Electronic Supplementary Information (ESI)

Coordination-insertion polymerization of polar allylbenzene monomers

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Contents

General Procedures and Materials: 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 monomers 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 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 ℃. Melting points (*Tm*) of copolymers were measured through DSC analyses, which were carried out on a Q 100 DSC from TA Instruments under a nitrogen atmosphere at heating and cooling rates of 10 °C/min (temperature range: 20−180 °C).

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Materials: [(2,6-^{i}PrC$_6$H$_3$NC(Me)C(Me)N-2,6-^{i}PrC$_6$H$_3$)Pd(CH$_3$)(Cl)][1], Pd(P(C$_6$H$_4$OCH$_3$)$_2$-C$_6$H$_4$SO$_3$)(CH$_3$)(DMSO)[2], Pd(P(C$_6$H$_{11}$)$_2$C$_6$H$_4$SO$_3$)(CH$_3$)(SO(CH$_3$)$_2$)[3], 2-methoxy allylbenzene[4], 2-acetoxy allylbenzene[5], 2-allylbenzaldehyde[6], 2-allylbromobenzene[6] and 2-(*N*,*N*-dimethylamino) allylbenzene[7] were prepared according to the literature procedures. All other reagents were commercially available and used as received.

A general procedure for the copolymerization of polar monomer with ethylene.

In a typical experiment, a 150 mL glass pressure reactor connected with a high pressure gas line was firstly dried at 90 ℃ under vacuum for at least 1 h. The glass reactor was then adjusted to the desired polymerization temperature. 23 mL of toluene and the desired polar allylbenzene monomer were added to the reactor under N_2 atmosphere, then the desired amount of Pd(II) catalyst in 2 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 the desired pressure of ethylene. After 1 h, the pressure reactor was vented and the copolymer was precipitated in ethanol, filtered and dried at 50 ℃ for at least 24 h under vacuum.

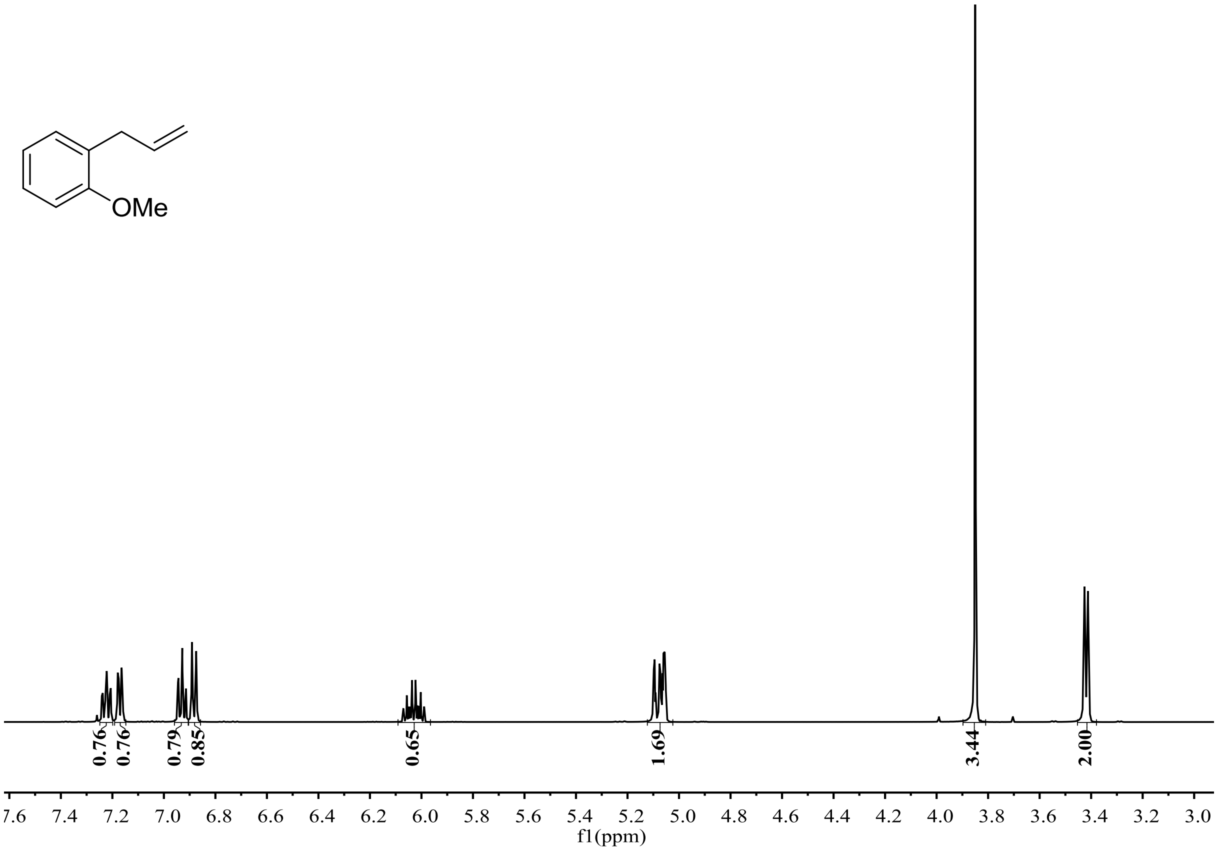


Figure S1. ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of **2-methoxy allylbenzene**.

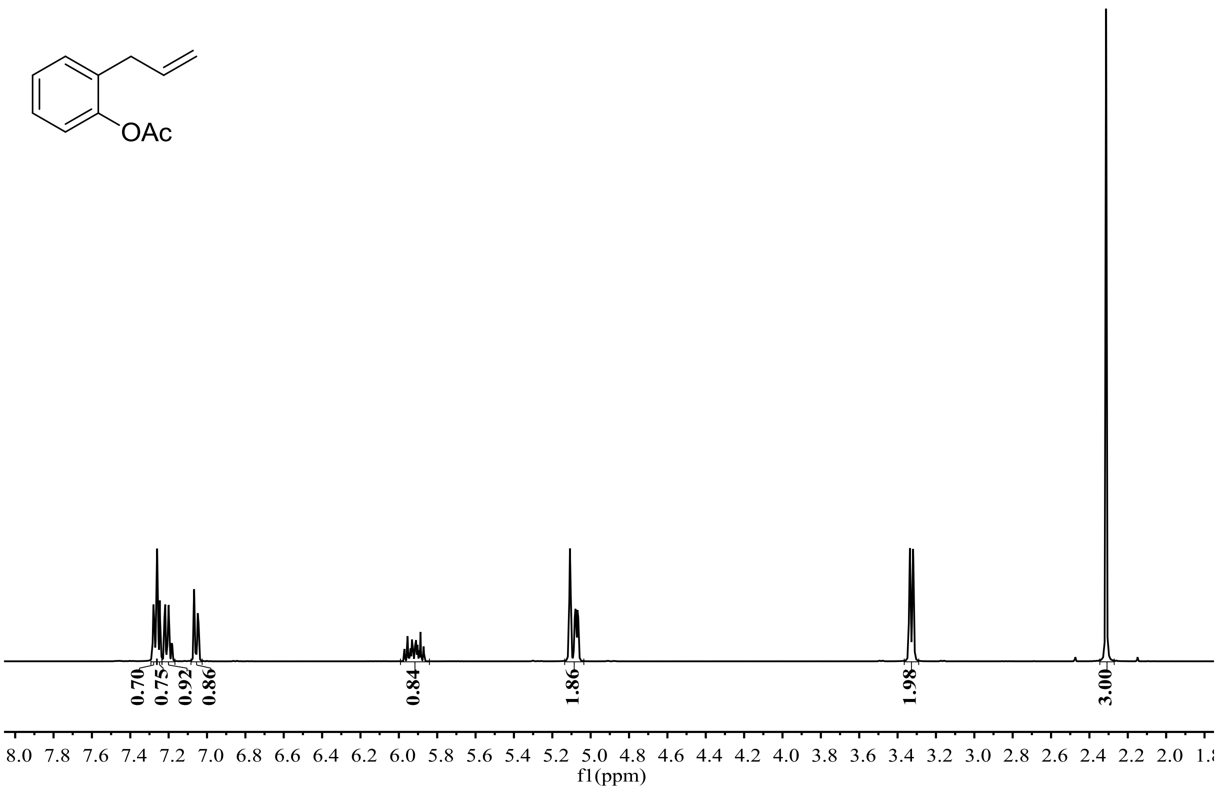


Figure S2. ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of **2-acetoxy allylbenzene**.

