic CO₂ reduction of a CO₂/ethylene mixture (Table 1, entry 1): A 300 mL stainless steel autoclave with a quartz window and a 30 mL glass tube were dried in an oven at 120 °C, and then allowed to cool inside a glovebox. The glass tube was charged with [Ru(bpy)₃]Cl₂ (20 μmol), BIH (500 μmol), 1 mL TEOA, 10 mL DMF, and then placed in the autoclave. The autoclave was then sealed, charged with carbon dioxide (0.5 MPa) and ethylene (3.0 MPa) and then stirred in an isothermal heating block at 60 °C under radiation of 455 nm Blue LEDs (10 W) for 3 h. After cooling the autoclave to room temperature, the gas mixture in the headspace were analyzed and quantified by a Shimadzu GC-2014C gas chromatograph. The column temperature was set to 40 °C. The carrier gas was argon which was supplied at a flow rate of 15.0 mL min⁻¹. A 2.0 m P-N column and a 2.0 m 13-X column were utilized within the gas chromatograph. Both a flame ionization detector (FID) equipped with a methanizer and a thermal conductivity detector (TCD) were used for gas component quantification (Figure S1). Hydrogen was supplied to the FID from a hydrogen generator at a flow rate of 40 mL min⁻¹. Air was also supplied to the FID at a flow rate of 300 mL min⁻¹. The standard curve of CO content with integral area of FID GC spectra was determined by using the standard gas with 0.01%, 0.02%, 0.04%, 0.06%, 0.08%, 0.10% CO contents (Figure S2). The CO content in the photocatalytic CO₂ reduction reaction was quantified according to standard curve. A control experiment in the absence of CO₂ was carried out and no CO was detected by GC after the reaction (Figure S14).

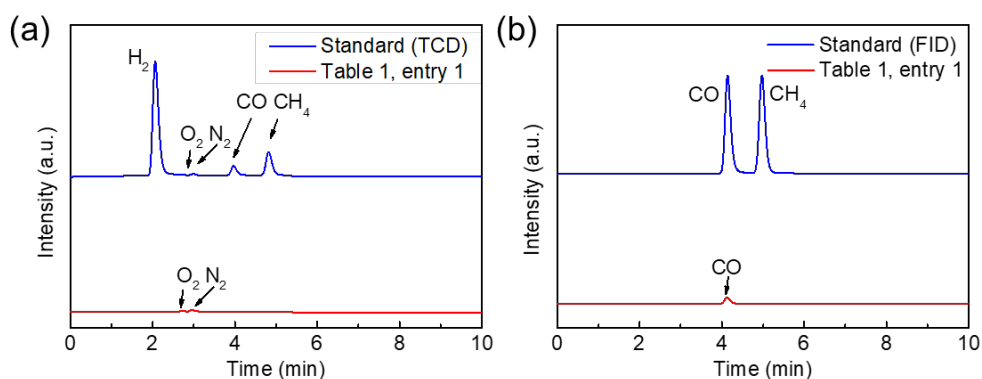


Figure S1. (a) GC-TCD spectra of standard gas (red line, 5 % H₂, 5 % CO, 5 % CH₄ in Ar) and gas sample for Table 1, entry 1 (blue line); (b) GC-FID spectra of standard gas (red line, 5 % H₂, 5 % CO, 5 % CH₄ in Ar) and gas sample for Table 1, entry 1 (blue line).

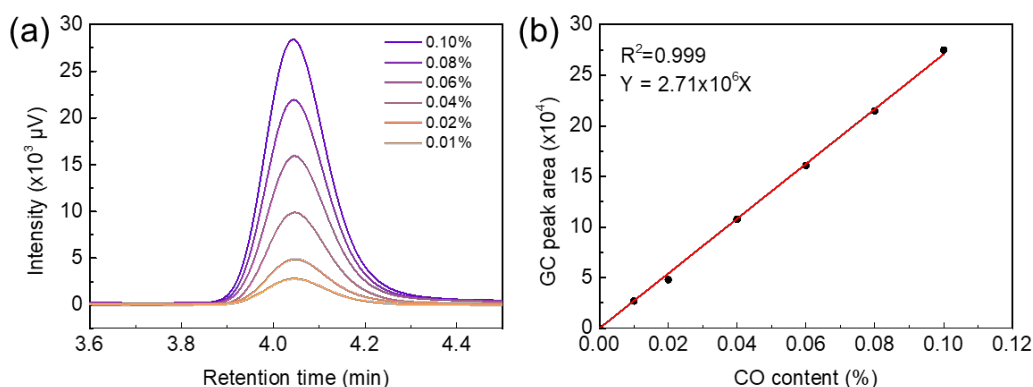


Figure S2. (a) GC spectra of 50 μL standard samples with 0.10%, 0.08%, 0.06%, 0.04%, 0.02% and 0.01% CO content, respectively; (b) Standard curve of CO content with integral area of GC spectra (FID).

Procedure for a ^{13}C labeling experiment for photocatalytic CO_2 reduction: A 20 mL optical reactor was charged with $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (20 μmol), BIH (50 mM) TEOA (1.0 mL) and DMF (10 mL), then evacuated and purged with $^{13}\text{CO}_2$ (1 bar). The mixture was stirred at 60 $^\circ\text{C}$ and irradiated under 455 nm Blue LEDs (10 W) for 3 h. After cooling to room temperature, the gas products were analyzed by an Agilent 7890B-5977B gas chromatographic mass spectrometer. The values of m/z were detected as 45 (Figure S3b) and 29 (Figure S3d) according to the gas chromatographic mass spectra, which belong to $^{13}\text{CO}_2$ and ^{13}CO , respectively (Figure S3). This experiment indicated that CO was derived from in situ CO_2 photoreduction.

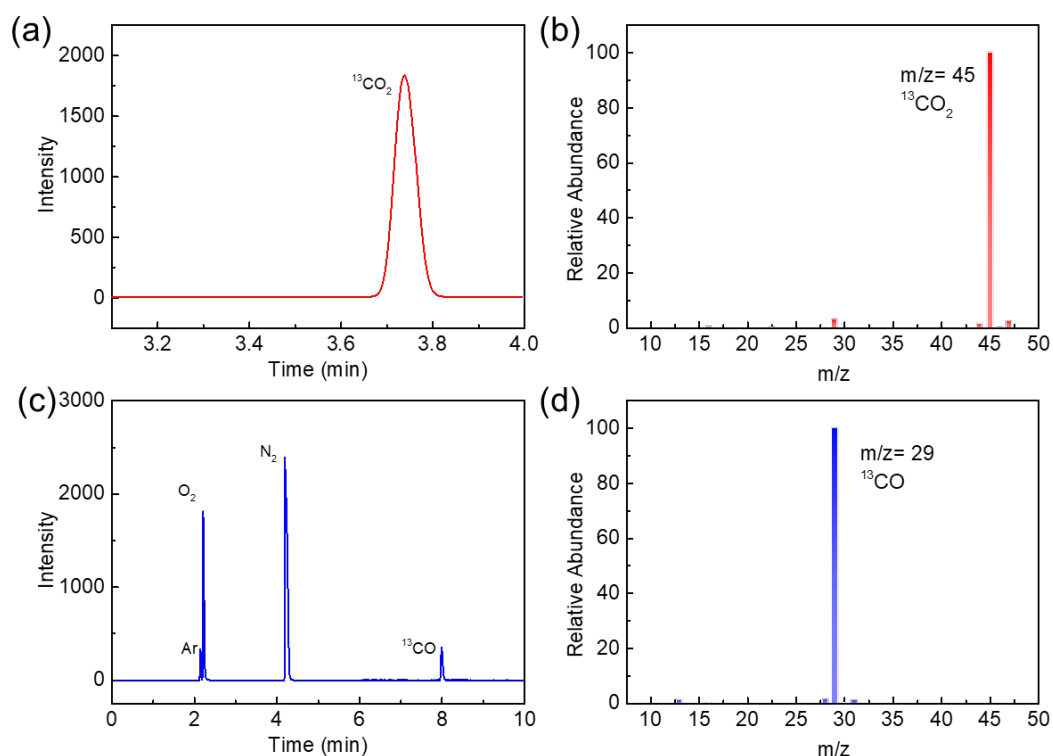


Figure S3. GC spectrum (a) and relative mass spectrum (b) of $^{13}\text{CO}_2$ from the headspace of reactor after 3 h photocatalytic reaction; GC spectrum (c) and relative mass spectrum (d) of ^{13}CO from the headspace of reactor after 3 h photocatalytic reaction.

A representative procedure for copolymerization of ethylene and carbon dioxide (Table 2, entry 1): A 300 mL stainless steel autoclave with a quartz window and two 30 mL glass tubes were dried in an oven at 120 $^\circ\text{C}$, and then allowed to cool inside a glovebox. One glass tube was charged with $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (20 μmol), BIH (500 μmol), 1 mL TEOA and 10 mL DMF; while the other glass tube was charged with **[Pd]-1** (10 μmol) and 10 mL toluene. Both of the tubes were then placed in the autoclave. The autoclave was then sealed, charged with CO_2 (0.5 MPa) and ethylene (3.0 MPa) and then stirred in an isothermal heating block at 60 $^\circ\text{C}$ under radiation of 455 nm Blue LEDs (10 W) for 3 h. After cooling the autoclave to room temperature, the excess gas pressure was carefully vented in a well ventilated fumehood. The polymerization reaction was quenched by addition of methanol (ca. 80 mL). The formed precipitate was filtered and washed with methanol. The obtained solid was dried under vacuum at 100 $^\circ\text{C}$ for 4 hours. The molecular weight and polydispersity were determined by size exclusion chromatography. CO incorporation ratio (i. r.) in mol% from the ^1H NMR spectra by the integration of the signals for isolated ketone unit (**B**, 2.42 ppm), alternating

copolymer unit (**H**, 2.70 ppm; **F**, 2.46 ppm; **B** = **F**) and those not adjacent to carbonyl groups. Assuming that there is no accumulating alternating ketone unit due to low CO incorporation, Isolated carbonyls/Alternating carbonyls (I/A) = (**B**+**F**-**H**)/2**H**, CO i. r. (%) = (**B**+**F**+**H**)/(a+c+d+e+f+g+h+j+n+i+b+2k+m+2o+2p+q+C+G+2B+2F+2H)×100%.

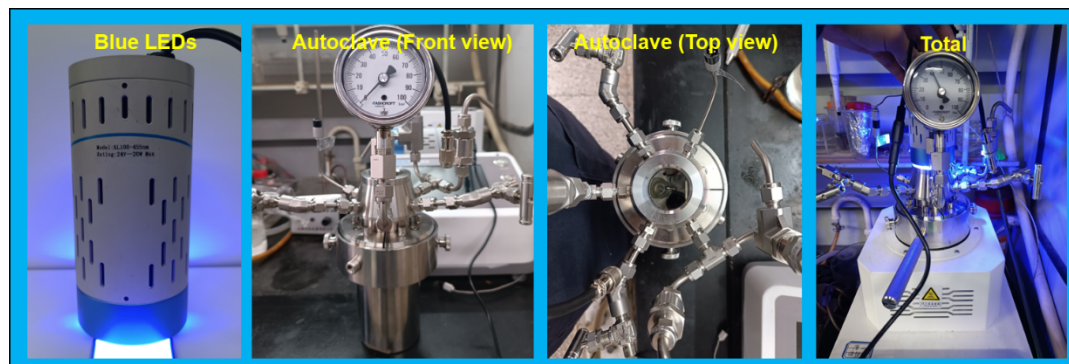


Figure S4. Reaction setup for the copolymer synthesis from CO₂ and ethylene.

Experimental procedure for copolymerization of ethylene with low pressure CO (Table 1, entry 6): A 45 mL stainless steel autoclave along with a 30 mL glass tube were dried in an oven at 120 °C, and then allowed to cool inside a glovebox. The glass tube was charged with [**Pd**]-**1** (10 μmol), toluene (10.0 mL) and then placed in the autoclave. The autoclave was then sealed, charged with CO (2.0 MPa, 10:1), released to atmosphere pressure, and charged with ethylene (3.5 MPa), then released to atmosphere pressure, and finally charged with ethylene (3.0 MPa). The autoclave was stirred in an isothermal heating block at 60 °C for 3 h. After cooling the autoclave to room temperature, the excess gas pressure was carefully vented in a well ventilated fumehood. The reaction was quenched by addition of methanol (ca. 80 mL). The formed precipitate was filtered and washed with methanol. The obtained solid was dried under vacuum for at 100 °C 4 hours. The molecular weight and polydispersity were determined by size exclusion chromatography. CO i. r. and I/A selectivity were determined by ¹H NMR analysis.

Copies of GC spectra of the photocatalytic CO₂ reduction

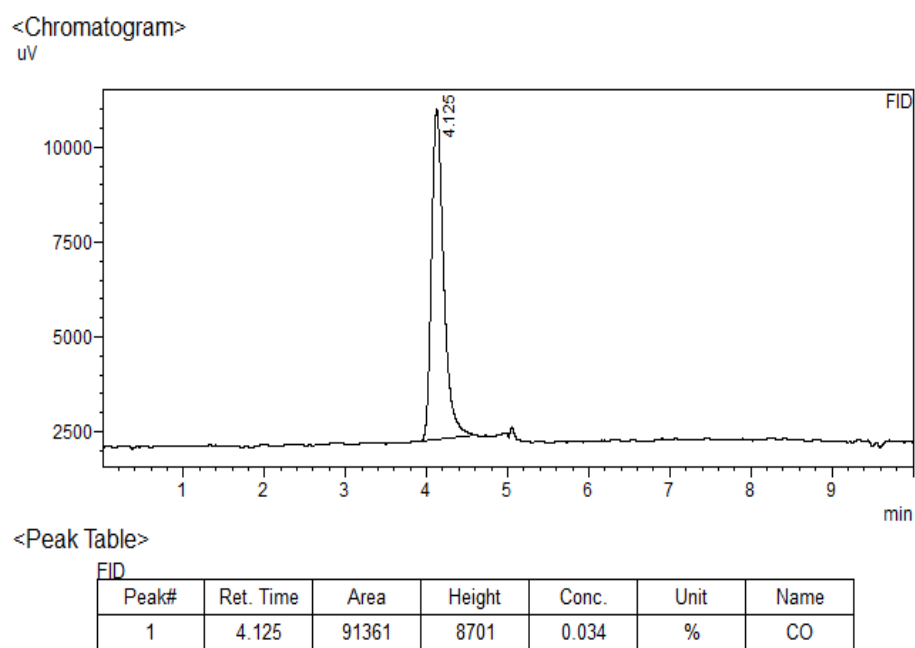


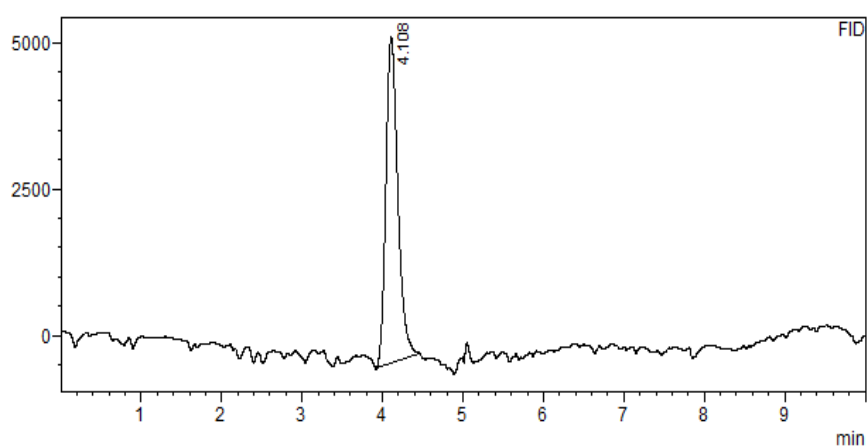
Figure S5. GC spectrum of the gas mixture obtained in Table 1, entry 1.

