Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Polar additive triggered chain walking copolymerization of ethylene and fundamental polar monomers

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Contents

Table S1. Effect of Polar Additive on Copolymerization of Ethylene and MA with Pd[a]

entry	[PA]/Pd	T (^{o}C)	yield (g)	act. (10^3)[b]	M_n (10^3)[c]	M_w (10^3)[c]	M_w/M_n[c]	brs[d]	X[e]
1	0	90	4.73	9.85	52	108	2.07	154	2.3
2	10	90	4.88	10.17	62	111	1.80	122	1.4
3	25	90	4.95	10.31	62	120	1.93	94	1.0
4	50	90	6.11	12.73	94	214	2.25	64	0.7
5	100	90	4.16	8.67	59	104	1.76	50	0.5
6[f]	1000	90	0.74	18.38	52	92	1.78	49	0.4

[a] Reaction conditions: Pd catalyst (60 μmol), NaBArF(1.5 eq.), toluene/CH_2Cl_2 (115 mL/5 mL), polymerization time (8 h), polymerization temperature (90 ^{o}C), MA(1.6 mol/L) all entries are based on at least two runs, unless noted otherwise. [b] Activity is in unit of 10^3 g mol^{-1} h^{-1}. [c] Determined by GPC in THF at 40 °C. [d] brs = Number of branches per 1000C, as determined by ^{1}H NMR spectroscopy. [e] X = Incorporation of MA in copolymer, as determined by ^{1}H NMR spectroscopy. [f] acrylonitrile was used instead of p-tolunitrile, ref 1.

1. General information

General Procedures: All syntheses involving air- and moisture sensitive compounds were carried out using standard Schlenk-type glassware (or in a glove box) under an atmosphere of nitrogen. All solvents were purified from the MBraun SPS system. NMR spectra for the ligand, complex, and polymers were recorded on a Bruker AV400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) or a Bruker AV500 (^{1}H: 500 MHz, ^{13}C: 125 MHz). NMR assignments were confirmed by ^{1}H−^{1}H COSY, ^{1}H−^{13}C HSQC and ^{1}H−^{13}C HMBC experiments when necessary. The molecular weights (M_n) and molecular weight distributions (M_w/M_n) of polyethylenes and copolymers were measured by means of gel permeation chromatography (GPC) on a PL-GPC 220-type high-temperature chromatograph equipped with three PL-gel 10 μm Mixed-B LS type columns at 150 °C.

A general procedure for produce the copolymers using Pd catalyst

In a typical experiment, a 75 mL or 350 mL glass pressure reactor connected with a high pressure gas line was firstly dried at 90 °C under vacuum for at least 1 h. The reactor was then adjusted to the desired polymerization temperature. 28 mL or 115 mL of toluene with NaBArF, galvinoxyl and additive (p-tolunitrile) were added to the reactor under N_2 atmosphere, then the desired polar monomer and the desired amount of Pd catalyst in 2 mL or 5 mL of CH_2Cl_2 was injected into the polymerization system via syringe subsequently. With a rapid stirring, the reactor was pressurized and maintained at desired ethylene pressure. After certain hours, the pressure reactor was vented and the polymerization was quenched via the addition of 200 mL MeOH, then the solvent was removed under vacuum and dried in a vacuum oven to constant weight.

2. Proposed mechanism of polar monomer insertion in copolymerization

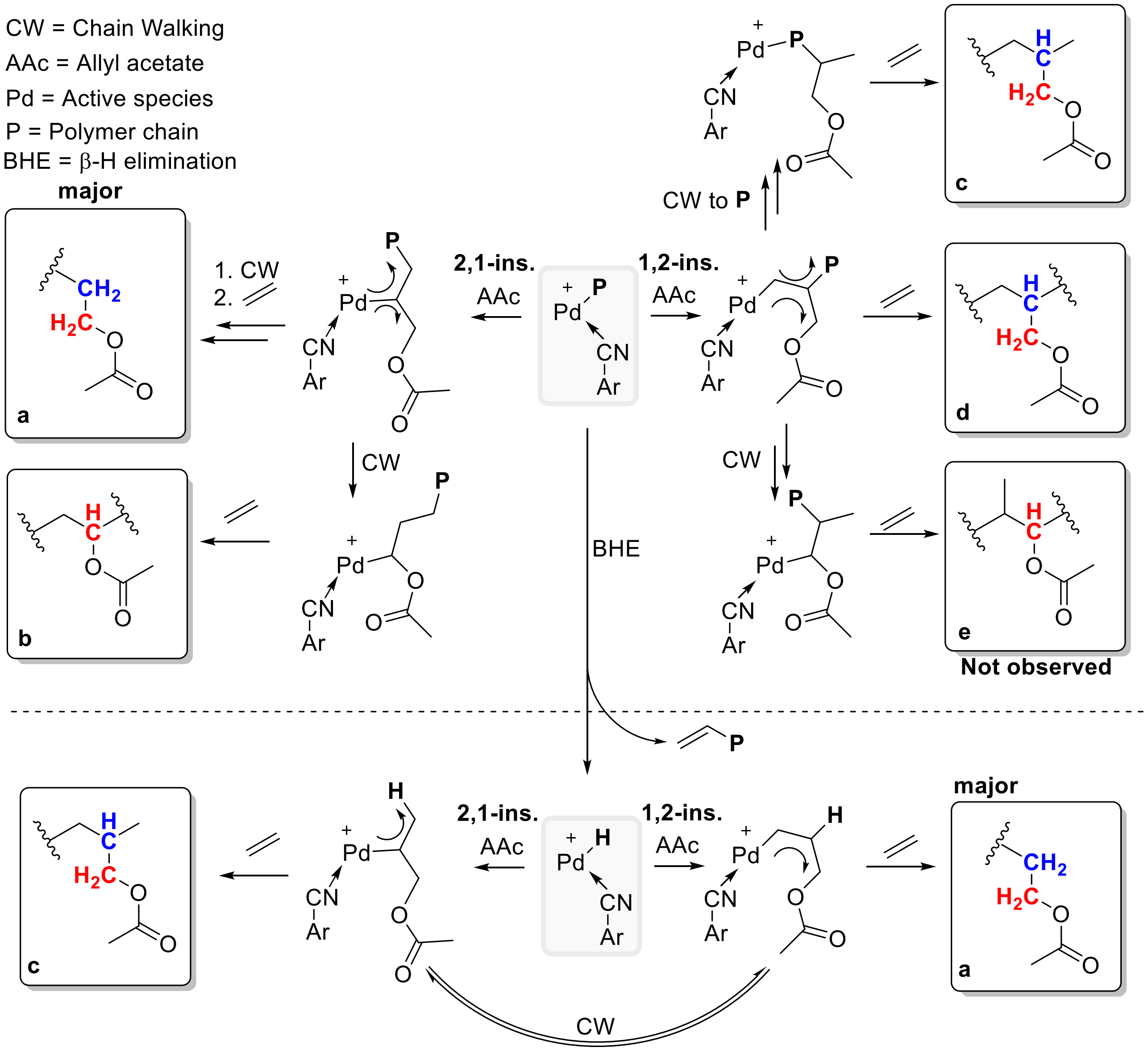


Figure S1. AAc (allyl acetate) insertion mechanism and corresponding incorporation patterns in copolymerization.

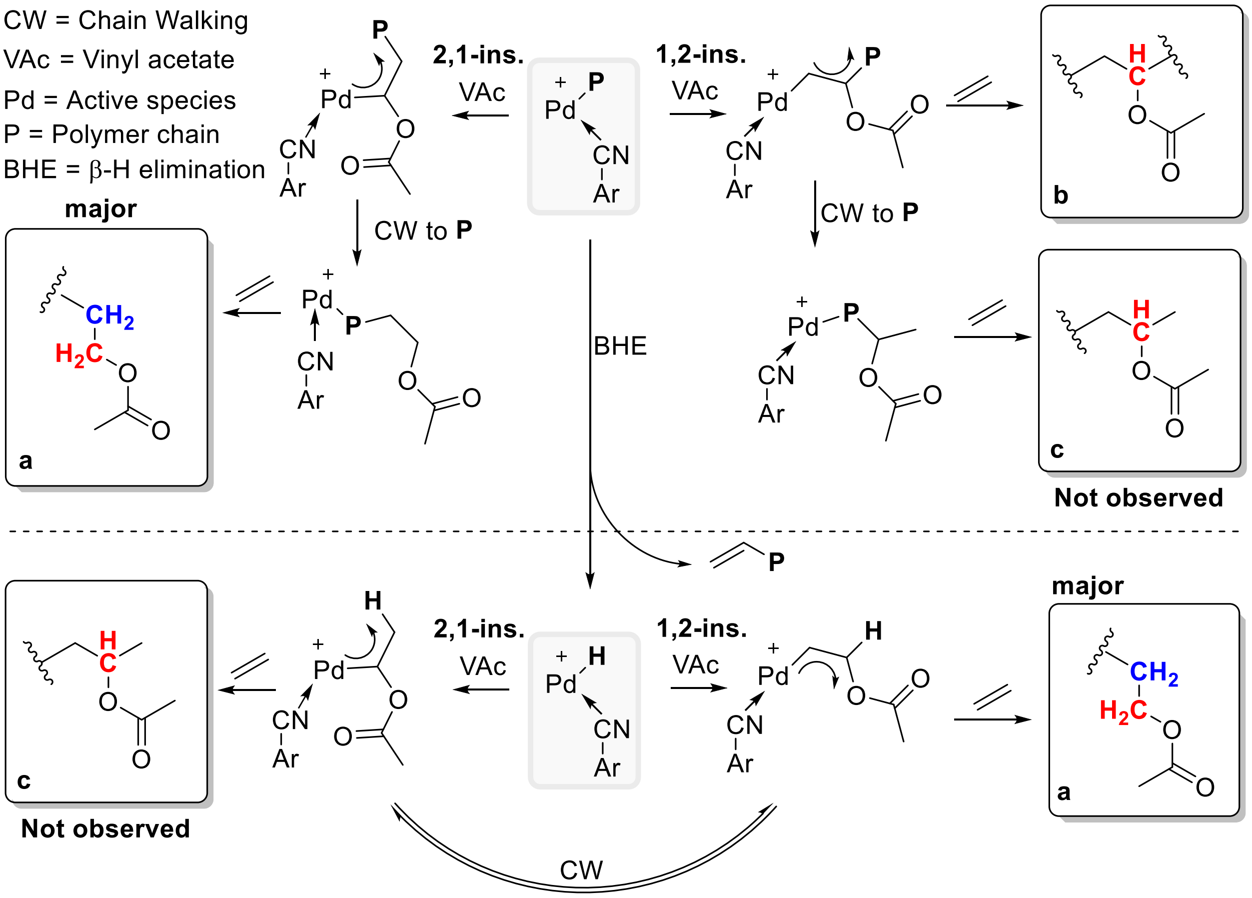


Figure S2. VAc (vinyl acetate) insertion mechanism and corresponding incorporation patterns in copolymerization.

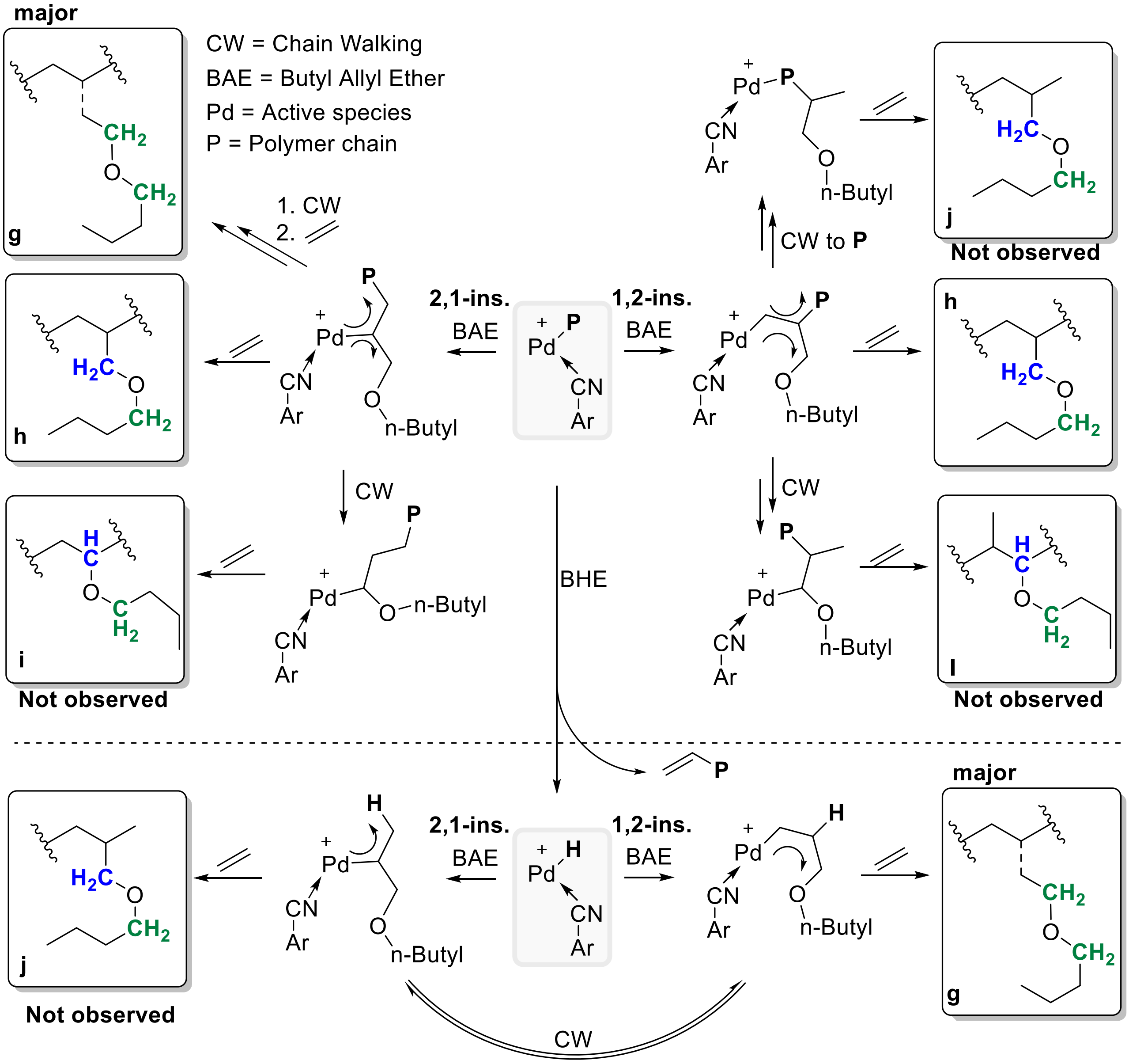


Figure S3. BAE (Butyl allyl ether) insertion mechanism and corresponding incorporation patterns in copolymerization.

3. NMR Figures of Polymers

3.1 NMR Spectra of Polymers in Table 1.

Equation 1: Branches = Me groups / 1000 C

Equation 2: Incorporation ratio = Polar monomer / (Polar monomer + Ethylene)

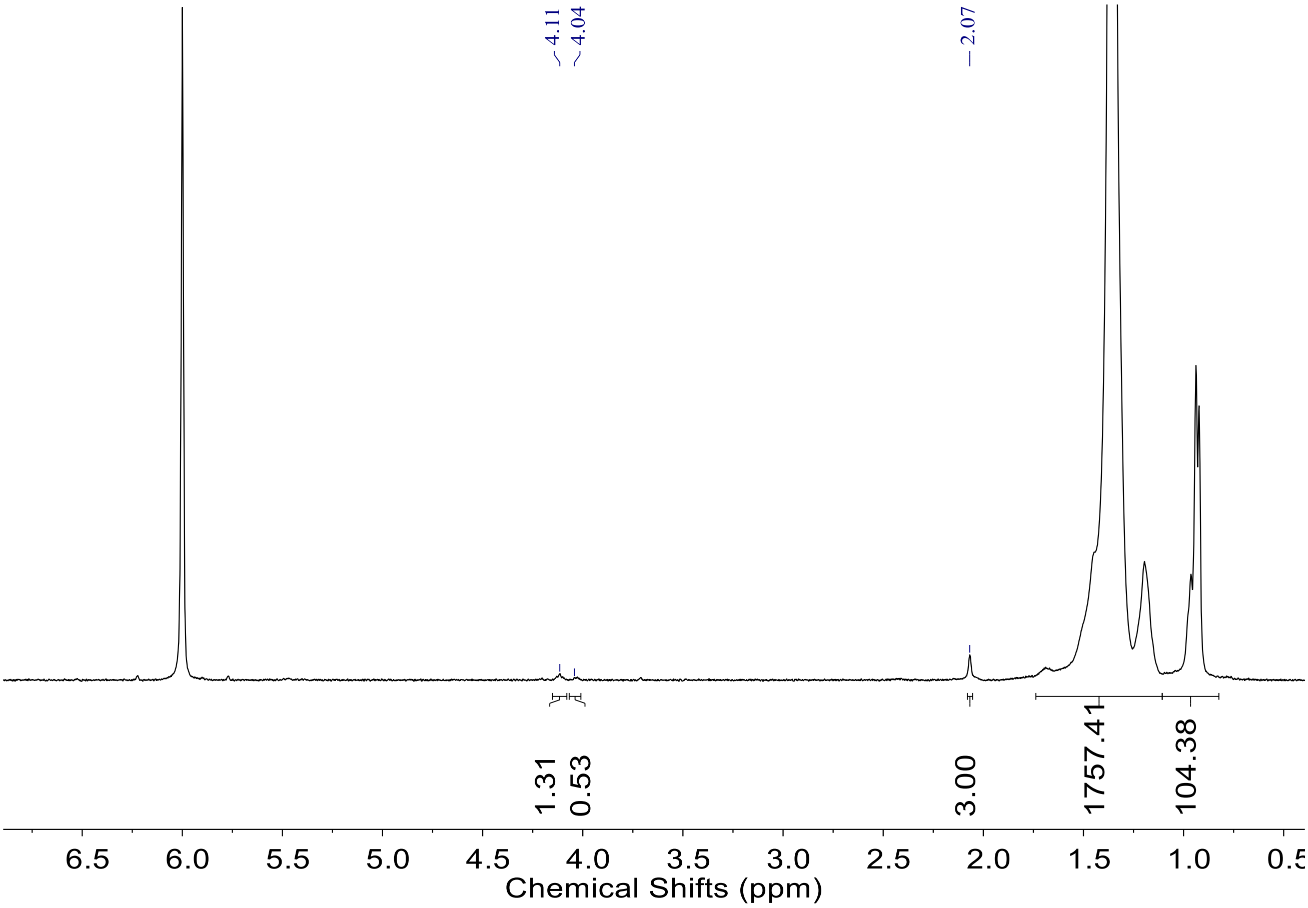


Figure S4. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 110 °C) of E-AAc copolymer from table 1, entry 3.

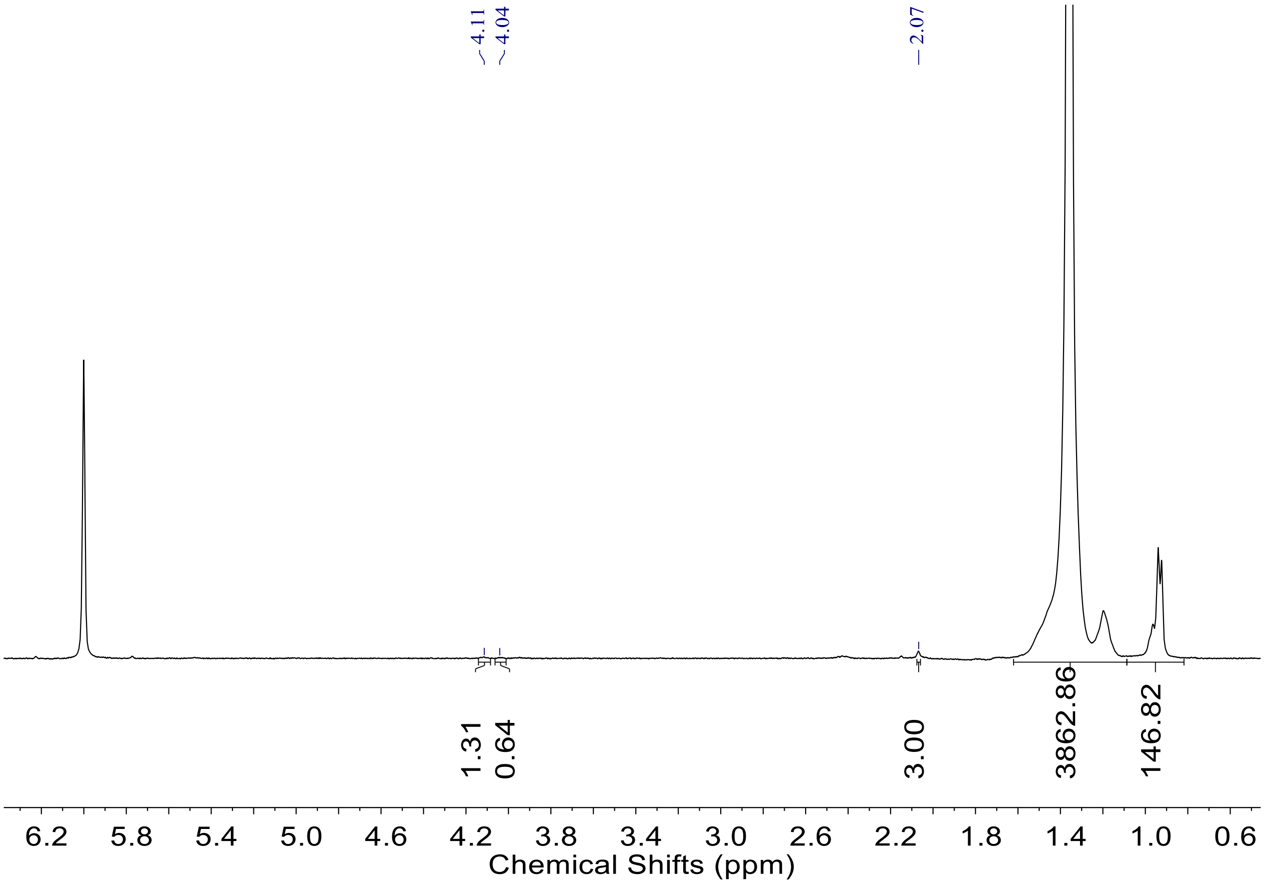


Figure S5. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 110 °C) of E-AAc copolymer from table 1, entry 4.

