Supplementary Information

High Density Polyethylenes Bearing Isolated In-Chain Carbonyls

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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 50-mL stainless steel autoclave. Ethylene (>99.9%) was purchased from Takachiho Chemical Industrial Co., Ltd. (Takachiho), and dried, by passing through a dry column DC-HDF300-A3 made by Nikka Seiko Co., Ltd. Dppp (>98.0%) and dppb (>98.0%) were purchased from TCI and opened and stored in an argon filled glovebox. PdMeCl(cod)[1], **[Pd]-1**,[2] **[Pd]-2**,[2] **[Pd]-3**,[2] **[Pd]-4**,[2] **[Pd]-5**,[3] and **[Pd]-6**[4] was prepared according to literature procedures. Anhydrous toluene was purchased from Kanto Chemical Co. Inc. (Kanto) and purified by the method of Pangborn et al. Anhydrous $PhCF_3$ was purchased from Aldrich and used as is in an argon filled glovebox. NMR spectra were recorded on a BRUKER Ascend 500 (^1H: 500 MHz, ^{13}C: 126 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 ($C_2D_2Cl_4$, δ: 6.00) or HFIP (9:1 $C_3H_2F_6O$ /C_6D_6, δ: 4.26; referenced to TMS). Chemical shift values for carbons are referenced to the carbon resonances of $CDCl_3$ (δ: 77.2 ppm), 1,1,2,2-tetrachloroethane (δ: 74.0 ppm) or HFIP (9:1 $C_3H_2F_6O/C_6D_6$, δ: 71.57 ppm; referenced to TMS). ^1H NMR analyses of polymers were performed in a 5-mm probe on ca. 5 wt % solutions of the polymers $C_2D_2Cl_4$ at 120 °C using a 30° pulse of 50.0 μs, a spectral width of 10 kHz, a relaxation time of 5.0 s, an acquisition time of 3.2 s (BRUKER Ascend500). Quantitative ^{13}C 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 using a 30° pulse of 16.8 μs, a spectral width of 30 kHz, a relaxation time of 2 s, an acquisition time = 1.1 s, and inverse-gated decoupling (BRUKER Ascend500). NMR assignments were assisted by ^{13}C-DEPT, ^1H-^{13}C HSQC, and ^1H-^{13}C HMBC data. Size exclusion chromatography (SEC) analyses were carried out with a Tosoh instrument (HLC-8321GPC/HT) equipped with two SEC columns (Tosoh TSKgel GMHHR- H(S)HT) and a refractive index (RI) detector by eluting the columns with 1,2-dichlorobenzene at 1.0 mL/min at 140 °C. Molecular weights were determined using narrow polystyrene standards and were corrected for polyethylene by universal calibration using the Mark–Houwink parameters of Rudin *et al.*: $K = 1.75 \times 10^{-2}$ cm^3/g and $\alpha = 0.67$ for polystyrene and $K = 5.90 \times 10^{-2}$ cm^3/g and $\alpha = 0.69$ for LLDPE. Differential scanning calorimetry (DSC) measurements of polymers were performed on a Seiko DSC 7020 analyzer at a heating and cooling rate of 20 °C/min. Thermogravimetric (TG) analyses were performed on a Seiko EXSTAR 6000 TG/DTA 6200 analyzer at a heating rate of 10 °C/min.

Experimental procedures

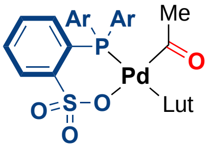
A representative procedure for copolymerization of ethylene and metal carbonyls (Table 1, entry 1): A 50 mL stainless steel autoclave along with a 40 mL glass tube were dried in an oven at 120 °C, and then allowed to cool inside a glovebox. The glass tube was charged with **[Pd]-1** (10 μmol), toluene (10.0 mL), $Fe_2(CO)_9$ (0.25 mmol) and then placed in the autoclave. The autoclave was then sealed, charged with ethylene (3.0 MPa) and stirred in an isothermal heating block at 80 °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 diluted hydrochloric acid and methanol. The obtained solid was dried under vacuum for 4 hours at 100 °C. 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+k+m+o+p+q+C+G+2B+2F+2H**)×100%. CO incorporation ratio (i. r.) can also be calculated from the quantitative $^{13}C\{^1H\}$ NMR spectra by the integration of the signals for carbonyl groups and those not adjacent to carbonyl groups, CO i.r. (%) = (**A+E**)/(**a+c+d+e+f+g+h+j+n+i+b+k+m+o+p+C+G+B+F+H+2A+2E**)×100%.

Experimental procedure for copolymerization of ethylene with $Fe_2(CO)_9$ outside the reaction mixture (Table 1, entry 5): A 50 mL stainless steel autoclave along with a 40 mL glass tube were dried in an oven at 120 °C, and then allowed to cool inside a glovebox. $Fe_2(CO)_9$ (0.25 mmol) and toluene (1.0 mL) were added to the autoclave. Meanwhile, 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 ethylene (3.0 MPa) and stirred in an isothermal heating block at 80 °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 diluted hydrochloric acid and methanol. The obtained solid was dried under vacuum for 4 hours at 100 °C. The molecular weight and polydispersity were determined by size exclusion chromatography. CO i. r. and I/A selectivity were determined by ^1H NMR analysis.

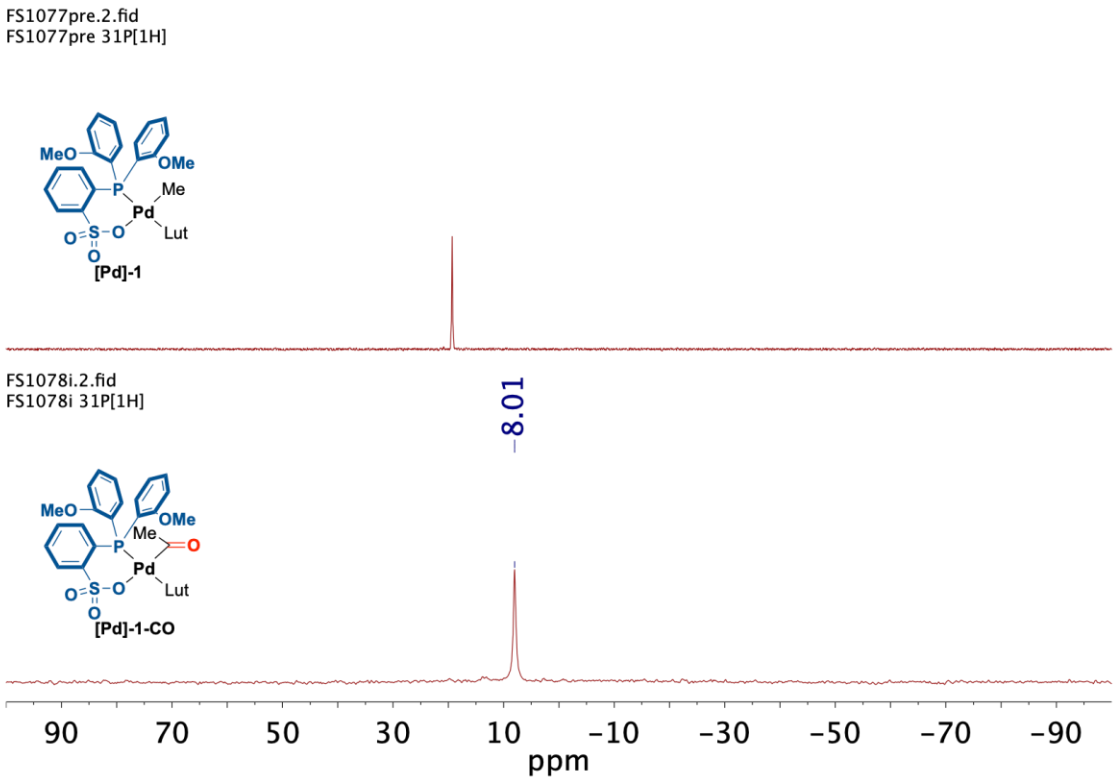
Experimental procedure for copolymerization of ethylene with low pressure CO (Table 1, entry 6): A 50 mL stainless steel autoclave along with a 40 mL glass tube were dried in an oven at 120 °C, and then allowed to cool inside a glovebox. The glass tube was charged with **[Pd]-1** (10 μmol), toluene (10.0 mL) and then placed in the autoclave. The autoclave was then sealed, charged with ethylene/CO feed (5.0 MPa, 10:1), released to atmosphere pressure, and finally charged with ethylene (3.0 MPa). The autoclave was stirred in an isothermal heating block at 80 °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 diluted hydrochloric acid and methanol. The obtained solid was dried under vacuum for 4 hours at 100 °C. The molecular weight and polydispersity were determined by size exclusion chromatography. CO i. r. and I/A selectivity were determined by ^{1}H NMR analysis.

Experimental procedure for the attempted polymerization reactions with the dppp and dppb ligands: In an argon filled glovebox was prepared a mixture of dppp (41.2 mg, 0.10 mmol) or dppb (42.6 mg, 0.10 mmol) and PdMeCl(cod) (26.5 mg, 100 mmol), NaBAr$^{F}_{4}$ (88.6 mg, 0.10 mmol), 2,6-lutidine (11.6 µL; 0.10 mmol) in anhydrous $PhCF_3$ (total volume 10.00 mL). The mixture was vigorously stirred at room temperature for 1 h, and then filtered through a syringe filter to remove some insolubles. The obtained clear, colorless stock solution (10 µmol/mL) of the catalyst was used within 1 d and stored in a freezer at -35 °C in between use. In an argon filled glovebox was charged an inert glass tube containing a strong stir bar with 1.0 mL of the respective catalyst stock solution (10 mmol), followed by 9.0 mL of dry toluene. For the polymerization experiments with $Fe_2(CO)_9$, the tube was at this point additionally charged with solid $Fe_2(CO)_9$ (90.9 mg, 0.25 mmol). The tube was placed in an autoclave, the autoclave was closed with wrenches and transferred out of the glovebox. The autoclave was then pressurized while vigorously stirring with 3.0 MPa ethylene for 2 min. The autoclave was stirred in an isothermal heating block at 80 °C for 3 h. After cooling the autoclaves 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). No precipitate was observed both with dppp or dppb.

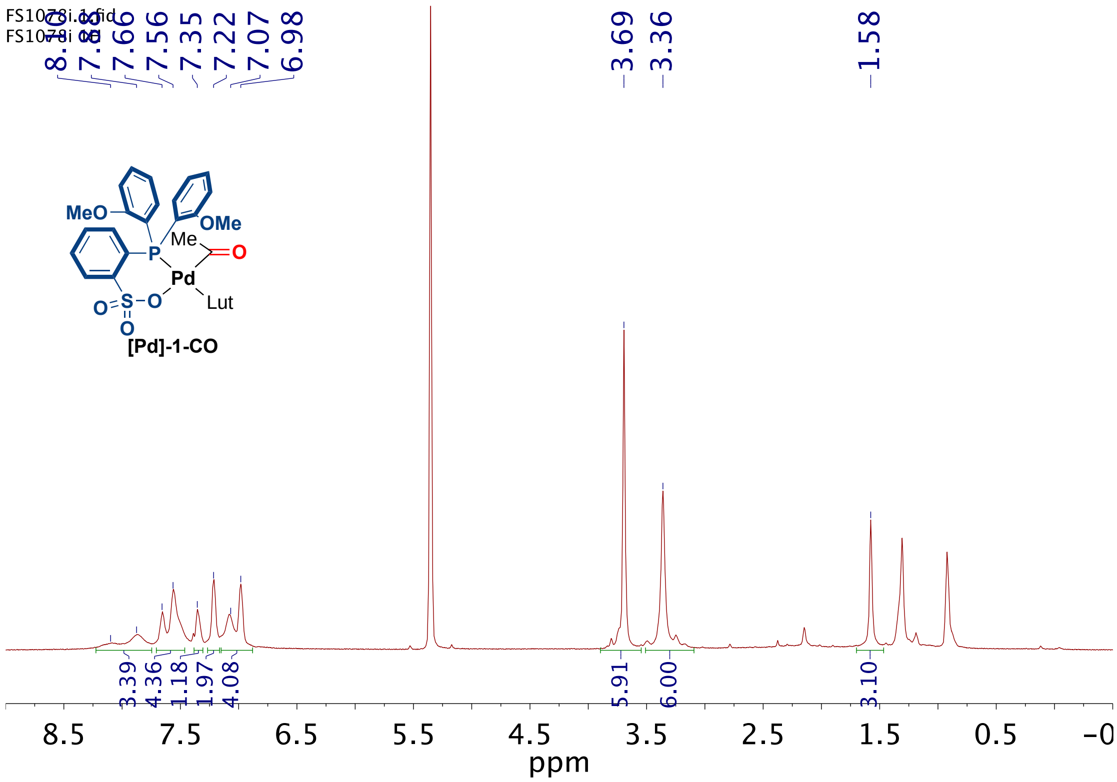
Stoichiometric experiment on carbonyl transfer from $Fe_2(CO)_9$ to catalyst [Pd]-1 to generate [Pd]-1-CO: In an argon filled glovebox were added **[Pd]-1** (10.0 mg; 15.9 mmol), $Fe_2(CO)_9$ (56.8 mg; 0.16 mmol) and dry CD_2Cl_2 (0.60 mL) to a J. Young NMR tube to give a gold-brownish suspension. After standing at room temperature for 1 h some conversion to **[Pd]-1-CO** was observed by ^{31}P[^{1}H]-NMR. Since $Fe_2(CO)_9$ has a poor solubility, ultrasonication was used occasionally during the reaction process. After 24 h, the sample was filtered in an argon filled glovebox through a pad of Celite (ca. 1cm) in a syringe equipped with a PTFE filter to remove dark solids. ^{31}P[^{1}H]/^{1}H analysis of the clear green filtrate at this stage indicated clean conversion to **[Pd]-1-CO** (Supplementary Fig. 1 and 2). The solution gradually showed signs of decomposition over the next two days. The sample was then layered with hexanes in an argon filled glovebox and placed in a freezer (-35 °C) for crystallization, which gave some poor-quality crystals that by preliminary scXRD analysis were identical to the reference sample of **[Pd]-1-CO**.



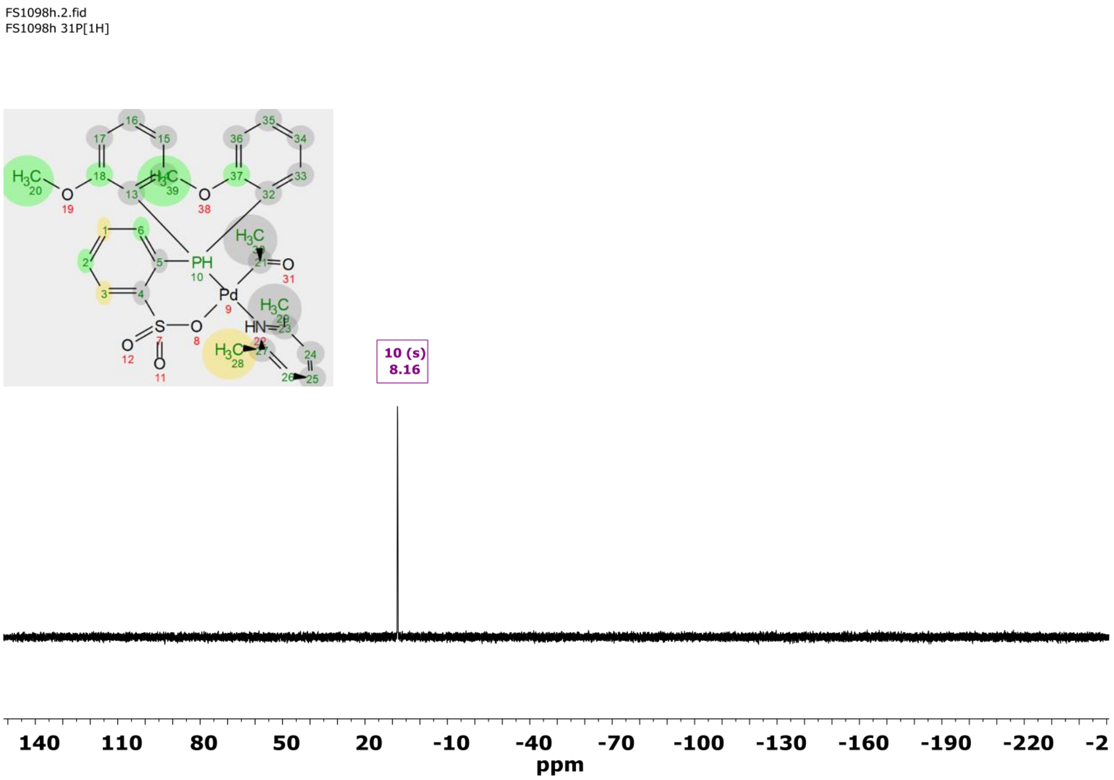
Synthesis of reference complex [Pd]-1-CO: A 10 mL J. Young Schlenk containing a stir bar was charged in an argon filled glovebox with **[Pd]-1** (20.0 mg; 0.032 mol) and dry CD_2Cl_2 (2.1 mL) to give a colorless solution. The Schlenk was closed and brought out of the glovebox and connected via a three-way valve to a nitrogen Schlenk manifold and a CO gas balloon (Valve closed towards the CO balloon during the degassing step; ***Careful***: Extremely toxic gas, only work with appropriate PPE and a CO and O_2 gas sensor in a well ventilated fumehood; a buddy system with a coworker that keeps watch is advised when working with CO). The reaction mixture was freeze-pump-thawed trice with liquid nitrogen, then the CO gas balloon was connected to the reaction vessel via valve manipulation. The reaction mixture was allowed to stir for 19 h at room temperature, after which NMR analysis of the reaction mixture showed full conversion to the target compound. The Schlenk was then closed, transferred into an argon filled glovebox. After filtering the reaction mixture through a GF/B plug in a pipet to remove some dark particles (presumably Pd black) into a vial, the colorless filtrate was carefully layered with dry n-hexane (8 mL) and allowed to stand at room temperature for crystallization. After 19 h the supernatant was decanted, and the remaining crystalline solids were washed with dry n-hexane (2 x 1.0 mL) and dried in HV for 9 h to give the product as a pale colored solid (FW (M + $(CD_2Cl_2)_{0.1}$ = 666.70 g/mol; 15.5 mg; 23.2 μmol; 73% yield). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.97 (ddd, *J* = 7.8, 5.0, 1.4 Hz, 1H), 7.87 (s, 2H), 7.64 (t, *J* = 7.7 Hz, 1H), 7.56 (tdd, *J* = 8.3, 1.7, 0.9 Hz, 2H), 7.45 – 7.36 (m, 2H), 7.32 – 7.26 (m, 1H), 7.19 (d, *J* = 7.7 Hz, 2H), 7.09 (tt, *J* = 7.6, 1.4 Hz, 2H), 6.97 (ddd, *J* = 8.3, 4.6, 1.0 Hz, 2H), 3.66 (s, 6H), 3.33 (s, 6H), 1.56 (d, *J* = 0.9 Hz, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 225.17 (d, *J* = 4.2 Hz, Pd-(*C*O)-Me), 161.10 (d, *J* = 1.8 Hz), 159.87, 148.74 (d, *J* = 15.6 Hz), 139.07, 138.02, 135.12 (d, *J* = 2.2 Hz), 133.71, 130.43 (d, *J* = 2.4 Hz), 128.06 (dd, *J* = 118.8, 7.8 Hz), 127.50 (d, *J* = 48.9 Hz), 123.08 (d, *J* = 2.3 Hz), 121.09 (d, *J* = 12.1 Hz), 116.05 (d, *J* = 53.2 Hz), 111.37 (d, *J* = 4.1 Hz), 55.26, 35.41 (d, *J* = 21.4 Hz), 26.24. ^{31}P NMR (202 MHz, CD_2Cl_2) δ 8.16. Analysis (% calcd, % found for $C_{29}H_{30}NO_6PPdS\cdot(CD_2Cl_2)_{0.1}$: C (52.33, 52.07), N (2.10, 2.15), H content was not determined due to co-crystalized CD_2Cl_2 which contains deuterium. Elemental analysis indicates that ca. 0.1 eq co-crystalized CD_2Cl_2 remains in the bulk sample after the drying step; CD_2Cl_2 was observed to co-crystalize with the target compound according to the single crystal XRD analysis. Some colorless X-ray quality crystals were taken from the bulk sample before the drying step, which decreased the isolated yield.



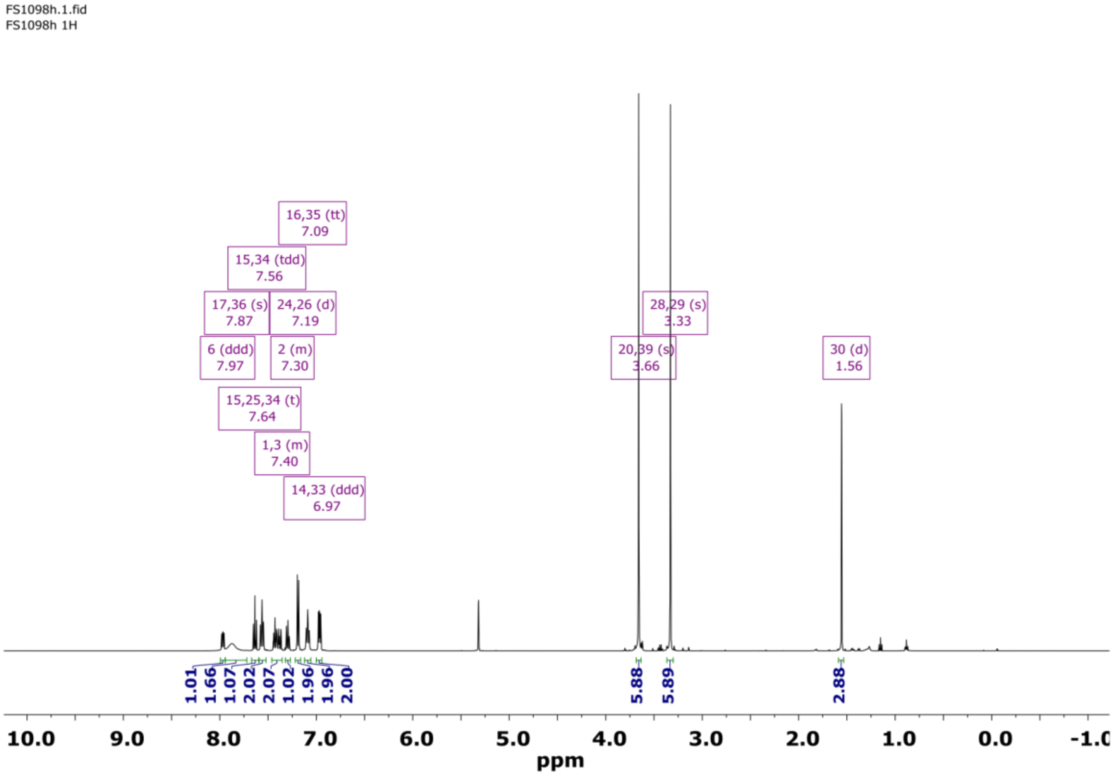
Supplementary Figure 1. $^{31}P[^{1}H]$ NMR spectrum of **[Pd]-1-CO** obtained from the NMR experiment (CD_2Cl_2, 202 MHz, 25°C).



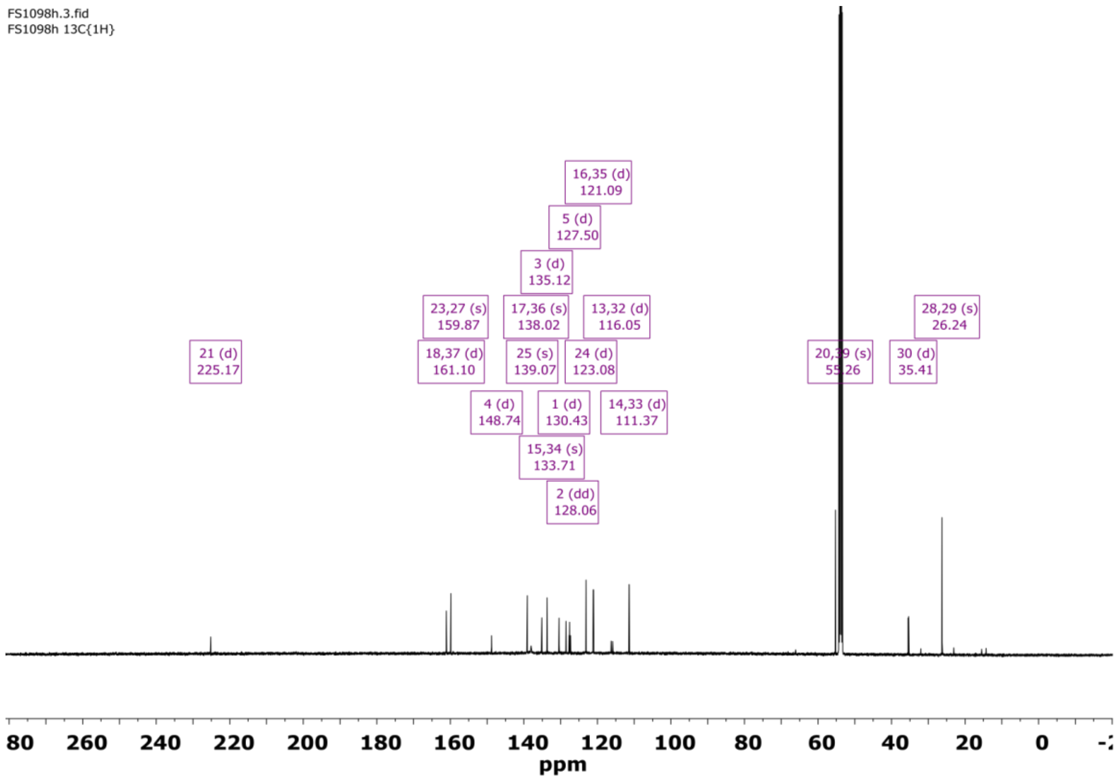
Supplementary Figure 2. ^{1}H NMR spectrum of **[Pd]-1-CO** obtained from the NMR experiment (CD_2Cl_2, 500 MHz, 25°C).