==== Shimadzu LabSolutions Analysis Report ====

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 Sample ID :
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 Method Filename : CO-BQ-2.gcm
 Batch Filename :
 Date Acquired : 2022/12/10 20:39:19
 Date Processed : 2023/2/21 15:20:01

<Chromatogram>

uV



<Peak Table>

FID						
Peak#	Ret. Time	Area	Height	Conc.	Unit	Name
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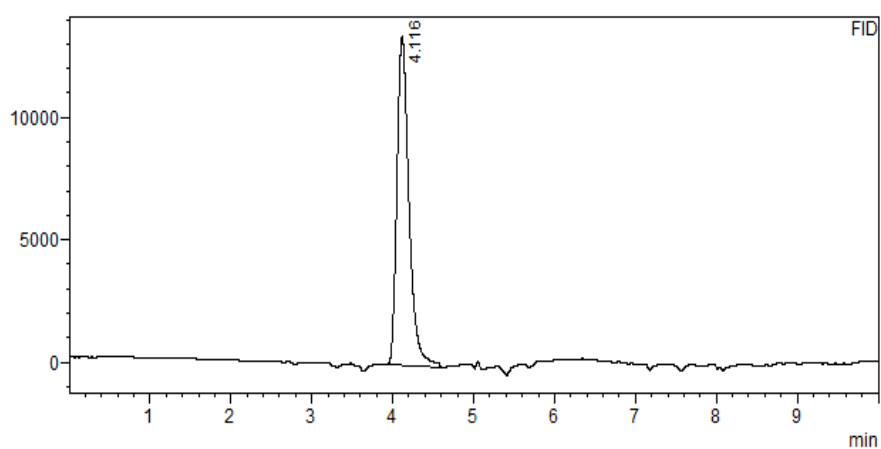
Figure S6. GC spectrum of the gas mixture obtained in Table 1, entry 2.

==== Shimadzu LabSolutions Analysis Report ====

Sample Name : 检测2
 Sample ID :
 Data Filename : CRR-23-50ul-3.gcd
 Method Filename : CO-BQ-2.gcm
 Batch Filename :
 Date Acquired : 2022/12/11 15:06:13
 Date Processed : 2023/2/21 15:22:04

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uV



<Peak Table>

FID						
Peak#	Ret. Time	Area	Height	Conc.	Unit	Name
1	4.116	139739	13432	0.052	%	CO

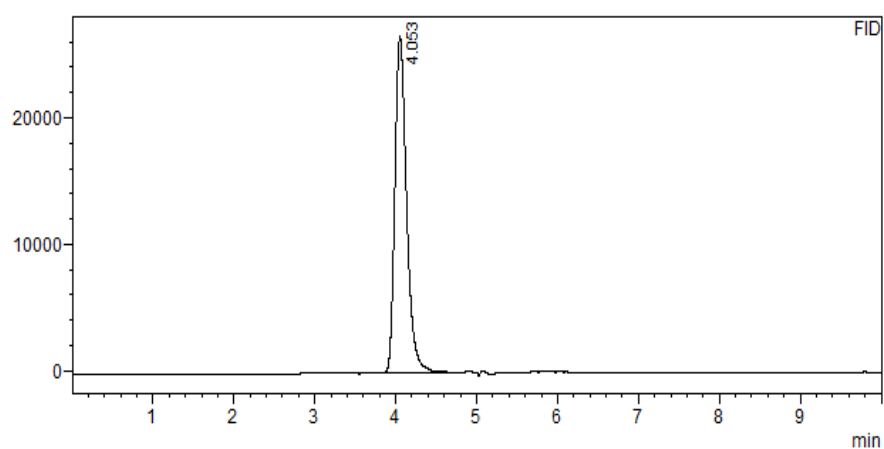
Figure S7. GC spectrum of the gas mixture obtained in Table 1, entry 3.

==== Shimadzu LabSolutions Analysis Report ====

Sample Name : 检测2
Sample ID :
Data Filename : CRR-41-50ul-2.gcd
Method Filename : CO-BQ-2.gcm
Batch Filename :
Date Acquired : 2023/1/9 21:56:52
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uV



<Peak Table>

FID						
Peak#	Ret. Time	Area	Height	Conc.	Unit	Name
1	4.053	268828	26622	0.099	%	CO

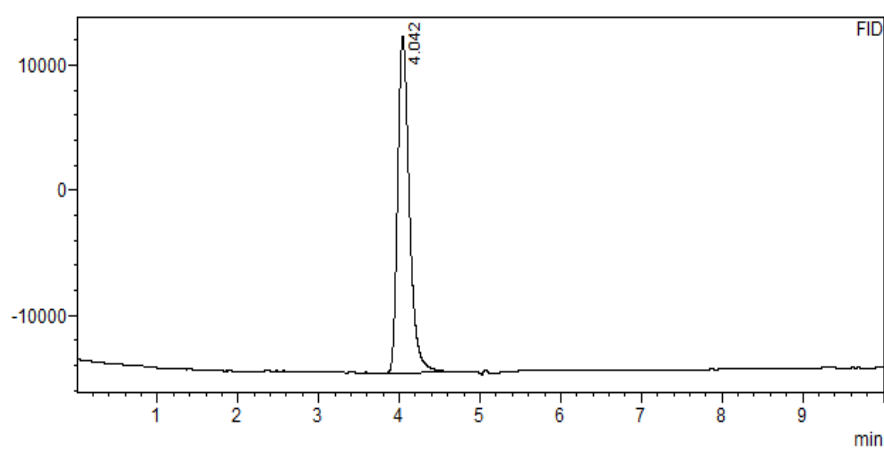
Figure S8. GC spectrum of the gas mixture obtained in Table 1, entry 4.

==== Shimadzu LabSolutions Analysis Report ====

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Sample ID :
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uv



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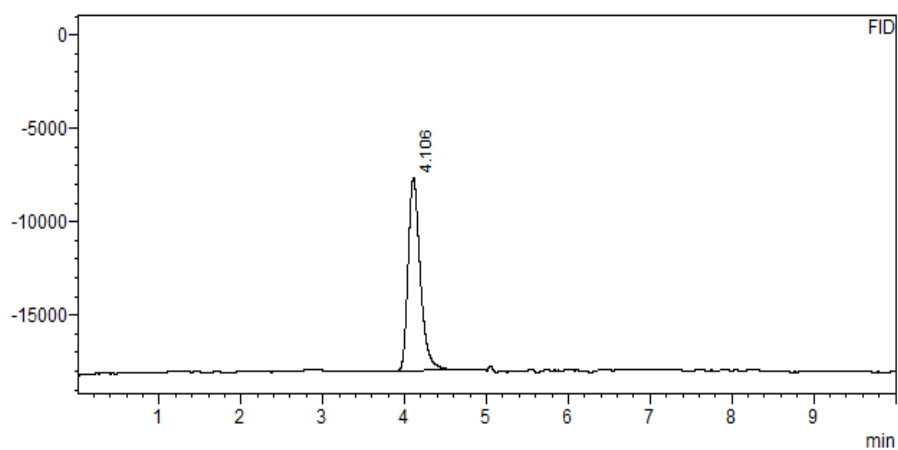
FID						
Peak#	Ret. Time	Area	Height	Conc.	Unit	Name
1	4.042	273093	26867	0.101	%	CO

Figure S9. GC spectrum of the gas mixture obtained in Table 1, entry 5.

==== Shimadzu LabSolutions Analysis Report ====

Sample Name : 检测2
Sample ID :
Data Filename : CRR-20-50ul-1.gcd
Method Filename : CO-BQ-2.gcm
Batch Filename :
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1	4.106	106575	10329	0.039	%	CO

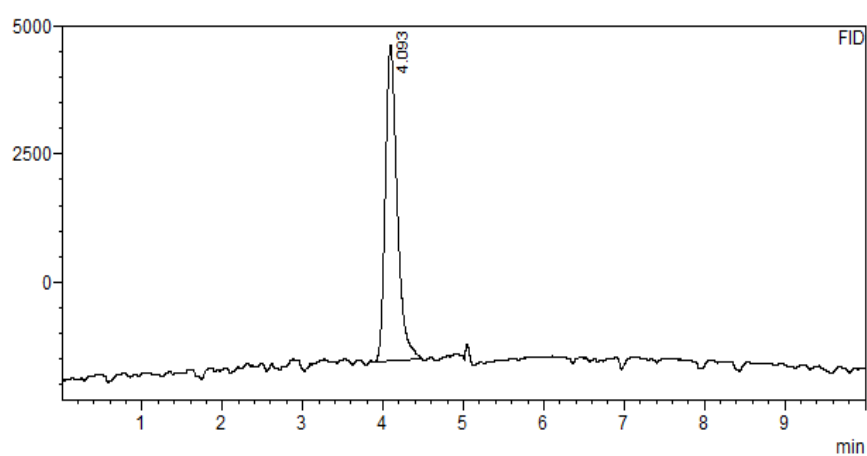
Figure S10. GC spectrum of the gas mixture obtained in Table 1, entry 6.

==== Shimadzu LabSolutions Analysis Report ====

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Sample ID :
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Method Filename : CO-BQ-2.gcm
Batch Filename :
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uV



<Peak Table>

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Peak#	Ret. Time	Area	Height	Conc.	Unit	Name
1	4.093	63121	6138	0.023	%	CO

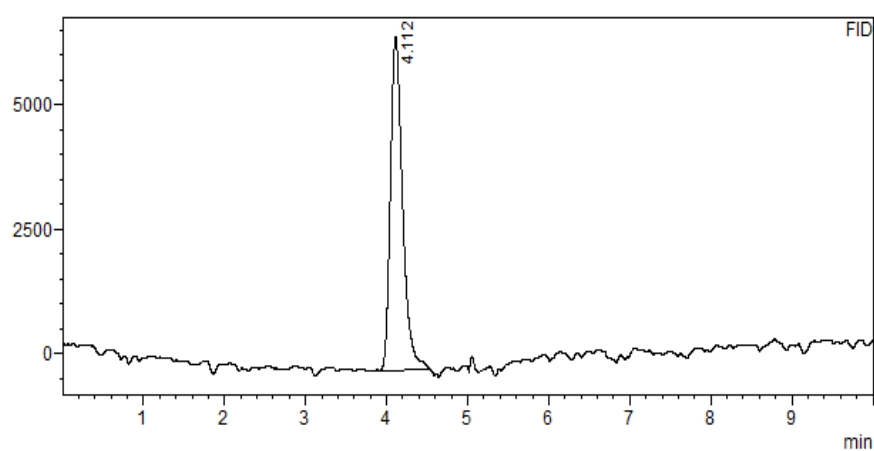
Figure S11. GC spectrum of the gas mixture obtained in Table 1, entry 7.

==== Shimadzu LabSolutions Analysis Report ====

Sample Name : 检测2
Sample ID :
Data Filename : CRR-25-50ul-2.gcd
Method Filename : CO-BQ-2.gcm
Batch Filename :
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Date Processed : 2023/2/21 15:30:59

<Chromatogram>

uV



<Peak Table>

FID						
Peak#	Ret. Time	Area	Height	Conc.	Unit	Name
1	4.112	69991	6679	0.026	%	CO

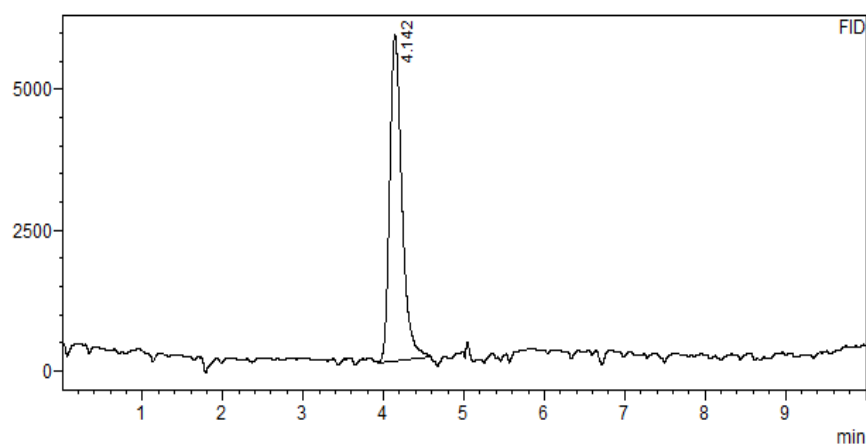
Figure S12. GC spectrum of the gas mixture obtained in Table 1, entry 8.

==== Shimadzu LabSolutions Analysis Report ====

Sample Name : 检测2
Sample ID :
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Method Filename : CO-BQ-2.gcm
Batch Filename :
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uV



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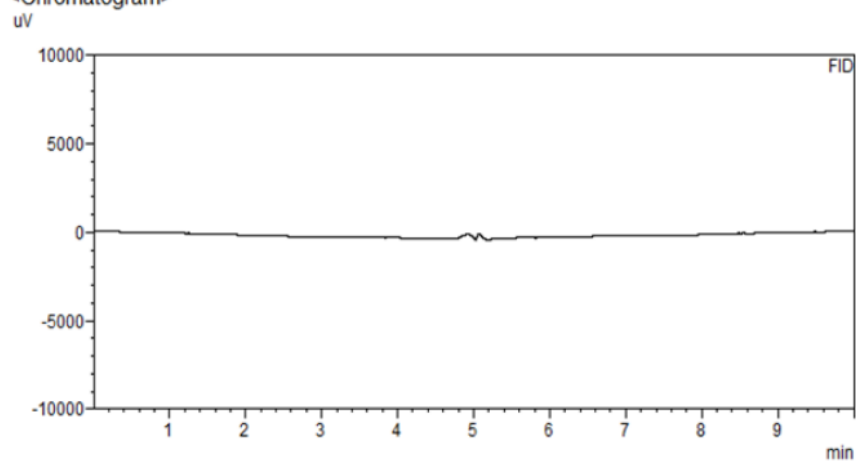
FID						
Peak#	Ret. Time	Area	Height	Conc.	Unit	Name
1	4.142	60793	5777	0.022	%	CO

Figure S13. GC spectrum of the gas mixture obtained in Table 1, entry 9.

==== Shimadzu LabSolutions Analysis Report ====

Sample Name : 检测2
Sample ID :
Data Filename : NoCO2-2.gcd
Method Filename : CO2-TEST-20200101.gcm
Batch Filename :
Date Acquired : 2023/2/25 22:15:45
Date Processed : 2023/2/25 22:36:19

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<Peak Table>

FID

Figure S14. GC spectrum of the gas mixture for photoreduction in the absence of CO₂.

The figure displays the ^1H NMR spectrum of poly(2,2,5-trimethyl-6-oxoheptanoate) in CDCl_3 . The x-axis represents the chemical shift δ in ppm, ranging from 6.5 to -0.5. The spectrum shows several distinct signals corresponding to different proton environments in the polymer chain.

