Supporting Information For

Copolymerization of Nonpolar Olefins and Allyl Acetate Using a Nickel Catalyst Bearing a Methylene-bridged Bisphosphine Monoxide Ligand

*Jin Jung, Hina Yasuda, and Kyoko Nozaki**

Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

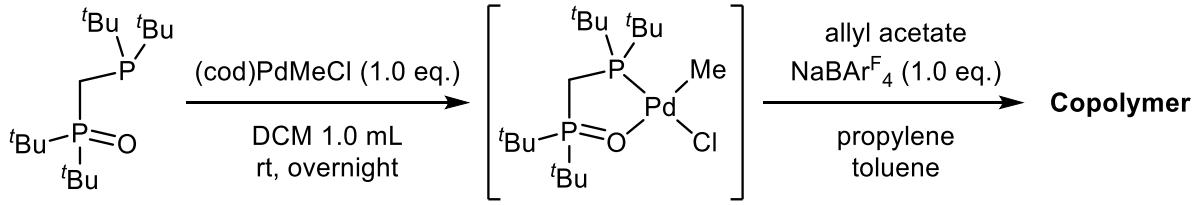
Table of Content

1. Experimental Section

Copolymerization of propylene with allyl acetate by *in-situ* generated palladium complex (Table S1).

Designated amount of ligand **1b**, anhydrous dichloromethane (1.0 mL), and (cod)PdMeCl (1.0 equiv.) were added into a 20 mL Schlenk under inert atmosphere, and then the reaction mixture was stirred for overnight at room temperature. Subsequently, the reaction mixture was injected *via* syringe into the 50 mL autoclave charged with $NaBAr^F_4$ (1.0 equiv.), designated amount of propylene, allyl acetate, and anhydrous toluene. After the autoclave was sealed, the reaction mixture was stirred in an isothermal heating block under designated condition. After cooling to room temperature and venting residual propylene, the volatile matters of reaction mixture were removed under reduced pressure. The product was then dried under vacuum for 6 h at 100 °C to afford a copolymer. The molecular weight and polydispersity were determined by SEC. The contents of polar functional groups were determined by ^{1}H NMR spectra (Figures S32 and S33).

Table S1. Copolymerization with allyl acetate using *in-situ* generated Pd catalyst.



1b

entry	propylene (g)	**1b** (mmol)	allyl acetate (mL)	temp. (°C)	time (h)	yield (g)	activity (g/mmol·h)	M_n (g/mol)[a]	M_w/M_n[a]	FG content (mol%)[b]
1	6.4	0.020	1.0	50	12	0.053	0.22	870	1.5	0.25
2	9.3	0.010	0.1	100	6	0.026	0.43	740	1.4	0.16

cod = 1,5-cyclooctadiene, Ar^F = 3,5-$(CF_3)_2C_6H_3$. [a] Determined by size-exclusion chromatography using polystyrene standards and corrected by universal calibration. [b] Determined by ^{1}H NMR analysis.

Complexation trial of phenylnickel chloride complex 2b

Ligand **1b** (50.0 mg, 0.156 mmol), $Ni(cod)_2$ (42.9 mg, 0.156 mmol), and anhydrous chlorobenzene (1.0 mL) were added into a 20 mL Schlenk under inert atmosphere, and then the reaction mixture was stirred for 14 h at room temperature. The color of reaction mixture changed from yellow to orange. Subsequently, the reaction mixture was concentrated under reduced pressure, and then *n*-hexane was added to afford an orange precipitate, but it rapidly decomposed during separation to black-brown solid.

Complexation trial of cationic phenylnickel complex

Ligand **1b** (25.0 mg, 78.0 μmol), $Ni(cod)_2$ (21.5 mg, 78.2 μmol), and anhydrous chlorobenzene (1.0 mL) were added into a 10 mL J. Young sample flask under inert atmosphere, and then the reaction mixture was stirred for 14 h at room temperature. The color of reaction mixture changed from yellow to orange. Subsequently, to the reaction mixture was added $NaBAr^F_4$ (69.1 mg, 78.0 μmol) and 2,6-lutidine (12.6 mg, 117 μmol). After stirring for 3 h at room temperature, *n*-hexane was added to the reaction mixture to afford a sticky solid which exhibited a complicated ^1H NMR spectrum and no polymerization activity.

Homopolymerization trial of allyl acetate by *in-situ* generated nickel η^3-allyl complex and MMAO.

Ligand **1b** (9.6 mg, 0.030 mmol), $NaBAr^F_4$ (28 mg, 0.030 mmol), $[Ni(\eta^3\text{-allyl})Br]_2$ (5.4 mg, 0.015 mmol), and anhydrous dichloromethane (3.0 mL) were added into a 20 mL Schlenk under inert atmosphere, and then the reaction mixture was stirred for overnight at room temperature. Subsequently, the yellow suspension including sodium bromide salt was injected *via* syringe into the mixture of AAc (5.0 mL), MMAO (4.6 mL, Al/Ni = 500), and anhydrous toluene (3.4 mL). The reaction mixture was stirred for 47 h at 50 °C, then poured into MeOH (300 mL). Trace amount of precipitated was obtained by filter, but it was not determined as poly(AAc).

2. NMR Spectra

NMR spectra of complex 3

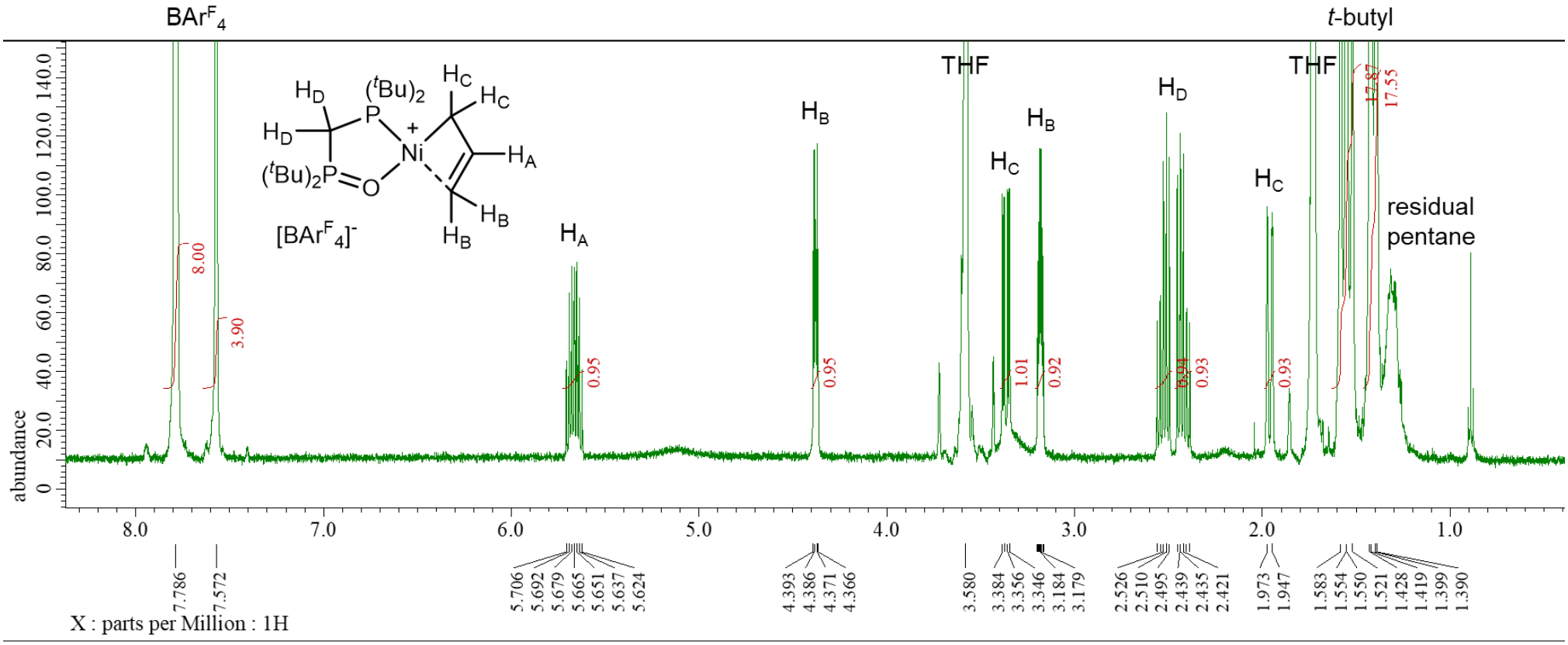


Figure S1. ^{1}H NMR spectrum of the complex **3** (THF-d_8, rt). Peak assignments were based on the previously reported palladium BPMO complex **VII**,[1] palladium BPMO complex **VI**,[2] and ^{1}H–^{1}H COSY NMR analysis.

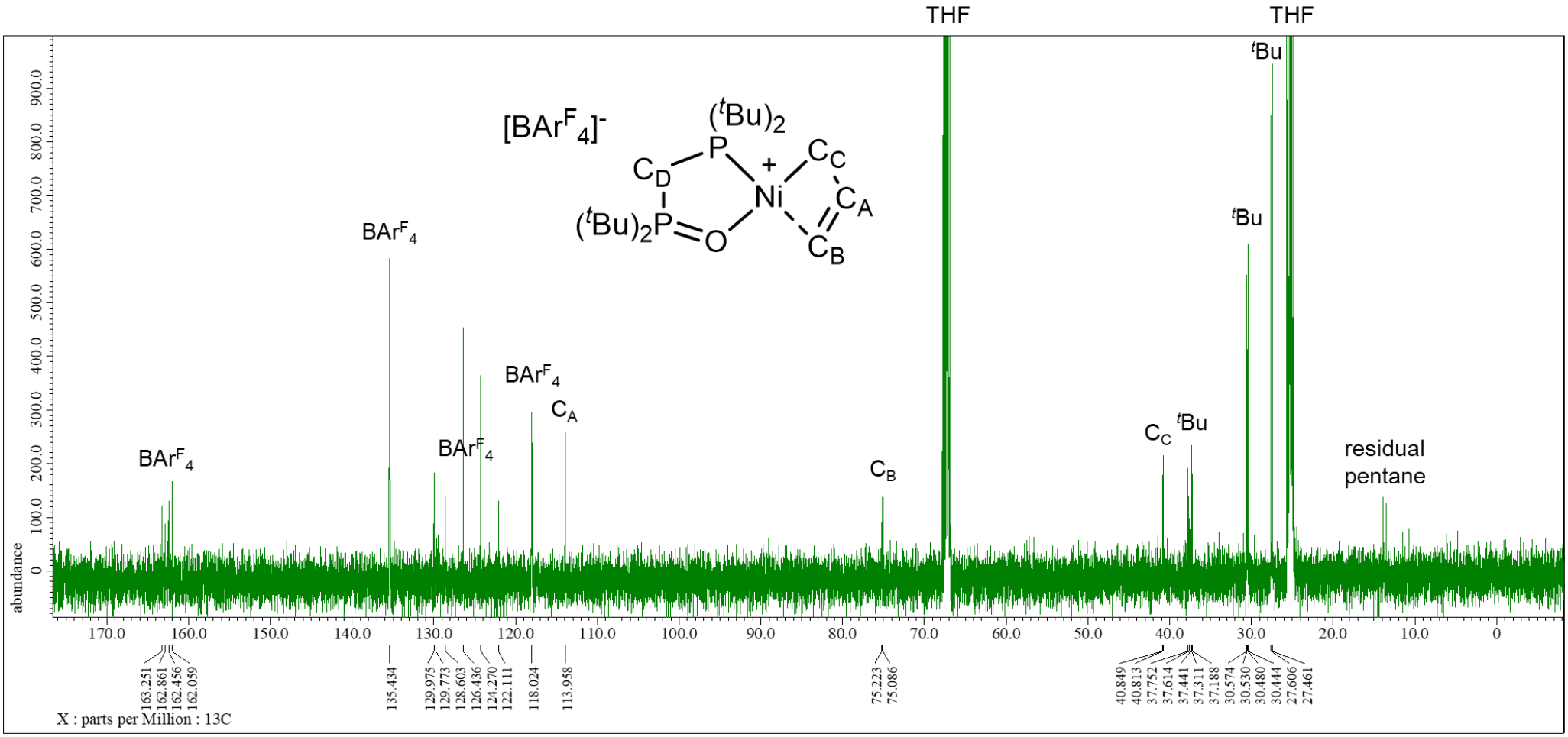


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of the complex **3** (THF-d_8, rt). Peak assignments were based on the previously reported palladium BPMO complex **VII**[1] and palladium BPMO complex **VI**.[2]

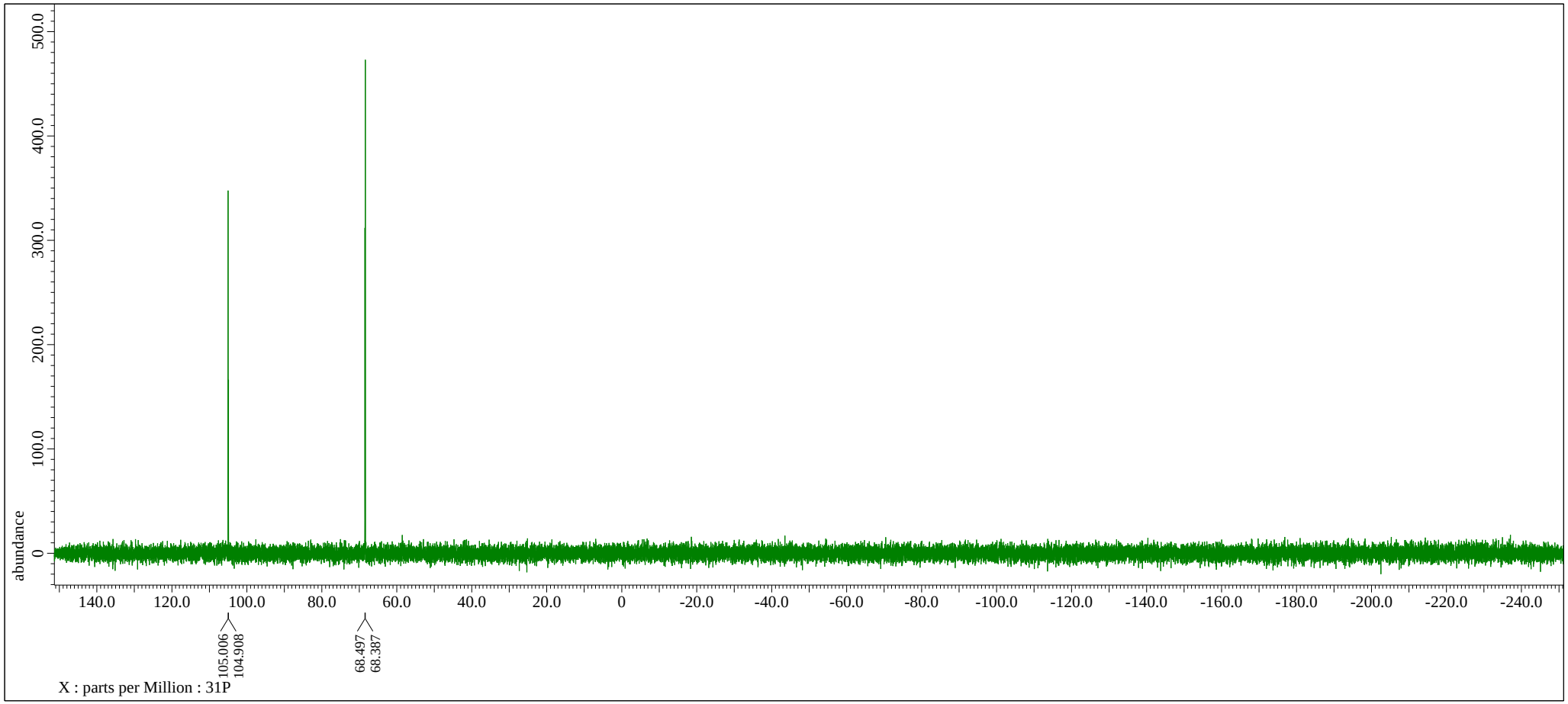


Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of the complex **3** (THF-d_8, rt).

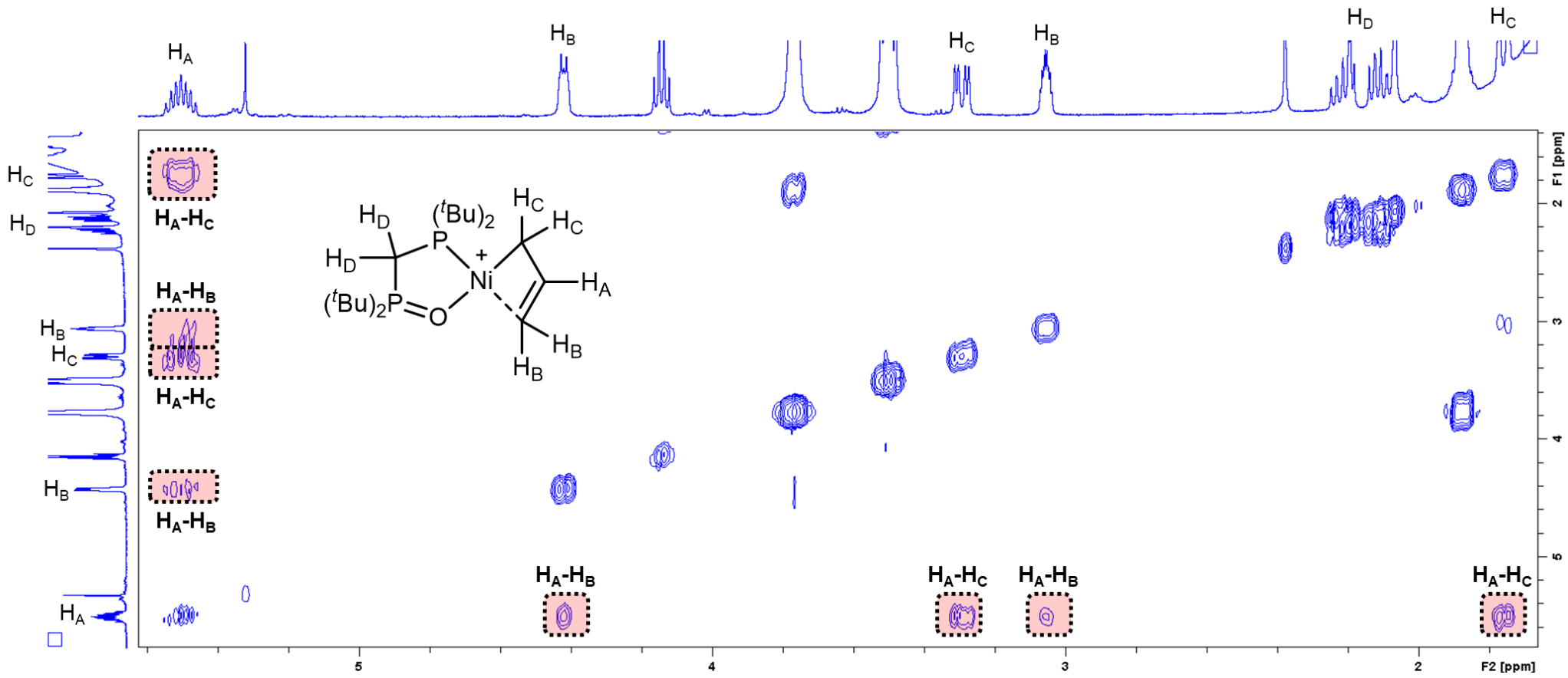


Figure S4. ^{1}H–^{1}H COSY NMR spectrum of the complex **3** ($CDCl_3$, rt).

NMR spectra of polymer from Table 2

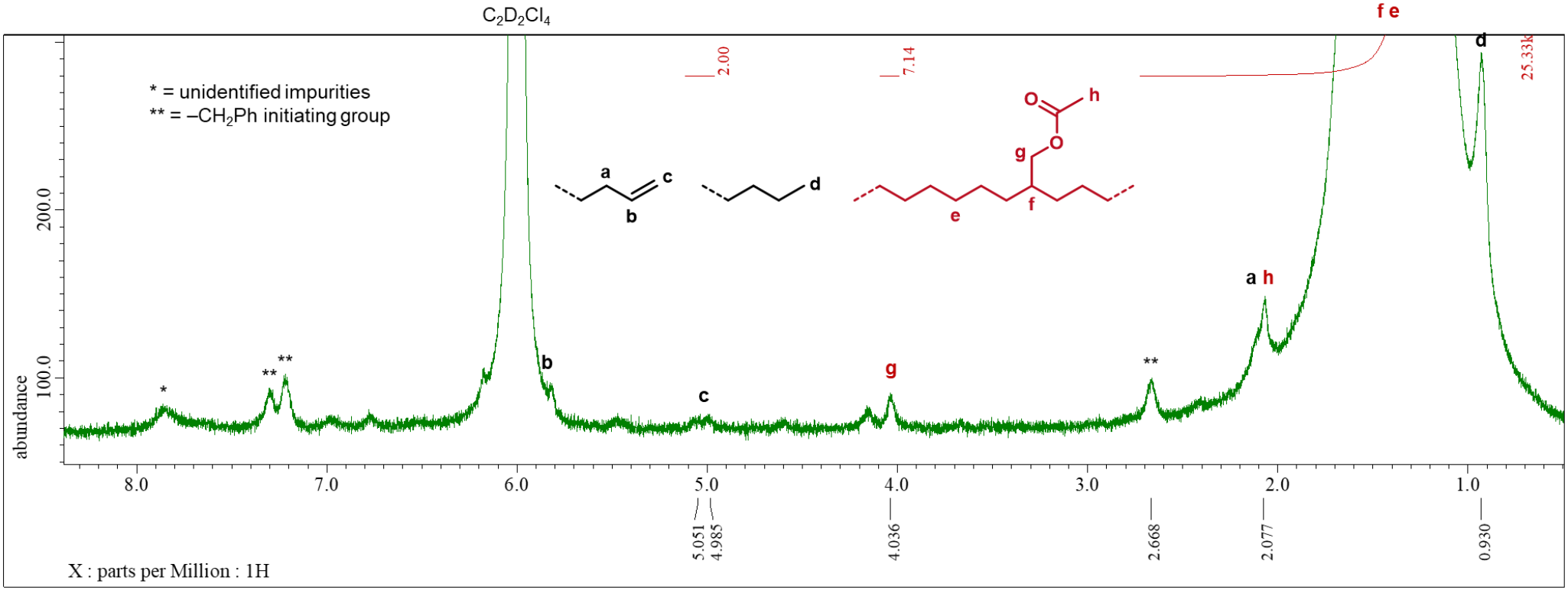


Figure S5. ^{1}H NMR spectrum of the ethylene / allyl acetate copolymer obtained in Table 2, entry 2 ($C_2D_2Cl_4$, 120 ºC, relaxation delay 5 s). Peak assignments were based on the literature.[3]

Note: Calculation of acetate group content in the polyethylene[3]: Assume (1-x) mol% ethylene and x mol% allyl acetate in the copolymer,

$$x = \frac{(\mathbf{g} \times 2 \times 100)}{(\mathbf{b} + \mathbf{c} + \mathbf{j} + \mathbf{a} + \mathbf{h} + \mathbf{f} + \mathbf{e} + \mathbf{d} - \mathbf{g})}$$

Therefore, the acetate group content is calculated as follows: (7.14×2×100)/(2.00+25330-7.14) = 0.06 mol%. This calculation was applied to entire cases in this paper.

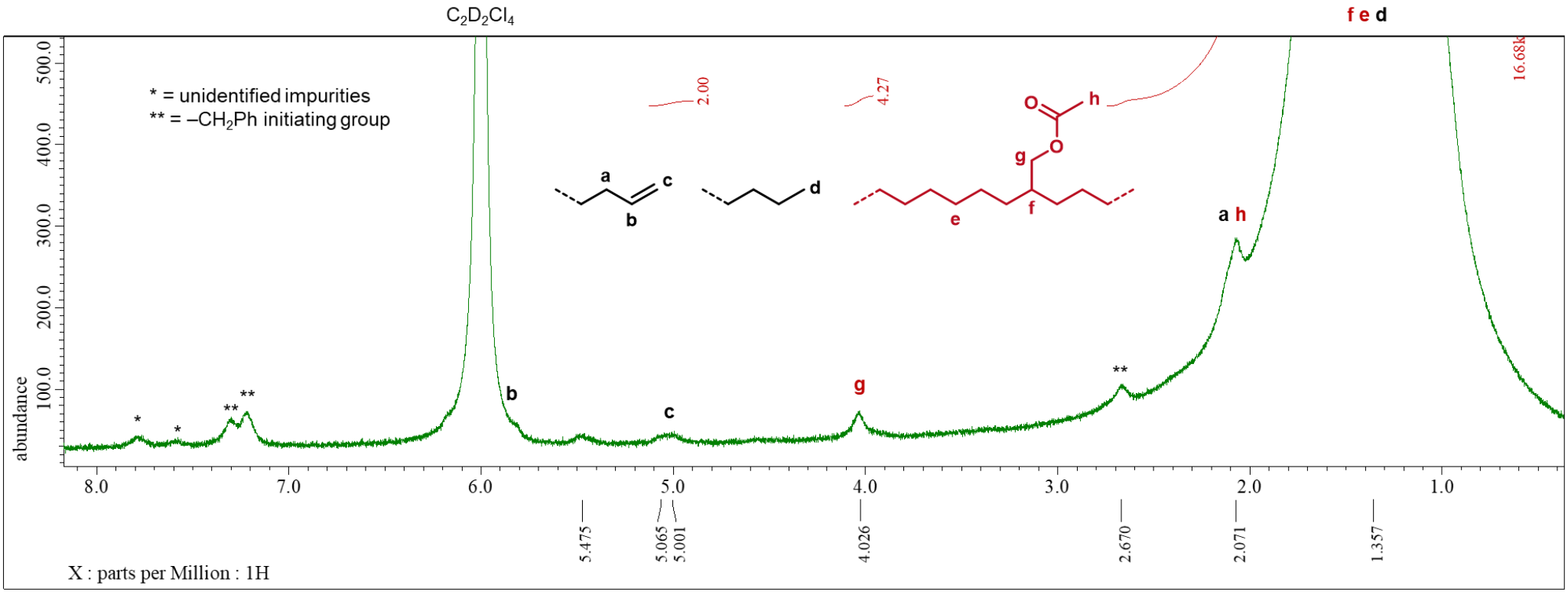


Figure S6. ^{1}H NMR spectrum of the ethylene / allyl acetate copolymer obtained in Table 2, entry 3 ($C_2D_2Cl_4$, 120 ºC, relaxation delay 5 s)

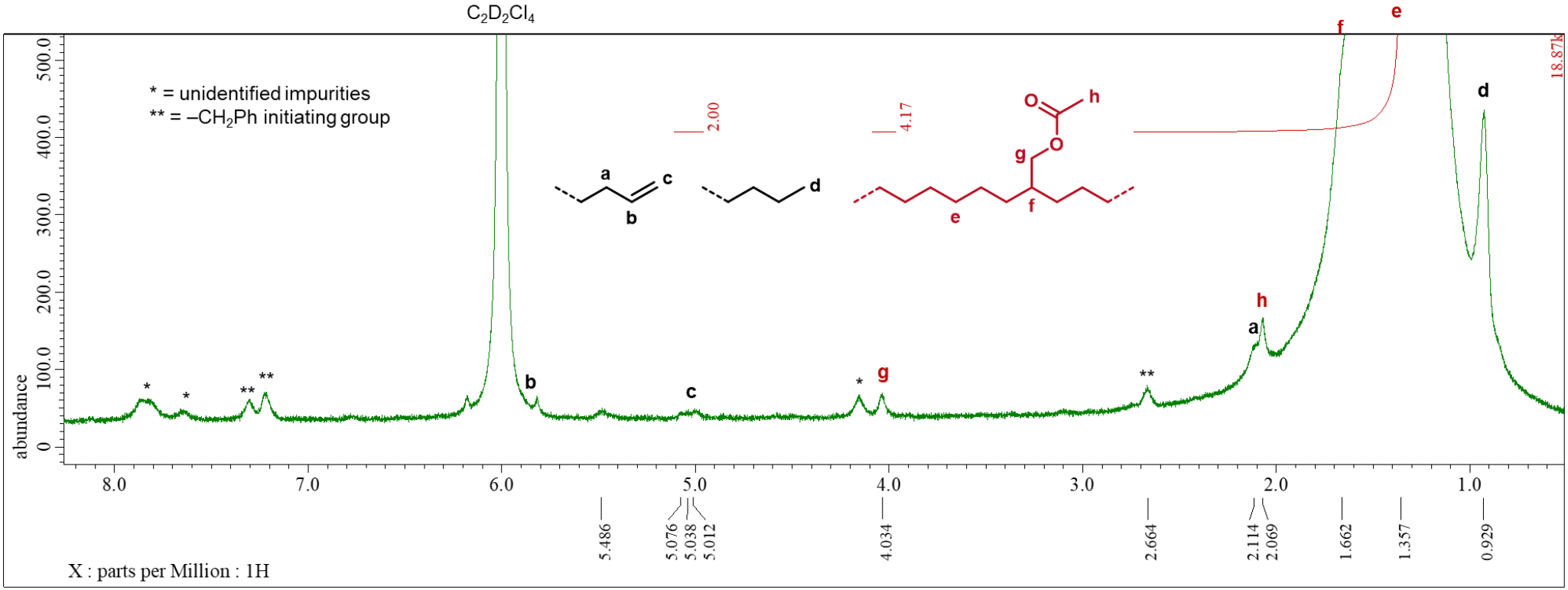


Figure S7. ^{1}H NMR spectrum of the ethylene / allyl acetate copolymer obtained in Table 2, entry 4 ($C_2D_2Cl_4$, 120 ºC, relaxation delay 5 s).