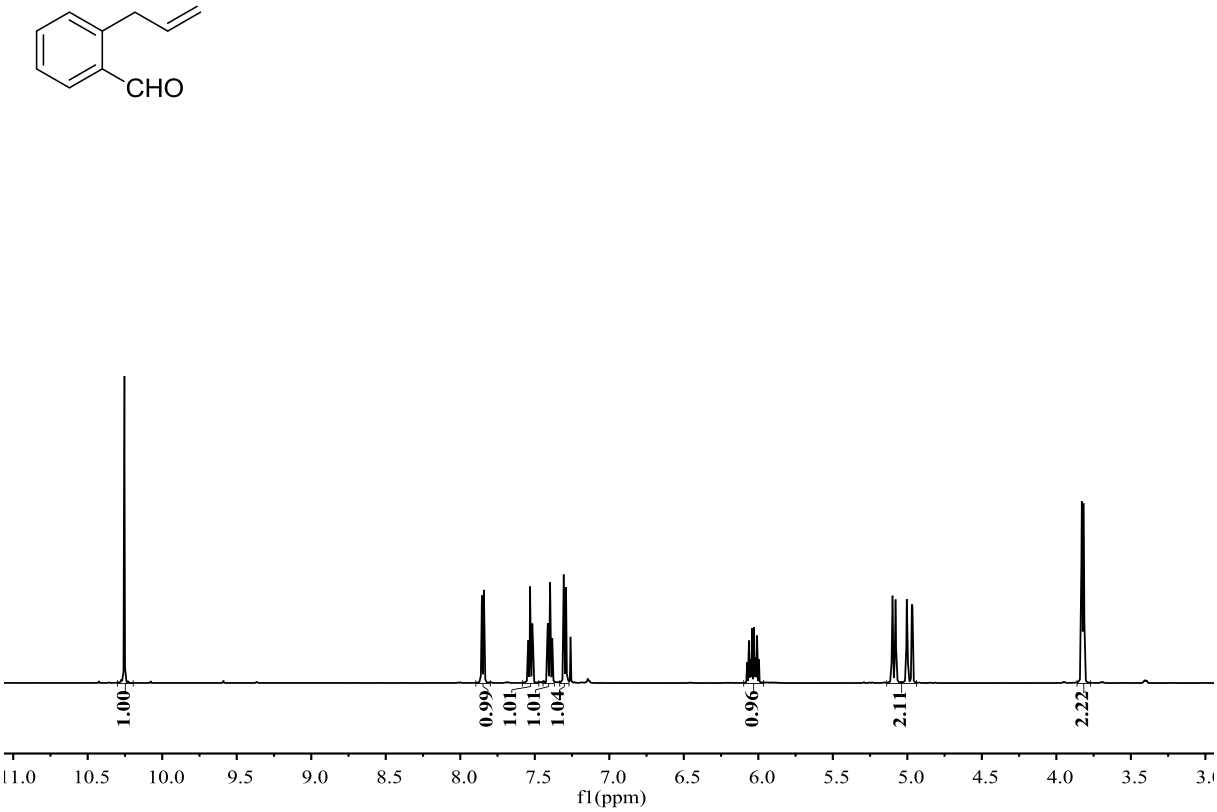


Figure S3. ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of **2-allylbenzaldehyde**.

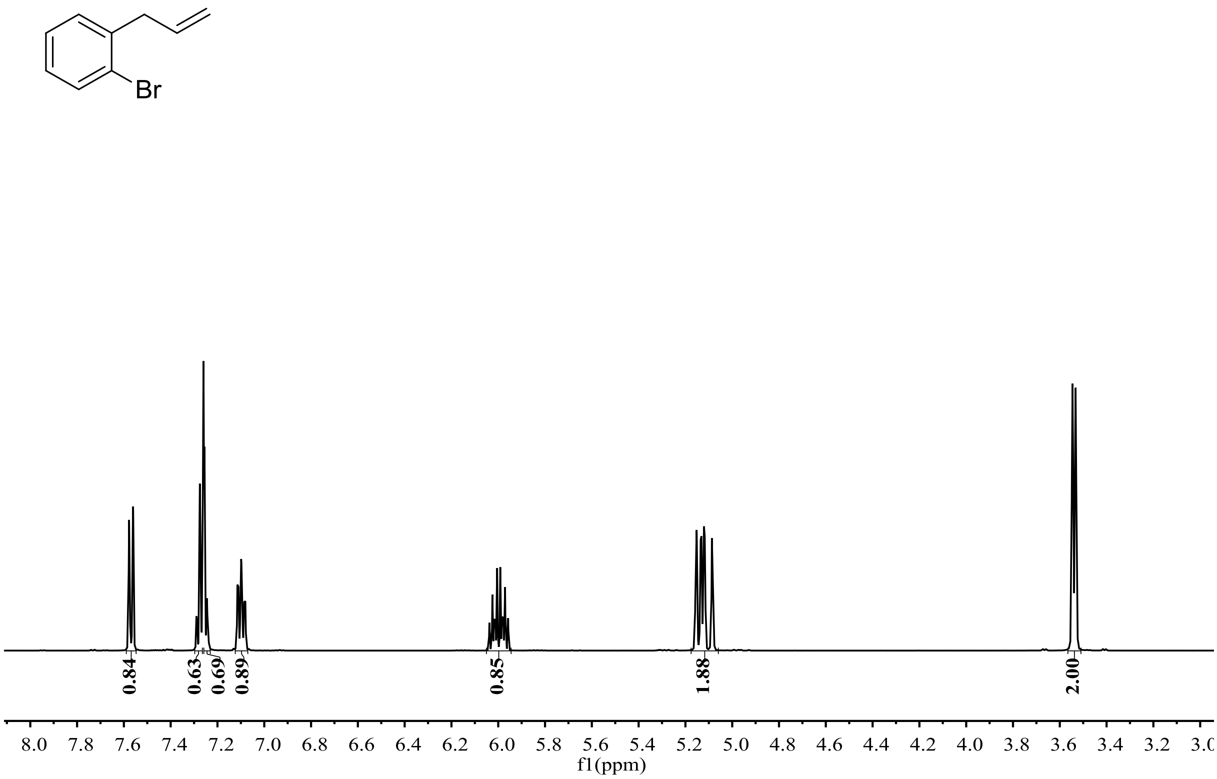


Figure S4. ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of **2-allylbromobenzene**.

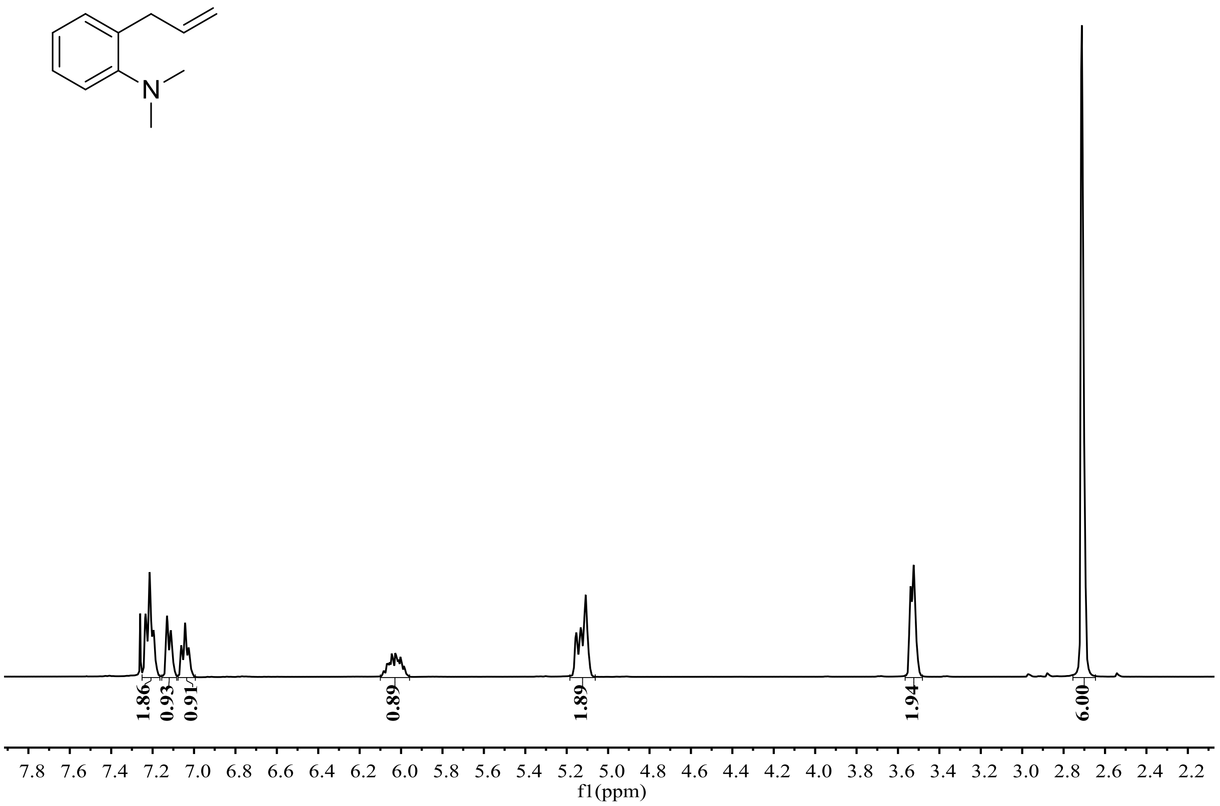


Figure S5. ^{1}H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of **2-(*N,N*-dimethylamino) allylbenzene**.