Chemical Structures and Proton Assignments:

- Top structure:** A segment of the polymer chain showing the repeating unit with protons labeled A through G. A carbonyl group is present, and the chain is terminated with dashed lines.
- Middle structure:** A segment of the polymer chain showing the repeating unit with protons labeled a through h. A carbonyl group is present, and the chain is terminated with dashed lines.
- Bottom structure:** A segment of the polymer chain showing the repeating unit with protons labeled i through n. A carbonyl group is present, and the chain is terminated with dashed lines.

Peak Assignments and Integration:

- 6.000 ppm:** A sharp singlet corresponding to the carbonyl protons (A, B, C, D, E, F, G, H, I, J, K, L, M, N, O, P).
- 5.455 and 5.414 ppm:** Two small peaks corresponding to the methine protons (a, b, c, d, e, f, g, h, i, j, k, l, m, n, o, p).
- 2.686 ppm:** A peak corresponding to the methylene protons (B, F).
- 2.385 ppm:** A peak corresponding to the methylene protons (C, G).
- 2.095 and 2.036 ppm:** Two small peaks corresponding to the methine protons (a, b, c, d, e, f, g, h, i, j, k, l, m, n, o, p).
- 1.613 ppm:** A peak corresponding to the methylene protons (B, F).
- 1.568 ppm:** A peak corresponding to the methylene protons (C, G).
- 1.491 ppm:** A peak corresponding to the methylene protons (B, F).
- 1.342 ppm:** A peak corresponding to the methylene protons (C, G).
- 1.194 ppm:** A peak corresponding to the methylene protons (B, F).
- 0.981, 0.967, and 0.953 ppm:** Three small peaks corresponding to the methyl protons (i, b, c, d, e, f, g, h, i, j, k, l, m, n, o, p).

Integration values:

- 0.03 (for 5.455 and 5.414 ppm)
- 0.04 (for 2.686 ppm)
- 1.00 (for 2.385 ppm)
- 0.09 (for 2.095 and 2.036 ppm)
- 2.07 (for 1.613 ppm)
- 49.37 (for 1.568 ppm)
- 0.29 (for 1.491 ppm)

The figure displays a ^{13}C NMR spectrum of poly(2,2,4,4-tetramethyl-5-oxo-1,3-dioxane). The x-axis represents the chemical shift δ in ppm, ranging from -20 to 210. The spectrum shows several distinct peaks corresponding to different carbon environments in the polymer structure.

Chemical structures are provided to illustrate the assignments:

- Top structure:** A cyclic dioxane ring with two carbonyl groups. Carbons are labeled A (carbonyl), B (CH₂), and C (CH₂).
- Second structure:** A linear chain segment with carbonyl groups. Carbons are labeled E (carbonyl), F (CH₂), G (CH₂), H (CH₂), and I (CH₂).
- Third structure:** A branched chain segment. Carbons are labeled a (CH₂), b (CH), c (CH₂), d (CH₂), e (CH₂), f (CH₂), g (CH₂), h (CH₂), and i (CH₂).
- Fourth structure:** A vinyl group. Carbons are labeled j (CH₂), k (CH), and m (CH₂).
- Fifth structure:** A carbonyl group. Carbons are labeled n (CH₂), o (C=O), and p (CH₂).
- Sixth structure:** A chlorinated carbon. Carbons are labeled r (CH), s (CH₂), and t (CH₂).

Peak assignments and chemical shifts are summarized in the table below:

Assignment	Chemical Shift δ (ppm)
A	210.628
o	130.608
74.090	74.090
B	42.654
a	29.630
C	23.925

S16

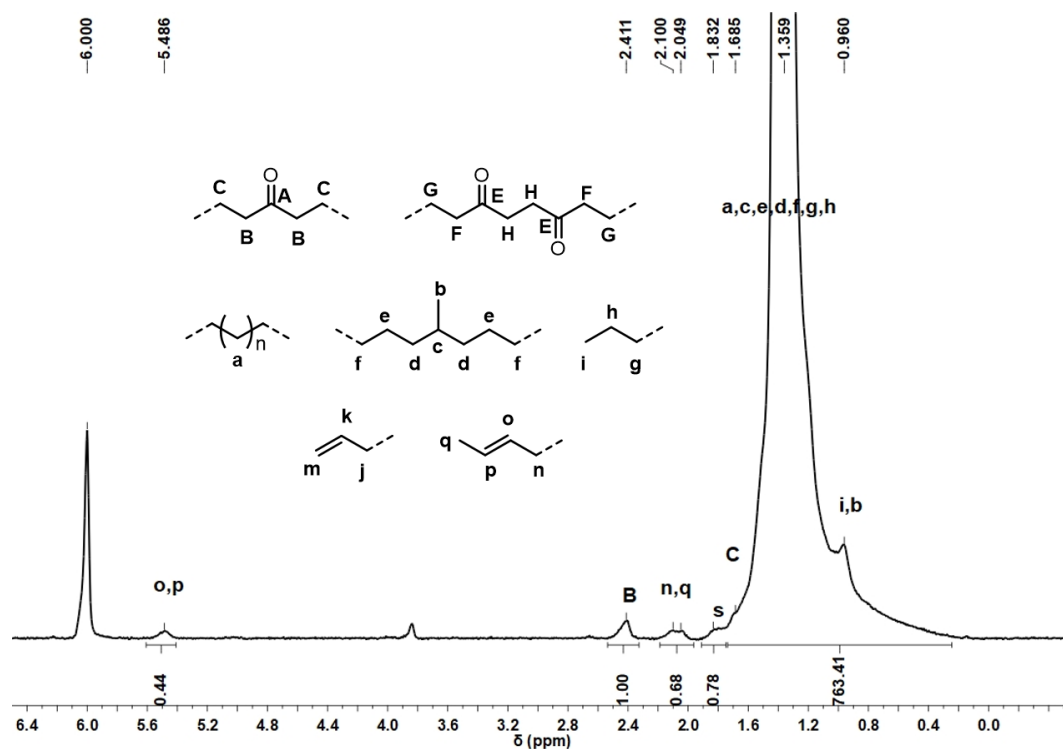


Figure S17. ^1H NMR spectrum of the polymer obtained in Table 2, entry 2 (1,1,2,2-tetrachloroethane- d_2 , 400 MHz, 120 $^\circ\text{C}$).

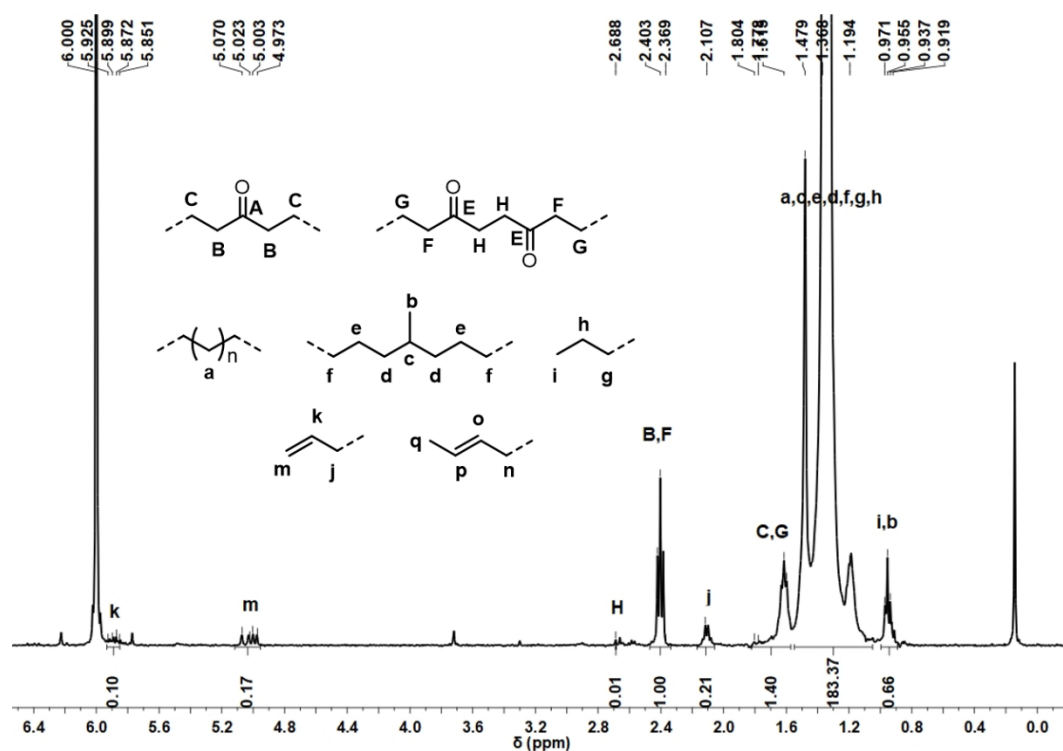


Figure S18. ^1H NMR spectrum of the polymer obtained in Table 2, entry 3 (1,1,2,2-tetrachloroethane- d_2 , 400 MHz, 120 $^\circ\text{C}$).

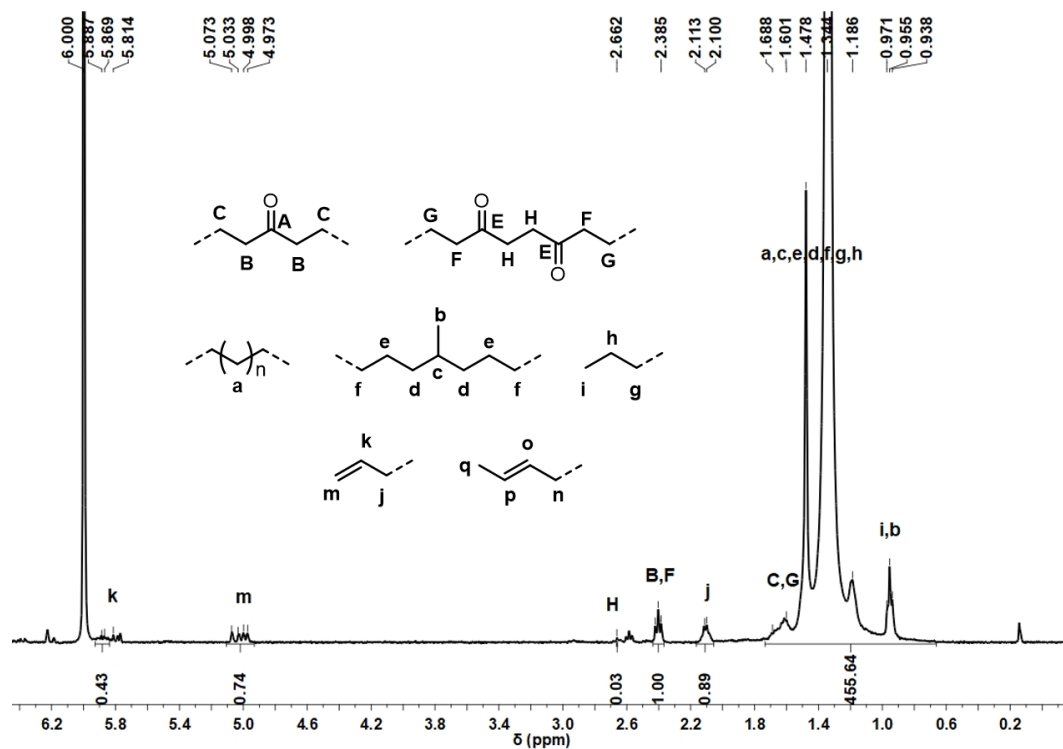


Figure S19. ^1H NMR spectrum of the polymer obtained in Table 2, entry 4 (1,1,2,2-tetrachloroethane- d_2 , 400 MHz, 120 $^\circ\text{C}$).

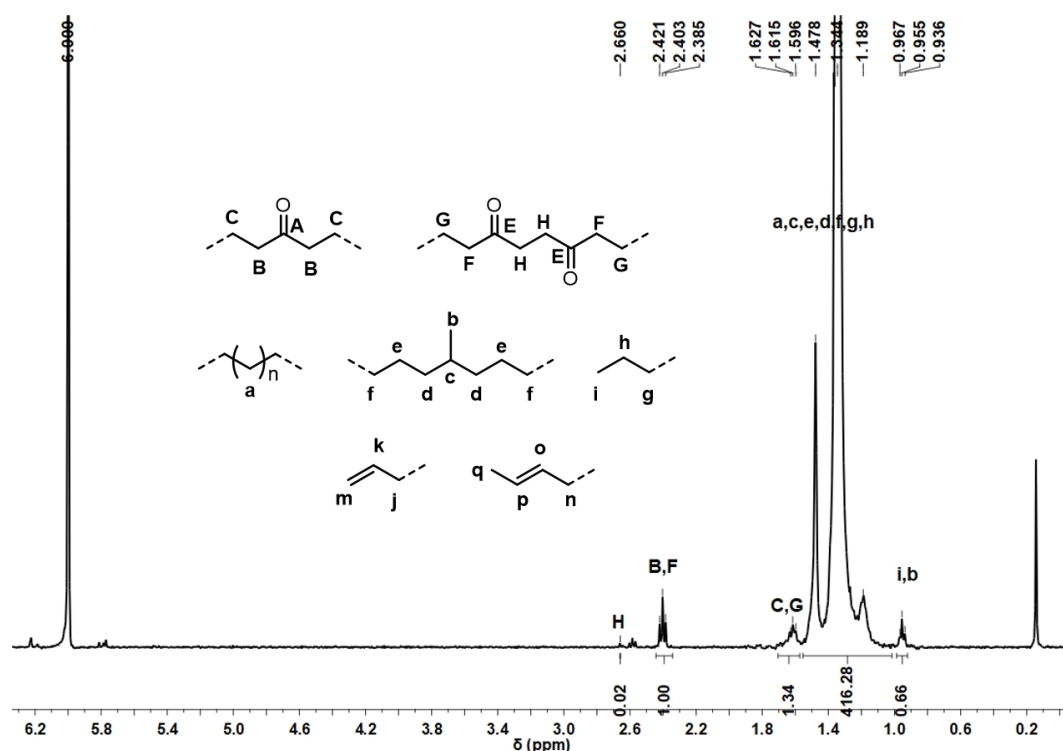


Figure S20. ^1H NMR spectrum of the polymer obtained in Table 2, entry 5 (1,1,2,2-tetrachloroethane- d_2 , 400 MHz, 120 $^\circ\text{C}$).