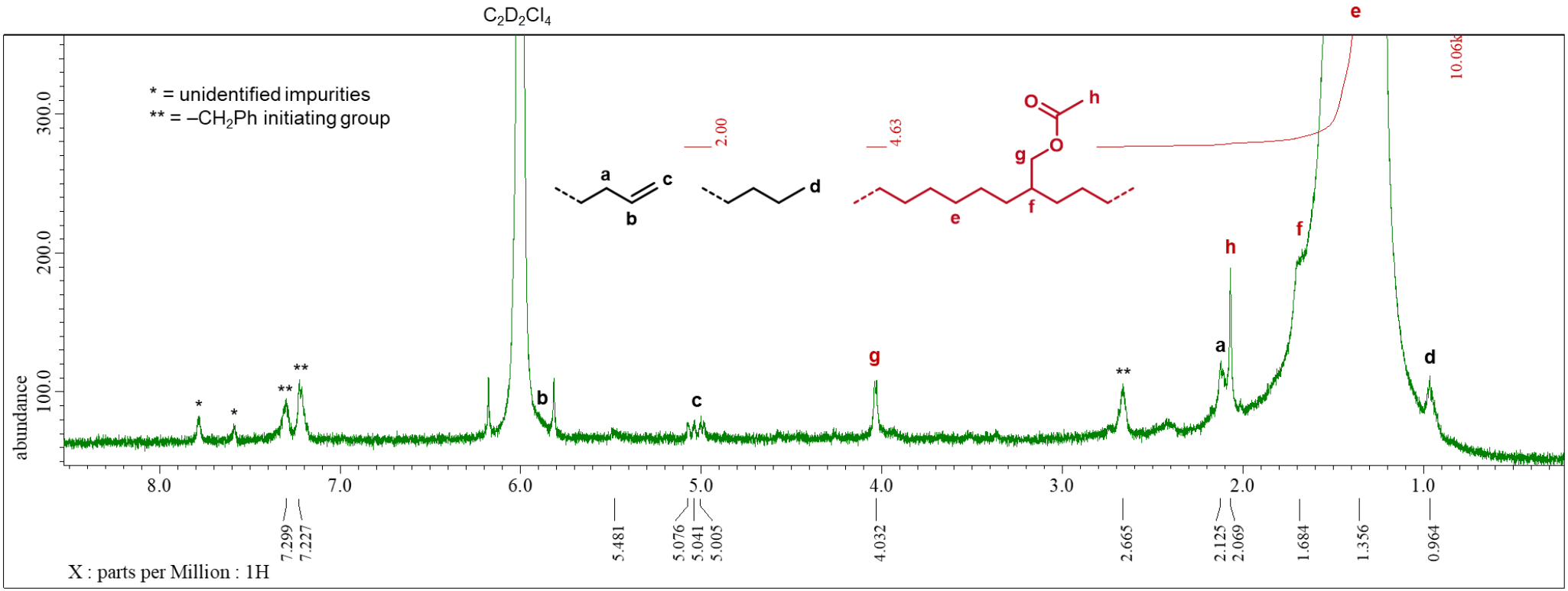


Figure S8. ^{1}H NMR spectrum of the ethylene / allyl acetate copolymer obtained in Table 2, entry 5 ($C_2D_2Cl_4$, 120 ºC, relaxation delay 5 s).

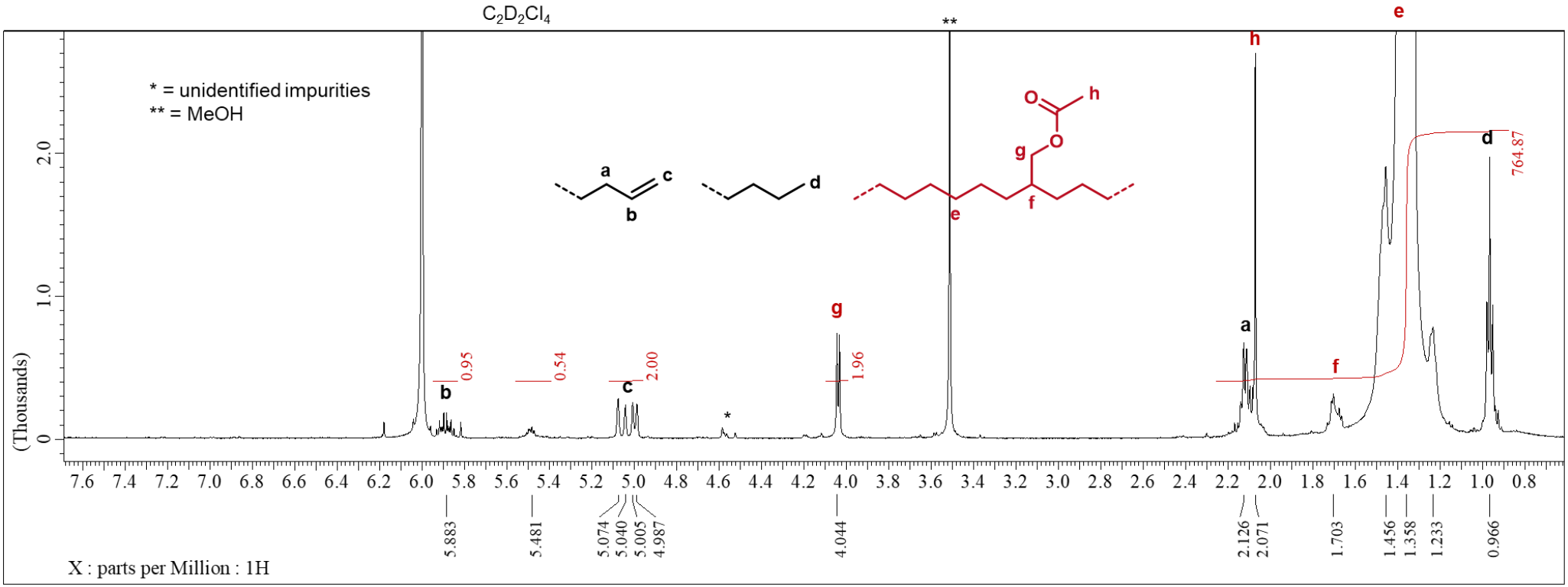


Figure S9. ^{1}H NMR spectrum of the ethylene / allyl acetate copolymer obtained in Table 2, entry 7 ($C_2D_2Cl_4$, 120 ºC, relaxation delay 5 s).

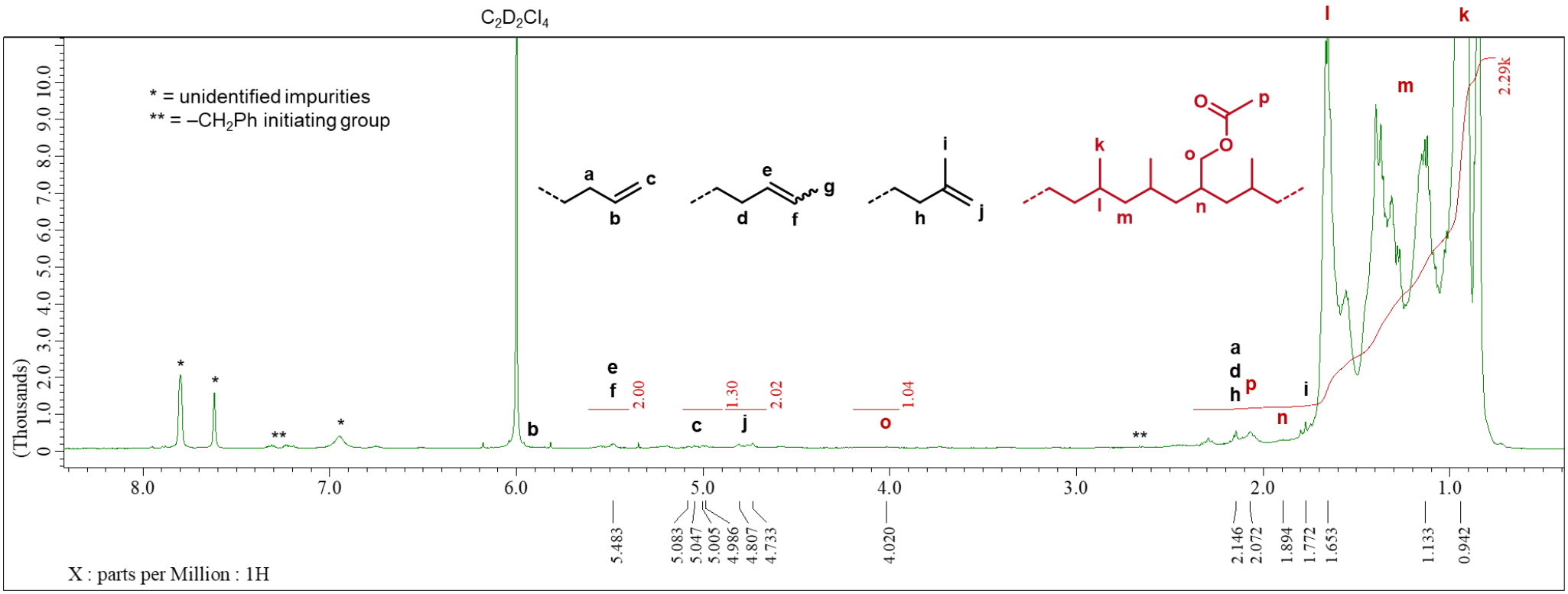


Figure S10. ^{1}H NMR spectrum of the propylene / allyl acetate copolymer obtained in Table 2, entry 6 ($C_2D_2Cl_4$, 120 ºC, relaxation delay 5 s). Peak assignments were based on the literatures.[4-5]

Note: Calculation of acetate group content in the polypropylene[4-5]:

Assume x mol% acetate group in the copolymer,

$$x = \frac{(\mathbf{o}/2) \times 100}{(\mathbf{b} + \mathbf{e} + \mathbf{f} + \mathbf{c} + \mathbf{j} + \mathbf{a} + \mathbf{d} + \mathbf{h} + \mathbf{p} + \mathbf{n} + \mathbf{i} + \mathbf{l} + \mathbf{m} + \mathbf{k})/6}$$

This calculation was applied to entire cases in this paper.

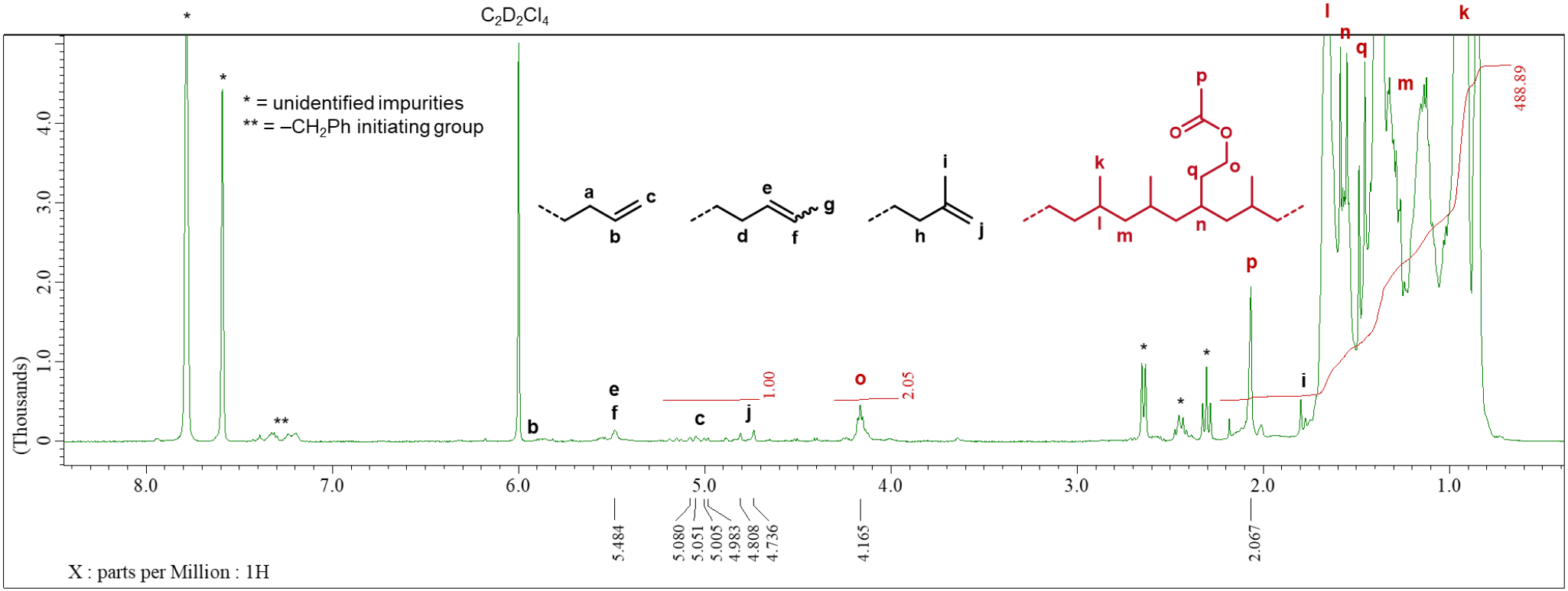


Figure S11. ^{1}H NMR spectrum of the propylene / 3-butenyl acetate copolymer obtained in Table 2, entry 7 ($C_2D_2Cl_4$, 120 ºC, relaxation delay 5 s). Peak assignments were based on the poly(propylene-*co*-allyl acetate)[4-5] and model compound (3-methyl-1-butyl acetate).[6]

NMR spectra of polymer from Table 3

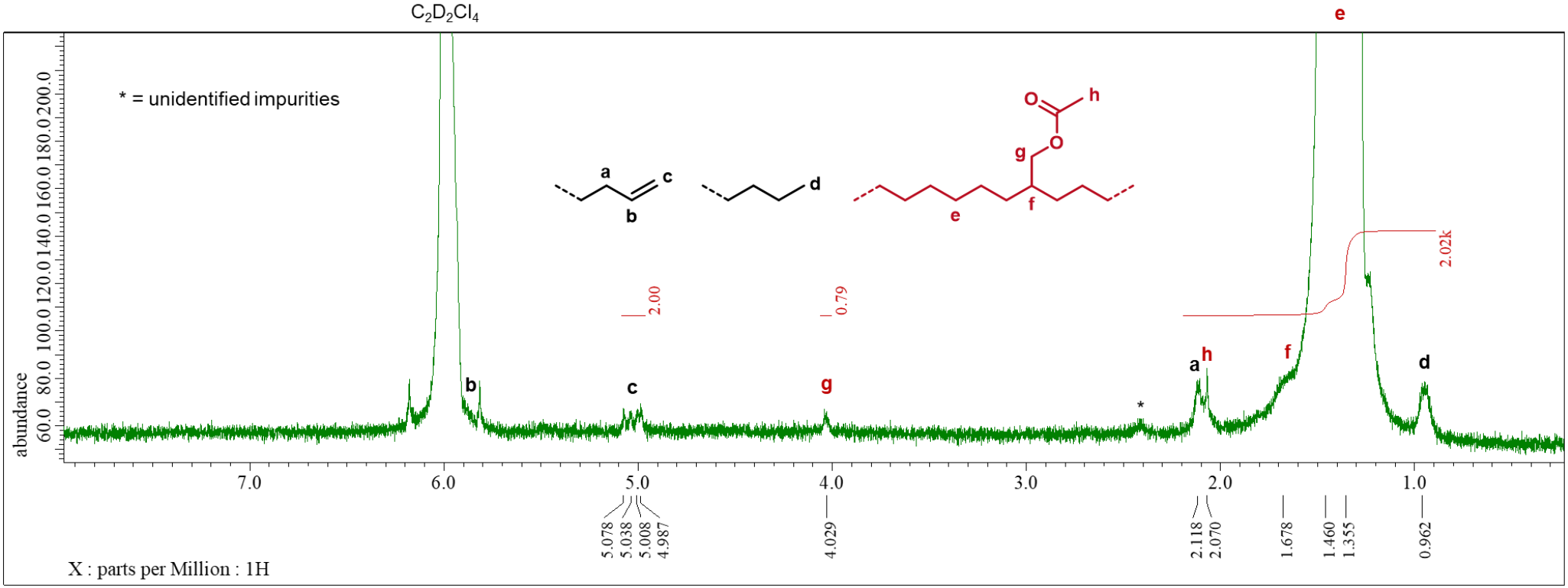


Figure S12. ^{1}H NMR spectrum of the ethylene / allyl acetate copolymer obtained in Table 3, entry 2 ($C_2D_2Cl_4$, 120 ºC, relaxation delay 5 s).

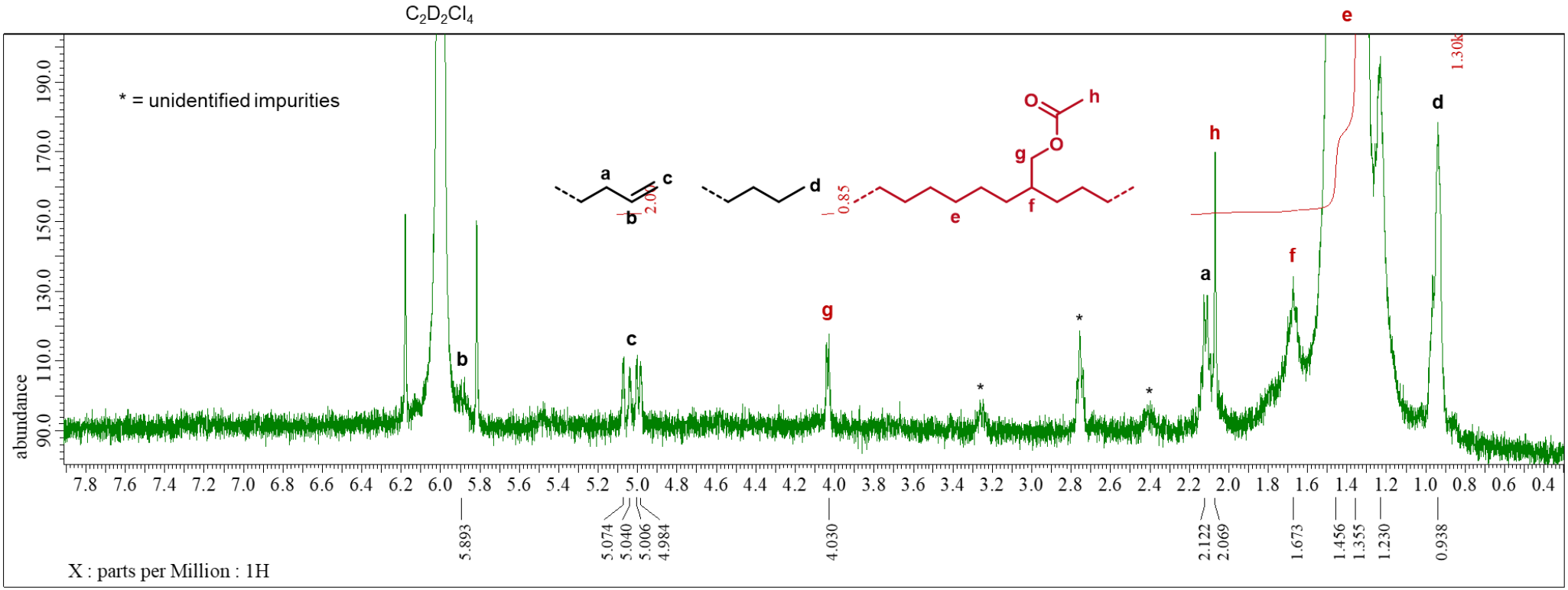


Figure S13. ^{1}H NMR spectrum of the ethylene / allyl acetate copolymer obtained in Table 3, entry 3 ($C_2D_2Cl_4$, 120 ºC, relaxation delay 5 s).

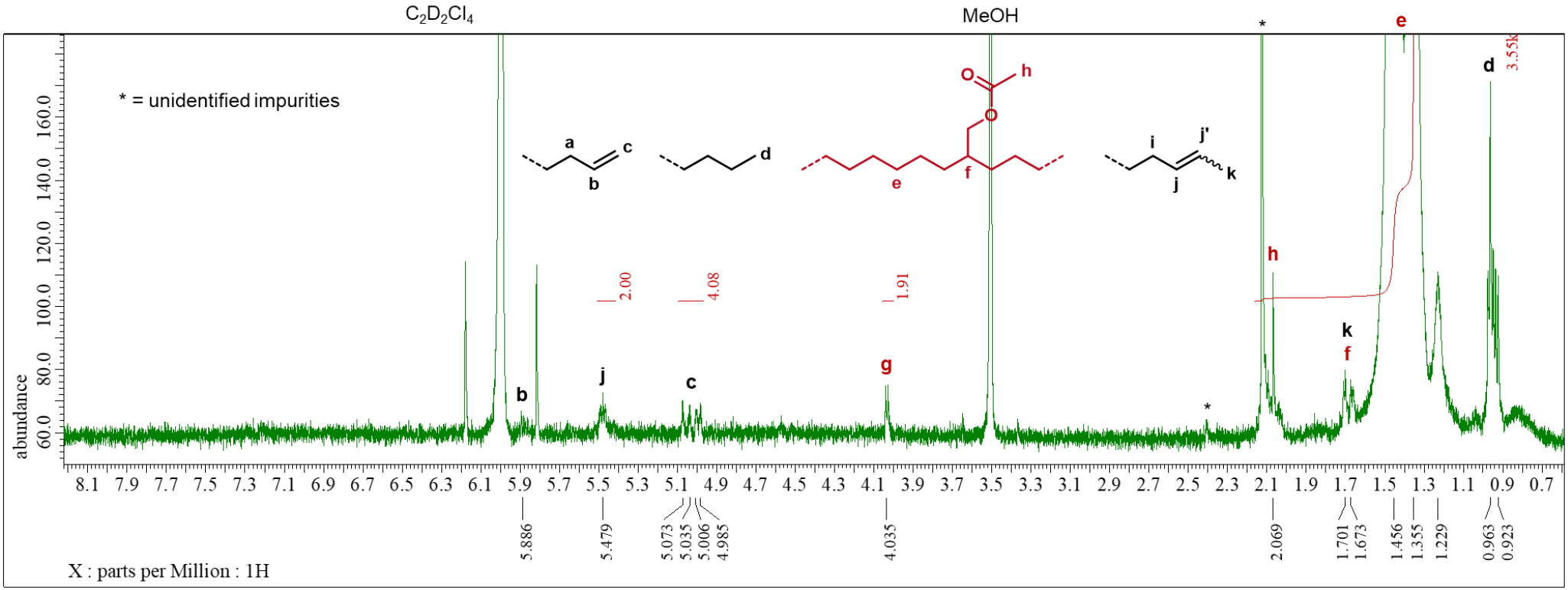


Figure S14. ^{1}H NMR spectrum of the ethylene / allyl acetate copolymer obtained in Table 3, entry 4 ($C_2D_2Cl_4$, 120 ºC, relaxation delay 5 s).

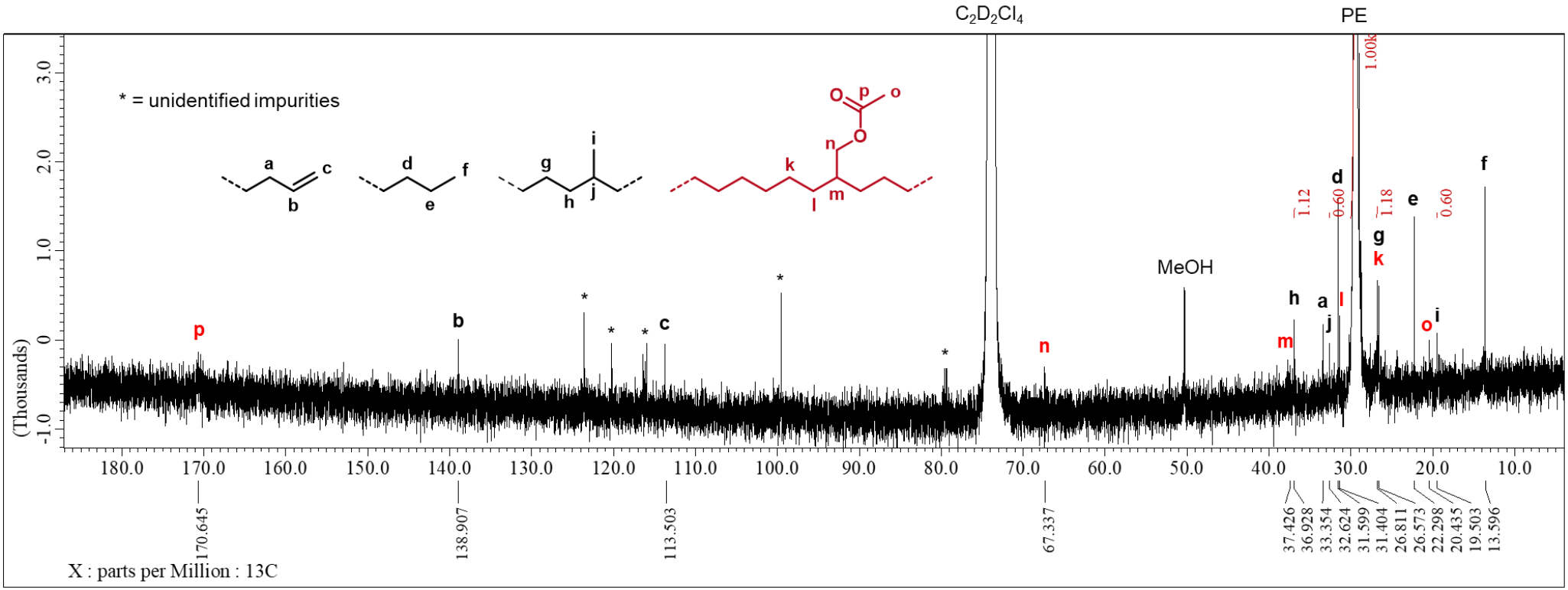


Figure S15. Quantitative ^{13}C NMR spectrum of the ethylene / allyl acetate copolymer obtained in Table 3, entry 4 ($C_2D_2Cl_4$, 120 ºC). Peak assignments were based on the literature.[1]

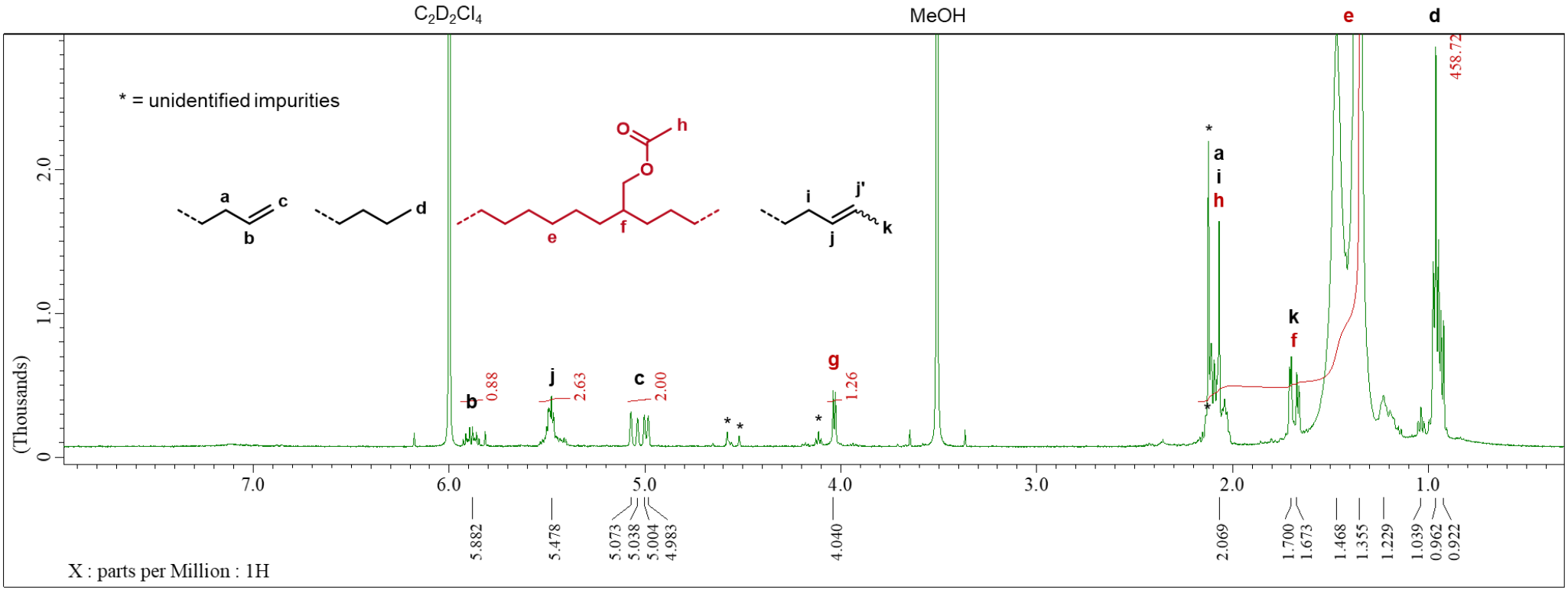


Figure S16. ^{1}H NMR spectrum of the ethylene / allyl acetate copolymer obtained in Table 3, entry 5 ($C_2D_2Cl_4$, 120 ºC, relaxation delay 5 s).

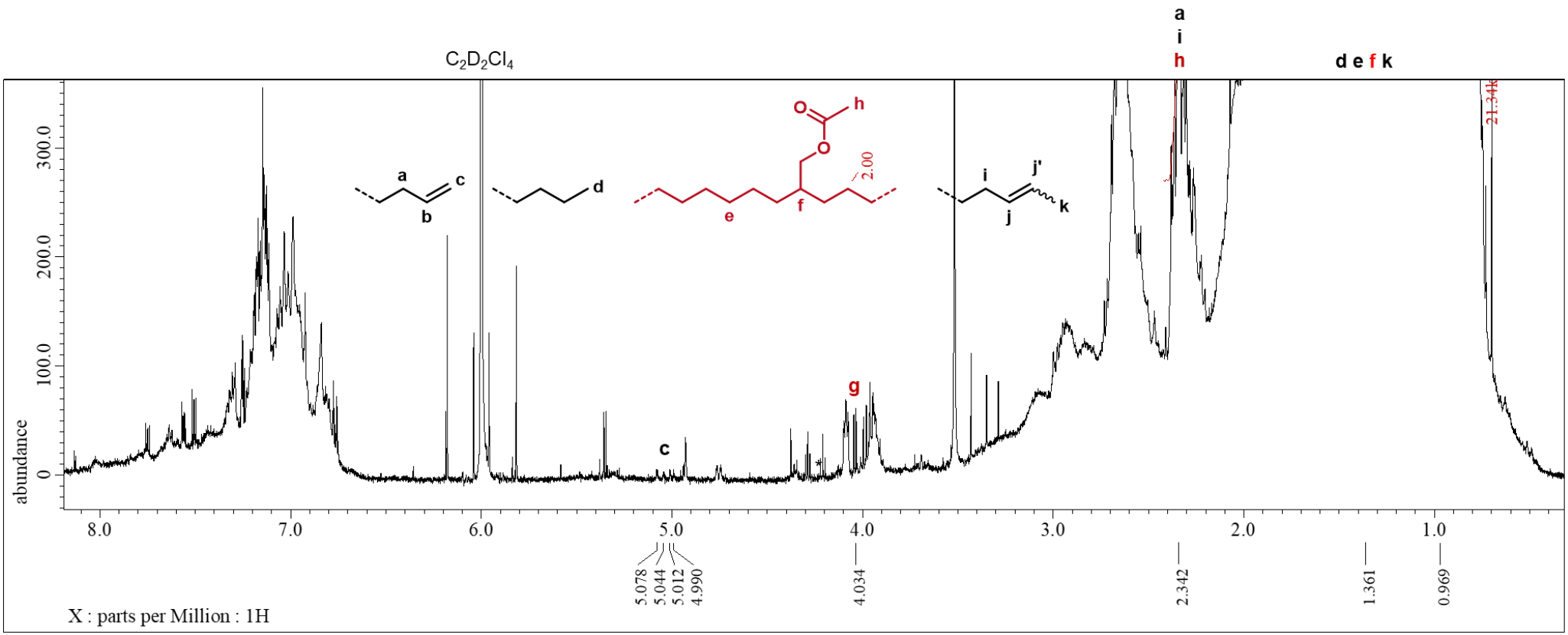


Figure S17. ^{1}H NMR spectrum of the polymer recovered from SEC eluent (retention time 18–20 min., $C_2D_2Cl_4$, 120 ºC, relaxation delay 5 s). Polymer from Table 3, entry 5 was used to the SEC measurement. Unassigned peaks were incorporated during SEC analysis and recollecting sample.