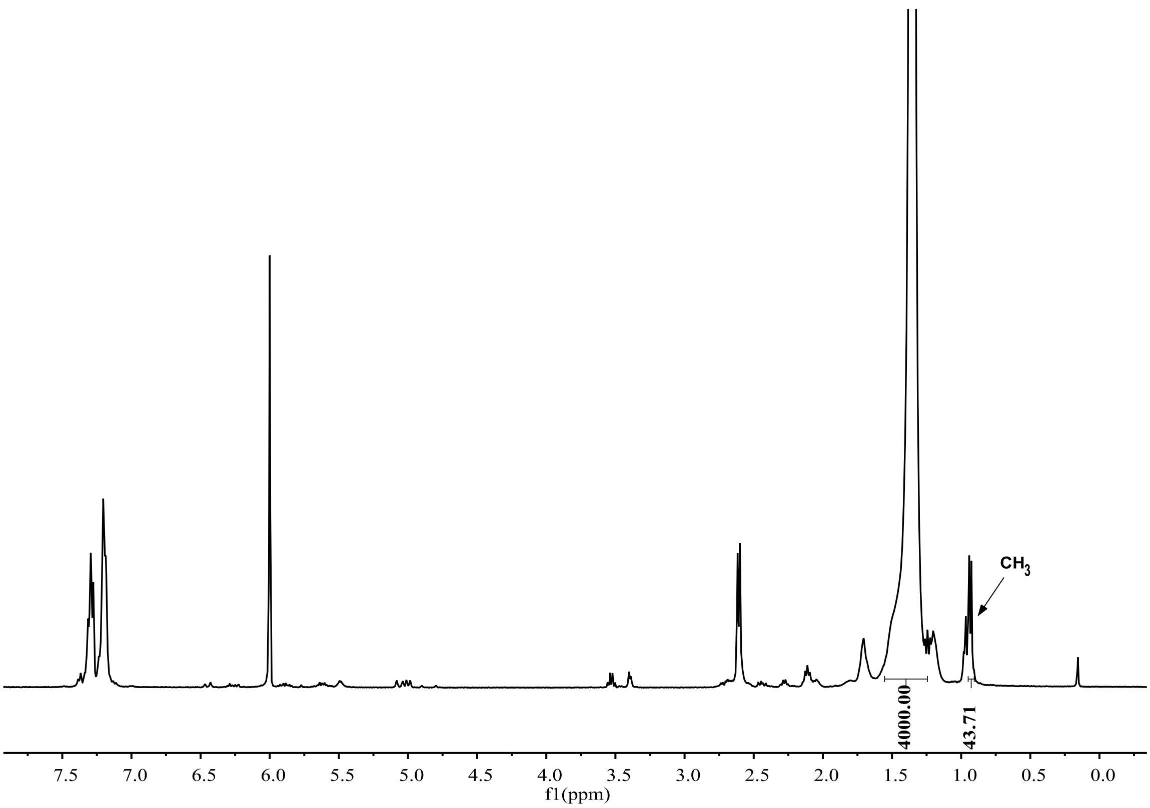


Figure S6. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 4.

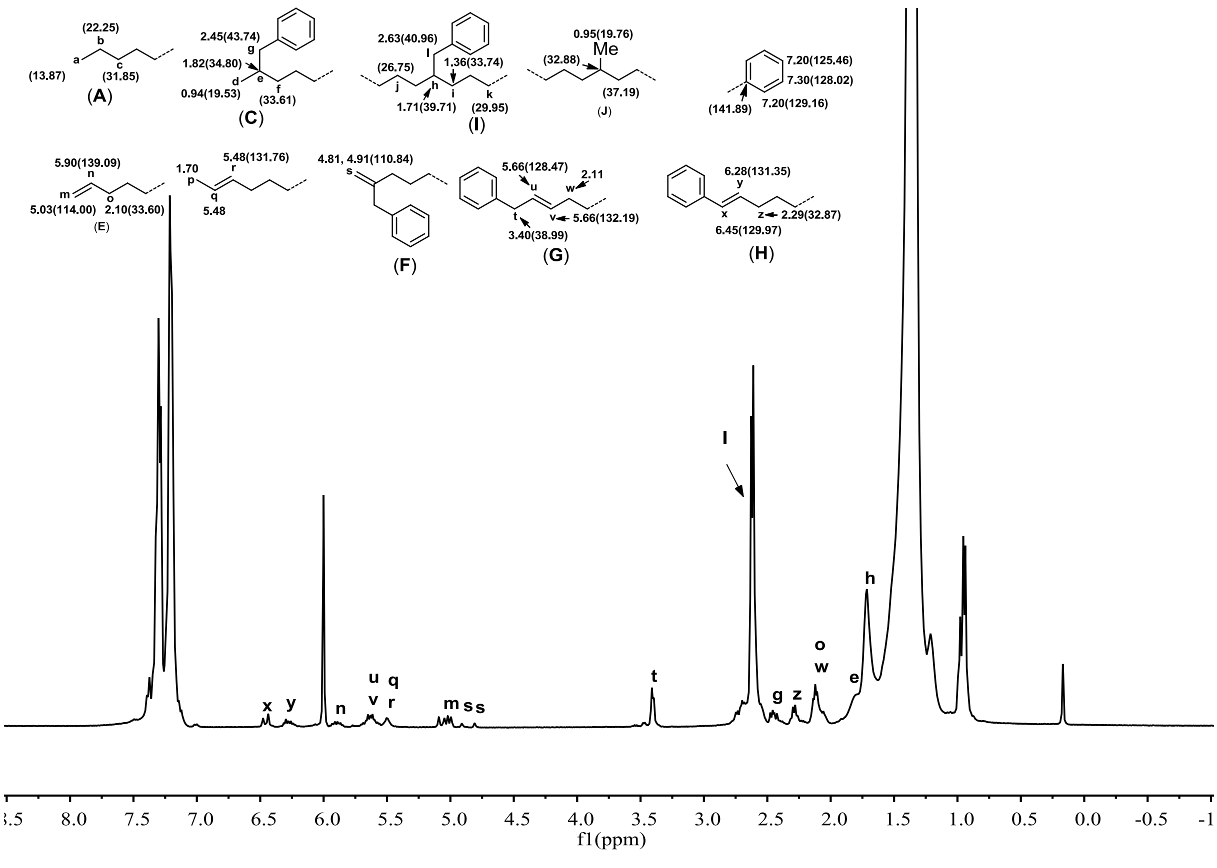


Figure S7. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 5.