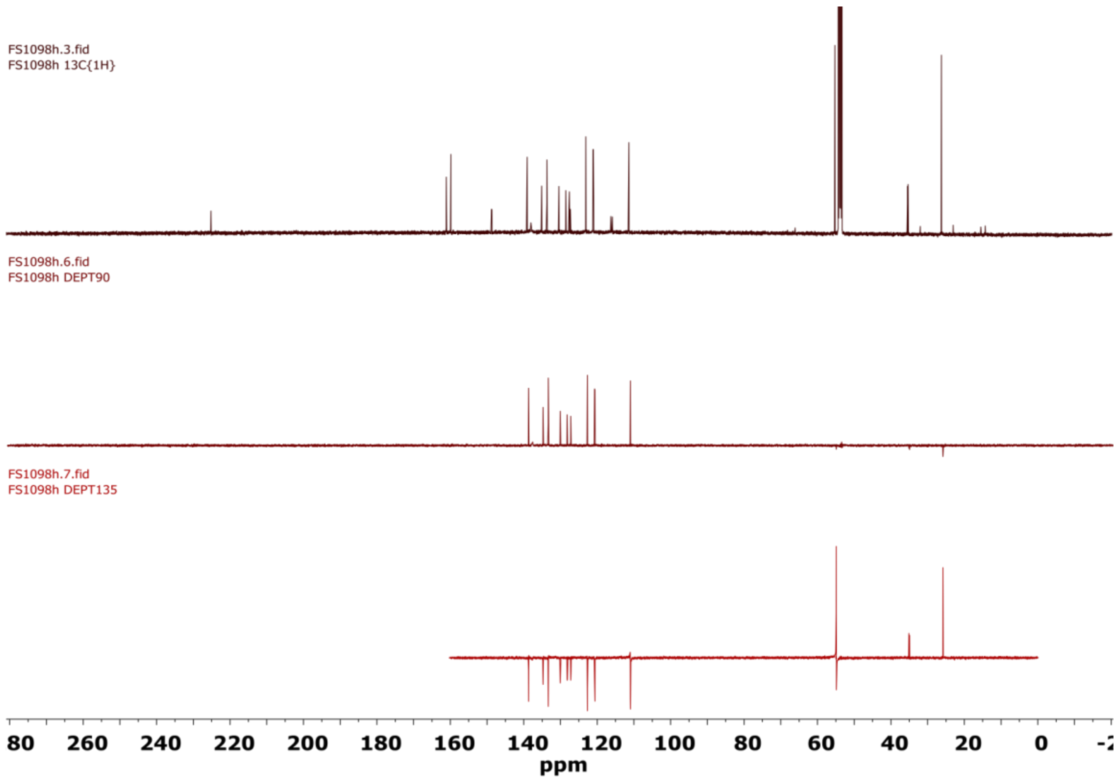
Supplementary Figure 3. $^{31}P[^1H]$ NMR spectrum of reference compound **[Pd]-1-CO** (CD_2Cl_2, 202 MHz, 25°C).



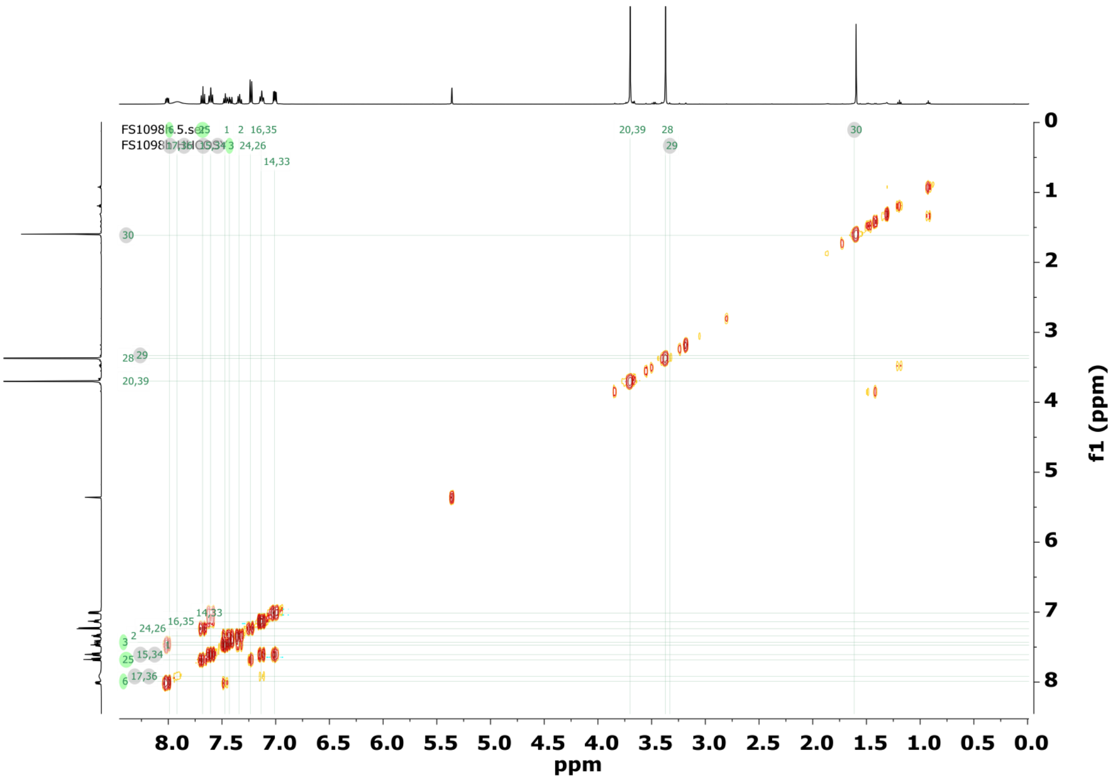
Supplementary Figure 4. ^1H NMR spectrum of reference compound **[Pd]-1-CO** (CD_2Cl_2, 500 MHz, 25°C).



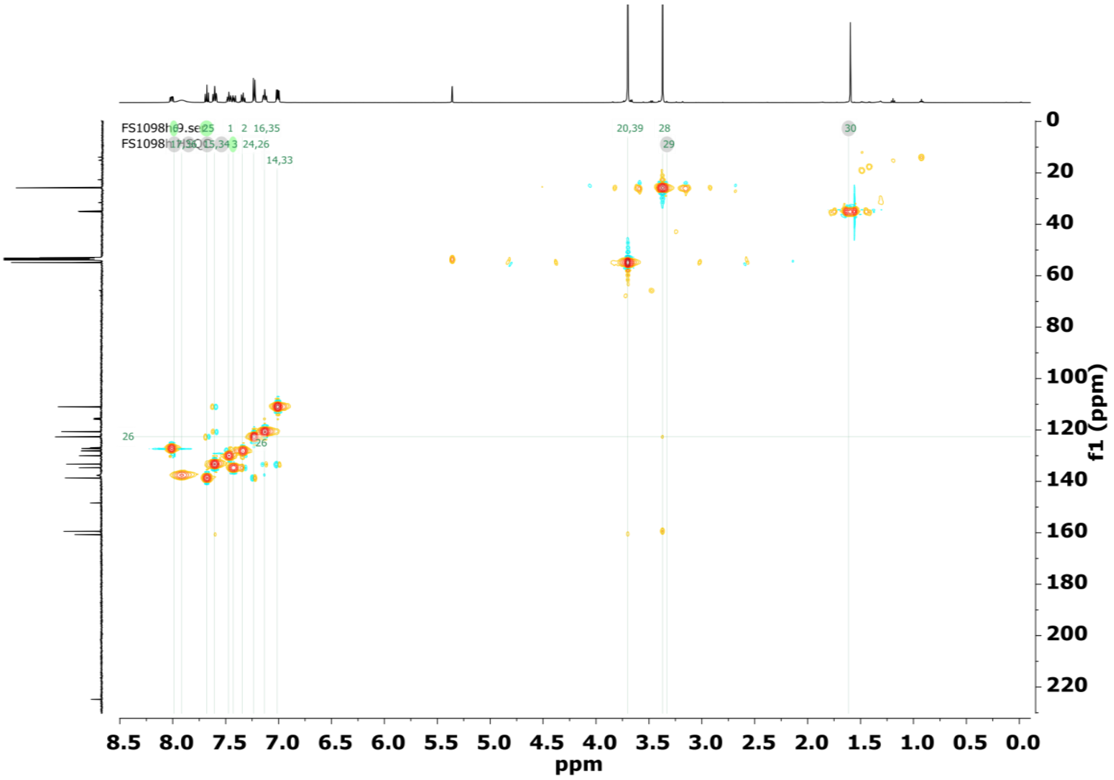
Supplementary Figure 5. $^{13}C\{^1H\}$ NMR spectrum of reference compound **[Pd]-1-CO** (CD_2Cl_2, 126 MHz, 25°C).



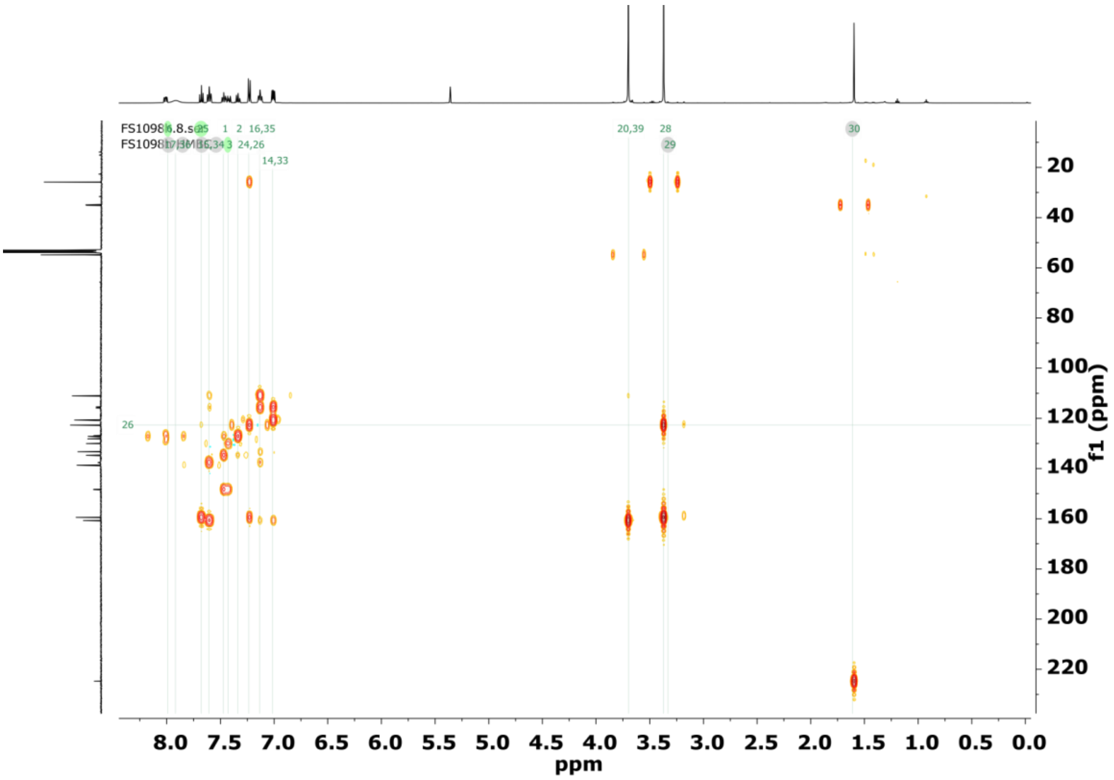
Supplementary Figure 6. Stacked $^{13}C\{^1H\}$ (top), DEPT90 (middle) and DEPT135 (bottom) spectra of reference compound **[Pd]-1-CO** (CD_2Cl_2, 25°C).



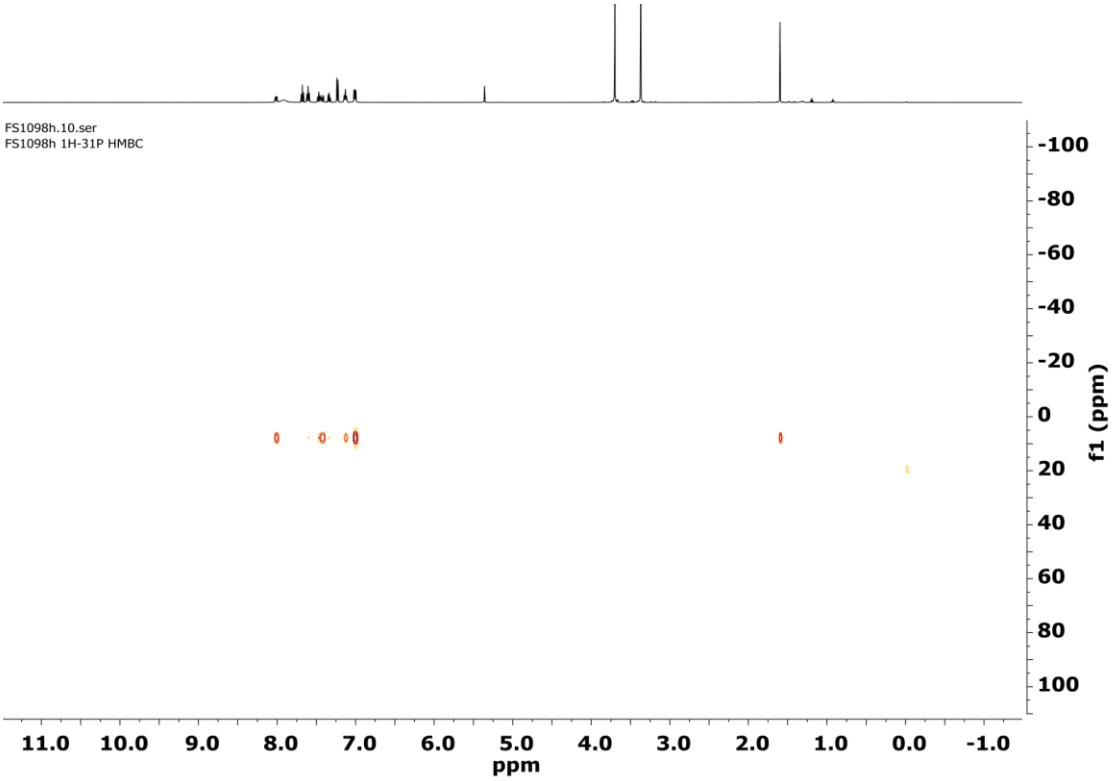
Supplementary Figure 7. ^{1}H-^{1}H COSY spectrum of reference compound **[Pd]-1-CO** (CD_2Cl_2, 25°C).



Supplementary Figure 8. ^{1}H-^{13}C HSQC spectrum of reference compound **[Pd]-1-CO** (CD_2Cl_2, 25°C).



Supplementary Figure 9. ^{1}H-^{13}C HMBC spectrum of reference compound **[Pd]-1-CO** (CD_2Cl_2, 25°C).



Supplementary Figure 10. ^{1}H-^{31}P HMBC spectrum of reference compound **[Pd]-1-CO** (CD_2Cl_2, 25°C).

X-ray crystallographic analysis for [Pd]-1-CO

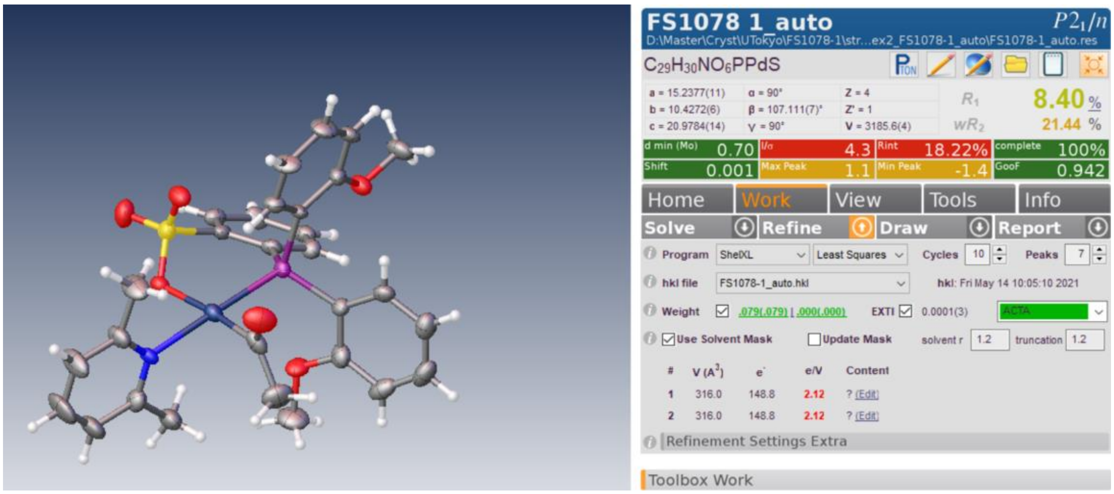
X-ray crystallographic analyses were performed on a Rigaku XtaLAB mini II diffractometer. For XRD measurements the samples were suspended in paraffin oil on a microscope slide (the samples were manipulated and transported under argon). Then - if necessary - a single crystalline piece was quickly cut out with a FEATHER brand ophthalmic scalpel utilizing polarizing light microscopy under air. Suitable crystals were quickly taken up on a loop and mounted on the goniometer head under a stream of chilled nitrogen (169.98(10) K). Processing of the raw diffraction data was done with CrysAlisPro. Via Olex2,[5] the structures were solved with the ShelXT[6] structure solution program using Intrinsic Phasing and refined with the ShelXL[7] refinement package using Least Squares minimization. Special refinement details are given for the respective structures as comments after the tables. Hydrogens were placed by AFIX instructions. **Deposition Number 2096472** contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures. Crystallographic data and refinement parameters are summarized in Table S1.

Table S1. Crystallographic data for complex ([Pd]-1-CO)[a]

Name(CCDC-#)	**[Pd]-1-CO** (CCDC-2096472)
Empirical formula	$C_{30.25}H_{30}D_2Cl_{2.5}NO_6PPdS$
Molecular Weight	765.63
Crystal shape, colour	block; colourless
Crystal size [mm]	0.38 x 0.34 x 0.21
Temperature [K]	169.98(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a [Å]	15.3814(3)
b [Å]	10.4079(2)
c [Å]	20.9108(4)
α [°]	90
β [°]	106.894(2)
γ [°]	90
V [Å^3]	3203.10(11)
Z	4
ρ [g cm^{-3}] (calcd)	1.588
μ [mm^{-1}]	0.947
F (000)	1552.0
Index ranges	$-21 \leq h \leq 21$, $-14 \leq k \leq 14$, $-29 \leq l \leq 29$
Radiation	Mo Kα (λ = 0.71073)
2*Θ* interval [°]	$4.412 \leq 2\Theta \leq 61.182$
Collected reflections	86390

Independent Refl.;R_{int}	9676; 0.0263
Data/restraints/ parameters	9676/13/426
wR$_2$ (all data)	0.0821
R$_1$ (I > 2σ(I))	0.0306
GooF on F^2	1.078
$\Delta\rho_{\text{max/min}}$ [e Å^{-3}]	1.15/-1.12

[a]The structure contains disordered CD_2Cl_2 molecules at the unit cell edges, which were modeled as Part -1/-2: Part -1 shows one non-disordered CD_2Cl_2 molecule (C1AA/Cl2/Cl3; occupancy: 0.5) and a four-fold disordered second CD_2Cl_2 molecule at a special position which was modeled by applying an occupancy of 0.5 to the carbon atom C and occupancies of 0.25 to the outer chlorine atoms Cl/Cl0A to account for the symmetry operations at the unit cell edge (The deuterium atoms in the latter CD_2Cl_2 molecule could not be refined). Part -2 shows one CD_2Cl_2 molecule (C0AA/Cl1/Cl4, occupancy: 0.5). The C-Cl distances of all CD_2Cl_2 molecules were restrained with DFIX instructions (1.78 Å) to allow refinement. A DELU instruction was used on Cl4/C0AA/Cl1, while EADP restraints were applied for C/Cl/Cl0A to allow refinement of the partial four-fold disorder.



FS1078 1_auto $P2_1/n$

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$C_{29}H_{30}NO_6PPdS$

a = 15.2377(11) α = 90° Z = 4

b = 10.4272(6) β = 107.111(7)° Z' = 1

c = 20.9784(14) γ = 90° V = 3185.6(4)

R$_1$ 8.40 %

wR$_2$ 21.44 %

d min (Mo) 0.70 | I/σ 4.3 | Rint 18.22% | complete 100%

Shift 0.001 | Max Peak 1.1 | Min Peak -1.4 | GooF 0.942

Program ShelXL · Least Squares · Cycles 10 · Peaks 7

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Weight ☑ .079(.079) | .000(.000) · EXTI ☑ 0.0001(3) · ACTA

☑ Use Solvent Mask · ☐ Update Mask · solvent r 1.2 · truncation 1.2

#	V (A^3)	e$^-$	e/V	Content
1	316.0	148.8	2.12	? (Edit)
2	316.0	148.8	2.12	? (Edit)

Supplementary Figure 11. Screenshot of the OLEX2 interface on the preliminary crystal structure of **[Pd]-1-CO** obtained from the green filtrate in the NMR experiment. SQUEEZE was used to account for the poorly disordered and co-crystalized CD_2Cl_2 molecules.

Proposed mechanism for CO transfer

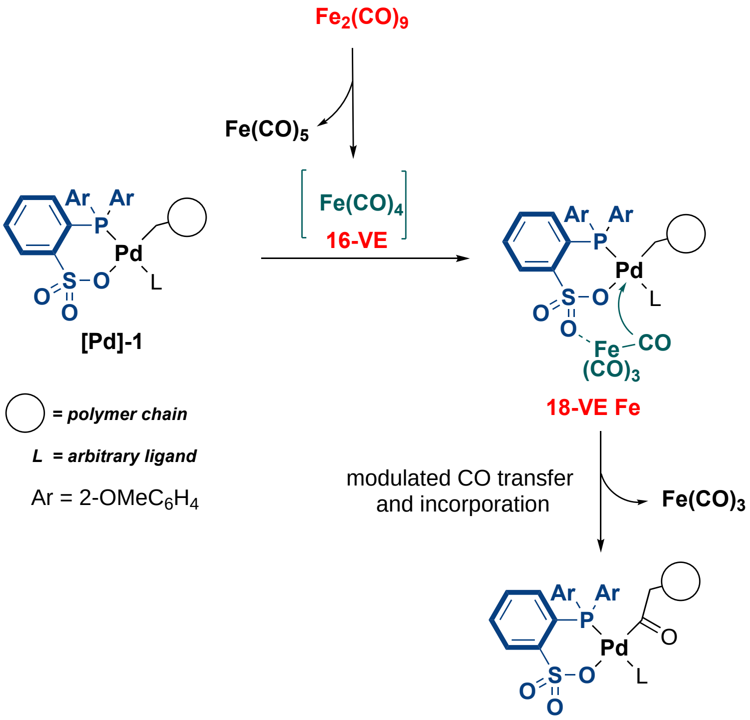
Reported M-M and M-CO bond enthalpies[8-10] for different metal carbonyls are summarized in *Supplementary Table 1*. The experimental results, namely the CO incorporation ratios and quantity in the copolymers by using different metal carbonyls and **[Pd]-1** as the catalyst, are compared. The incorporated CO quantity in the copolymer per metal atom followed the order of $Fe(CO)_5$ > $Fe_2(CO)_9$ > $Mn_2(CO)_{10}$ (>> $Co_2(CO)_8$ = 0), which qualitatively follows the M-CO bond enthalpies (Entries 1/2/4/6). Nevertheless, the incorporated CO quantity in the copolymers is higher when CO gas is employed as the carbonyl source (Entry 7). It is worthy of noting that the reported M-M bond enthalpies for the bimetallic metal carbonyls $Fe_2(CO)_9$ and $Co_2(CO)_8$ are lower when compared with the corresponding M-CO bond dissociation energies. Therefore, 16/17-VE species can be formed from the bimetallic metal carbonyls via M-M bond scission, which are energetically more feasible than the direct M-CO dissociation by comparison of the bond enthalpies (Entries 1,3 and 6). For $Mn_2(CO)_{10}$, a wide range of M-M bond enthalpies have been reported that partially seem to exceed the M-CO bond enthalpies.[8,9]

Supplementary Table 1. Bond enthalpies of metal carbonyls and their effects on carbonyl incorporation with [Pd]-1 as the catalyst

Entry	Carbonyl source	*E*(M-M) (kJ mol^{-1})	*E*(M-CO) (kJ mol^{-1})	n ($M_x(CO)_Y$) or n(CO gas) (mmol)	Incorporation ratio (i. r. %)	Incorporated CO (µmol)[a]	I/A[b]
1	**$Mn_2(CO)_{10}$**	94[8] / 159[9]	151[9]	0.25	0.14	31.8	>99:1
2	**$Fe(CO)_5$**	-	117[10]	0.50	0.16	91.8	>99:1
3	**$Fe_2(CO)_9$**	70[10]	123[10]	0.10	1.1	76.5	99:1
4	**$Fe_2(CO)_9$**	70[10]	123[10]	0.25	1.6	65.6	96:4
5	**$Fe_2(CO)_9$**	70[10]	123[10]	0.50	3.1	64.1	91:9
6	**$Co_2(CO)_8$**	70[10]	136[10]	0.25	-		-
7	**CO gas**			ca. 0.25	0.31	119	67:33

[a] Approximate amount of total incorporated CO in µmol calculated as follows: i. r. × m(polymer) / MW(ethylene).
[b] The I/A ratio was determined by ^1H NMR analysis. I/A = Isolated carbonyls/Alternating carbonyls.