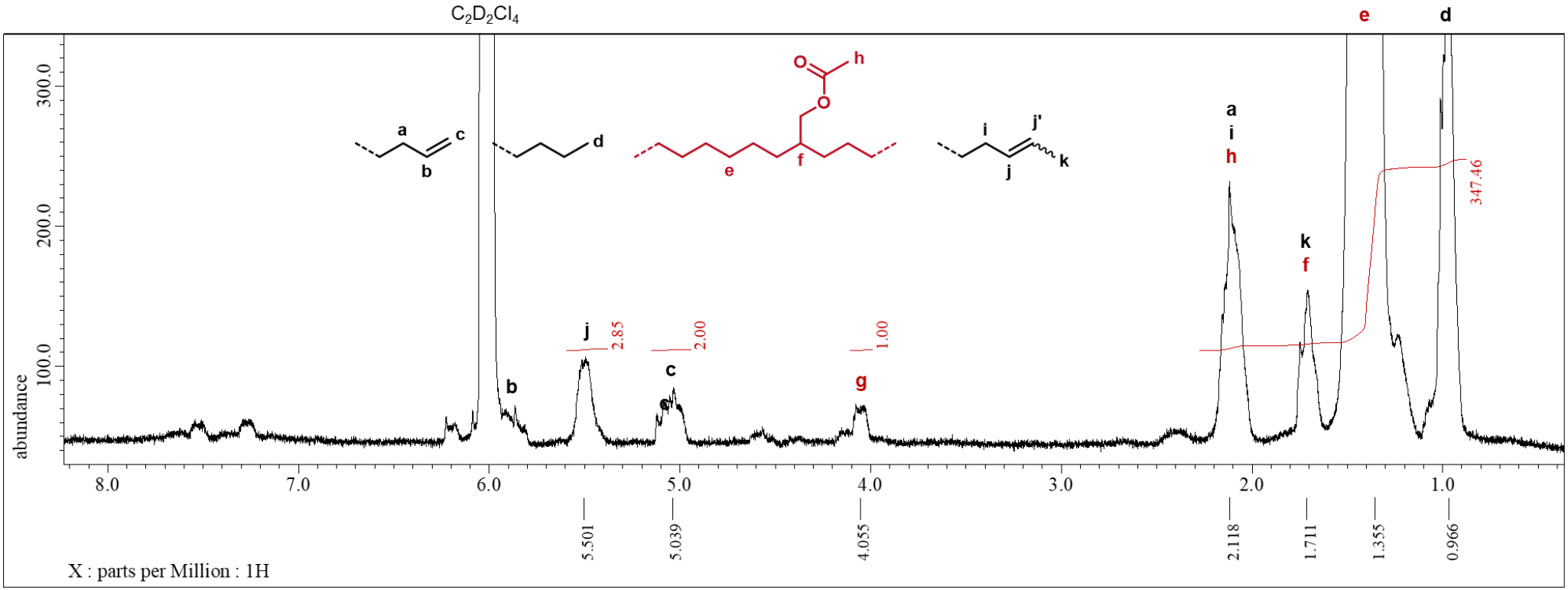


Figure S18. ^{1}H NMR spectrum of the polymer recovered from SEC eluent (retention time 21−23 min., $C_2D_2Cl_4$, 120 ºC, relaxation delay 5 s). Polymer from Table 3, entry 5 was used to the SEC measurement. Unassigned peaks were incorporated during SEC analysis and recollecting sample.

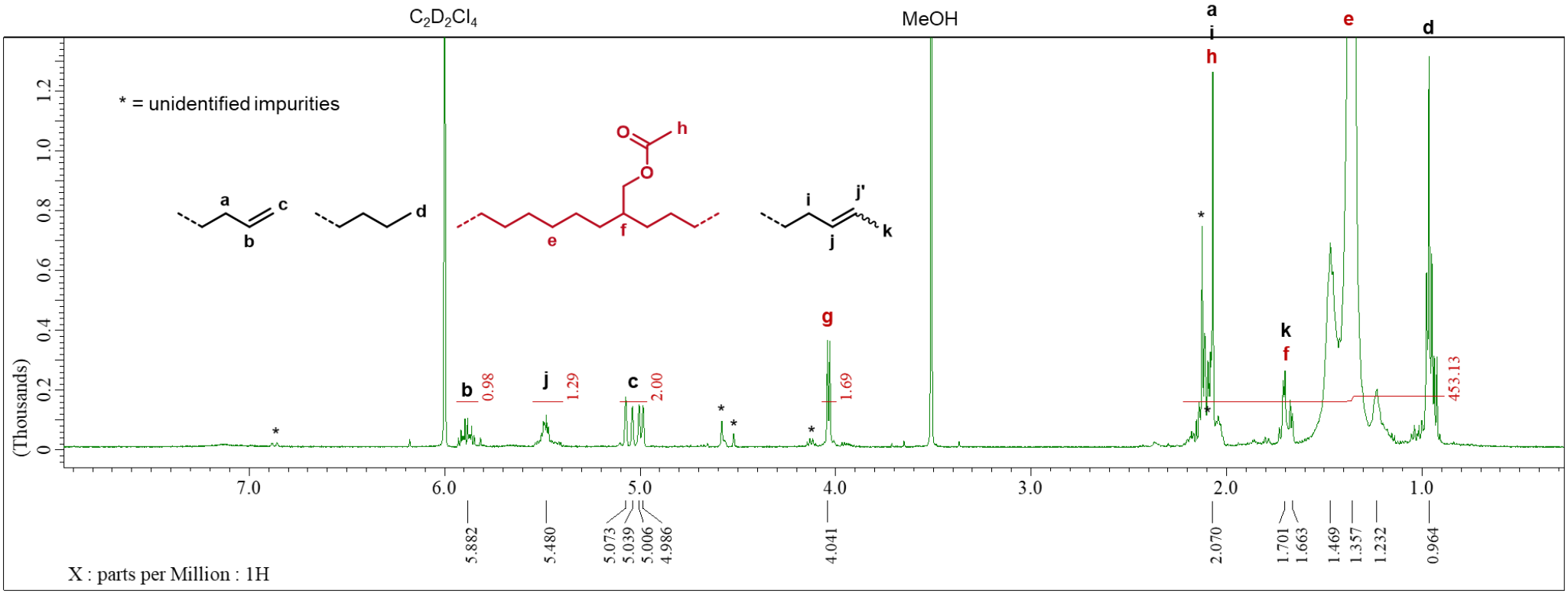


Figure S19. ^{1}H NMR spectrum of the ethylene / allyl acetate copolymer obtained in Table 3, entry 6 ($C_2D_2Cl_4$, 120 ºC, relaxation delay 5 s).

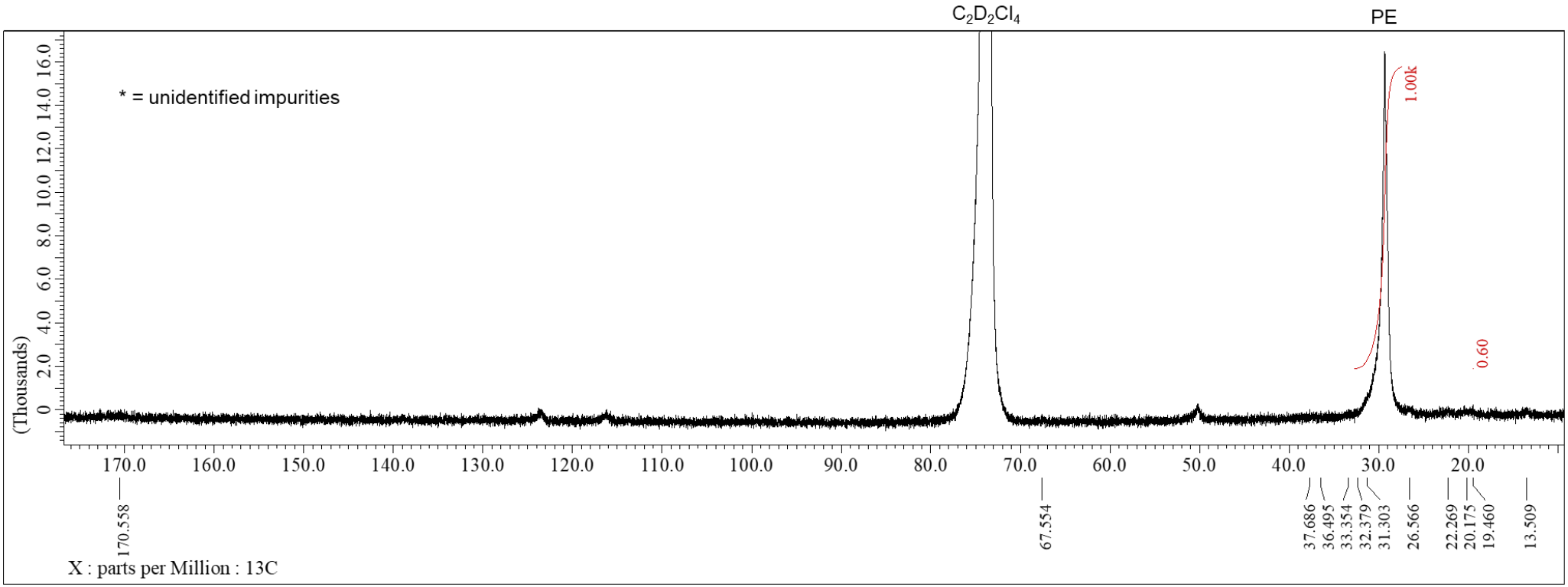


Figure S20. Quantitative ^{13}C NMR spectrum of the ethylene / allyl acetate copolymer obtained in Table 3, entry 6 ($C_2D_2Cl_4$, 120 ºC).

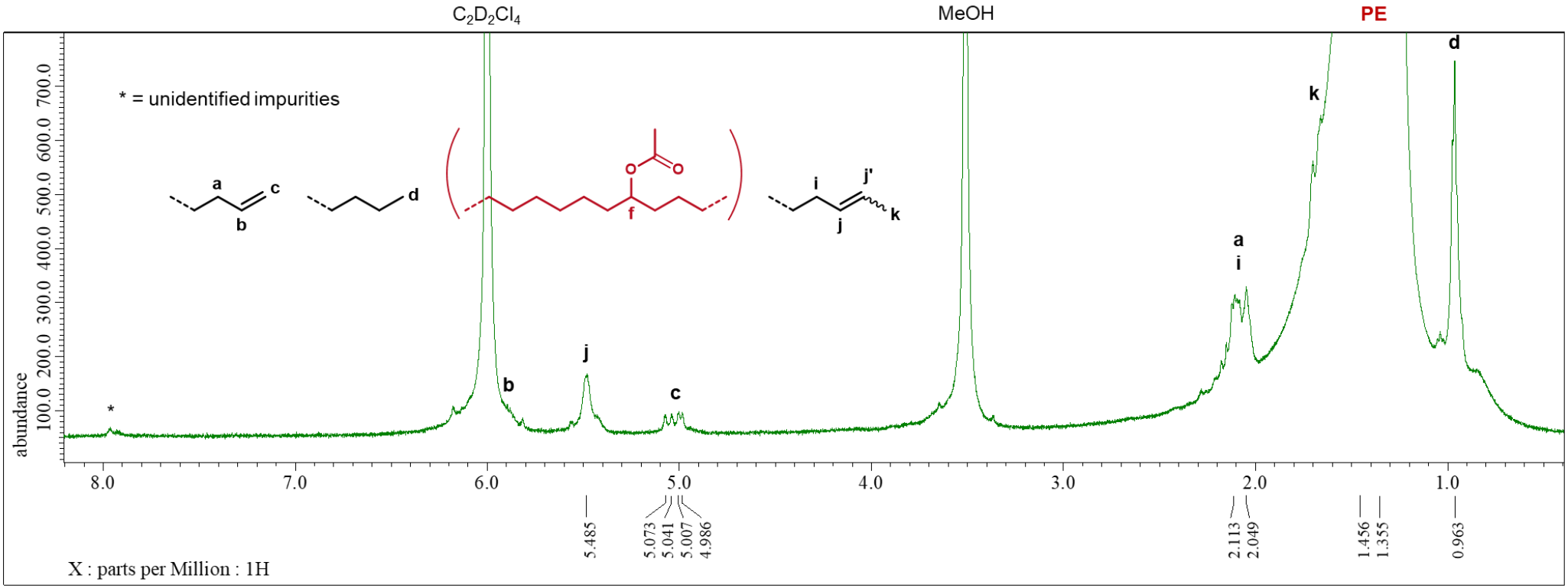


Figure S21. ^{1}H NMR spectrum of the polyethylene obtained in Table 3, entry 7 ($C_2D_2Cl_4$, 120 ºC, relaxation delay 5 s). Characteristic peak of acetoxy group (f at 4.90–4.80 ppm)[7] was not detected.

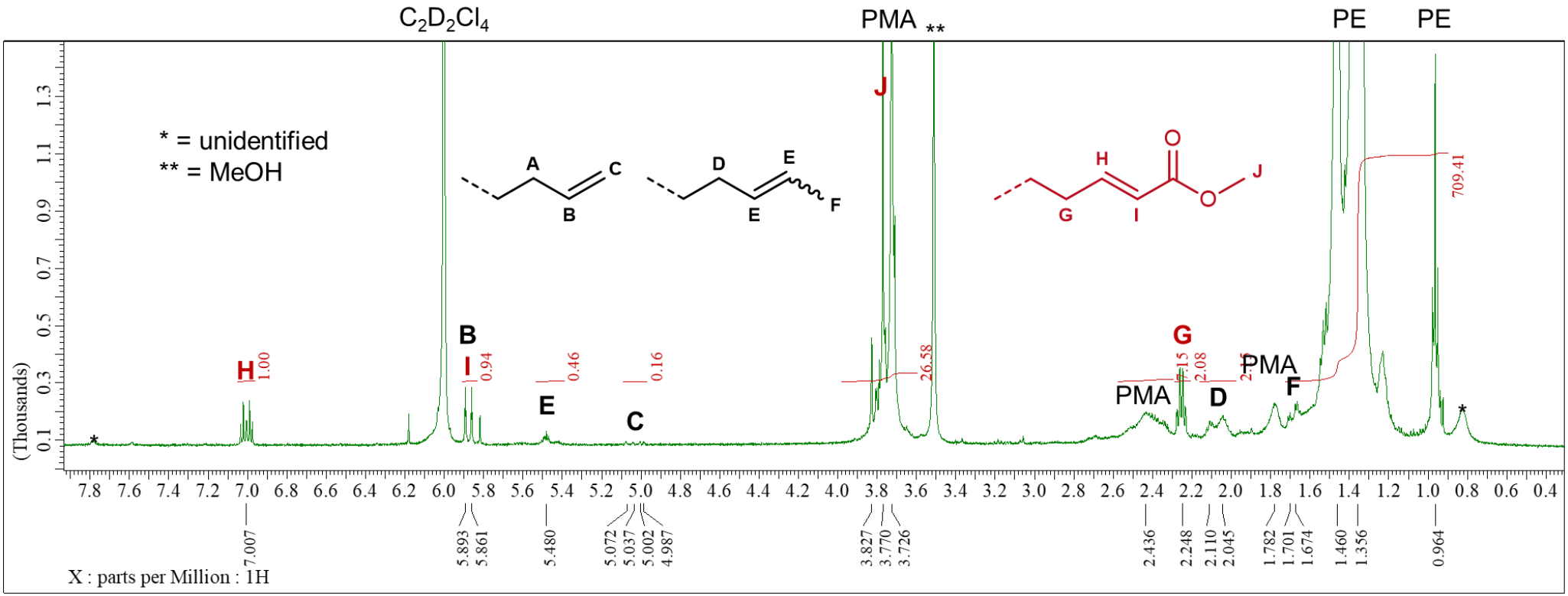


Figure S22. ^{1}H NMR spectrum of the ethylene / methyl acrylate copolymer obtained in Table 3, entry 8 ($C_2D_2Cl_4$, 120 ºC, relaxation delay 5 s). Peak assignments were based on the literatures.[8-9]

Note: Calculation of terminal α,β-unsaturated ester group content: Assume (1-x) mol% ethylene and x mol% terminal α,β-unsaturated ester group in the copolymer,

$$\frac{x}{x+4(1-x)} = \frac{\mathbf{H}}{\mathbf{H}+\mathbf{E}+\mathbf{C}+\mathbf{D}+\mathbf{F}+\mathrm{PE}} \qquad x = \frac{4\times\mathbf{H}\times 100}{(4\times\mathbf{H})+\mathbf{E}+\mathbf{C}+\mathbf{D}+\mathbf{F}+\mathrm{PE}}$$

Therefore, the terminal α,β-unsaturated ester group content is calculated as follows: (4×1.00×100)/{(4×1.00)+0.46+0.16+2.15+709.41 = 0.56 mol%

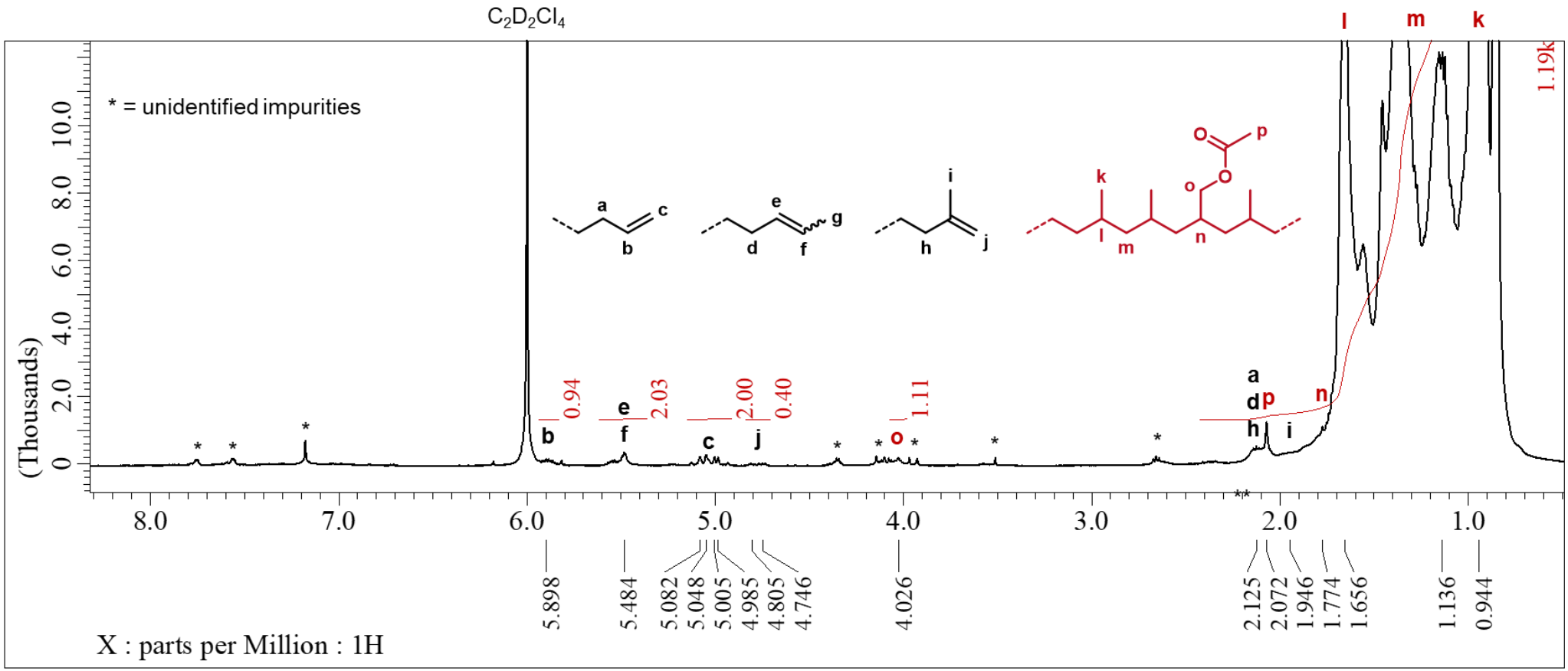


Figure S23. ^{1}H NMR spectrum of the propylene / allyl acetate copolymer obtained in Table 3, entry 9 ($C_2D_2Cl_4$, 120 ºC, relaxation delay 5 s).

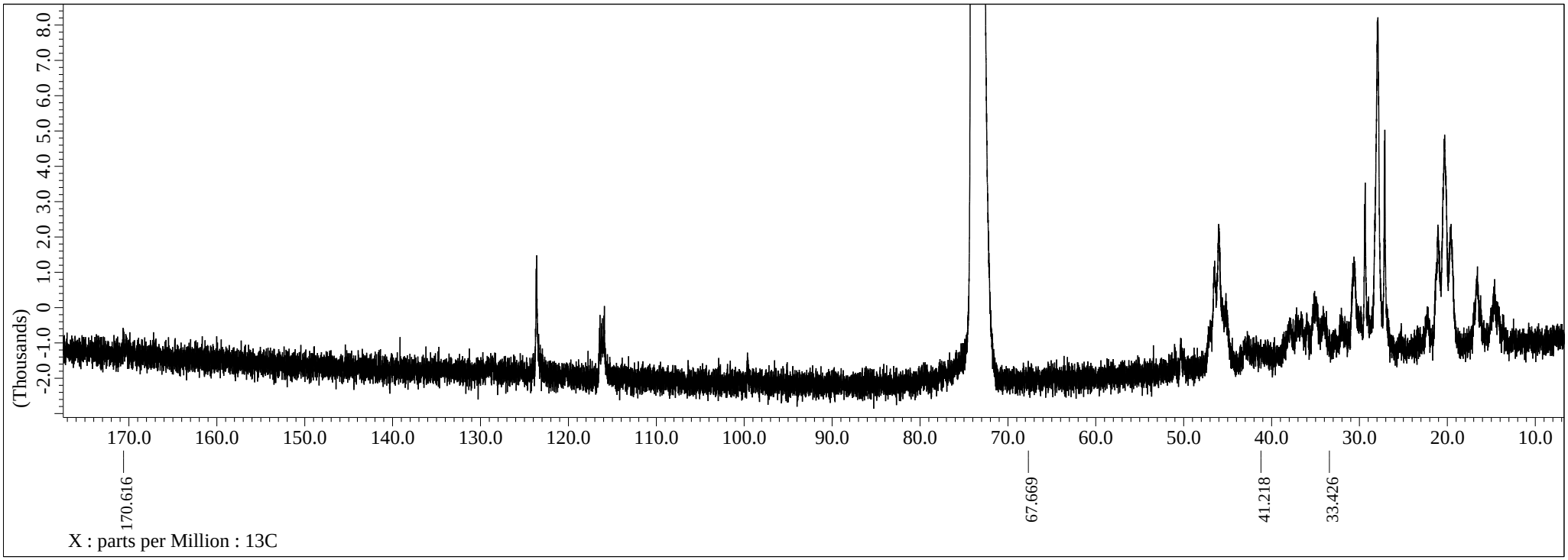


Figure S24. Quantitative ^{13}C NMR spectrum of the propylene / allyl acetate copolymer obtained in Table 3, entry 9 ($C_2D_2Cl_4$, 120 ºC).

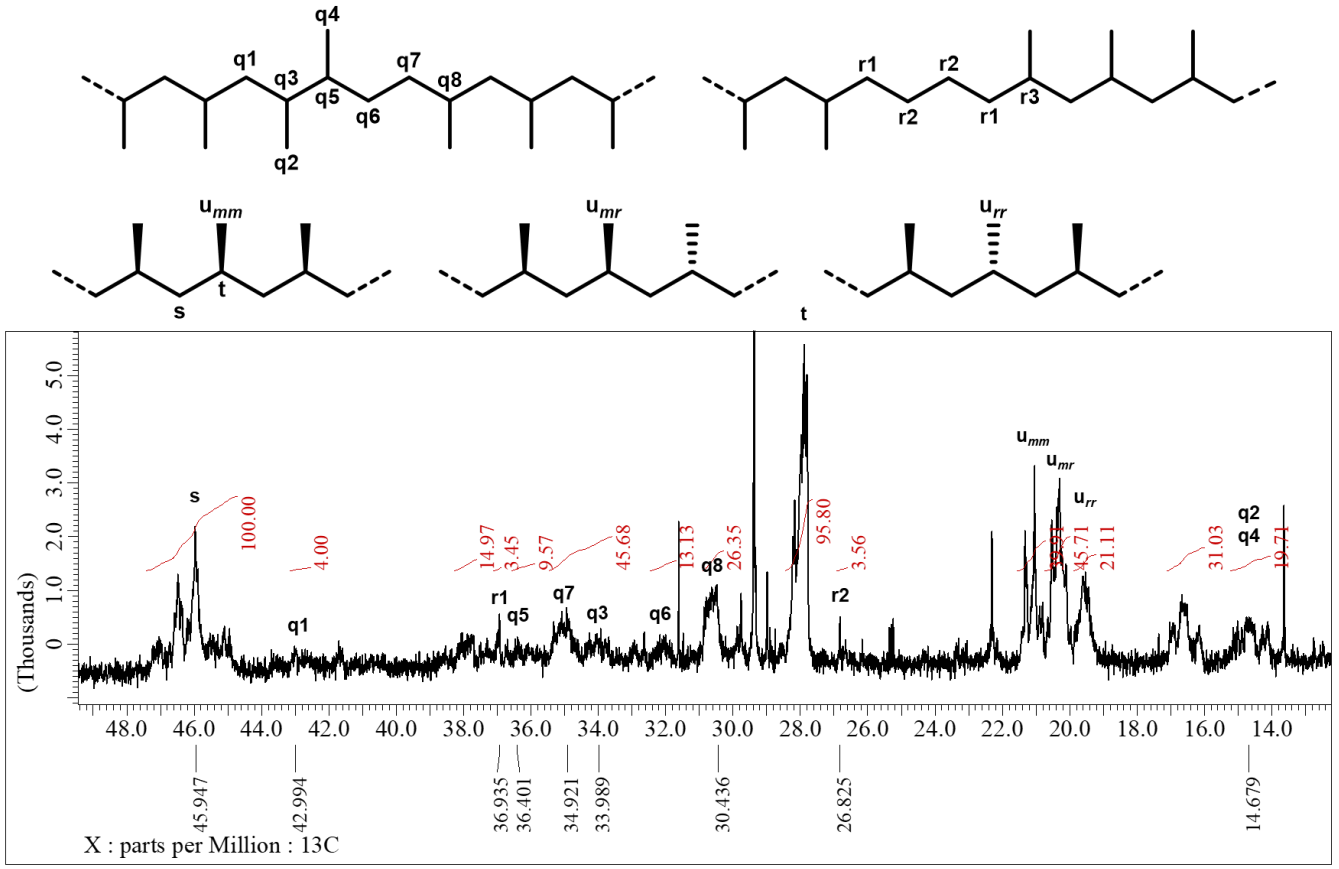


Figure S25. Amplified quantitative ^{13}C NMR spectrum from Figure S24.

Note: Calculation of regiodefect (mol%)

$$x = \frac{[(\mathbf{q2}+\mathbf{q4})/2]+(\mathbf{r2}/2)}{\text{all carbons}/3} \times 100$$

Therefore, the regiodefect is calculated as follows: [{(19.71/2)+(3.56/2)}/{(100+4+14.97+3.45+9.57+45.68+13.13+26.35+95.80+3.56+39.91+45.71+21.11+31.03+19.71)/3}] = 7.36 mol%. Among them, 1,2-/2,1-regiodefect (q1–q8) is estimated to be *ca.* 5.91 mol% while 1,3-enchainment (r1–r3) is estimated to be *ca.* 0.28 mol%

There are some other unidentified signals possibly from other defects structures. On the other hand, the triad abundances were determined by integral values of $\mathbf{u}_{mm}$, $\mathbf{u}_{mr}$, $\mathbf{u}_{rr}$.