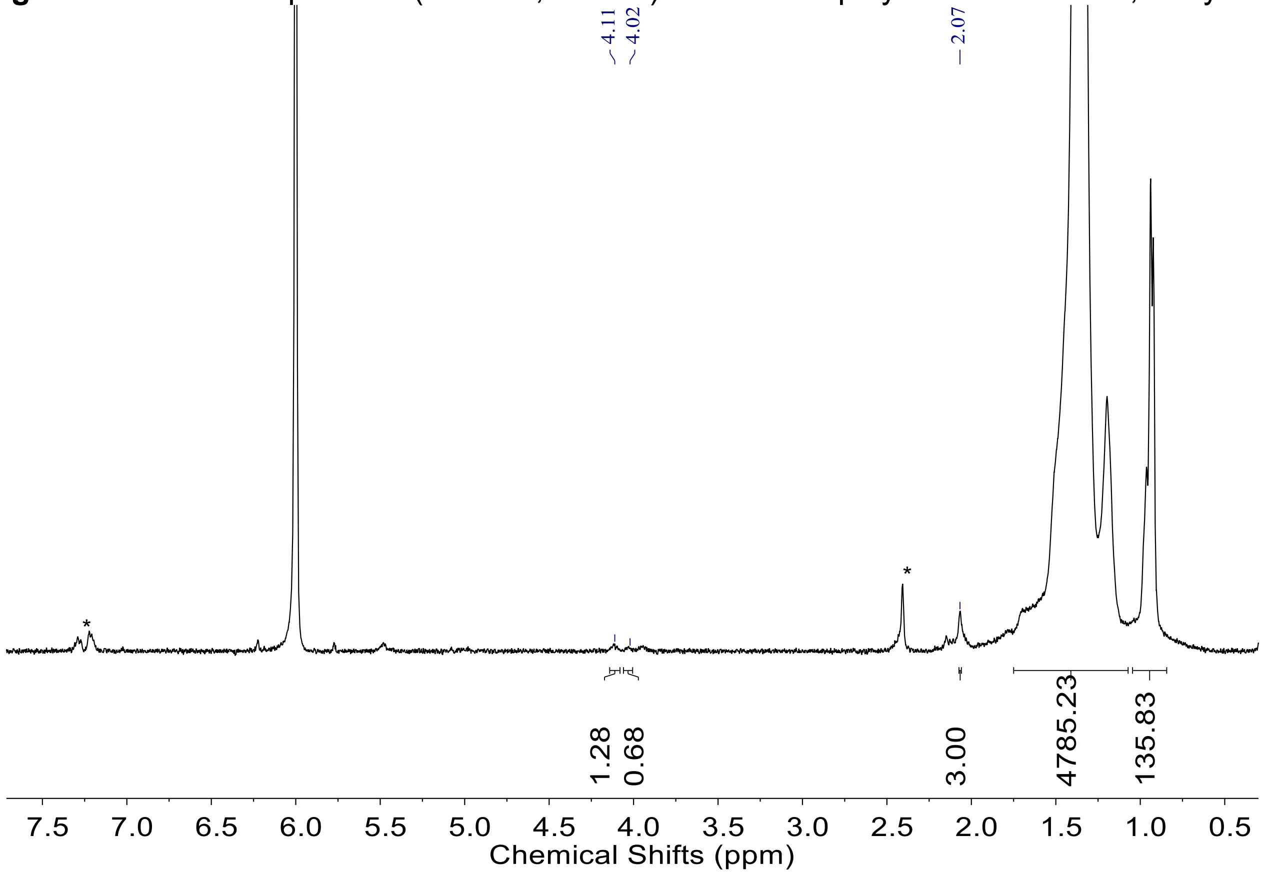


Figure S6. ^{1}H NMR spectrum ($4C_2D_2Cl_4$, 110 °C) of E-AAc copolymer from table 1, entry 5. (*: toluene)

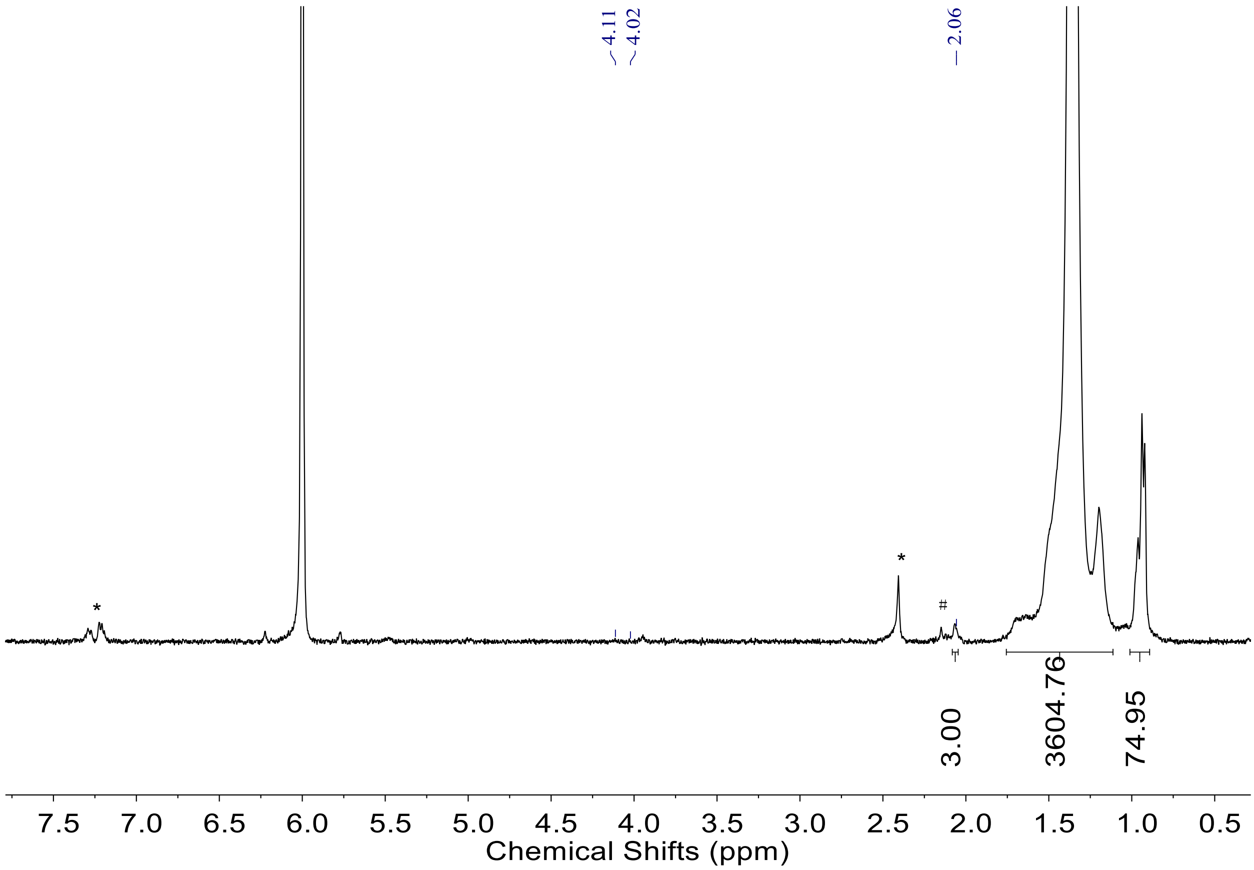


Figure S7. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 110 °C) of E-AAc copolymer from table 1, entry 6. (*: toluene, #: impurity)

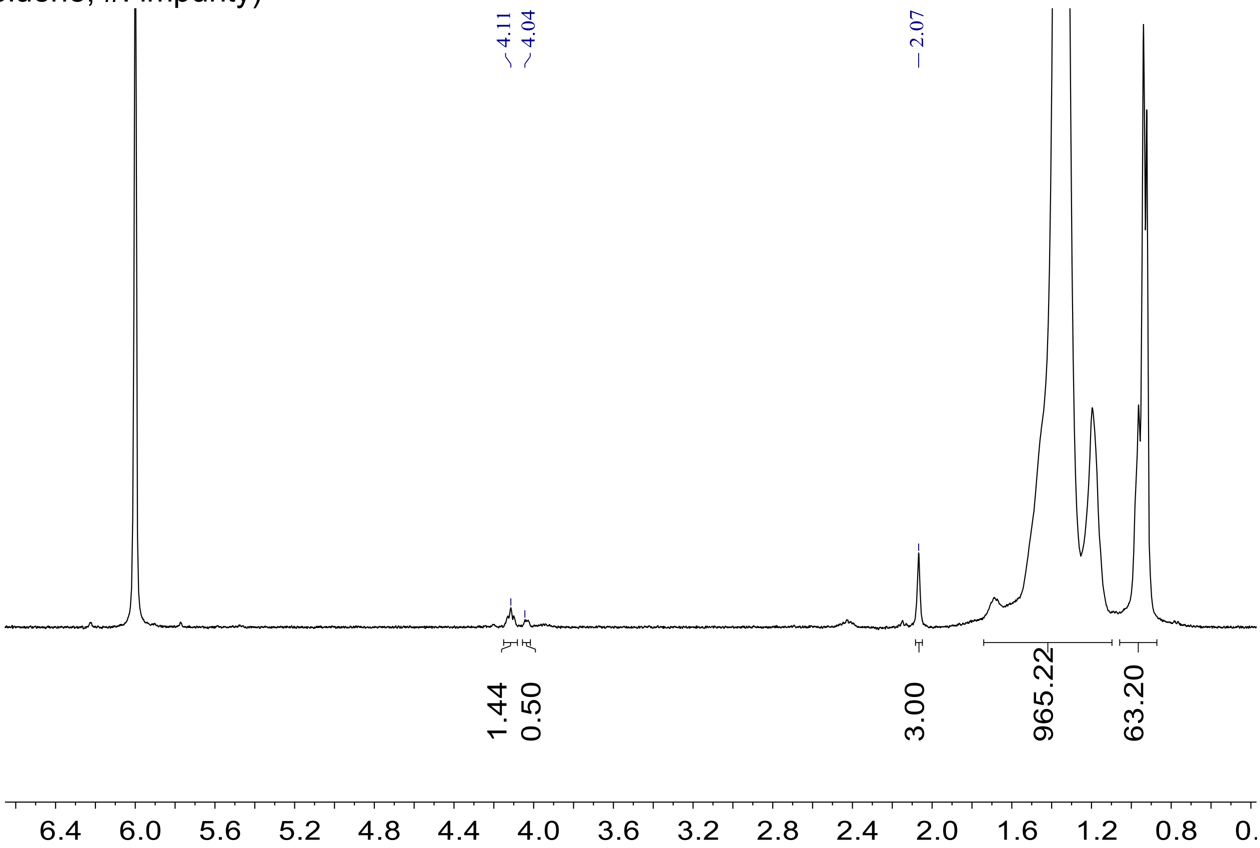


Figure S8. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 110 °C) of E-AAc copolymer from table 1, entry 9.

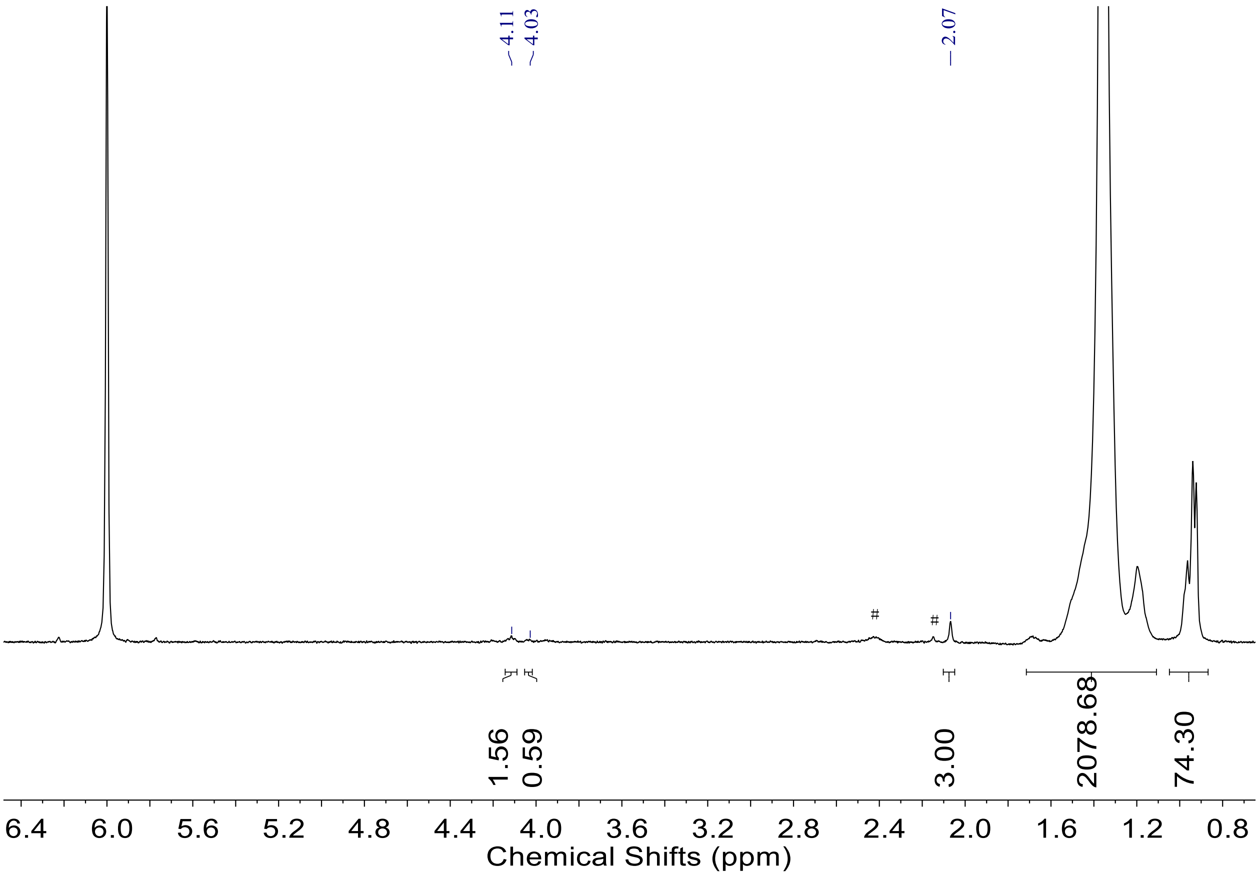


Figure S9. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 110 °C) of E-AAc copolymer from table 1, entry 10.

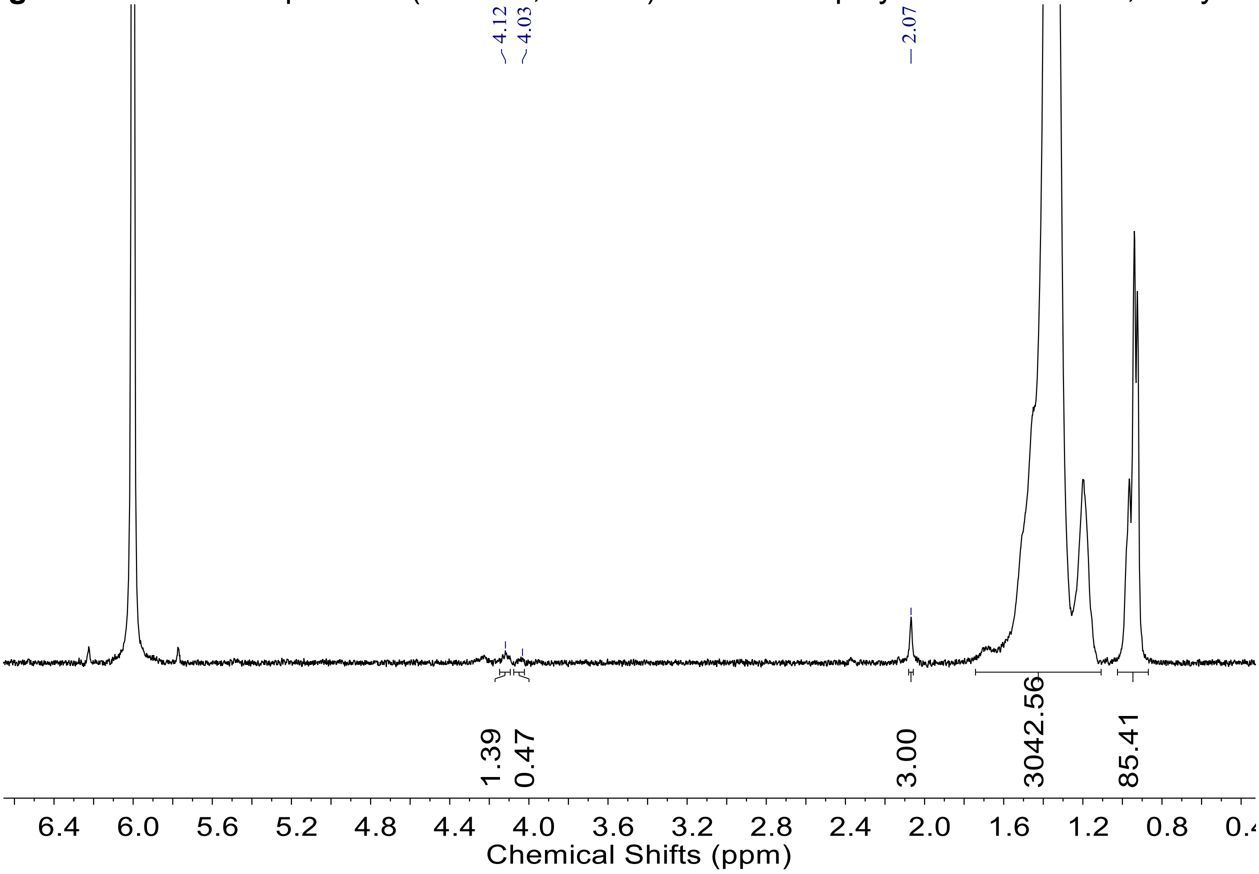


Figure S10. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 110 °C) of E-AAc copolymer from table 1, entry 11.

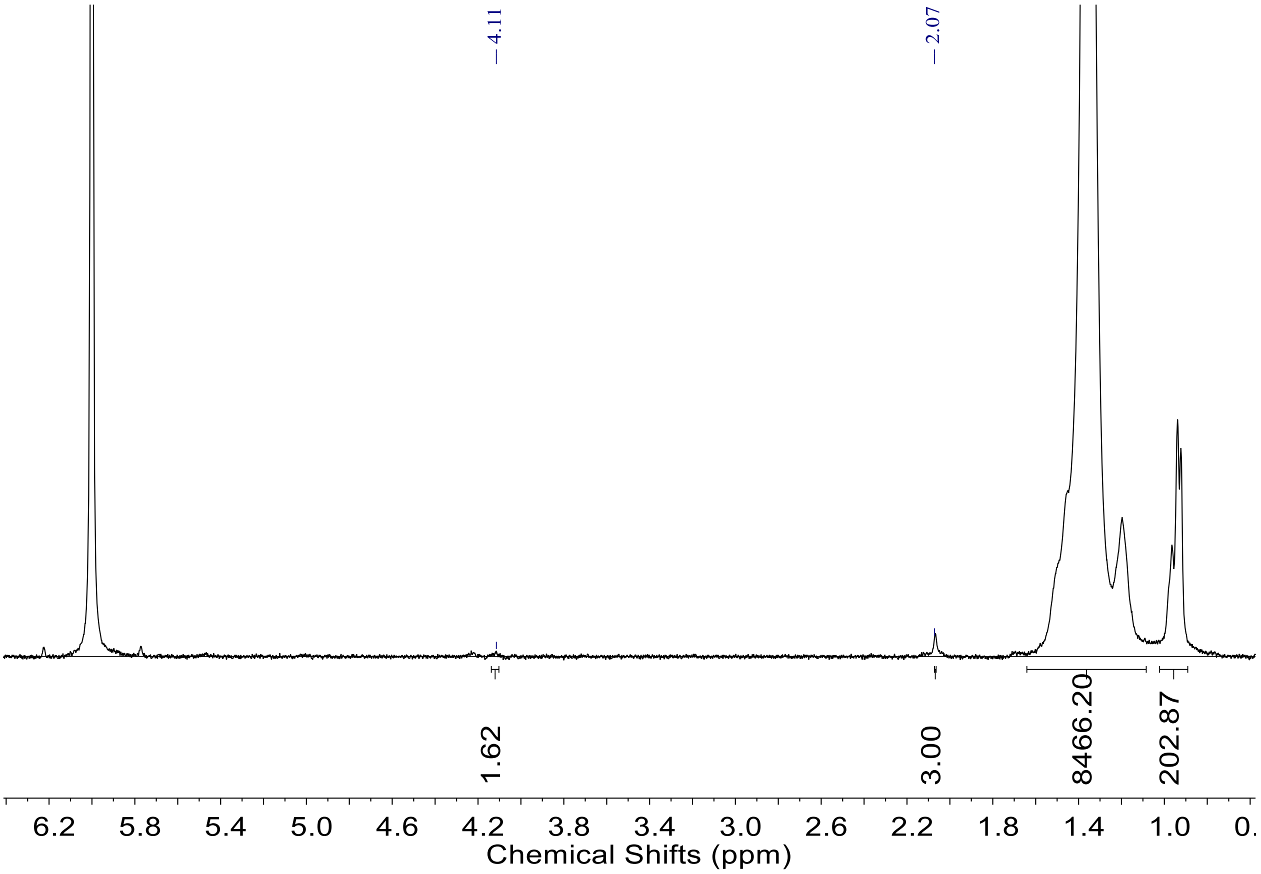


Figure S11. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 110 °C) of E-AAc copolymer from table 1, entry 12.

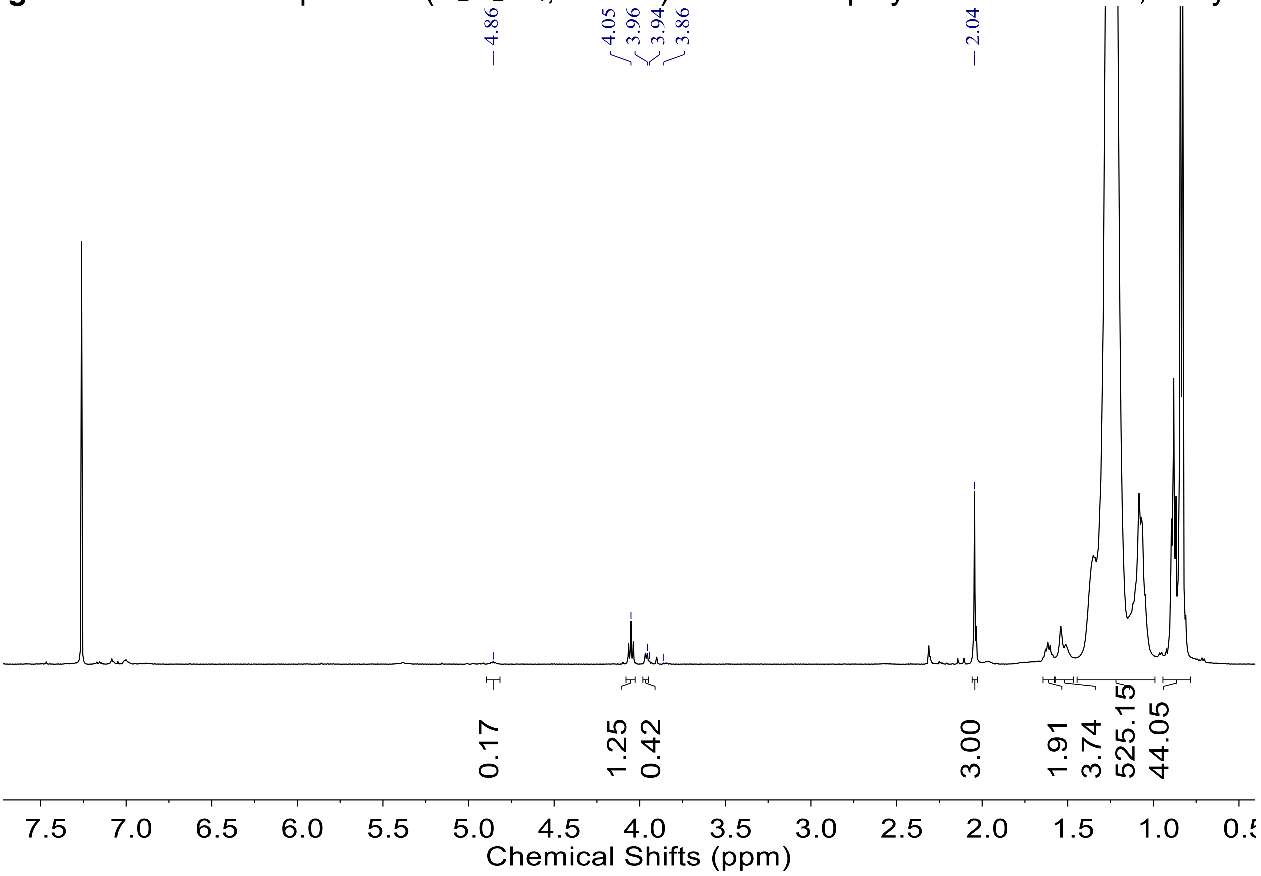


Figure S12. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of E-AAc copolymer from table 1, entry 15.

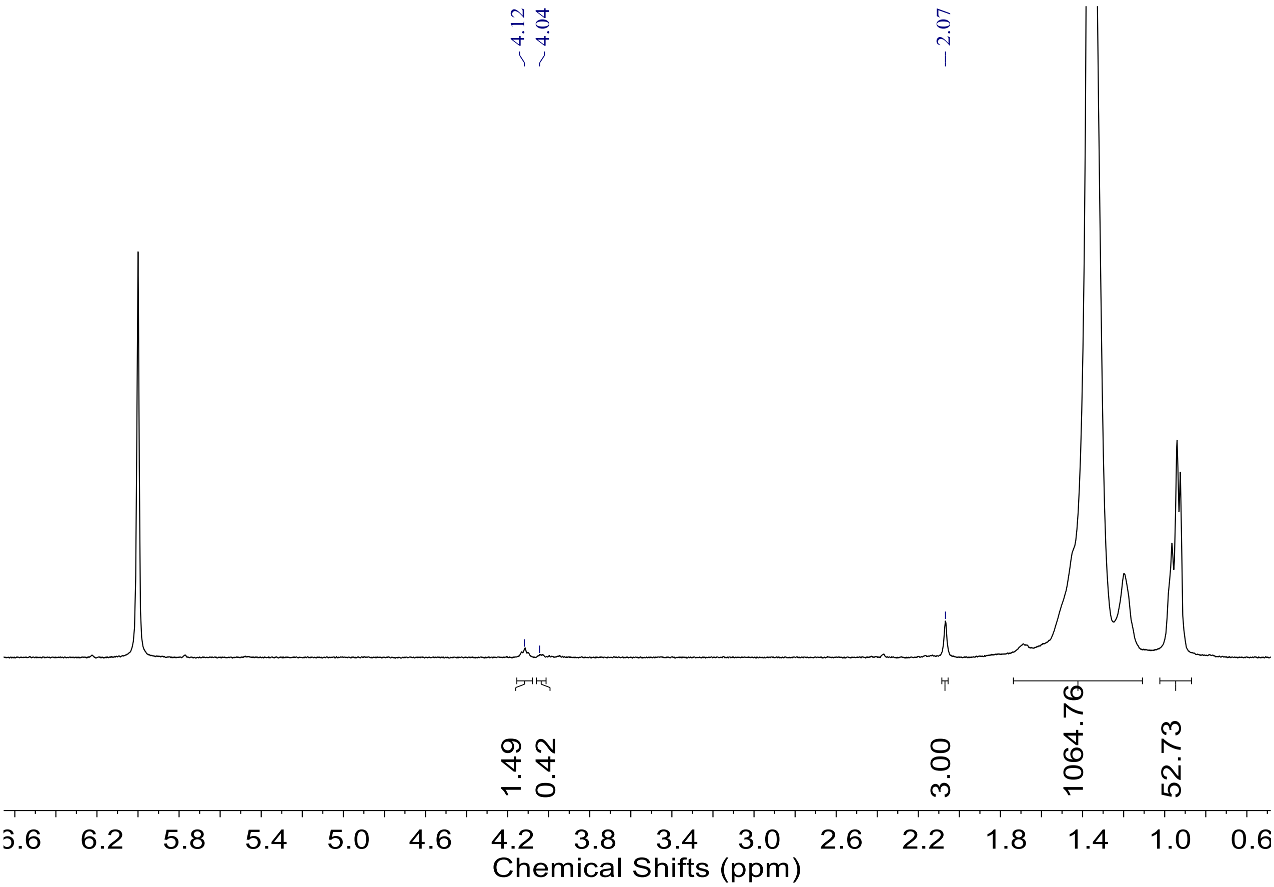


Figure S13. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 110 °C) of E-AAc copolymer from table 1, entry 16.