As revealed in Table 1 of the main text, palladium phosphine-sulfonate complexes are important for successful carbonyl incorporation. Almost no CO incorporation was observed with palladium NHC-phenolate and bisphosphine-monoxide complexes. One potential reason for this could be that the pending S=O arms of the sulfonate moiety acted as ligands, which allows dissociation of CO from the metal carbonyls or cause intramolecular CO transfer from the coordinated metal carbonyls to the palladium center. A plausible mechanism for CO transfer from $Fe_2(CO)_9$ to **[Pd]-1** is presented in Supplementary Figure S12. First, disproportionation of $Fe_2(CO)_9$ would lead to the formation of a 16-VE $Fe(CO)_4$ and a 18-VE $Fe(CO)_5$. Coordination of S=O units of the phosphine-sulfonate complexes to $Fe(CO)_4$ would afford a more stable 18-VE species. At last, slow intramolecular CO transfer might take place at the nearby polymerization site. Based on the control experiments for thermal decomposition of $Fe_2(CO)_9$ for slow CO release (See main text, Table 1, entry 5) and the experiment with CO gas (See main text, Table 1, entry 6), an interaction of the catalyst with the metal carbonyl precursors was likely to be the key for efficient incorporation of isolated CO units into the copolymers.

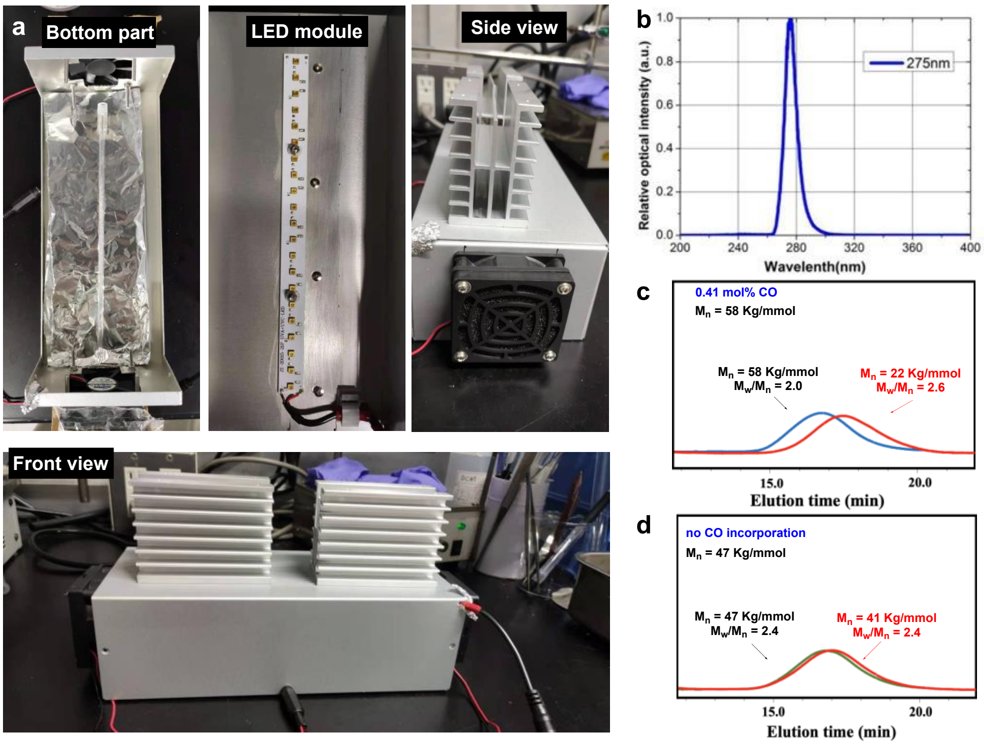


Supplementary Figure 12. Proposed mechanism for the CO transfer from $Fe_2(CO)_9$ to **[Pd]-1**.

Photodegradation experiment

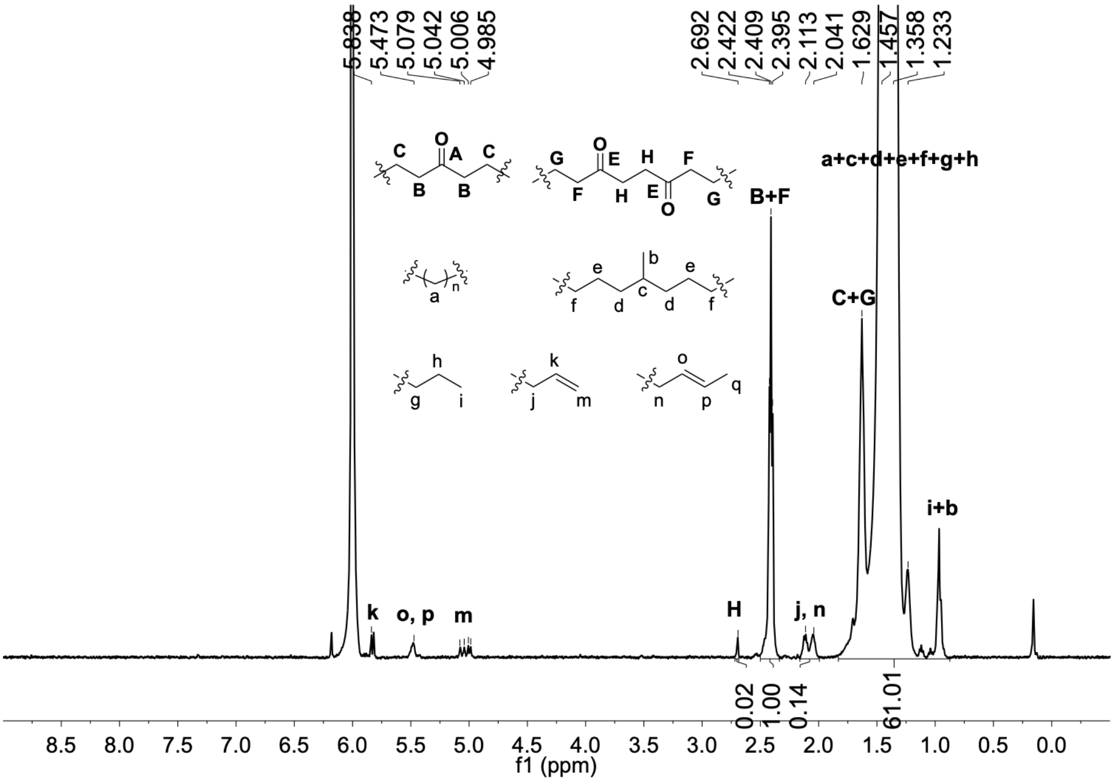
UV photoreactor setup: A 24.5 x 11 x 7.5 cm (length x width x height) aluminum box was equipped with two fans on the long sides to control heat buildup during operation, which kept the internal temperature at ca. 30 °C. To the outside of the fans was attached a foam filter to prevent dust buildup in the reaction chamber. The filters were further covered on the outside with paper towels to prevent UV light leakage during experiments. An array of 21 LED lamps (Qingdao Jason Electric Co.: www.qdjason.com; Model: P35-10A; 275 nm peak wavelength; for further information see the LED data specification sheet under: http://qdjason.hubers.cn/uploads/soft/210507/1_1735383781.pdf) was attached to the inside of the aluminum cover with screws. On the outside of the cover, above the LED module, two passively cooled aluminum heat sinks were attached which kept the LED module at ca. 36 °C during 50 h operation. The floor of the irradiation chamber was covered with aluminum foil. The polymer samples were spread out in a quartz NMR tube to prevent the samples to be blown away by the fans. The tube was placed on the aluminum foil on the chamber floor, 7 cm away from the LED module. The LED array was powered by a 19V / 3.4 A power supply (Go Forward Enterprise Corp.; Model No: GF65L-US1934), the fans were powered by a switching power supply at 7.5 V / 900 mA (MW; Model No.: MW7EA08EL).

Experimental procedure for polymer degradation: The powdery polymer samples in quartz NMR tubes were placed on the bottom of the UV photoreactor. Irradiation test was then carried out at 30 ºC under UV irradiation for 50 h. The molecular weight and polydispersity were determined by size exclusion chromatography.

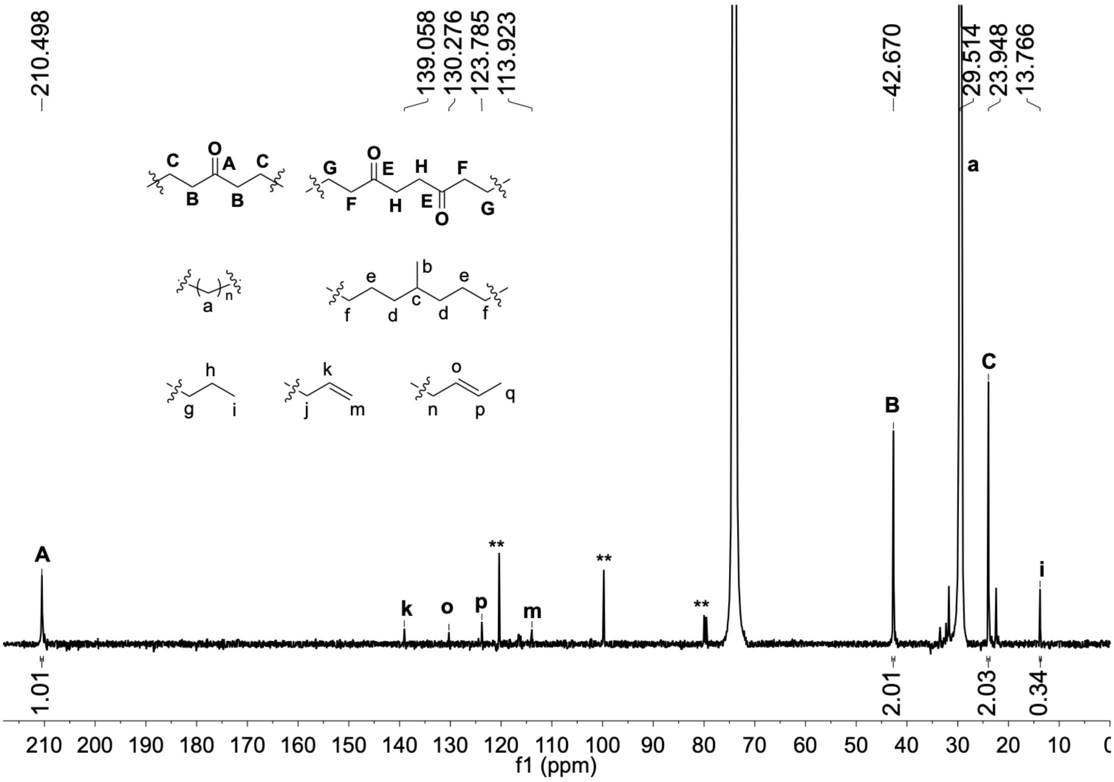


Supplementary Figure 13. Photodegradation experiments. (**a**) UV photoreactor setup. (**b**) Spectrum of the UV-LED light emission. (**e**) SEC trace of the polymer in Table 1, entry 12 before (Blue line) and after (Red line) UV irradiation. (**f**) SEC trace of the polyethylene in Table 1, entry 15 before (Green line) and after (Red line) UV irradiation.

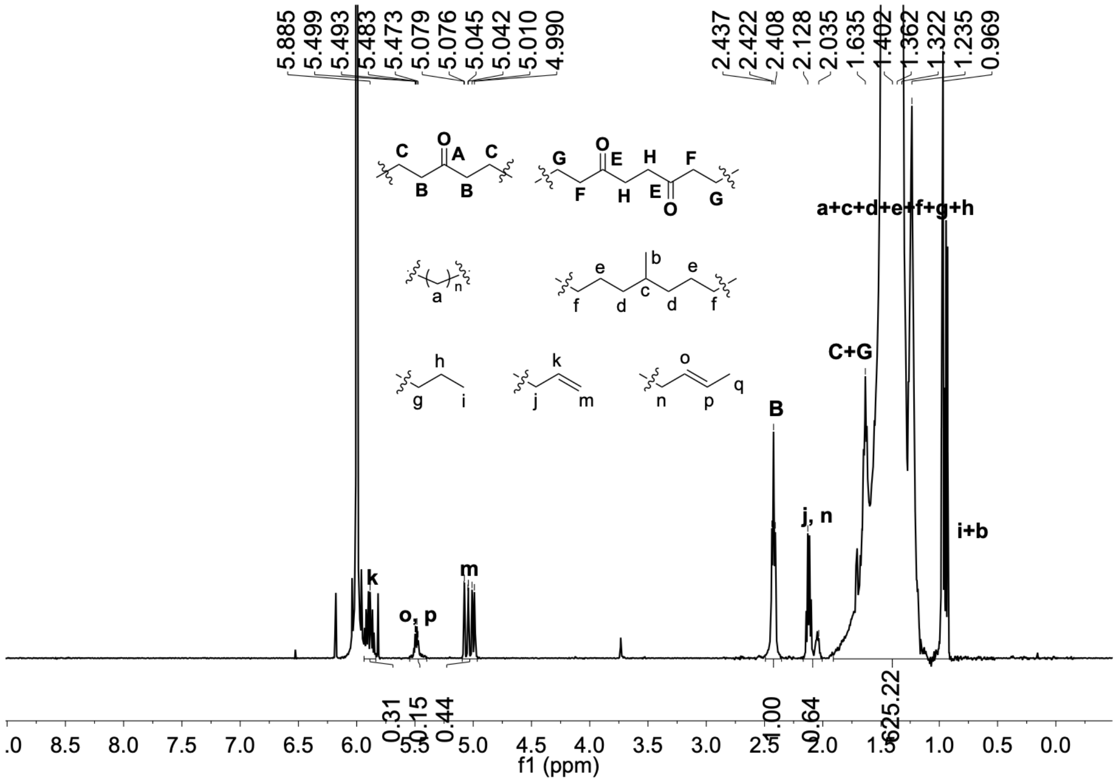
Copies of NMR spectra of the polymers



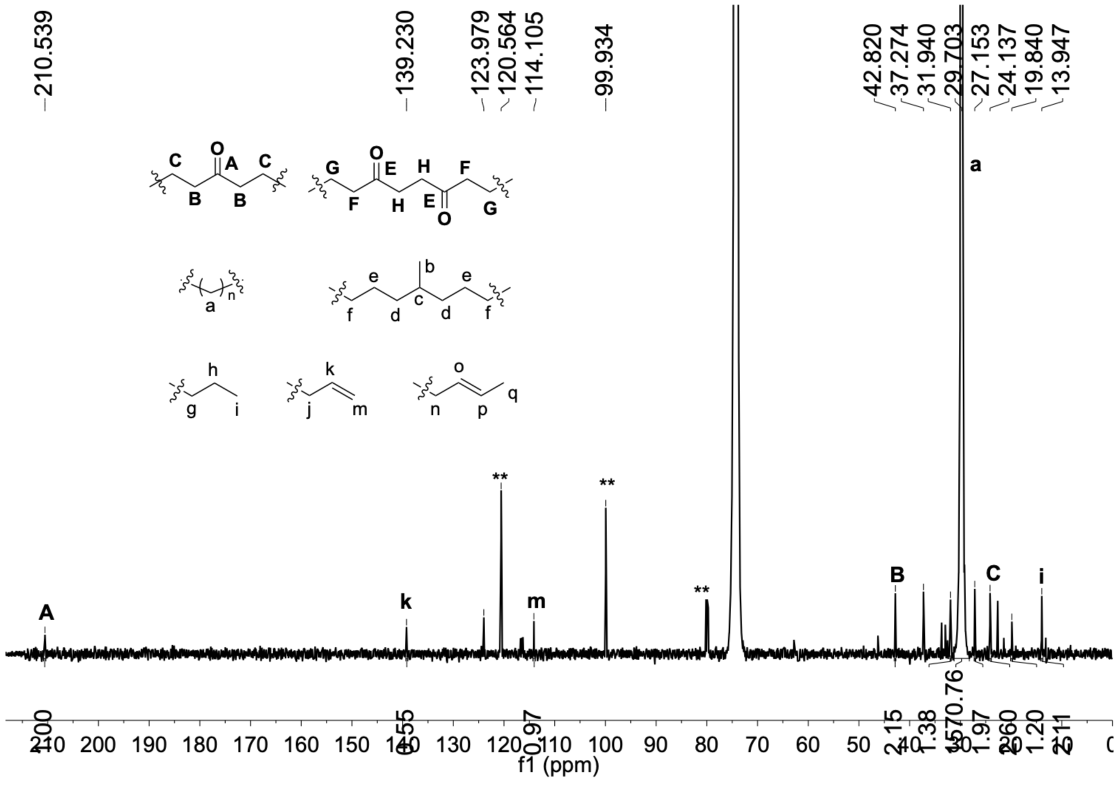
Supplementary Figure 14. ^{1}H NMR spectrum of the polymer obtained in Table 1, entry 1 (1,1,2,2-tetrachloroethane-d_2, 500 MHz, 120 ^{o}C).



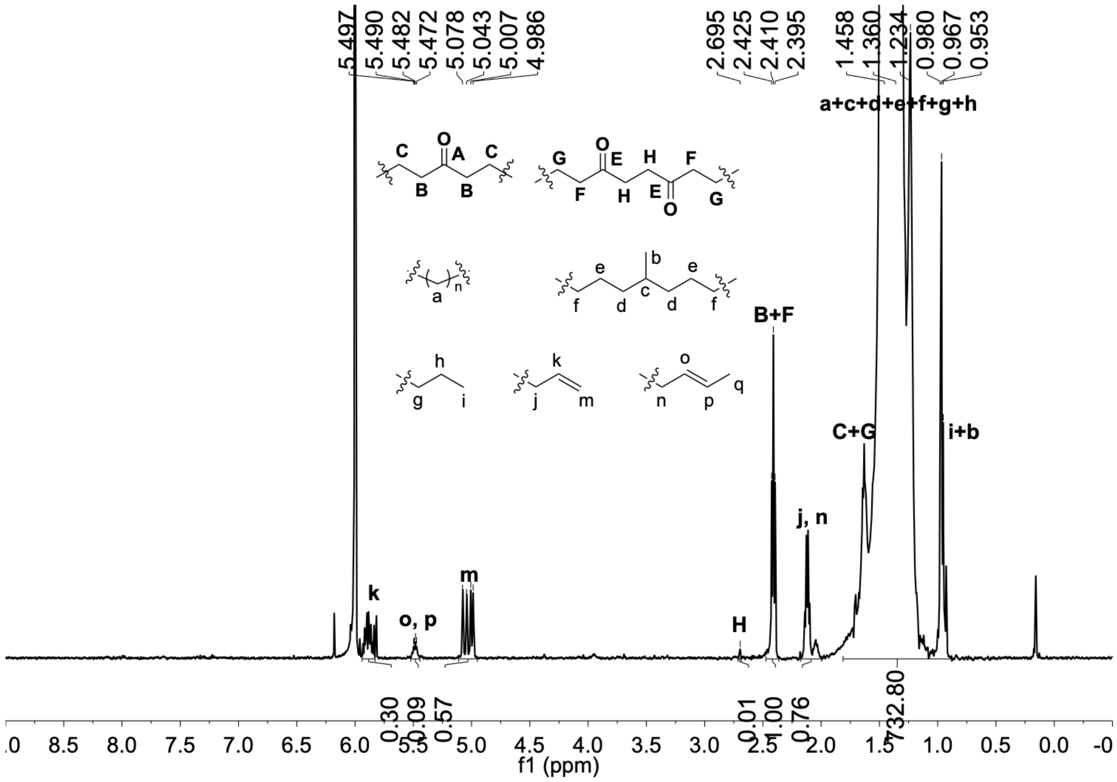
Supplementary Figure 15. Quantitative ^{13}C NMR spectrum of the polymer obtained in Table 1, entry 1 (1,1,2,2-tetrachloroethane-d_2, 126 MHz, 120 ^{o}C).



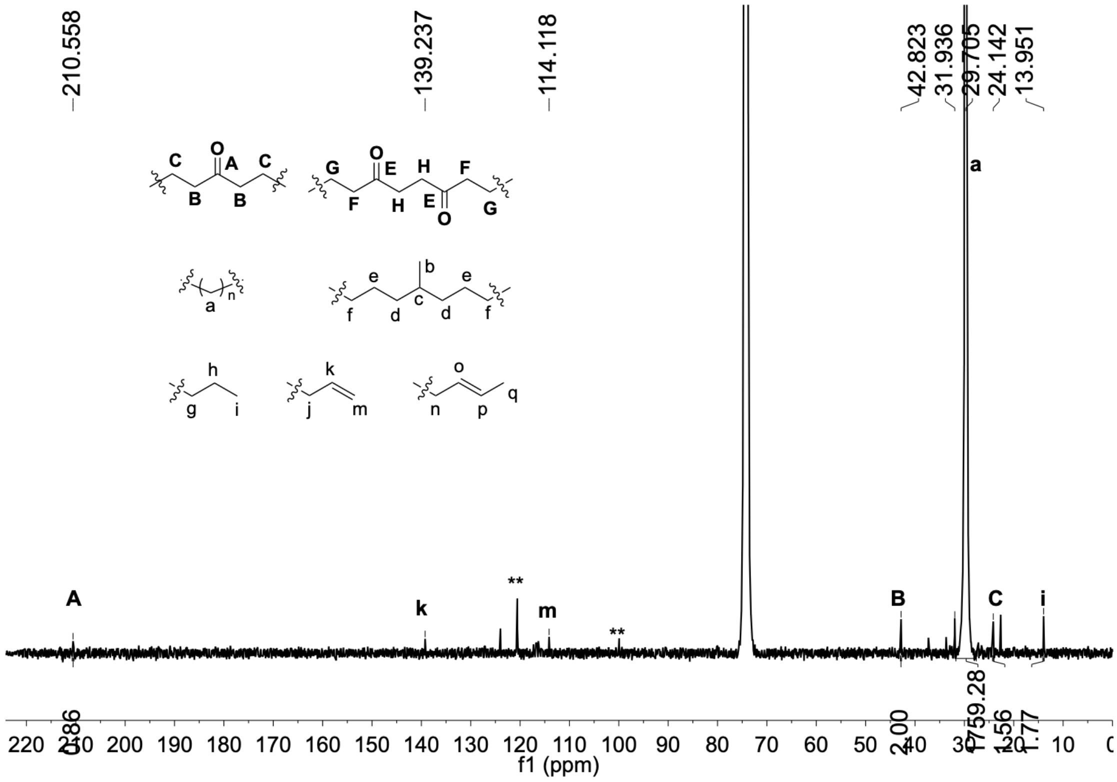
Supplementary Figure 16. ^{1}H NMR spectrum of the polymer obtained in Table 1, entry 2 (1,1,2,2-tetrachloroethane-d_2, 500 MHz, 120 °C).



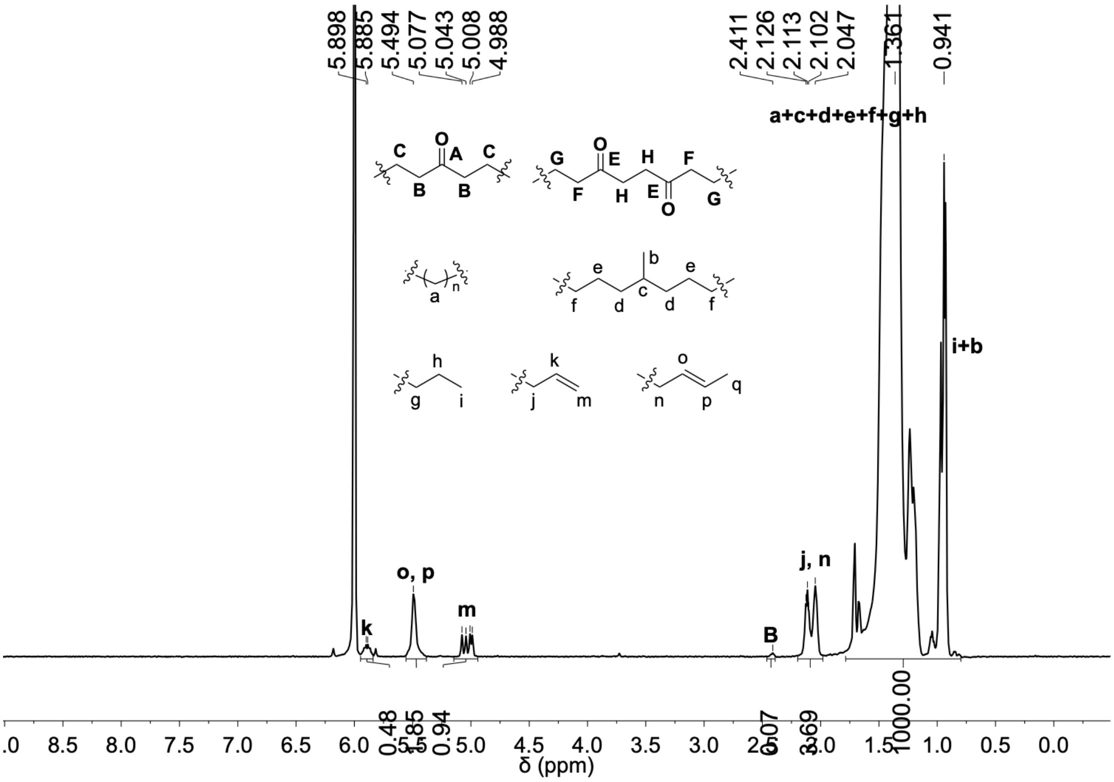
Supplementary Figure 17. Quantitative ^{13}C NMR spectrum of the polymer obtained in Table 1, entry 2 (1,1,2,2-tetrachloroethane-d_2, 126 MHz, 120 °C).