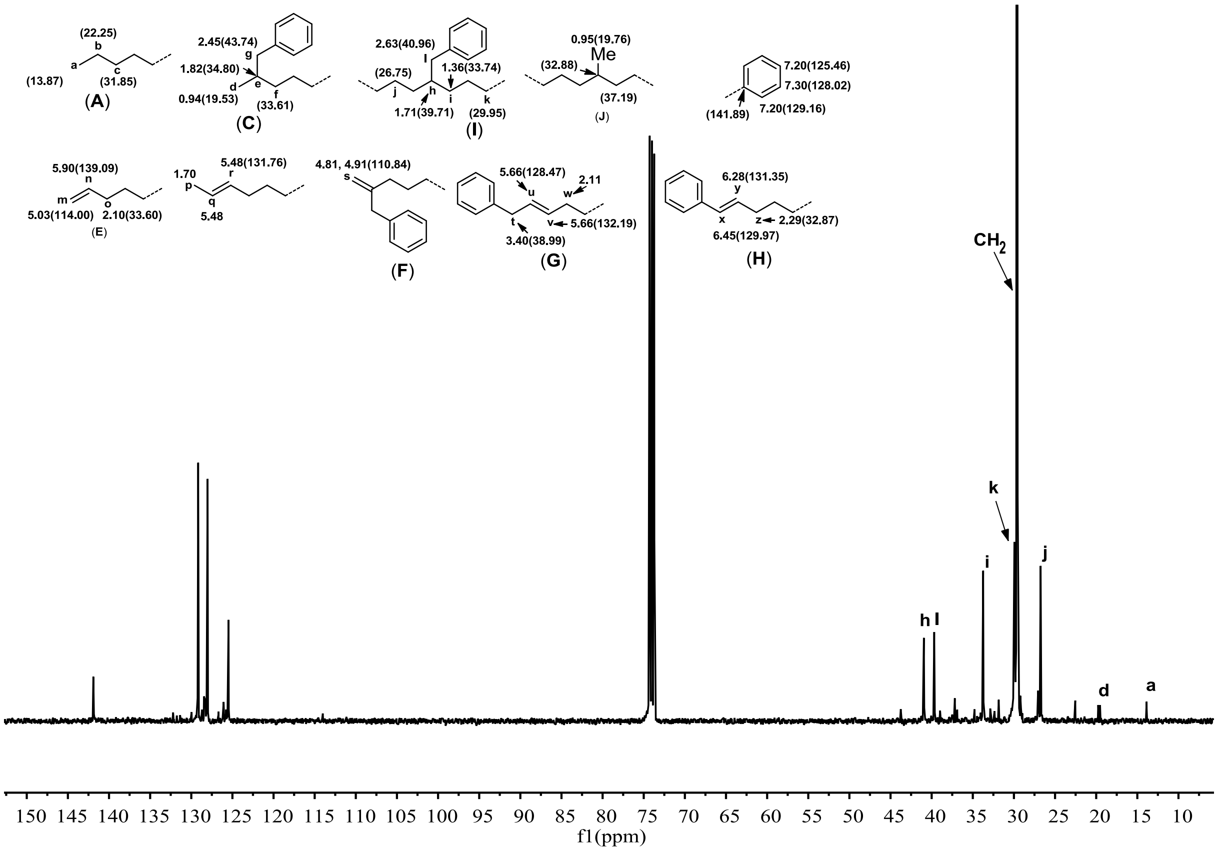


Figure S8. [13]C NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 5.

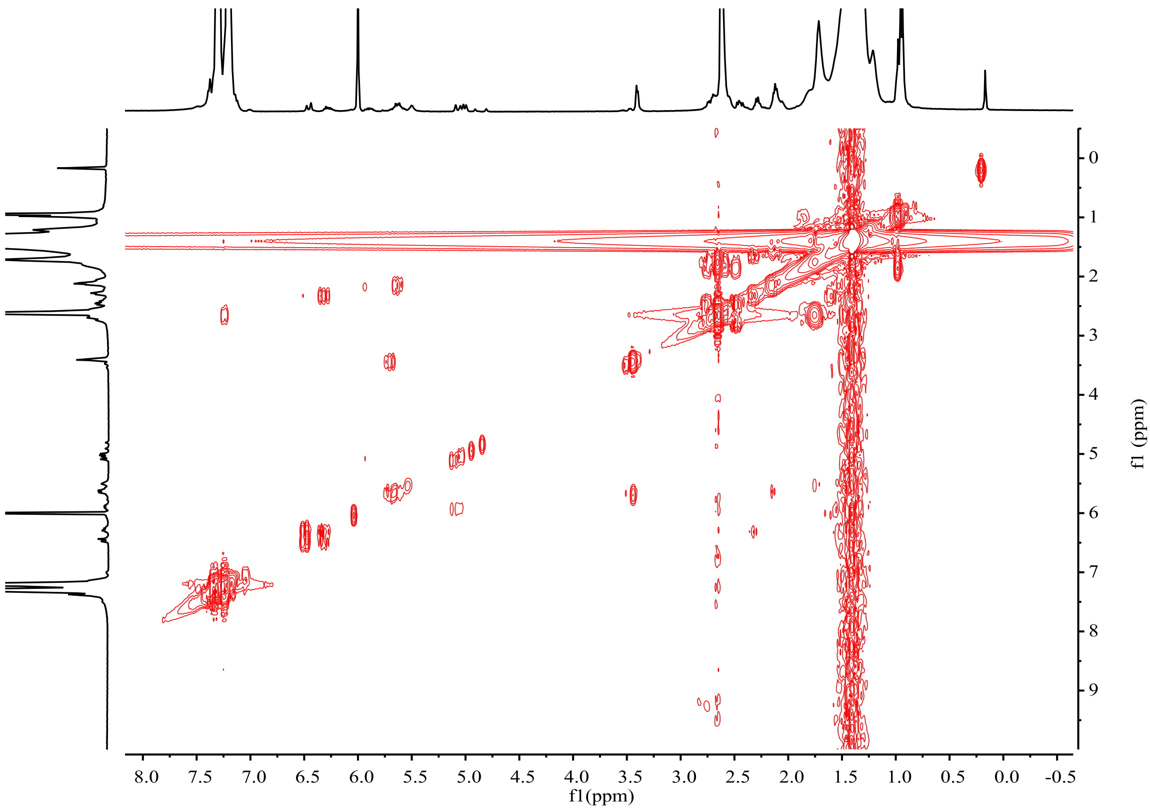


Figure S9. [1]H-[1]H COSY NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 5.

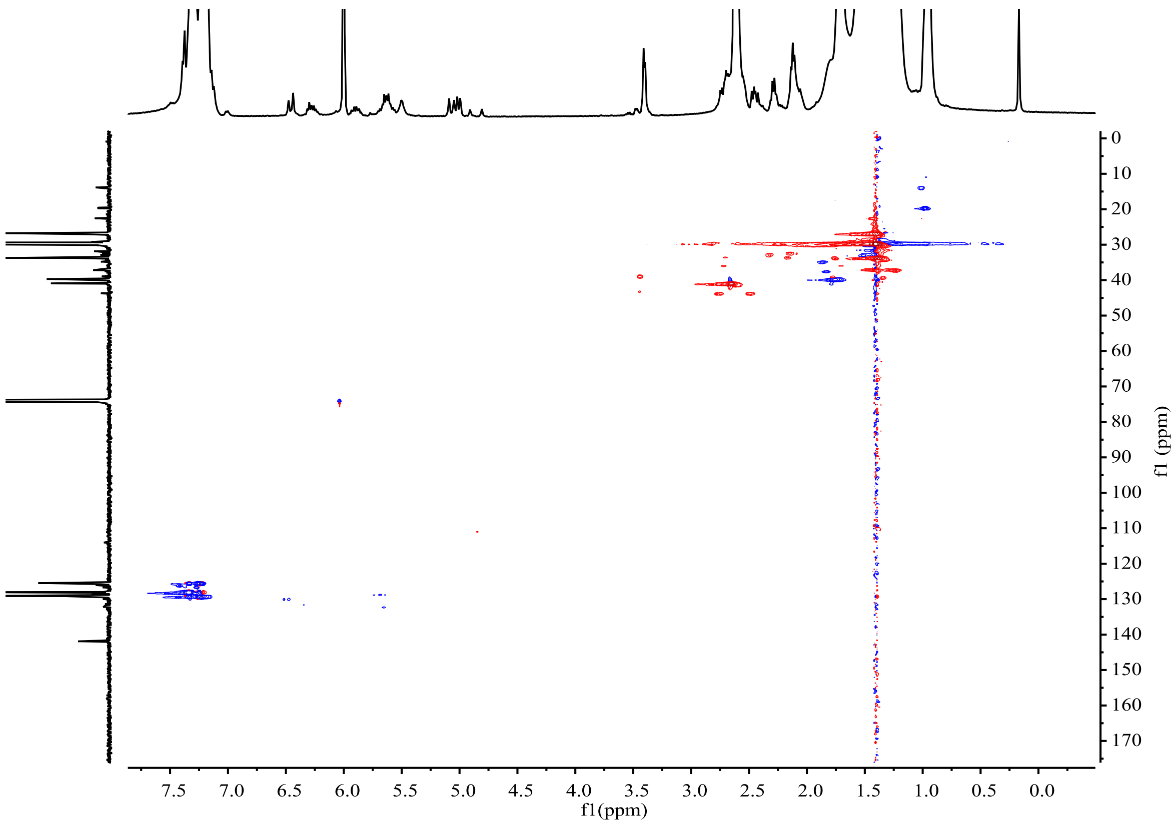


Figure S10. ^{1}H-^{13}C HSQC NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 5.