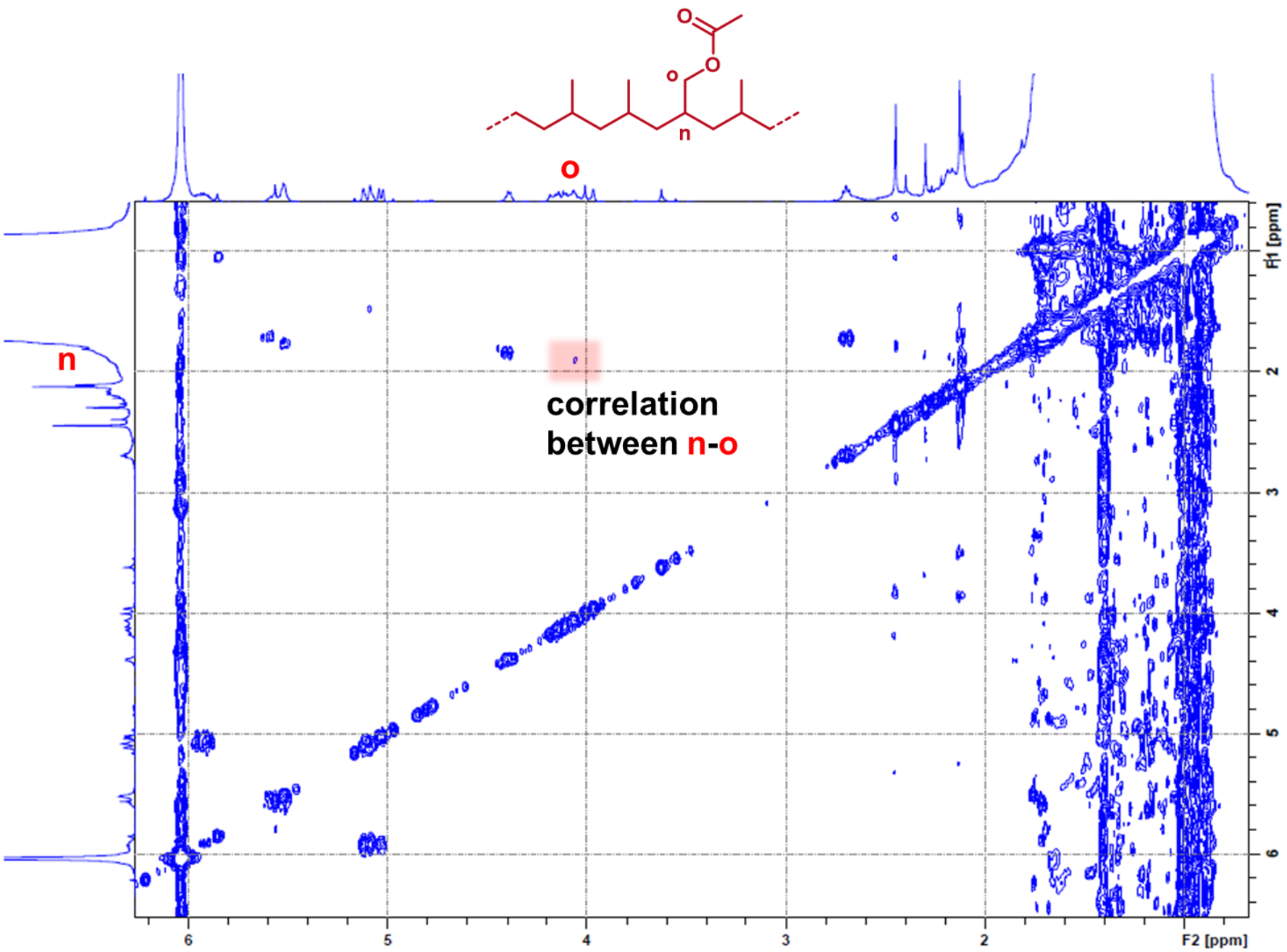


Figure S26. ^{1}H–^{1}H COSY spectrum of the propylene / allyl acetate copolymer obtained in Table 3, entry 9 ($C_2D_2Cl_4$, 120 ºC).

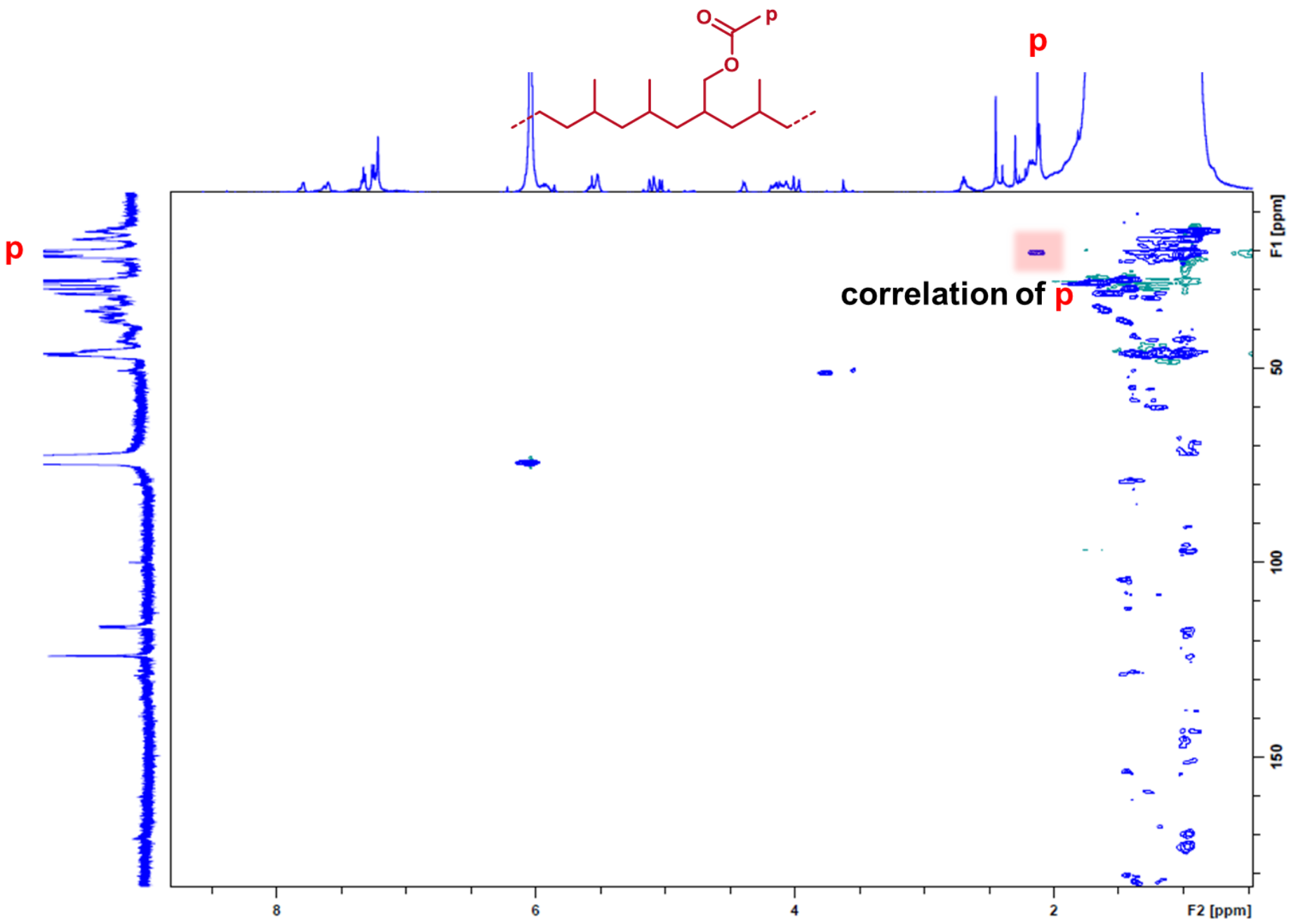


Figure S27. ^{1}H–^{13}C HSQC spectrum of the propylene / allyl acetate copolymer obtained in Table 3, entry 9 ($C_2D_2Cl_4$, 120 ºC).

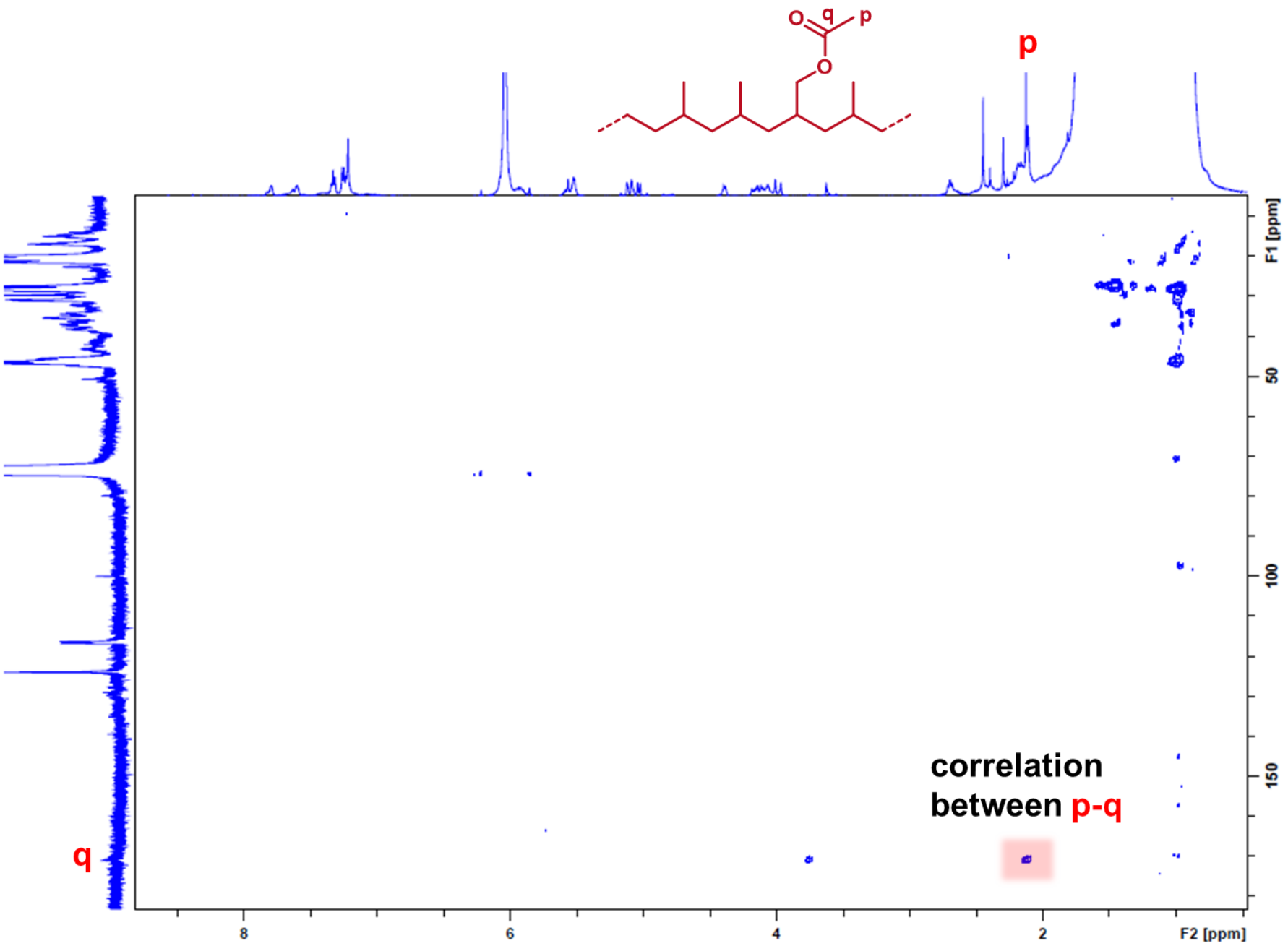


Figure S28. ^{1}H–^{13}C HMBC spectrum of the propylene / allyl acetate copolymer obtained in Table 3, entry 9 ($C_2D_2Cl_4$, 120 ºC).

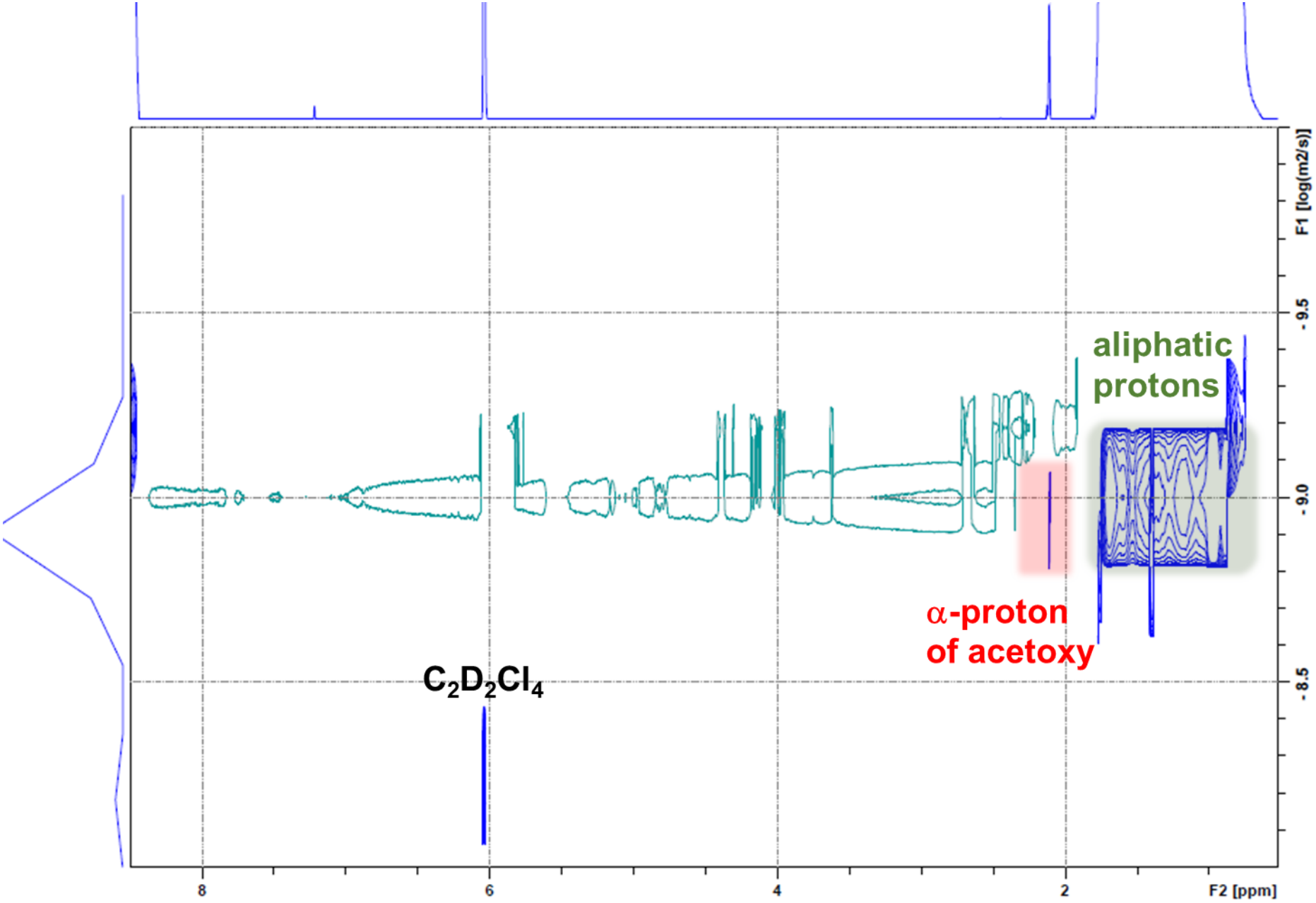


Figure S29. DOSY spectrum of the propylene / allyl acetate copolymer obtained in Table 3, entry 9 ($C_2D_2Cl_4$, 120 ºC).

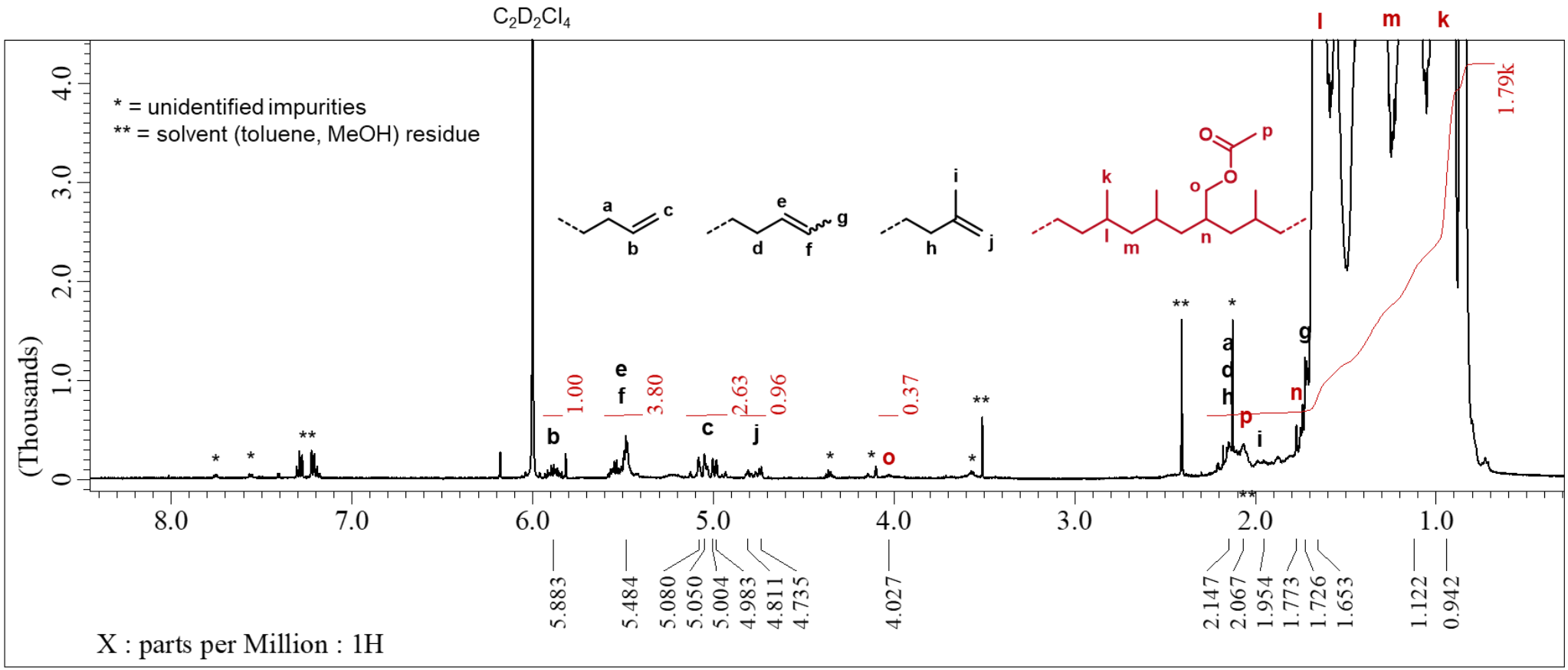


Figure S30. ^{1}H NMR spectrum of the propylene / allyl acetate copolymer obtained in Table 3, entry 10 ($C_2D_2Cl_4$, 120 ºC, relaxation delay 5 s).

Figure S31. DOSY spectrum of the propylene / allyl acetate copolymer obtained in Table 3, entry 10 ($C_2D_2Cl_4$, 120 ºC, relaxation delay 5 s).

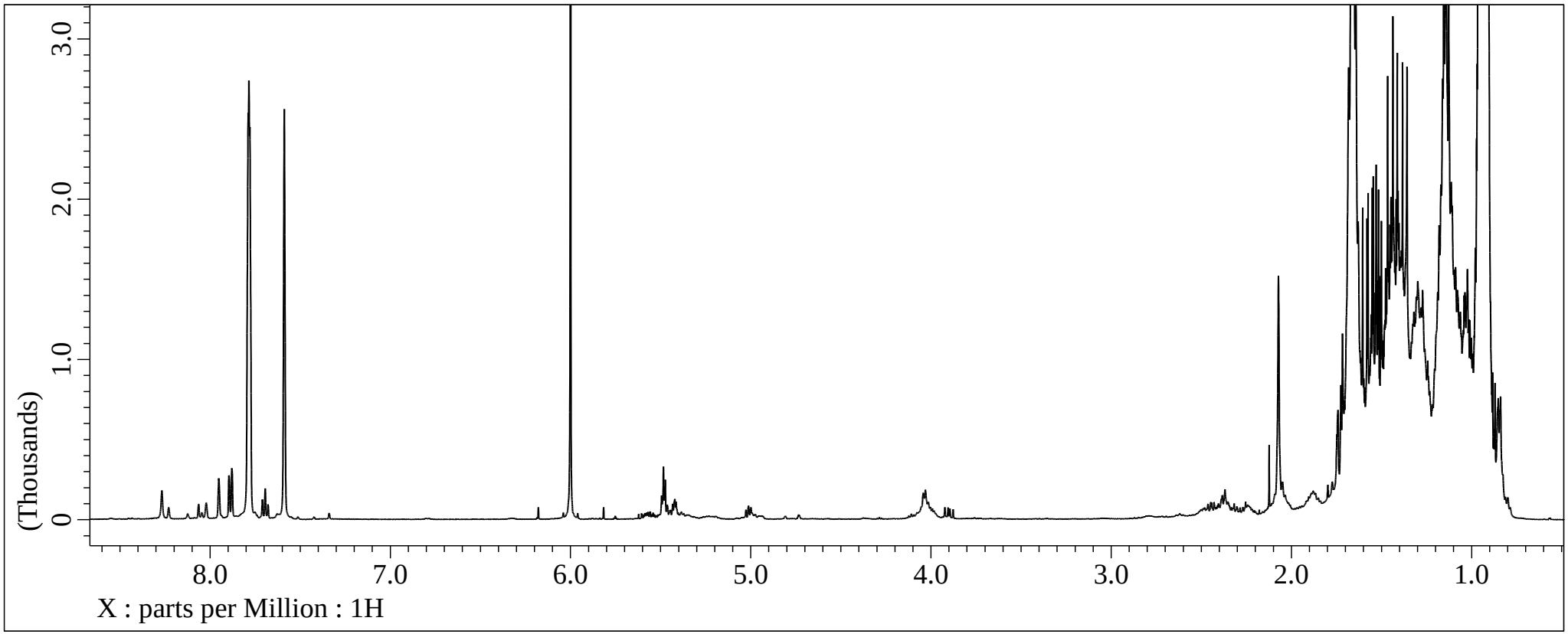


Figure S32. ^{1}H NMR spectrum of the propylene / allyl acetate copolymer obtained in Table S1, entry 1 ($C_2D_2Cl_4$, 120 ºC, relaxation delay 5 s).

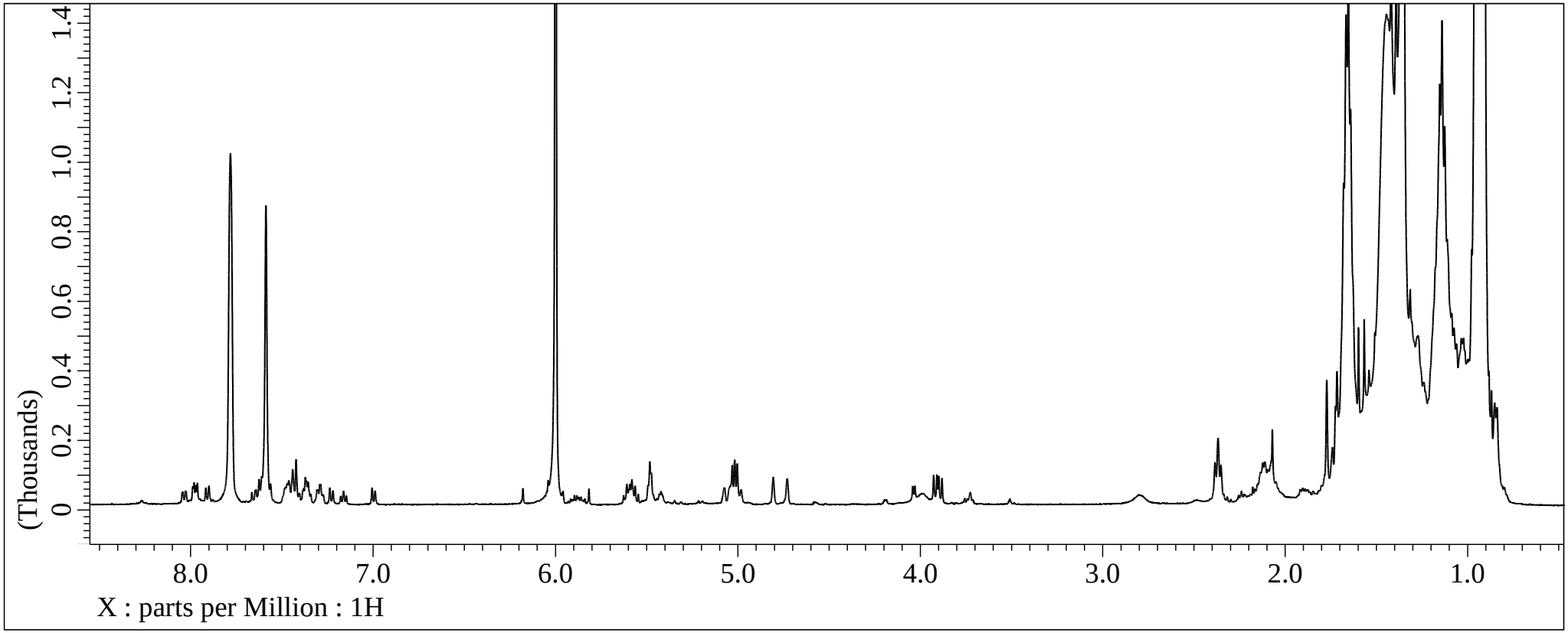
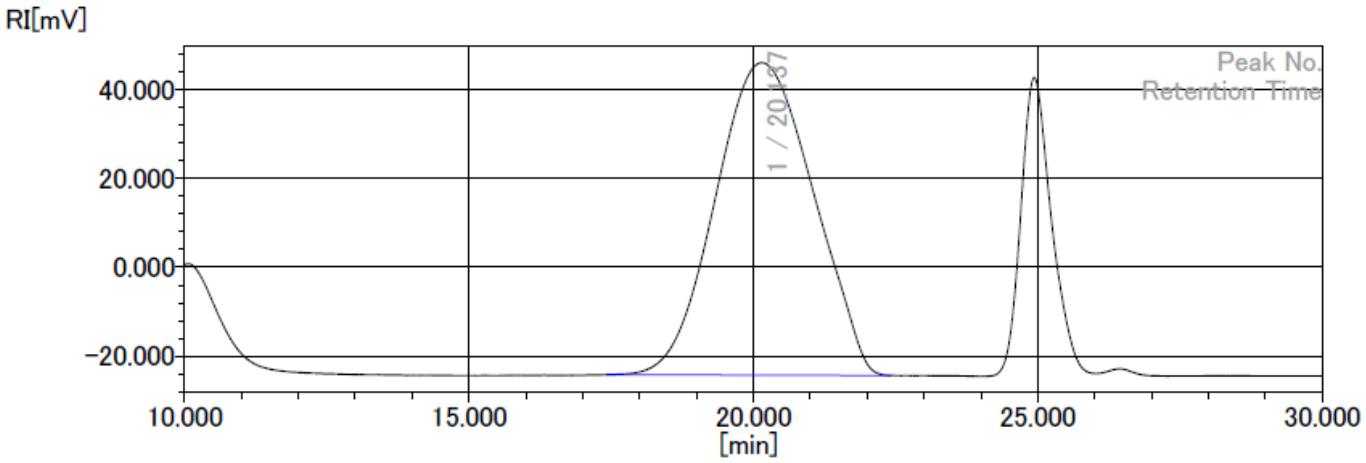


Figure S33. ^{1}H NMR spectrum of the propylene / allyl acetate copolymer obtained in Table S1, entry 2 ($C_2D_2Cl_4$, 120 ºC, relaxation delay 5 s).