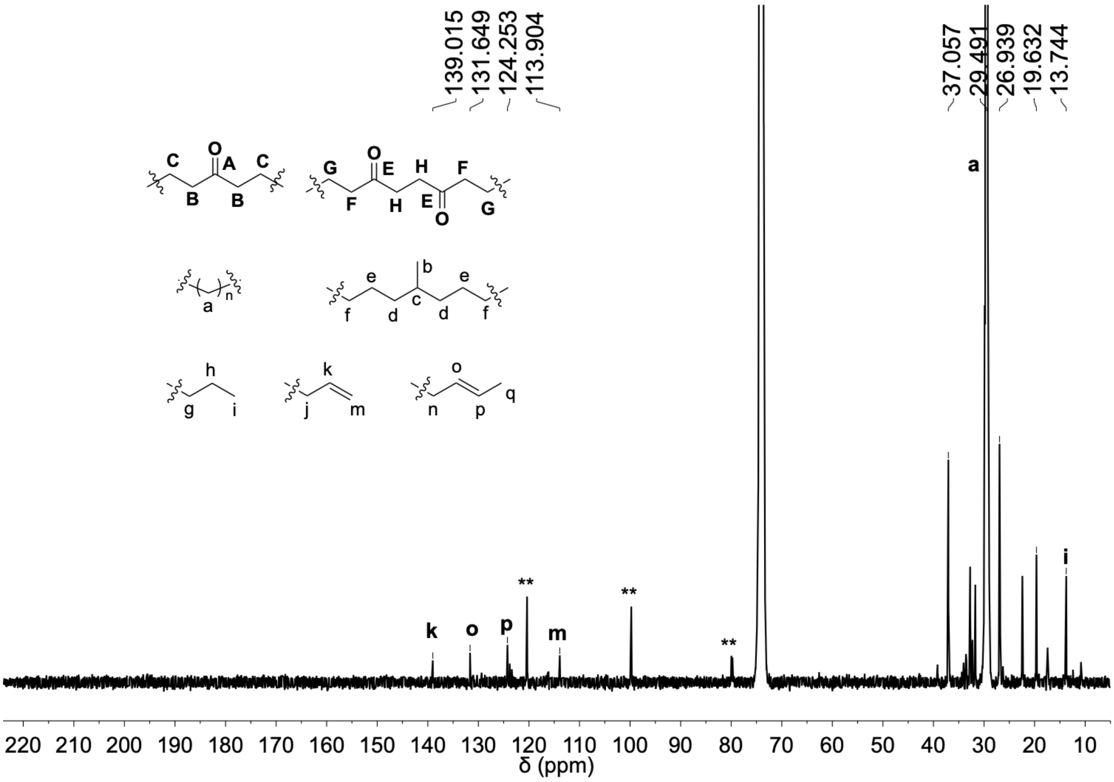
Supplementary Figure 18. ^{1}H NMR spectrum of the polymer obtained in Table 1, entry 3 (1,1,2,2-tetrachloroethane-d_2, 500 MHz, 120 ^{o}C).



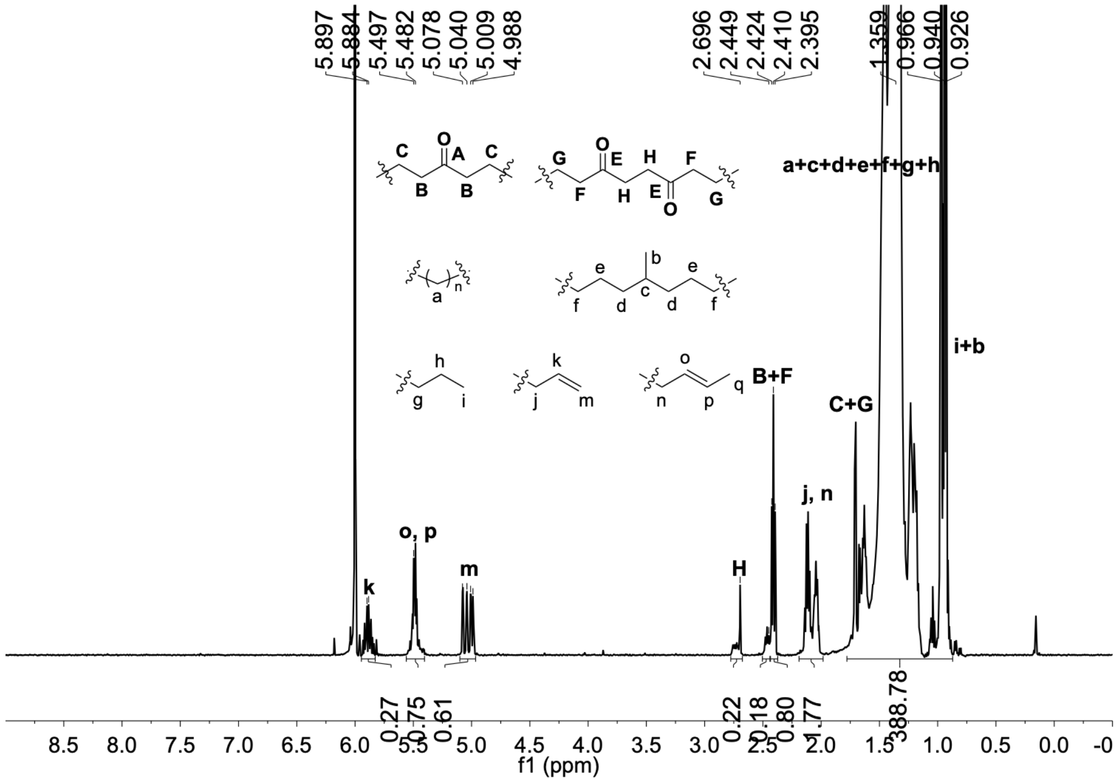
Supplementary Figure 19. Quantitative ^{13}C NMR spectrum of the polymer obtained in Table 1, entry 3 (1,1,2,2-tetrachloroethane-d_2, 126 MHz, 120 ^{o}C).



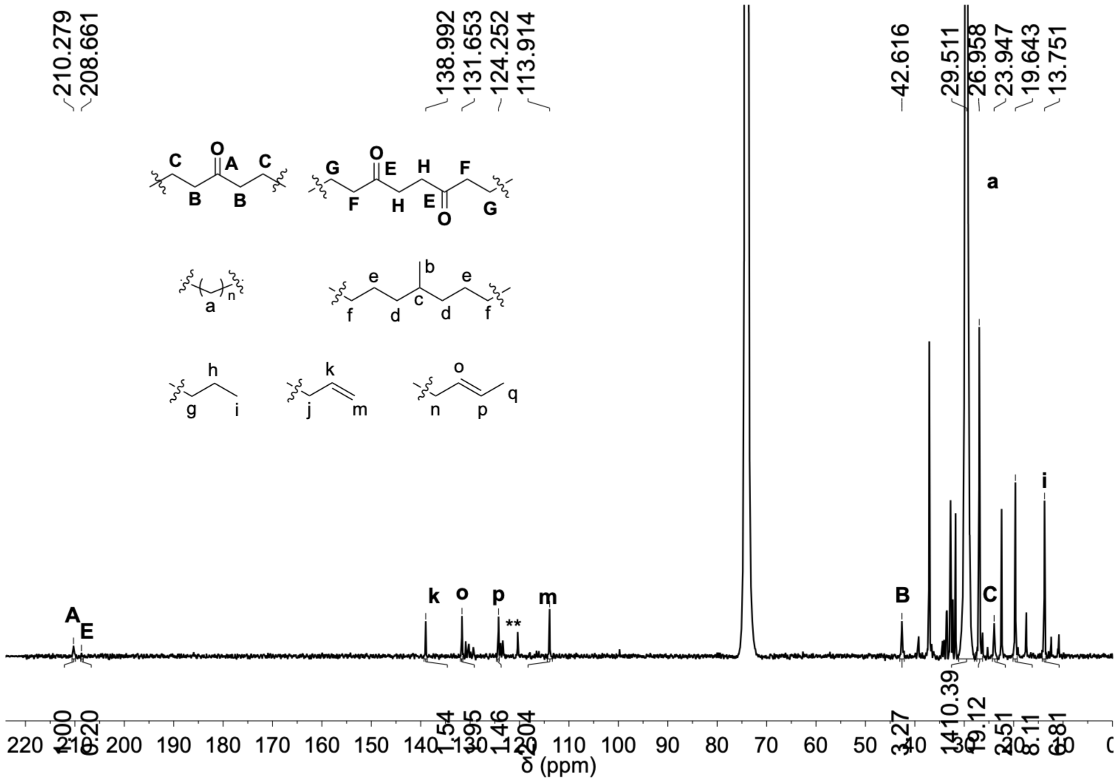
Supplementary Figure 20. ^{1}H NMR spectrum of the polymer obtained in Table 1, entry 5 (1,1,2,2-tetrachloroethane-d_2, 500 MHz, 120 ^{o}C).



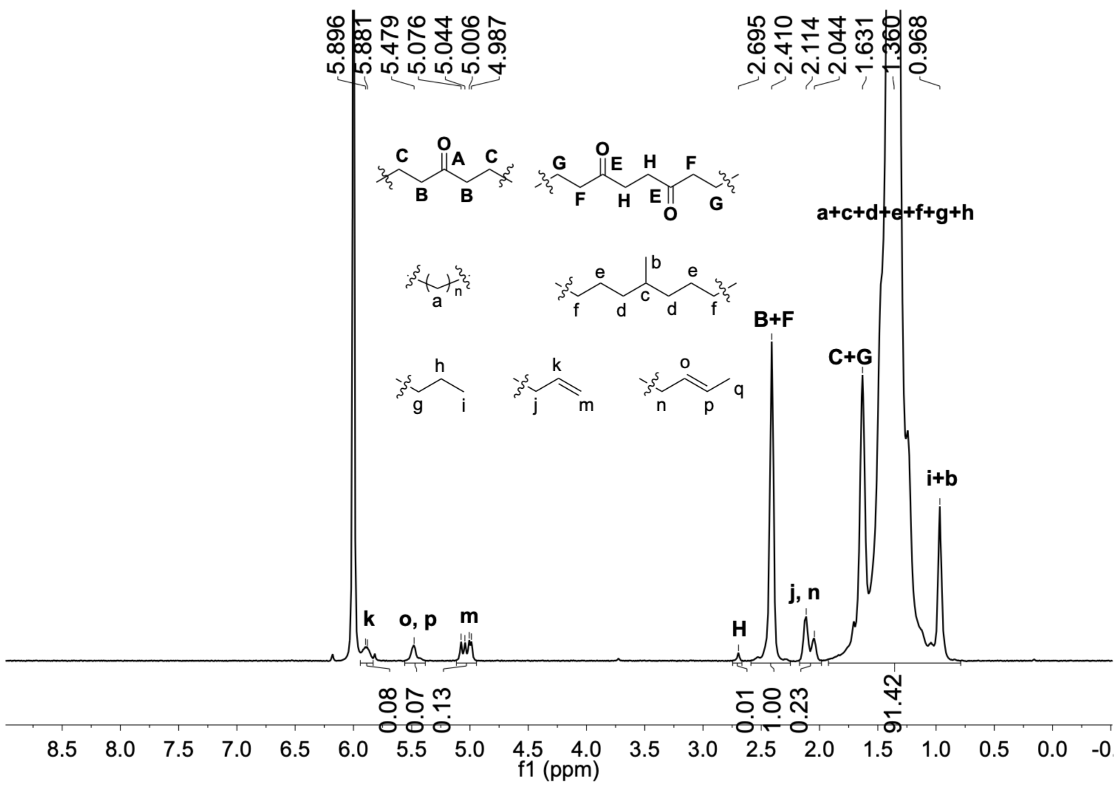
Supplementary Figure 21. Quantitative ^{13}C NMR spectrum of the polymer obtained in Table 1, entry 5 (1,1,2,2-tetrachloroethane-d_2, 126 MHz, 120 ^{o}C).



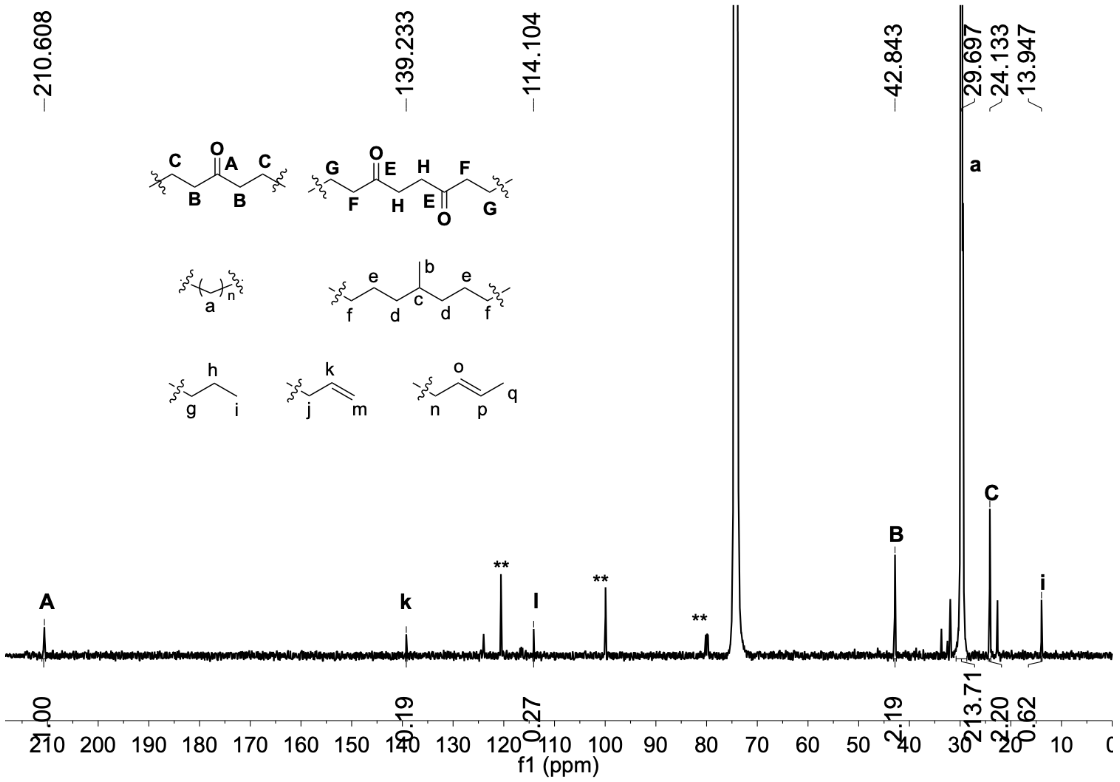
Supplementary Figure 22. Supplementary Figure 1. ^{1}H NMR spectrum of the polymer obtained in Table 1, entry 6 (1,1,2,2-tetrachloroethane-*d*$_2$, 500 MHz, 120 °C).



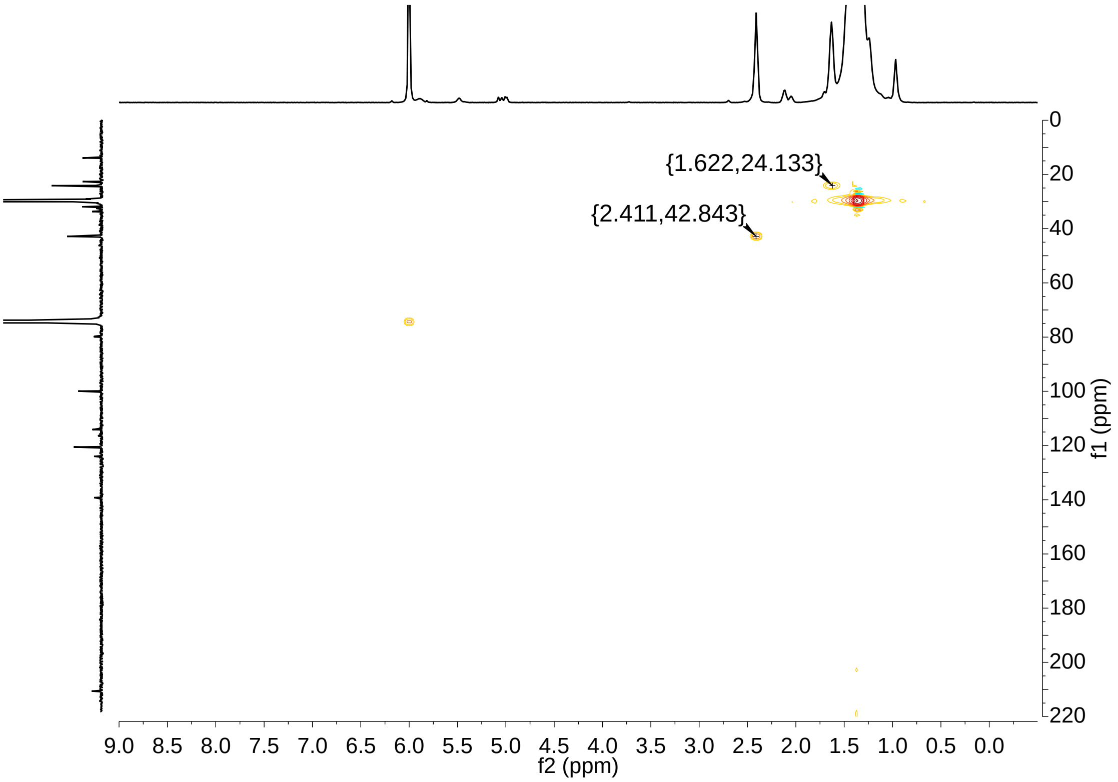
Supplementary Figure 23. Quantitative ^{13}C NMR spectrum of the polymer obtained in Table 1, entry 6 (1,1,2,2-tetrachloroethane-*d*$_2$, 126 MHz, 120 °C).



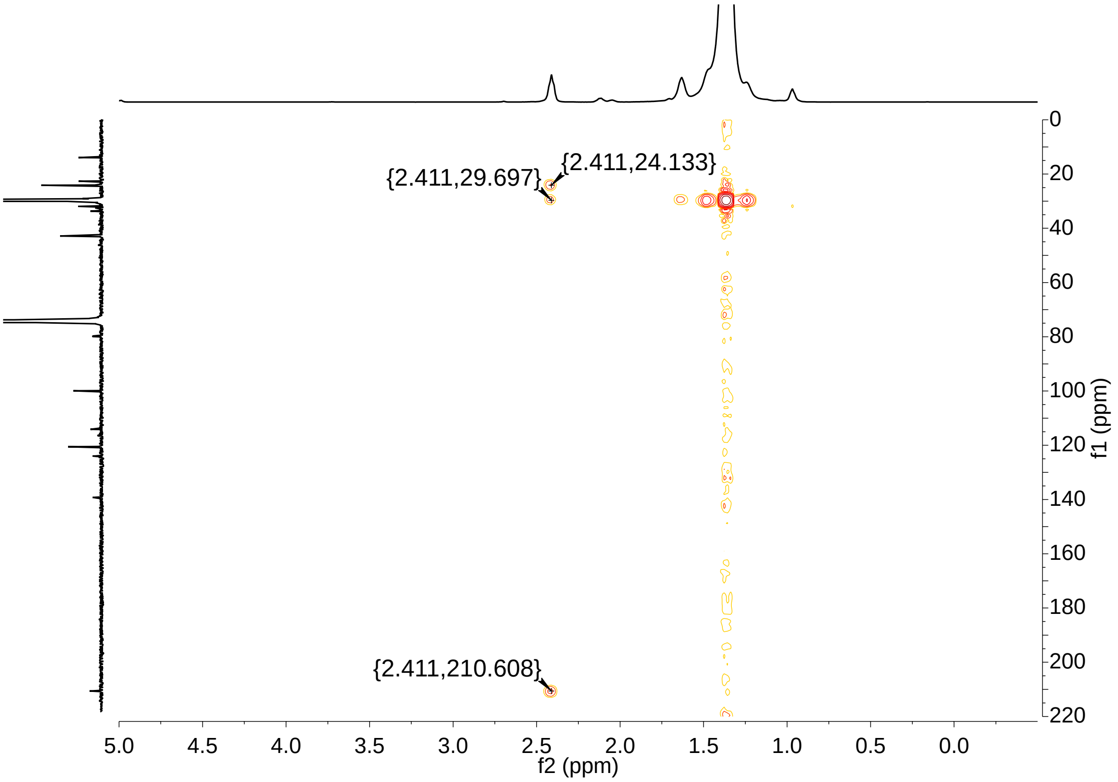
Supplementary Figure 24. ^{1}H NMR spectrum of the polymer obtained in Table 1, entry 7 (1,1,2,2-tetrachloroethane-d_2, 500 MHz, 120 ^{o}C).



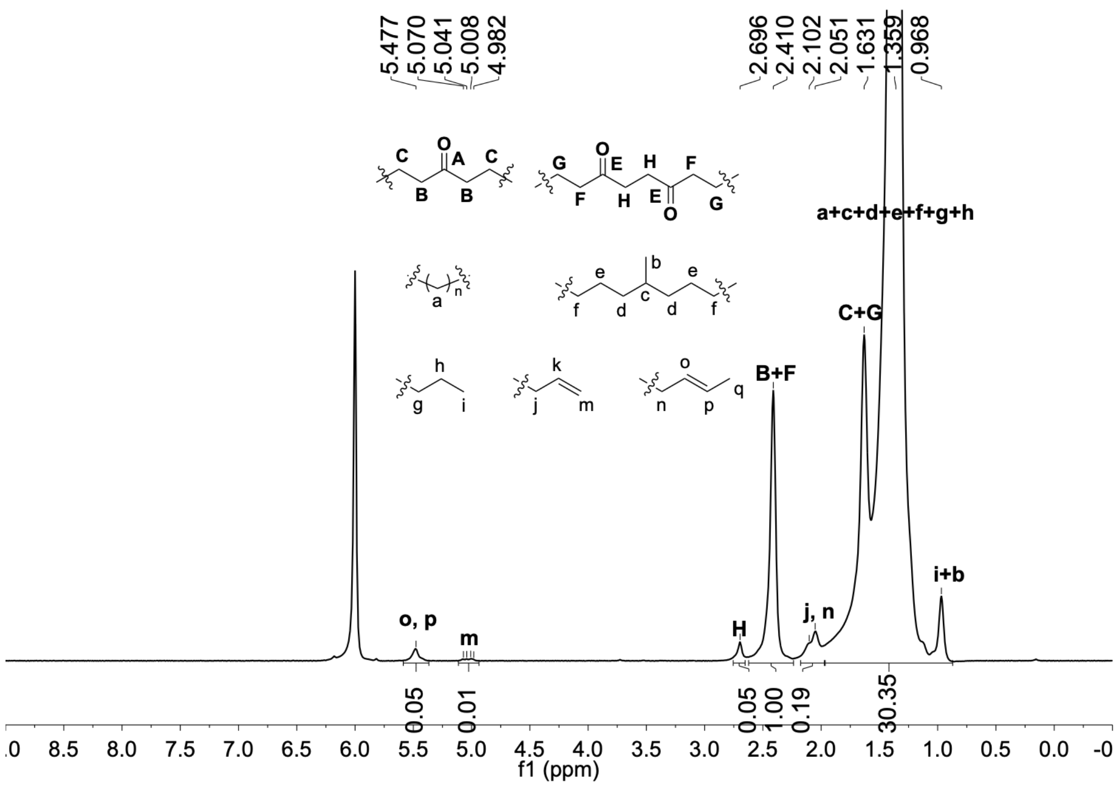
Supplementary Figure 25. Quantitative ^{13}C NMR spectrum of the polymer obtained in Table 1, entry 7 (1,1,2,2-tetrachloroethane-d_2, 126 MHz, 120 ^{o}C).



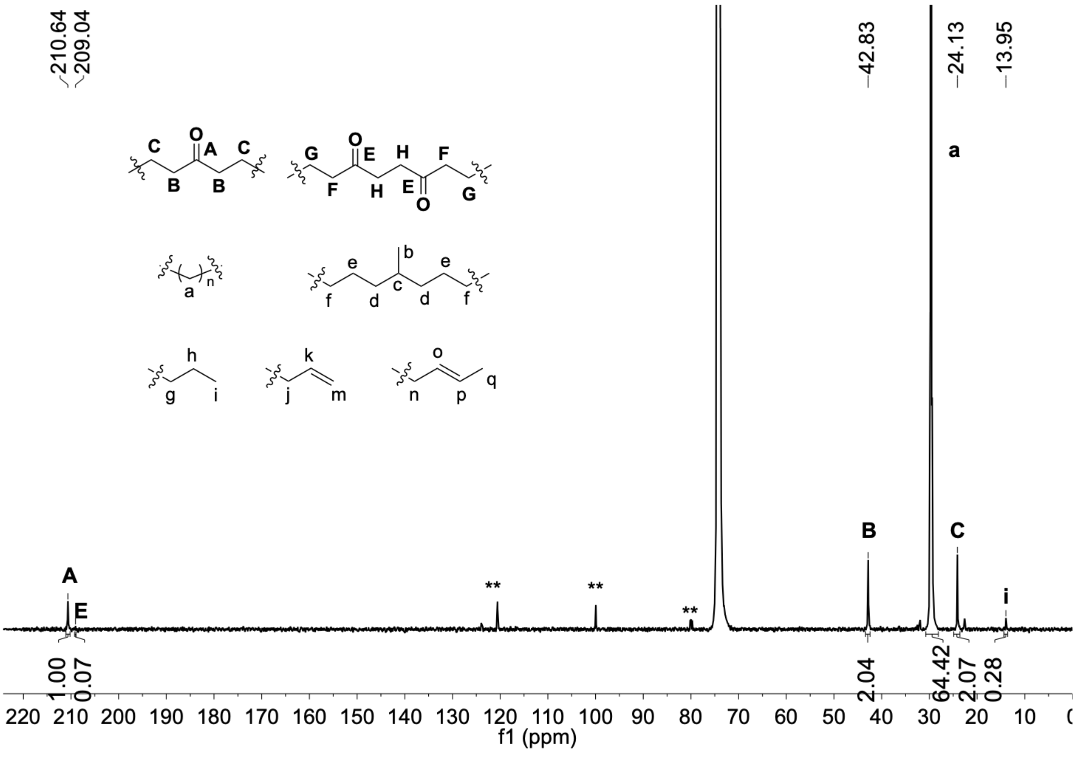
Supplementary Figure 26. ^{1}H-^{13}C HSQC spectrum of the polymer obtained in Table 1, entry 7 (1,1,2,2-tetrachloroethane-d_2, 500 MHz, 120 ºC).