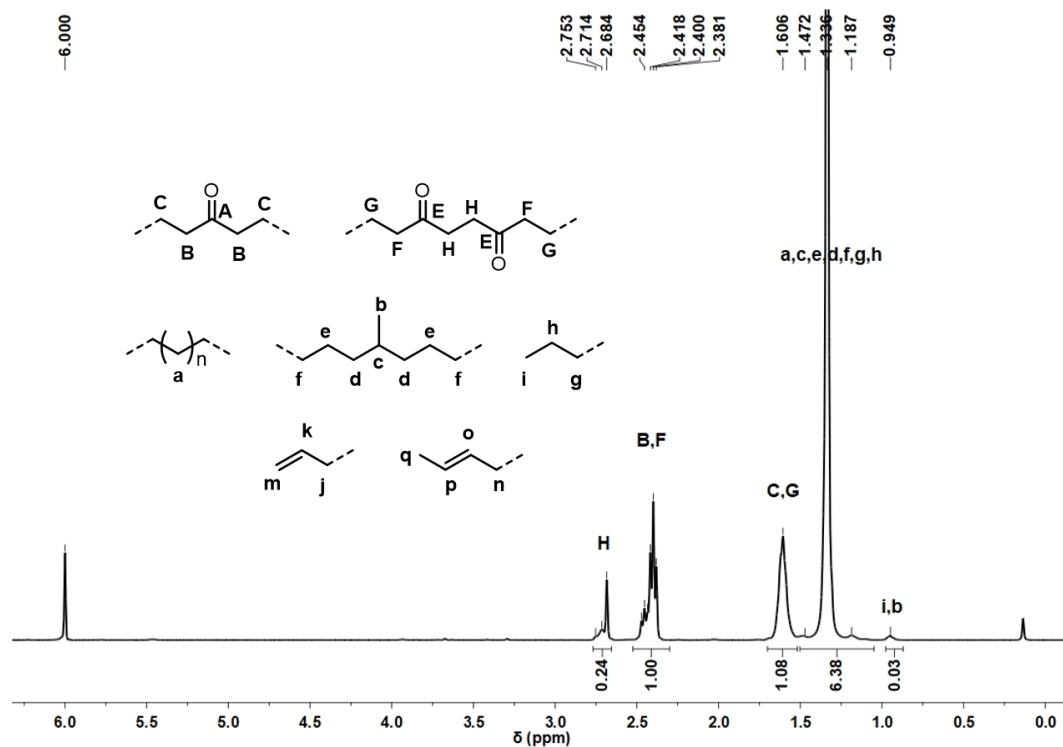


Figure S21. ^1H NMR spectrum of the polymer obtained in Table 2, entry 7 (1,1,2,2-tetrachloroethane- d_2 , 400 MHz, 120 $^\circ\text{C}$).

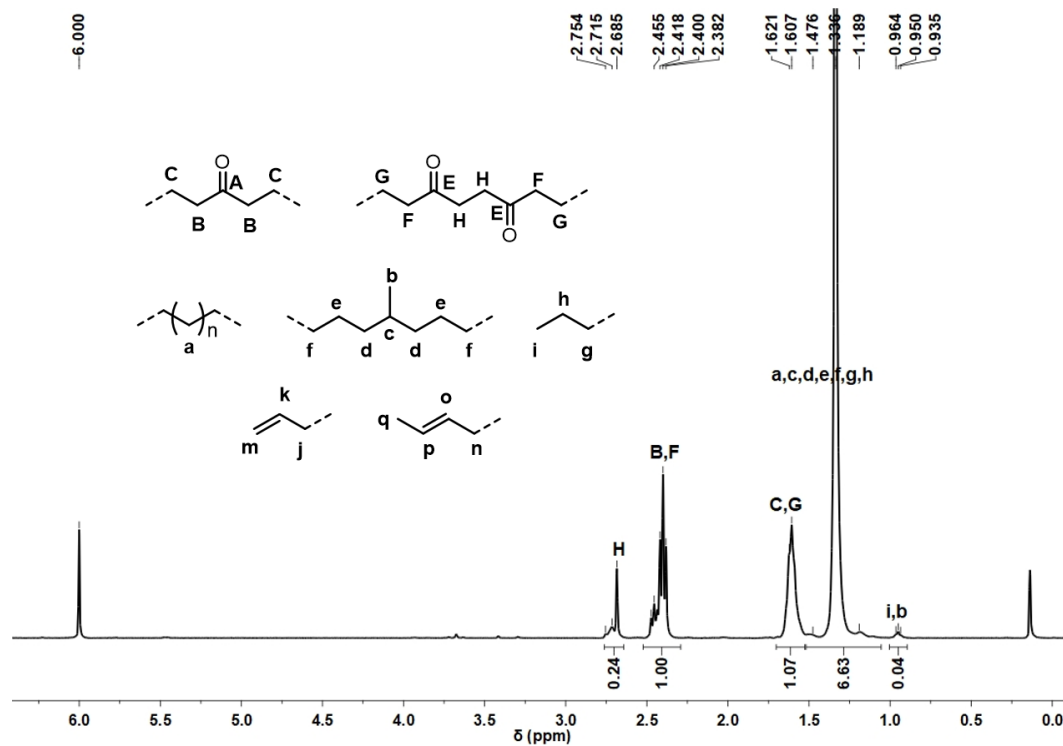


Figure S22. ^1H NMR spectrum of the polymer obtained in Table 2, entry 8 (1,1,2,2-tetrachloroethane- d_2 , 400 MHz, 120 $^\circ\text{C}$).

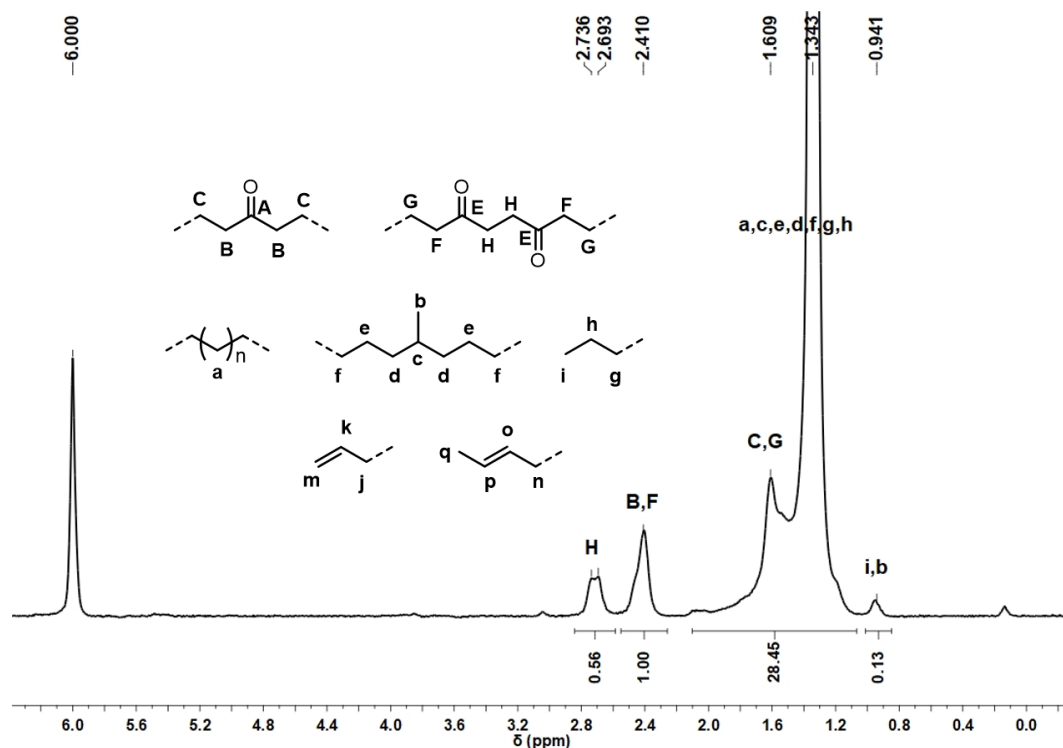


Figure S23. ^1H NMR spectrum of the polymer obtained in Table 2, entry 9 (1,1,2,2-tetrachloroethane- d_2 , 400 MHz, 120 $^\circ\text{C}$).

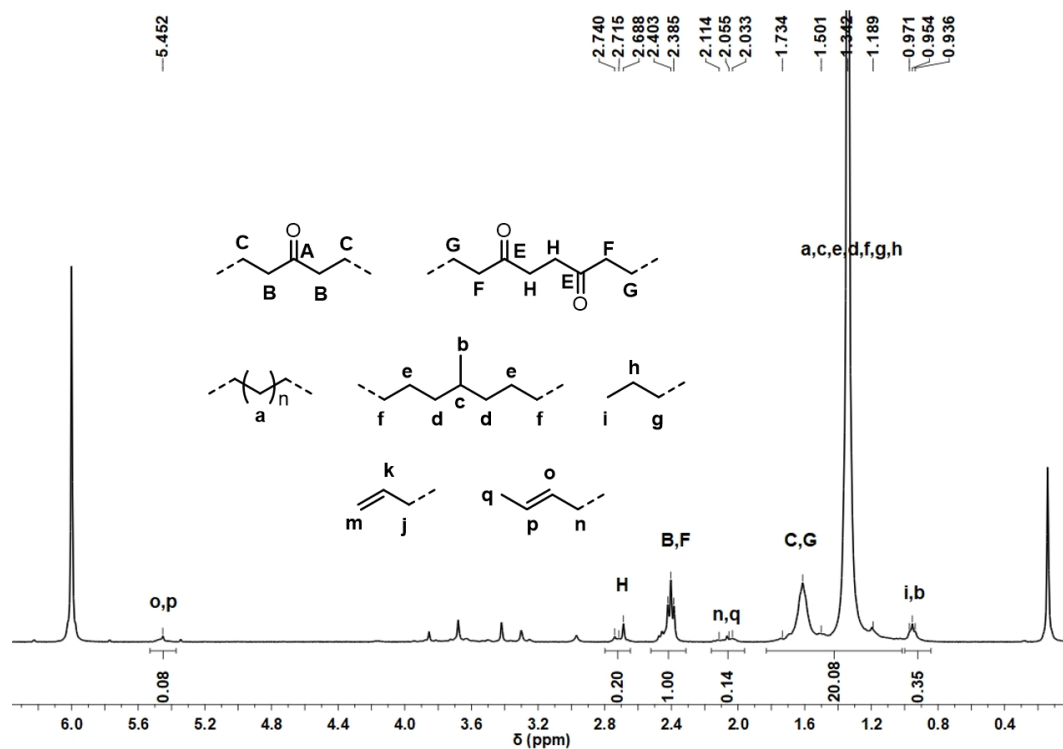


Figure S24. ^1H NMR spectrum of the polymer obtained in Table 2, entry 10 (1,1,2,2-tetrachloroethane- d_2 , 400 MHz, 120 $^\circ\text{C}$).

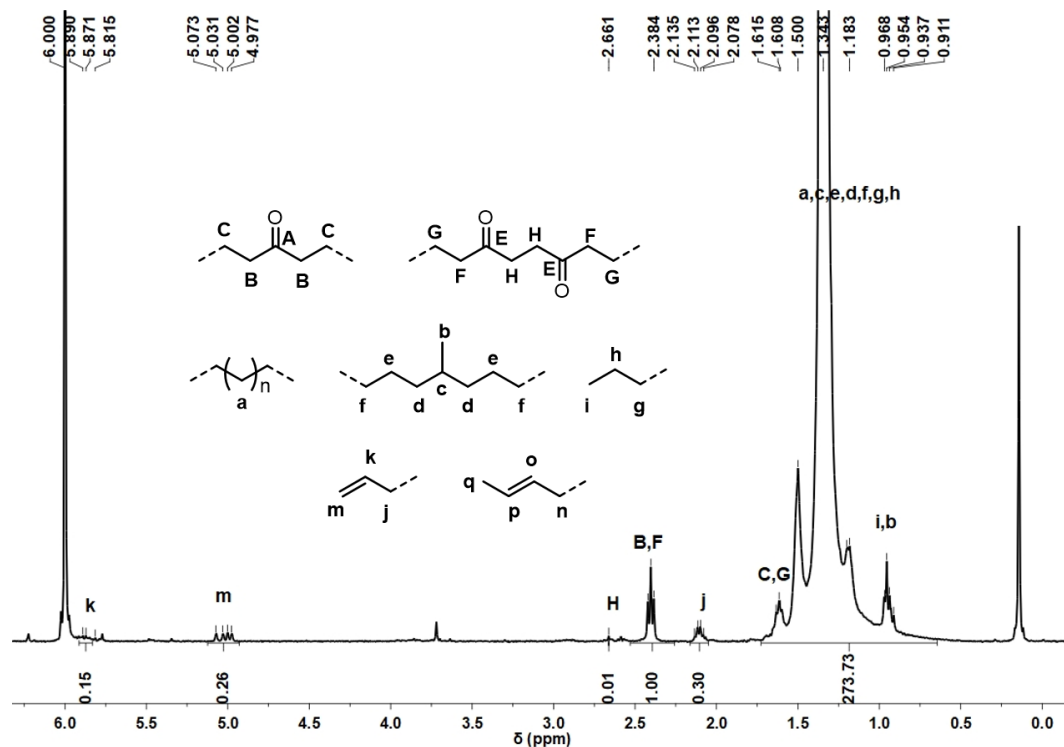


Figure S25. ^1H NMR spectrum of the polymer obtained in Table 2, entry 11 (1,1,2,2-tetrachloroethane- d_2 , 400 MHz, 120 $^\circ\text{C}$).

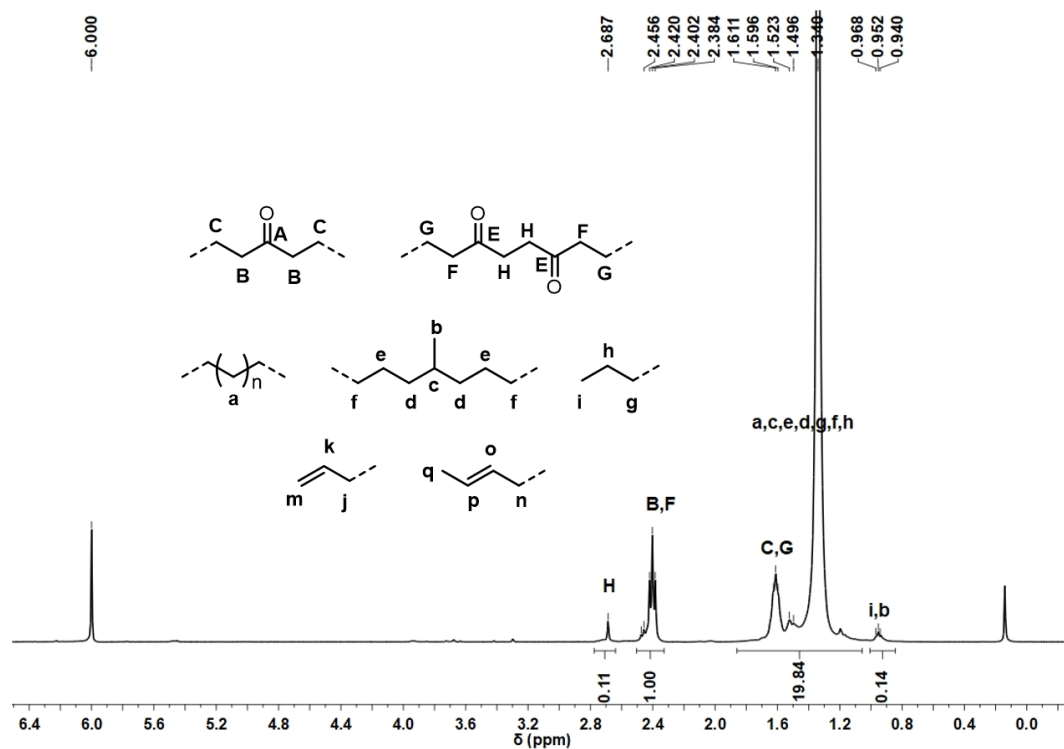


Figure S26. ^1H NMR spectrum of the polymer obtained in Table 2, entry 12 (1,1,2,2-tetrachloroethane- d_2 , 400 MHz, 120 $^\circ\text{C}$).