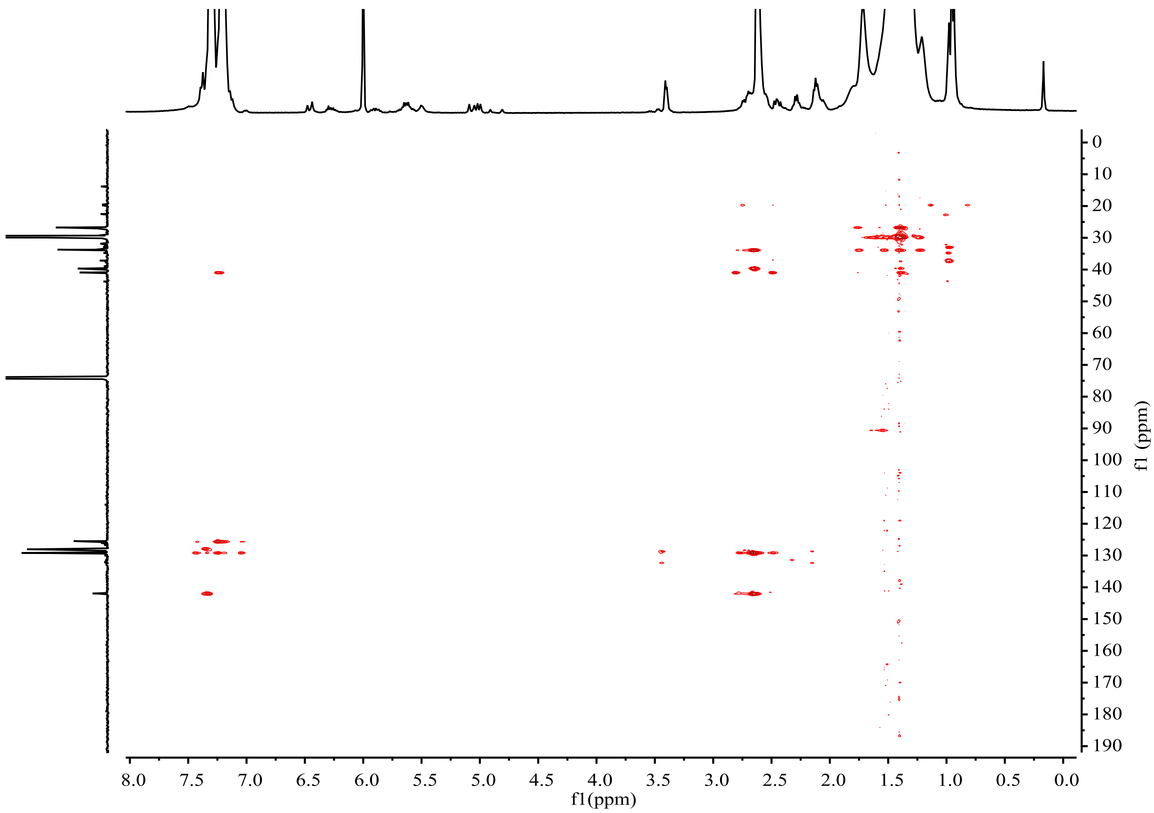


Figure S11. ^{1}H-^{13}C HMBC NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 5.

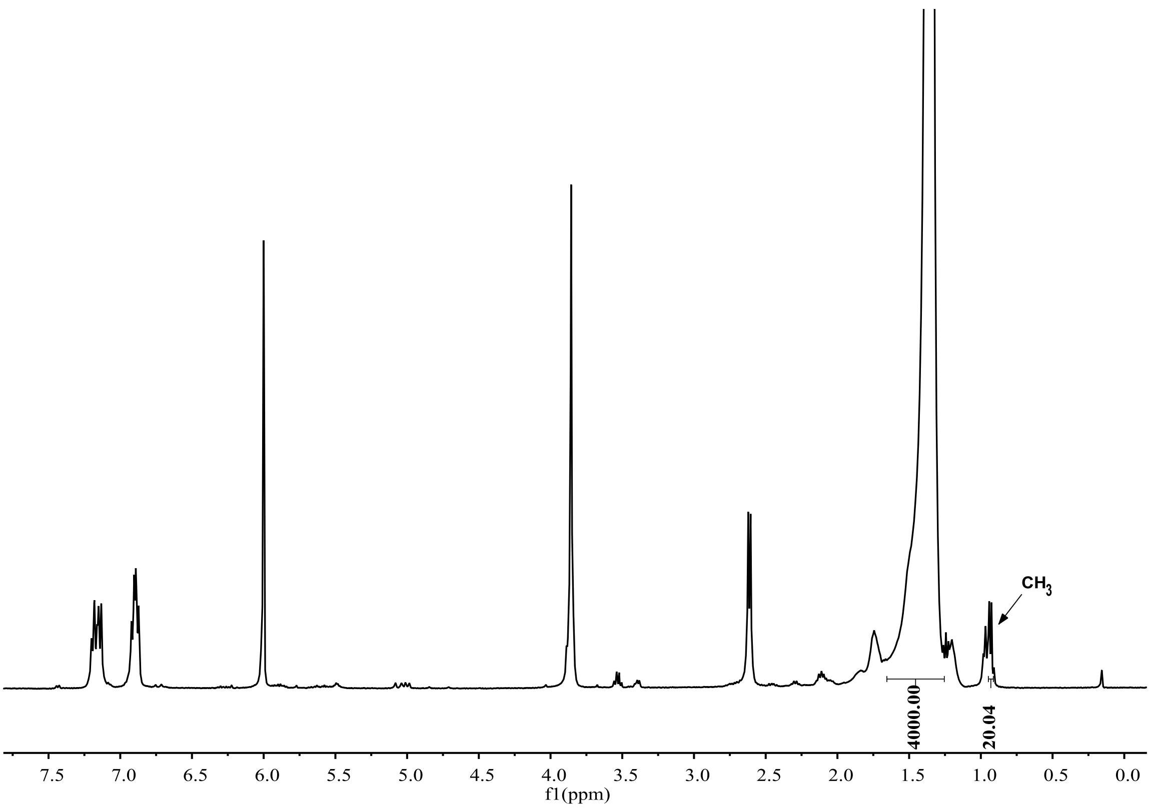


Figure S12. [1]H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 6.

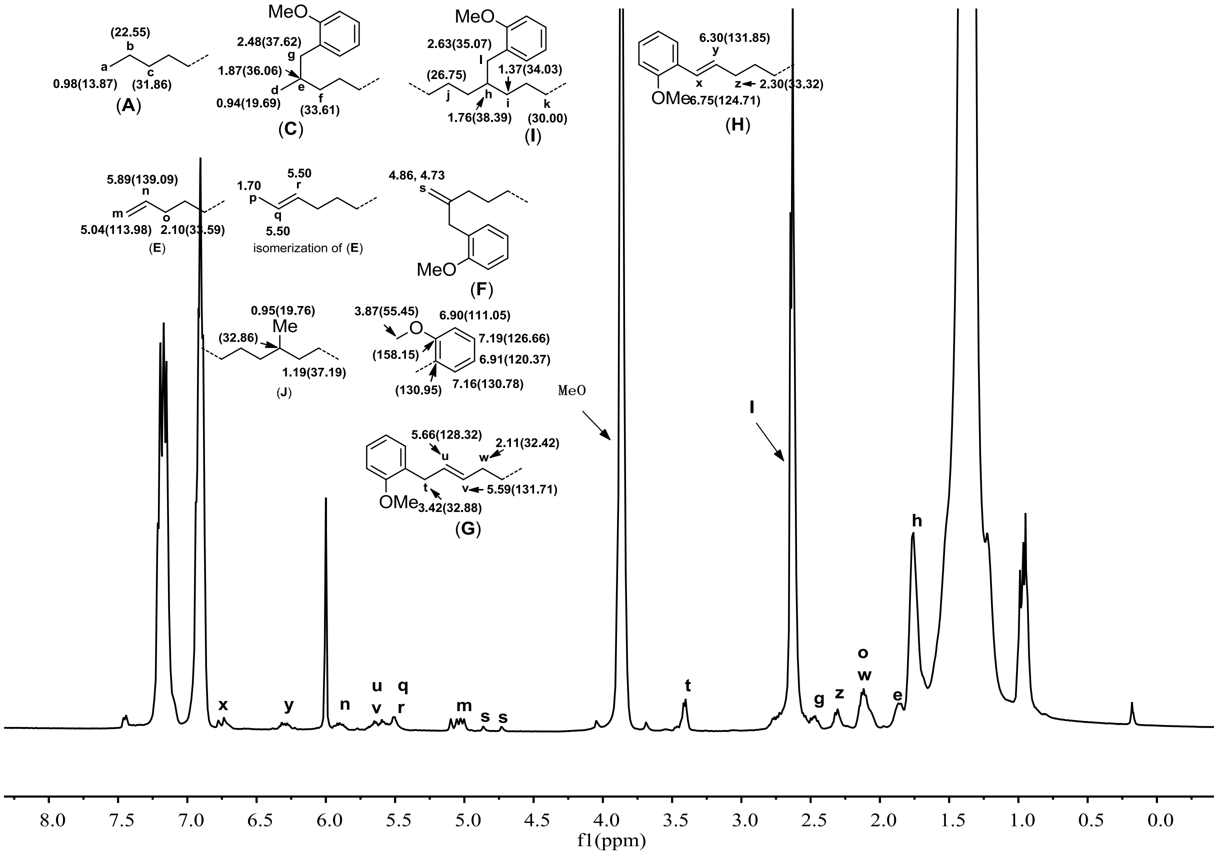


Figure S13. [1]H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 7.