3. SEC Traces

Chromatography Report

Title		Measurement Date & Time	2020/03/03 17:20:46
Sample Name	09-018-A55PE	Calculation Date & Time	2020/03/03 18:30:33
Database Name	2020-03-03.chd	Acquisition Time [min] [min]	10.000 - 30.000
Saved File Name	RSLT0597	Sampling Pitch [ms] [ms]	100
Method Data	meth8509_standard	Vial Number	11
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test



Result of Calculation (RI) (RI)

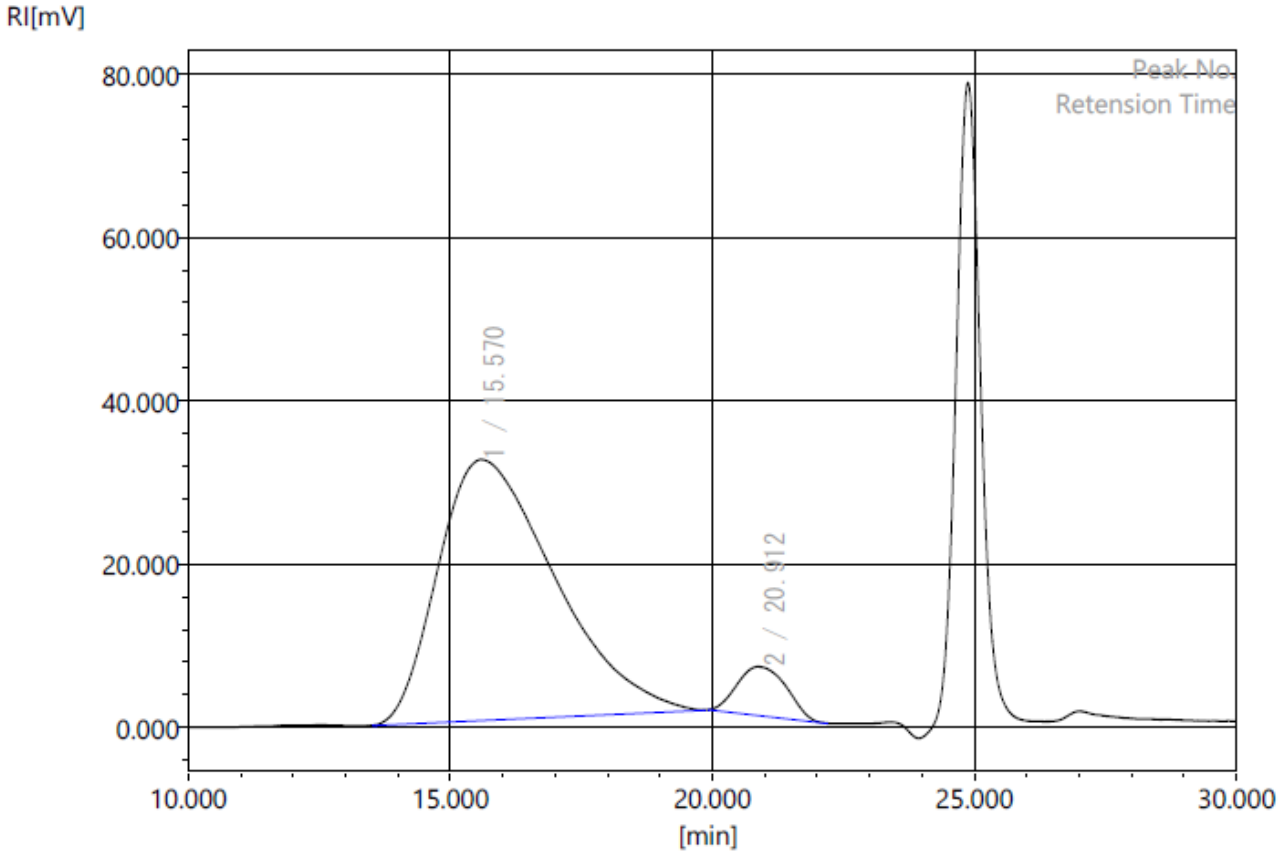
Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak Start	17.423	-24.179	114,599	Mn	3,772
Peak Top	20.137	46.184	7,438	Mw	9,399
Peak End	22.390	-24.395	157	Mz	17,462
				Mz+1	26,857
				Mv	9,399
Height [mV]			70.481	Mp	8,824
Area [mV*s]			8398.050	Mz/Mw	1.858
Area% [%]			100.000	Mw/Mn	2.492
[eta]			9399.39415	Mz+1/Mw	2.857

Figure S34. SEC trace of the polyethylene obtained in Table 1, entry 1 (1,2-dichlorobenzene, 145 ºC)

Chromatography Report

Title		Measurement Date	2018/10/17 17:05:55
Sample Name	133-03-116	Calculation Date	2018/10/17 18:01:07
Database Name	2018-10-17.chd	Measurement Time [min]	10.000 - 30.000
Saved File Name	RSLT0332	Sampling Pitch [ms]	100
Method Data	meth8509_standard	Cup Number	4
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test



Result of Calculation (RI)

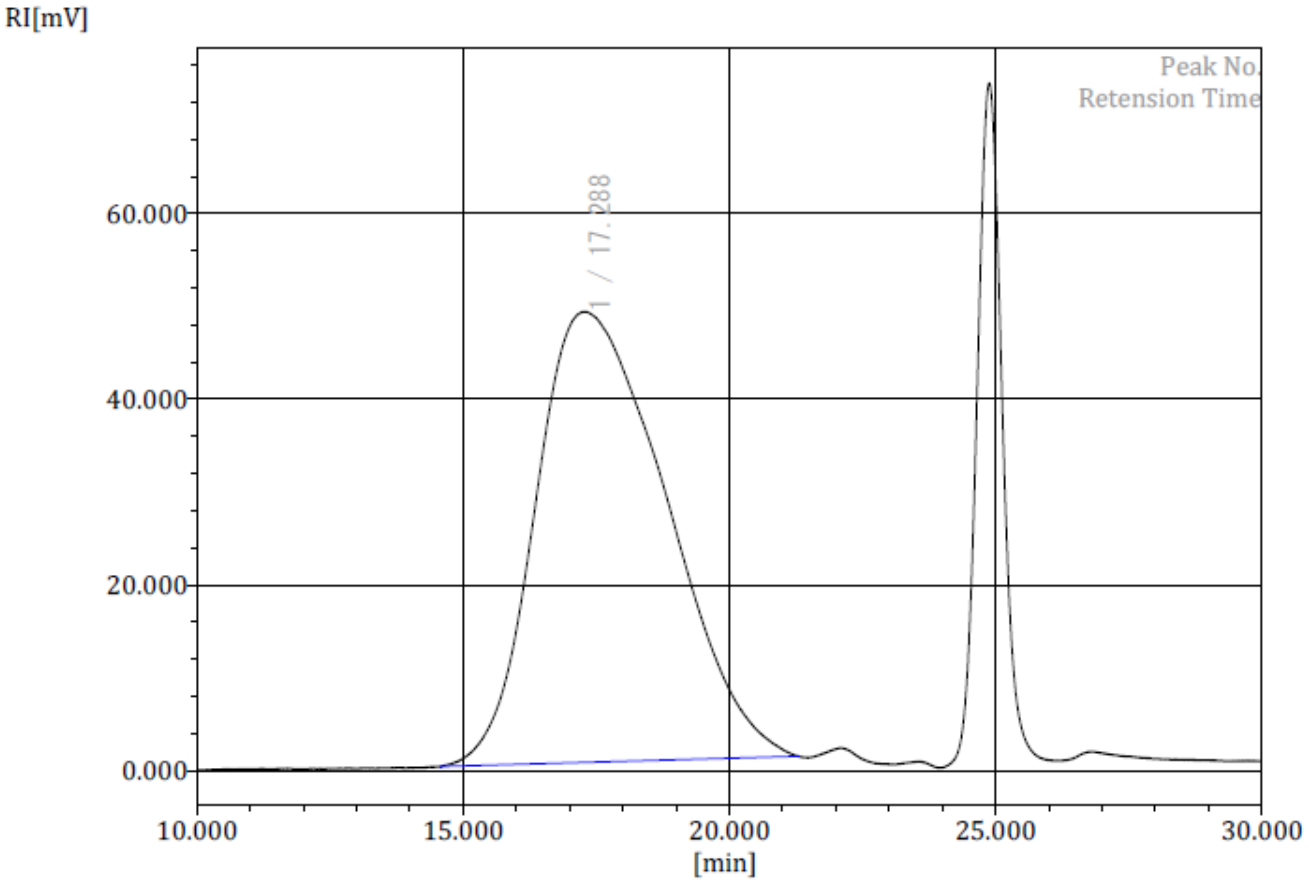
Peak No. 1 Base Peak

	[min]	[mV]	[mol]		
Peak Start	13.530	0.239	3,540,928	Mn	227,255
Peak Top	15.570	32.830	601,437	Mw	558,635
Peak End	19.853	2.104	10,415	Mz	938,928
				Mz+1	1,285,245
				Mv	558,635
Height [mV]			31.989	Mp	601,438
Area [mV*s]			4944.986	Mz/Mw	1.681
Area% [%]			92.593	Mw/Mn	2.458
[eta]			558635.26300	Mz+1/Mw	2.301

Figure S35. SEC trace of the polyethylene obtained in Table 1, entry 2 (1,2-dichlorobenzene, 145 ºC)

High-temperature GPC Report

Title		Measurement Date	2018/10/22 18:10:32
Sample Name	133-03-121	Calculation Date	2018/10/22 18:26:13
Database Name	2018-10-22.chd	Measurement Time [min]	10.000 - 30.000
Saved File Name	RSLT0334	Sampling Pitch [ms]	100
Method Data	meth8509_standard	Cup Number	2
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test



Calculation Results (RI)

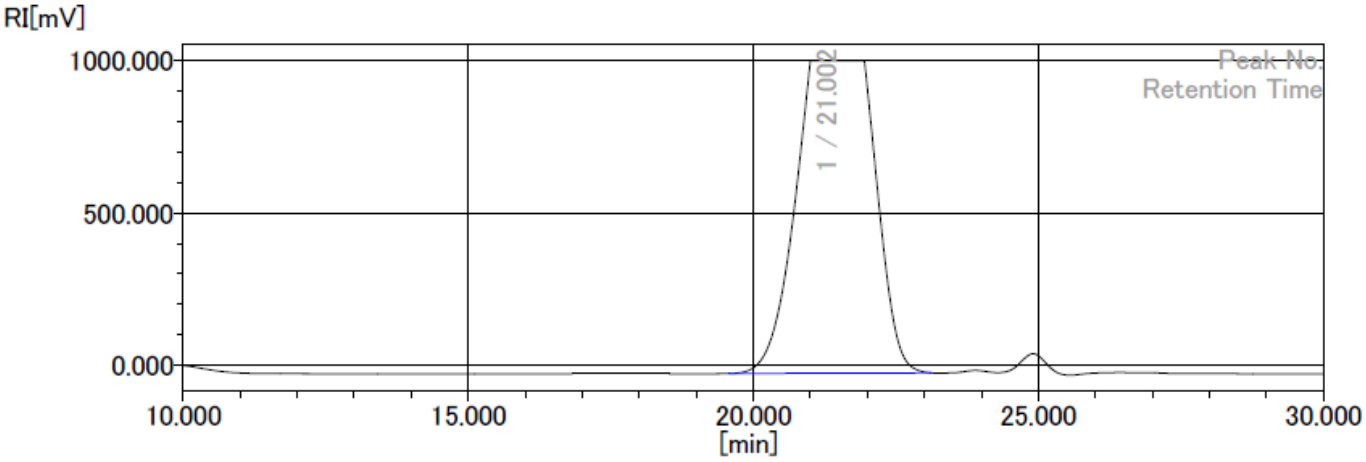
Peak No. 1 Base Peak

	[min]	[mV]	[mol]		
Peak Start	14.583	0.432	1,438,609	Mn	45,461
Peak Top	17.288	49.457	129,440	Mw	132,657
Peak End	21.298	1.544	1,418	Mz	258,245
				Mz+1	406,886
				Mv	132,657
Height [mV]			48.577	Mp	132,786
Area [mV*s]			8256.070	Mz/Mw	1.947
Area% [%]			100.000	Mw/Mn	2.918
[eta]			132656.70351	Mz+1/Mw	3.067

Figure S36. SEC trace of the polyethylene obtained in Table 1, entry 3 (1,2-dichlorobenzene, 145 ºC)

Chromatography Report

Title		Measurement Date & Time	2020/03/10 18:21:07
Sample Name	019-PP50	Calculation Date & Time	2020/03/10 18:56:03
Database Name	2020-03-10.chd	Acquisition Time [min] [min]	10.000 - 30.000
Saved File Name	RSLT0605	Sampling Pitch [ms] [ms]	100
Method Data	meth8509_standard	Vial Number	18
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test



Result of Calculation (RI) (RI)

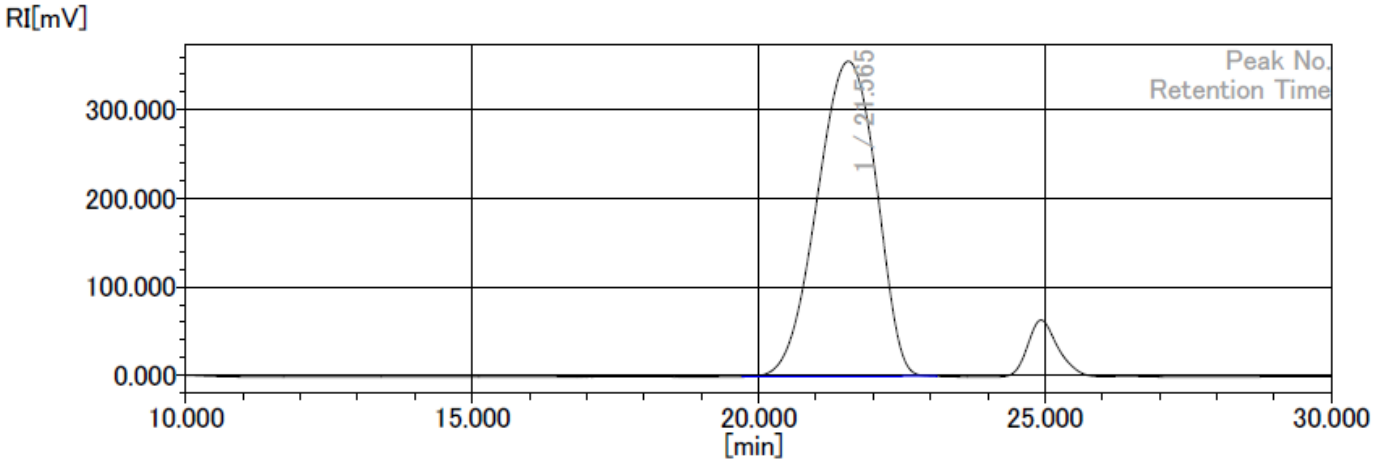
Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak Start	19.587	-26.976	14,057	Mn	647
Peak Top	21.002	1000.000	2,281	Mw	1,501
Peak End	23.110	-24.636	21	Mz	2,685
				Mz+1	3,887
				Mv	1,501
Height [mV]			1026.036	Mp	2,288
Area [mV*s]			98821.272	Mz/Mw	1.788
Area% [%]			100.000	Mw/Mn	2.322
[eta]			1501.42498	Mz+1/Mw	2.589

Figure S37. SEC trace of the polypropylene obtained in Table 1, entry 4 (1,2-dichlorobenzene, 145 ºC)

Chromatography Report

Title		Measurement Date & Time	2020/03/10 18:51:08
Sample Name	020-PP80	Calculation Date & Time	2020/03/18 05:26:43
Database Name	2020-03-10.chd	Acquisition Time [min] [min]	10.000 - 30.000
Saved File Name	RSLT0606	Sampling Pitch [ms] [ms]	100
Method Data	meth8509_standard	Vial Number	19
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test



Result of Calculation (RI) (RI)

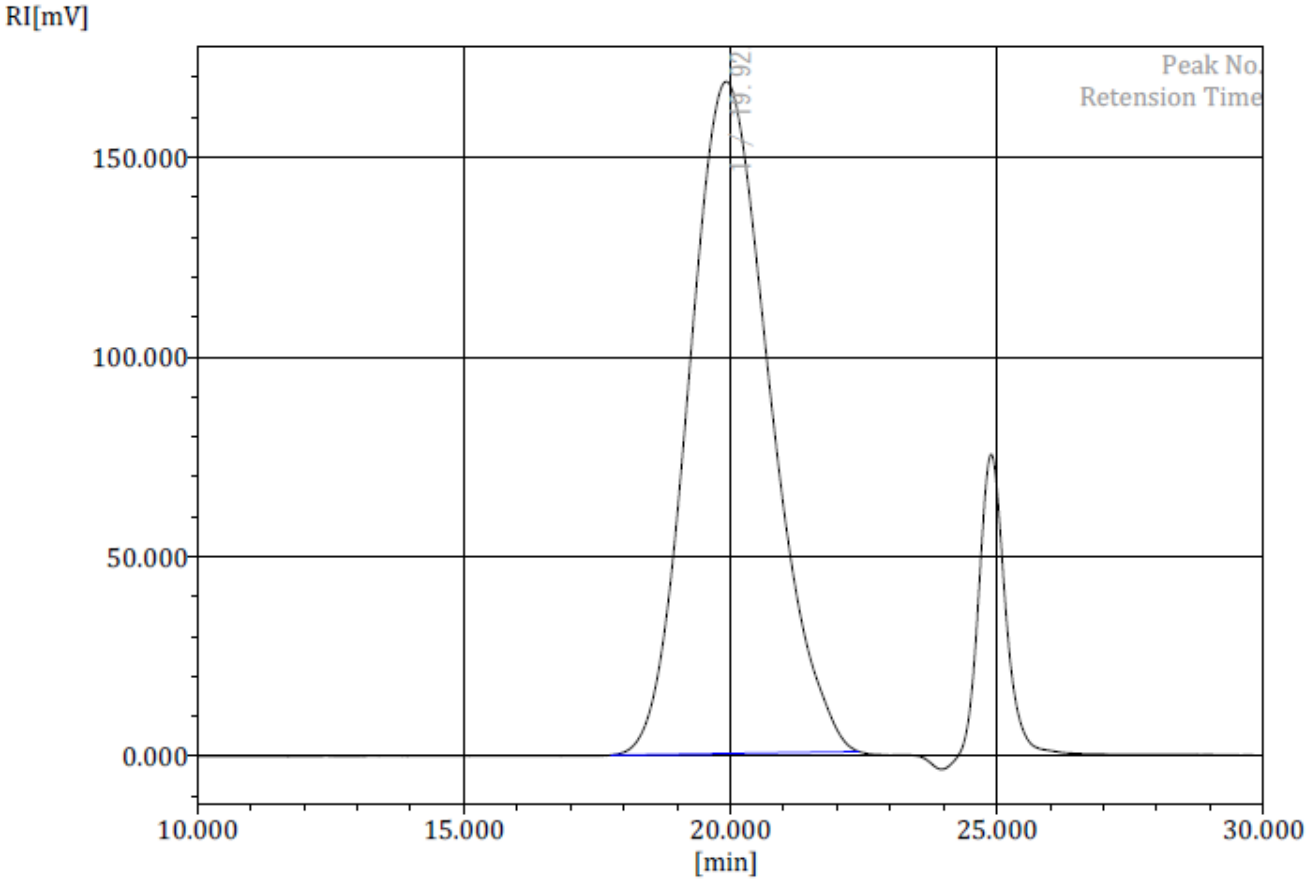
Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak Start	19.720	-1.786	12,122	Mn	640
Peak Top	21.565	355.071	890	Mw	1,232
Peak End	23.110	-1.110	21	Mz	2,082
				Mz+1	3,068
				Mv	1,232
Height [mV]			356.489	Mp	1,038
Area [mV*s]			25594.820	Mz/Mw	1.690
Area% [%]			100.000	Mw/Mn	1.925
[eta]			1231.68501	Mz+1/Mw	2.491

Figure S38. SEC trace of the polypropylene obtained in Table 1, entry 5 (1,2-dichlorobenzene, 145 ºC)

High-temperature GPC Report

Title		Measurement Date	2019/02/06 17:35:15
Sample Name	133-04-063	Calculation Date	2019/02/06 18:14:03
Database Name	2019-02-06.chd	Measurement Time [min]	10.000 - 30.000
Saved File Name	RSLT0421	Sampling Pitch [ms]	100
Method Data	meth8509_standard	Cup Number	1
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test



Calculation Results (RI)

Peak No. 1 Base Peak

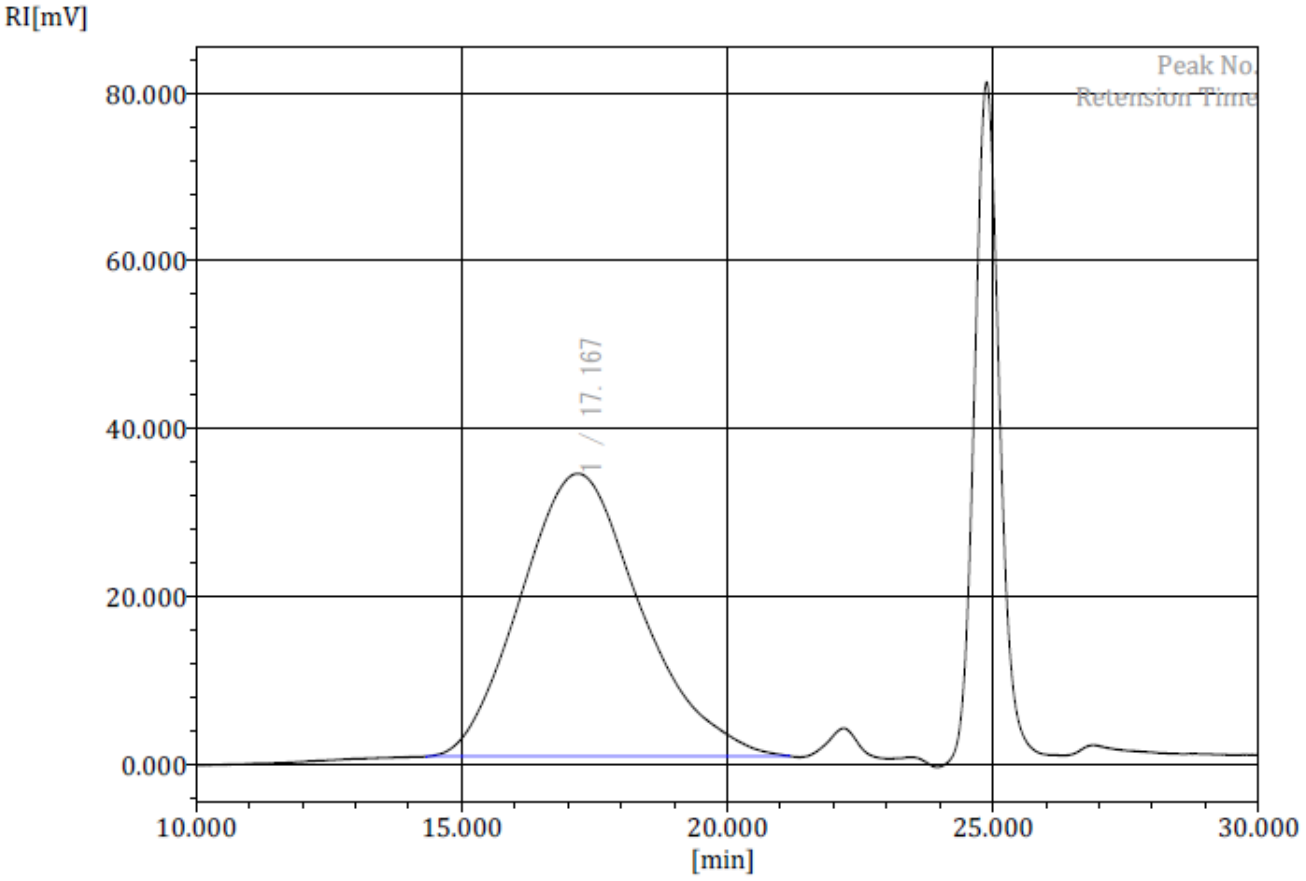
	[min]	[mV]	[mol]
Peak Start	17.770	0.215	83,650
Peak Top	19.922	169.004	9,620
Peak End	22.402	1.109	153
Height [mV]			168.374
Area [mV*s]			17685.165
Area% [%]			100.000
[eta]			10858.41942

Mn	4,820
Mw	10,858
Mz	17,546
Mz+1	24,441
Mv	10,858
Mp	10,617
Mz/Mw	1.616
Mw/Mn	2.253
Mz+1/Mw	2.251

Figure S39. SEC trace of the polypropylene obtained in Table 1, entry 6 (1,2-dichlorobenzene, 145 ºC)

High-temperature GPC Report

Title		Measurement Date	2018/10/22 17:40:32
Sample Name	133-03-119	Calculation Date	2018/10/22 18:25:26
Database Name	2018-10-22.chd	Measurement Time [min]	10.000 - 30.000
Saved File Name	RSLT0333	Sampling Pitch [ms]	100
Method Data	meth8509_standard	Cup Number	1
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test



Calculation Results (RI)

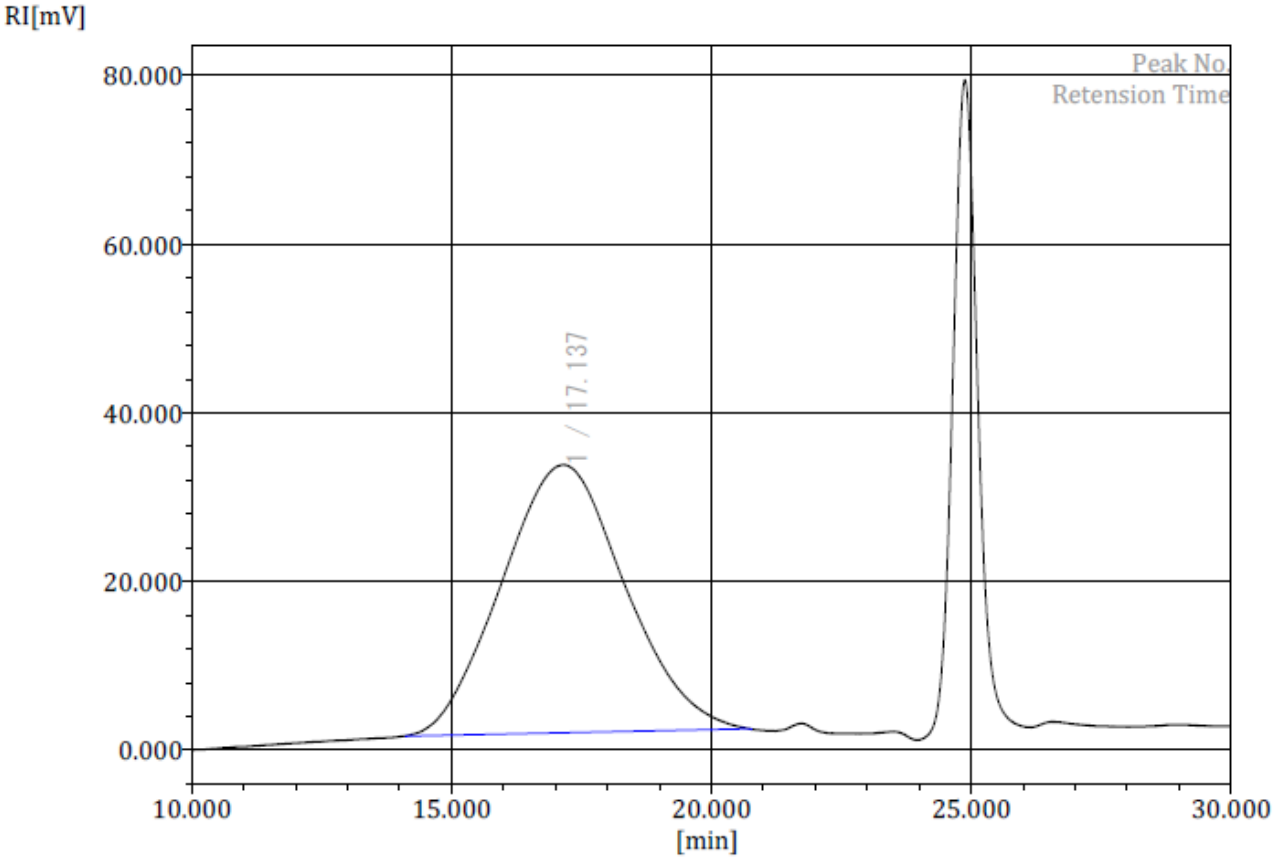
Peak No. 1 Base Peak

	[min]	[mV]	[mol]		
Peak Start	14.338	1.043	1,780,805	Mn	67,612
Peak Top	17.167	34.721	144,416	Mw	186,426
Peak End	21.177	1.048	1,733	Mz	356,813
				Mz+1	548,510
				Mv	186,426
Height [mV]			33.676	Mp	144,416
Area [mV*s]			5290.055	Mz/Mw	1.914
Area% [%]			100.000	Mw/Mn	2.757
[eta]			186425.75017	Mz+1/Mw	2.942

Figure S40. SEC trace of the ethylene / allyl acetate copolymer obtained in Table 2, entry 2 (1,2-dichlorobenzene, 145 ºC)

High-temperature GPC Report

Title		Measurement Date	2018/12/07 16:39:00
Sample Name	133-04-010	Calculation Date	2018/12/07 16:48:34
Database Name	2018-12-07.chd	Measurement Time [min]	10.000 - 30.000
Saved File Name	RSLT0384	Sampling Pitch [ms]	100
Method Data	meth8509_standard	Cup Number	1
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test



Calculation Results (RI)

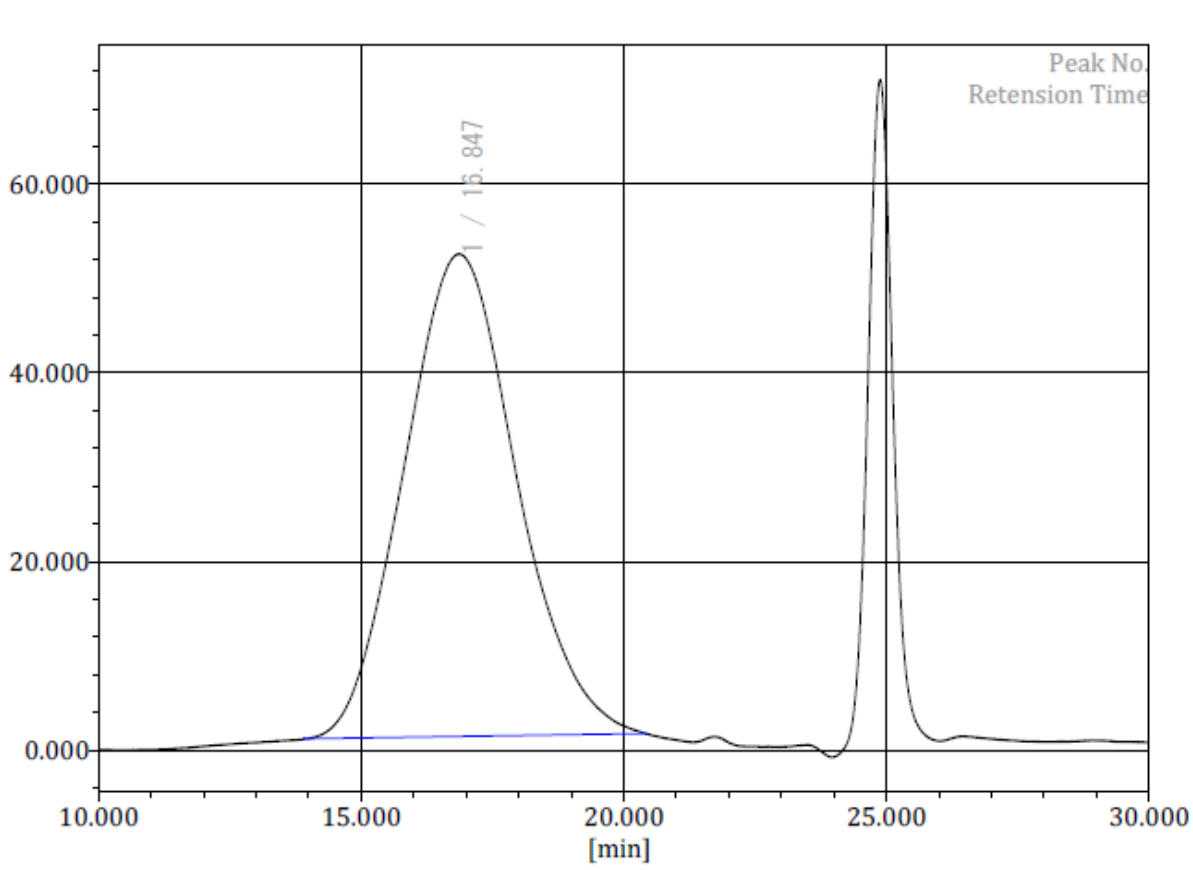
Peak No. 1 Base Peak

	[min]	[mV]	[mol]		
Peak Start	14.118	1.661	2,153,247	Mn	81,297
Peak Top	17.137	33.872	148,362	Mw	216,818
Peak End	20.760	2.544	3,263	Mz	444,101
				Mz+1	711,246
				Mv	216,818
Height [mV]			31.810	Mp	148,362
Area [mV*s]			5229.402	Mz/Mw	2.048
Area% [%]			100.000	Mw/Mn	2.667
[eta]			216818.11663	Mz+1/Mw	3.280