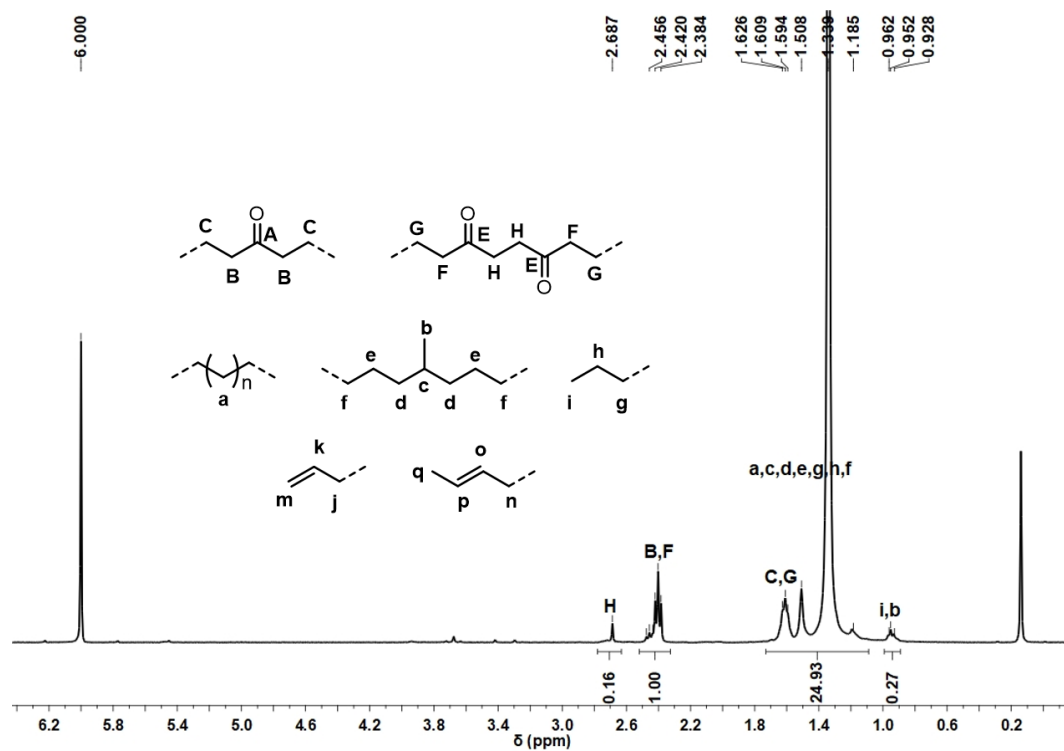


Figure S27. ^1H NMR spectrum of the polymer obtained in Table 2, entry 13 (1,1,2,2-tetrachloroethane- d_2 , 400 MHz, 120 $^\circ\text{C}$).

Copies of ATR-IR Spectra

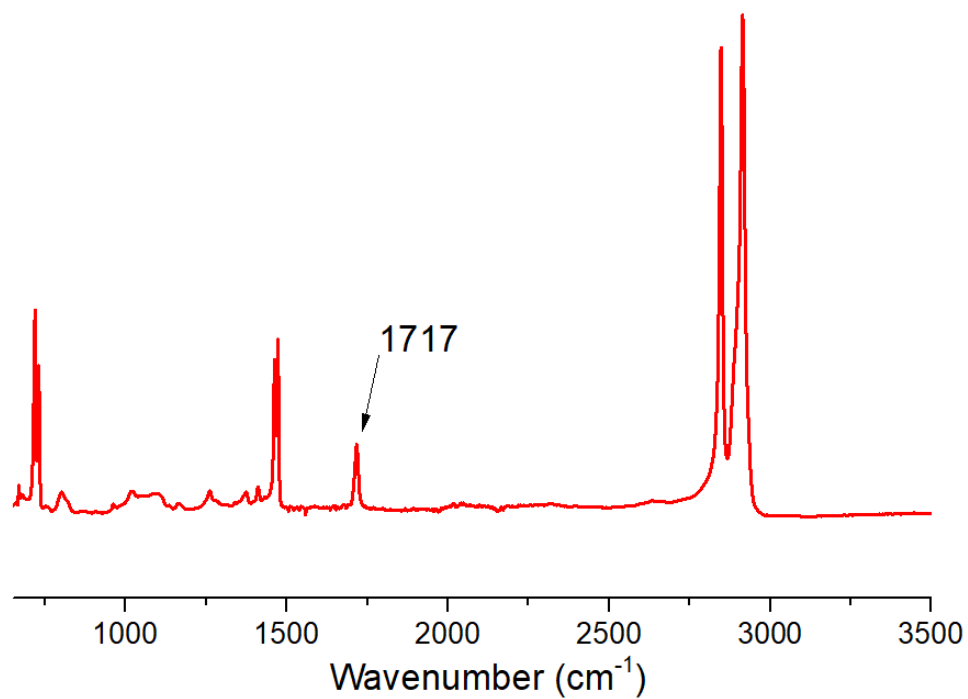


Figure S28. IR spectrum of the polymer obtained in Table 2, entry 1.

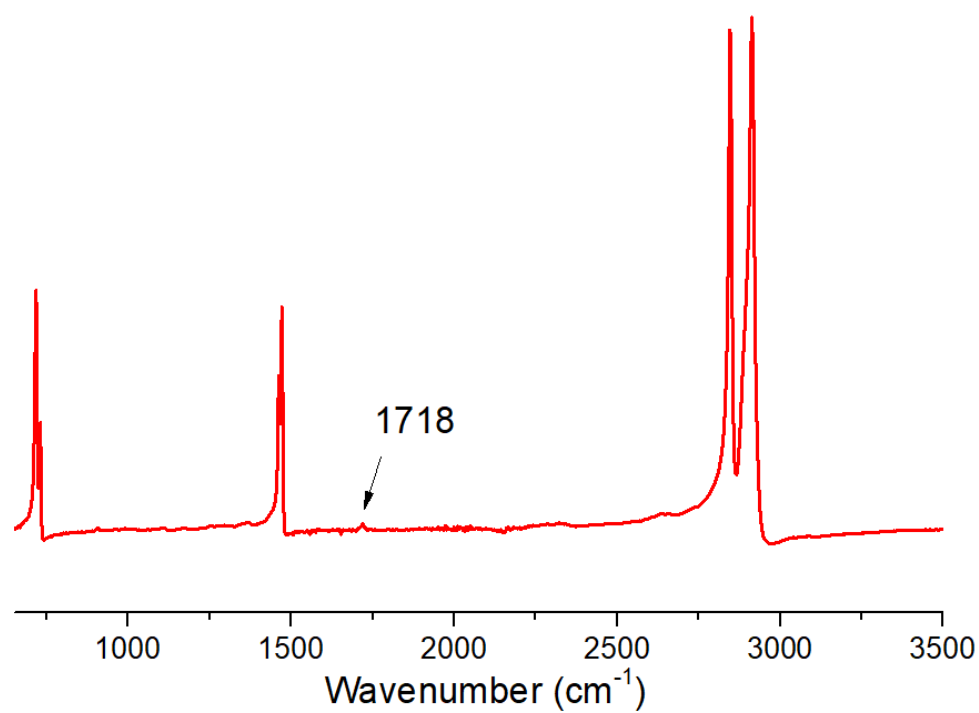


Figure S29. IR spectrum of the polymer obtained in Table 2, entry 2.

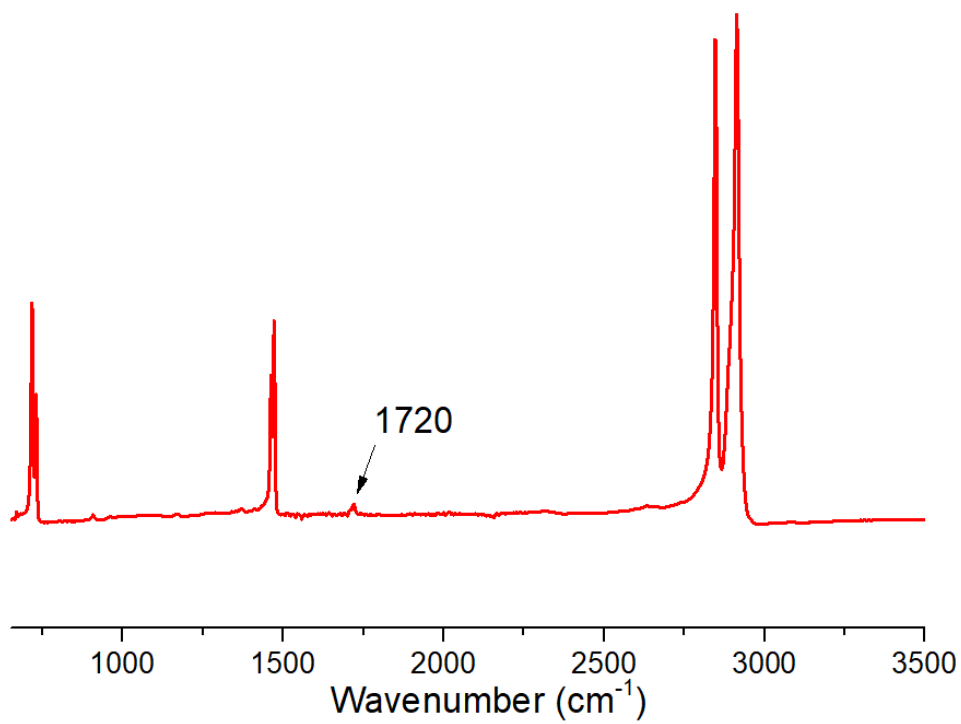


Figure S30. IR spectrum of the polymer obtained in Table 2, entry 3.

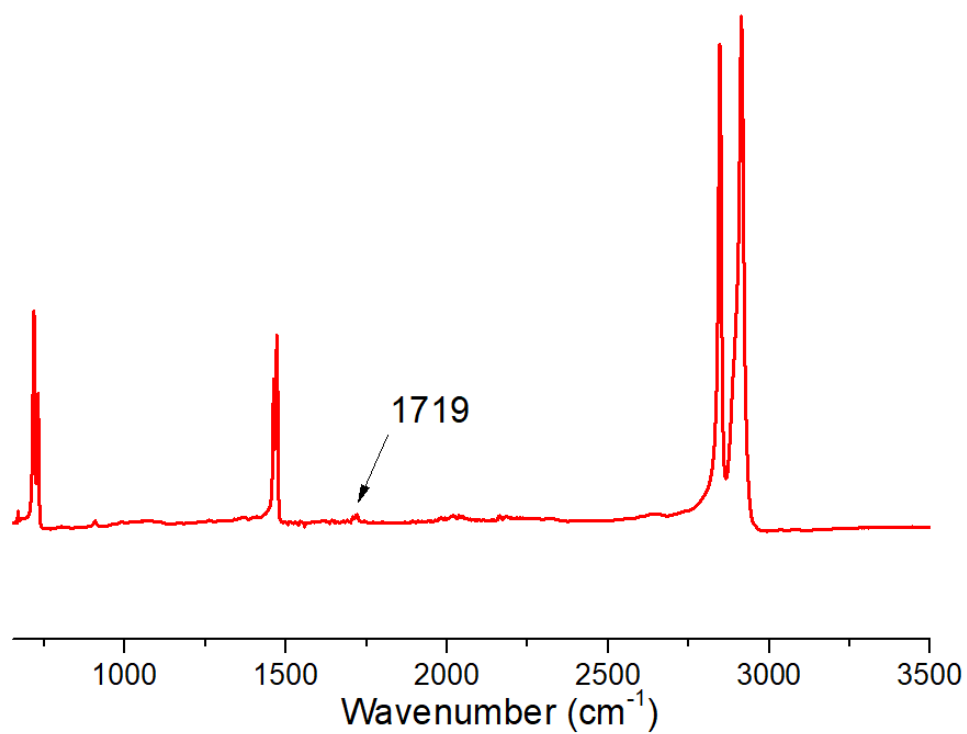


Figure S31. IR spectrum of the polymer obtained in Table 2, entry 4.

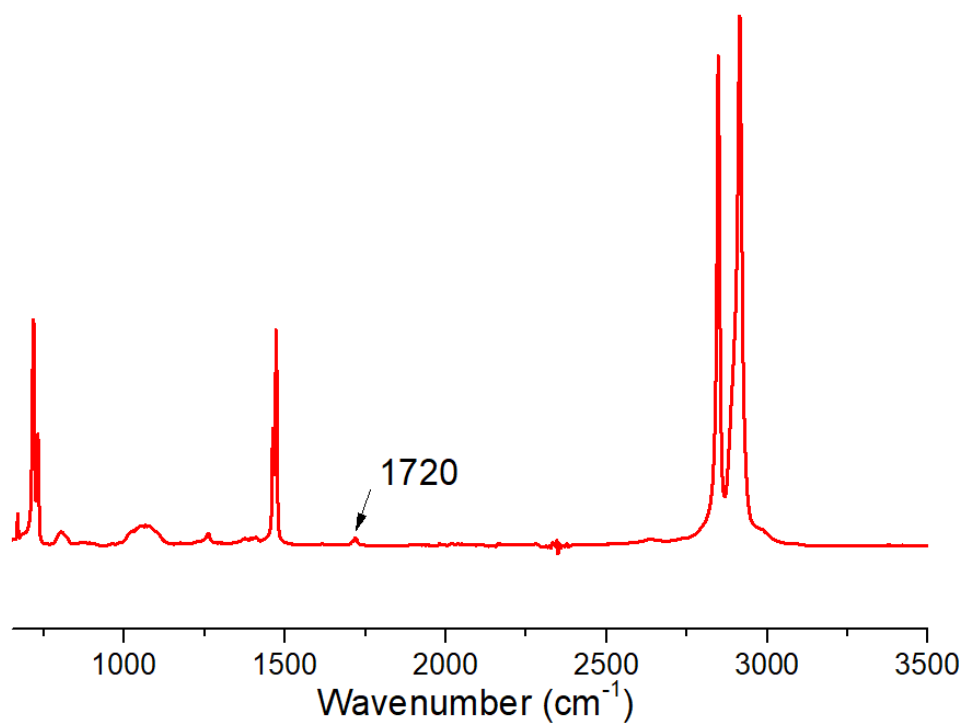


Figure S32. IR spectrum of the polymer obtained in Table 2, entry 5.

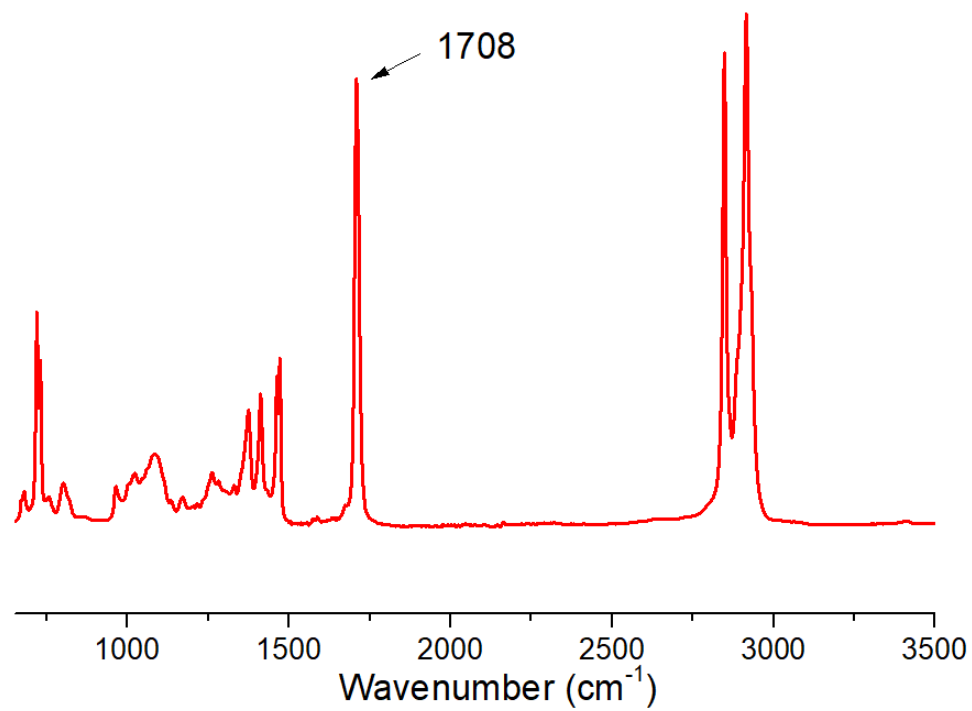


Figure S33. IR spectrum of the polymer obtained in Table 2, entry 7.