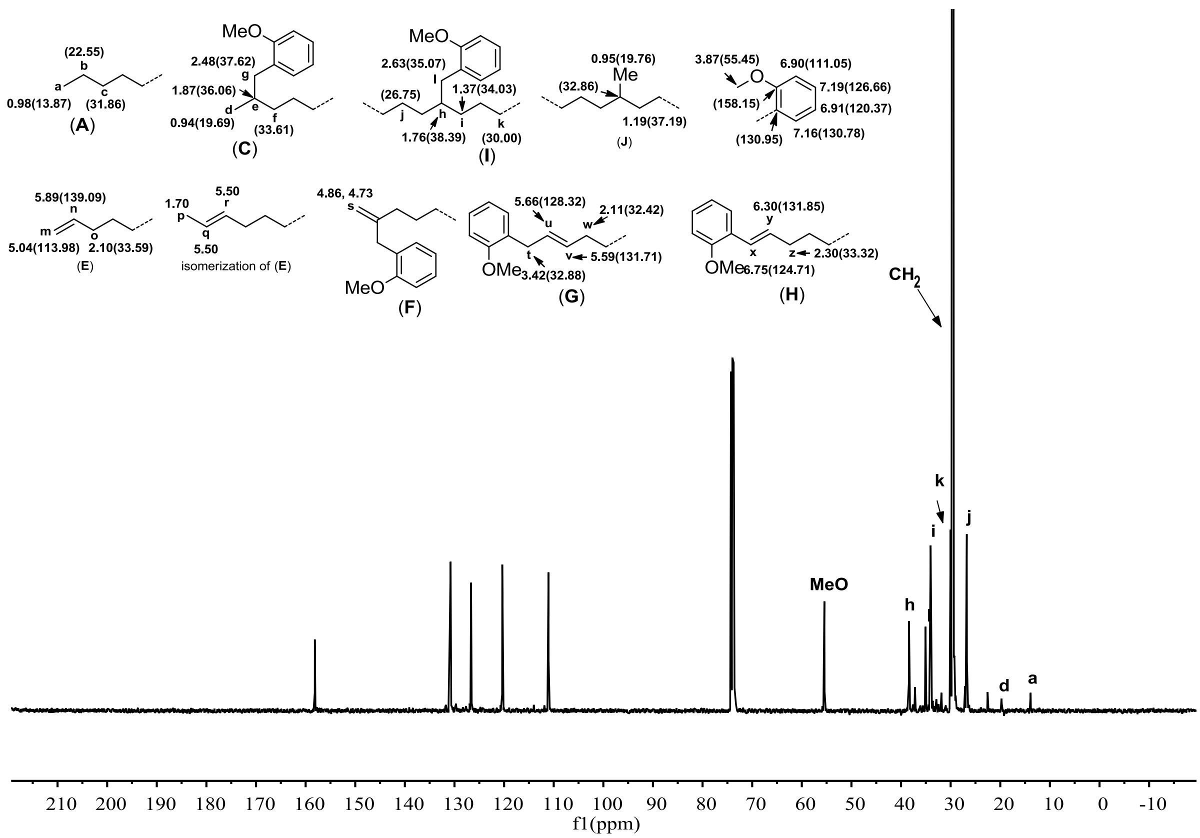


Figure S14. ^{13}C NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 7.

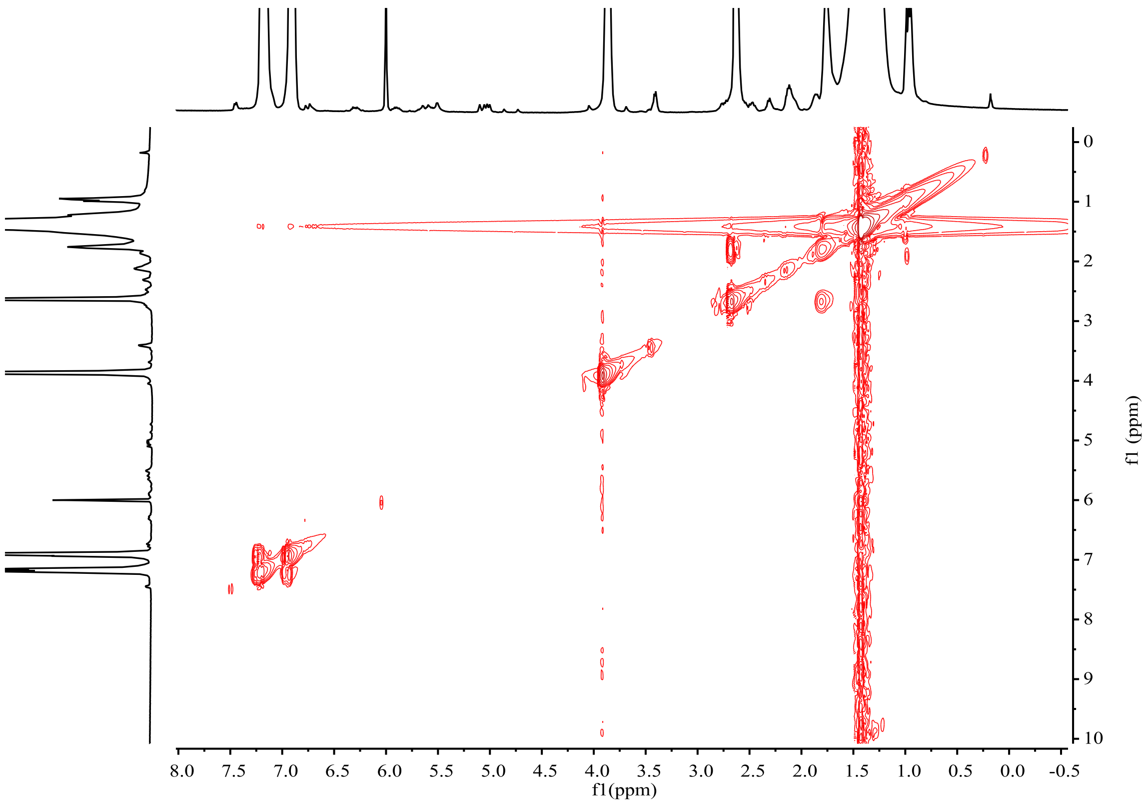


Figure S15. ^{1}H-^{1}H COSY NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 7.