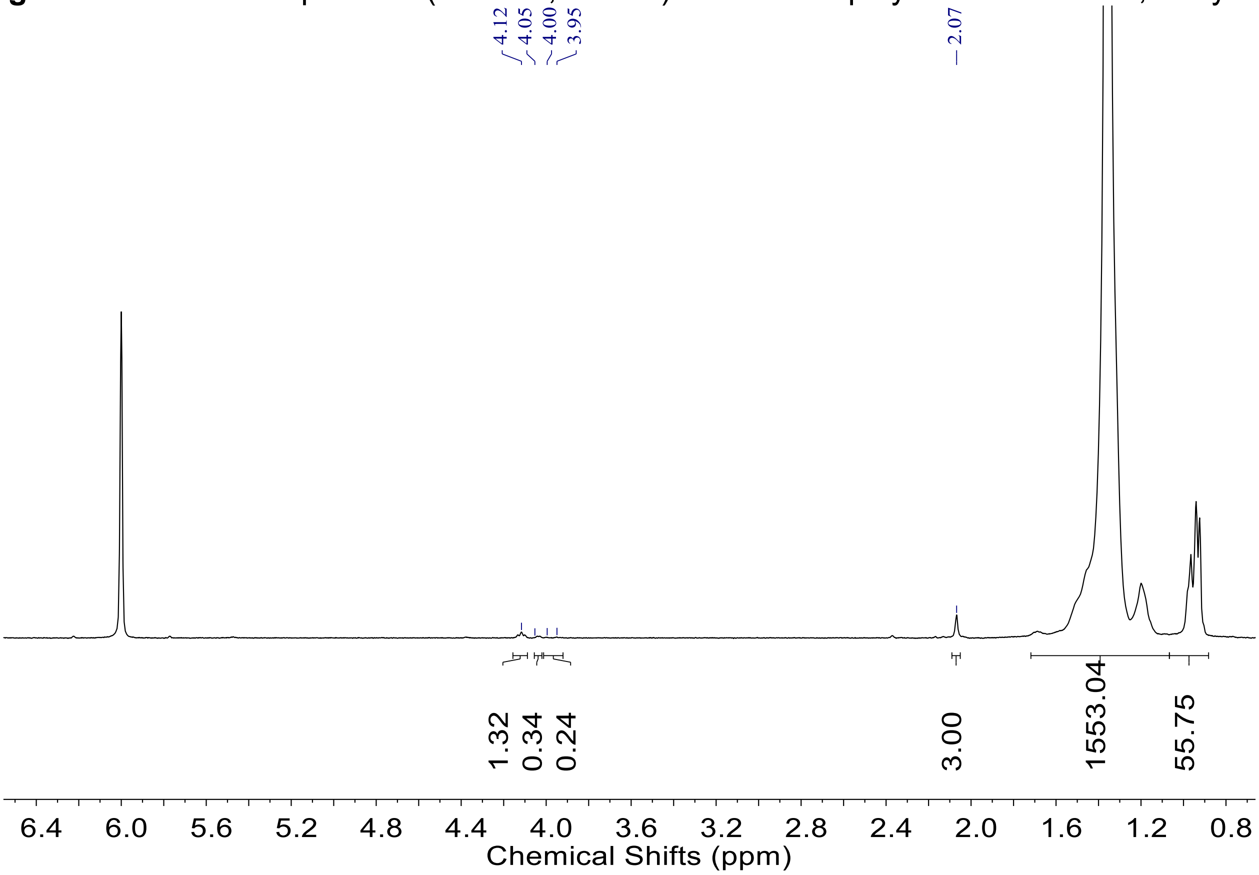


Figure S14. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 110 °C) of E-AAc copolymer from table 1, entry 17.

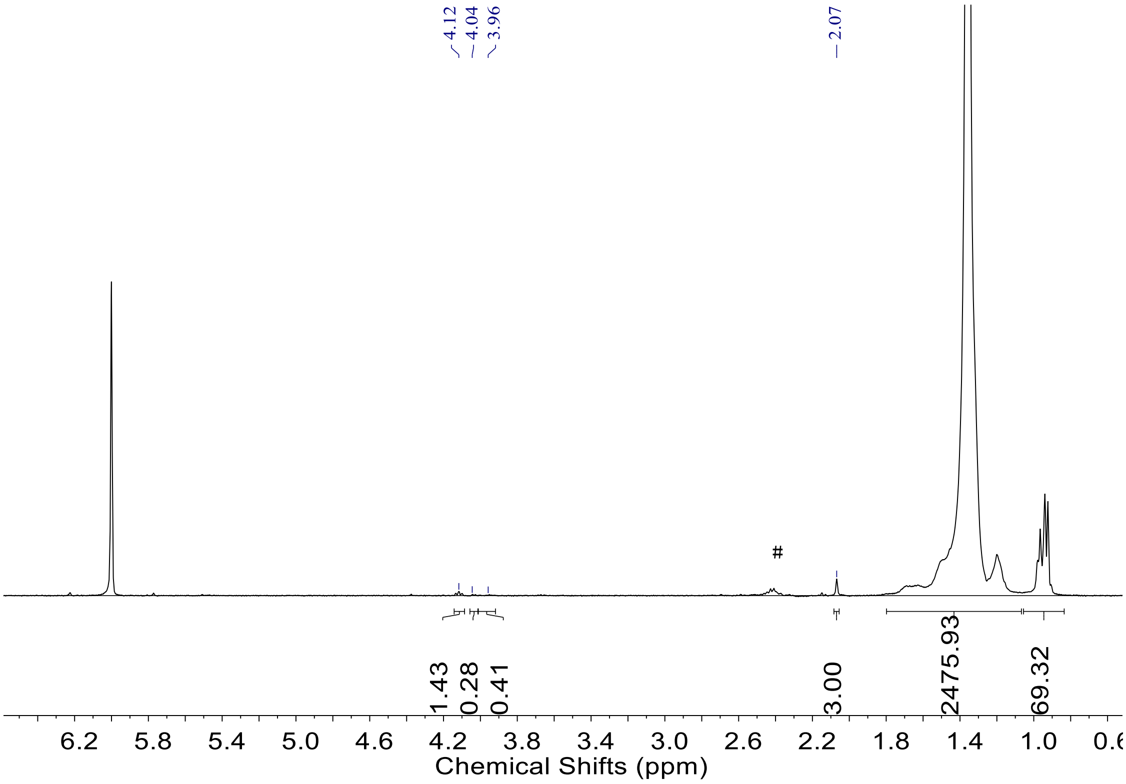


Figure S15. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 110 °C) of E-AAc copolymer from table 1, entry 18. (#: impurity)

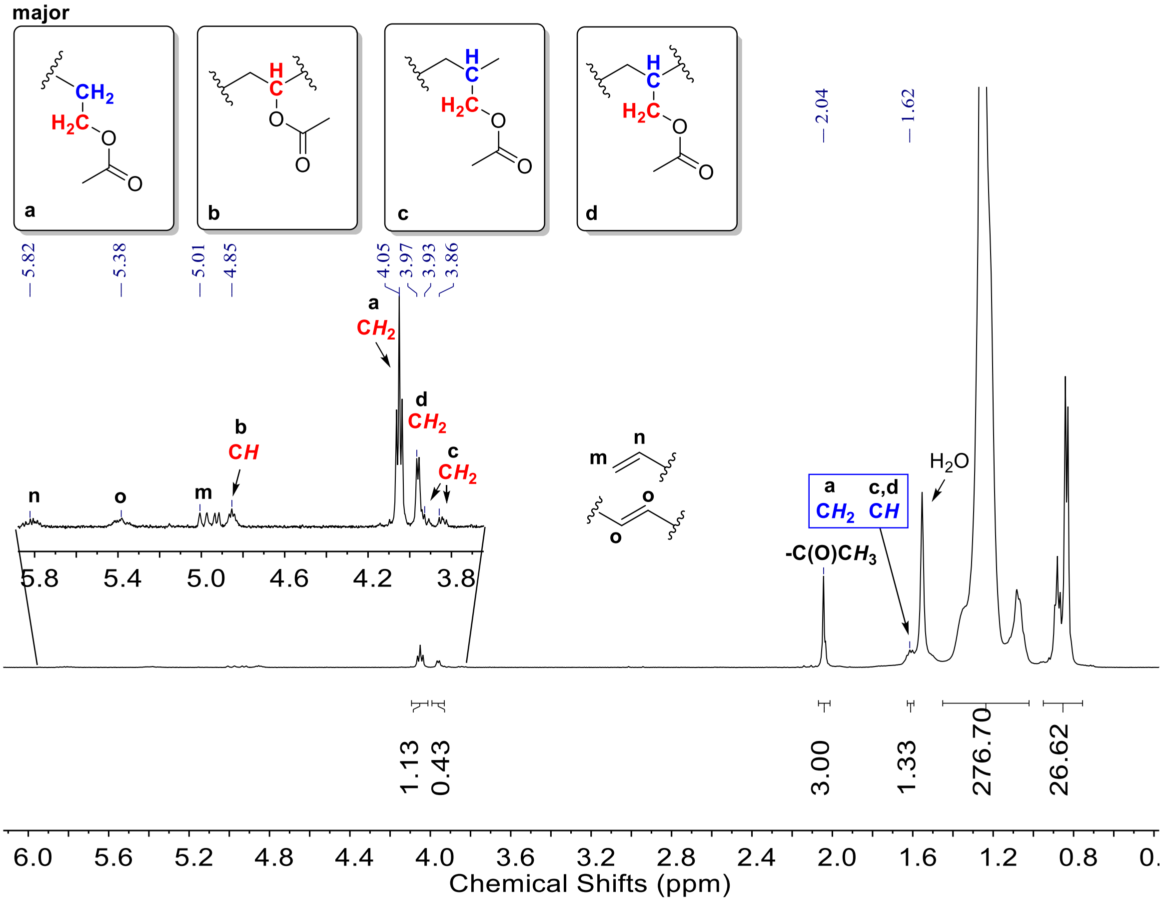


Figure S16. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of E-AAc copolymer from table 1, entry 21. (Structure c was assigned according to a report of Takeuchi[2])

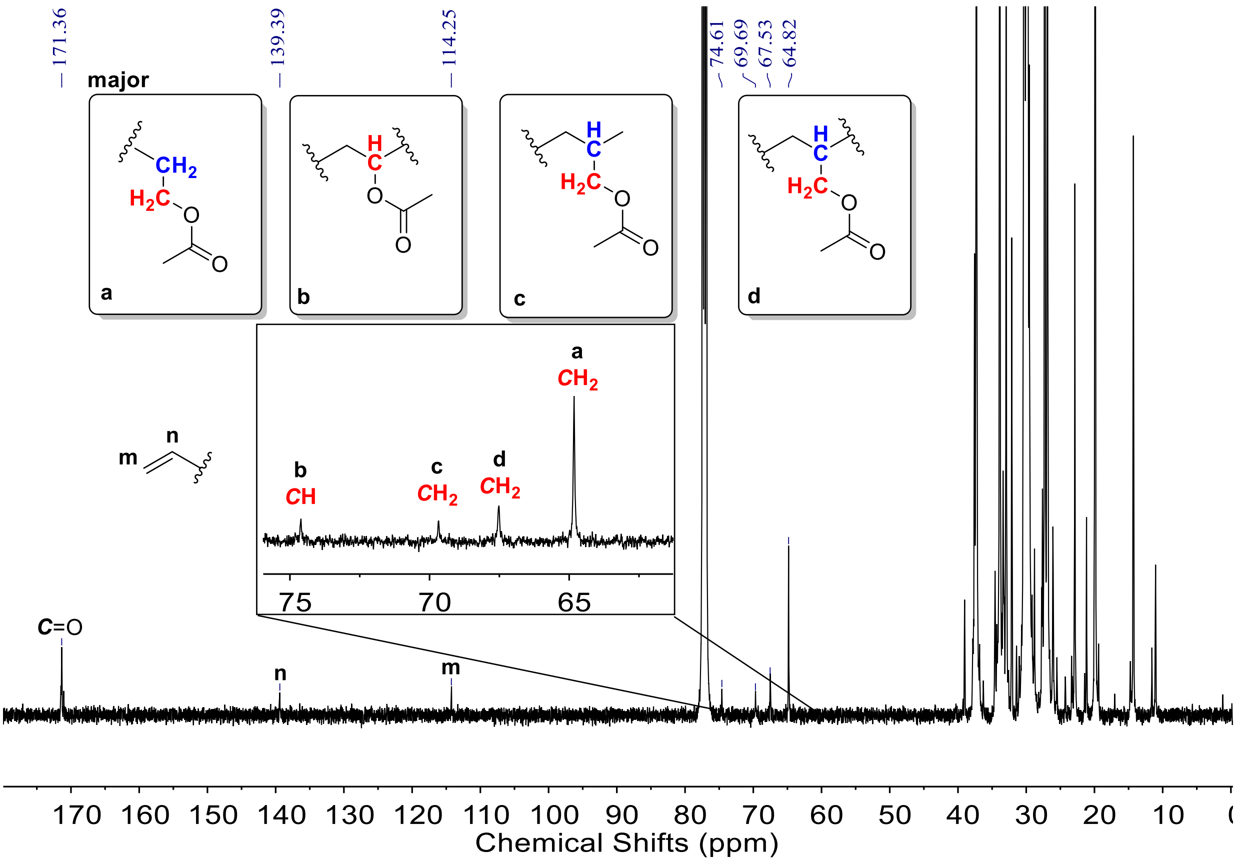


Figure S17. ^{13}C NMR ($CDCl_3$, 25 °C) of E-AAc copolymer from table 1, entry 21.(Assignment was according to reports of Nozaki[3,4])

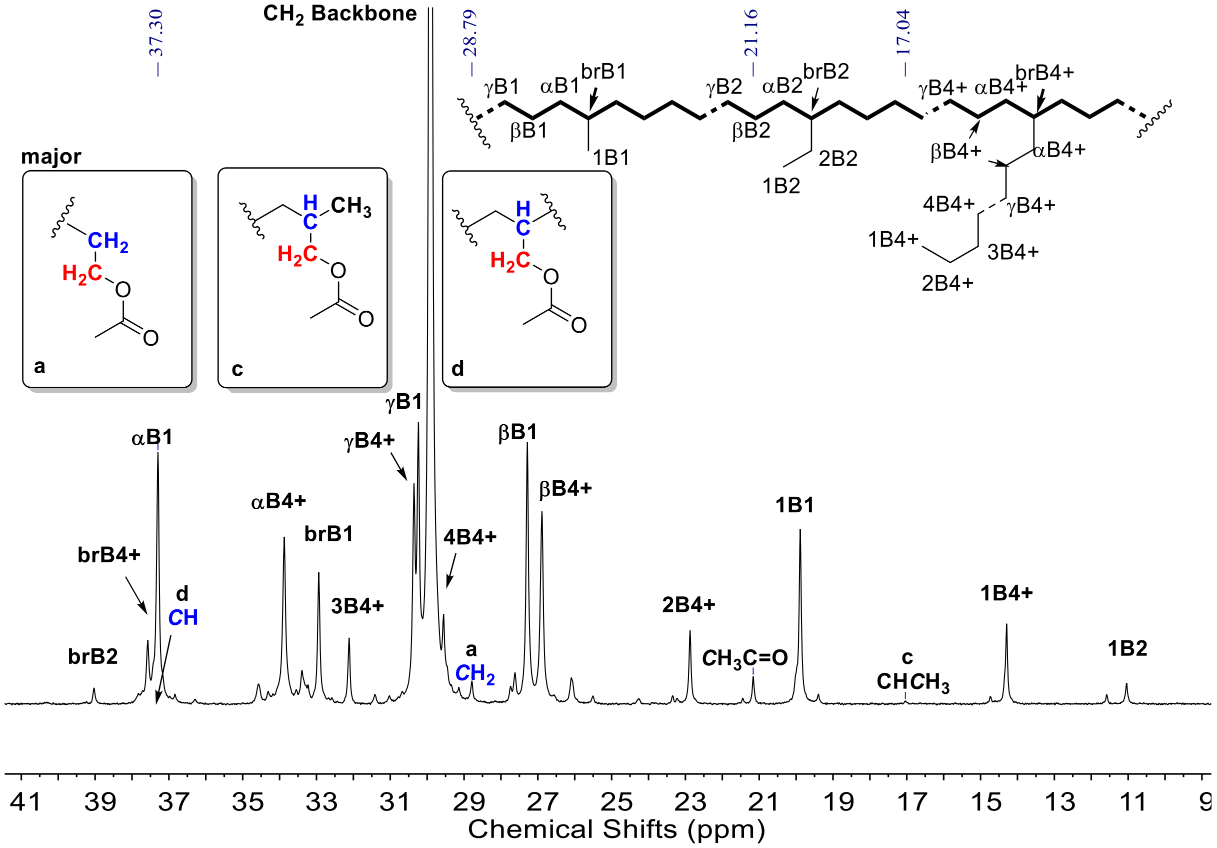


Figure S18. ^{13}C NMR ($CDCl_3$, 25 °C) of E-AAc copolymer from table 1, entry 21. (enlarged)

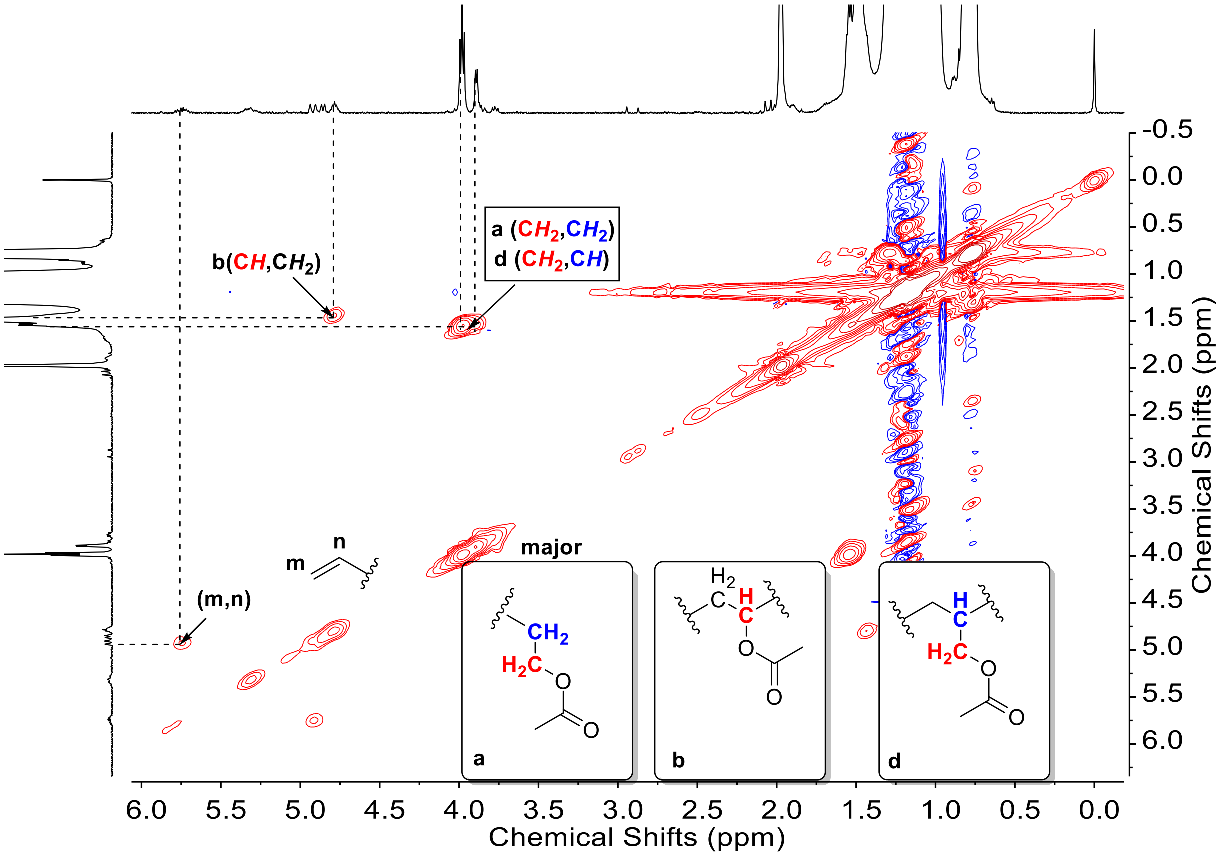


Figure S19. ^{1}H-^{1}H COSY NMR (CDCl$_3$, 25 °C) of E-AAc copolymer from table 1, entry 21.

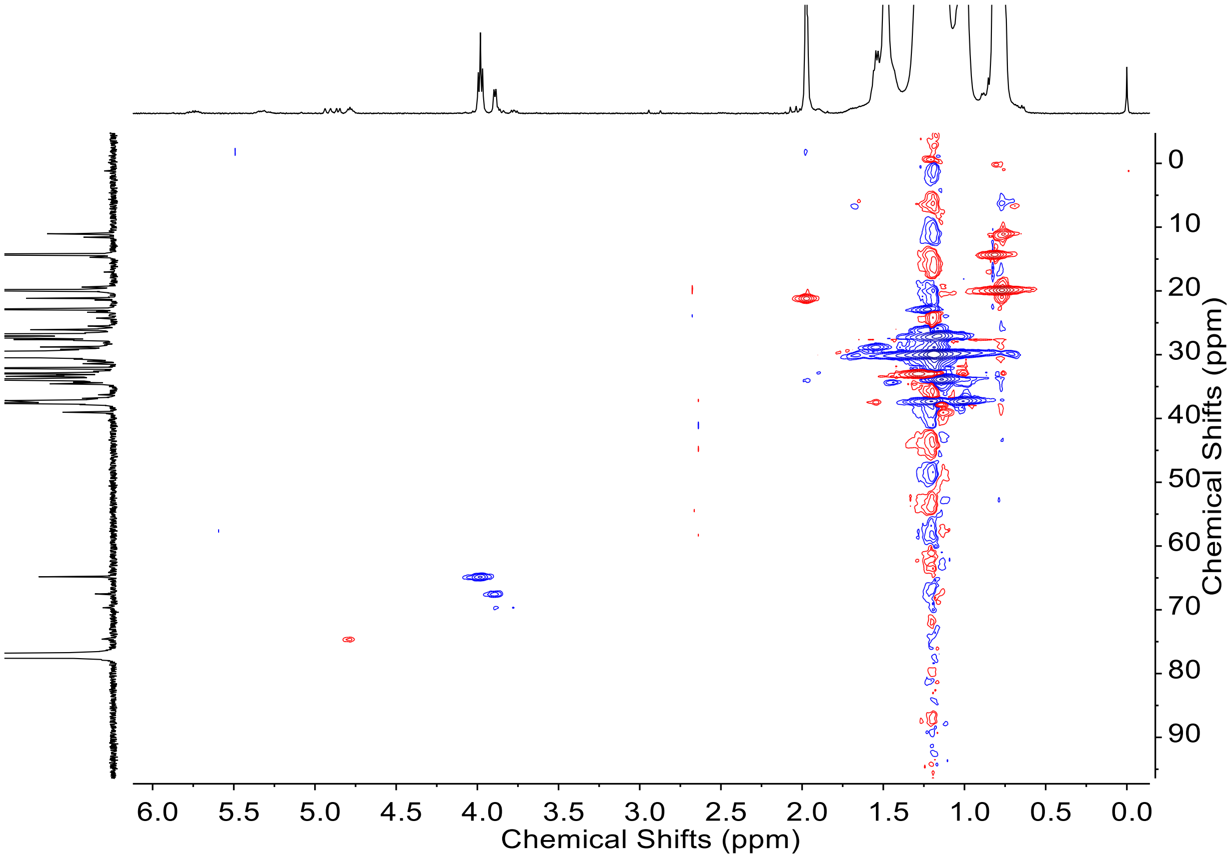


Figure S20. ^{1}H-^{13}C HSQC NMR (CDCl$_3$, 25 °C) of E-AAc copolymer from table 1, entry 21.