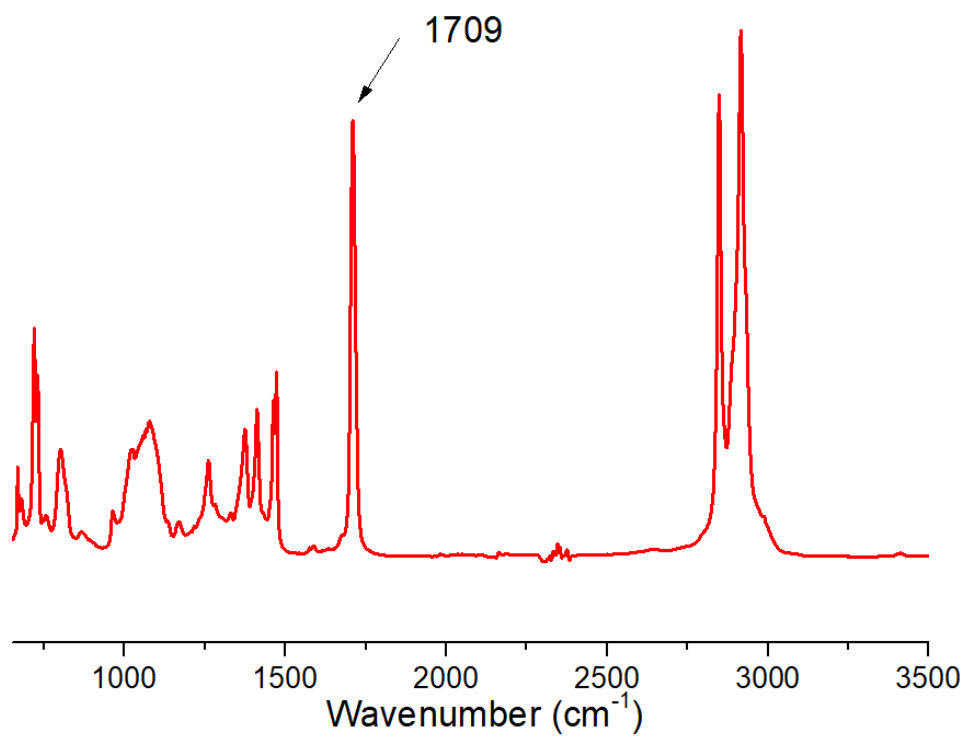


Figure S34. IR spectrum of the polymer obtained in Table 2, entry 8.

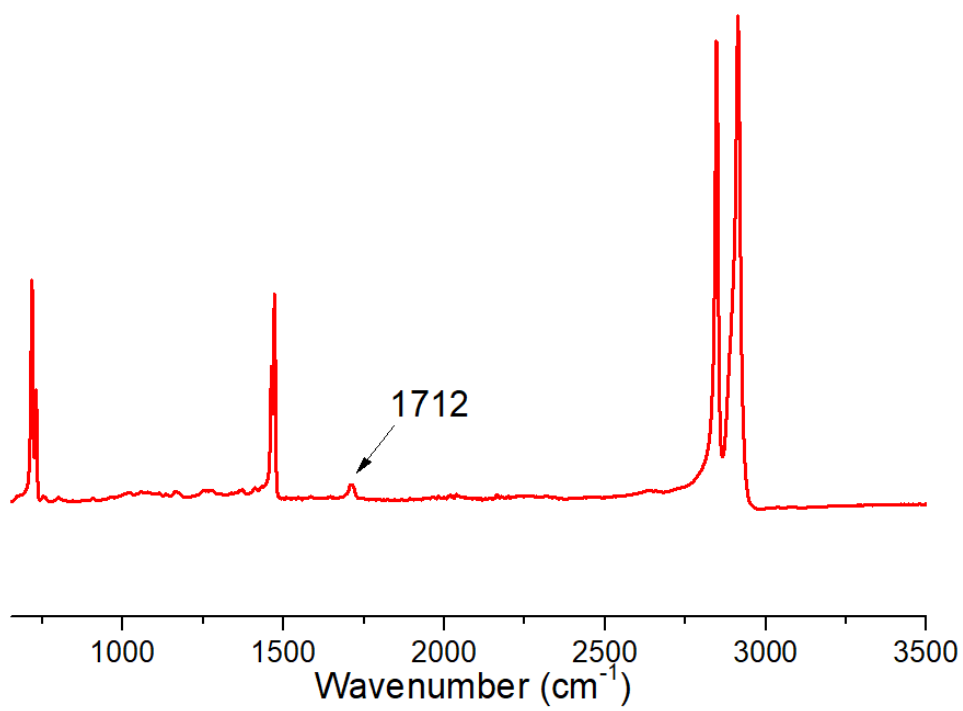


Figure S35. IR spectrum of the polymer obtained in Table 2, entry 9.

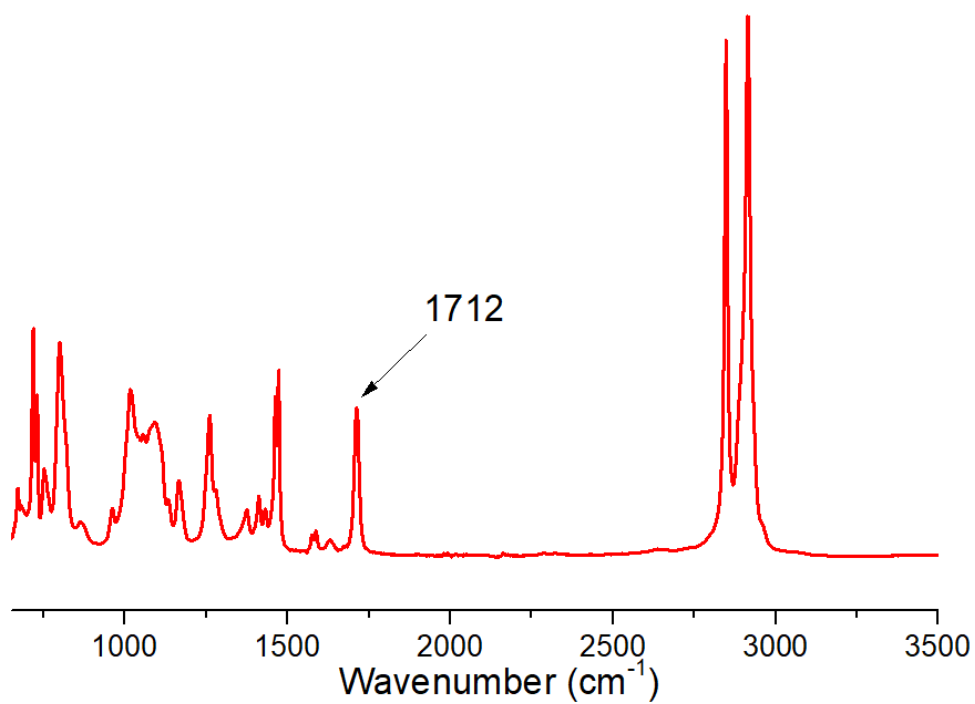


Figure S36. IR spectrum of the polymer obtained in Table 2, entry 10.

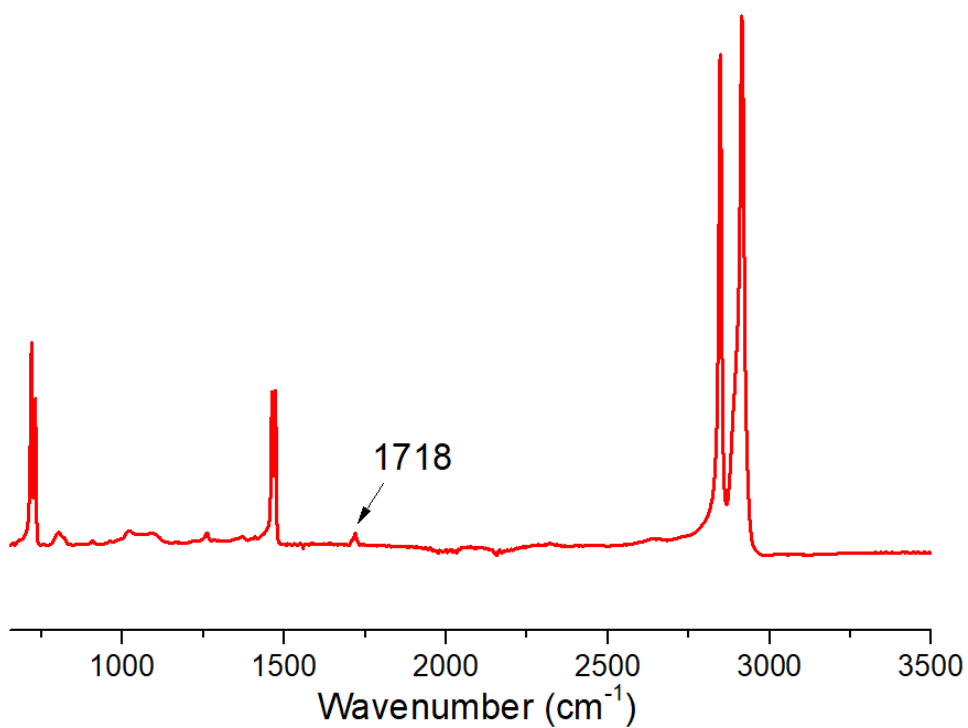


Figure S37. IR spectrum of the polymer obtained in Table 2, entry 11.

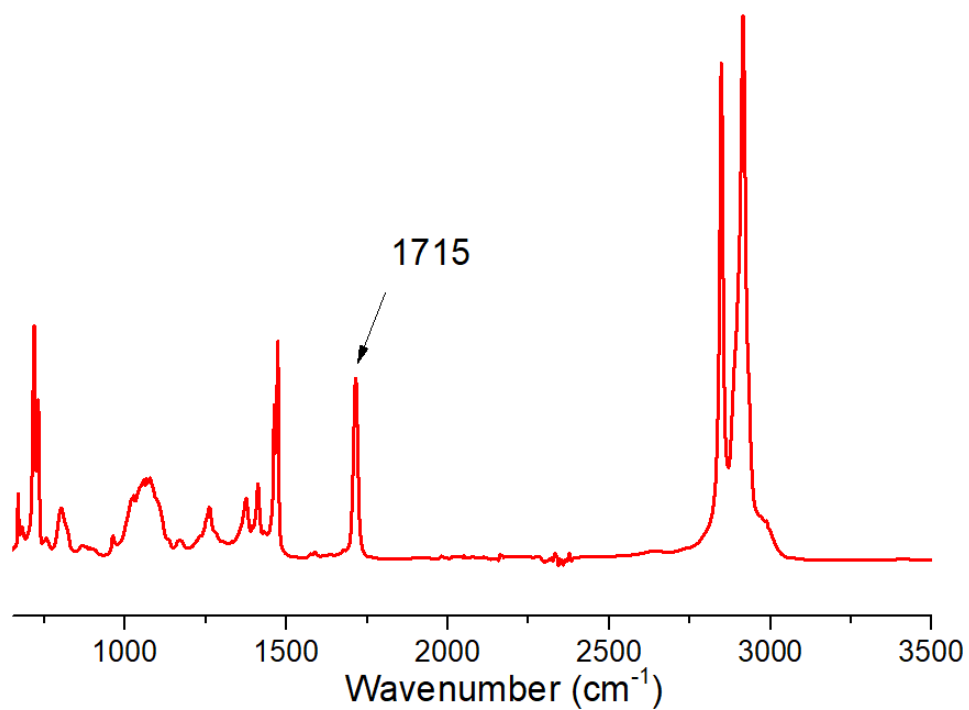


Figure S38. IR spectrum of the polymer obtained in Table 2, entry 12.

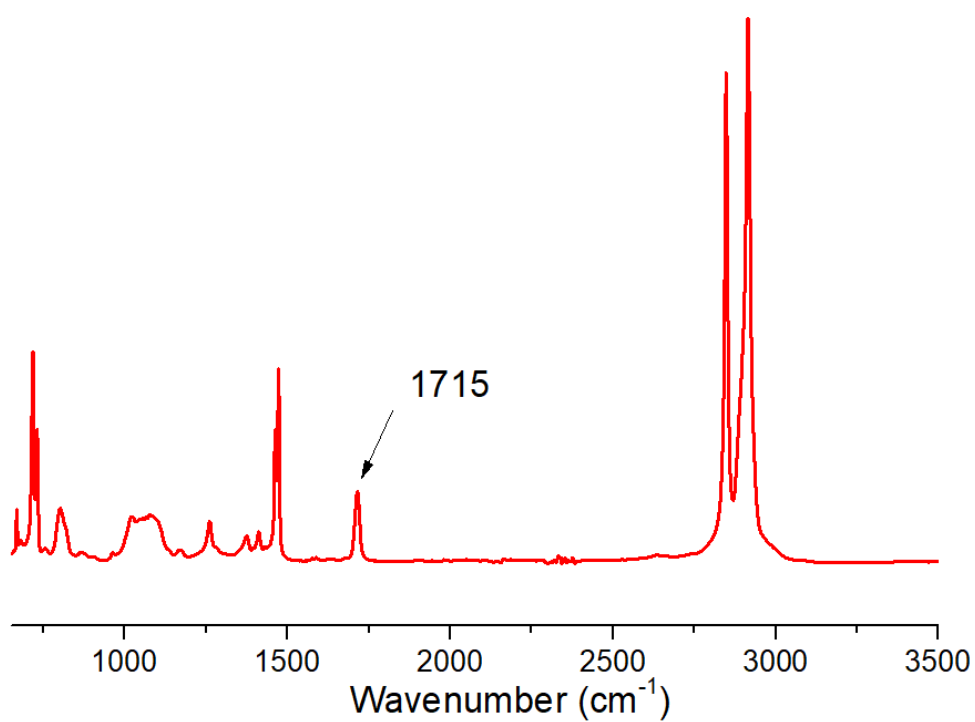


Figure S39. IR spectrum of the polymer obtained in Table 2, entry 13.