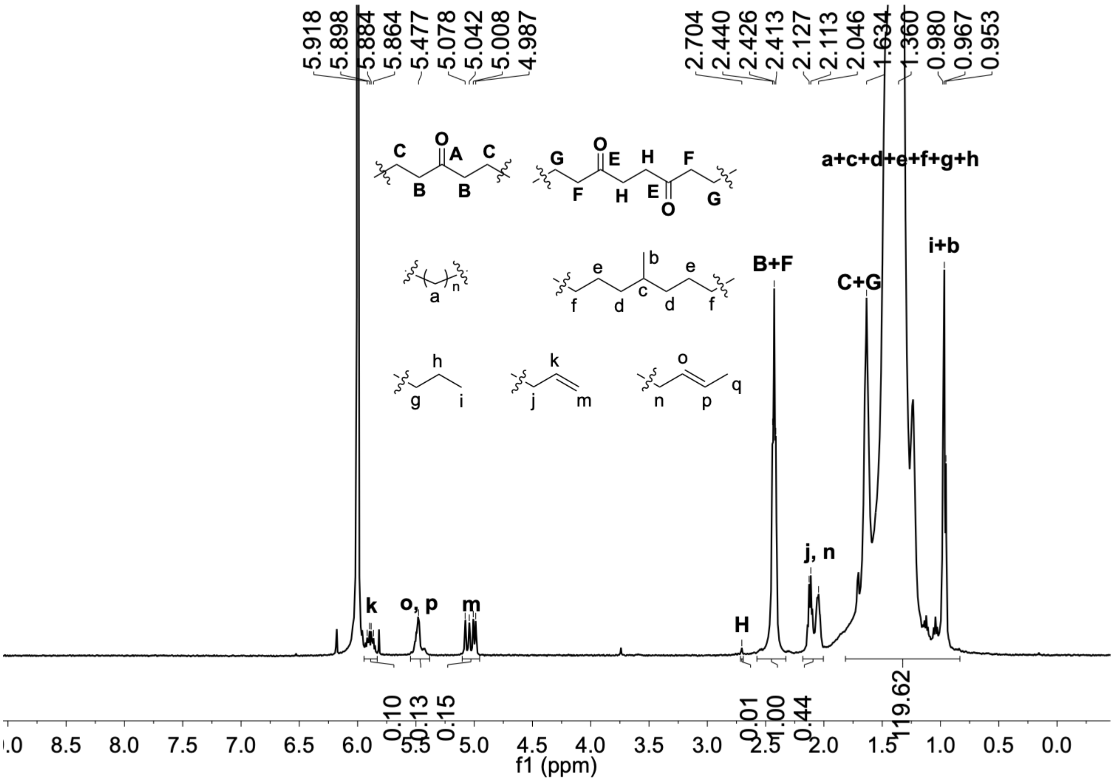
Supplementary Figure 27. ^{1}H-^{13}C HMBC spectrum of the polymer obtained in Table 1, entry 7 (1,1,2,2-tetrachloroethane-d_2, 500 MHz, 120 ºC).



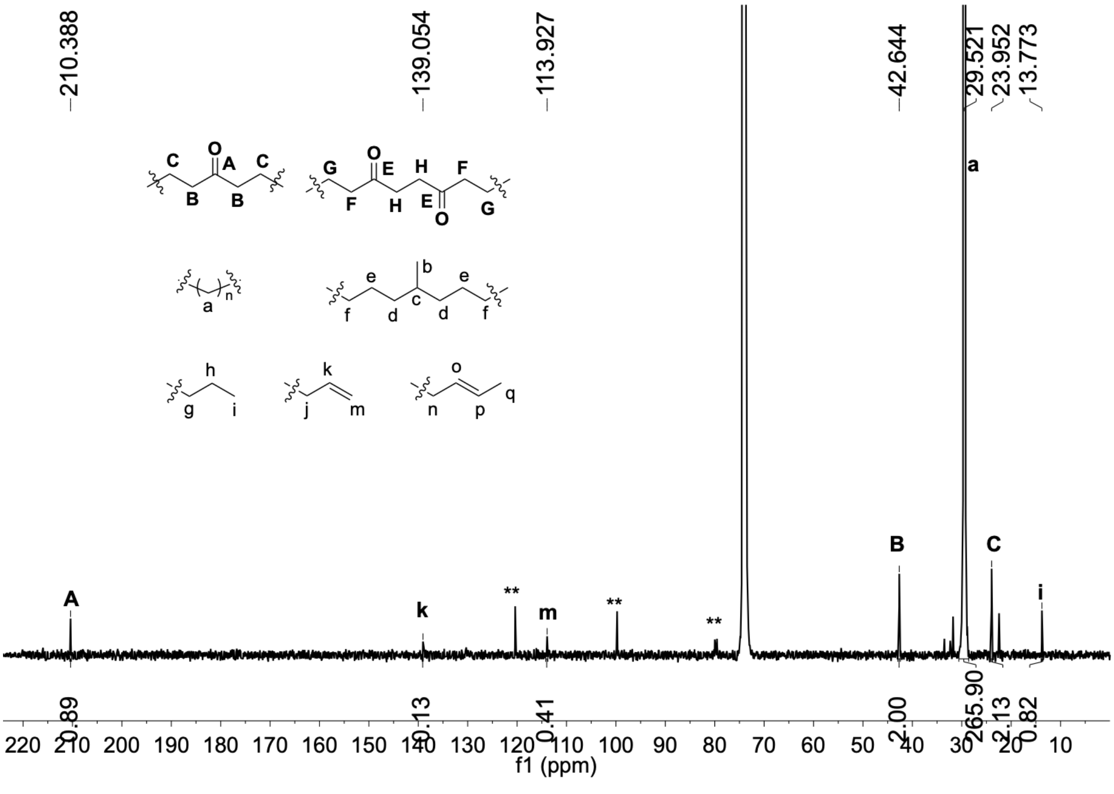
Supplementary Figure 28. ^{1}H NMR spectrum of the polymer obtained in Table 1, entry 8 (1,1,2,2-tetrachloroethane-d_2, 500 MHz, 120 °C).



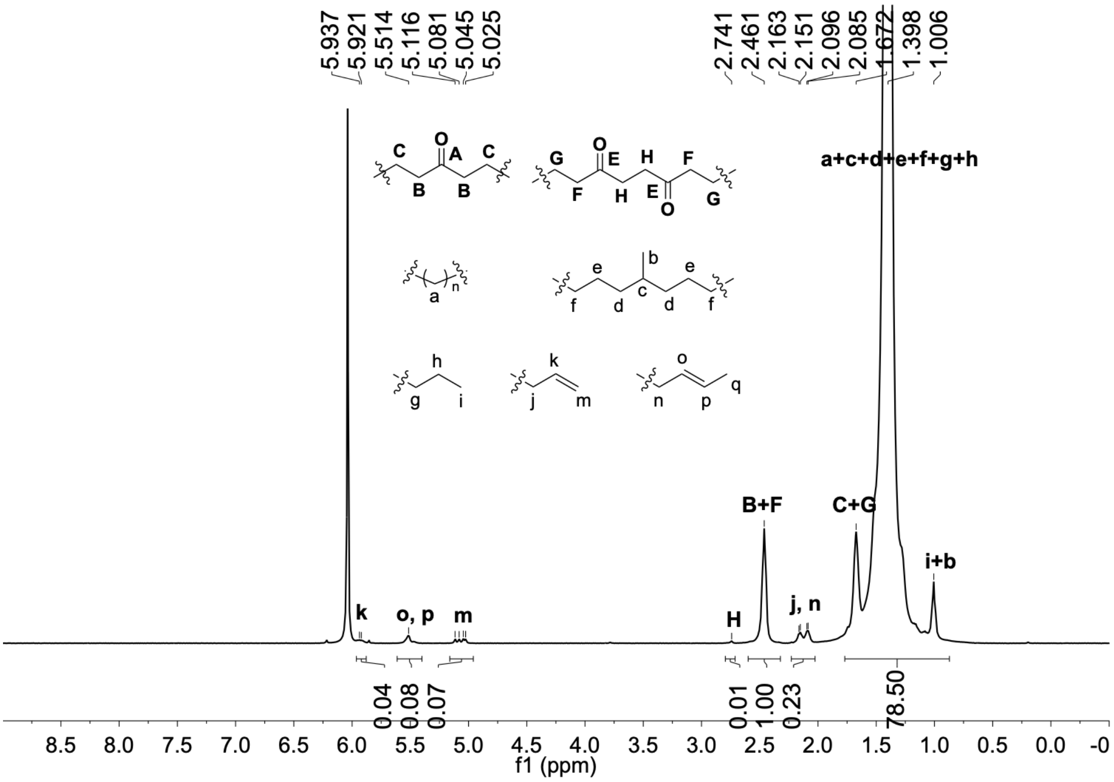
Supplementary Figure 29. Quantitative ^{13}C NMR spectrum of the polymer obtained in Table 1, entry 8 (1,1,2,2-tetrachloroethane-d_2, 126 MHz, 120 °C).



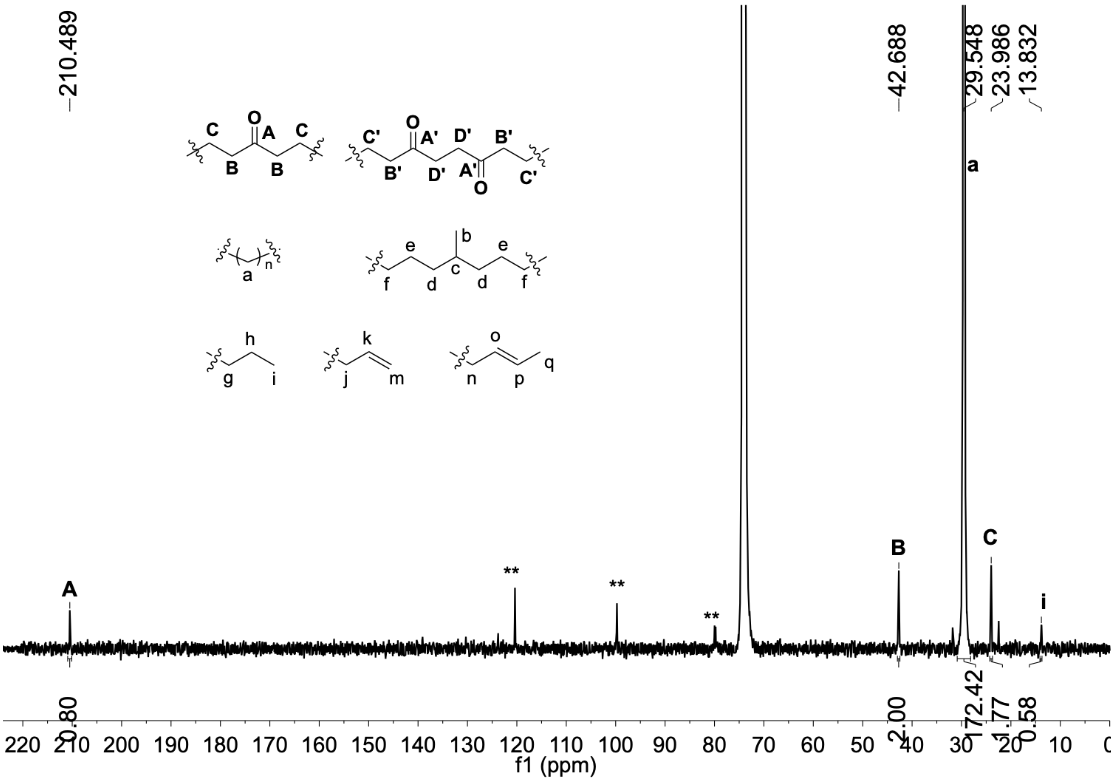
Supplementary Figure 30. ^{1}H NMR spectrum of the polymer obtained in Table 1, entry 9 (1,1,2,2-tetrachloroethane-d_2, 500 MHz, 120 °C).



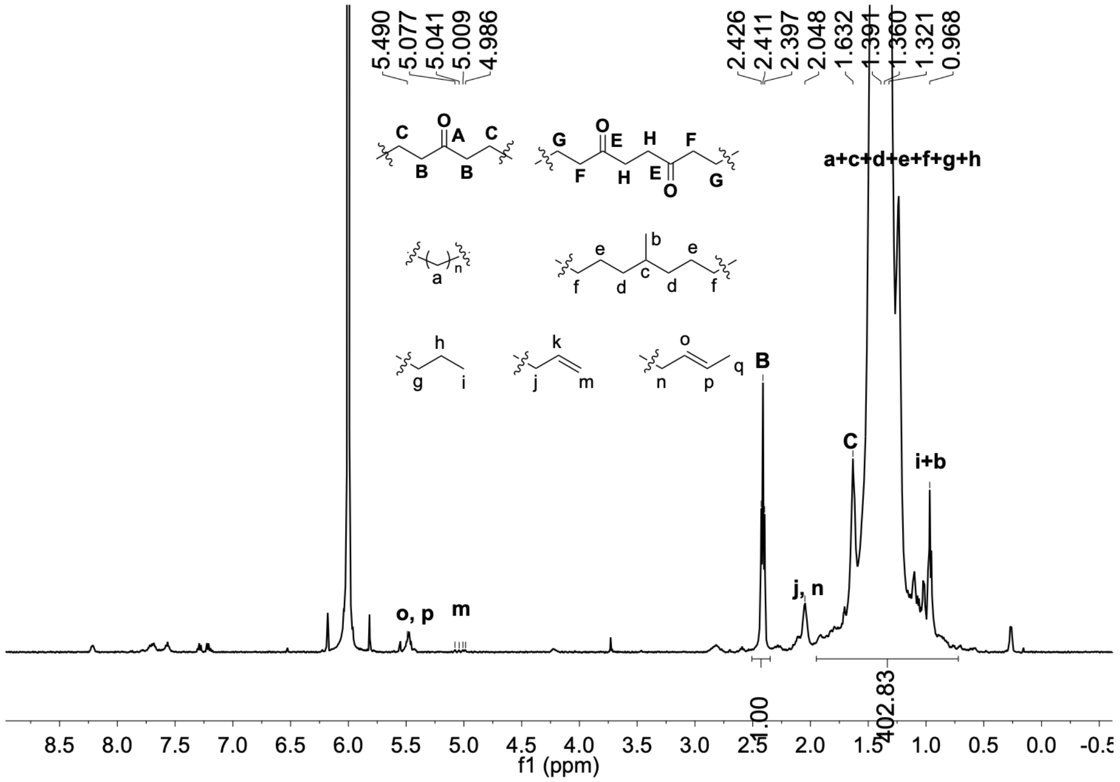
Supplementary Figure 31. Quantitative ^{13}C NMR spectrum of the polymer obtained in Table 1, entry 9 (1,1,2,2-tetrachloroethane-d_2, 126 MHz, 120 °C).



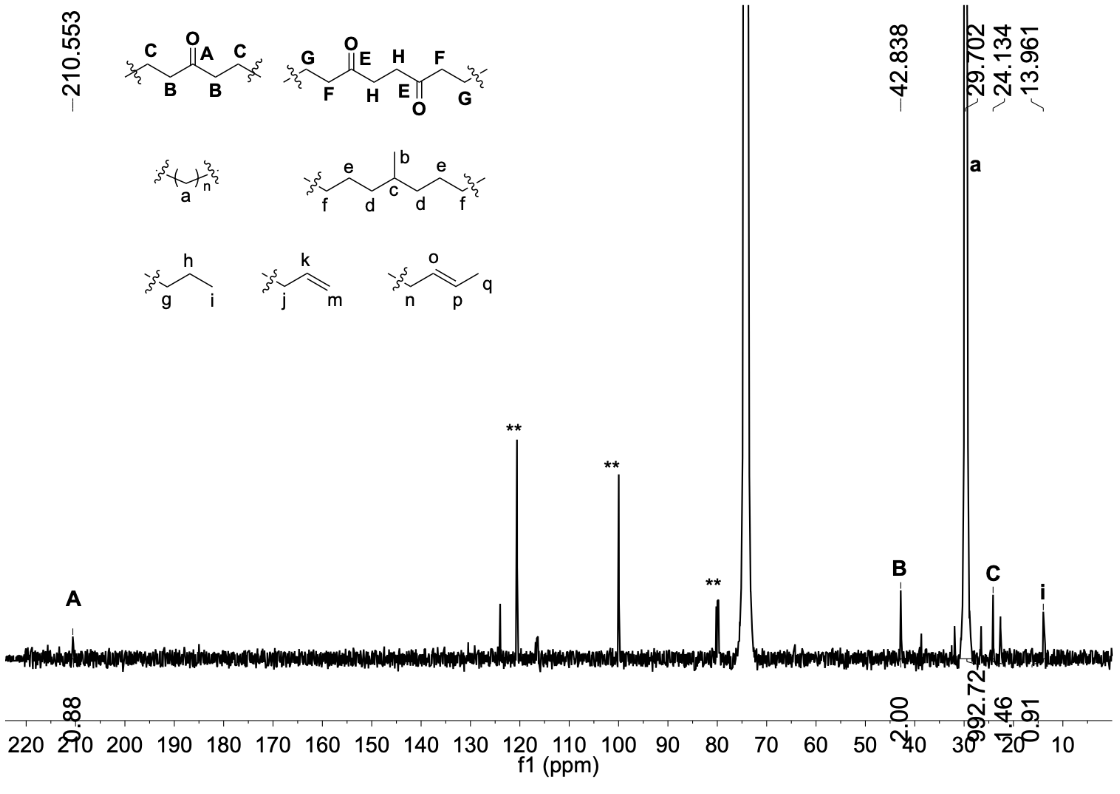
Supplementary Figure 32. ^{1}H NMR spectrum of the polymer obtained in Table 1, entry 10 (1,1,2,2-tetrachloroethane-d_2, 500 MHz, 120 °C).



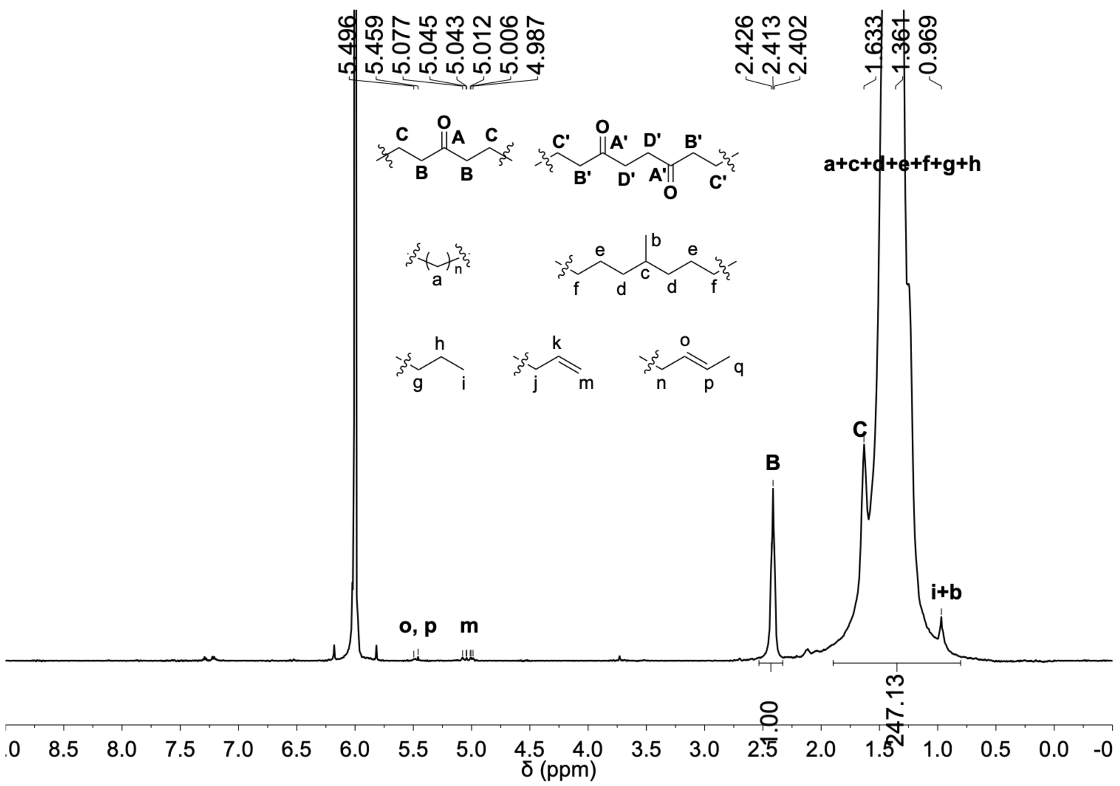
Supplementary Figure 33. Quantitative ^{13}C NMR spectrum of the polymer obtained in Table 1, entry 10 (1,1,2,2-tetrachloroethane-d_2, 126 MHz, 120 °C).



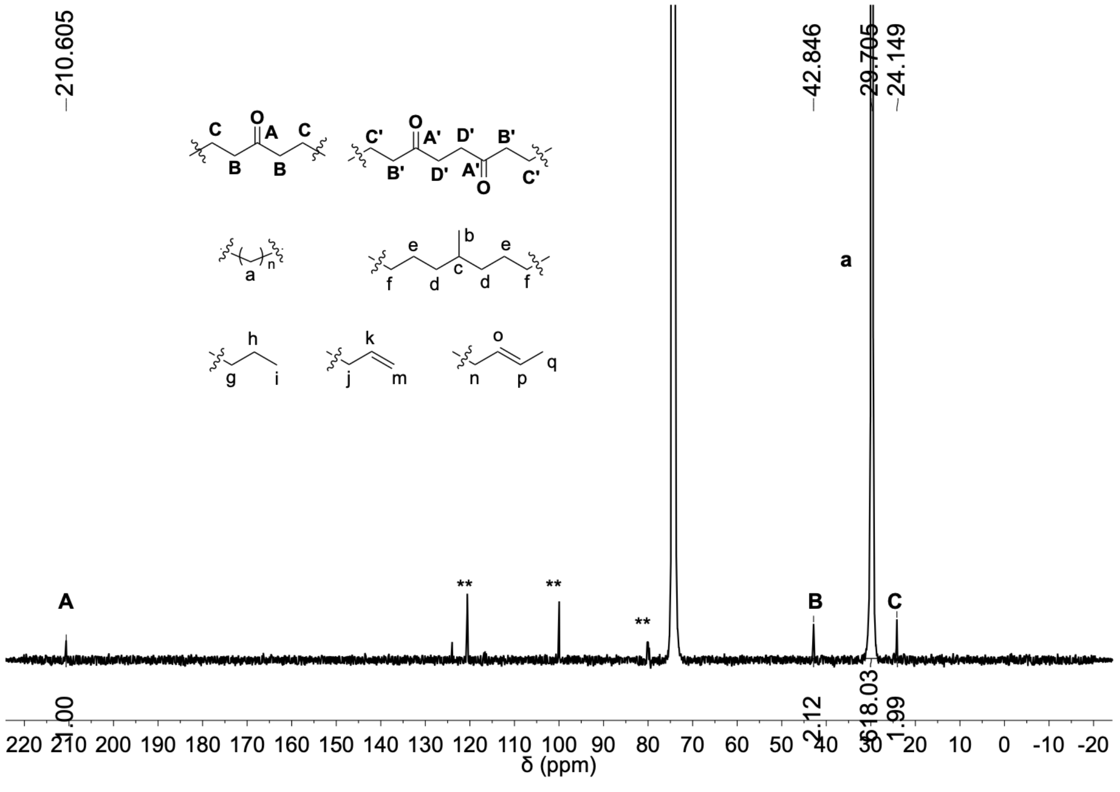
Supplementary Figure 34. ^{1}H NMR spectrum of the polymer obtained in Table 1, entry 11 (1,1,2,2-tetrachloroethane-d_2, 500 MHz, 120 °C).