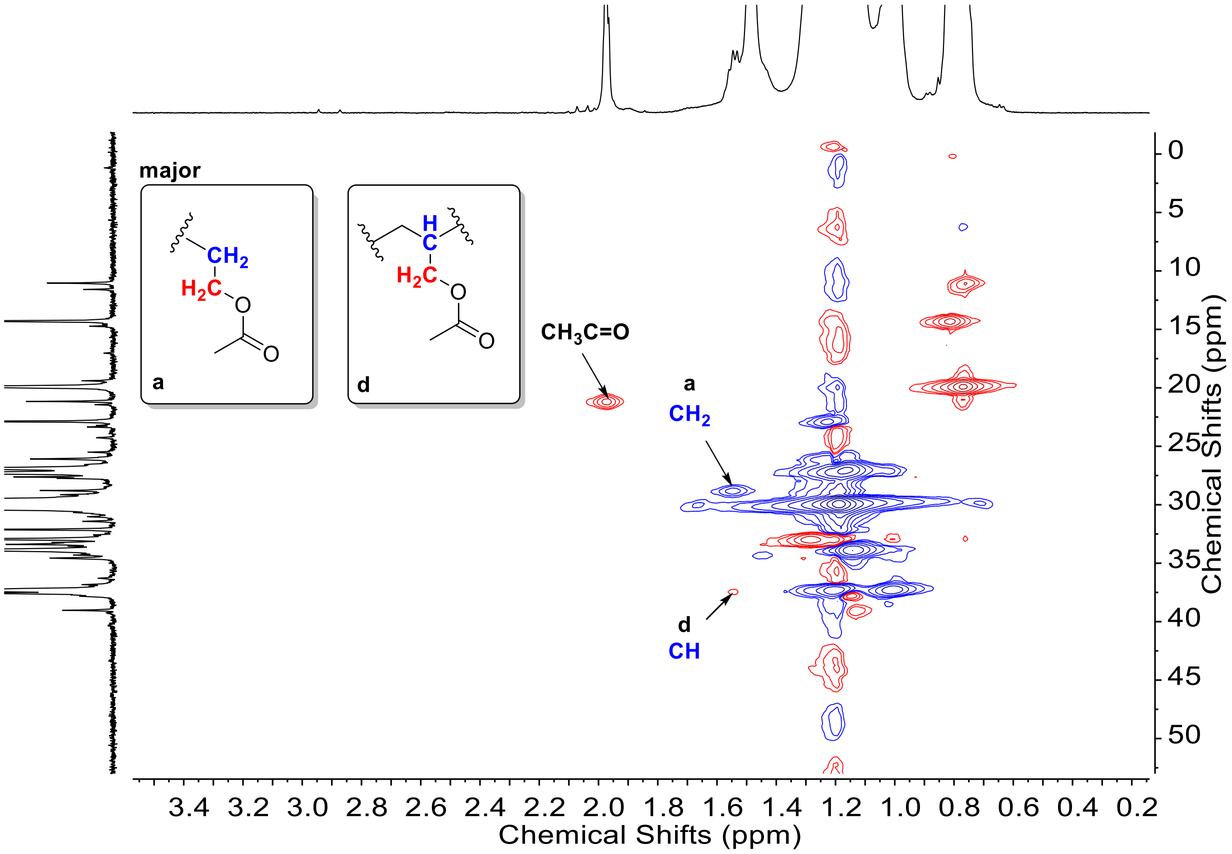


Figure S21. ^{1}H-^{13}C HSQC NMR ($CDCl_3$, 25 °C) of E-AAc copolymer from table 1, entry 21. (enlarged)

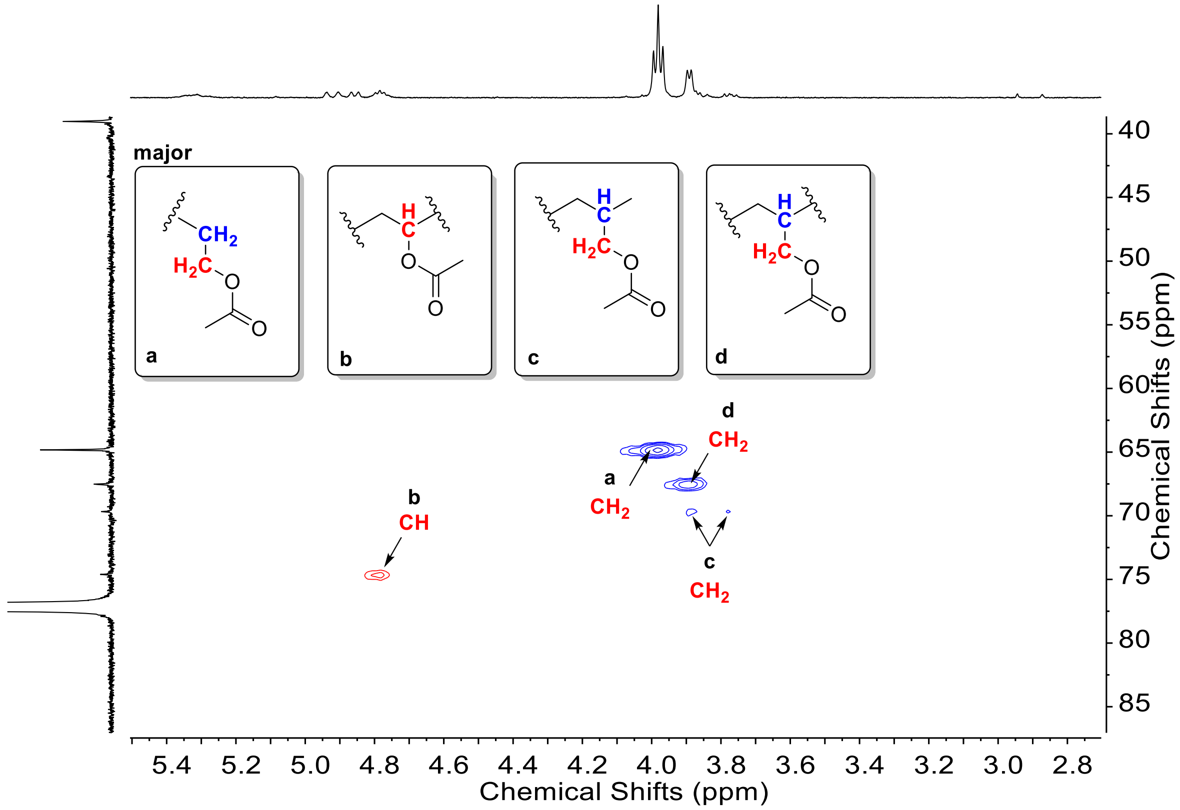


Figure S22. ^{1}H-^{13}C HSQC NMR ($CDCl_3$, 25 °C) of E-AAc copolymer from table 1, entry 21. (enlarged)

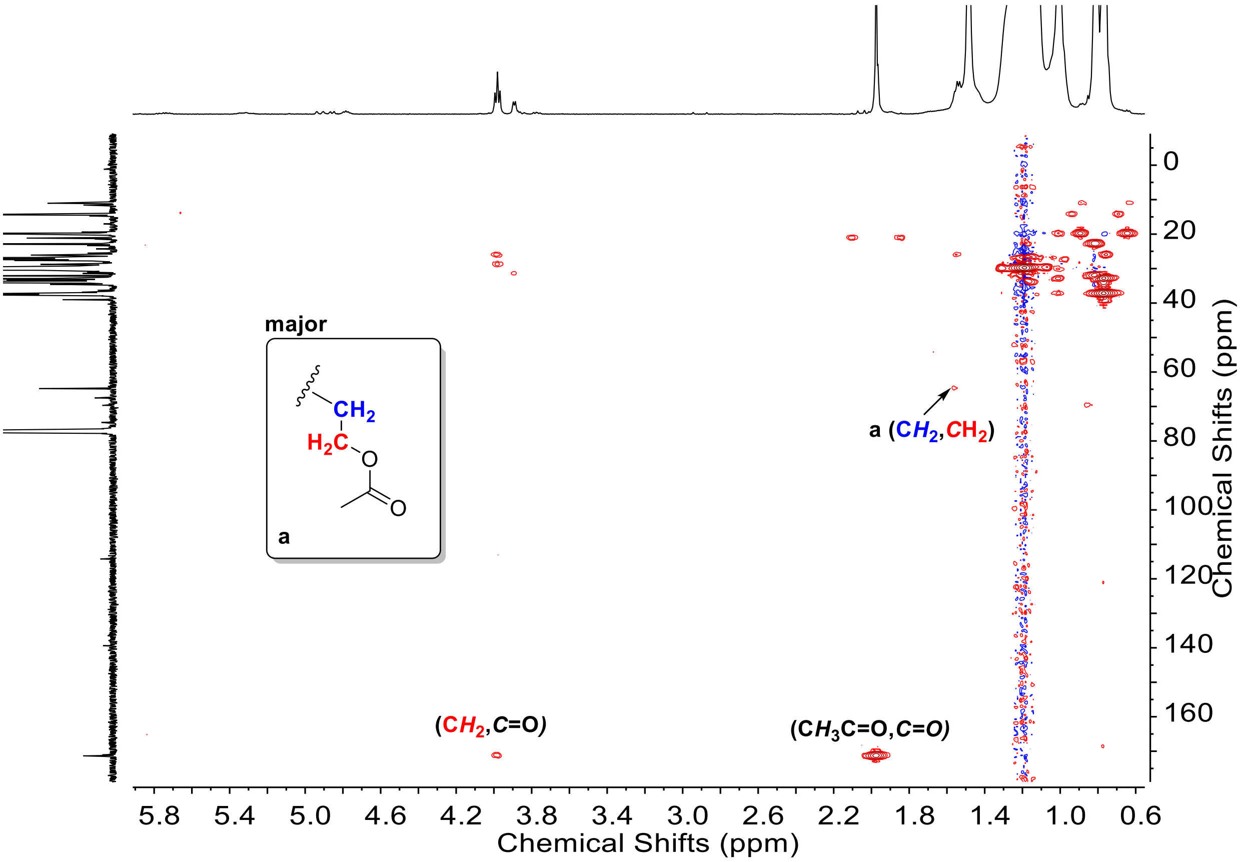


Figure S23. ^{1}H-^{13}C HMBC NMR (CDCl₃, 25 °C) of E-AAc copolymer from table 1, entry 21.

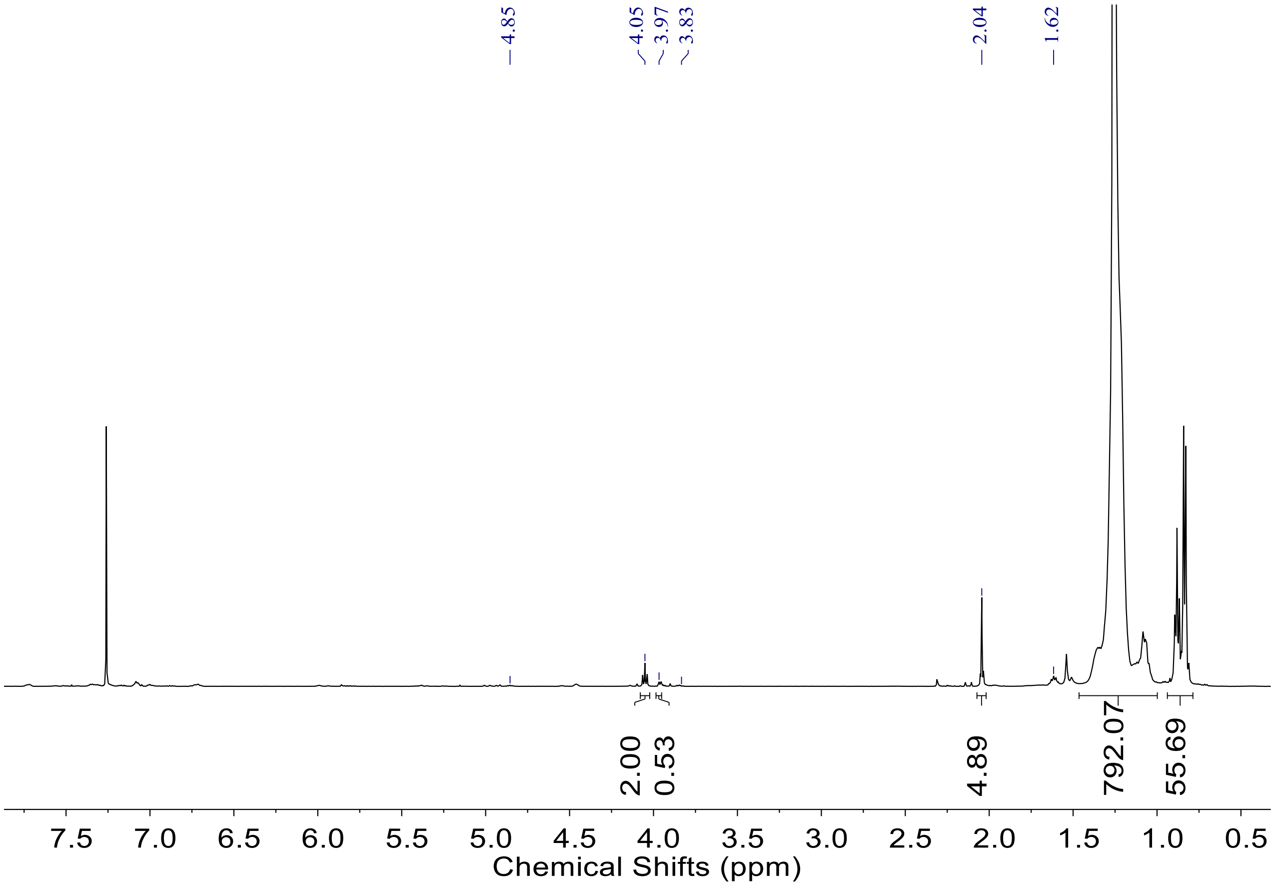


Figure S24. ^{1}H NMR spectrum (CDCl₃, 25 °C) of E-AAc copolymer from table 1, entry 22.

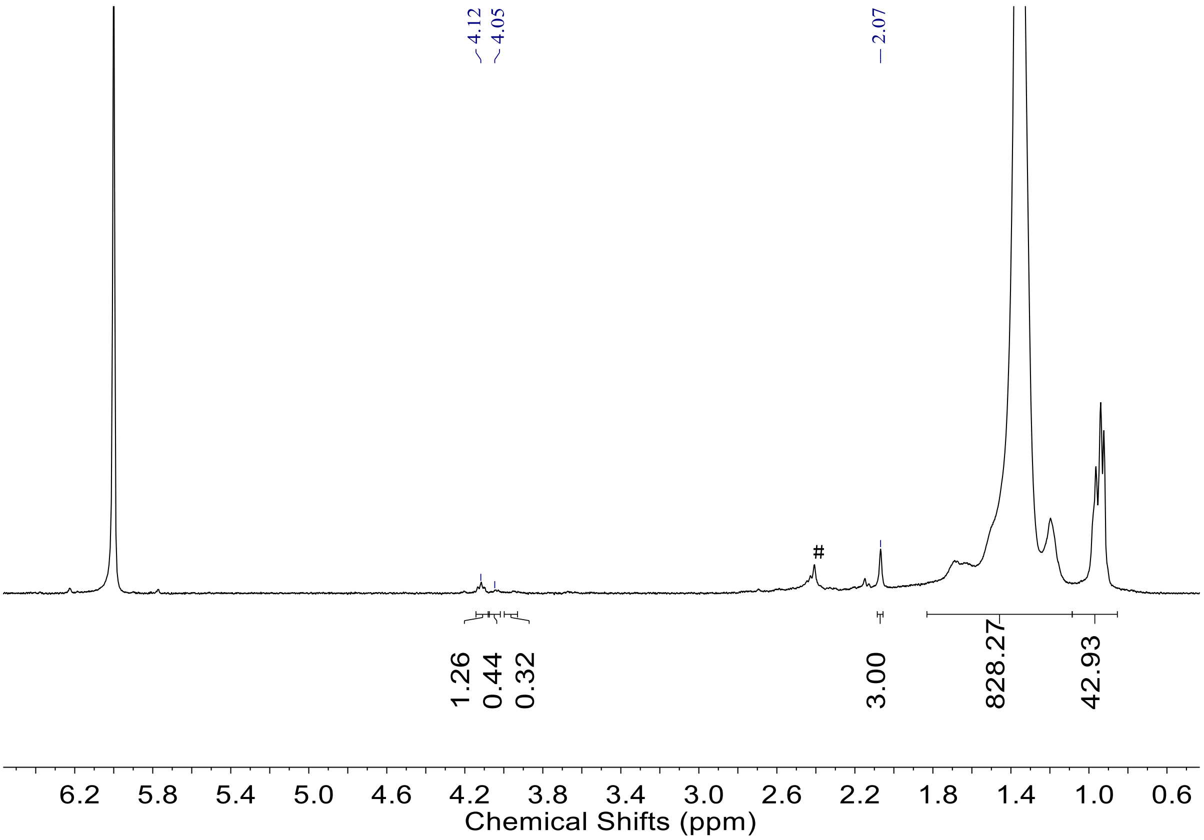


Figure S25. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 110 °C) of E-AAc copolymer from table 1, entry 23. (#: impurity)

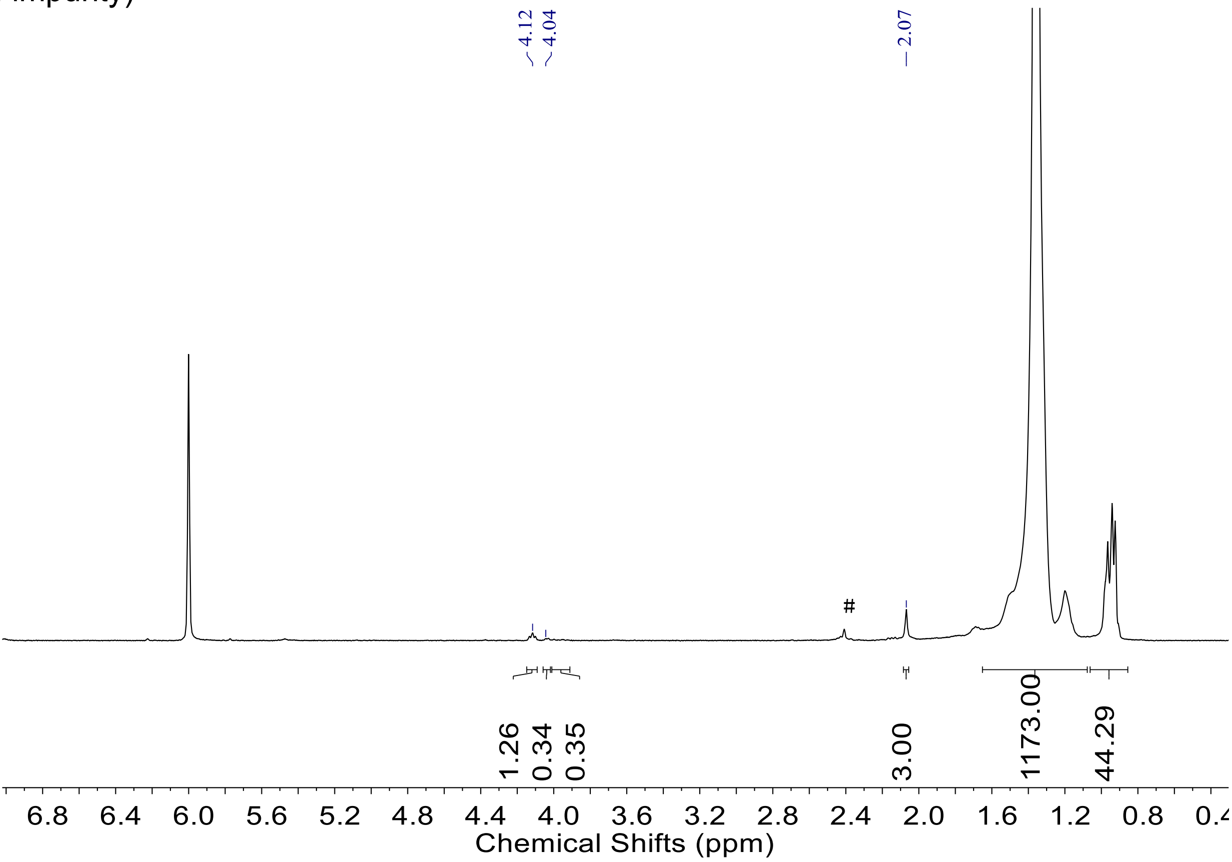


Figure S26. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 110 °C) of E-AAc copolymer from table 1, entry 24. (#: impurity)

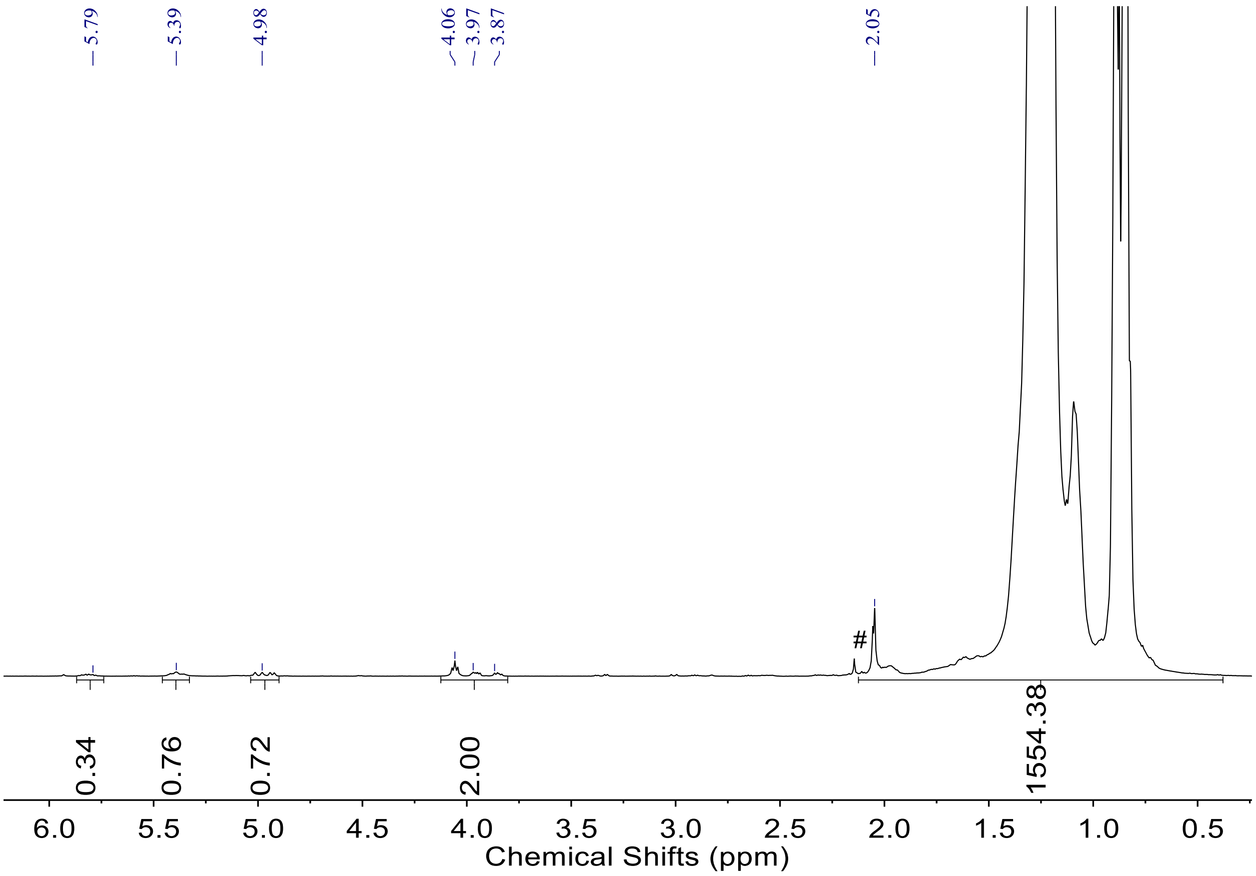


Figure S27. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of E-AAc copolymer from table 1, entry 26. (#: impurity)

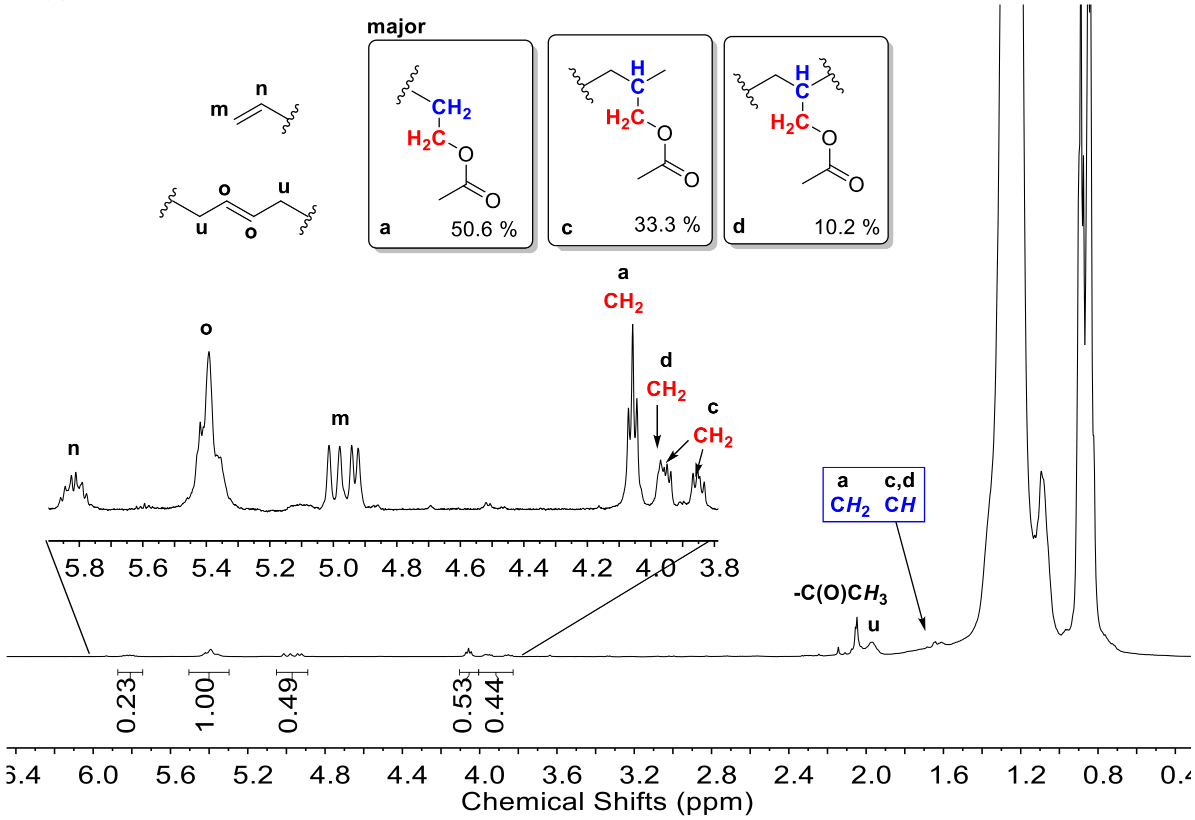


Figure S28. ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of E-AAc copolymer from table 1, entry 27. (Structure c was assigned according to a report of Takeuchi[2])

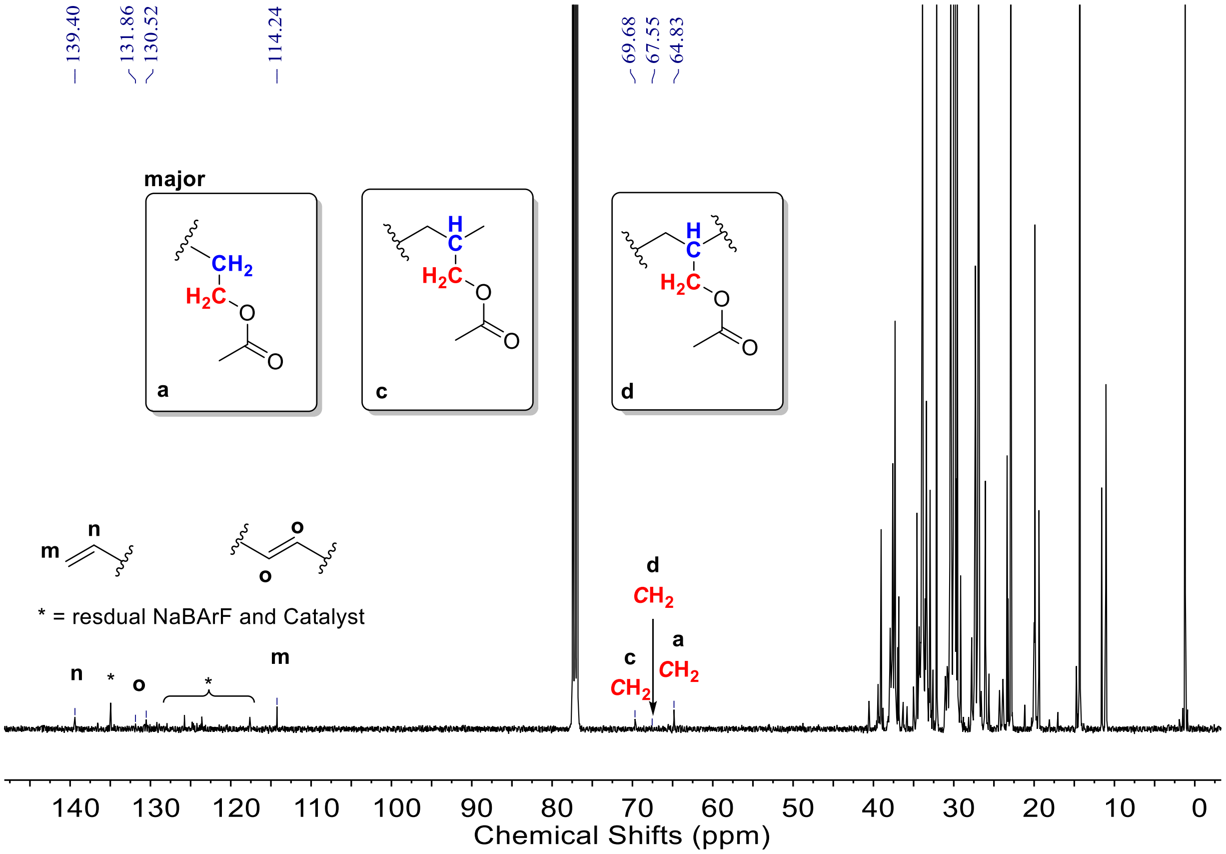


Figure S29. ^{13}C NMR ($CDCl_3$, 25 °C) of E-AAc copolymer from table 1, entry 27.