TGA curve and DSC Trace

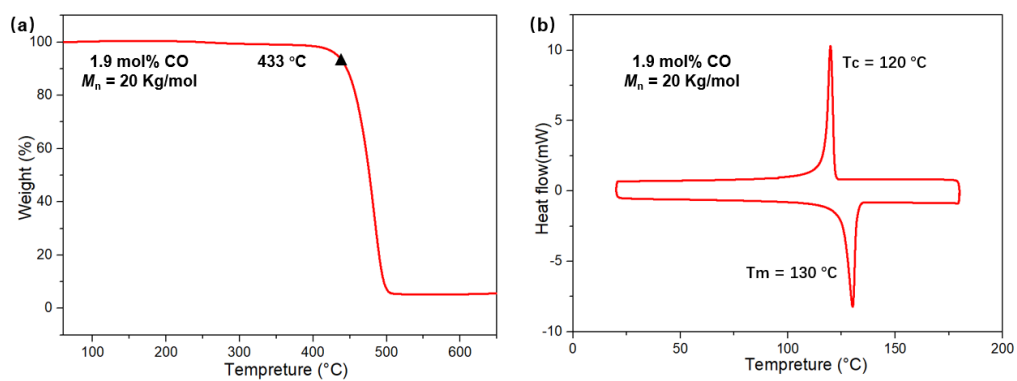


Figure S40. TGA curve (a) and DSC Trace (b) of the polymer obtained in Table 2, entry 1.

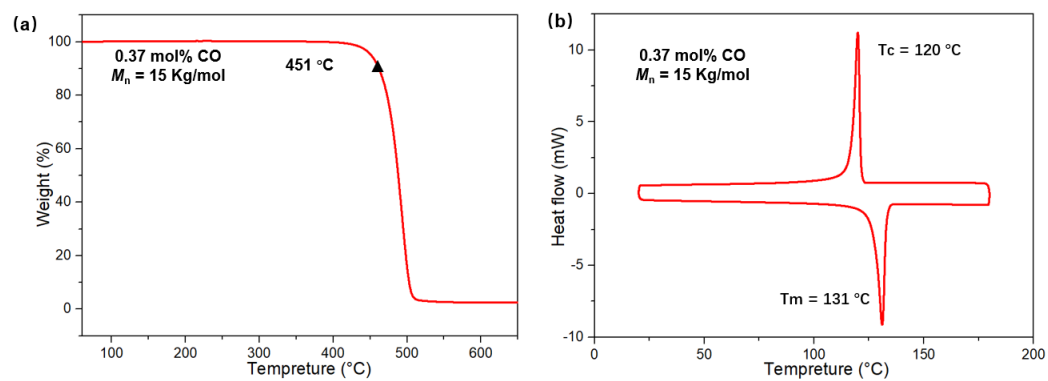


Figure S41. TGA curve (a) and DSC Trace (b) of the polymer obtained in Table 2, entry 11.

Copies of SEC Charts

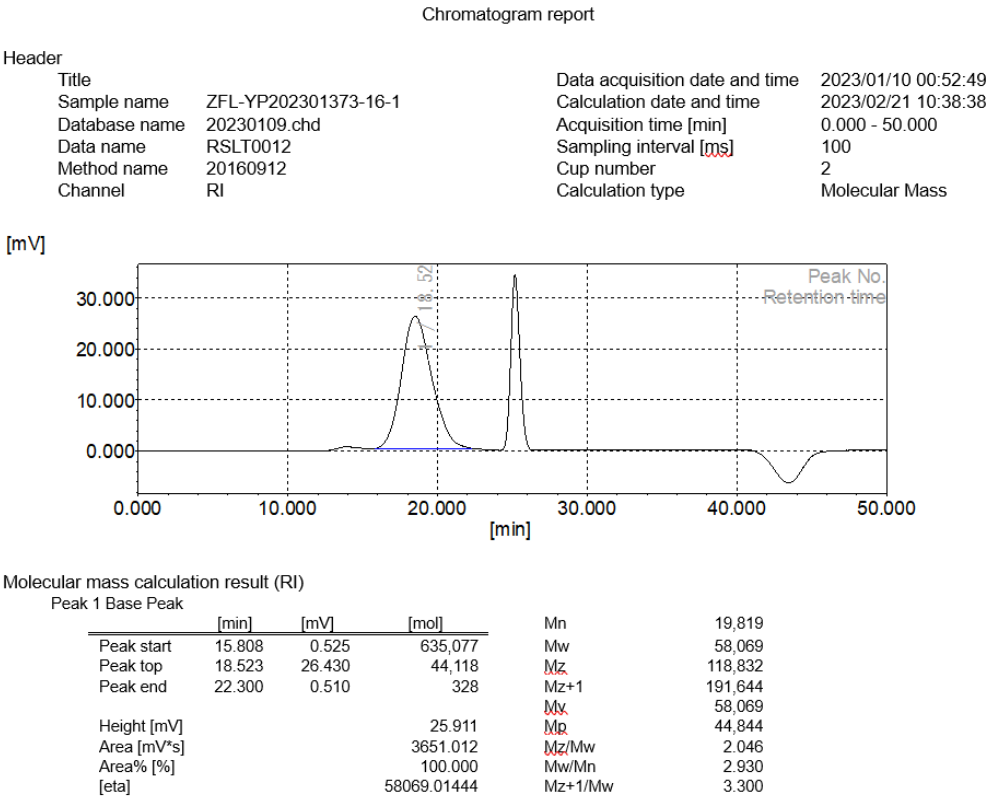
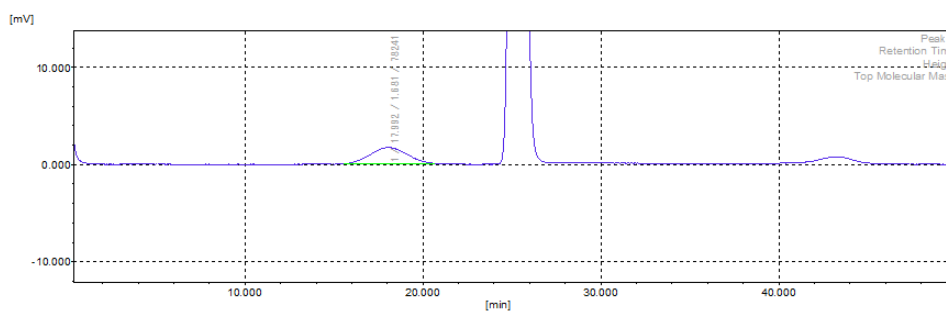


Figure S42. SEC chart of the polymer obtained in Table 2, entry 1.

Chromatogram report

Header

Title		Data acquisition date and time	2023/01/09 20:42:44
Sample name	ZFL-YP202301373-20-2	Calculation date and time	2023/02/13 15:35:24
Database name	20230109.chd	Acquisition time [min]	0.000 - 50.000
Data name	RSLT0007	Sampling interval [ms]	100
Method name	20160912	Cup number	8
Channel	RI	Calculation type	Molecular Mass



Molecular mass calculation result (RI)

Peak 1 Base Peak

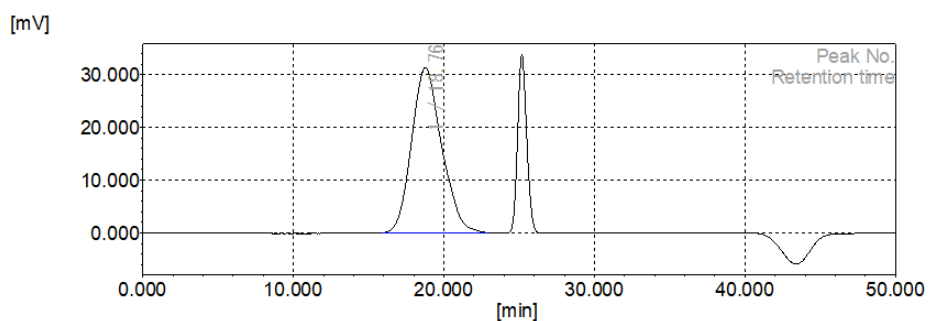
	[min]	[mV]	[mol]		
Peak start	15.442	0.027	899,893	Mn	38,437
Peak top	17.992	1.767	78,241	Mw	105,982
Peak end	21.672	0.061	1,155	Mz	215,339
				Mz+1	334,283
				Mx	105,982
Height [mV]			1.726	Mp	78,242
Area [mV*s]			253.227	Mz/Mw	2.032
Area% [%]			100.000	Mw/Mn	2.757
[eta]			105981.90143	Mz+1/Mw	3.154

Figure S43. SEC chart of the polymer obtained in Table 2, entry 2.

Chromatogram report

Header

Title		Data acquisition date and time	2023/01/09 21:32:45
Sample name	ZFL-YP202301373-21-1	Calculation date and time	2023/02/13 15:31:56
Database name	20230109.chd	Acquisition time [min]	0.000 - 50.000
Data name	RSLT0008	Sampling interval [ms]	100
Method name	20160912	Cup number	9
Channel	RI	Calculation type	Molecular Mass



Molecular mass calculation result (RI)

Peak 1 Base Peak

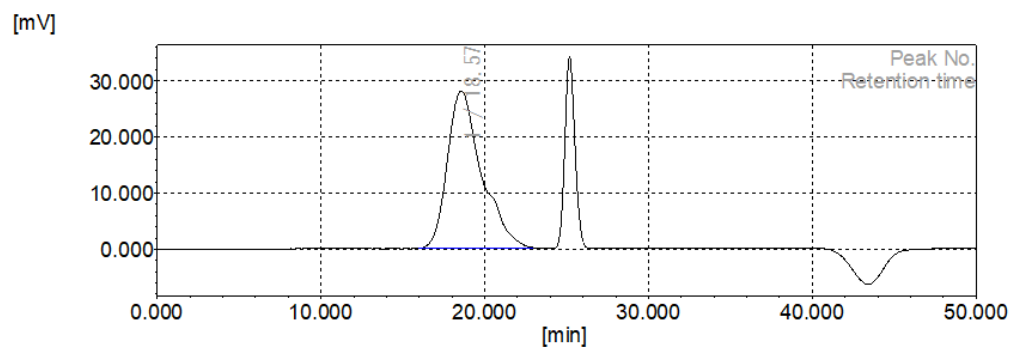
	[min]	[mV]	[mol]		
Peak start	15.877	0.016	596,719	Mn	13,602
Peak top	18.768	31.378	33,805	Mw	44,620
Peak end	22.903	0.048	52	Mz	93,479
				Mz+1	155,809
				Mv	44,620
Height [mV]			31.349	Mp	33,259
Area [mV*s]			4344.361	Mz/Mw	2.095
Area% [%]			100.000	Mw/Mn	3.280
[eta]			44620.38515	Mz+1/Mw	3.492

Figure S44. SEC chart of the polymer obtained in Table 2, entry 3.

Chromatogram report

Header

Title		Data acquisition date and time	2023/01/09 19:52:43
Sample name	ZFL-YP202301373-20-1	Calculation date and time	2023/02/20 17:15:55
Database name	20230109.chd	Acquisition time [min]	0.000 - 50.000
Data name	RSLT0006	Sampling interval [ms]	100
Method name	20160912	Cup number	7
Channel	RI	Calculation type	Molecular Mass



Molecular mass calculation result (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	15.955	0.164	555,911	Mn	10,050
Peak top	18.578	28.209	41,559	Mw	46,726
Peak end	22.982	0.268	39	Mz	96,690
				Mz+1	153,789
Height [mV]			28.006	Mv	46,726
Area [mV*s]			4059.546	Mp	42,243
Area% [%]			100.000	Mz/Mw	2.069
[eta]			46726.30346	Mw/Mn	4.650
				Mz+1/Mw	3.291

Figure S45. SEC chart of the polymer obtained in Table 2, entry 4.

Cirrus GPC Sample Injection Report

Generated by: Administrator

2023年2月22日 19:00

Workbook: D:\Cirrus Workbooks\PS-20220902\PS-20220902.plw

Sample Details

Sample Name: zfl-2

Acquired: 2023/2/22 16:54:54

By Analyst: Administrator

Batch Name: 2023_2_22

Concentration: 0.10 mg/ml Injection Volume: 200.0 ul K of Sample: 12.1000 Alpha of Sample: 0.7000

Analysis Using Method: PS Standard-20220815

Calibration Used: 2022/9/2 9:53:18

Calibration Type: Narrow Standard

Curve Fit Used: 3

K: 12.1000

Alpha: 0.7000

Calibration Curve: $y = 20.441758 - 2.418866x^1 + 0.141132x^2 - 0.003640x^3$

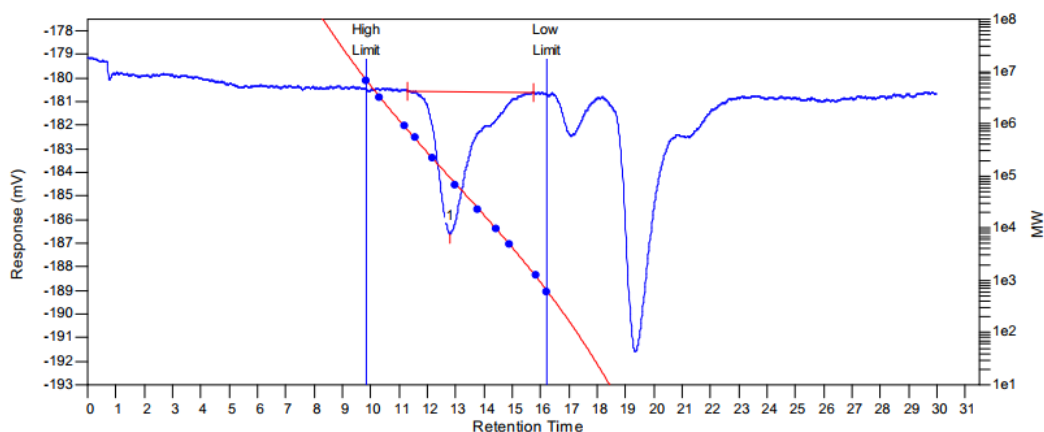
High Limit MW RT: 9.87 mins

Low Limit MW RT: 16.23 mins

Flow Marker RT: 0.00 mins

FRCF: 1.0000

FRM Name:



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	90934	31682	82423	134223	191226	75238	2.60157

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.30	12.82	15.73	-6.02279	0	481.029	100

Figure S46. SEC chart of the polymer obtained in Table 2, entry 5.

Cirrus GPC Sample Injection Report

Generated by: Administrator

2023年2月22日 19:00

Workbook: D:\Cirrus Workbooks\PS-20220902\PS-20220902.plw

Sample Details

Sample Name: zfl-1

Acquired: 2023/2/22 16:21:58

By Analyst: Administrator

Batch Name: 2023_2_22

Concentration: 0.10 mg/ml Injection Volume: 200.0 ul K of Sample: 12.1000 Alpha of Sample: 0.7000

Analysis Using Method: PS Standard-20220815

Calibration Used: 2022/9/2 9:53:18

Calibration Type: Narrow Standard Curve Fit Used: 3 K: 12.1000 Alpha: 0.7000

Calibration Curve: $y = 20.441758 - 2.418866x^1 + 0.141132x^2 - 0.003640x^3$

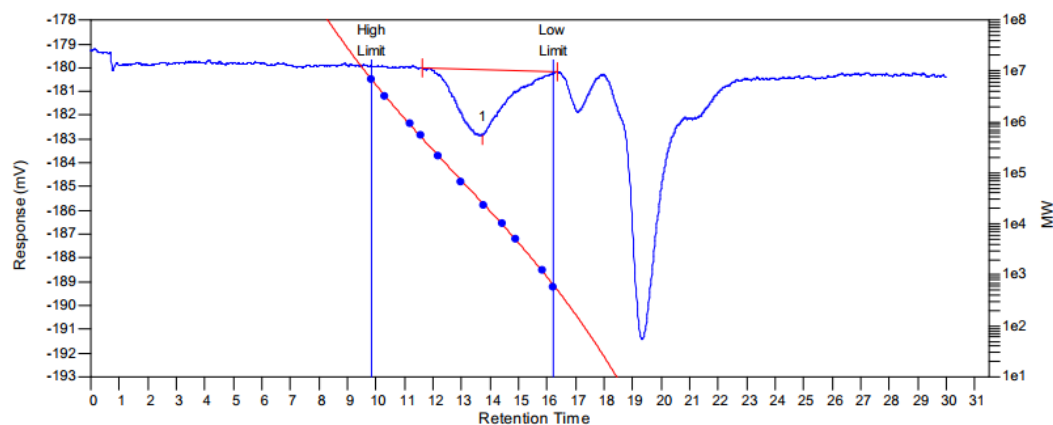
High Limit MW RT: 9.87 mins

Low Limit MW RT: 16.23 mins

Flow Marker RT: 0.00 mins

FRCF: 1.0000

FRM Name:



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	30298	10640	39647	87345	147921	34322	3.72622

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.62	13.72	16.37	-2.75566	0	315.866	100

Figure S47. SEC chart of the polymer obtained in Table 2, entry 7.