Figure S41. SEC trace of the ethylene / allyl acetate copolymer obtained in Table 2, entry 3 (1,2-dichlorobenzene, 145 ºC)

High-temperature GPC Report

Title		Measurement Date	2018/12/07 17:09:01
Sample Name	133-04-011	Calculation Date	2018/12/07 17:14:21
Database Name	2018-12-07.chd	Measurement Time [min]	10.000 - 30.000
Saved File Name	RSLT0385	Sampling Pitch [ms]	100
Method Data	meth8509_standard	Cup Number	2
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test



Calculation Results (RI)

Peak No. 1 Base Peak

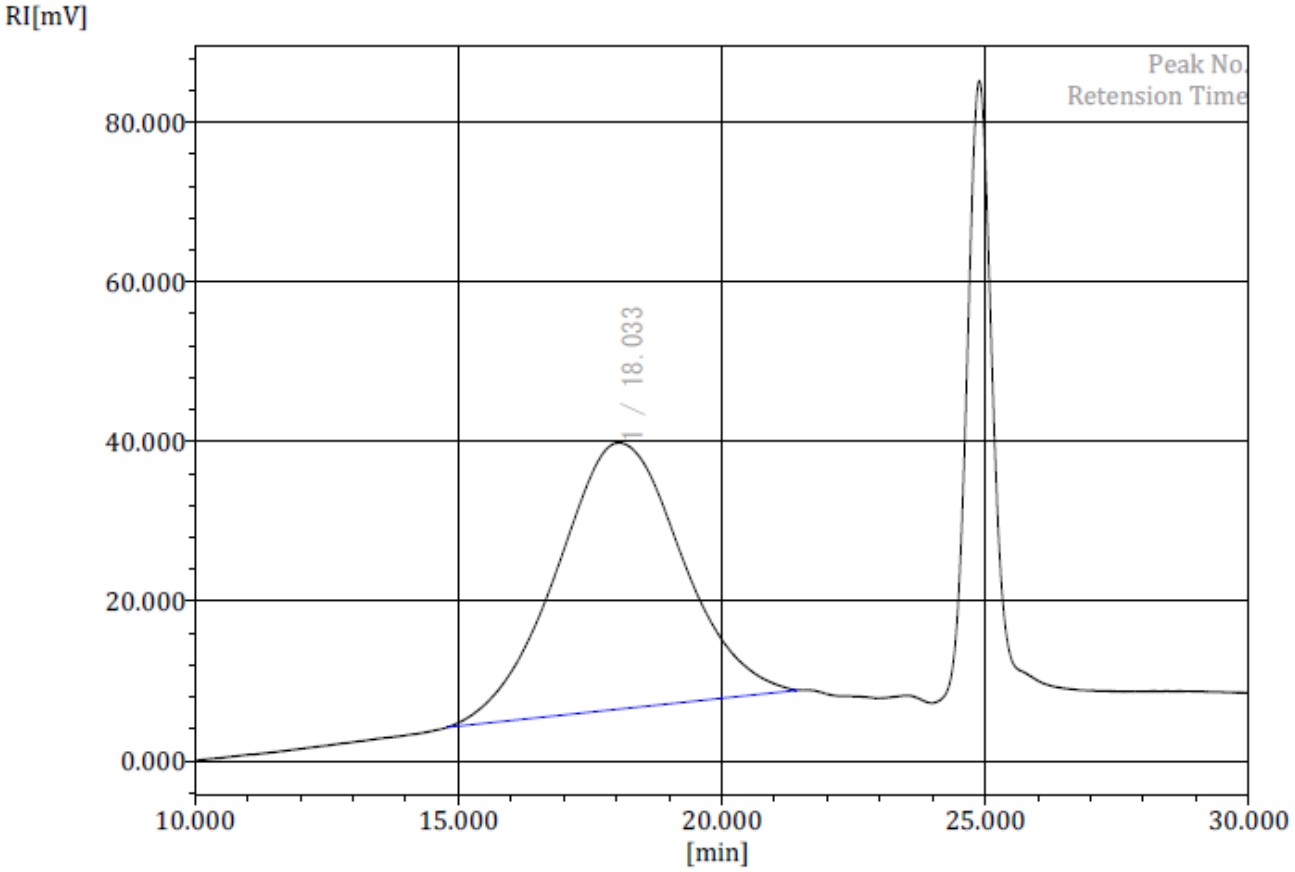
	[min]	[mV]	[mol]
Peak Start	13.922	1.195	2,547,503
Peak Top	16.847	52.631	192,428
Peak End	20.417	1.757	5,219
Height [mV]			51.183
Area [mV*s]			7601.737
Area% [%]			100.000
[eta]			253439.01617

Mn	111,591
Mw	253,439
Mz	470,118
Mz+1	732,011
Mv	253,439
Mp	192,428
Mz/Mw	1.855
Mw/Mn	2.271
Mz+1/Mw	2.888

Figure S42. SEC trace of the ethylene / allyl acetate copolymer obtained in Table 2, entry 4 (1,2-dichlorobenzene, 145 ºC)

High-temperature GPC Report

Title		Measurement Date	2019/01/11 16:27:12
Sample Name	133-04-028	Calculation Date	2019/01/11 18:07:43
Database Name	2019-01-11.chd	Measurement Time [min]	10.000 - 30.000
Saved File Name	RSLT0400	Sampling Pitch [ms]	100
Method Data	meth8509_standard	Cup Number	1
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test



Calculation Results (RI)

Peak No. 1 Base Peak

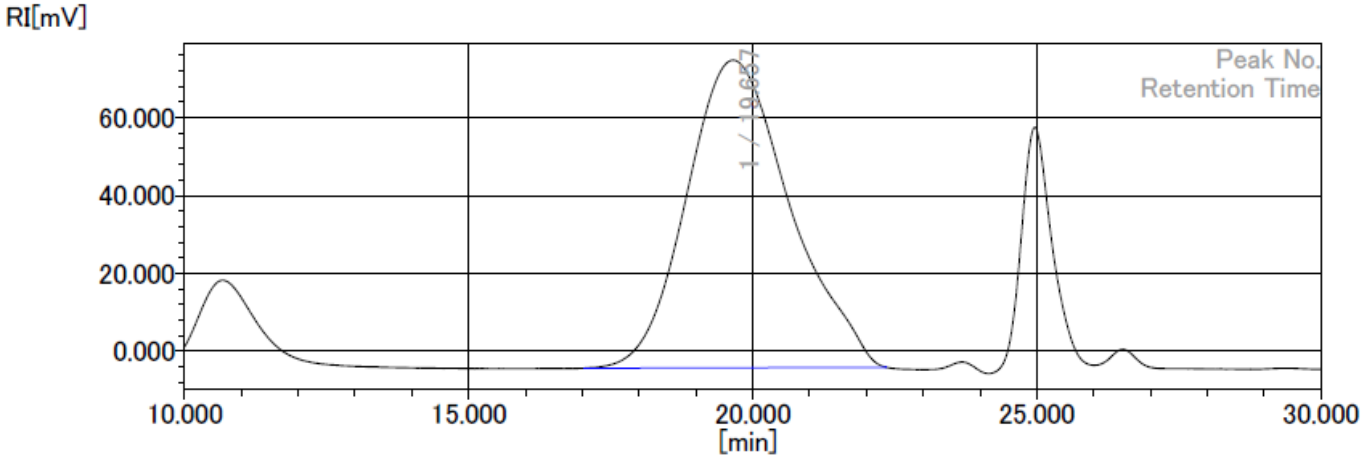
	[min]	[mV]	[mol]
Peak Start	14.803	4.213	1,186,113
Peak Top	18.033	39.893	65,675
Peak End	21.422	8.820	1,149
Height [mV]			33.432
Area [mV*s]			5505.964
Area% [%]			100.000
[eta]			101150.56782

Mn	33,187
Mw	101,151
Mz	231,507
Mz+1	402,513
Mv	101,151
Mp	70,166
Mz/Mw	2.289
Mw/Mn	3.048
Mz+1/Mw	3.979

Figure S43. SEC trace of the ethylene / allyl acetate copolymer obtained in Table 2, entry 5 (1,2-dichlorobenzene, 145 ºC)

Chromatography Report

Title		Measurement Date & Time	2020/03/17 22:27:31
Sample Name	09-031	Calculation Date & Time	2020/03/18 05:34:34
Database Name	2020-03-17(3).chd	Acquisition Time [min] [min]	10.000 - 30.000
Saved File Name	RSLT0633	Sampling Pitch [ms] [ms]	100
Method Data	meth8509_standard	Vial Number	10
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test



Result of Calculation (RI) (RI)

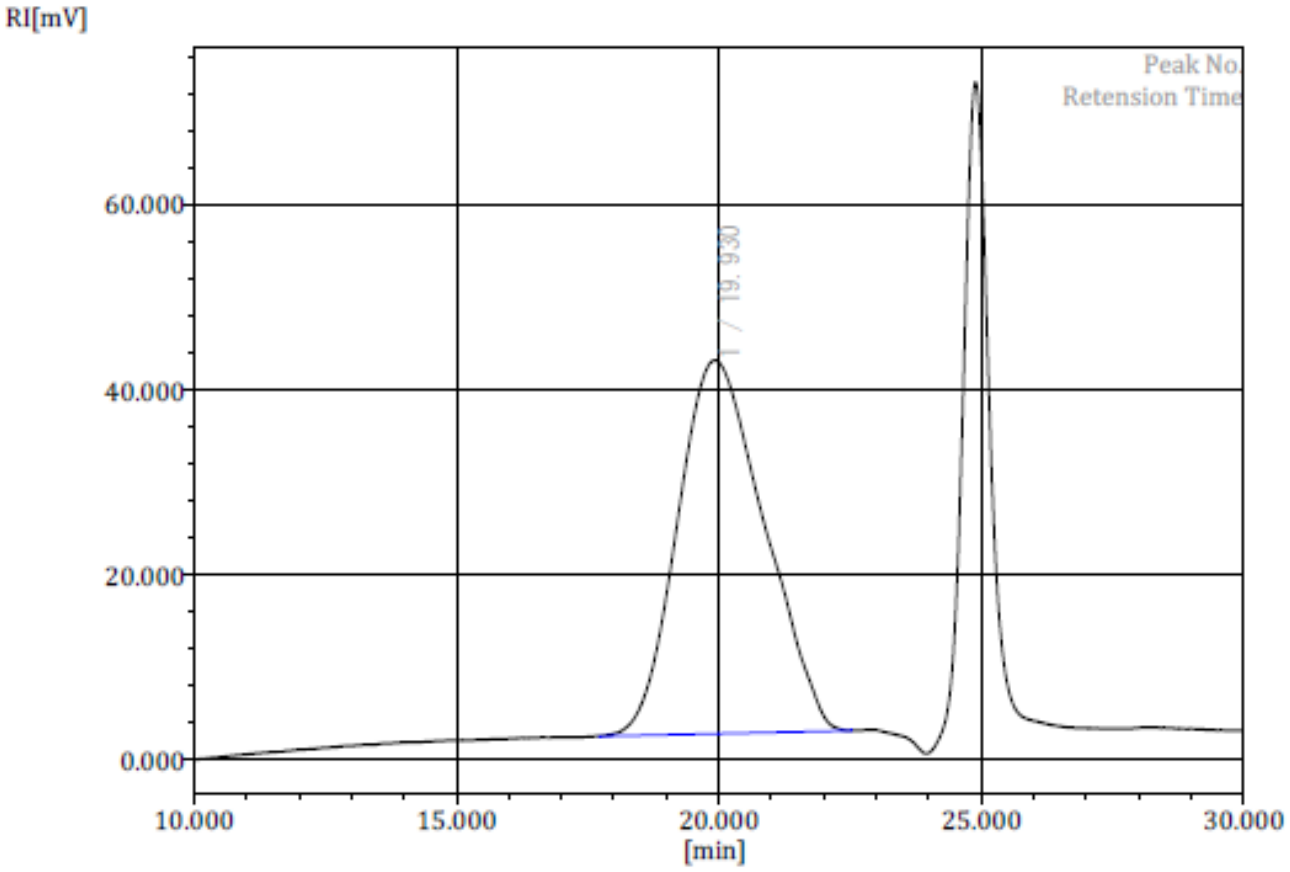
Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak Start	17.035	-4.417	162,541	Mn	5,155
Peak Top	19.657	74.793	13,011	Mw	15,313
Peak End	22.353	-4.167	172	Mz	28,253
				Mz+1	43,158
				Mv	15,313
Height [mV]			79.087	Mp	14,766
Area [mV*s]			9995.126	Mz/Mw	1.845
Area% [%]			100.000	Mw/Mn	2.970
[eta]			15313.26166	Mz+1/Mw	2.818

Figure S44. SEC trace of the ethylene / allyl acetate copolymer obtained in Table 2, entry 7 (1,2-dichlorobenzene, 145 ºC)

High-temperature GPC Report

Title		Measurement Date	2019/02/12 17:30:40
Sample Name	133-04-071	Calculation Date	2019/02/12 18:12:18
Database Name	2019-02-12.chd	Measurement Time [min]	10.000 - 30.000
Saved File Name	RSLT0423	Sampling Pitch [ms]	100
Method Data	meth8509_standard	Cup Number	1
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test



Calculation Results (RI)

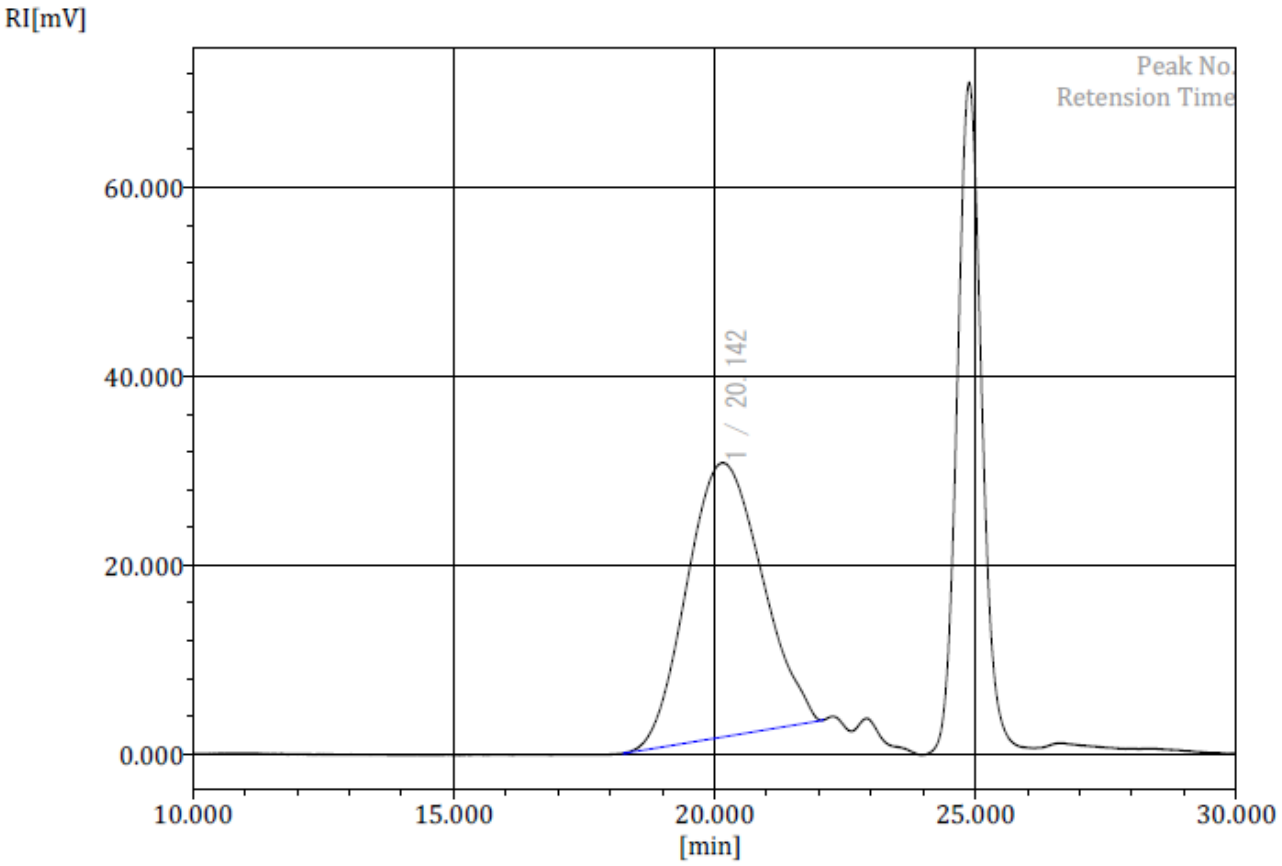
Peak No. 1 Base Peak

	[min]	[mV]	[mol]		
Peak Start	17.720	2.572	87,555	Mn	4,159
Peak Top	19.930	43.230	9,527	Mw	10,395
Peak End	22.525	3.190	113	Mz	17,783
				Mz+1	25,320
				Mv	10,395
Height [mV]			40.374	Mp	10,699
Area [mV*s]			4632.445	Mz/Mw	1.711
Area% [%]			100.000	Mw/Mn	2.500
[eta]			10395.25528	Mz+1/Mw	2.436

Figure S45. SEC trace of the propylene / allyl acetate copolymer obtained in Table 2, entry 9 (1,2-dichlorobenzene, 145 ºC)

High-temperature GPC Report

Title		Measurement Date	2018/11/02 17:33:55
Sample Name	133-03-128	Calculation Date	2018/11/02 18:10:16
Database Name	2018-11-02.chd	Measurement Time [min]	10.000 - 30.000
Saved File Name	RSLT0365	Sampling Pitch [ms]	100
Method Data	meth8509_standard	Cup Number	2
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test



Calculation Results (RI)

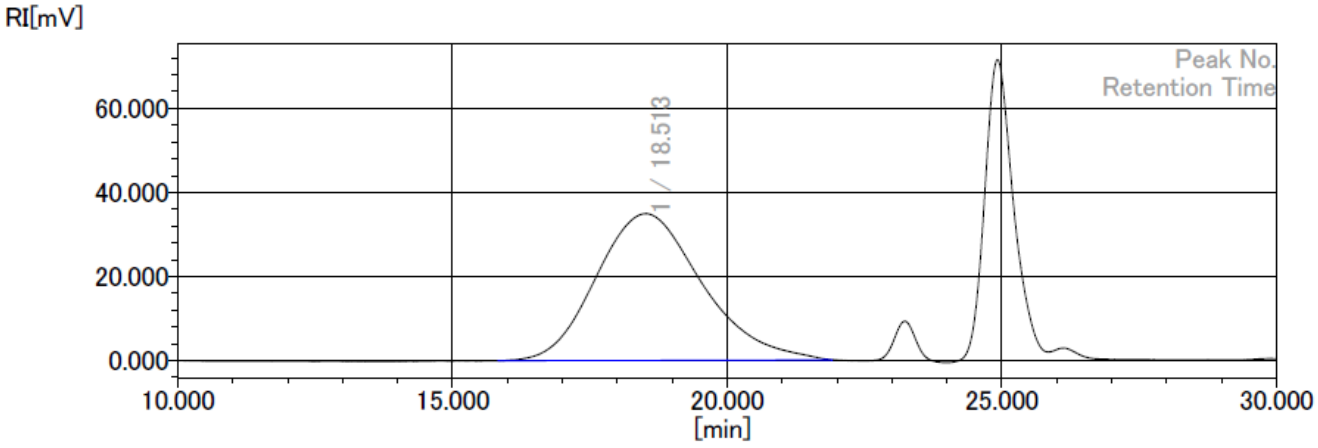
Peak No. 1 Base Peak

	[min]	[mV]	[mol]		
Peak Start	18.260	0.073	53,184	Mn	4,285
Peak Top	20.142	30.853	7,393	Mw	8,439
Peak End	22.083	3.580	318	Mz	13,195
				Mz+1	17,801
				Mv	8,439
Height [mV]			29.054	Mp	8,346
Area [mV*s]			2900.175	Mz/Mw	1.564
Area% [%]			100.000	Mw/Mn	1.969
[eta]			8438.80311	Mz+1/Mw	2.109

Figure S46. SEC trace of the propylene / 3-butetyl acetate copolymer obtained in Table 2, entry 10 (1,2-dichlorobenzene, 145 ºC)

Chromatography Report

Title		Measurement Date & Time	2019/09/06 19:24:39
Sample Name	068-Zn	Calculation Date & Time	2019/12/24 15:59:56
Database Name	2019-09-06.chd	Acquisition Time [min] [min]	10.000 - 30.000
Saved File Name	RSLT0496	Sampling Pitch [ms] [ms]	100
Method Data	meth8509_standard	Vial Number	24
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test



Result of Calculation (RI) (RI)

Peak 1 Base Peak

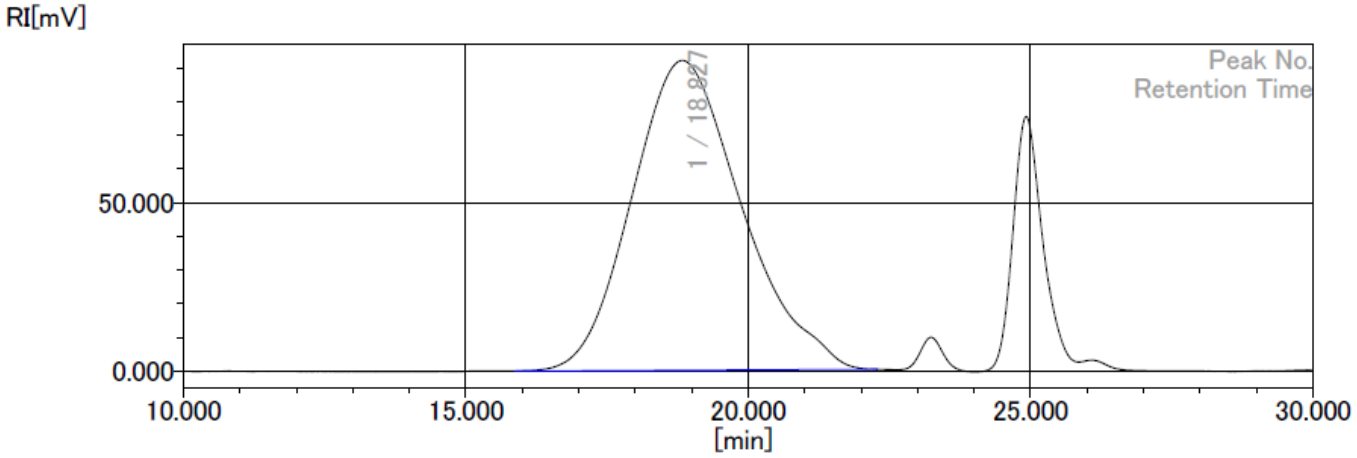
	[min]	[mV]	[mol]
Peak Start	15.833	-0.059	475,684
Peak Top	18.513	34.998	41,850
Peak End	21.912	0.175	456
Height [mV]			34.954
Area [mV*s]			4674.963
Area% [%]			100.000
[eta]			49895.32259

Mn	19,231
Mw	49,895
Mz	86,809
Mz+1	129,945
Mv	49,895
Mp	44,243
Mz/Mw	1.740
Mw/Mn	2.595
Mz+1/Mw	2.604

Figure S47. SEC trace of the ethylene / allyl acetate copolymer obtained in Table 3, entry 2 (1,2-dichlorobenzene, 145 ºC)

Chromatography Report

Title		Measurement Date & Time	2019/09/06 18:24:37
Sample Name	062-BCF	Calculation Date & Time	2019/12/24 16:02:08
Database Name	2019-09-06.chd	Acquisition Time [min] [min]	10.000 – 30.000
Saved File Name	RSLT0494	Sampling Pitch [ms] [ms]	100
Method Data	meth8509_standard	Vial Number	22
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test



Result of Calculation (RI) (RI)

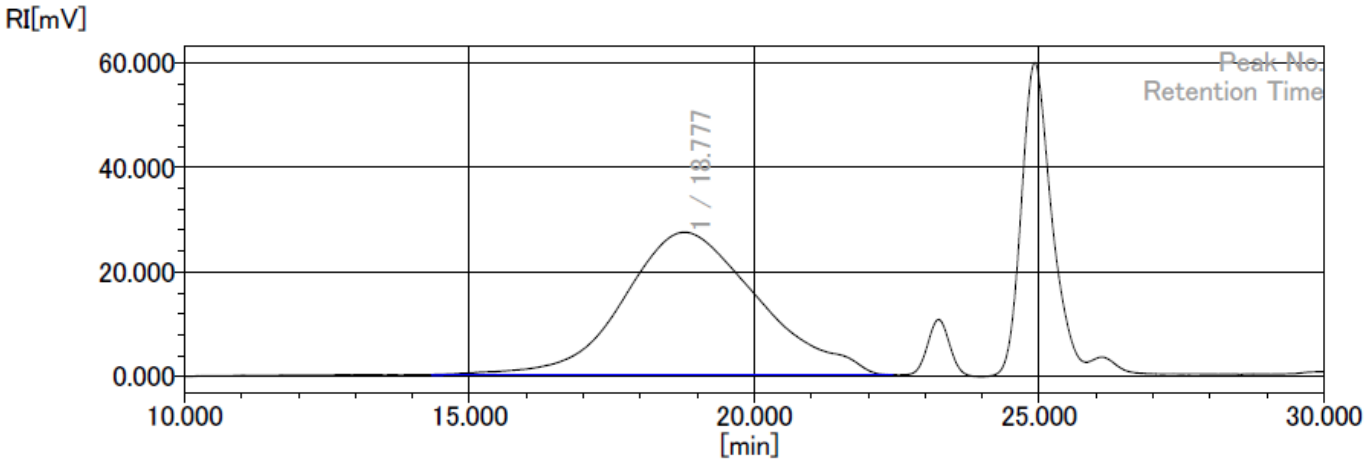
Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak Start	15.882	0.085	455,622	Mn	13,386
Peak Top	18.827	92.189	30,885	Mw	36,736
Peak End	22.280	0.638	204	Mz	66,491
				Mz+1	102,518
				Mv	36,736
Height [mV]			91.849	Mp	33,082
Area [mV*s]			12380.172	Mz/Mw	1.810
Area% [%]			100.000	Mw/Mn	2.744
[eta]			36736.19678	Mz+1/Mw	2.791

Figure S48. SEC trace of the ethylene / allyl acetate copolymer obtained in Table 3, entry 3 (1,2-dichlorobenzene, 145 ºC)

Chromatography Report

Title		Measurement Date & Time	2019/09/06 18:54:37
Sample Name	063-MAO	Calculation Date & Time	2019/12/24 16:01:18
Database Name	2019-09-06.chd	Acquisition Time [min] [min]	10.000 - 30.000
Saved File Name	RSLT0495	Sampling Pitch [ms] [ms]	100
Method Data	meth8509_standard	Vial Number	23
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test



Result of Calculation (RI) (RI)

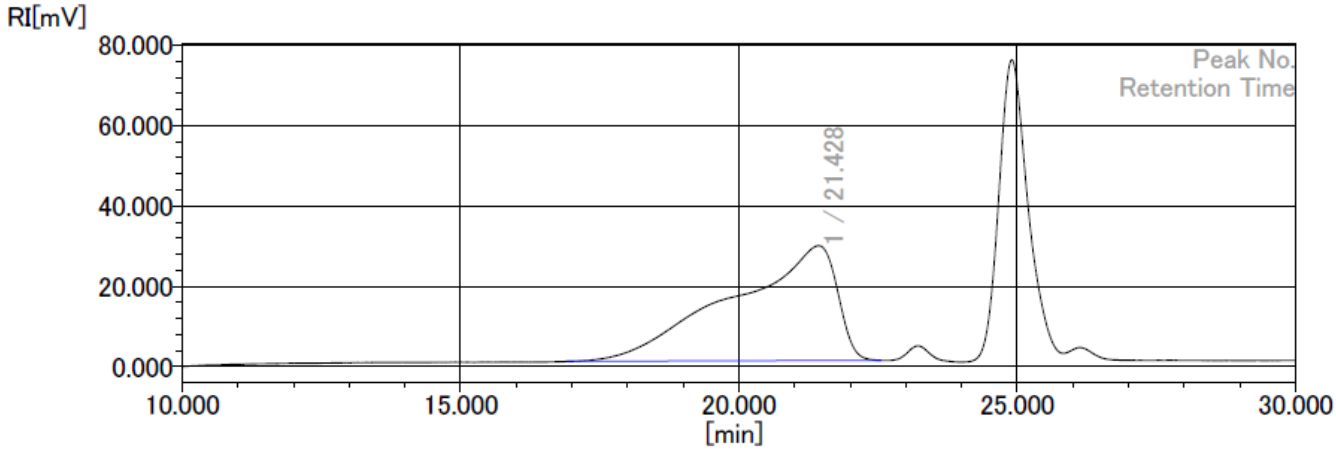
Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak Start	14.338	0.345	1,780,805	Mn	9,488
Peak Top	18.777	27.634	32,440	Mw	50,582
Peak End	22.427	0.377	144	Mz	203,918
				Mz+1	599,884
				Mv	50,582
Height [mV]			27.271	Mp	35,245
Area [mV*s]			4480.479	Mz/Mw	4.031
Area% [%]			100.000	Mw/Mn	5.331
[eta]			50582.42709	Mz+1/Mw	11.860

Figure S49. SEC trace of the ethylene / allyl acetate copolymer obtained in Table 3, entry 4 (1,2-dichlorobenzene, 145 ºC)

Chromatography Report

Title		Measurement Date & Time	2019/09/28 19:22:20
Sample Name	70-08-079-5mL	Calculation Date & Time	2019/12/24 16:05:37
Database Name	2019-09-28(2).chd	Acquisition Time [min] [min]	10.000 - 30.000
Saved File Name	RSLT0503	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	16.912	1.355	181,545	Mn	2,062
Peak Top	21.428	30.158	1,136	Mw	10,068
Peak End	22.548	1.607	106	Mz	31,633
				Mz+1	54,735
				Mv	10,068
Height [mV]			28.601	Mp	1,315
Area [mV*s]			3726.658	Mz/Mw	3.142
Area% [%]			100.000	Mw/Mn	4.882
[eta]			10068.04385	Mz+1/Mw	5.436

Figure S50. SEC trace of the ethylene / allyl acetate copolymer obtained in Table 3, entry 5 (1,2-dichlorobenzene, 145 ºC)