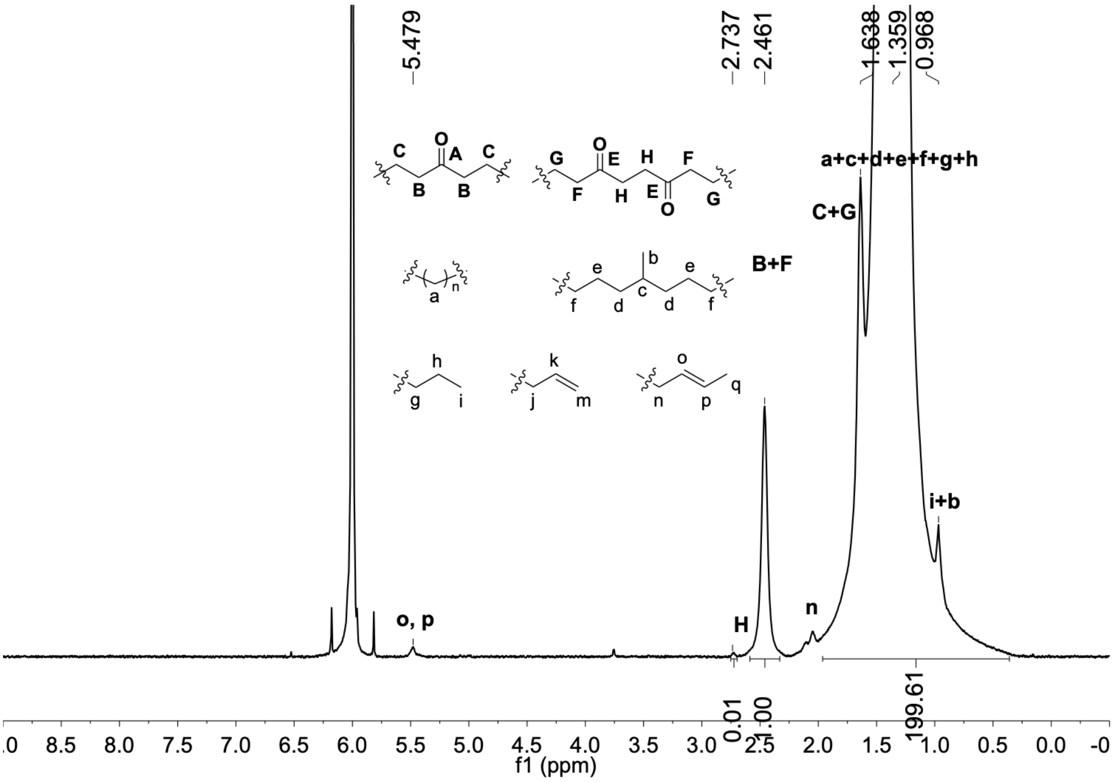
Supplementary Figure 35. Quantitative ^{13}C NMR spectrum of the polymer obtained in Table 1, entry 11 (1,1,2,2-tetrachloroethane-d_2, 126 MHz, 120 °C).



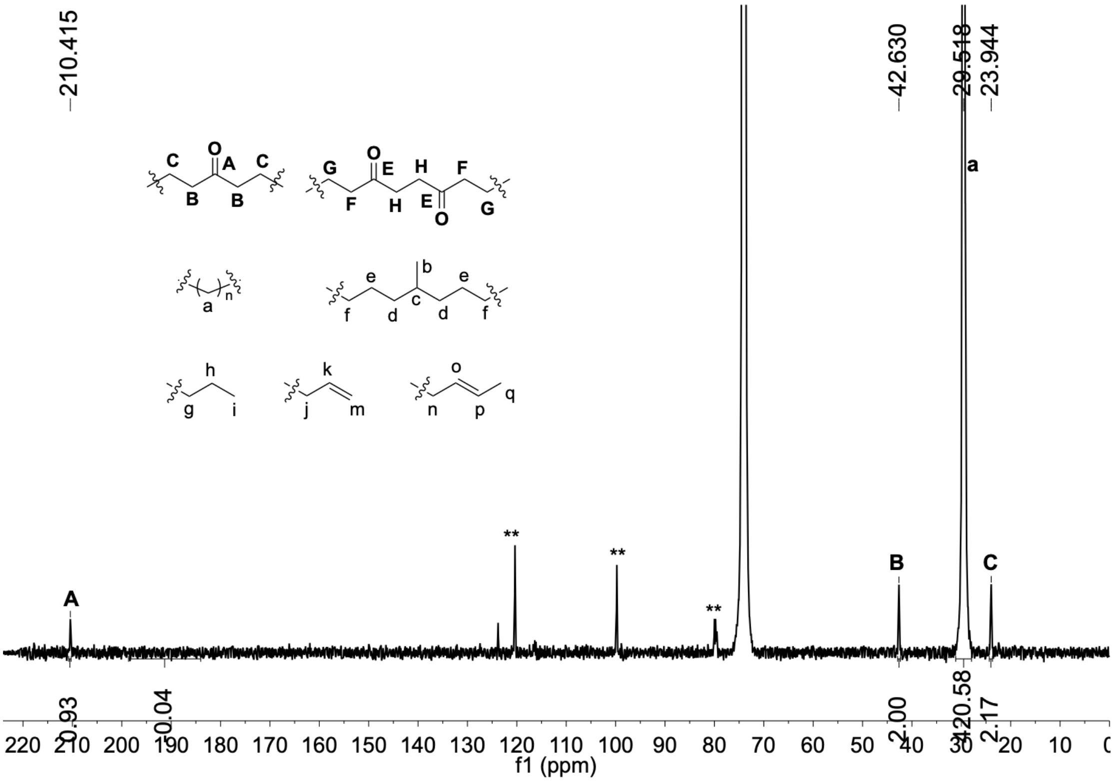
Supplementary Figure 36. ^{1}H NMR spectrum of the polymer obtained in Table 1, entry 12 (1,1,2,2-tetrachloroethane-d_2, 500 MHz, 120 °C).



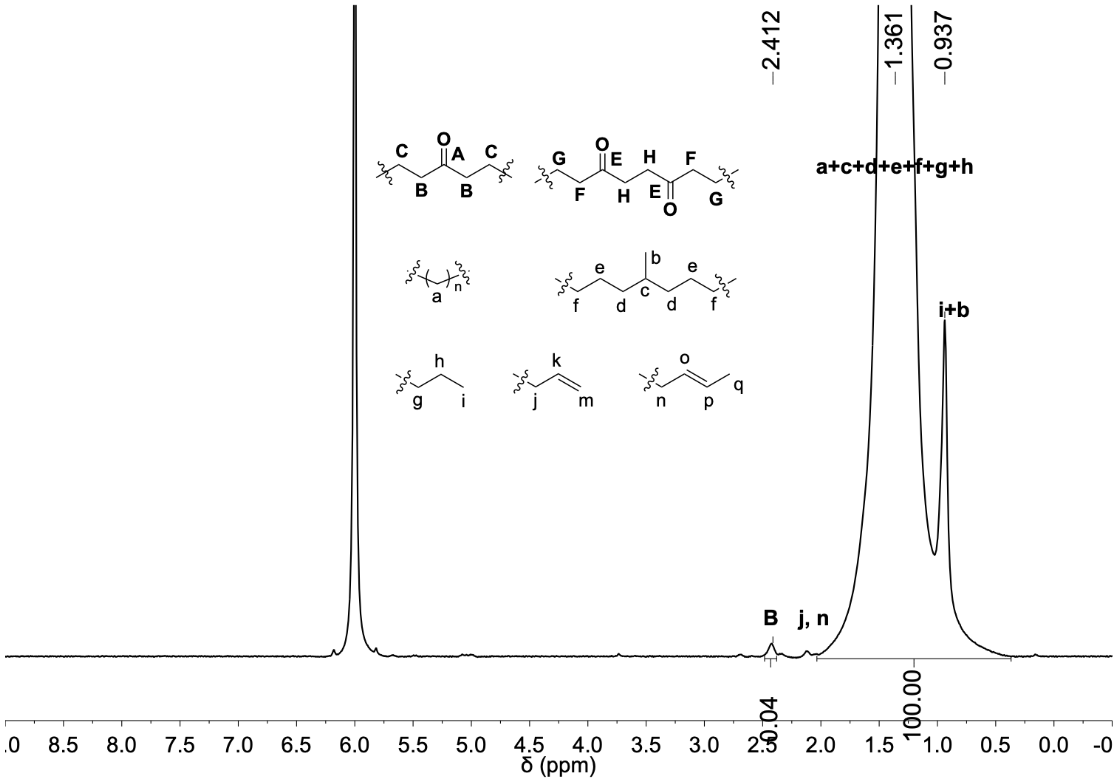
Supplementary Figure 37. Quantitative ^{13}C NMR spectrum of the polymer obtained in Table 1, entry 12 (1,1,2,2-tetrachloroethane-d_2, 126 MHz, 120 °C).



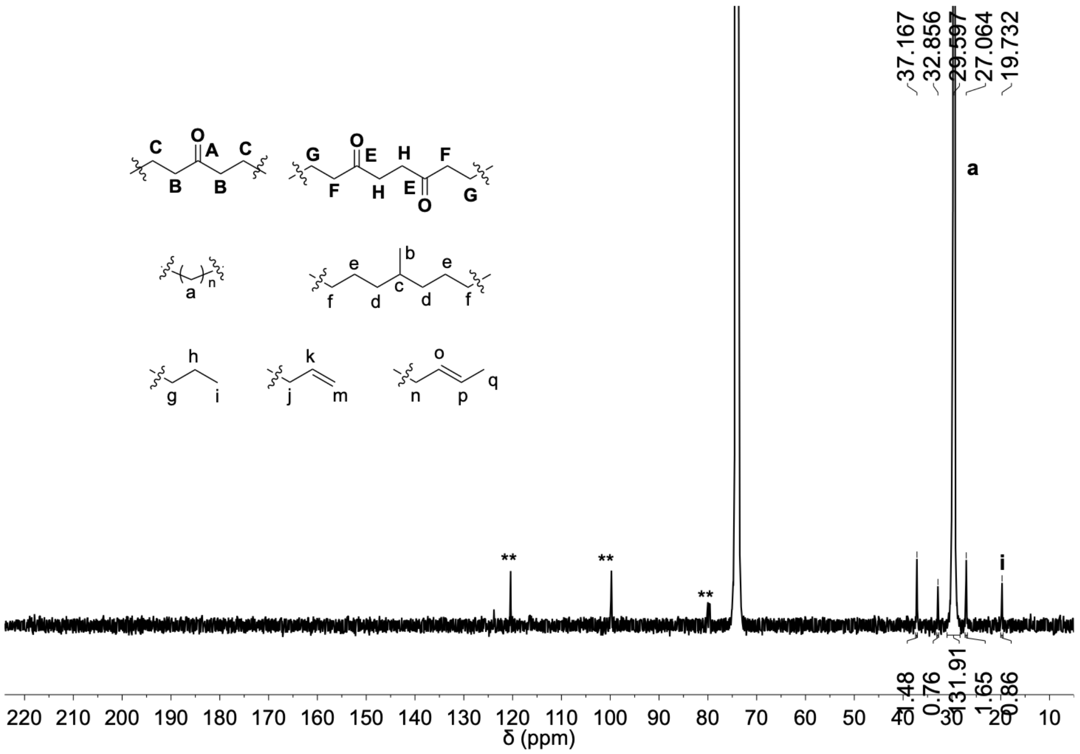
Supplementary Figure 38. ^{1}H NMR spectrum of the polymer obtained in Table 1, entry 13 (1,1,2,2-tetrachloroethane-d_2, 500 MHz, 120 °C).



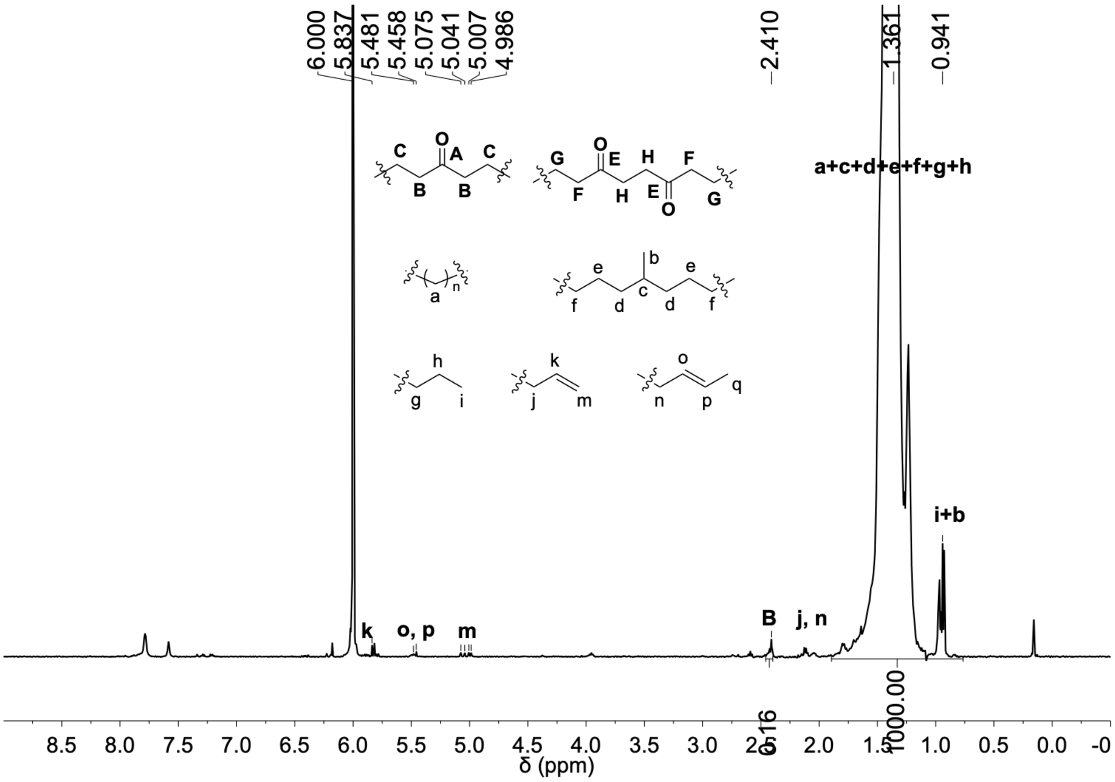
Supplementary Figure 39. Quantitative ^{13}C NMR spectrum of the polymer obtained in Table 1, entry 13 (1,1,2,2-tetrachloroethane-d_2, 126 MHz, 120 °C).



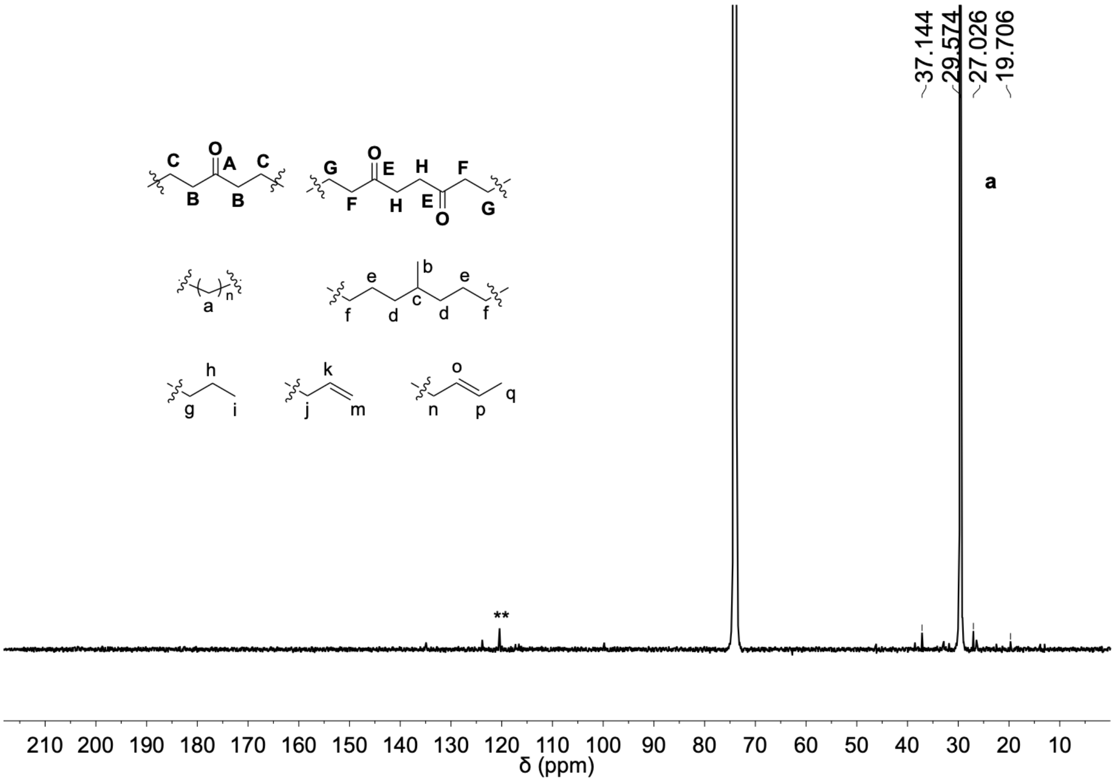
Supplementary Figure 40. ^{1}H NMR spectrum of the polymer obtained in Table 1, entry 14 (1,1,2,2-tetrachloroethane-d_2, 500 MHz, 120 °C).



Supplementary Figure 41. Quantitative ^{13}C NMR spectrum of the polymer obtained in Table 1, entry 14 (1,1,2,2-tetrachloroethane-d_2, 126 MHz, 120 °C).

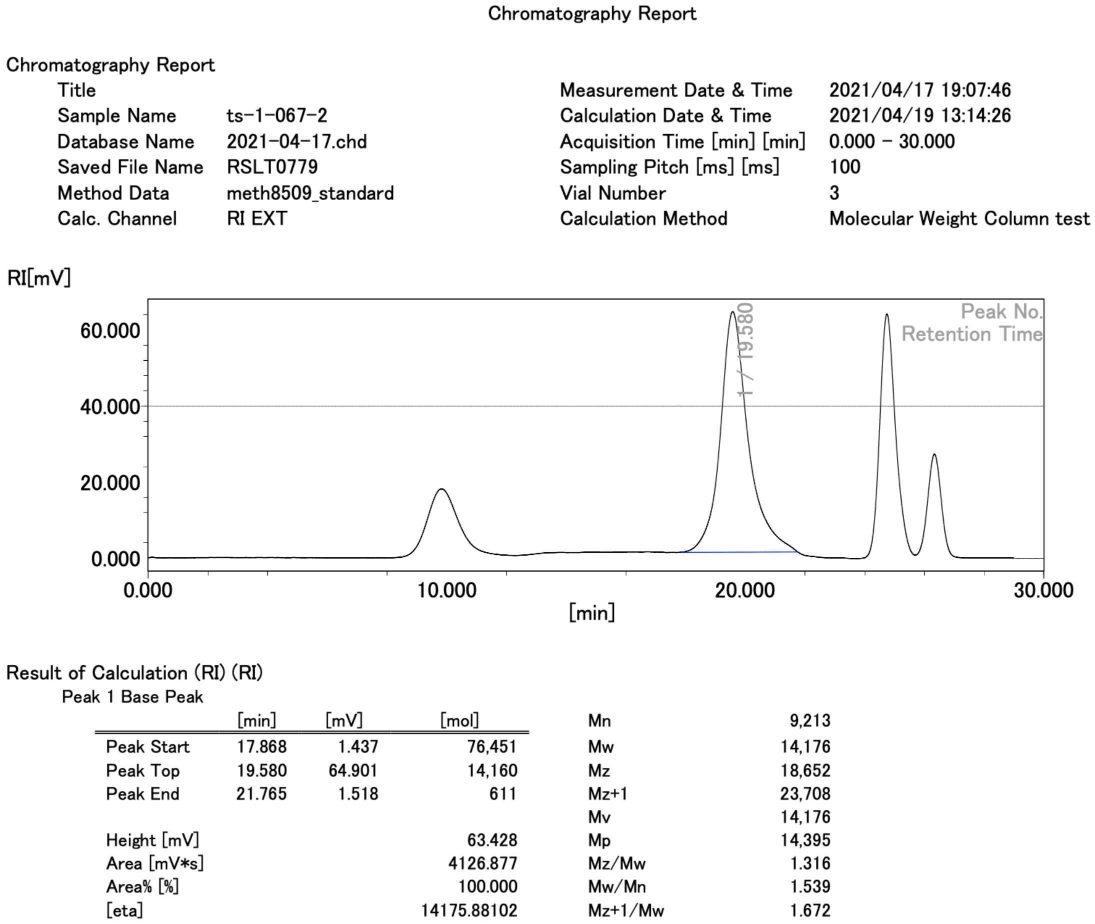


Supplementary Figure 42. ^{1}H NMR spectrum of the polymer obtained in Table 1, entry 15 (1,1,2,2-tetrachloroethane-d_2, 500 MHz, 120 °C).



Supplementary Figure 43. Quantitative ^{13}C NMR spectrum of the polymer obtained in Table 1, entry 15 (1,1,2,2-tetrachloroethane-d_2, 126 MHz, 120 °C).

Copies of SEC Charts



Chromatography Report

Chromatography Report

Title		Measurement Date & Time	2021/04/17 19:07:46
Sample Name	ts-1-067-2	Calculation Date & Time	2021/04/19 13:14:26
Database Name	2021-04-17.chd	Acquisition Time [min] [min]	0.000 - 30.000
Saved File Name	RSLT0779	Sampling Pitch [ms] [ms]	100
Method Data	meth8509_standard	Vial Number	3
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test

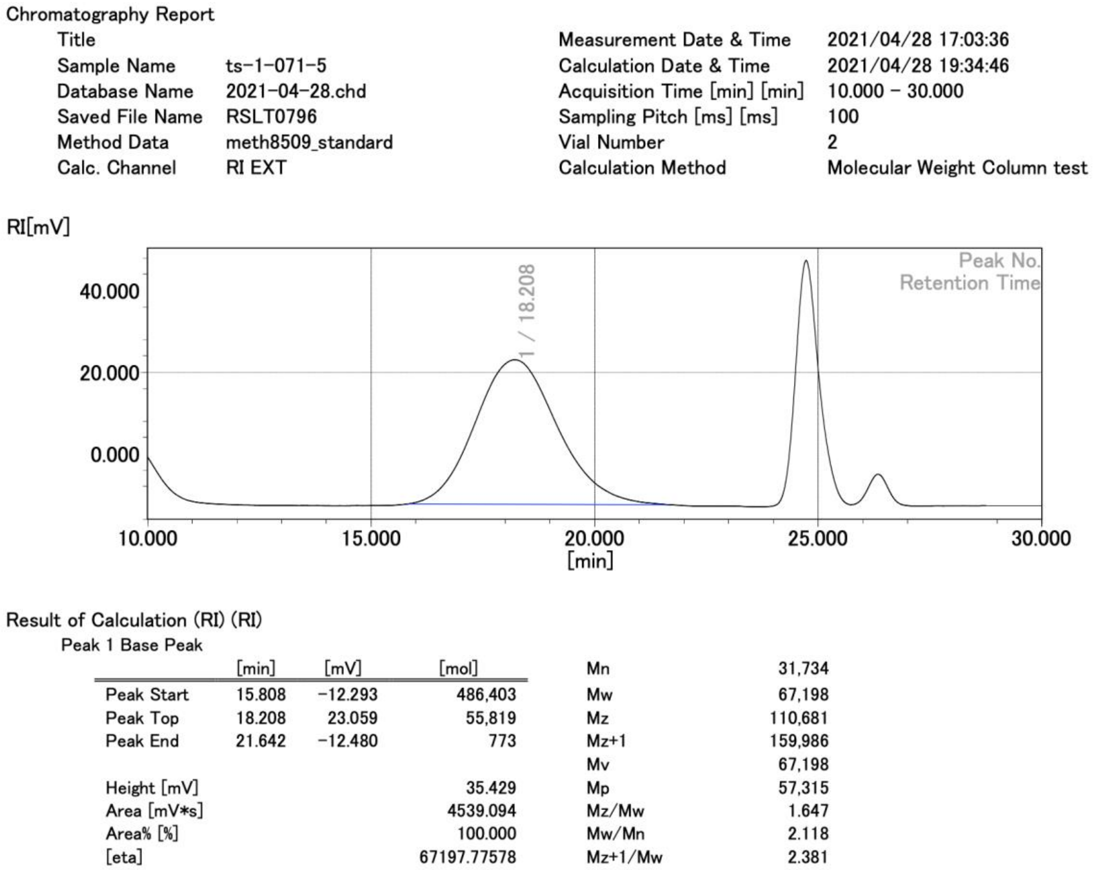
Result of Calculation (RI) (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]
Peak Start	17.868	1.437	76,451
Peak Top	19.580	64.901	14,160
Peak End	21.765	1.518	611
Height [mV]			63.428
Area [mV*s]			4126.877
Area% [%]			100.000
[eta]			14175.88102

Mn	9,213
Mw	14,176
Mz	18,652
Mz+1	23,708
Mv	14,176
Mp	14,395
Mz/Mw	1.316
Mw/Mn	1.539
Mz+1/Mw	1.672

Supplementary Figure 44. SEC chart of the polymer obtained in Table 1, entry 1. M_n (PS) = 9,213 was corrected to M_n (PE) = 4,000 by universal calibration.