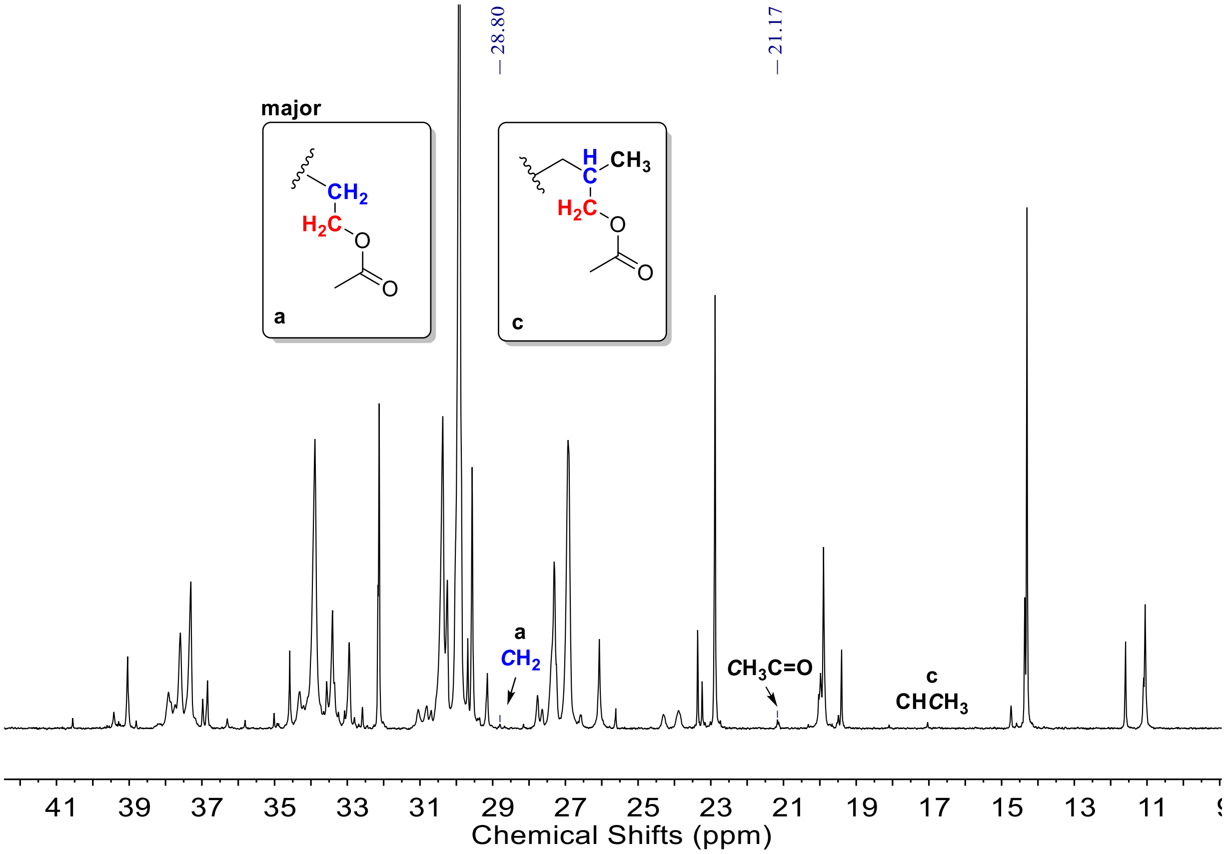


Figure S30. ^{13}C NMR ($CDCl_3$, 25 °C) of E-AAc copolymer from table 1, entry 27. (enlarged)

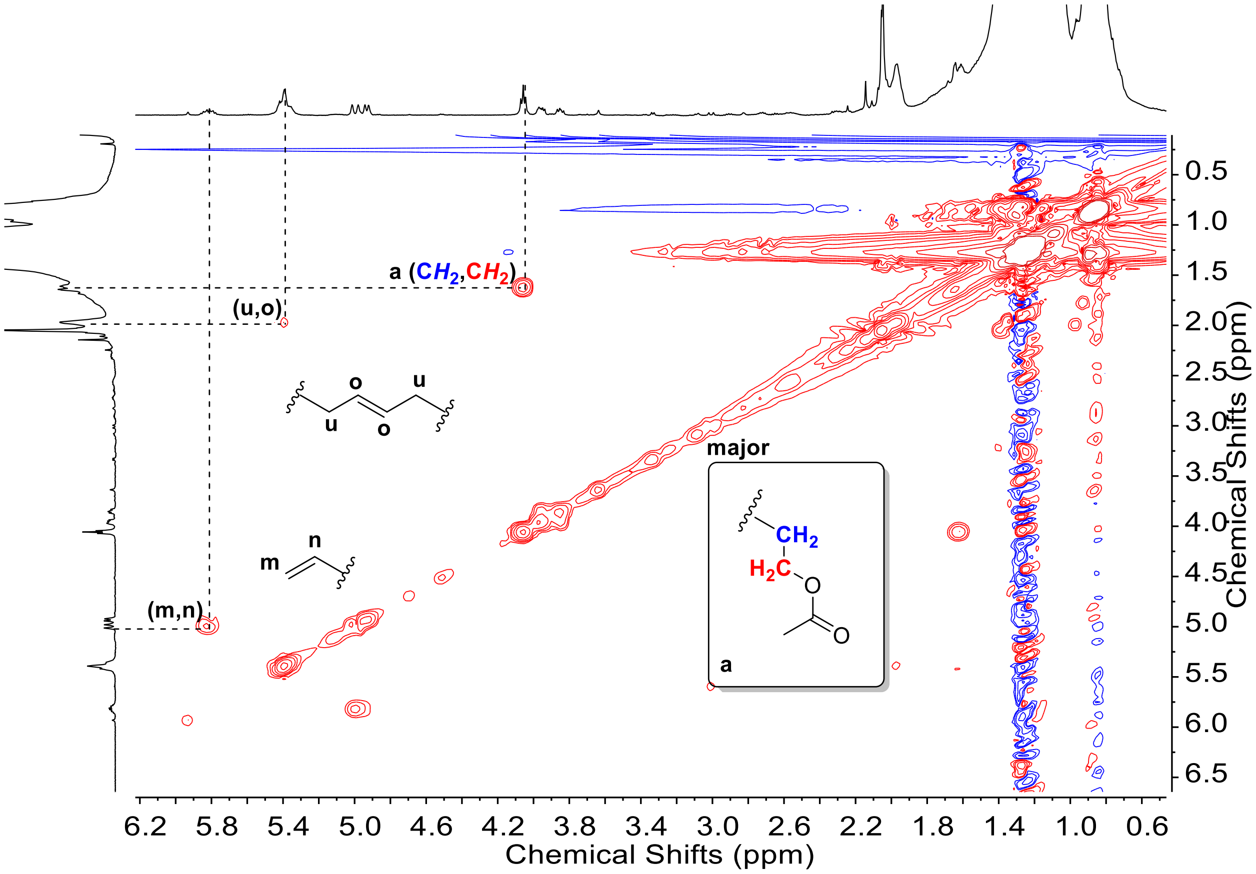


Figure S31. ^{1}H-^{1}H COSY NMR (CDCl$_3$, 25 °C) of E-AAc copolymer from table 1, entry 27.

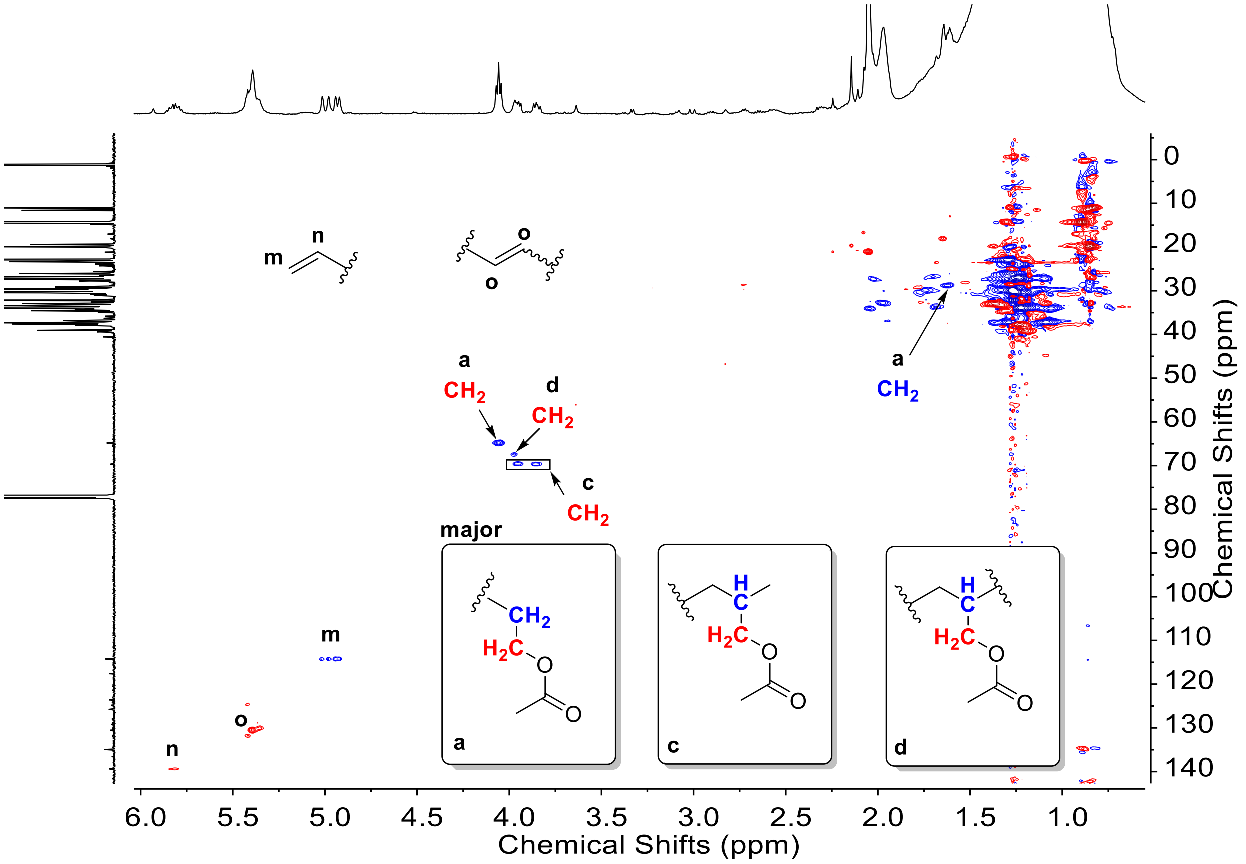


Figure S32. ^{1}H-^{13}C HSQC NMR (CDCl$_3$, 25 °C) of E-AAc copolymer from table 1, entry 27.

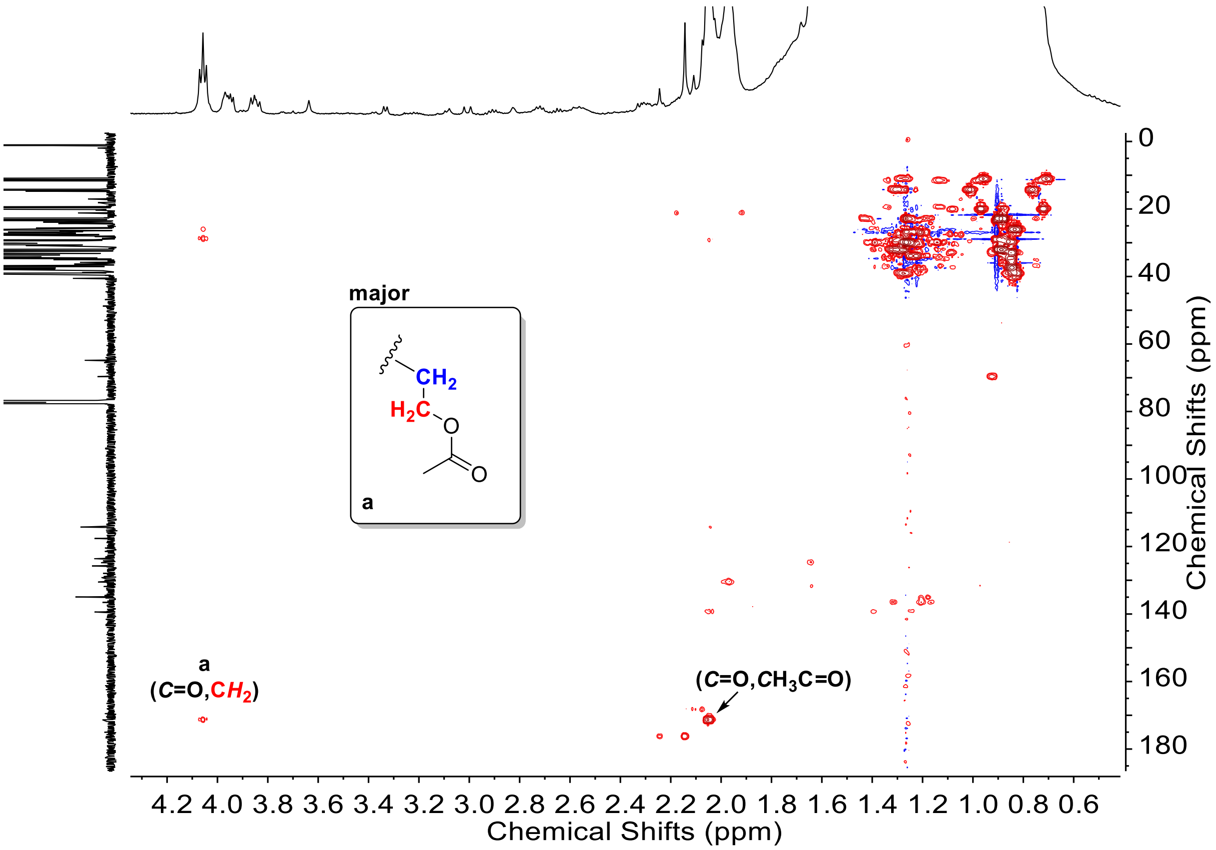


Figure S33. ^{1}H-^{13}C HMBC NMR ($CDCl_3$, 25 °C) of E-AAc copolymer from table 1, entry 27.

3.2 NMR Spectra of Polymers in Table 2.

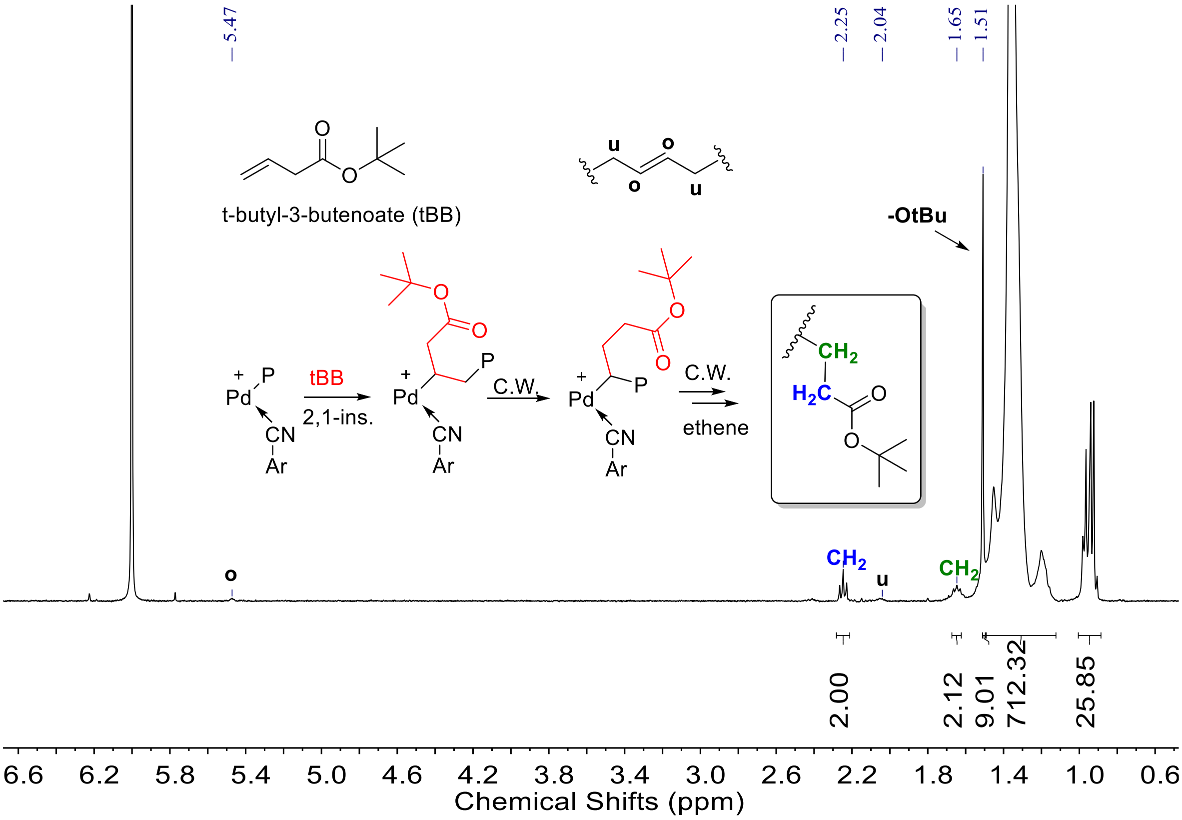


Figure S34. ^{1}H NMR ($C_2D_2Cl_4$, 110 °C) of E-tBB copolymer from table 2, entry 2.

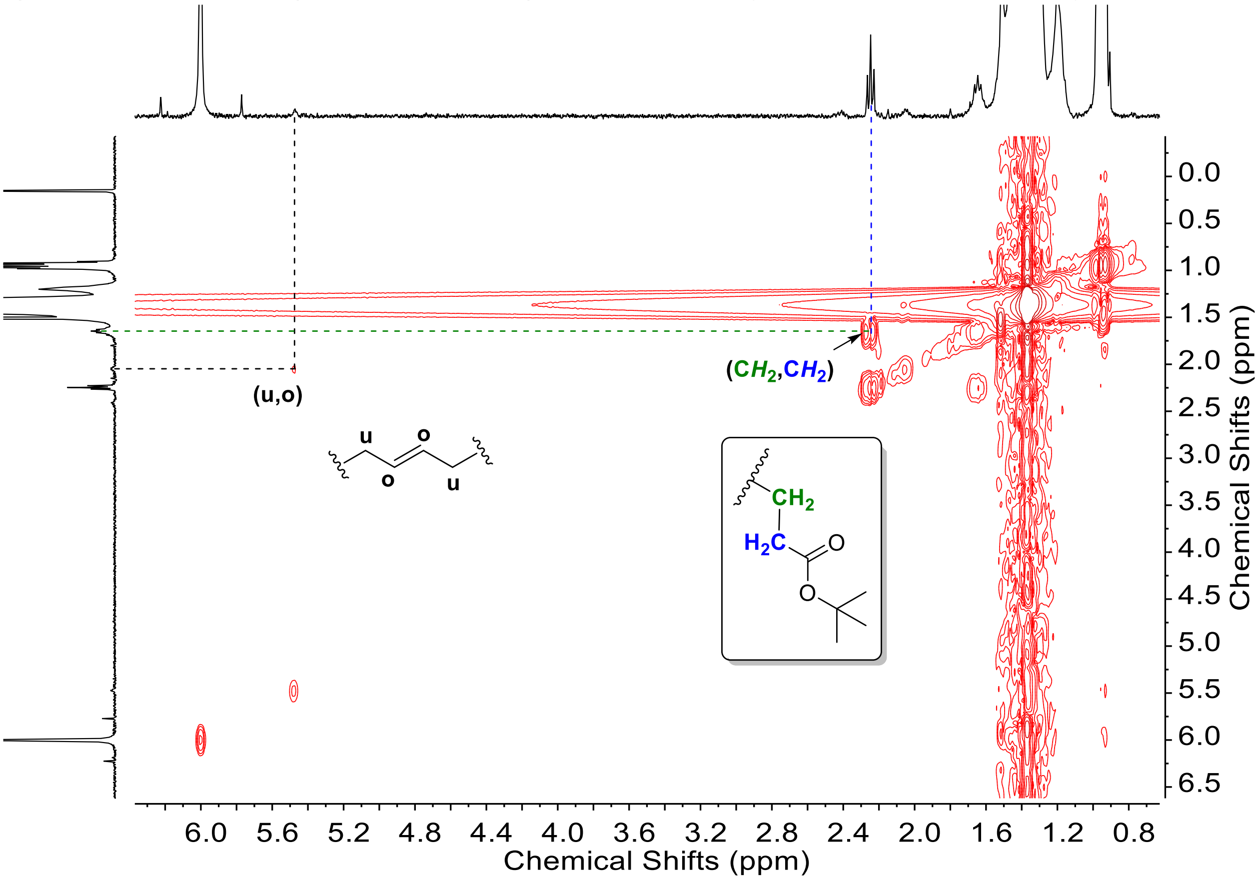


Figure S35. ^{1}H-^{1}H COSY NMR ($C_2D_2Cl_4$, 110 °C) of E-tBB copolymer from table 2, entry 2.

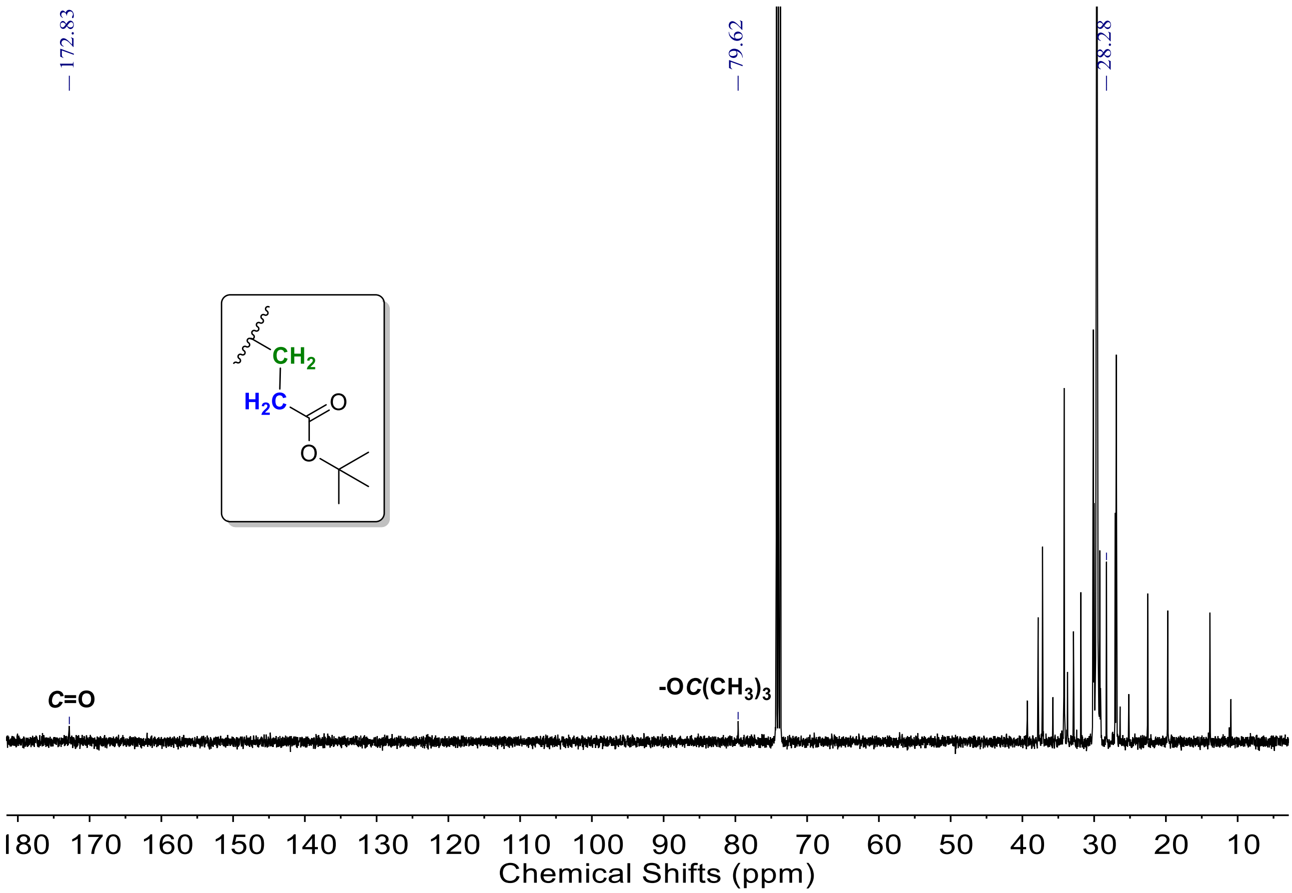


Figure S36. ^{13}C NMR ($C_2D_2Cl_4$, 110 °C) of E-tBB copolymer from table 2, entry 2.