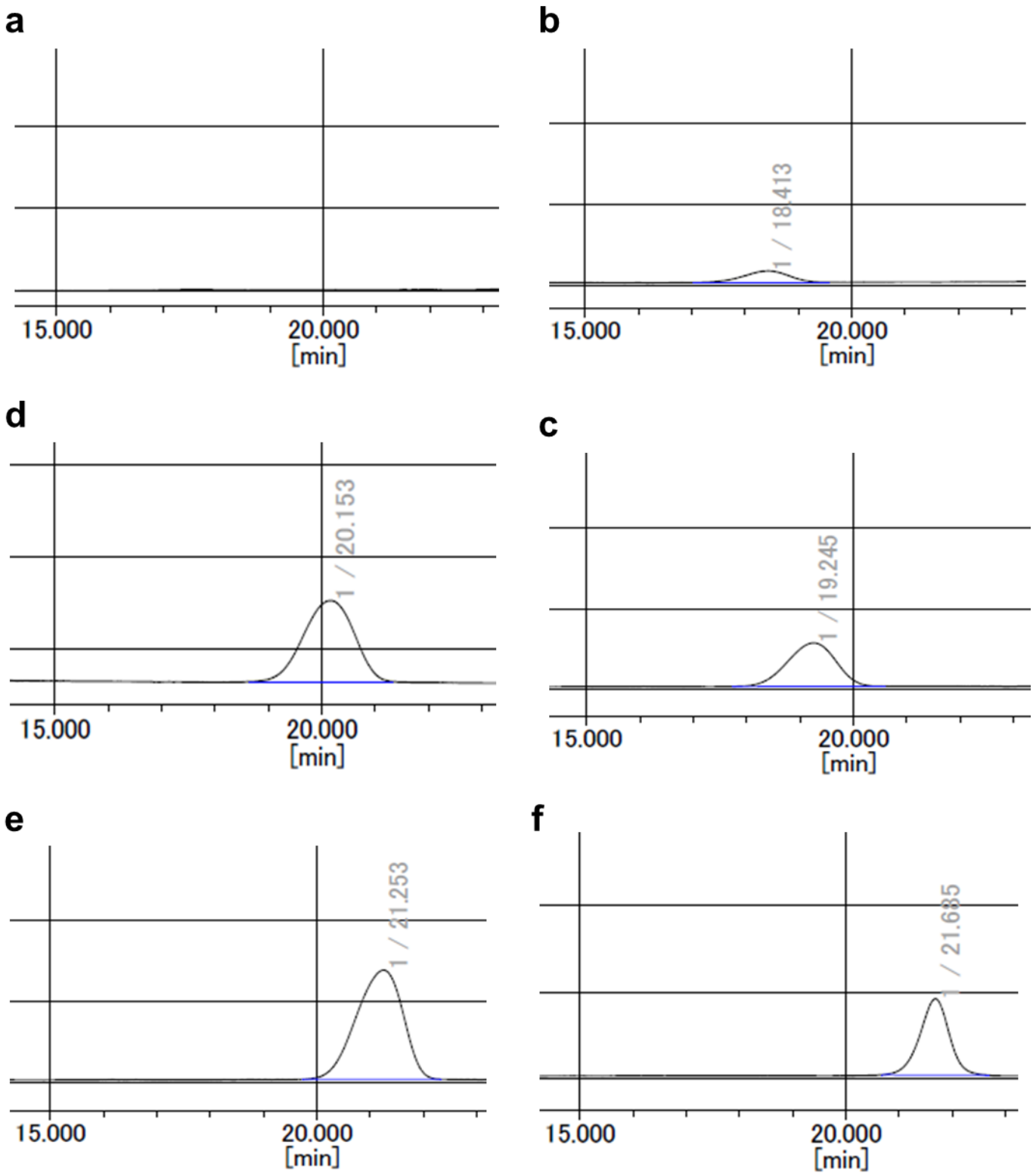
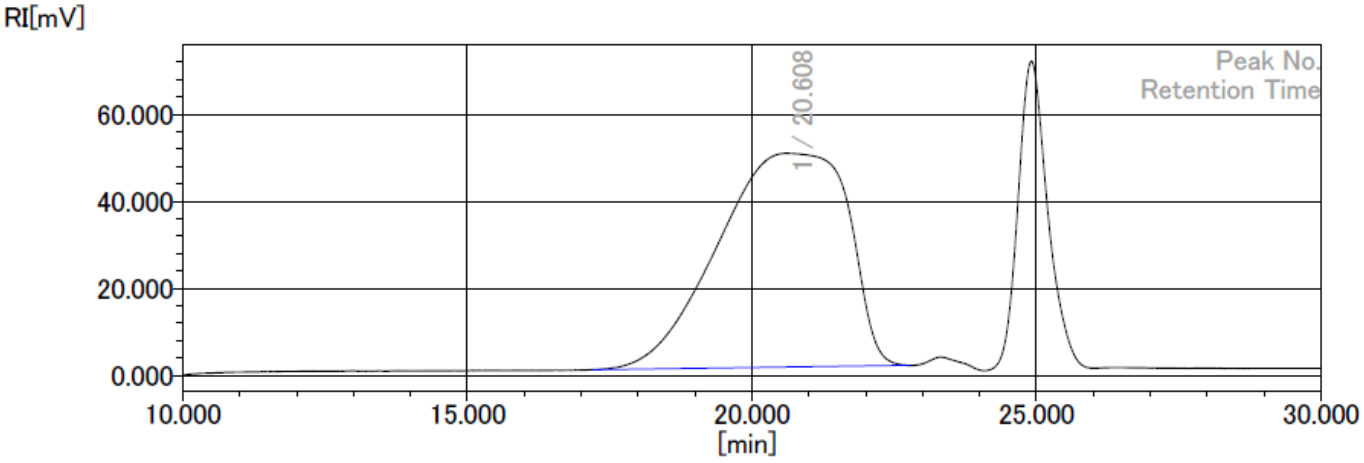


Figure S51. SEC traces of the collected eluents from SEC measurement of polymer from Table 3, entry 5 (1,2-dichlorobenzene, 145 ºC). Eluent of **a**, retention time 17–18 min. **b**, retention time 18–19 min. **c**, retention time 19–20 min. **d**, retention time 20–21 min. **e**, retention time 21–22 min. and **f**, retention time 22–23 min.

Chromatography Report

Title		Measurement Date & Time	2019/09/30 06:35:13
Sample Name	70-08-085-500eq	Calculation Date & Time	2019/12/24 16:09:32
Database Name	2019-09-30.chd	Acquisition Time [min] [min]	10.000 - 30.000
Saved File Name	RSLT0508	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)

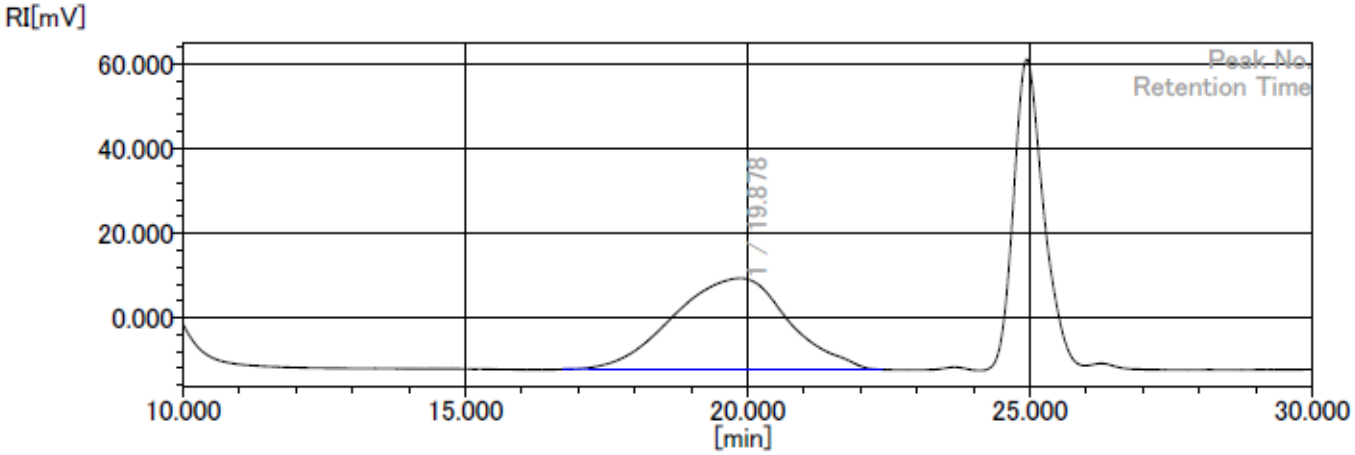
Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak Start	17.207	1.305	139,314	Mn	2,062
Peak Top	20.608	51.047	4,036	Mw	8,528
Peak End	22.770	2.352	59	Mz	22,870
				Mz+1	39,886
				Mv	8,528
Height [mV]			49.102	Mp	6,545
Area [mV*s]			7794.272	Mz/Mw	2.682
Area% [%]			100.000	Mw/Mn	4.136
[eta]			8528.06827	Mz+1/Mw	4.677

Figure S52. SEC trace of the ethylene / allyl acetate copolymer obtained in Table 3, entry 6 (1,2-dichlorobenzene, 145 ºC)

Chromatography Report

Title		Measurement Date & Time	2019/11/08 23:20:14
Sample Name	70-08-111-EVA	Calculation Date & Time	2019/11/09 11:10:46
Database Name	2019-11-08(2).chd	Acquisition Time [min] [min]	10.000 - 30.000
Saved File Name	RSLT0537	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)

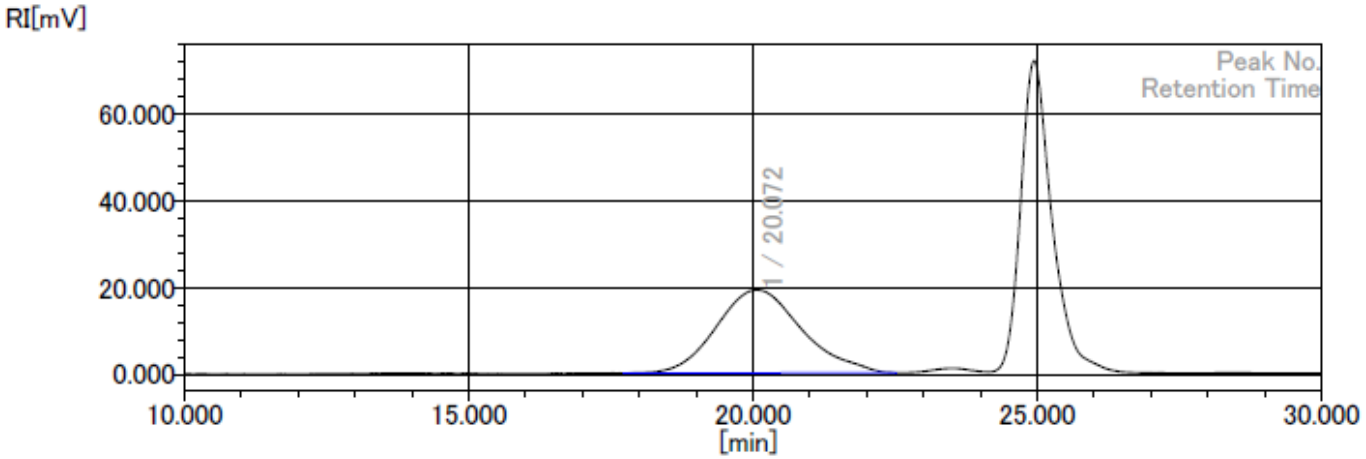
Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak Start	16.740	-12.181	211,704	Mn	5,914
Peak Top	19.878	9.409	10,118	Mw	18,629
Peak End	22.377	-12.247	163	Mz	38,471
				Mz+1	61,280
				Mv	18,629
Height [mV]			21.627	Mp	13,084
Area [mV*s]			3053.674	Mz/Mw	2.065
Area% [%]			100.000	Mw/Mn	3.150
[eta]			18629.24937	Mz+1/Mw	3.289

Figure S53. SEC trace of the polyethylene obtained in Table 3, entry 7 (1,2-dichlorobenzene, 145 ºC)

Chromatography Report

Title		Measurement Date & Time	2019/11/08 22:50:13
Sample Name	70-08-105-EMA	Calculation Date & Time	2019/11/09 11:10:29
Database Name	2019-11-08(2).chd	Acquisition Time [min] [min]	10.000 – 30.000
Saved File Name	RSLT0536	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)

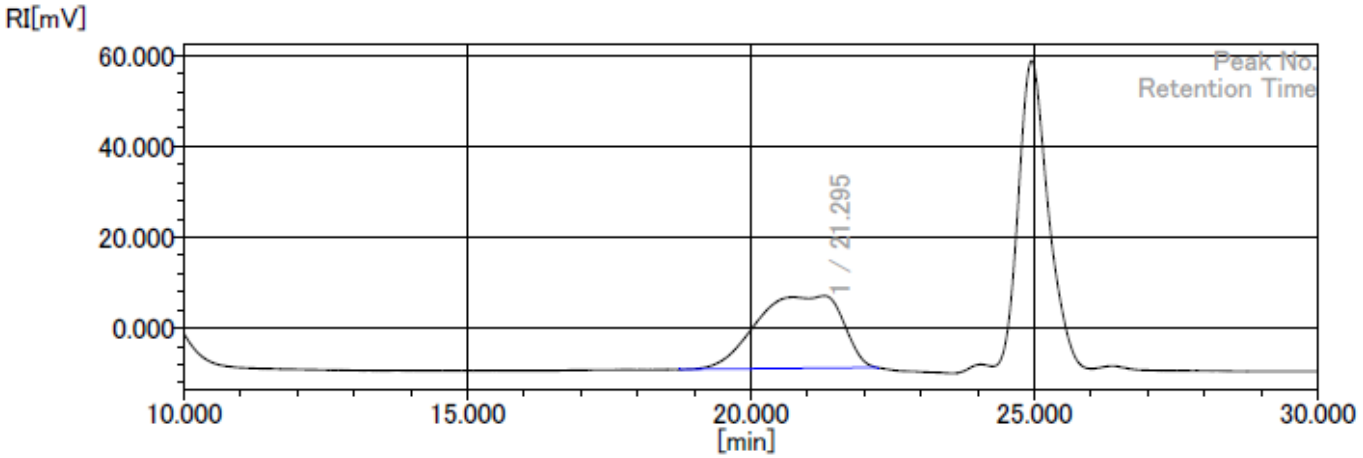
Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak Start	17.720	0.187	87,555	Mn	4,010
Peak Top	20.072	19.497	8,050	Mw	9,612
Peak End	22.500	0.373	120	Mz	16,205
				Mz+1	23,813
				Mv	9,612
Height [mV]			19.218	Mp	9,215
Area [mV*s]			1999.713	Mz/Mw	1.686
Area% [%]			100.000	Mw/Mn	2.397
[eta]			9611.76027	Mz+1/Mw	2.478

Figure S54. SEC trace of the ethylene / methyl acrylate copolymer obtained in Table 3, entry 8 (1,2-dichlorobenzene, 145 ºC)

Chromatography Report

Title		Measurement Date & Time	2020/01/14 22:25:47
Sample Name	70-08-133-2	Calculation Date & Time	2020/01/15 09:19:11
Database Name	2020-01-14.chd	Acquisition Time [min] [min]	10.000 – 30.000
Saved File Name	RSLT0563	Sampling Pitch [ms] [ms]	100
Method Data	meth8509_standard	Vial Number	8
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test



Result of Calculation (RI) (RI)

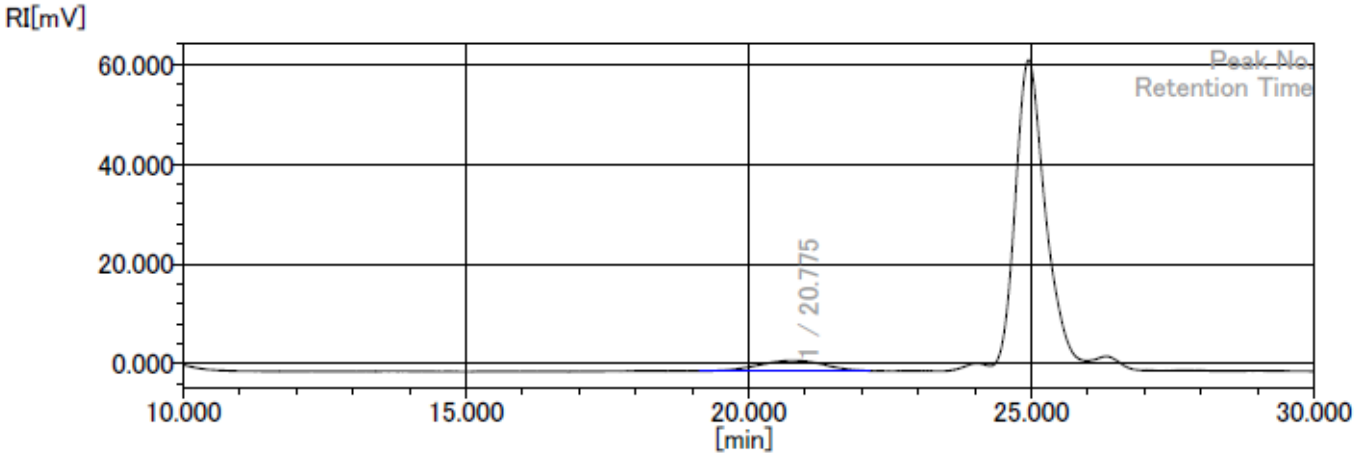
Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak Start	18.750	-9.021	33,297	Mn	1,982
Peak Top	21.295	7.185	1,426	Mw	4,051
Peak End	22.230	-8.600	229	Mz	7,059
				Mz+1	10,104
				Mv	4,051
Height [mV]			15.898	Mp	4,254
Area [mV*s]			1674.795	Mz/Mw	1.742
Area% [%]			100.000	Mw/Mn	2.044
[eta]			4051.40028	Mz+1/Mw	2.494

Figure S55. SEC trace of the propylene / allyl acetate copolymer obtained in Table 3, entry 9 (1,2-dichlorobenzene, 145 ºC).

Chromatography Report

Title		Measurement Date & Time	2020/01/14 22:55:48
Sample Name	70-08-134	Calculation Date & Time	2020/01/16 18:49:08
Database Name	2020-01-14.chd	Acquisition Time [min] [min]	10.000 - 30.000
Saved File Name	RSLT0564	Sampling Pitch [ms] [ms]	100
Method Data	meth8509_standard	Vial Number	9
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test



Result of Calculation (RI) (RI)

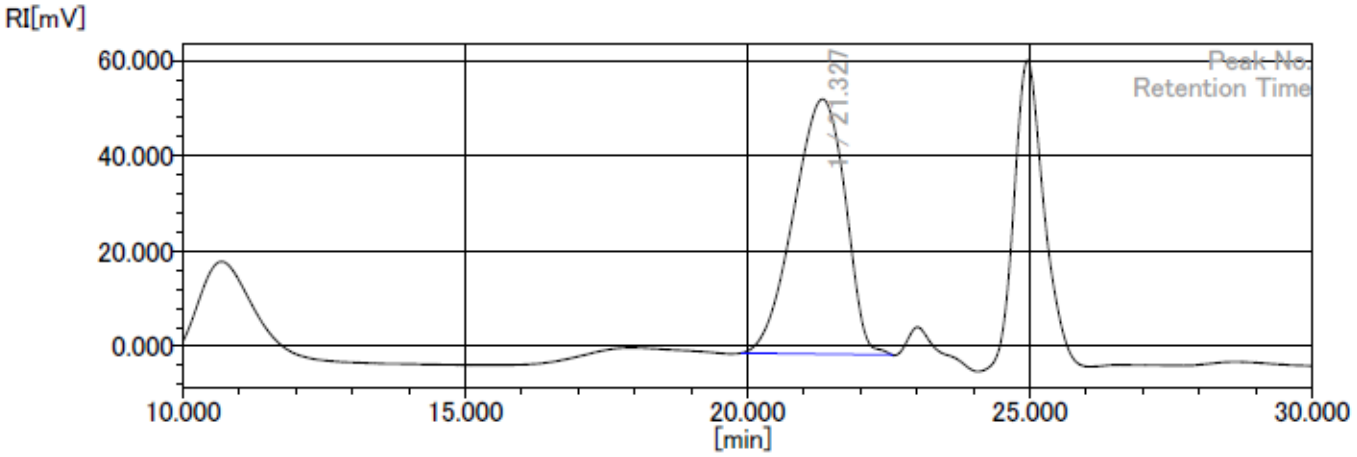
Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak Start	19.138	-1.424	22,591	Mn	2,403
Peak Top	20.775	0.706	3,194	Mw	4,011
Peak End	22.142	-1.384	279	Mz	6,045
				Mz+1	8,229
				Mv	4,011
Height [mV]			2.108	Mp	3,750
Area [mV*s]			164.479	Mz/Mw	1.507
Area% [%]			100.000	Mw/Mn	1.670
[eta]			4011.04032	Mz+1/Mw	2.052

Figure S56. SEC trace of the propylene / allyl acetate copolymer obtained in Table 3, entry 10 (1,2-dichlorobenzene, 145 ºC).

Chromatography Report

Title		Measurement Date & Time	2020/03/17 19:52:10
Sample Name	09-032	Calculation Date & Time	2020/03/18 05:32:48
Database Name	2020-03-17(2).chd	Acquisition Time [min] [min]	10.000 – 30.000
Saved File Name	RSLT0631	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)

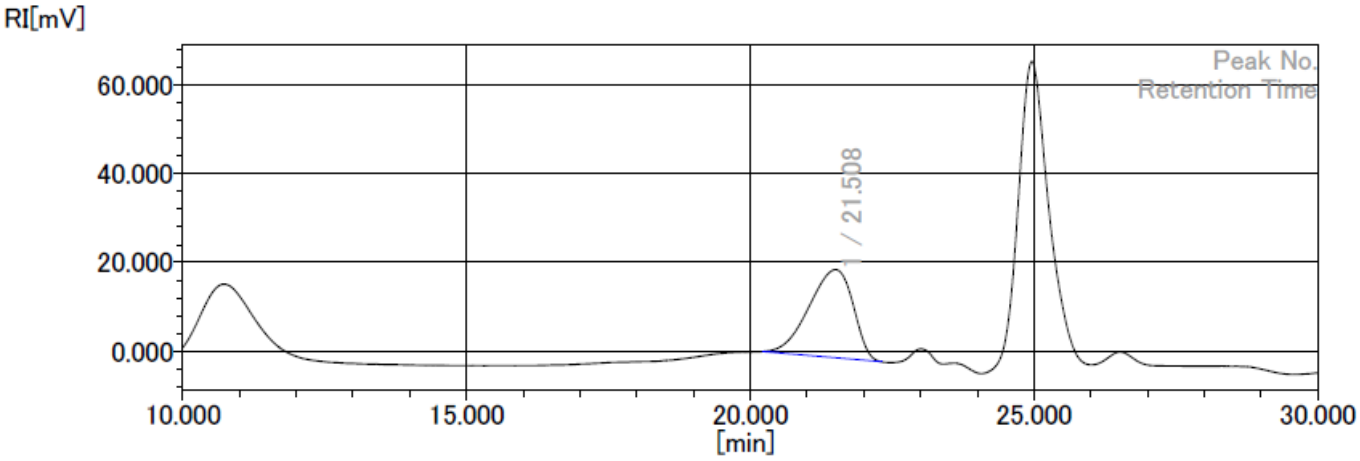
Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak Start	19.913	−1.378	9,714	Mn	1,165
Peak Top	21.327	51.945	1,352	Mw	1,827
Peak End	22.557	−1.774	104	Mz	2,696
				Mz+1	3,649
				Mv	1,827
Height [mV]			53.535	Mp	1,488
Area [mV*s]			3399.011	Mz/Mw	1.475
Area% [%]			100.000	Mw/Mn	1.568
[eta]			1827.32879	Mz+1/Mw	1.997

Figure S57. SEC trace of the propylene / allyl acetate copolymer obtained in Table S1, entry 1 (1,2-dichlorobenzene, 145 ºC).

Chromatography Report

Title		Measurement Date & Time	2020/03/17 22:57:32
Sample Name	09-034	Calculation Date & Time	2020/03/18 05:35:25
Database Name	2020-03-17(3).chd	Acquisition Time [min] [min]	10.000 - 30.000
Saved File Name	RSLT0634	Sampling Pitch [ms] [ms]	100
Method Data	meth8509_standard	Vial Number	11
Calc. Channel	RI EXT	Calculation Method	Molecular Weight Column test



Result of Calculation (RI) (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak Start	20.220	-0.115	6,710	Mn	991
Peak Top	21.508	18.421	986	Mw	1,396
Peak End	22.303	-2.376	193	Mz	1,950
				Mz+1	2,581
				Mv	1,396
Height [mV]			19.934	Mp	1,091
Area [mV*s]			1070.835	Mz/Mw	1.396
Area% [%]			100.000	Mw/Mn	1.409
[eta]			1396.41967	Mz+1/Mw	1.848

Figure S58. SEC trace of the propylene / allyl acetate copolymer obtained in Table S1, entry 2 (1,2-dichlorobenzene, 145 ºC).

4. DSC Traces

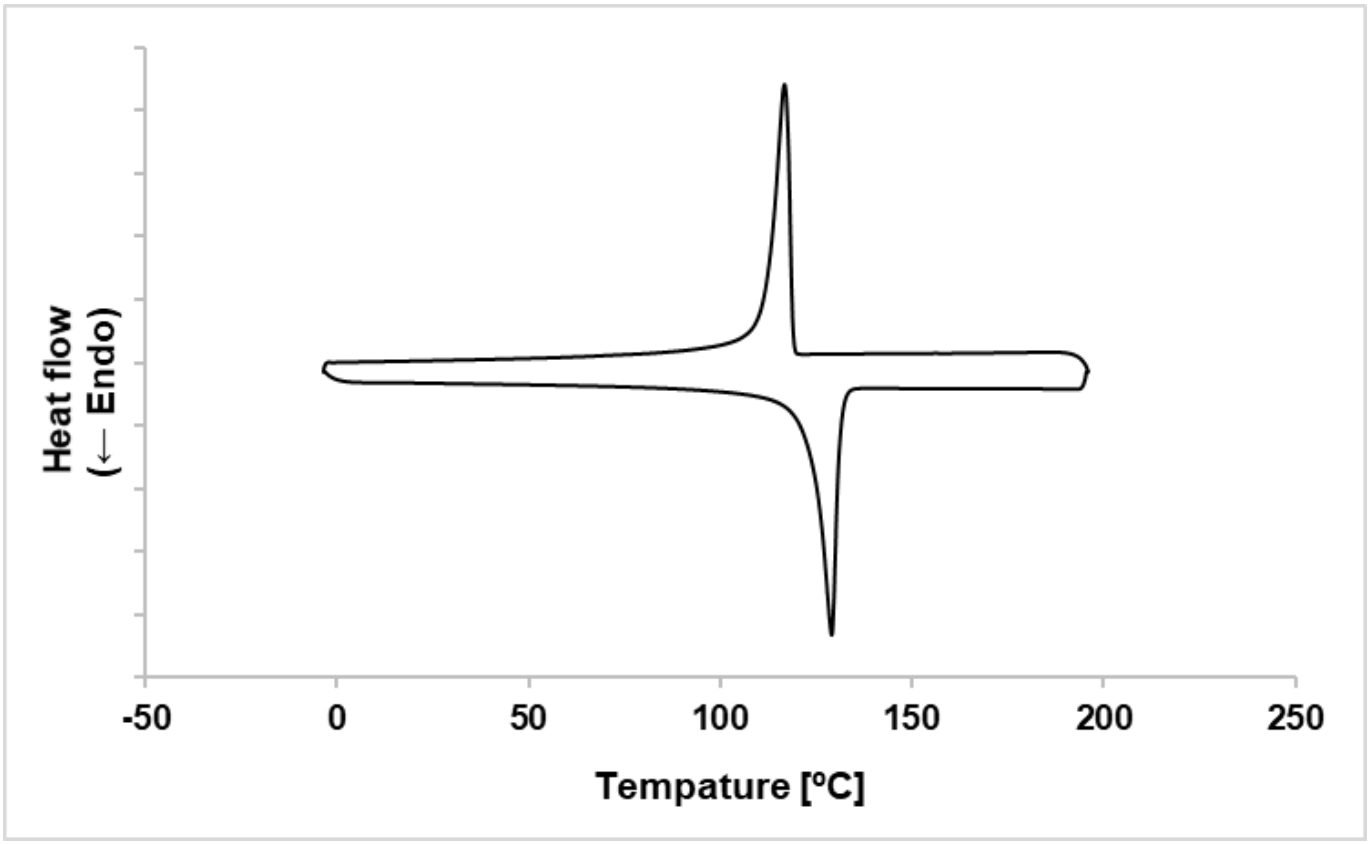


Figure S59. DSC trace of the ethylene / allyl acetate copolymer obtained in Table 3, entry 2.