Chromatography Report

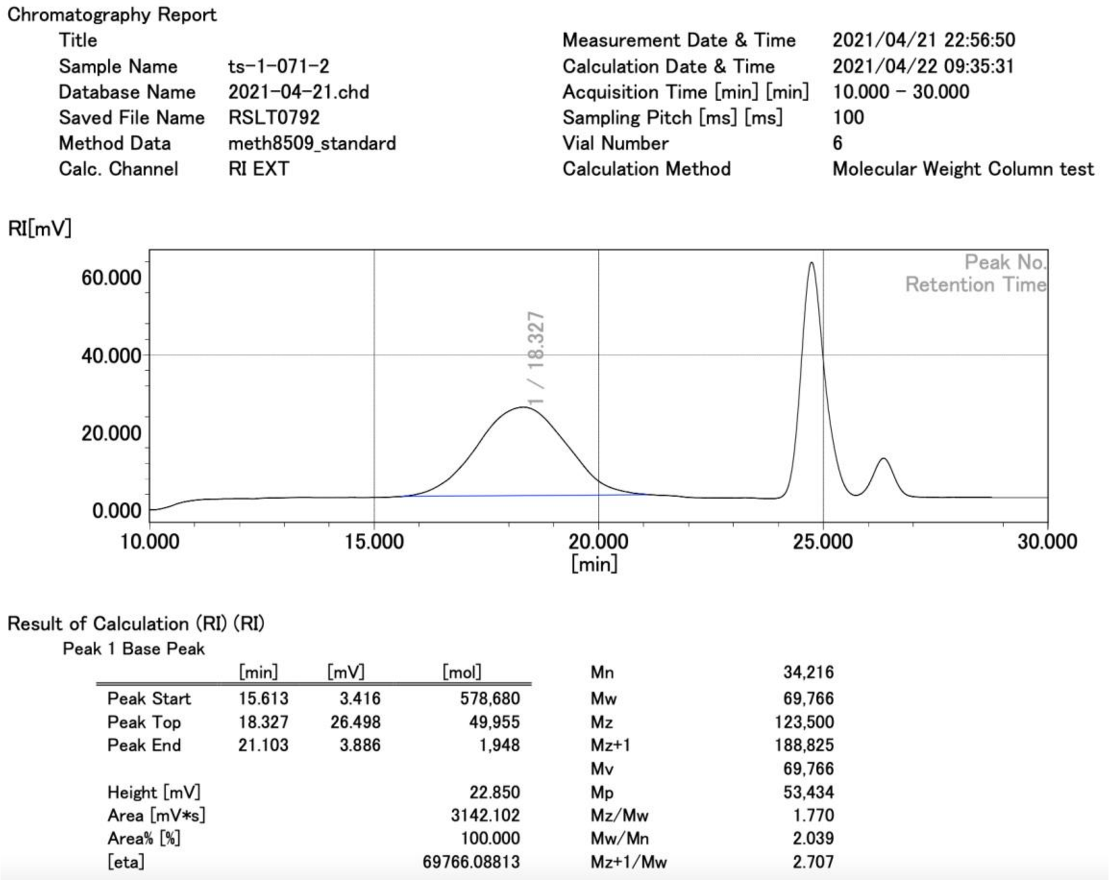
Title		Measurement Date & Time	2021/04/28 17:03:36
Sample Name	ts-1-071-5	Calculation Date & Time	2021/04/28 19:34:46
Database Name	2021-04-28.chd	Acquisition Time [min] [min]	10.000 - 30.000
Saved File Name	RSLT0796	Sampling Pitch [ms] [ms]	100
Method Data	meth8509_standard	Vial Number	2
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test

Result of Calculation (RI) (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak Start	15.808	-12.293	486,403	Mn	31,734
Peak Top	18.208	23.059	55,819	Mw	67,198
Peak End	21.642	-12.480	773	Mz	110,681
				Mz+1	159,986
				Mv	67,198
Height [mV]			35.429	Mp	57,315
Area [mV*s]			4539.094	Mz/Mw	1.647
Area% [%]			100.000	Mw/Mn	2.118
[eta]			67197.77578	Mz+1/Mw	2.381

Supplementary Figure 45. SEC chart of the polymer obtained in Table 1, entry 2. M_n (PS) = 31,734 was corrected to M_n (PE) = 14,000 by universal calibration.



Chromatography Report

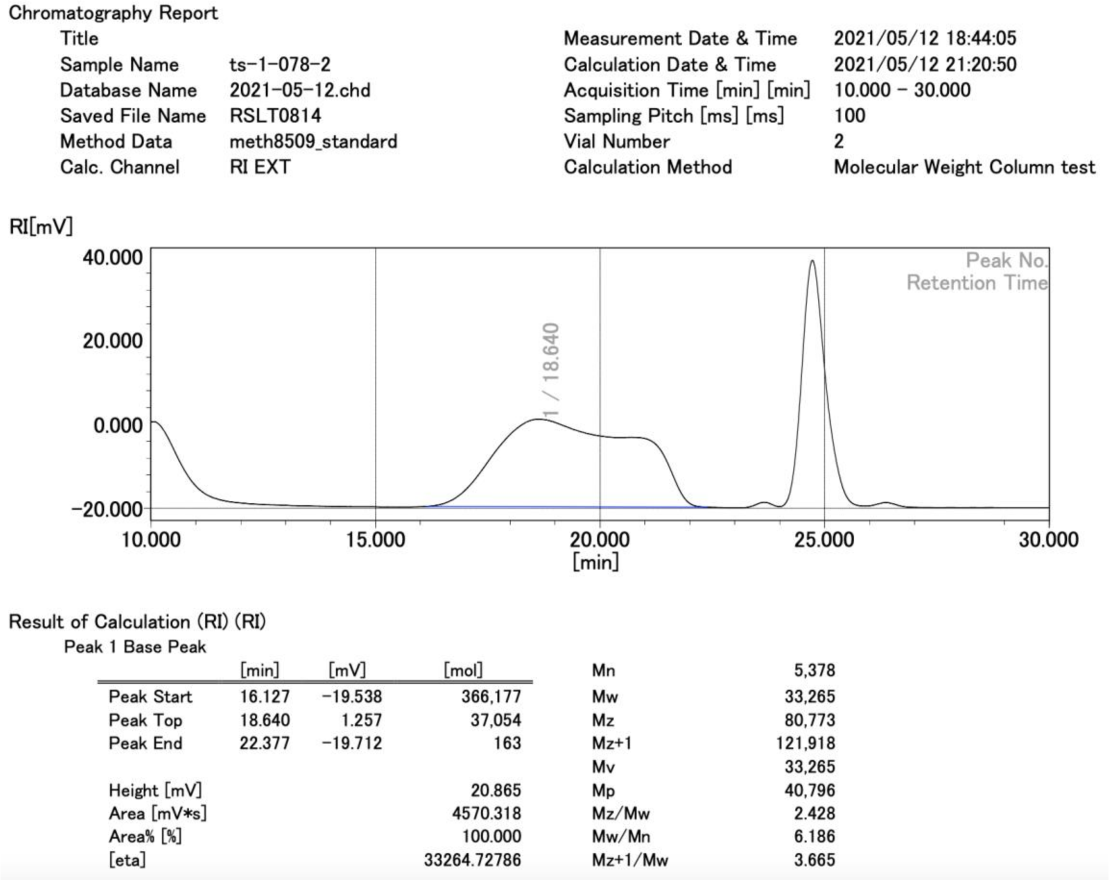
Title		Measurement Date & Time	2021/04/21 22:56:50
Sample Name	ts-1-071-2	Calculation Date & Time	2021/04/22 09:35:31
Database Name	2021-04-21.chd	Acquisition Time [min] [min]	10.000 - 30.000
Saved File Name	RSLT0792	Sampling Pitch [ms] [ms]	100
Method Data	meth8509_standard	Vial Number	6
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test

Result of Calculation (RI) (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
				Mn	34,216
Peak Start	15.613	3.416	578,680	Mw	69,766
Peak Top	18.327	26.498	49,955	Mz	123,500
Peak End	21.103	3.886	1,948	Mz+1	188,825
				Mv	69,766
Height [mV]			22.850	Mp	53,434
Area [mV*s]			3142.102	Mz/Mw	1.770
Area% [%]			100.000	Mw/Mn	2.039
[eta]			69766.08813	Mz+1/Mw	2.707

Supplementary Figure 46. SEC chart of the polymer obtained in Table 1, entry 3. M_n (PS) = 34,216 was corrected to M_n (PE) = 14,000 by universal calibration.



Chromatography Report

Title		Measurement Date & Time	2021/05/12 18:44:05
Sample Name	ts-1-078-2	Calculation Date & Time	2021/05/12 21:20:50
Database Name	2021-05-12.chd	Acquisition Time [min] [min]	10.000 - 30.000
Saved File Name	RSLT0814	Sampling Pitch [ms] [ms]	100
Method Data	meth8509_standard	Vial Number	2
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test

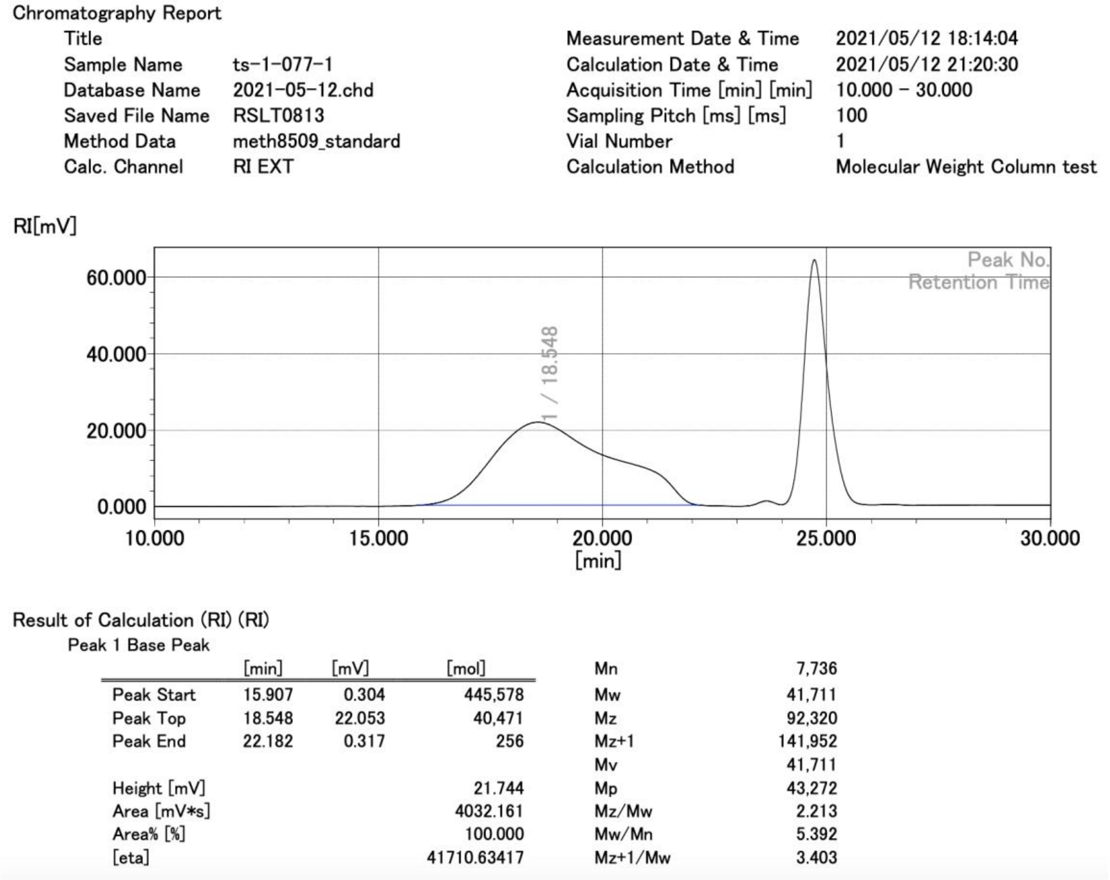
Result of Calculation (RI) (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak Start	16.127	-19.538	366,177	Mw	33,265
Peak Top	18.640	1.257	37,054	Mz	80,773
Peak End	22.377	-19.712	163	Mz+1	121,918
				Mv	33,265
Height [mV]			20.865	Mp	40,796
Area [mV*s]			4570.318	Mz/Mw	2.428
Area% [%]			100.000	Mw/Mn	6.186
[eta]			33264.72786	Mz+1/Mw	3.665

Mn 5,378

Supplementary Figure 47. SEC chart of the polymer obtained in Table 1, entry 5. M_n (PS) = 5,378 was corrected to M_n (PE) = 3,400 by universal calibration.



Chromatography Report

Title		Measurement Date & Time	2021/05/12 18:14:04
Sample Name	ts-1-077-1	Calculation Date & Time	2021/05/12 21:20:30
Database Name	2021-05-12.chd	Acquisition Time [min] [min]	10.000 - 30.000
Saved File Name	RSLT0813	Sampling Pitch [ms] [ms]	100
Method Data	meth8509_standard	Vial Number	1
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test

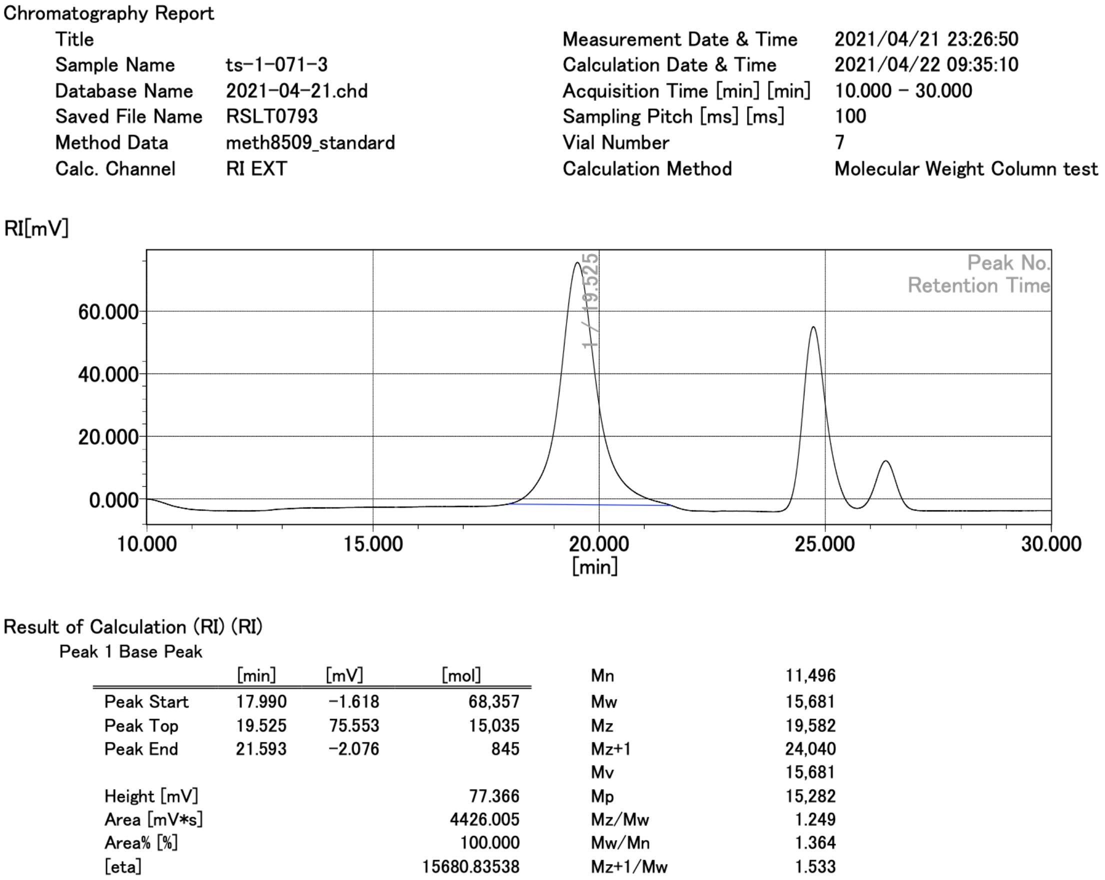
Result of Calculation (RI) (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]
Peak Start	15.907	0.304	445,578
Peak Top	18.548	22.053	40,471
Peak End	22.182	0.317	256
Height [mV]			21.744
Area [mV*s]			4032.161
Area% [%]			100.000
[eta]			41710.63417

Mn	7,736
Mw	41,711
Mz	92,320
Mz+1	141,952
Mv	41,711
Mp	43,272
Mz/Mw	2.213
Mw/Mn	5.392
Mz+1/Mw	3.403

Supplementary Figure 48. SEC chart of the polymer obtained in Table 1, entry 6. M_n (PS) = 7,736 was corrected to M_n (PE) = 2,400 by universal calibration.



Chromatography Report

Title		Measurement Date & Time	2021/04/21 23:26:50
Sample Name	ts-1-071-3	Calculation Date & Time	2021/04/22 09:35:10
Database Name	2021-04-21.chd	Acquisition Time [min] [min]	10.000 - 30.000
Saved File Name	RSLT0793	Sampling Pitch [ms] [ms]	100
Method Data	meth8509_standard	Vial Number	7
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test

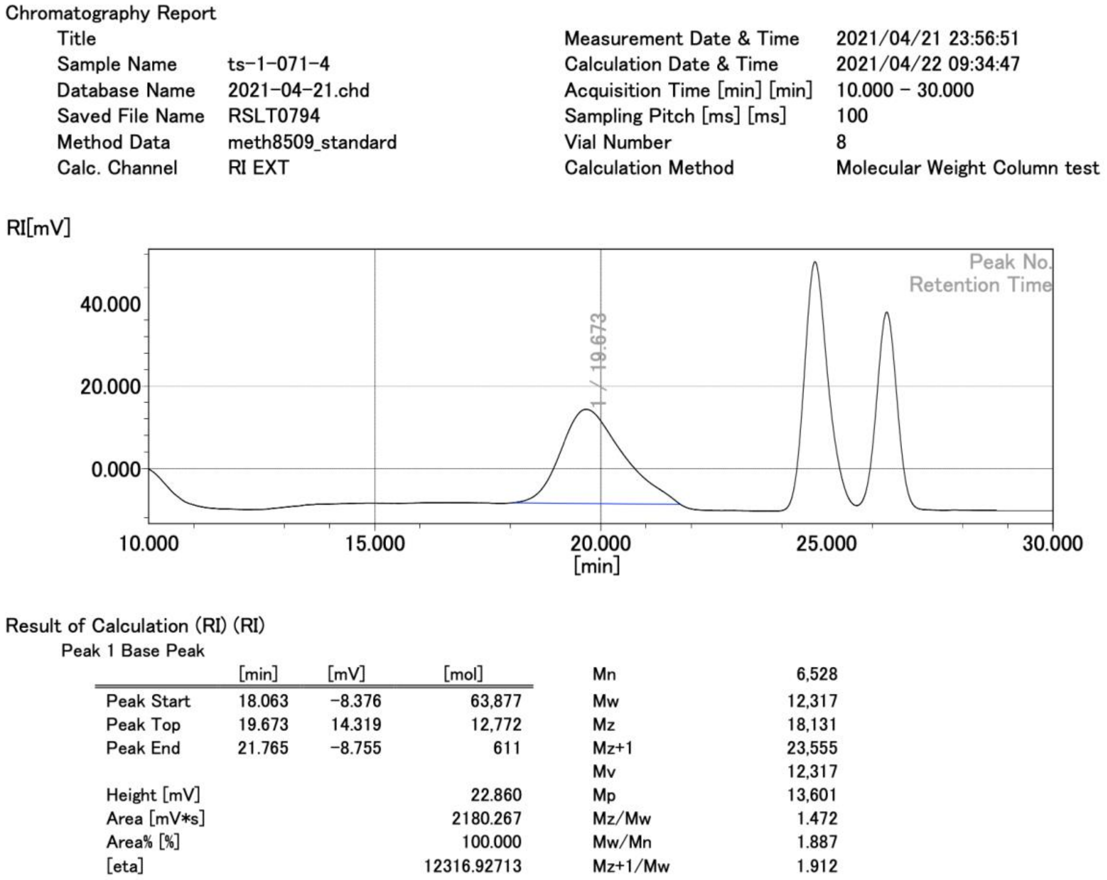
Result of Calculation (RI) (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]
Peak Start	17.990	-1.618	68,357
Peak Top	19.525	75.553	15,035
Peak End	21.593	-2.076	845
Height [mV]			77.366
Area [mV*s]			4426.005
Area% [%]			100.000
[eta]			15680.83538

Mn	11,496
Mw	15,681
Mz	19,582
Mz+1	24,040
Mv	15,681
Mp	15,282
Mz/Mw	1.249
Mw/Mn	1.364
Mz+1/Mw	1.533

Supplementary Figure 49. SEC chart of the polymer obtained in Table 1, entry 7. M_n (PS) = 11,496 was corrected to M_n (PE) = 5,000 by universal calibration.



Chromatography Report

Title	
Sample Name	ts-1-071-4
Database Name	2021-04-21.chd
Saved File Name	RSLT0794
Method Data	meth8509_standard
Calc. Channel	RI EXT

Measurement Date & Time	2021/04/21 23:56:51
Calculation Date & Time	2021/04/22 09:34:47
Acquisition Time [min] [min]	10.000 - 30.000
Sampling Pitch [ms] [ms]	100
Vial Number	8
Calculation Method	Molecular Weight Column test

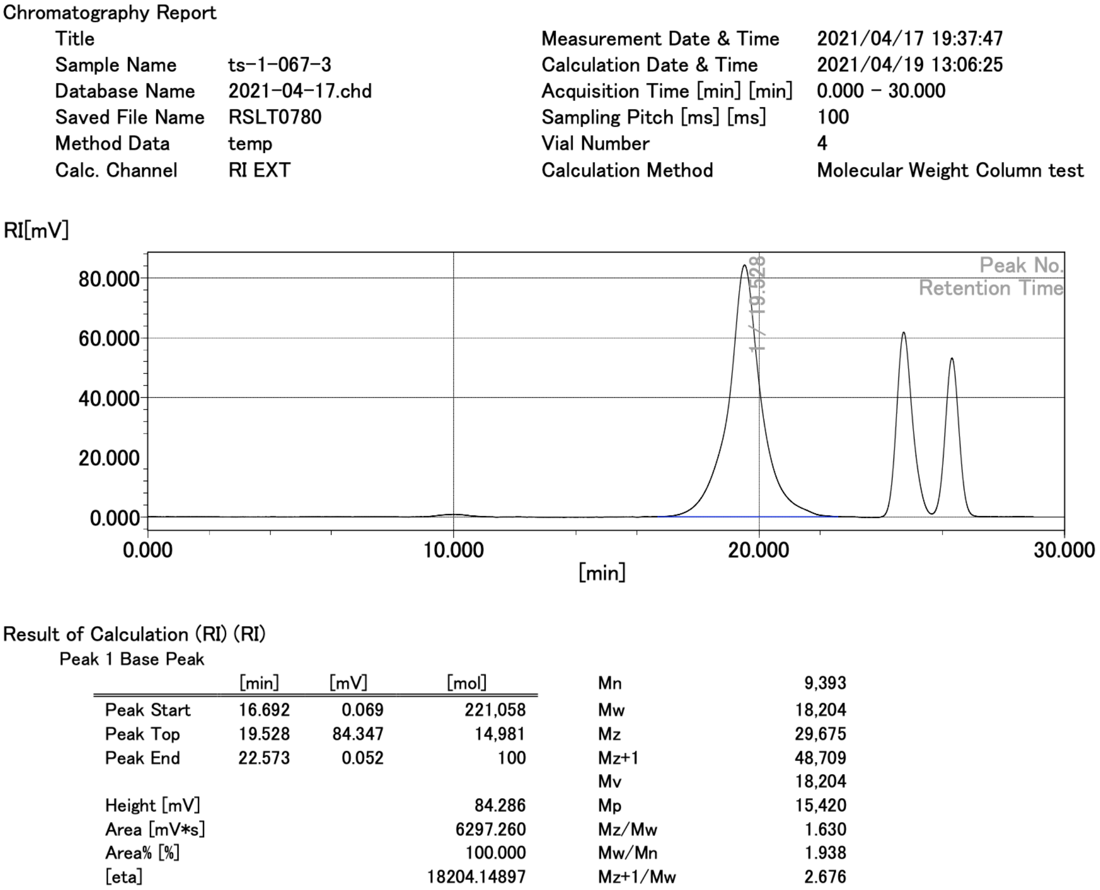
Result of Calculation (RI) (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]
Peak Start	18.063	-8.376	63,877
Peak Top	19.673	14.319	12,772
Peak End	21.765	-8.755	611
Height [mV]			22.860
Area [mV*s]			2180.267
Area% [%]			100.000
[eta]			12316.92713

Mn	6,528
Mw	12,317
Mz	18,131
Mz+1	23,555
Mv	12,317
Mp	13,601
Mz/Mw	1.472
Mw/Mn	1.887
Mz+1/Mw	1.912

Supplementary Figure 50. SEC chart of the polymer obtained in Table 1, entry 8. M_n (PS) = 6,528 was corrected to M_n (PE) = 2,900 by universal calibration.