Cirrus GPC Sample Injection Report

Generated by: Administrator

2023年2月27日 17:13

Workbook: D:\Cirrus Workbooks\PS-20220902\PS-20220902.plw

Sample Details

Sample Name: zfl-36-1

Acquired: 2023/2/27 16:39:48

By Analyst: Administrator

Batch Name: 2023_2_27

Concentration: 0.10 mg/ml Injection Volume: 200.0 ul K of Sample: 12.1000 Alpha of Sample: 0.7000

Analysis Using Method: PS Standard-20220815

Calibration Used: 2022/9/2 9:53:18

Calibration Type: Narrow Standard Curve Fit Used: 3 K: 12.1000 Alpha: 0.7000

Calibration Curve: $y = 20.441758 - 2.418866x^1 + 0.141132x^2 - 0.003640x^3$

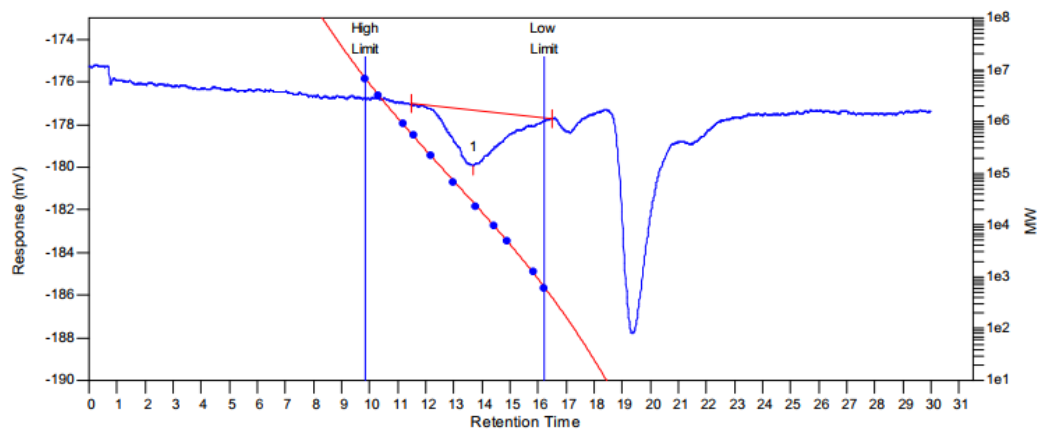
High Limit MW RT: 9.87 mins

Low Limit MW RT: 16.23 mins

Flow Marker RT: 0.00 mins

FRCF: 1.0000

FRM Name:



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	27628	7966	34999	92004	192653	29599	4.39355

Processed Peaks

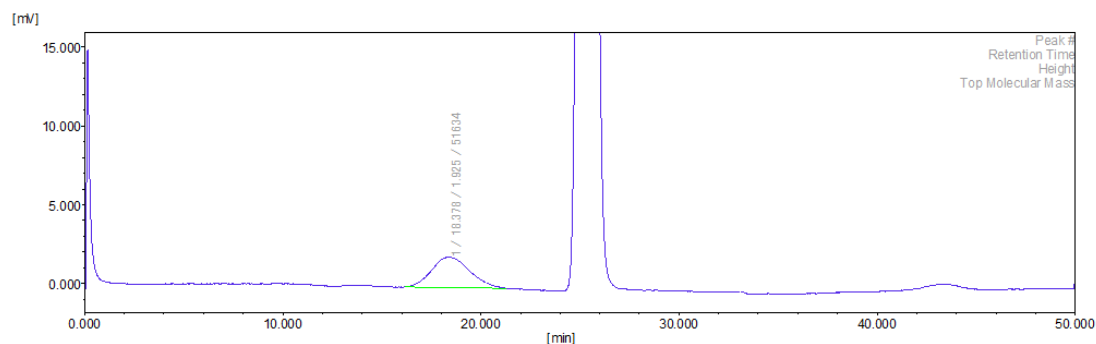
Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.48	13.68	16.50	-2.58108	0	311.112	100

Figure S48. SEC chart of the polymer obtained in Table 2, entry 8.

Chromatogram report

Header

Title		Data acquisition date and time	2023/01/09 17:22:40
Sample name	ZFL-YP202301373-18-1	Calculation date and time	2023/02/21 10:57:30
Database name	20230109.chd	Acquisition time [min]	0.000 - 50.000
Data name	RSLT0003	Sampling interval [ms]	100
Method name	20160912	Cup number	3
Channel	RI	Calculation type	Molecular Mass



Molecular mass calculation result (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]	Mn	27,406
Peak start	16.162	-0.199	461,922	Mw	63,223
Peak top	18.378	1.687	51,634	Mz	116,390
Peak end	21.277	-0.289	2,082	Mz+1	173,290
				Mx	63,223
Height [mV]		1.925		My	53,243
Area [mV*s]		256.270		Mz/Mw	1.841
Area% [%]		100.000		Mw/Mn	2.307
[eta]		63223.45844		Mz+1/Mw	2.741

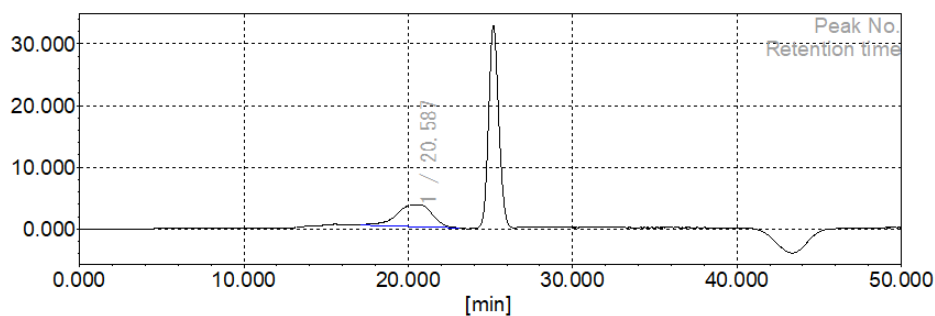
Figure S49. SEC chart of the polymer obtained in Table 2, entry 9.

Chromatogram report

Header

Title		Data acquisition date and time	2023/01/09 19:02:42
Sample name	ZFL-YP202301373-19-2	Calculation date and time	2023/02/21 10:52:37
Database name	20230109.chd	Acquisition time [min]	0.000 - 50.000
Data name	RSLT0005	Sampling interval [ms]	100
Method name	20160912	Cup number	6
Channel	RI	Calculation type	Molecular Mass

[mV]



Molecular mass calculation result (RI)

Pe⁺ 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	17.113	0.632	191,956	Mn	3,021
Peak top	20.587	3.892	4,807	Mw	11,463
Peak end	23.112	0.170	22	Mz	37,805
				Mz+1	78,769
				Mv	11,463
Height [mV]			3.528	Mp	6,762
Area [mV*s]			532.465	Mz/Mw	3.298
Area% [%]			100.000	Mw/Mn	3.794
[eta]			11462.83260	Mz+1/Mw	6.872

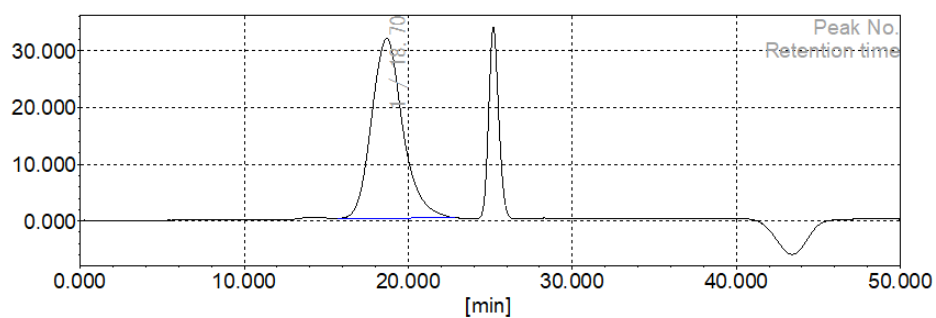
Figure S50. SEC chart of the polymer obtained in Table 2, entry10.

Chromatogram report

Header

Title		Data acquisition date and time	2023/01/09 18:12:41
Sample name	ZFL-YP202301373-19-1	Calculation date and time	2023/01/11 11:45:09
Database name	20230109.chd	Acquisition time [min]	0.000 - 50.000
Data name	RSLT0004	Sampling interval [ms]	100
Method name	20160912	Cup number	4
Channel	RI	Calculation type	Molecular Mass

[mV]



Molecular mass calculation result (RI)

Peak 1 Base Peak

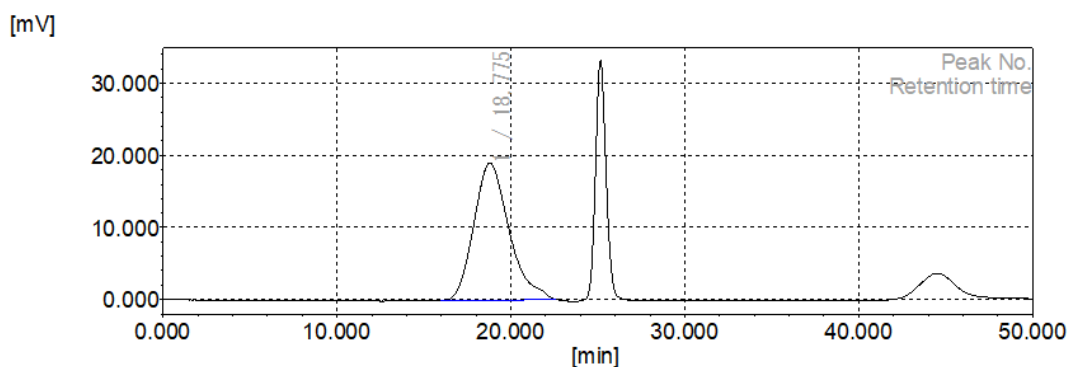
	[min]	[mV]	[mol]		
Peak start	15.678	0.456	716,286	Mn	14,670
Peak top	18.702	32.215	36,345	Mw	49,905
Peak end	22.882	0.551	57	Mz	99,455
				Mz+1	162,840
Height [mV]			31.719	Mv	49,905
Area [mV*s]			4193.159	Mp	36,345
Area% [%]			100.000	Mz/Mw	1.993
[eta]			49905.21657	Mw/Mn	3.402
				Mz+1/Mw	3.263

Figure S51. SEC chart of the polymer obtained in Table 2, entry 11.

Chromatogram report

Header

Title		Data acquisition date and time	2023/02/27 21:06:00
Sample name	ZFL-35-2	Calculation date and time	2023/02/27 21:39:13
Database name	20230227.chd	Acquisition time [min]	0.000 - 50.000
Data name	RSLT0010	Sampling interval [ms]	100
Method name	20160912	Cup number	13
Channel	RI	Calculation type	Molecular Mass



Molecular mass calculation result (RI)

Peak 1 Base Peak

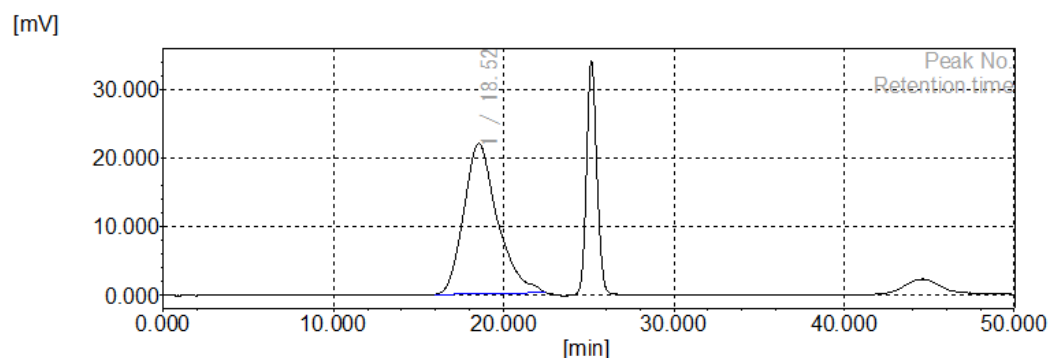
	[min]	[mV]	[mol]		
Peak start	15.978	-0.192	544,354	Mn	11,714
Peak top	18.775	18.982	33,561	Mw	43,225
Peak end	22.598	0.002	146	Mz	90,908
				Mz+1	148,720
				Mv	43,225
Height [mV]			19.092	Mp	33,501
Area [mV*s]			2687.525	Mz/Mw	2.103
Area% [%]			100.000	Mw/Mn	3.690
[eta]			43225.25022	Mz+1/Mw	3.441

Figure S52. SEC chart of the polymer obtained in Table 2, entry 12.

Chromatogram report

Header

Title		Data acquisition date and time	2023/02/27 20:15:59
Sample name	ZFL-35-1	Calculation date and time	2023/02/27 21:23:07
Database name	20230227.chd	Acquisition time [min]	0.000 - 50.000
Data name	RSLT0009	Sampling interval [ms]	100
Method name	20160912	Cup number	12
Channel	RI	Calculation type	Molecular Mass



Molecular mass calculation result (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	15.943	0.161	561,788	Mn	14,482
Peak top	18.525	22.178	44,039	Mw	53,858
Peak end	22.455	0.467	220	Mz	107,859
				Mz+1	168,126
				Mv	53,858
Height [mV]			21.896	Mp	44,039
Area [mV*s]			3007.862	Mz/Mw	2.003
Area% [%]			100.000	Mw/Mn	3.719
[eta]			53857.64817	Mz+1/Mw	3.122

Figure S53. SEC chart of the polymer obtained in Table 2, entry 12.

References

- [1] X.-Q. Zhu, M.-T. Zhang, A. Yu, C.-H. Wang, J.-P. Cheng, *J. Am. Chem. Soc.* **2008**, *130*, 2501.
- [2] J. M. Kelly, C.M. O'Connell, J. G. Vos, *J. Chem. Soc., Dalton Trans.* **1986**, 253.
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- [4] Y. Ota, S. Ito, J.-i. Kuroda, Y. Okumura, K. Nozaki, *J. Am. Chem. Soc.* **2014**, *136*, 11898.
- [5] B. Neuwald, L. Caporaso, L. Cavallo, S. Mecking, *J. Am. Chem. Soc.* **2013**, *135*, 1026.
- [6] T. Fujita, K. Nakano, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2006**, *128*, 1968.