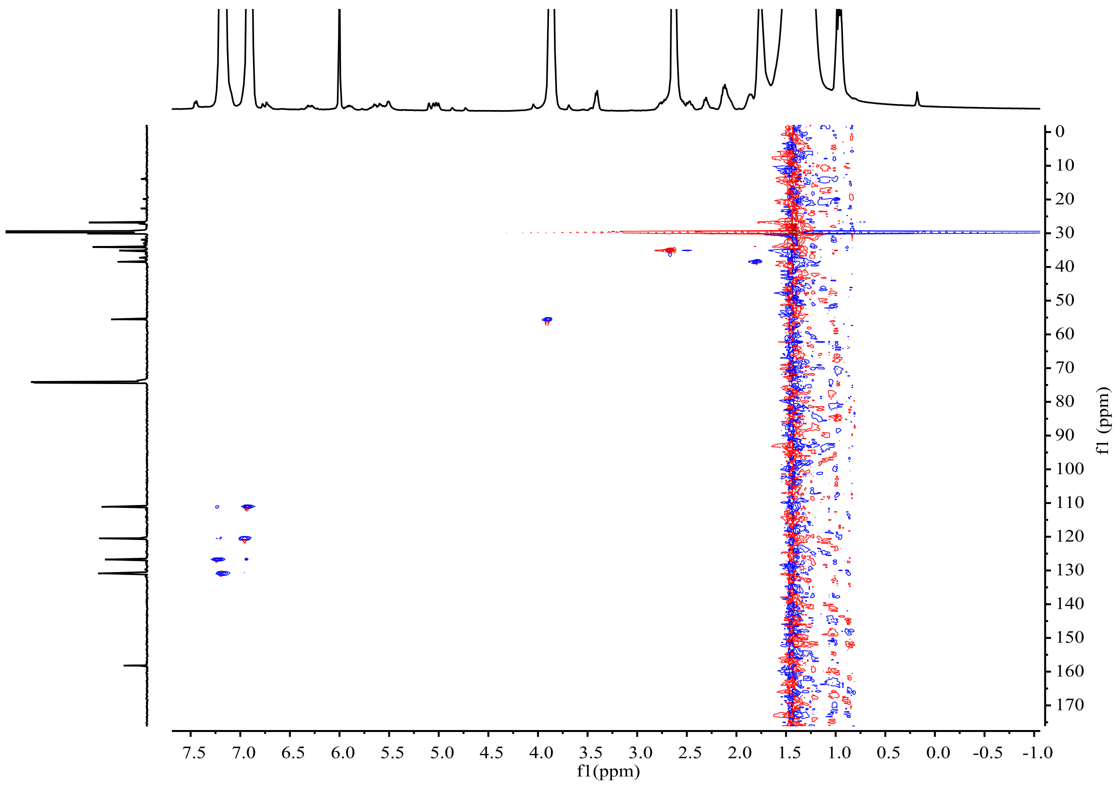


Figure S16. ^{1}H-^{13}C HSQC NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 7.

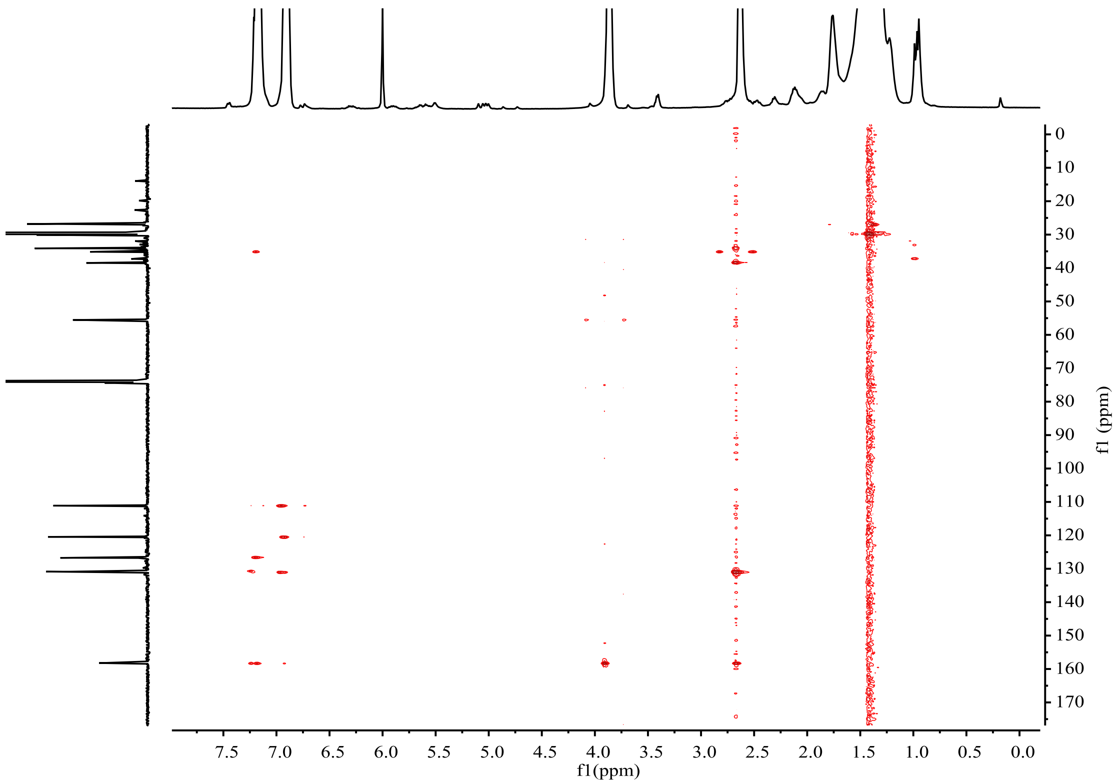


Figure S17. ^{1}H-^{13}C HMBC NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 7.

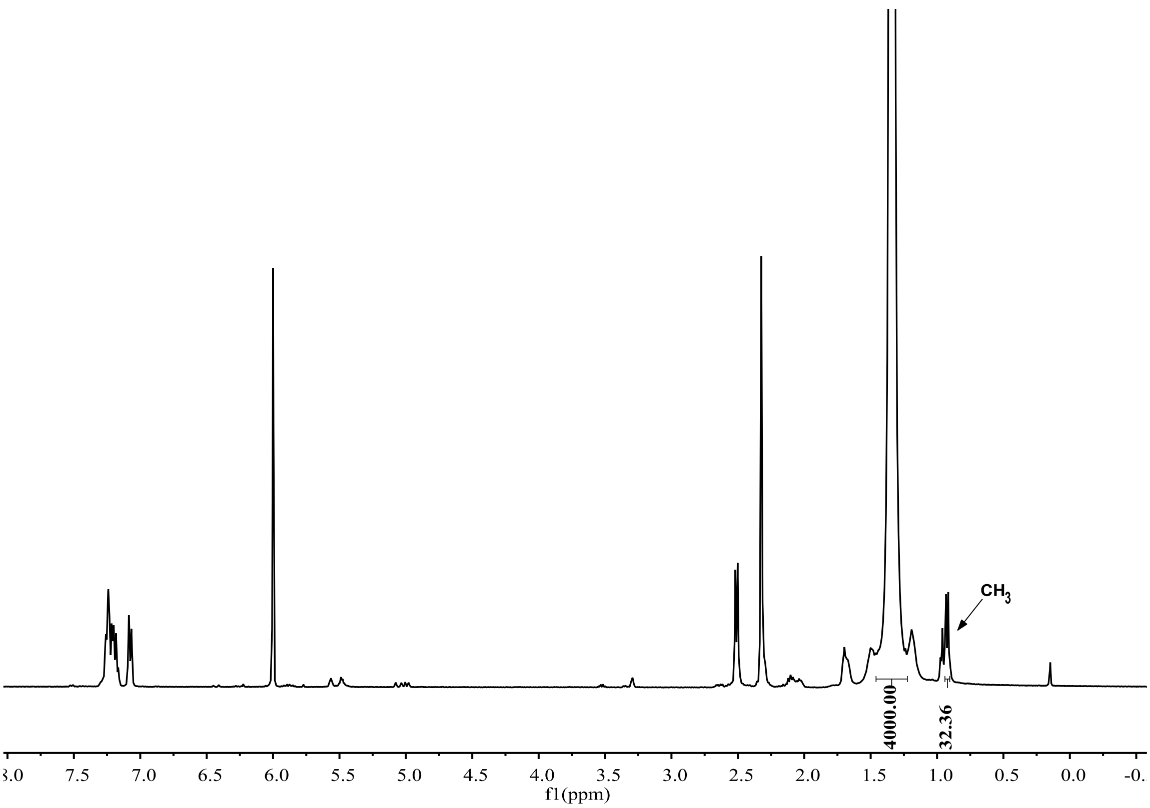


Figure S18. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 8.