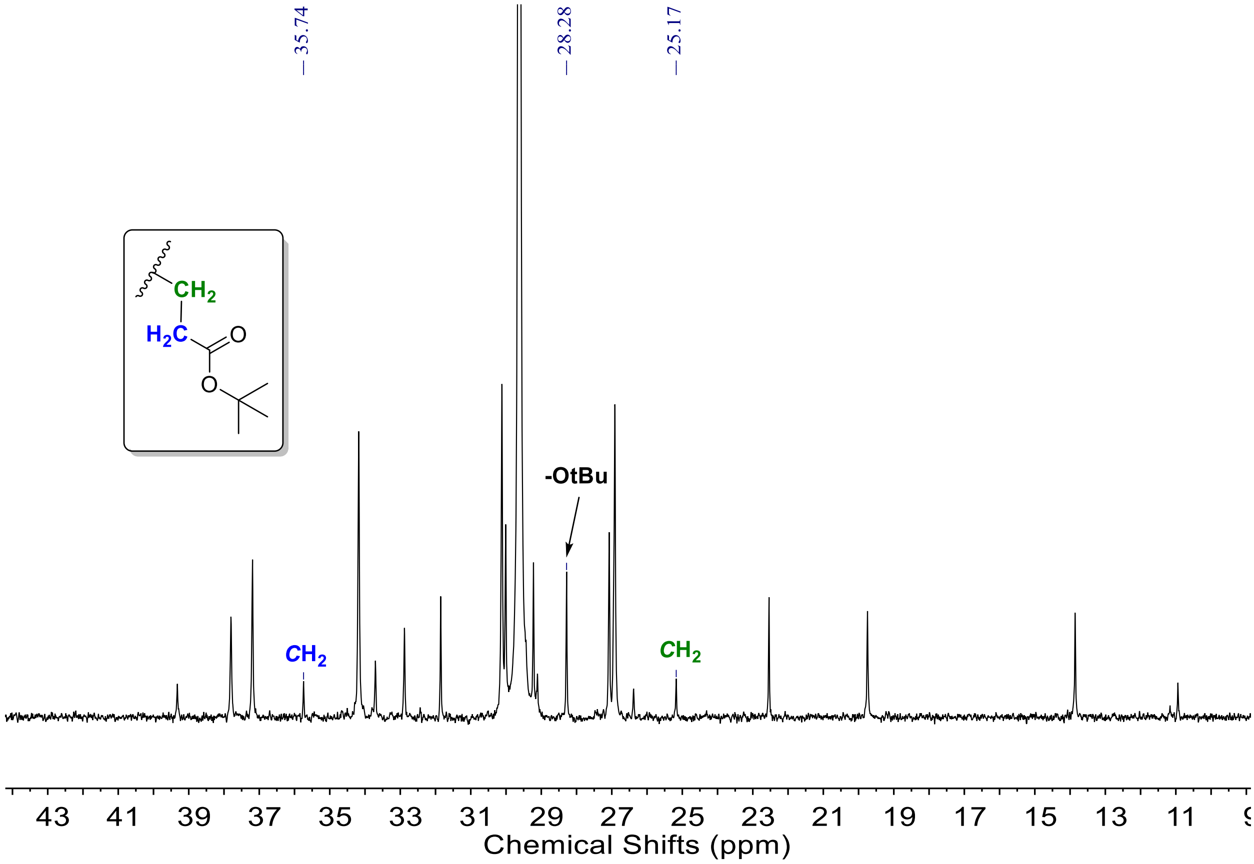


Figure S37. ^{13}C NMR ($C_2D_2Cl_4$, 110 °C) of E-tBB copolymer from table 2, entry 2. (enlarged)

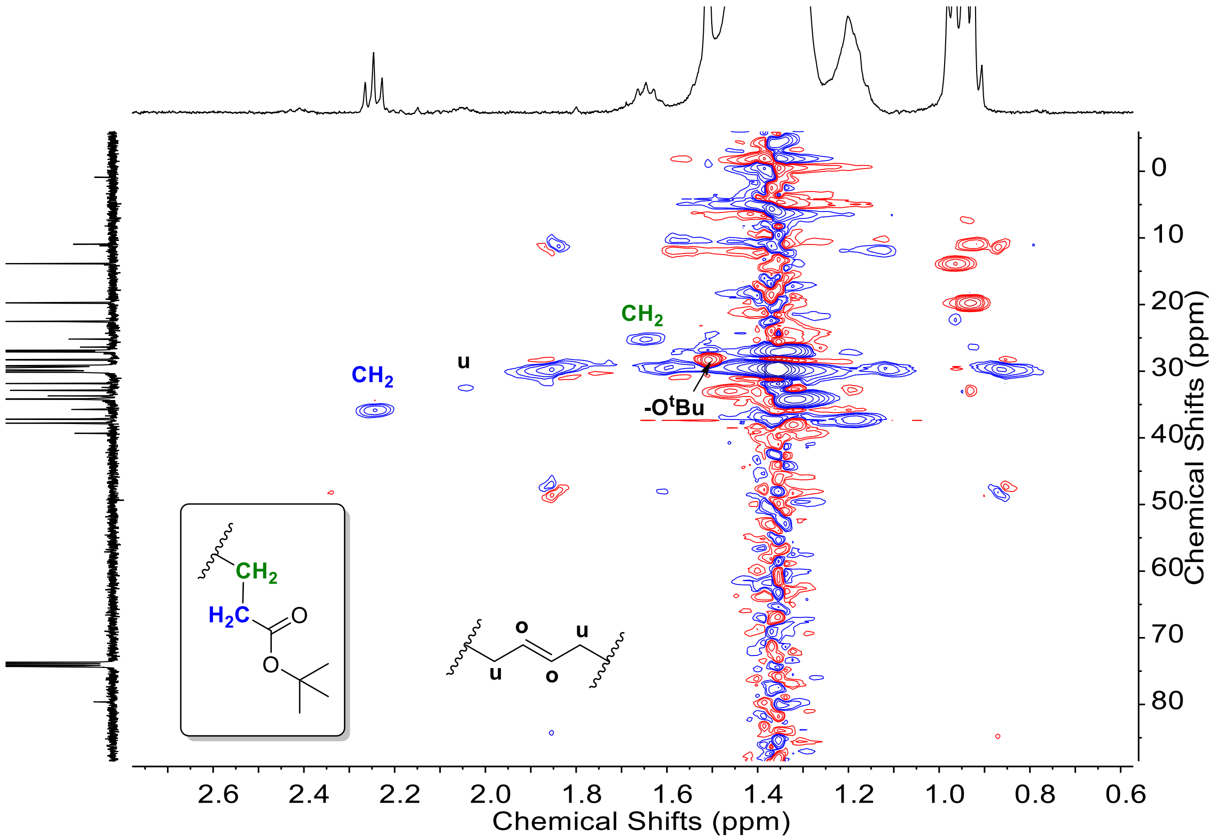


Figure S38. ^1H-^{13}C HSQC NMR ($C_2D_2Cl_4$, 110 °C) of E-tBB copolymer from table 2, entry 2. (enlarged)

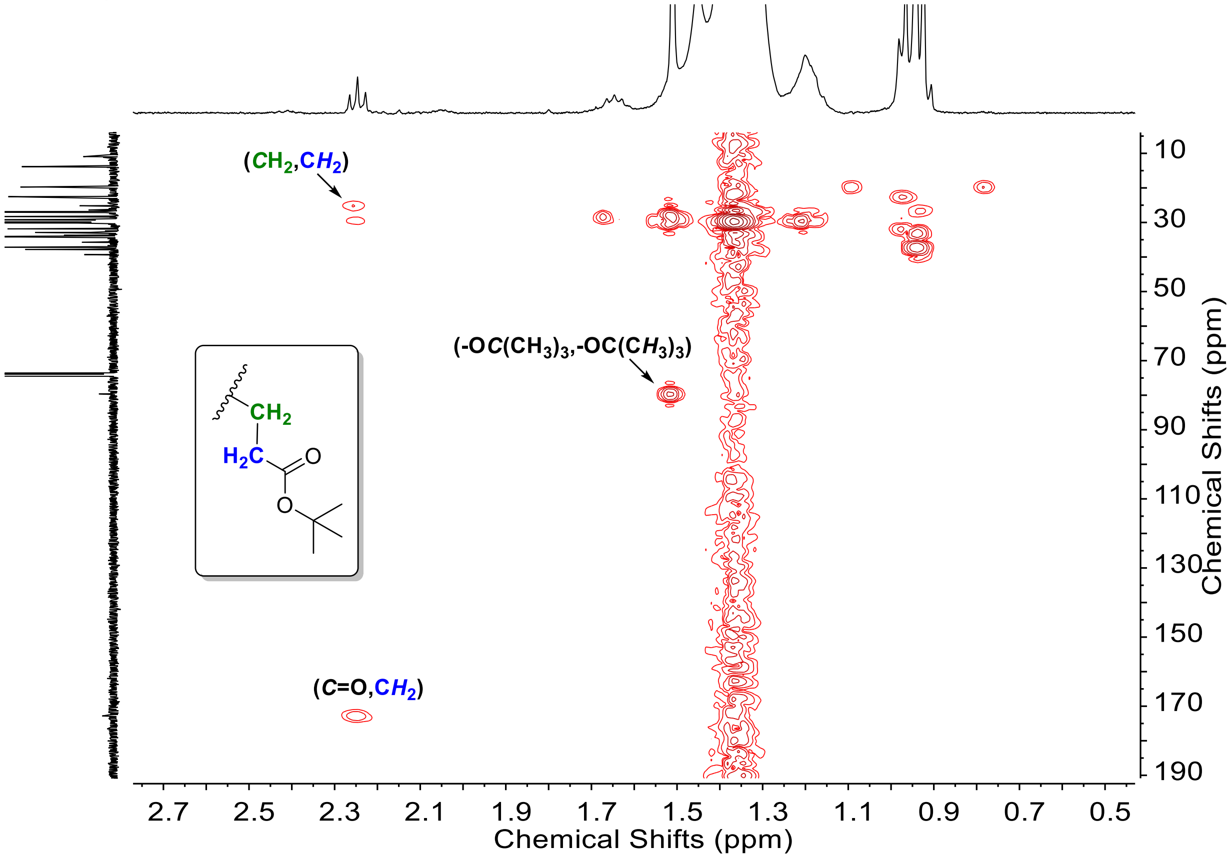


Figure S39. ^1H-^{13}C HMBC NMR ($C_2D_2Cl_4$, 110 °C) of E-tBB copolymer from table 2, entry 2. (enlarged)

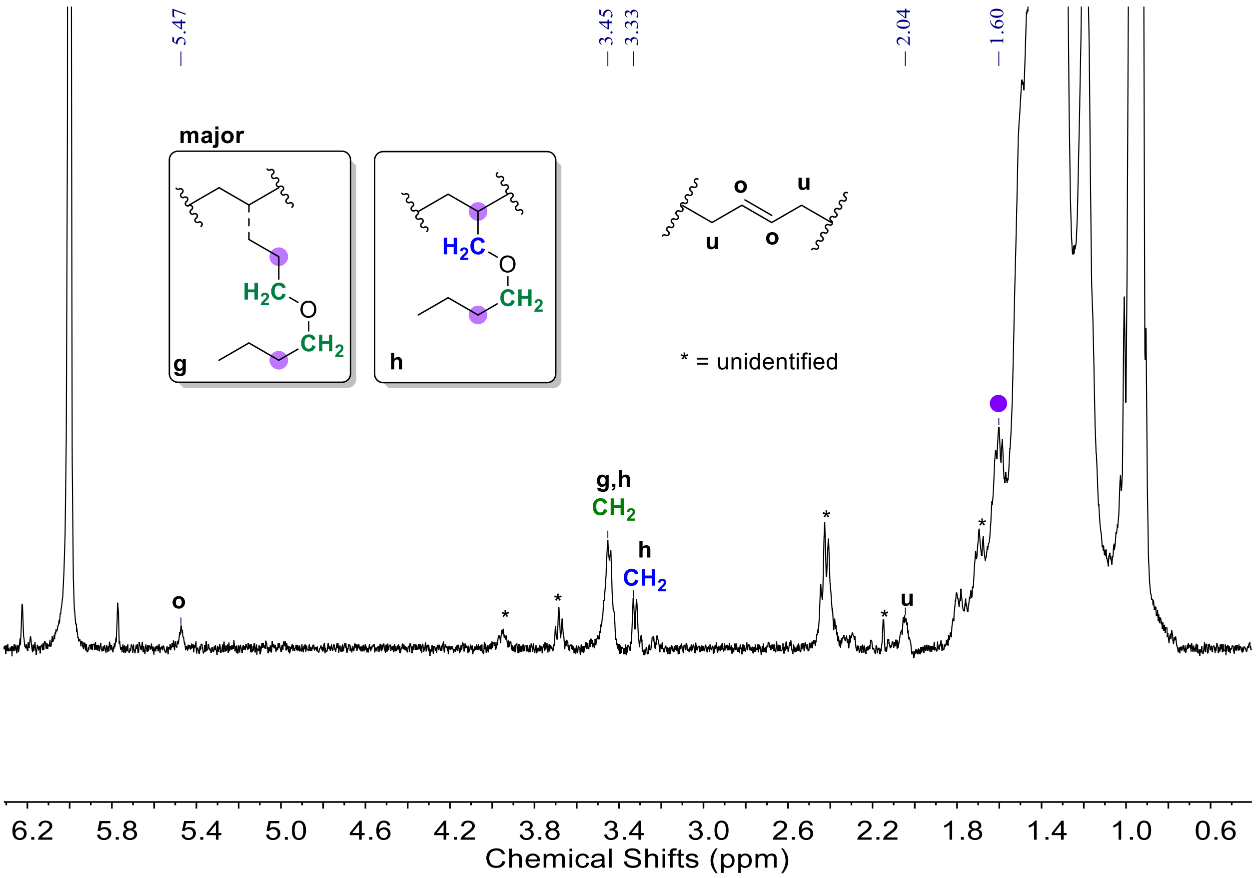


Figure S40. ^{1}H NMR ($C_2D_2Cl_4$, 110 °C) of E-BAE copolymer from table 2, entry 4.

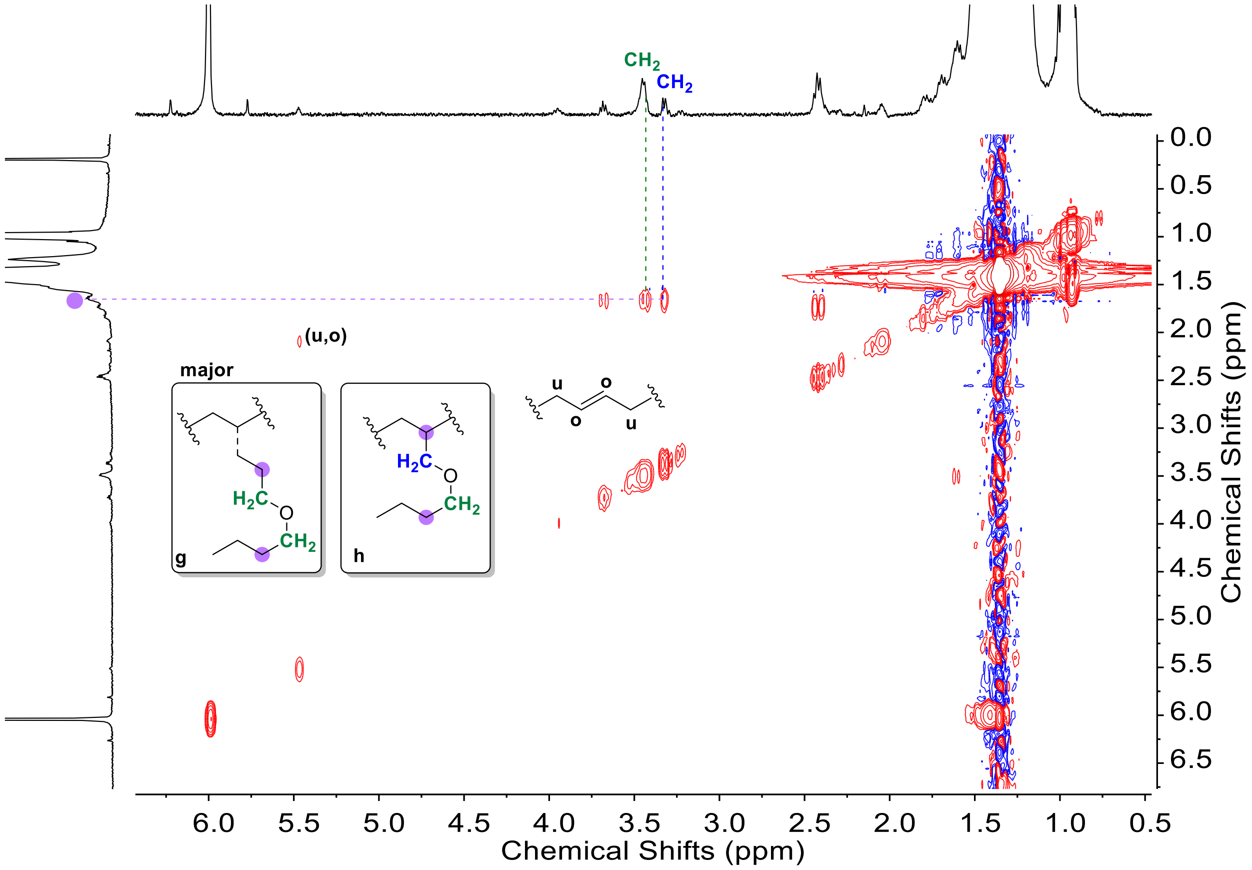


Figure S41. ^{1}H-^{1}H COSY NMR ($C_2D_2Cl_4$, 110 °C) of E-BAE copolymer from table 2, entry 4.

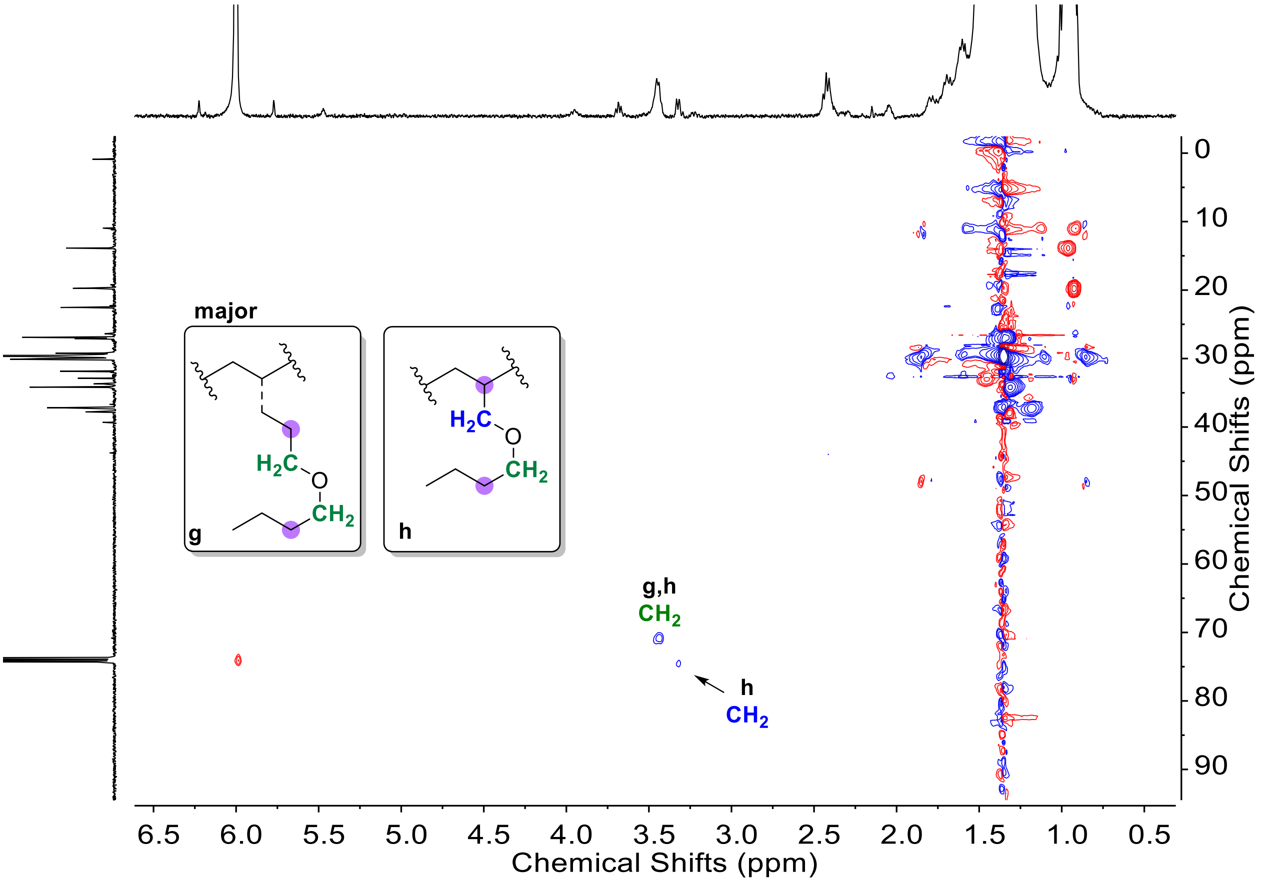


Figure S42. ^{1}H-^{13}C HSQC NMR ($C_2D_2Cl_4$, 110 °C) of E-BAE copolymer from table 2, entry 4.