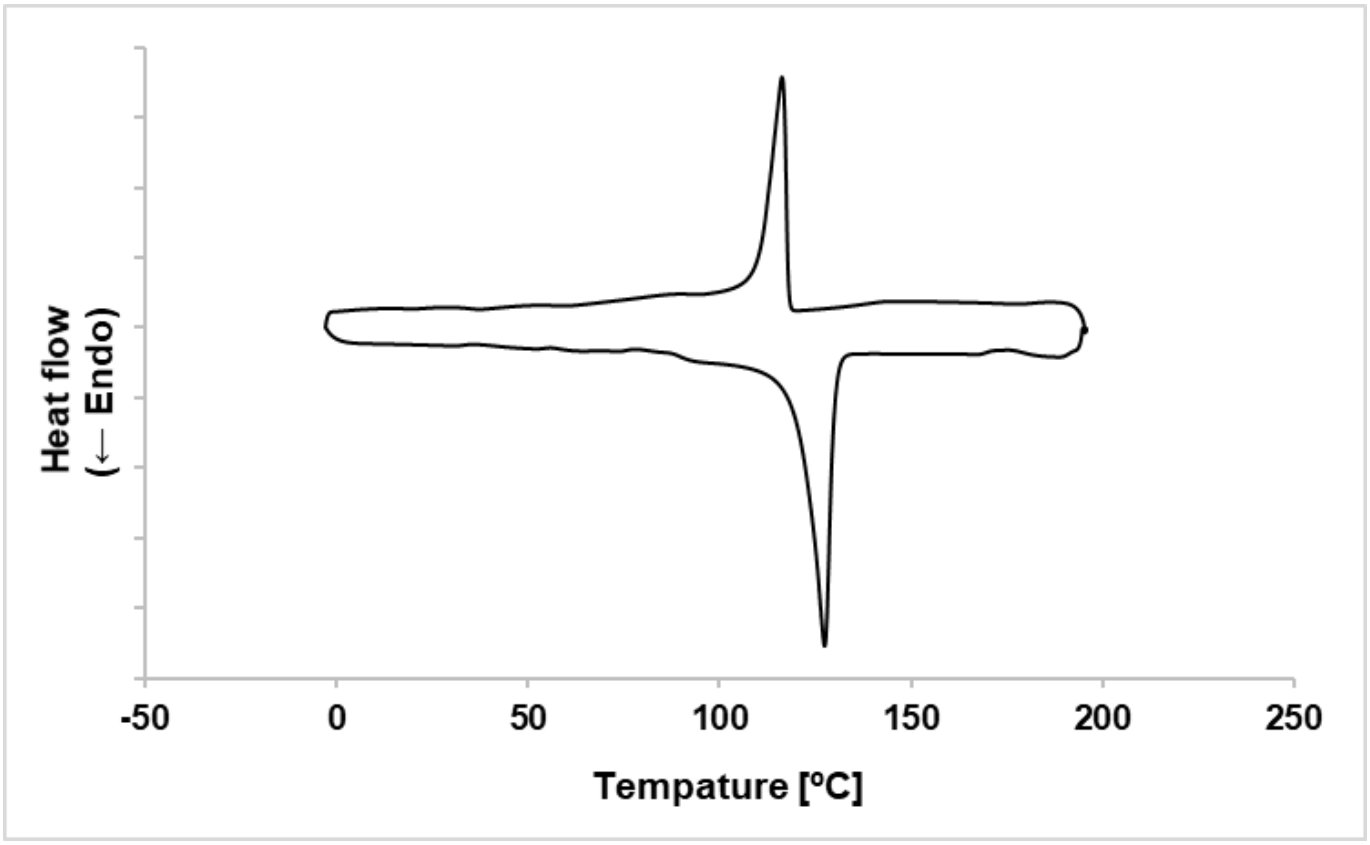


Figure S60. DSC trace of the ethylene / allyl acetate copolymer obtained in Table 3, entry 3.

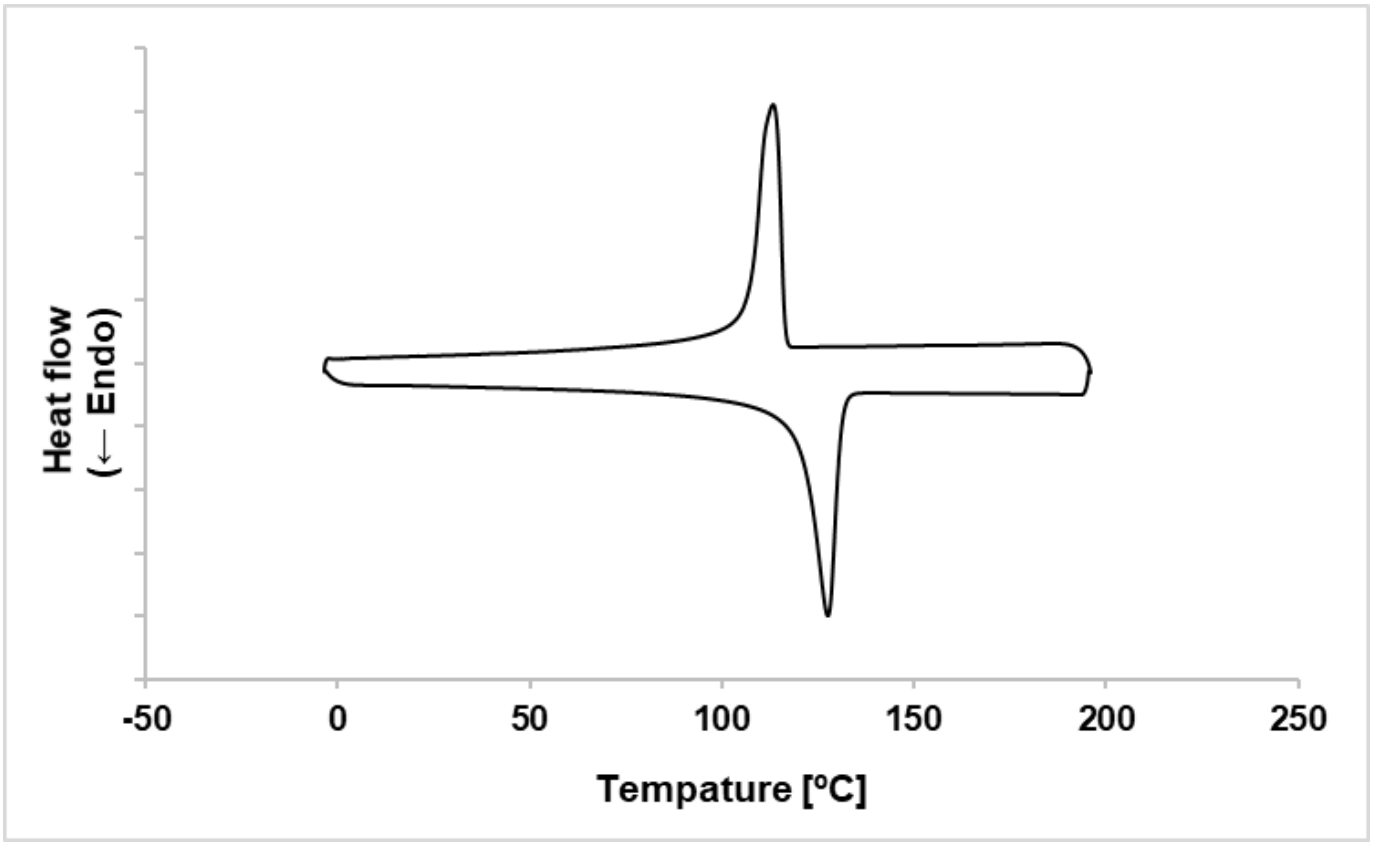


Figure S61. DSC trace of the ethylene / allyl acetate copolymer obtained in Table 3, entry 4.

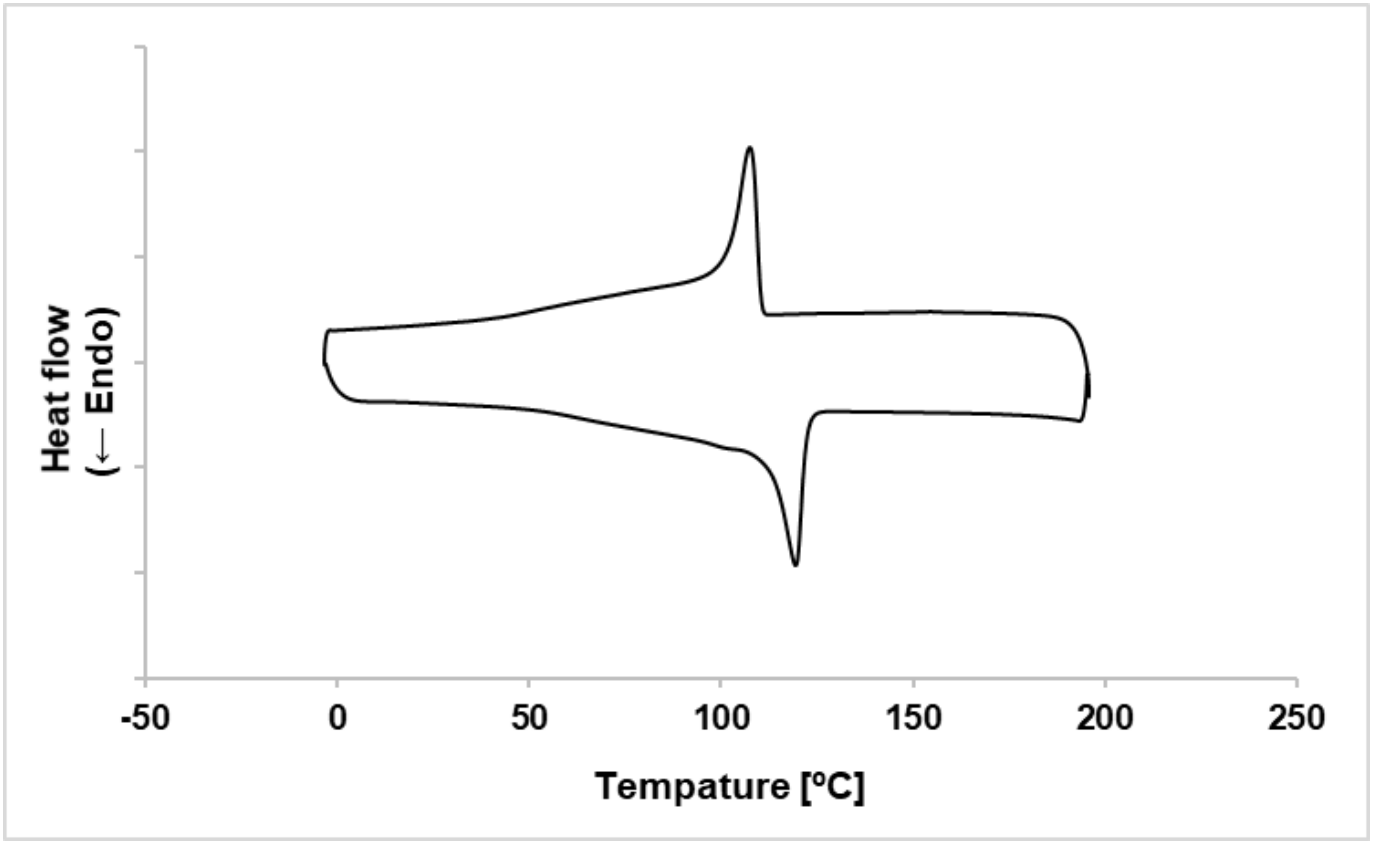


Figure S62. DSC trace of the ethylene / allyl acetate copolymer obtained in Table 3, entry 5.

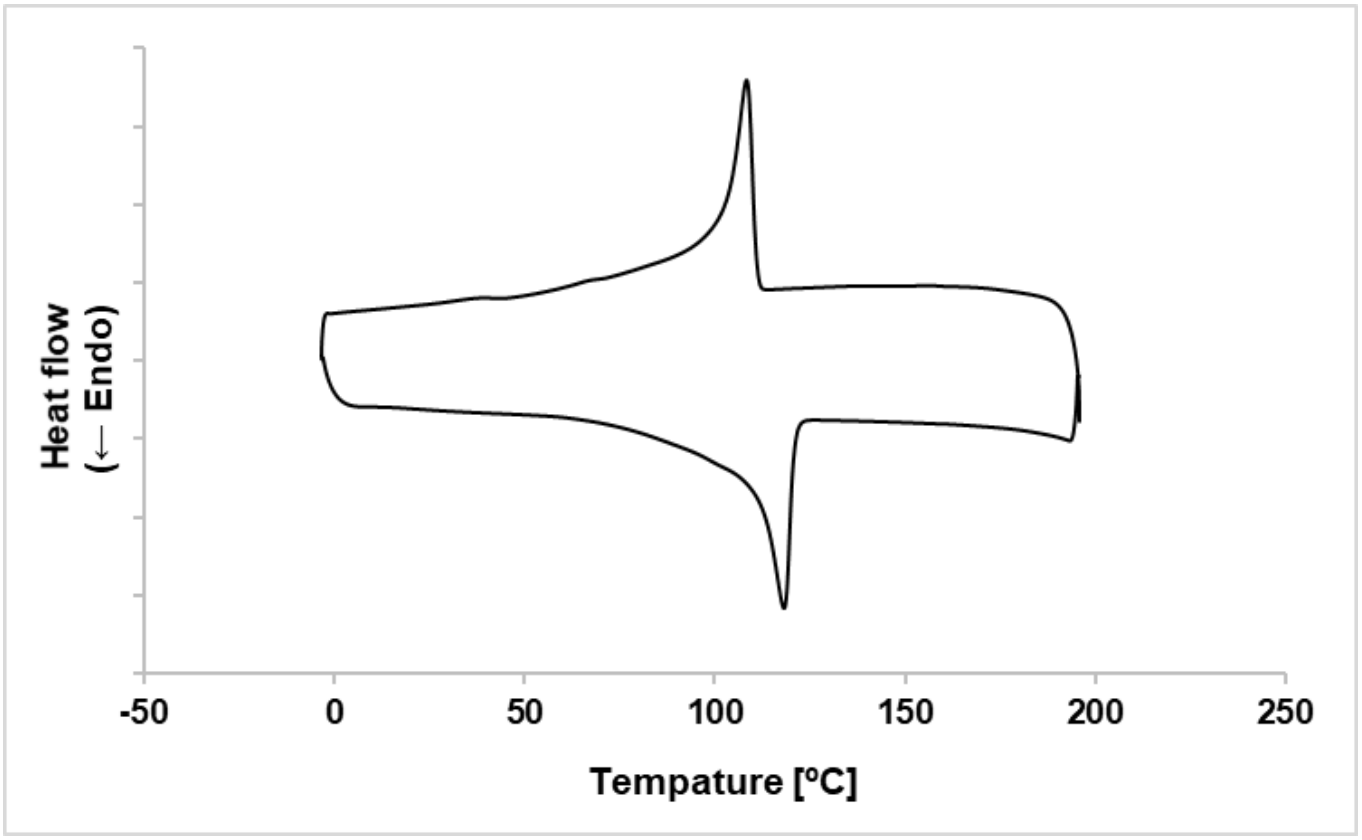


Figure S63. DSC trace of the ethylene / allyl acetate copolymer obtained in Table 3, entry 6.

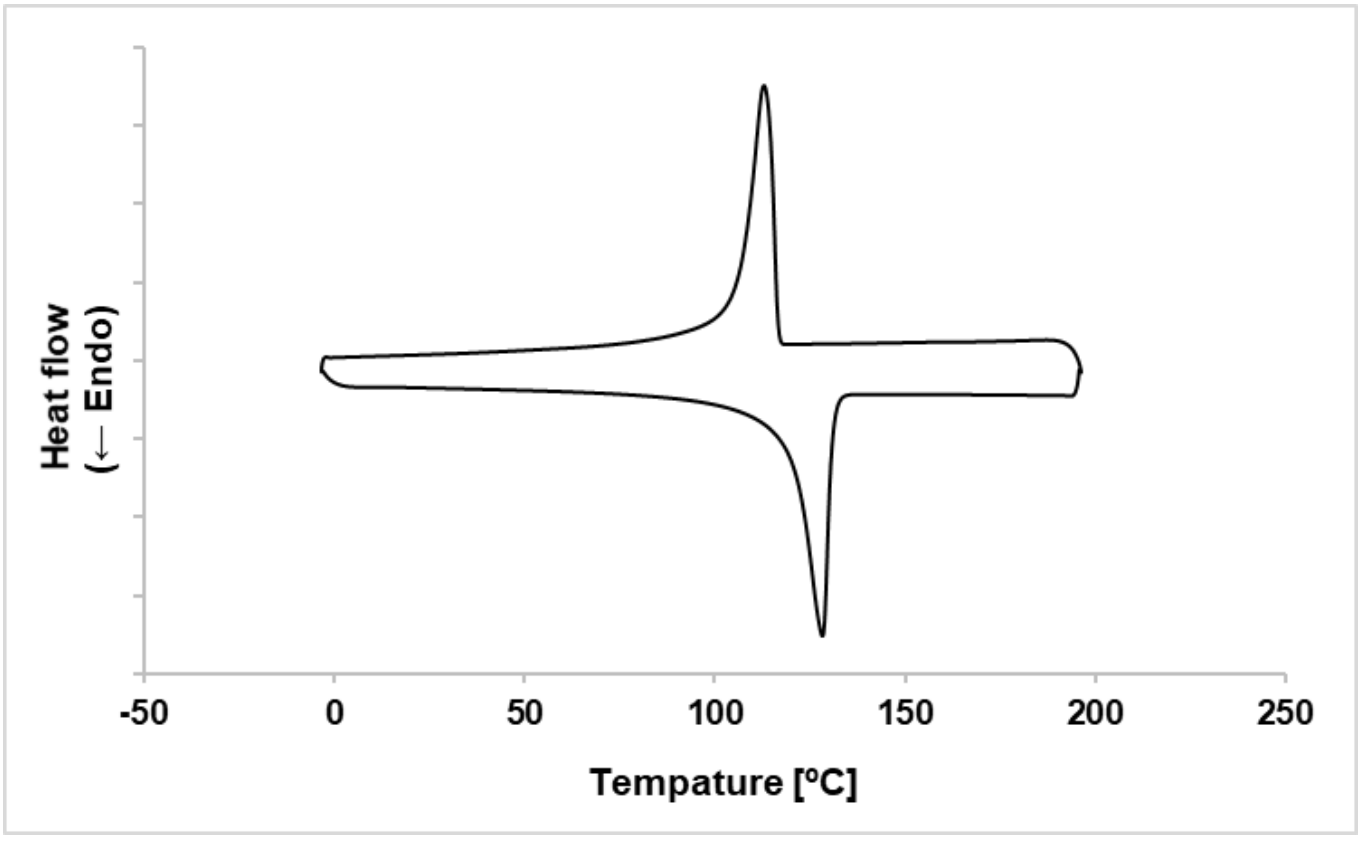


Figure S64. DSC trace of the polyethylene obtained in Table 3, entry 7.

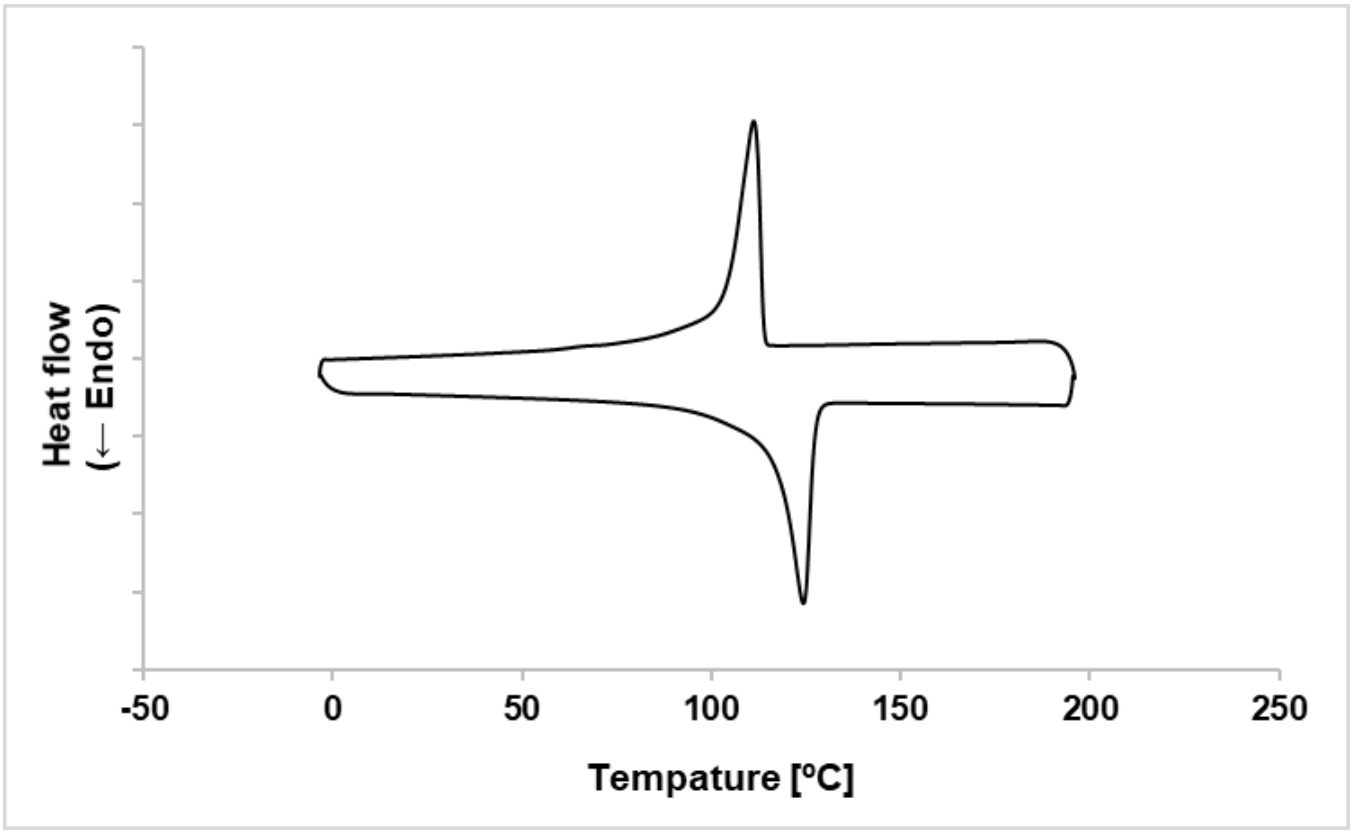


Figure S65. DSC trace of the polyethylene end-capped with ester obtained in Table 3, entry 8.

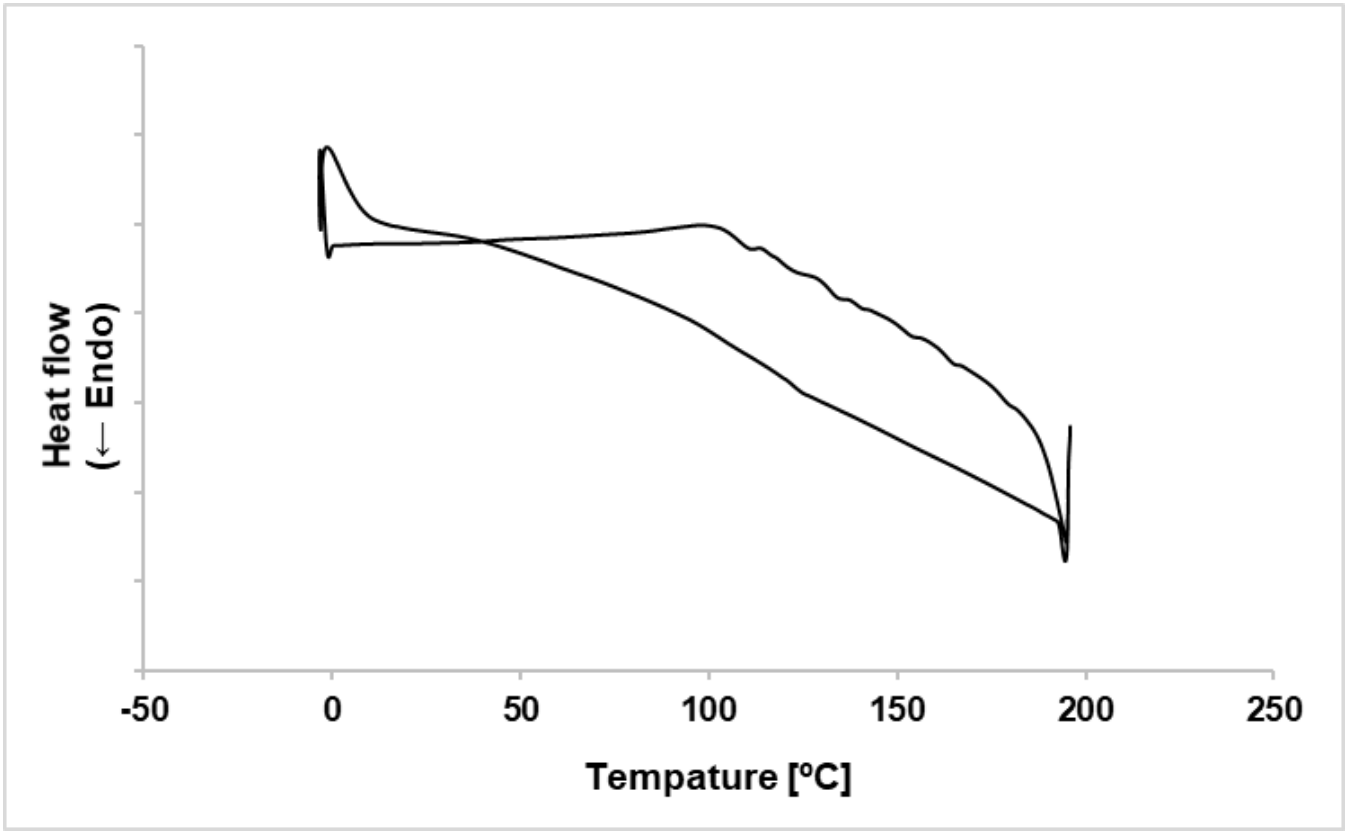


Figure S66. DSC trace of the propylene / allyl acetate copolymer obtained in Table 3, entry 9.

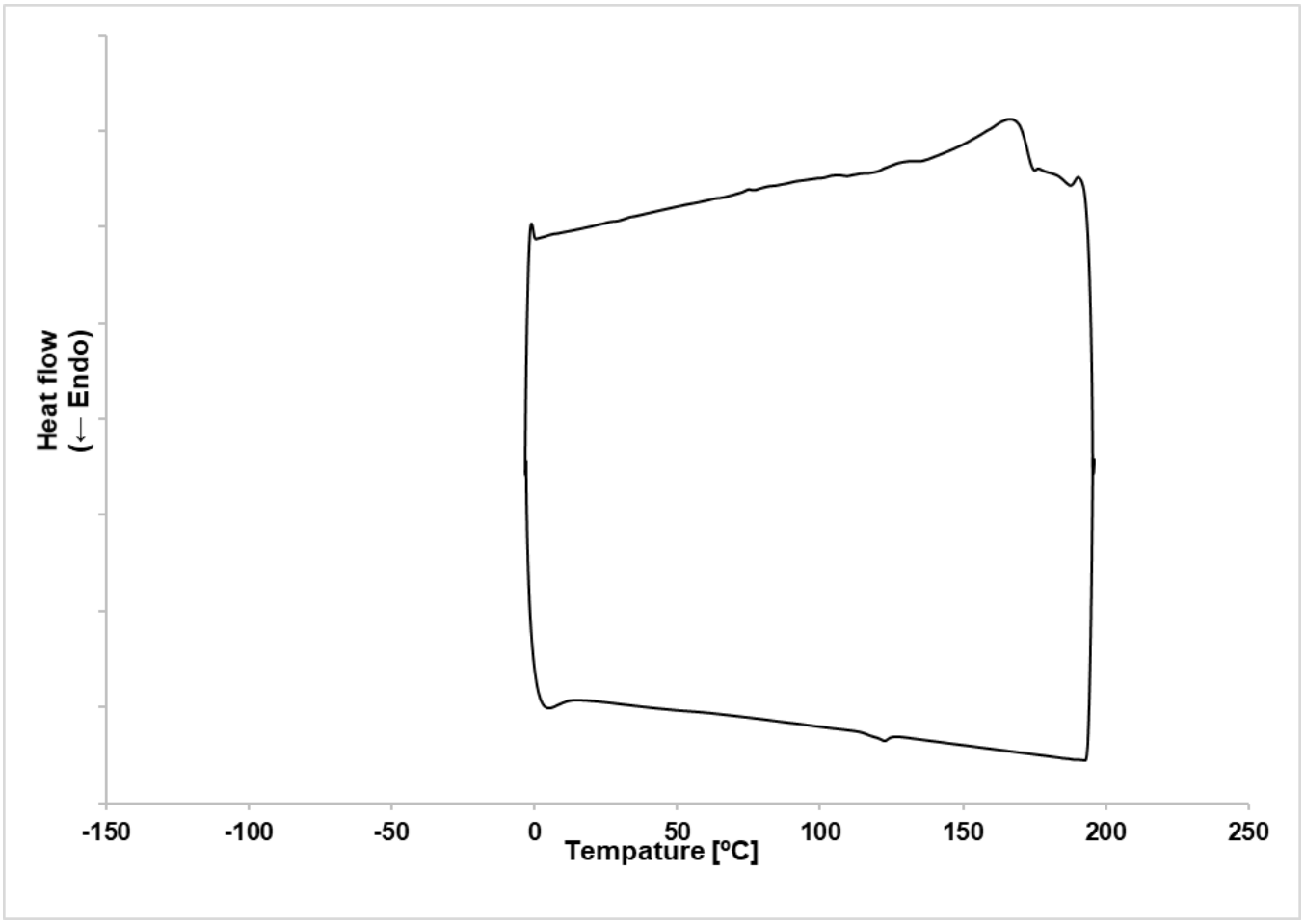


Figure S67. DSC trace of the propylene / allyl acetate copolymer obtained in Table 3, entry 10.

5. X-ray Crystallographic Data of Complex 3

Single crystal of **3** was mounted with mineral oil on a loop-type mount and transferred to the goniometer of a Rigaku Saturn CCD diffractometer. The radiation was performed with graphite-monochromated Mo Kα (λ = 0.71075 Å). The structure was solved by direct methods with (SHELXT 2018)[10] and refined by full-matrix least-squares techniques against F^2 (SHELXL 2018)[10] on the Olex[2] program.[11] The intensities was corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions. The data are summarized in Table S1.

Table S1. Crystal Data and Structure Refinement for Complex **3**.

Empirical formula		$C_{52}H_{55}BF_{24}NiOP_2$
Formula weight		1283.42
Temperature (K)		293
Crystal system		triclinic
Space group		P_{-1}
Unit cell dimensions	a (Å)	12.36430(10)
	b (Å)	21.2593(2)
	c (Å)	25.0961(3)
	α (°)	65.7360(10)
	β (°)	76.1750(10)
	γ (°)	76.5800(10)
Volume (Å^3)		5772.53(11)
Z		2
Density (calculated) (g/cm^3)		1.528
Absorption coefficient (mm^{-1})		0.50
F(000)		2714.0
Crystal size (mm^3)		0.50 × 0.25 × 0.40
Theta range		2.2960–28.9450
Index ranges		-16<=h<=16
		-28<=k<=28
		-34<=l<=34
Reflections collected		202560
Independent reflections		28130
R(int)		0.0299
Data / restraints / parameters		28130 / 0 / 1484
Goodness-of-fit on F^2		1.032
Final *R* indices [I > 2σ(*I*)]		R_1 = 0.0953
		wR_2 = 0.2809
R indices (all data) [I > 2σ(*I*)]		R_1 = 0.1054
		wR_2 = 0.2919

5. References

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