Chromatography Report

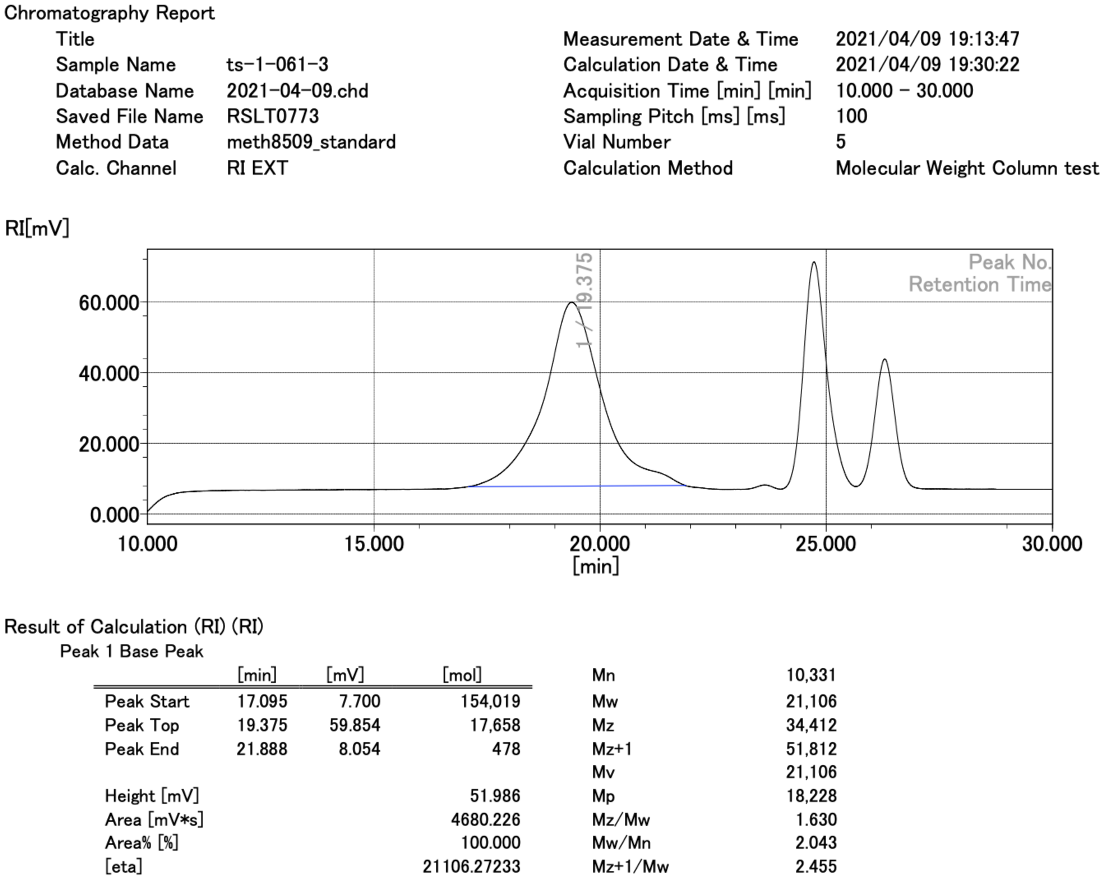
Title		Measurement Date & Time	2021/04/17 19:37:47
Sample Name	ts-1-067-3	Calculation Date & Time	2021/04/19 13:06:25
Database Name	2021-04-17.chd	Acquisition Time [min] [min]	0.000 - 30.000
Saved File Name	RSLT0780	Sampling Pitch [ms] [ms]	100
Method Data	temp	Vial Number	4
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test

Result of Calculation (RI) (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
				Mn	9,393
Peak Start	16.692	0.069	221,058	Mw	18,204
Peak Top	19.528	84.347	14,981	Mz	29,675
Peak End	22.573	0.052	100	Mz+1	48,709
				Mv	18,204
Height [mV]			84.286	Mp	15,420
Area [mV*s]			6297.260	Mz/Mw	1.630
Area% [%]			100.000	Mw/Mn	1.938
[eta]			18204.14897	Mz+1/Mw	2.676

Supplementary Figure 51. SEC chart of the polymer obtained in Table 1, entry 9. M_n (PS) = 9,393 was corrected to M_n (PE) = 4,100 by universal calibration.



Chromatography Report

Title		Measurement Date & Time	2021/04/09 19:13:47
Sample Name	ts-1-061-3	Calculation Date & Time	2021/04/09 19:30:22
Database Name	2021-04-09.chd	Acquisition Time [min] [min]	10.000 - 30.000
Saved File Name	RSLT0773	Sampling Pitch [ms] [ms]	100
Method Data	meth8509_standard	Vial Number	5
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test

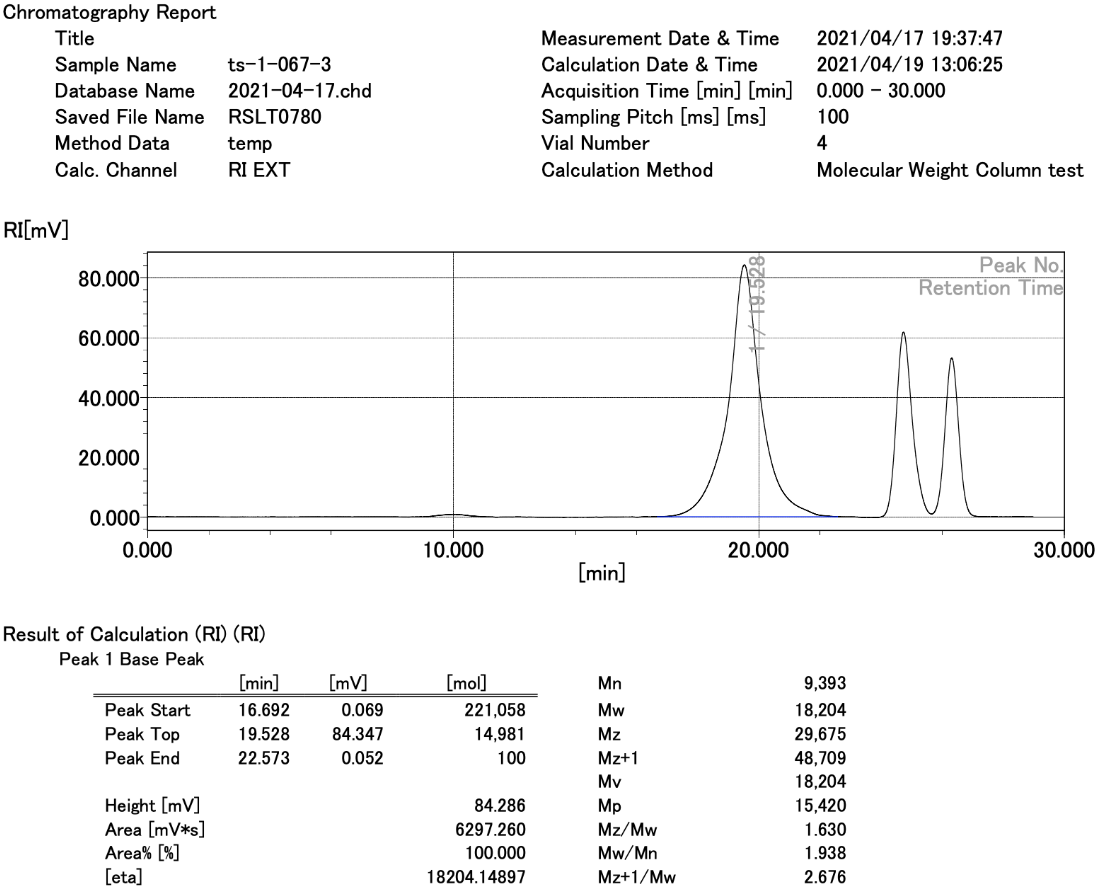
Result of Calculation (RI) (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]
Peak Start	17.095	7.700	154,019
Peak Top	19.375	59.854	17,658
Peak End	21.888	8.054	478
Height [mV]			51.986
Area [mV*s]			4680.226
Area% [%]			100.000
[eta]			21106.27233

Mn	10,331
Mw	21,106
Mz	34,412
Mz+1	51,812
Mv	21,106
Mp	18,228
Mz/Mw	1.630
Mw/Mn	2.043
Mz+1/Mw	2.455

Supplementary Figure 52. SEC chart of the polymer obtained in Table 1, entry 10. M_n (PS) = 10,331 was corrected to M_n (PE) = 4,500 by universal calibration.



Chromatography Report

Title		Measurement Date & Time	2021/04/17 19:37:47
Sample Name	ts-1-067-3	Calculation Date & Time	2021/04/19 13:06:25
Database Name	2021-04-17.chd	Acquisition Time [min] [min]	0.000 - 30.000
Saved File Name	RSLT0780	Sampling Pitch [ms] [ms]	100
Method Data	temp	Vial Number	4
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test

Result of Calculation (RI) (RI)

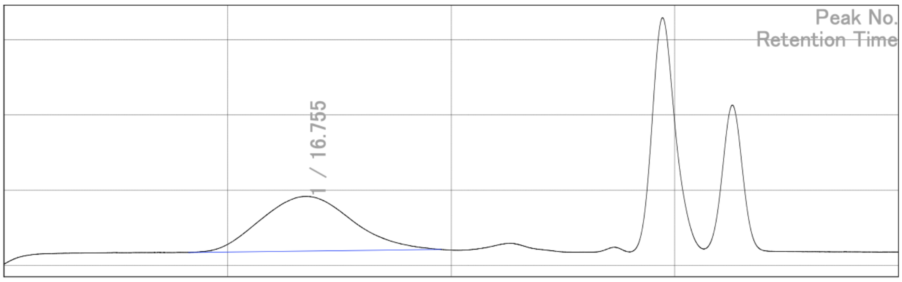
Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak Start	16.692	0.069	221,058	Mn	9,393
Peak Top	19.528	84.347	14,981	Mw	18,204
Peak End	22.573	0.052	100	Mz	29,675
				Mz+1	48,709
				Mv	18,204
Height [mV]			84.286	Mp	15,420
Area [mV*s]			6297.260	Mz/Mw	1.630
Area% [%]			100.000	Mw/Mn	1.938
[eta]			18204.14897	Mz+1/Mw	2.676

Supplementary Figure 53. SEC chart of the polymer obtained in Table 1, entry 11. M_n (PS) = 9,393 was corrected to M_n (PE) = 26,000 by universal calibration.

Chromatography Report

Title		Measurement Date & Time	2021/04/09 18:43:46
Sample Name	ts-1-061-2	Calculation Date & Time	2021/07/13 19:24:18
Database Name	2021-04-09.chd	Acquisition Time [min] [min]	10.000 - 30.000
Saved File Name	RSLT0772	Sampling Pitch [ms] [ms]	100
Method Data	meth8509_standard	Vial Number	4
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test

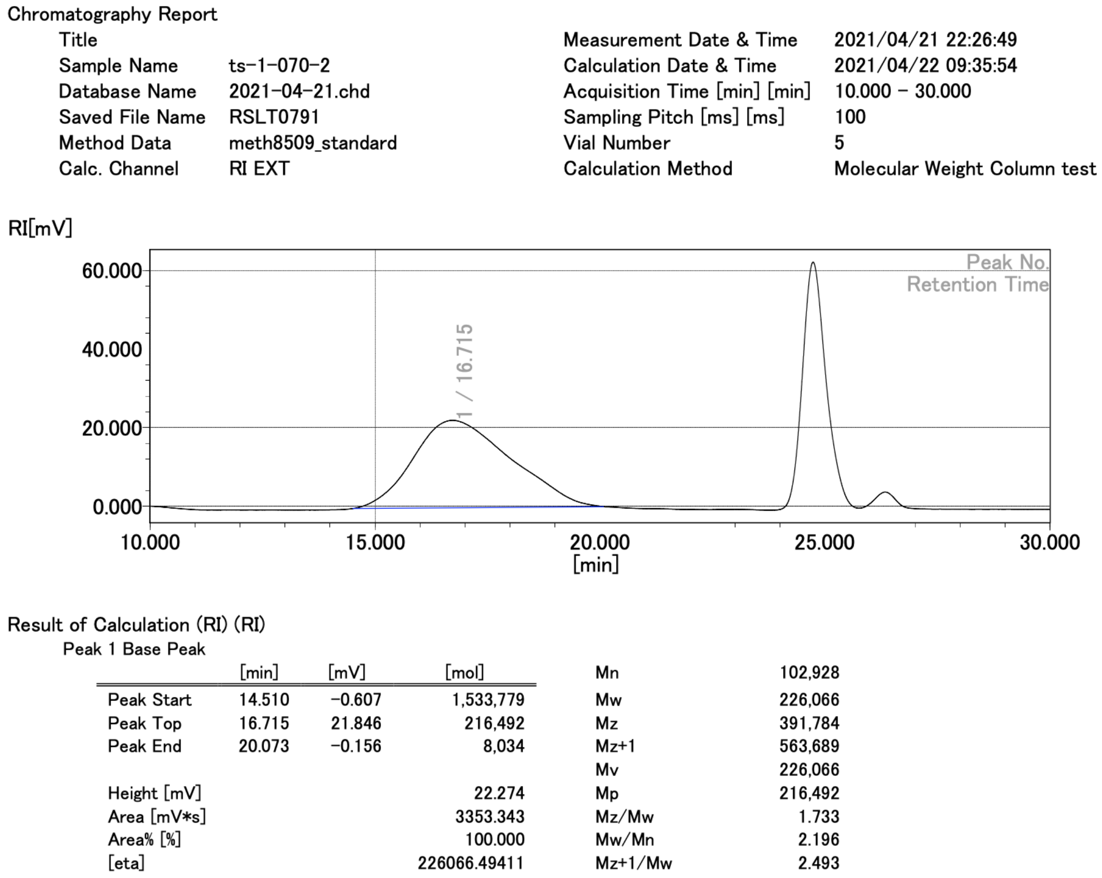


Result of Calculation (RI) (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
				Mn	136,010
Peak Start	14.118	3.435	2,153,247	Mw	270,908
Peak Top	16.755	18.361	208,882	Mz	460,049
Peak End	19.780	4.249	11,327	Mz+1	672,511
				Mv	270,908
Height [mV]			14.547	Mp	208,882
Area [mV*s]			2068.328	Mz/Mw	1.698
Area% [%]			100.000	Mw/Mn	1.992
[eta]			270908.30659	Mz+1/Mw	2.482

Supplementary Figure 54. SEC chart of the polymer obtained in Table 1, entry 12. M_n (PS) = 136,010 was corrected to M_n (PE) = 58,000 by universal calibration.



Chromatography Report

Title		Measurement Date & Time	2021/04/21 22:26:49
Sample Name	ts-1-070-2	Calculation Date & Time	2021/04/22 09:35:54
Database Name	2021-04-21.chd	Acquisition Time [min] [min]	10.000 - 30.000
Saved File Name	RSLT0791	Sampling Pitch [ms] [ms]	100
Method Data	meth8509_standard	Vial Number	5
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test

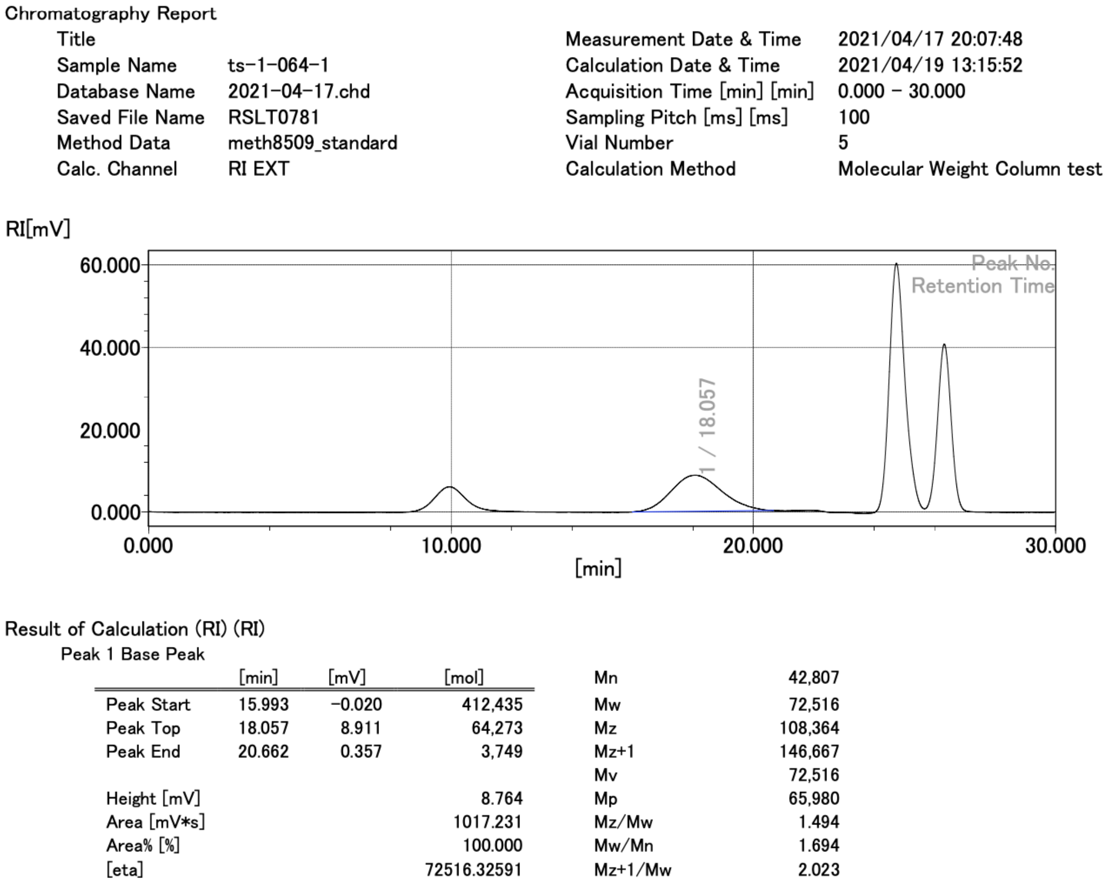
Result of Calculation (RI) (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]
Peak Start	14.510	-0.607	1,533,779
Peak Top	16.715	21.846	216,492
Peak End	20.073	-0.156	8,034
Height [mV]			22.274
Area [mV*s]			3353.343
Area% [%]			100.000
[eta]			226066.49411

Mn	102,928
Mw	226,066
Mz	391,784
Mz+1	563,689
Mv	226,066
Mp	216,492
Mz/Mw	1.733
Mw/Mn	2.196
Mz+1/Mw	2.493

Supplementary Figure 55. SEC chart of the polymer obtained in Table 1, entry 13. M_n (PS) = 102,928 was corrected to M_n (PE) = 44,000 by universal calibration.



Chromatography Report

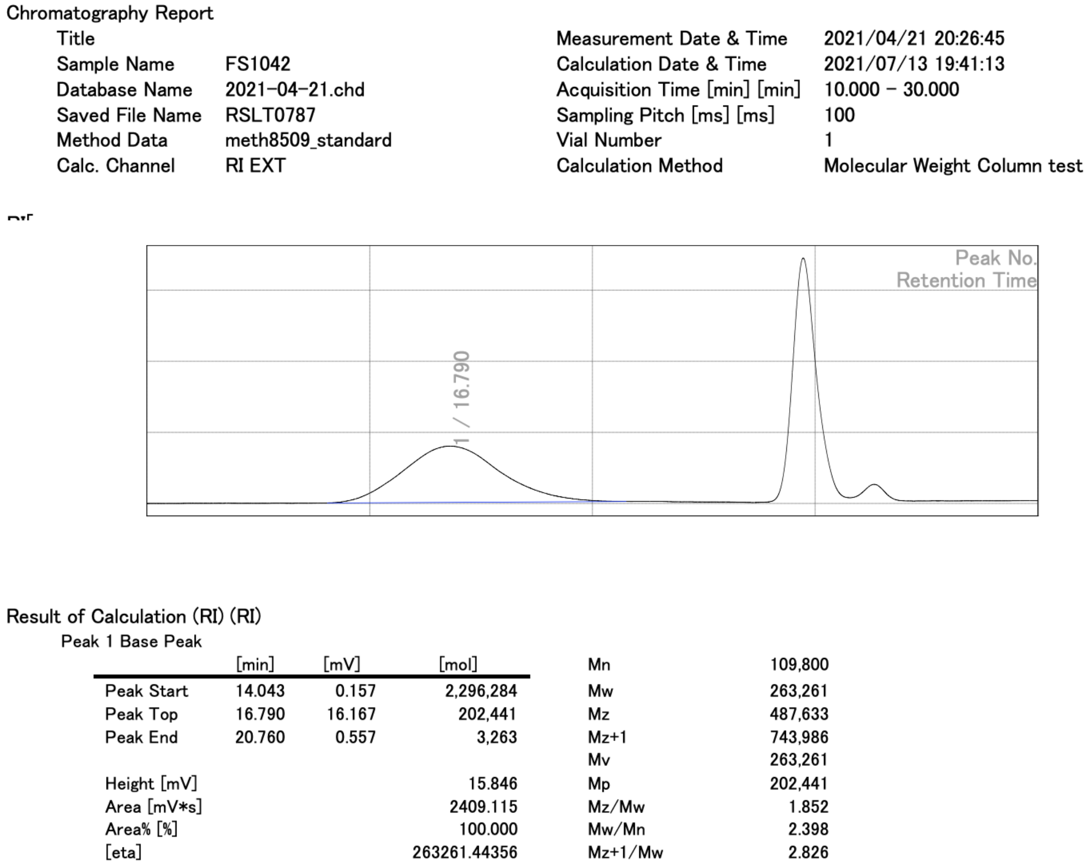
Title		Measurement Date & Time	2021/04/17 20:07:48
Sample Name	ts-1-064-1	Calculation Date & Time	2021/04/19 13:15:52
Database Name	2021-04-17.chd	Acquisition Time [min] [min]	0.000 - 30.000
Saved File Name	RSLT0781	Sampling Pitch [ms] [ms]	100
Method Data	meth8509_standard	Vial Number	5
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test

Result of Calculation (RI) (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
				Mn	42,807
Peak Start	15.993	-0.020	412,435	Mw	72,516
Peak Top	18.057	8.911	64,273	Mz	108,364
Peak End	20.662	0.357	3,749	Mz+1	146,667
				Mv	72,516
Height [mV]			8.764	Mp	65,980
Area [mV*s]			1017.231	Mz/Mw	1.494
Area% [%]			100.000	Mw/Mn	1.694
[eta]			72516.32591	Mz+1/Mw	2.023

Supplementary Figure 56. SEC chart of the polymer obtained in Table 1, entry 14. M_n (PS) = 42807 was corrected to M_n (PE) = 17,000 by universal calibration.



Chromatography Report

Title		Measurement Date & Time	2021/04/21 20:26:45
Sample Name	FS1042	Calculation Date & Time	2021/07/13 19:41:13
Database Name	2021-04-21.chd	Acquisition Time [min] [min]	10.000 - 30.000
Saved File Name	RSLT0787	Sampling Pitch [ms] [ms]	100
Method Data	meth8509_standard	Vial Number	1
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test

Result of Calculation (RI) (RI)

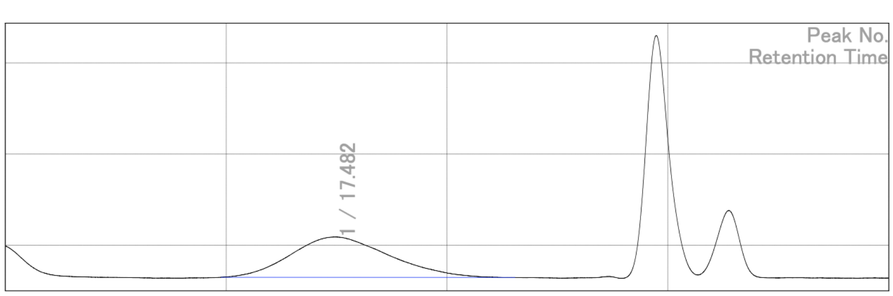
Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak Start	14.043	0.157	2,296,284	Mn	109,800
Peak Top	16.790	16.167	202,441	Mw	263,261
Peak End	20.760	0.557	3,263	Mz	487,633
				Mz+1	743,986
				Mv	263,261
Height [mV]			15.846	Mp	202,441
Area [mV*s]			2409.115	Mz/Mw	1.852
Area% [%]			100.000	Mw/Mn	2.398
[eta]			263261.44356	Mz+1/Mw	2.826

Supplementary Figure 57. SEC chart of polymer obtained in Table 1, entry 15. M_n (PS) = 109,800 was corrected to M_n (PE) = 47,000 by universal calibration.

Chromatography Report

Title		Measurement Date & Time	2021/07/13 18:35:10
Sample Name	ts-1-105-1	Calculation Date & Time	2021/07/13 19:11:05
Database Name	2021-07-13.chd	Acquisition Time [min] [min]	10.000 - 30.000
Saved File Name	RSLT0872	Sampling Pitch [ms] [ms]	100
Method Data	meth8509_standard	Vial Number	5
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test



Result of Calculation (RI) (RI)

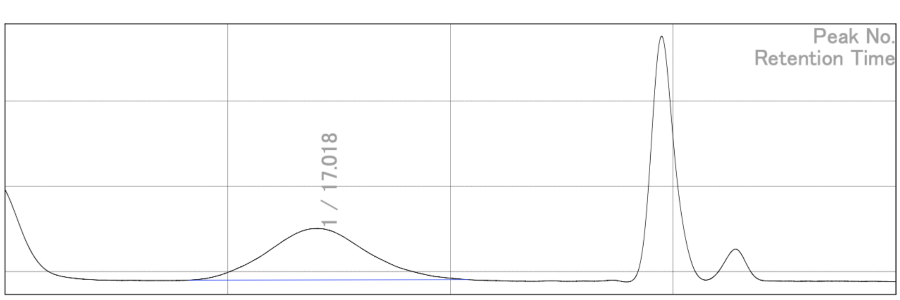
Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak Start	14.877	-7.018	1,111,943	Mn	51,101
Peak Top	17.482	1.837	108,711	Mw	135,232
Peak End	21.543	-7.040	926	Mz	255,266
				Mz+1	390,564
				Mv	135,232
Height [mV]			8.864	Mp	114,427
Area [mV*s]			1372.141	Mz/Mw	1.888
Area% [%]			100.000	Mw/Mn	2.646
[eta]			135231.84317	Mz+1/Mw	2.888

Supplementary Figure 58. SEC chart of the polymer obtained in Table 1, entry 12 after UV irradiation. M_n (PS) = 51,101 was corrected to M_n (PE) = 22,000 by universal calibration.

Chromatography Report

Title		Measurement Date & Time	2021/07/13 19:05:11
Sample Name	ts-1-105-2	Calculation Date & Time	2021/07/13 19:14:06
Database Name	2021-07-13.chd	Acquisition Time [min] [min]	10.000 - 30.000
Saved File Name	RSLT0873	Sampling Pitch [ms] [ms]	100
Method Data	meth8509_standard	Vial Number	6
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test



Result of Calculation (RI) (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak Start	14.118	-22.001	2,153,247	Mn	96,329
Peak Top	17.018	-9.859	164,989	Mw	235,968
Peak End	20.417	-21.878	5,219	Mz	464,371
				Mz+1	735,207
				Mv	235,968
Height [mV]			12.085	Mp	164,990
Area [mV*s]			1881.649	Mz/Mw	1.968
Area% [%]			100.000	Mw/Mn	2.450
[eta]			235968.19697	Mz+1/Mw	3.116

Supplementary Figure 59. SEC chart of the polymer in Table 1, entry 15 after UV irradiation. M_n (PS) = 96329 was corrected to M_n (PE) = 41,000 by universal calibration.

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