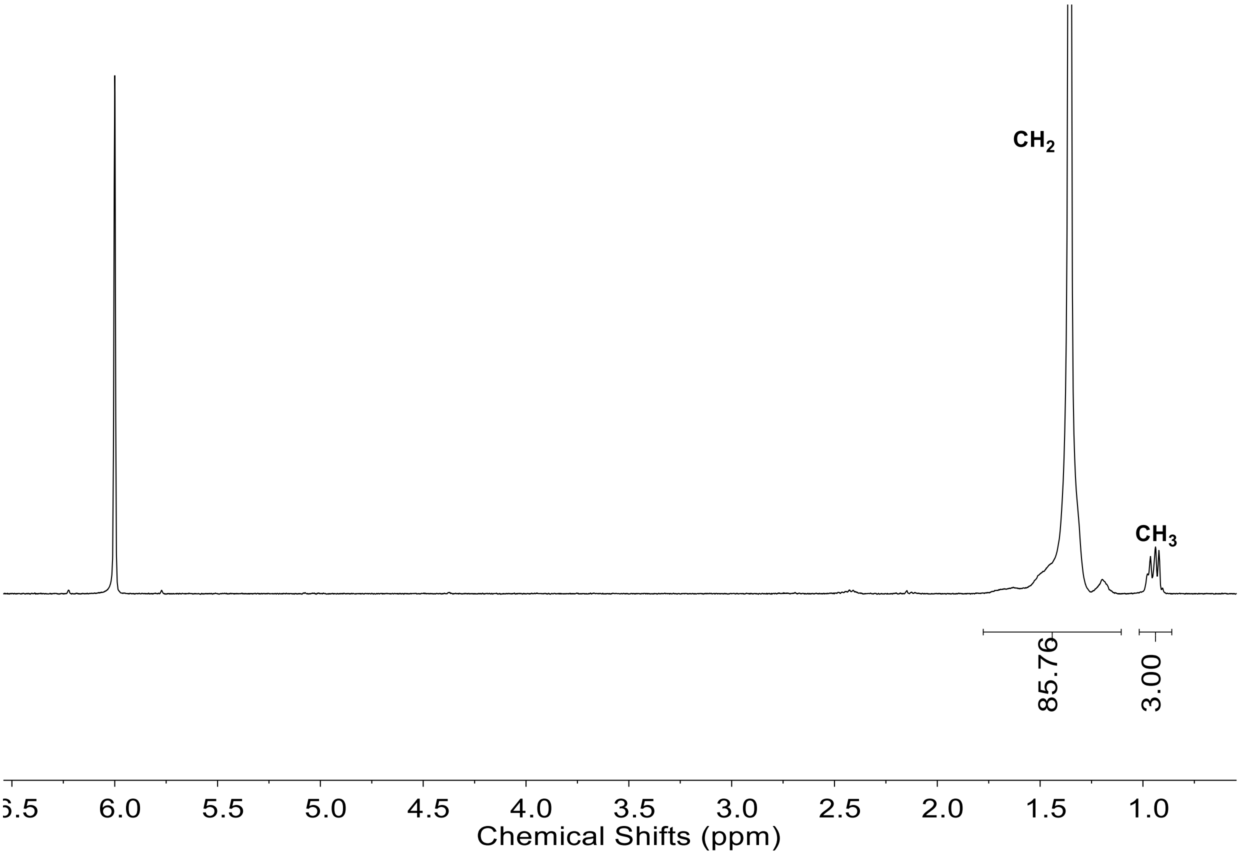


Figure S43. ^{1}H NMR ($C_2D_2Cl_4$, 110 °C) of E-ACl copolymer from table 2, entry 6. (no ACl incorporation)

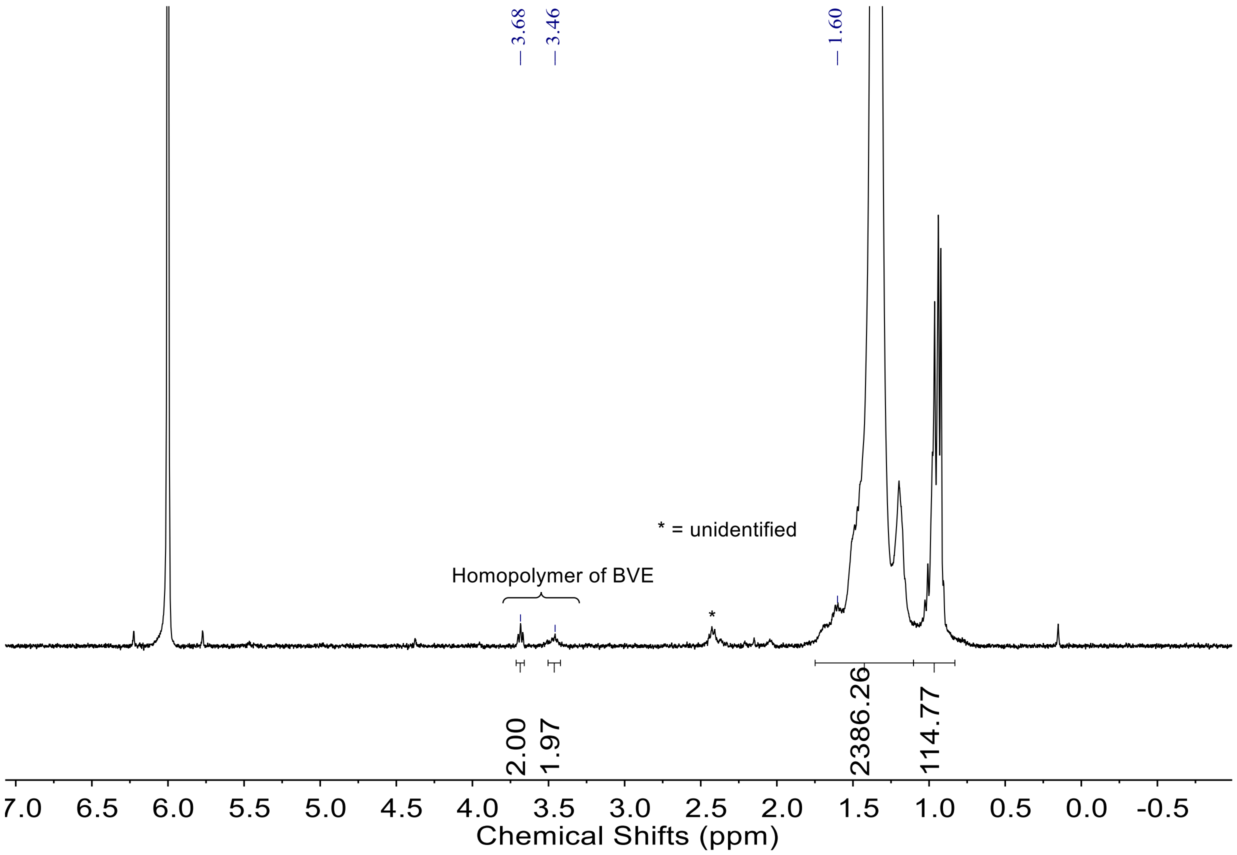


Figure S44. ^{1}H NMR ($C_2D_2Cl_4$, 110 °C) of E-BVE copolymer from table 2, entry 8. (no BVE incorporation)

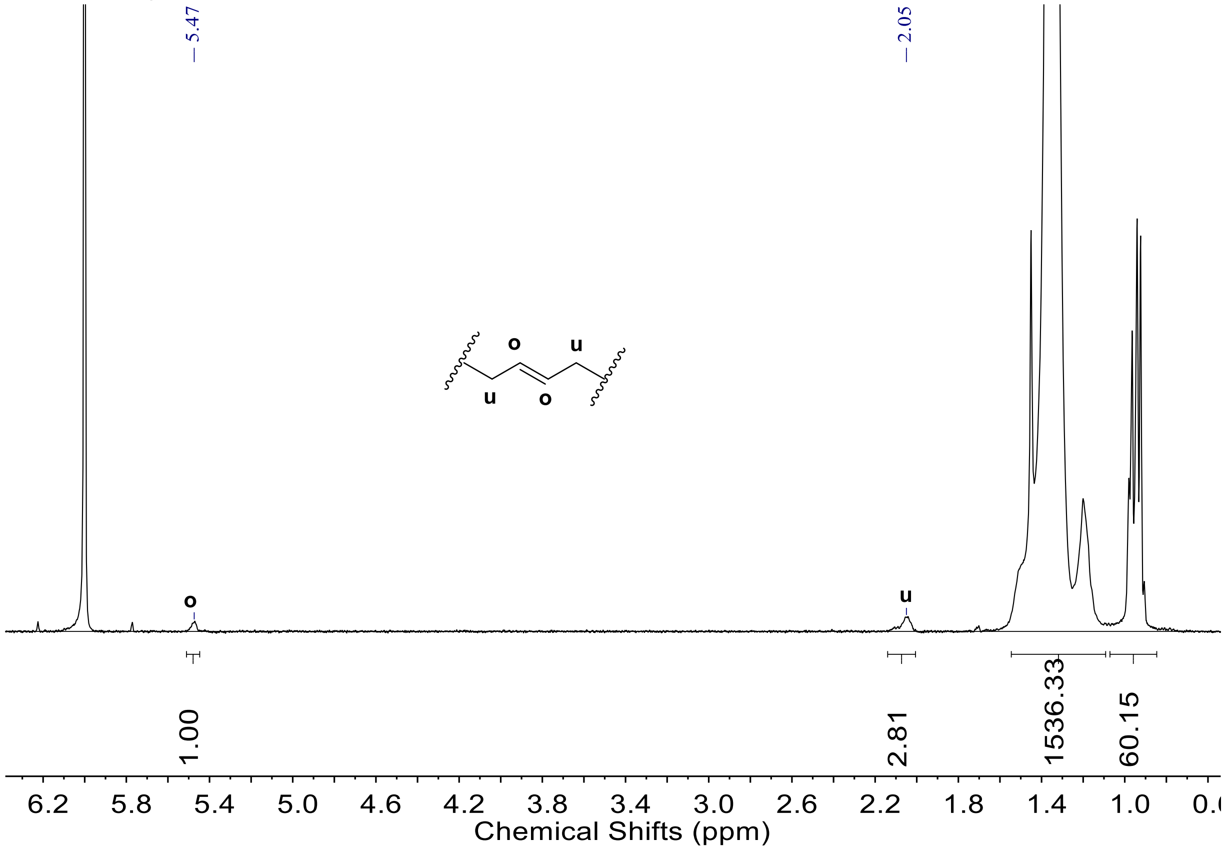


Figure S45. ^{1}H NMR ($C_2D_2Cl_4$, 110 °C) of E-AA copolymer from table 2, entry 10. (no AA incorporation)

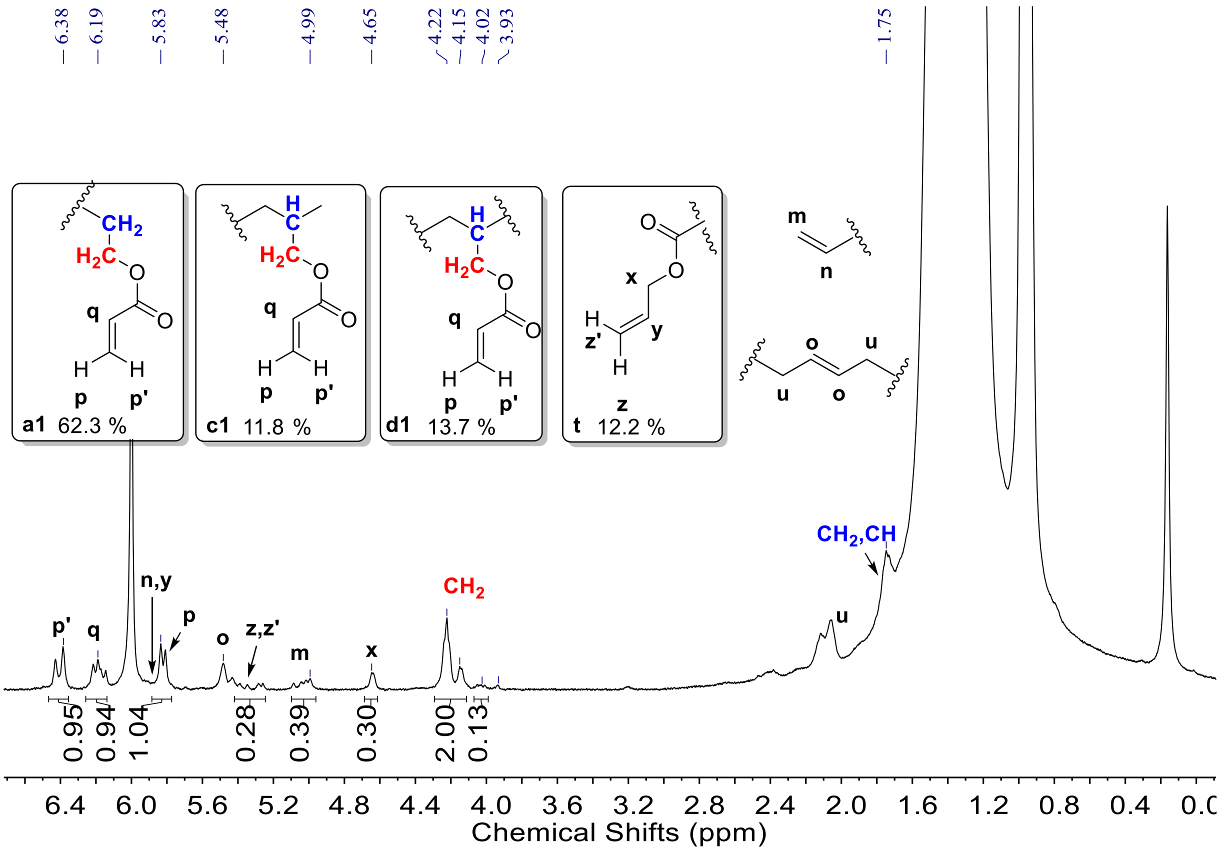


Figure S46. ^{1}H NMR ($C_2D_2Cl_4$, 110 °C) of E-AIA copolymer from table 2, entry 12. (Assignment was according to a report of Claverie [5])

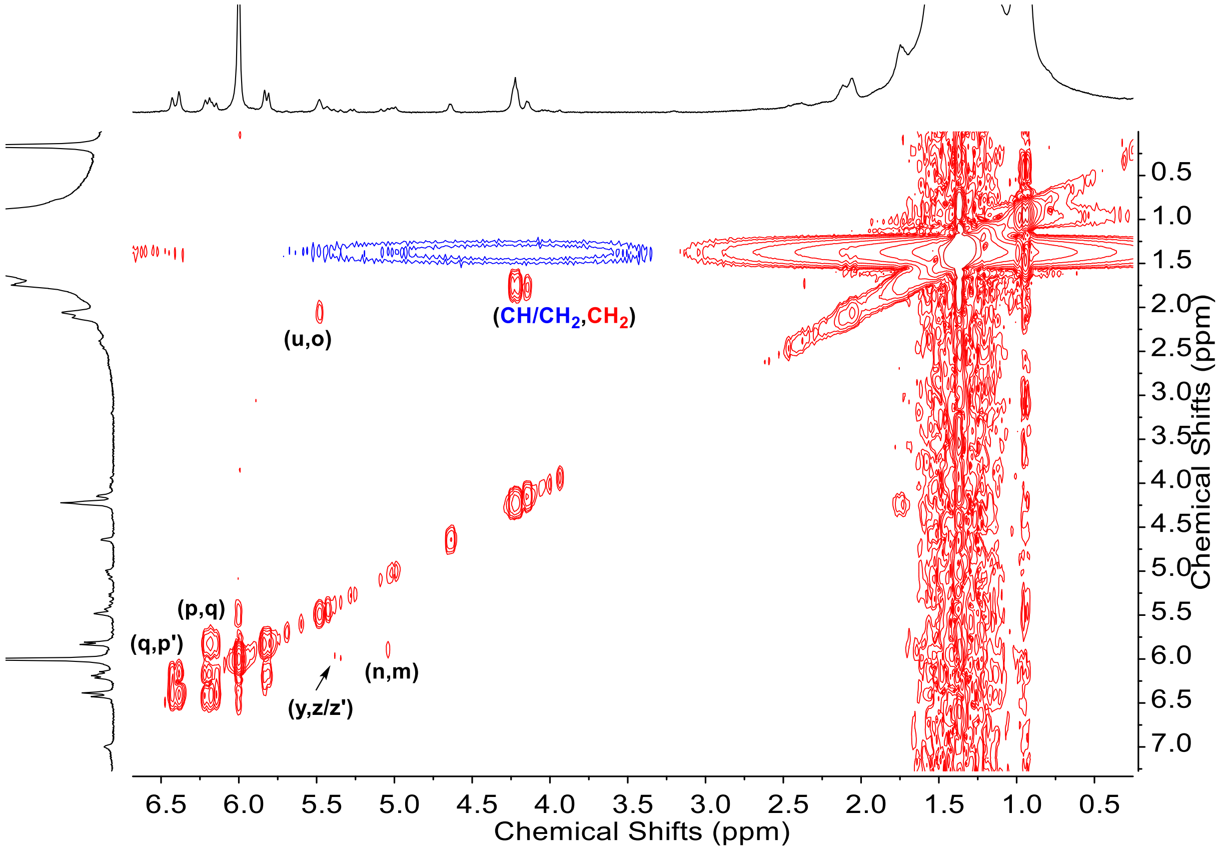


Figure S47. ^{1}H-^{1}H COSY NMR ($C_2D_2Cl_4$, 110 °C) of E-AIA copolymer from table 2, entry 12.

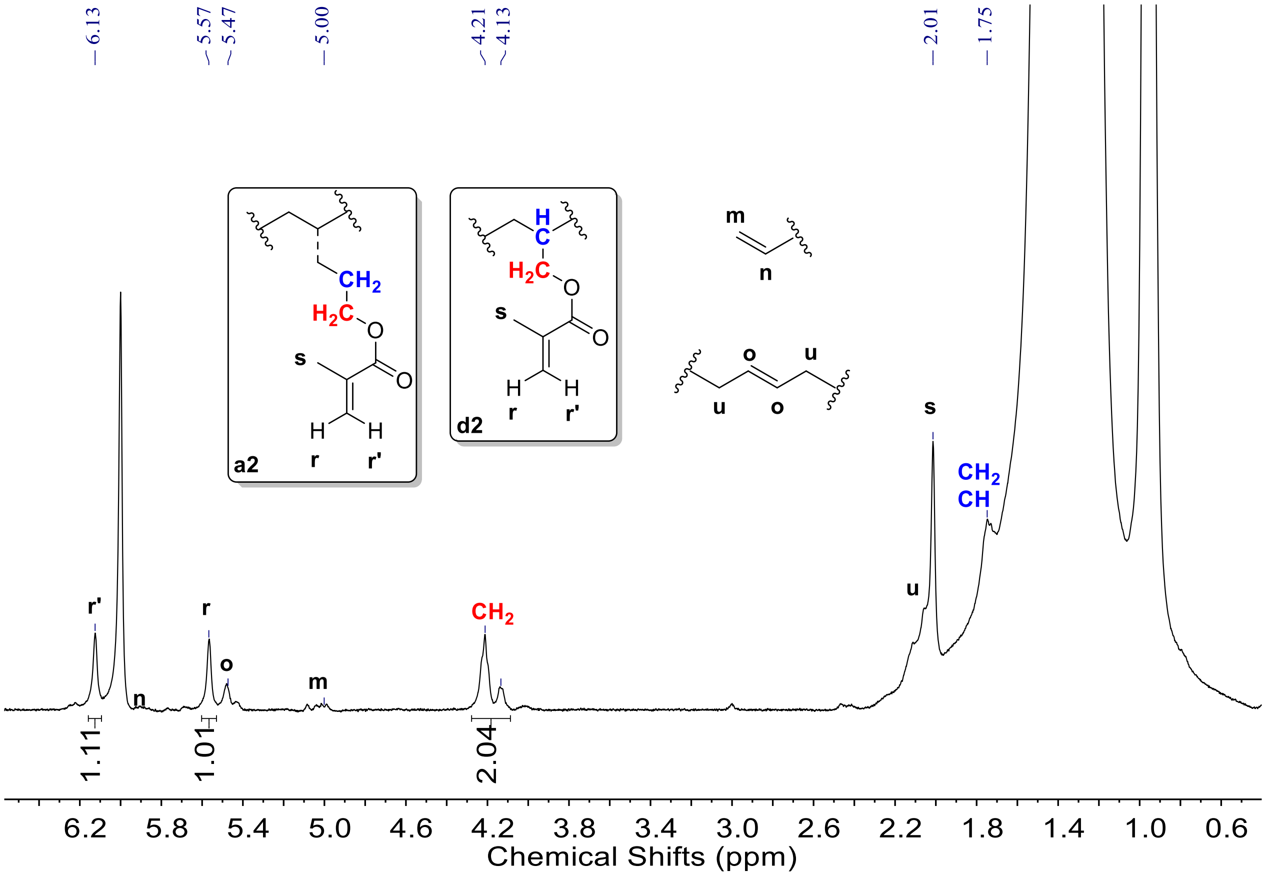


Figure S48. ^{1}H NMR ($C_2D_2Cl_4$, 110 °C) of E-AMA copolymer from table 2, entry 14.

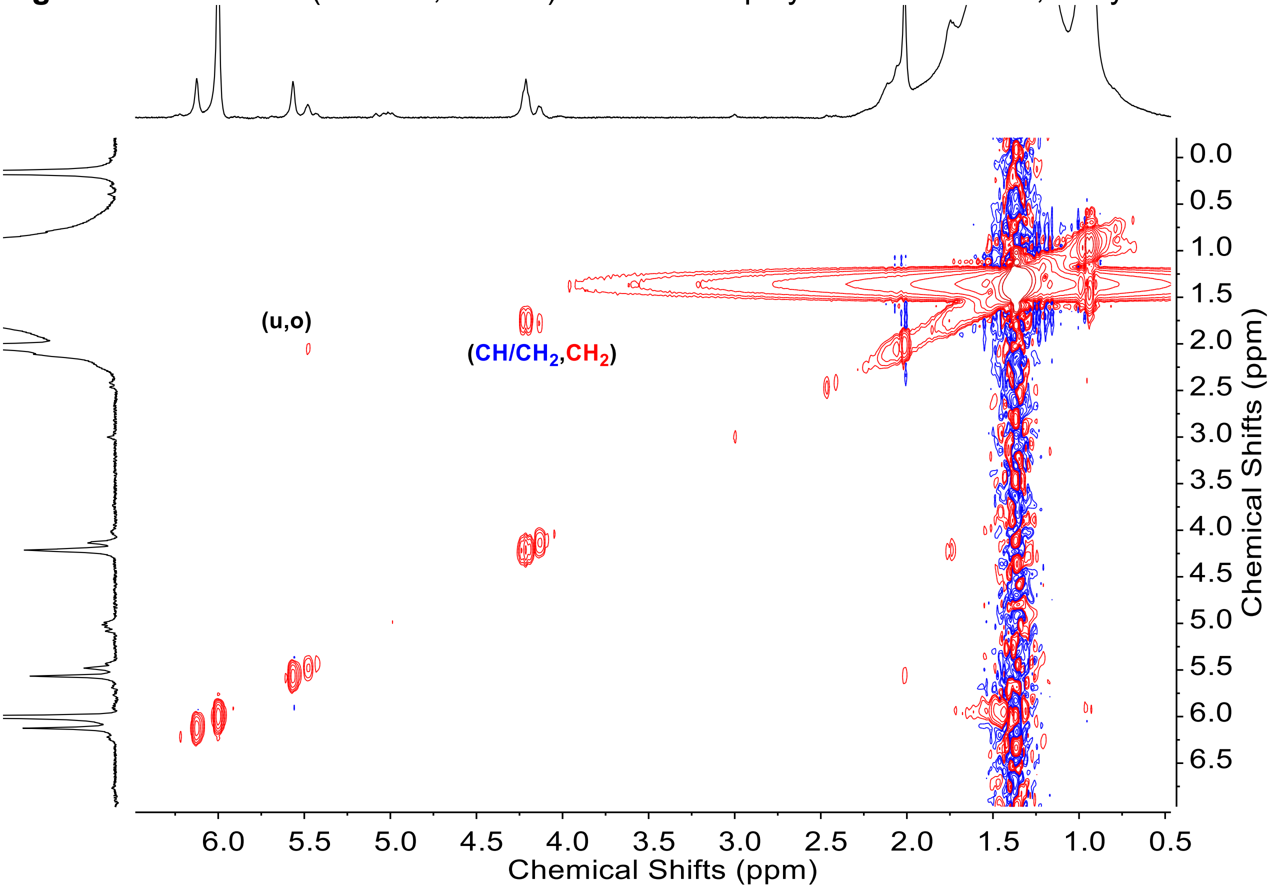


Figure S49. ^{1}H NMR ($C_2D_2Cl_4$, 110 °C) of E-AMA copolymer from table 2, entry 14.

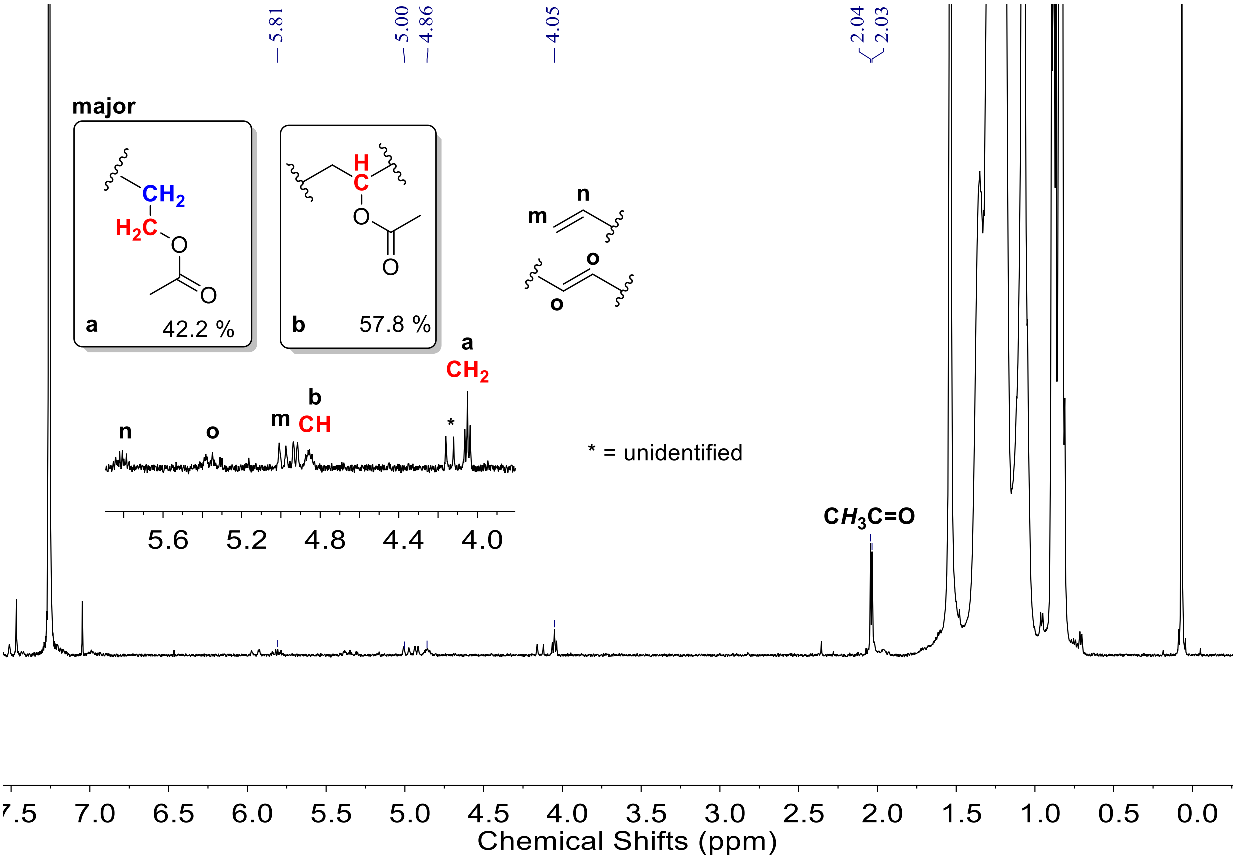


Figure S50. ^{1}H NMR ($CDCl_3$, 25 °C) of E-VAc copolymer from table 2, entry 20.

4. FT-IR spectra of Polymers

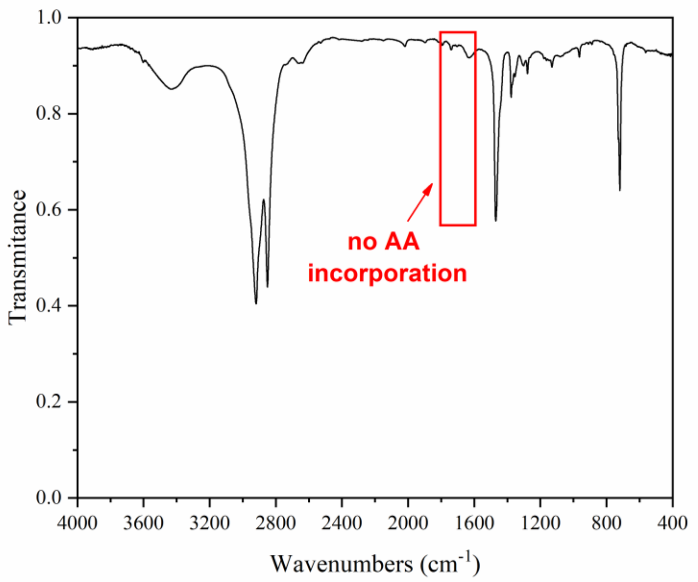


Figure S51. FT-IR (ATR) of E-AA copolymer from table 2, entry 10 (no AA incorporation)

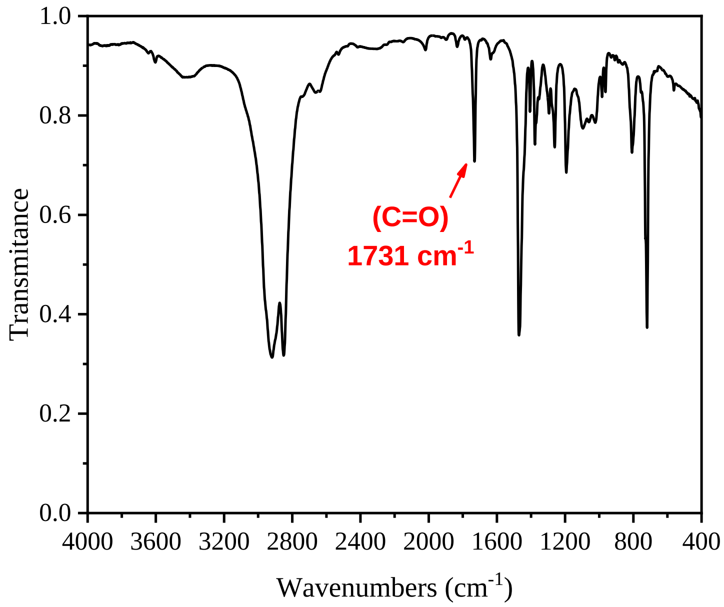


Figure S52. FT-IR (ATR) of E-AIA copolymer from table 2, entry 12 (acyclic incorporation)

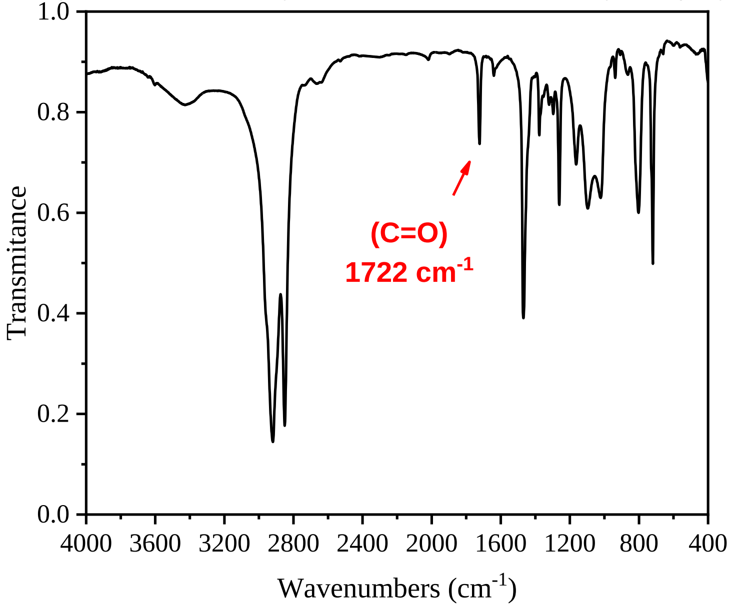
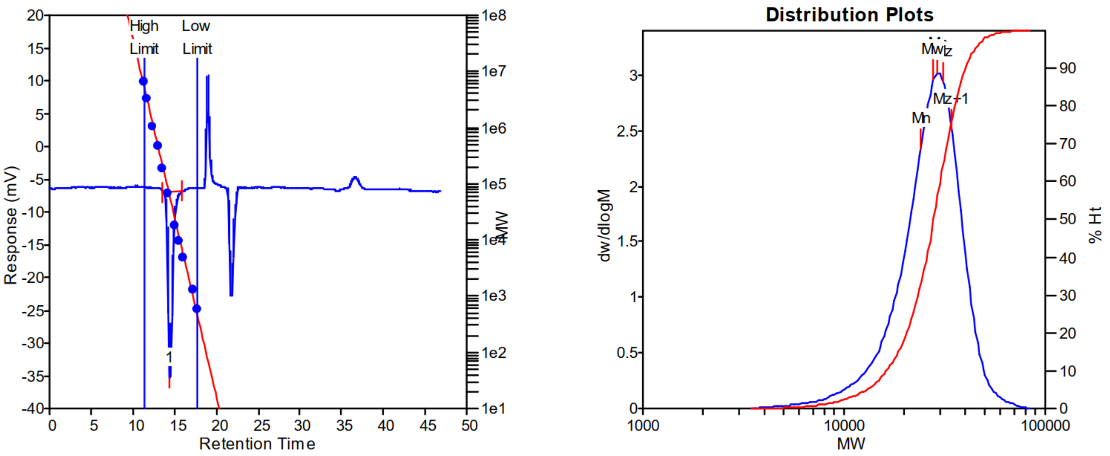


Figure S53. FT-IR (ATR) of E-AMA copolymer from table 2, entry 14 (acyclic incorporation)

5. GPC of Polymers



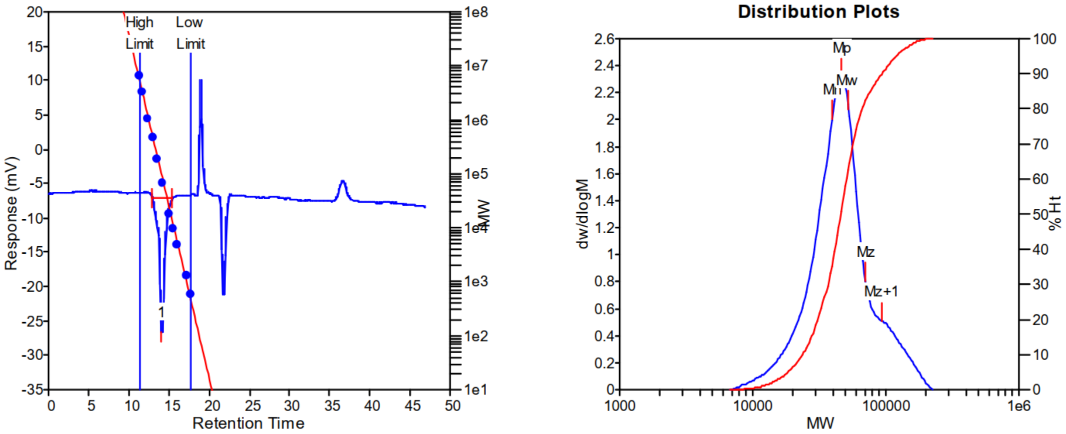
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	29396	24069	28005	31303	34434	27538	1.16353

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.60	14.33	15.83	-28.3204	100	913.603	100

Figure S54. GPC trace of the copolymer from table 1, entry 1.



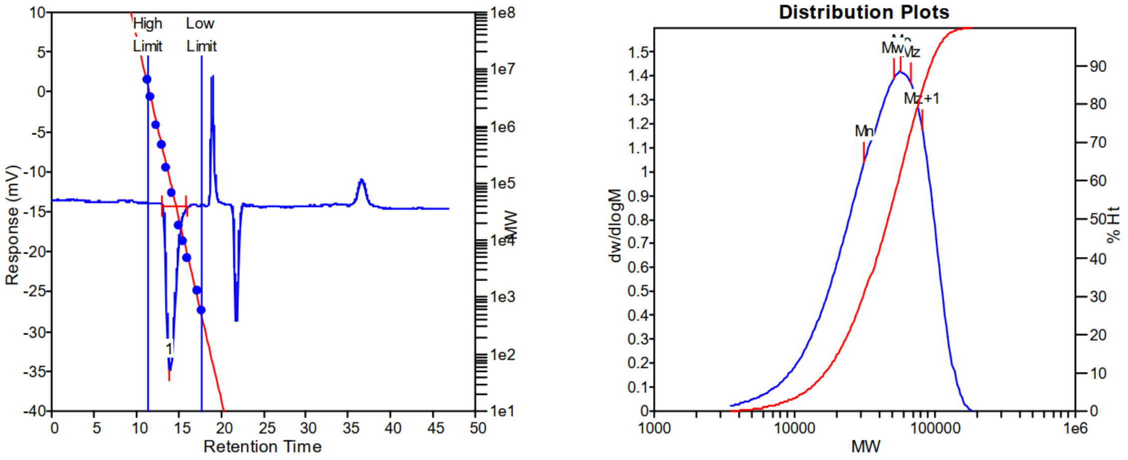
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	46090	39239	52409	70453	93621	50351	1.33564

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.90	14.02	15.37	-19.5197	100	820.119	100

Figure S55. GPC trace of the copolymer from table 1, entry 11.



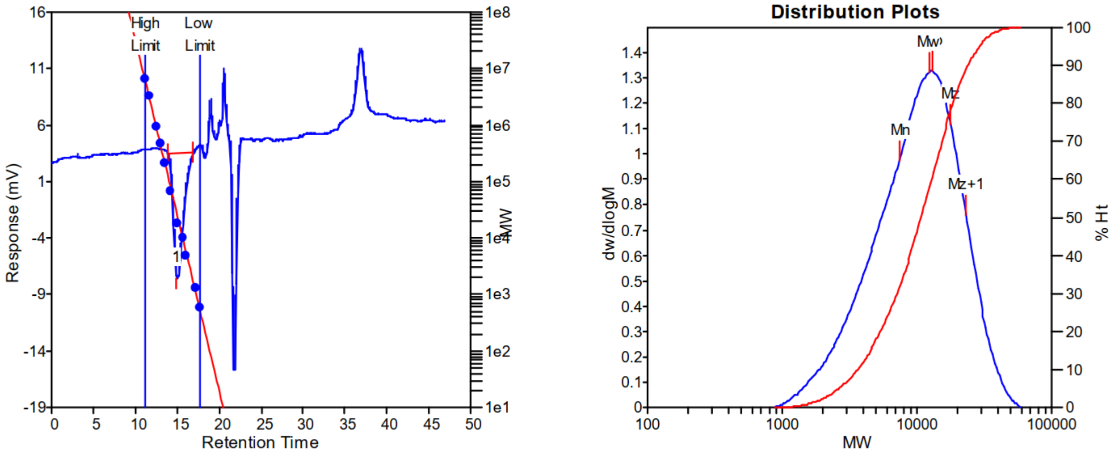
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	57033	31589	50462	67659	81811	48069	1.59745

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.05	13.87	15.83	-20.6227	100	1417.85	100

Figure S56. GPC trace of the copolymer from table 1, entry 17.



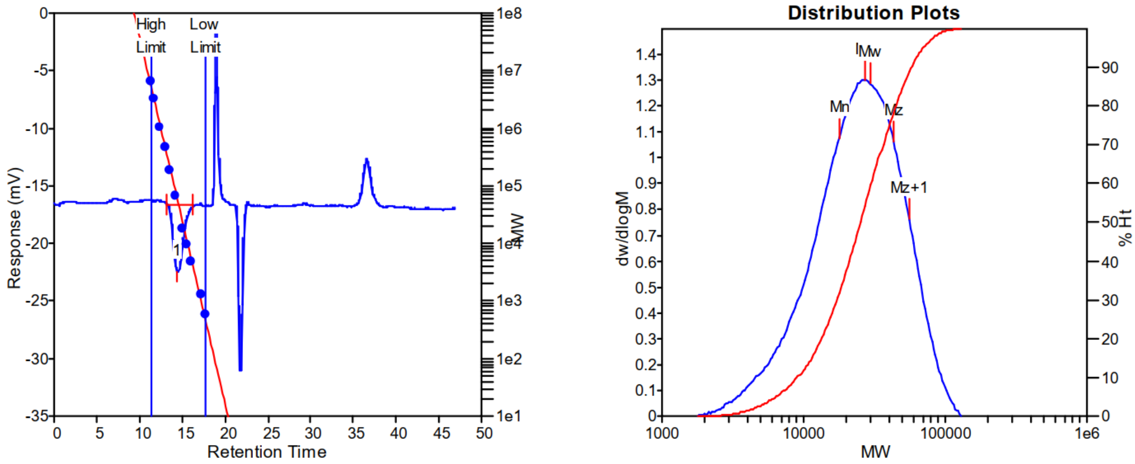
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	12982	7410	12437	17974	23288	11727	1.67841

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.83	14.92	16.85	-11.1312	100	835.037	100

Figure S57. GPC trace of the copolymer from table 1, entry 21.



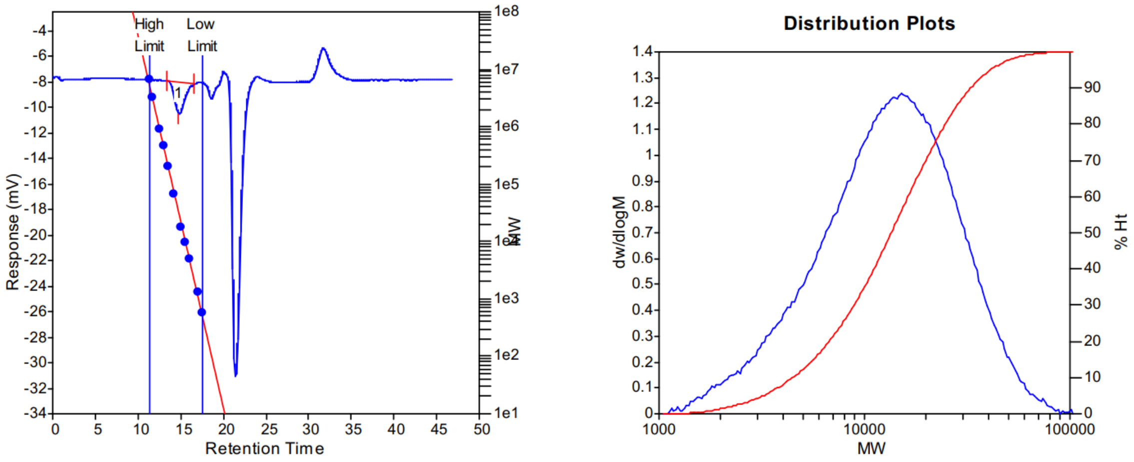
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	27380	17788	29699	42842	55480	28023	1.66961

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.28	14.38	16.30	-5.81545	100	434.325	100

Figure S58. GPC trace of the copolymer from table 1, entry 23.



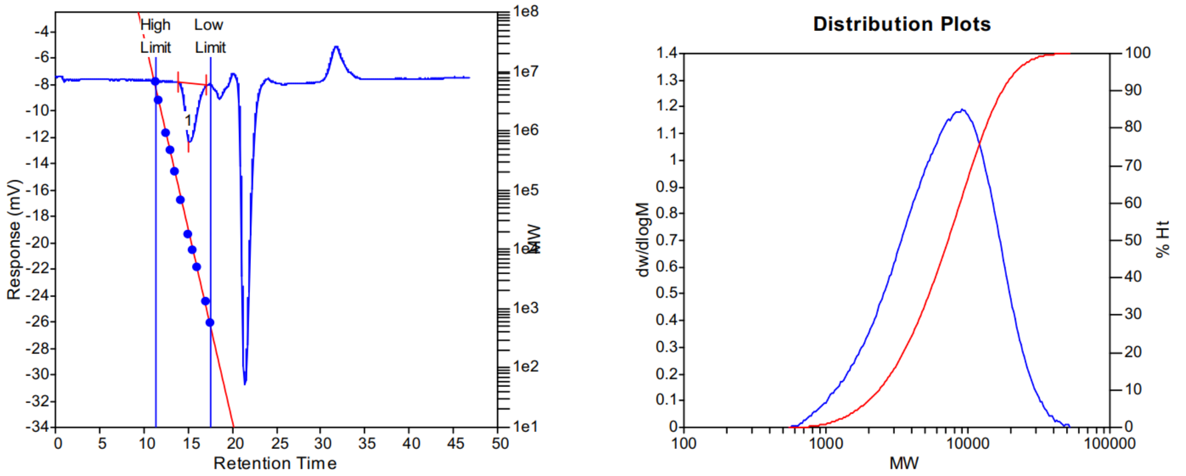
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	15143	9208	16463	25566	35554	15376	1.7879

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.38	14.72	16.57	-2.46444	100	189.941	100

Figure S59. GPC trace of the copolymer from table 1, entry 26.



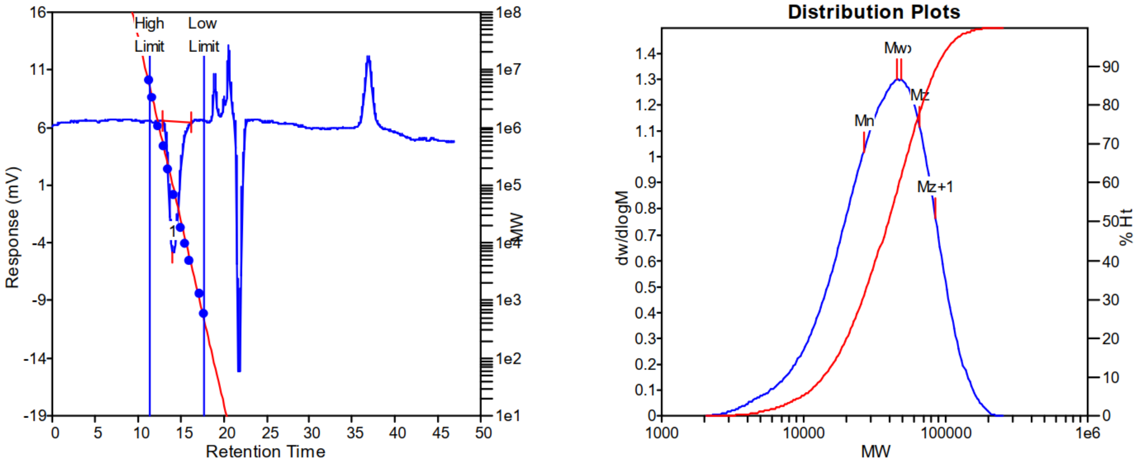
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	9132	4896	8805	13601	18615	8222	1.79841

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.87	15.07	17.02	-4.49339	100	360.785	100

Figure S60. GPC trace of the copolymer from table 1, entry 27.



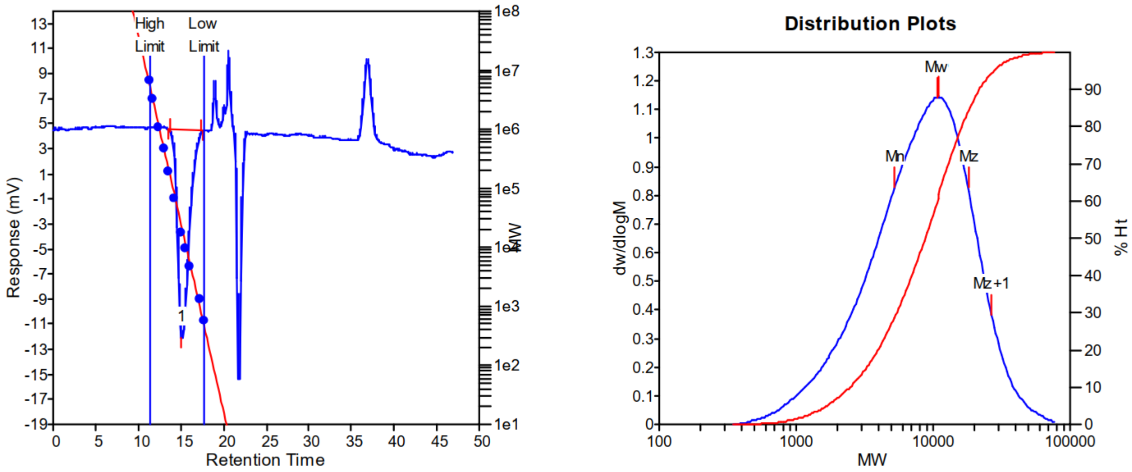
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	48324	26594	45404	65545	85138	42822	1.7073

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.82	14.03	16.20	-11.3975	100	853.555	100

Figure S61. GPC trace of the copolymer from table 2, entry 2.



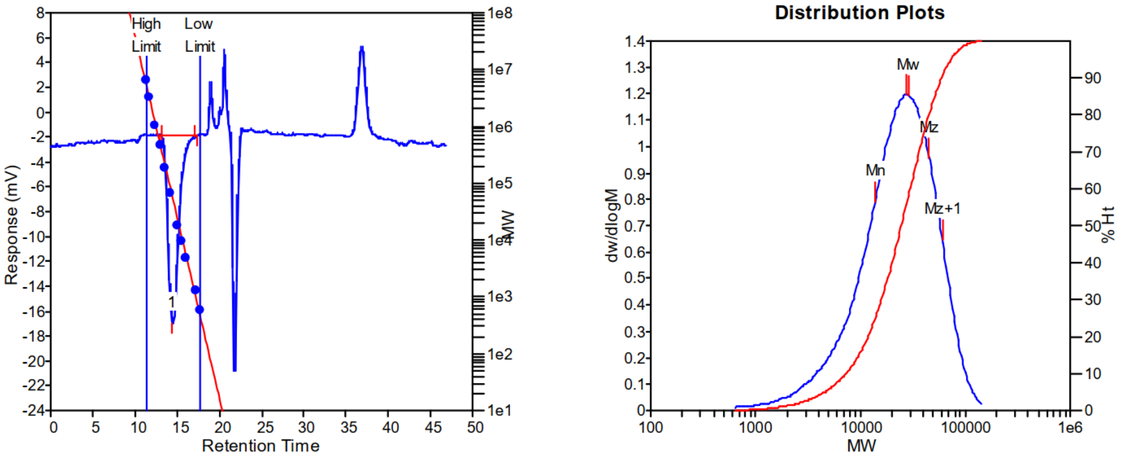
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	10877	5265	10840	18099	26825	10005	2.05888

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.65	15.03	17.45	-16.644	100	1415.41	100

Figure S62. GPC trace of the copolymer from table 2, entry 4.



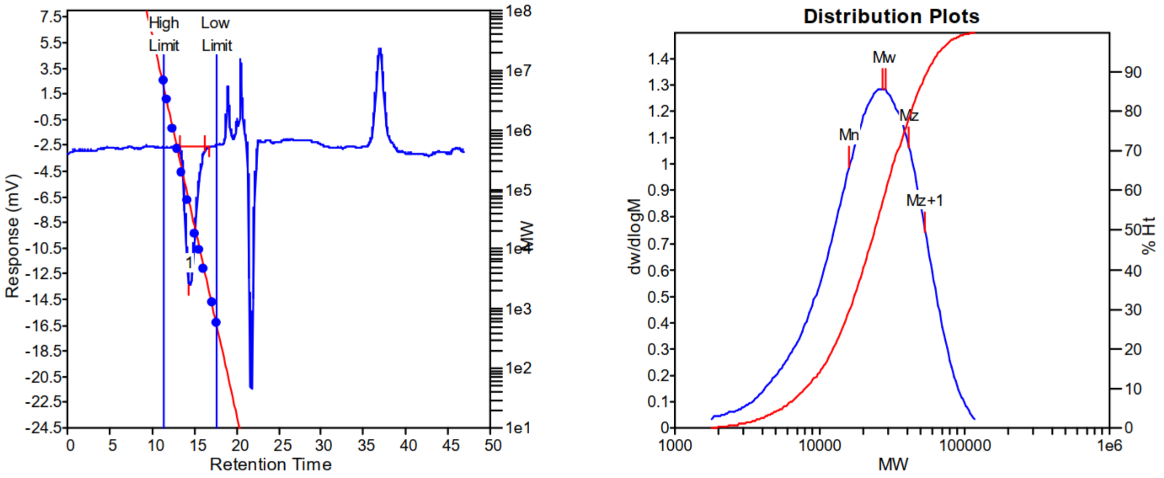
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	27380	13876	29543	45450	60676	27515	2.12907

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.23	14.38	17.03	-15.1104	100	1228.73	100

Figure S63. GPC trace of the copolymer from table 2, entry 12.



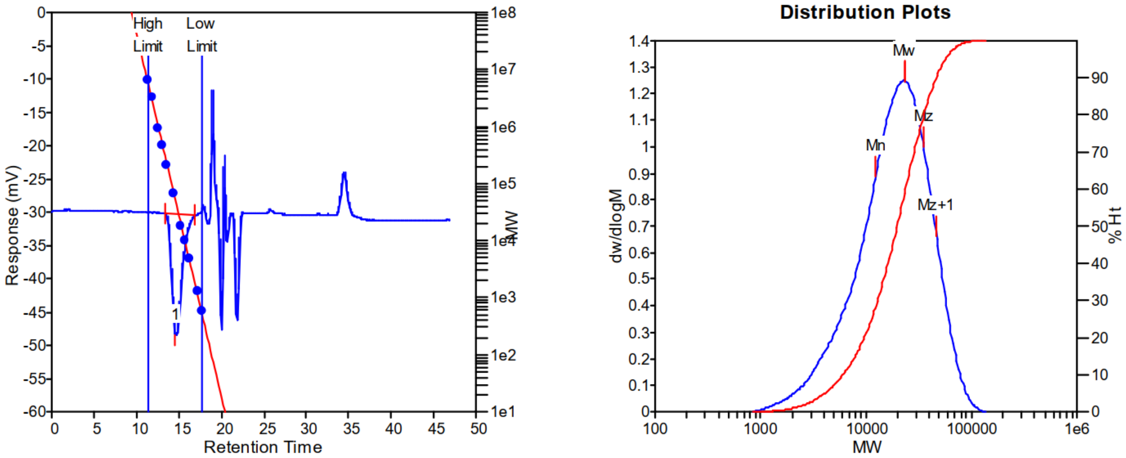
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	27380	16004	28199	41218	53626	26527	1.762

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.35	14.38	16.30	-10.7531	100	812.722	100

Figure S64. GPC trace of the copolymer from table 2, entry 14.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	23232	12399	23404	35295	46925	21895	1.88757

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.32	14.57	16.90	-18.1942	100	1418.94	100

Figure S65. GPC trace of the copolymer from table 2, entry 18.

6. References

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5. J.-C. Daigle, L. Piche, A. Arnold and J. P. Claverie, *Acs Macro Lett.*, 2012, **1**, 343-346.