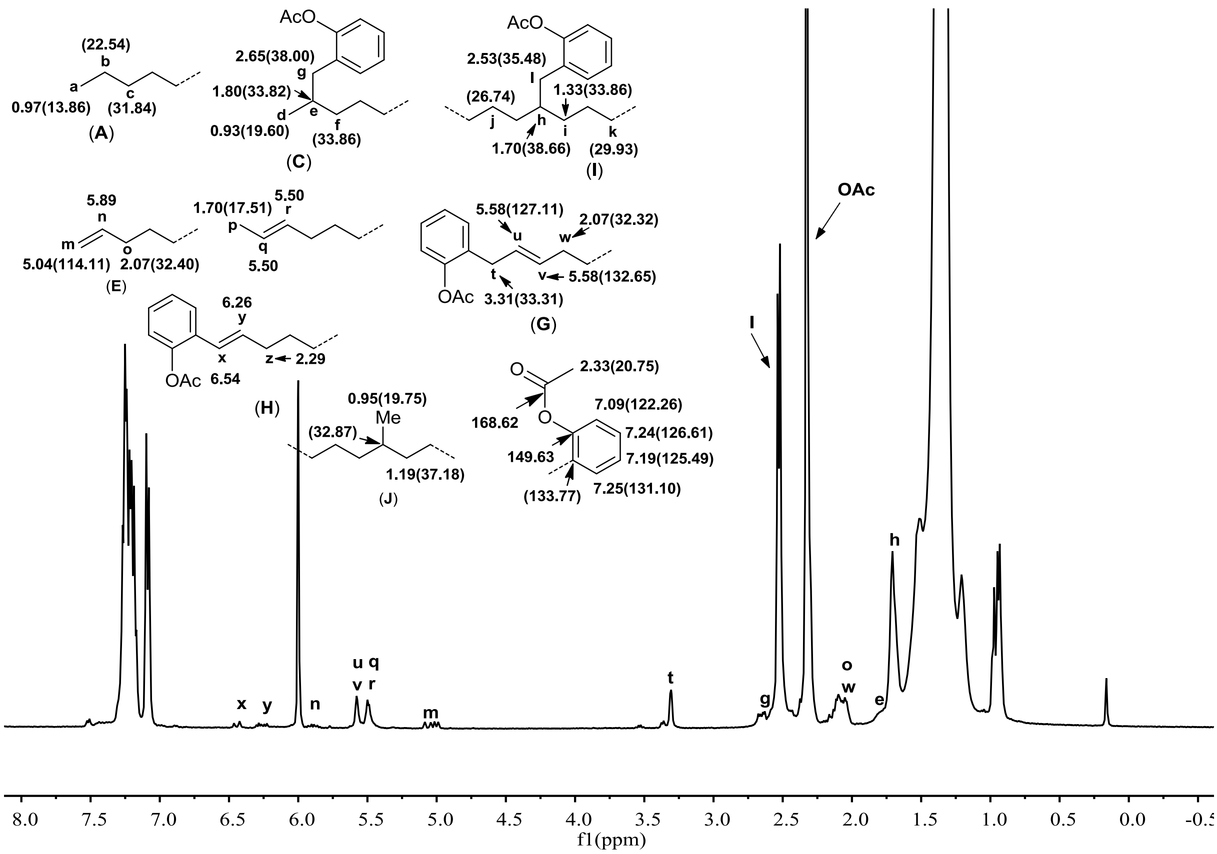


Figure S19. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 9.

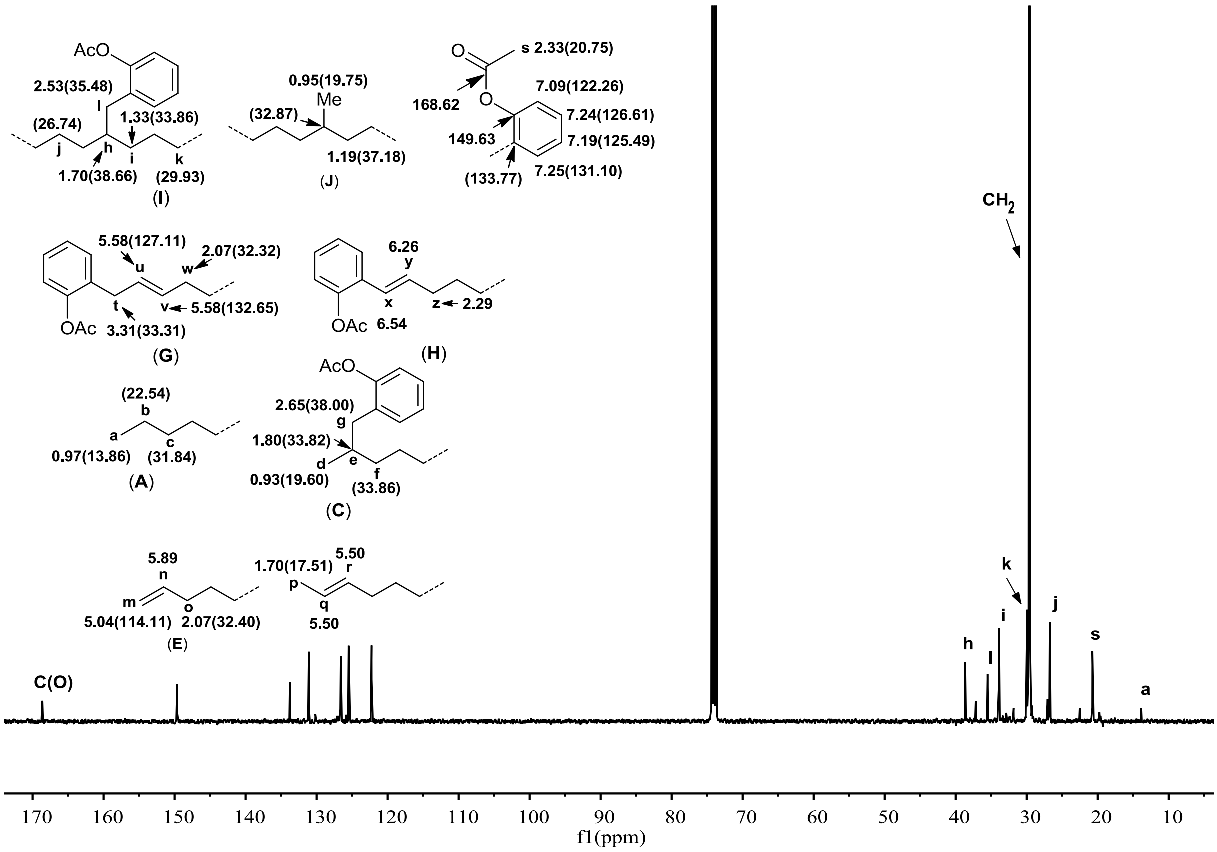


Figure S20. ^{13}C NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 9.

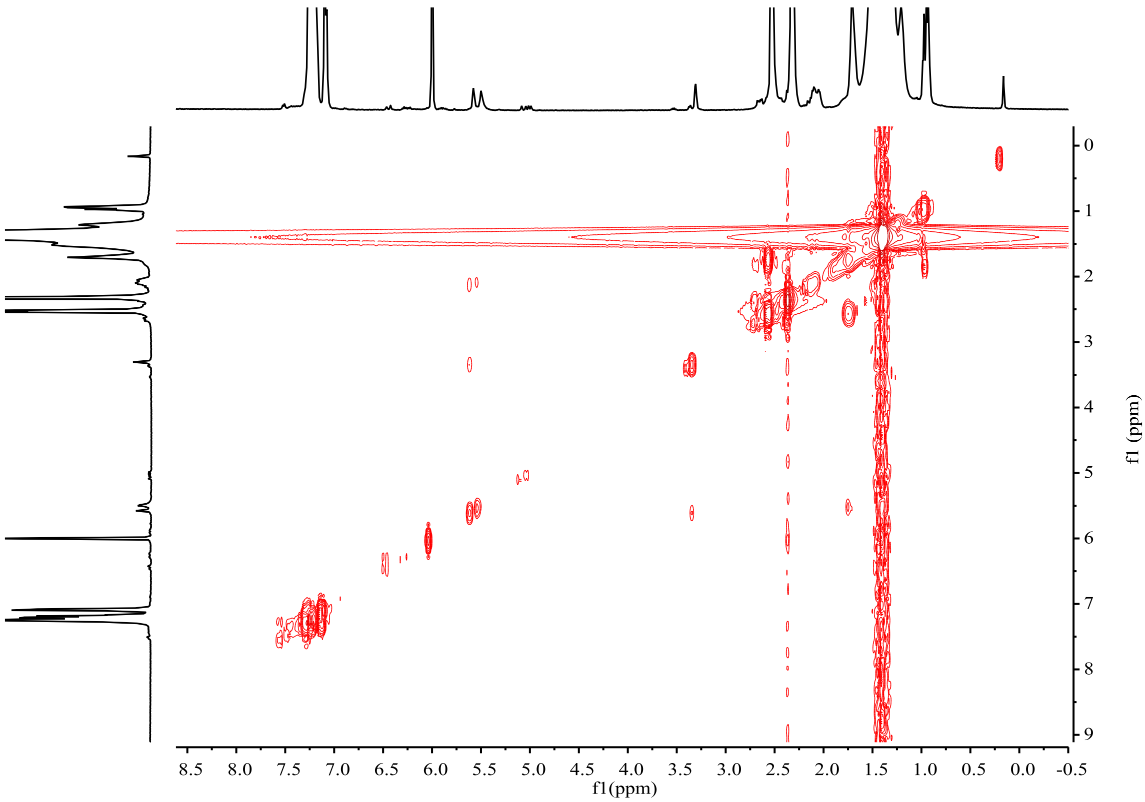


Figure S21. ^{1}H-^{1}H COSY NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 9.

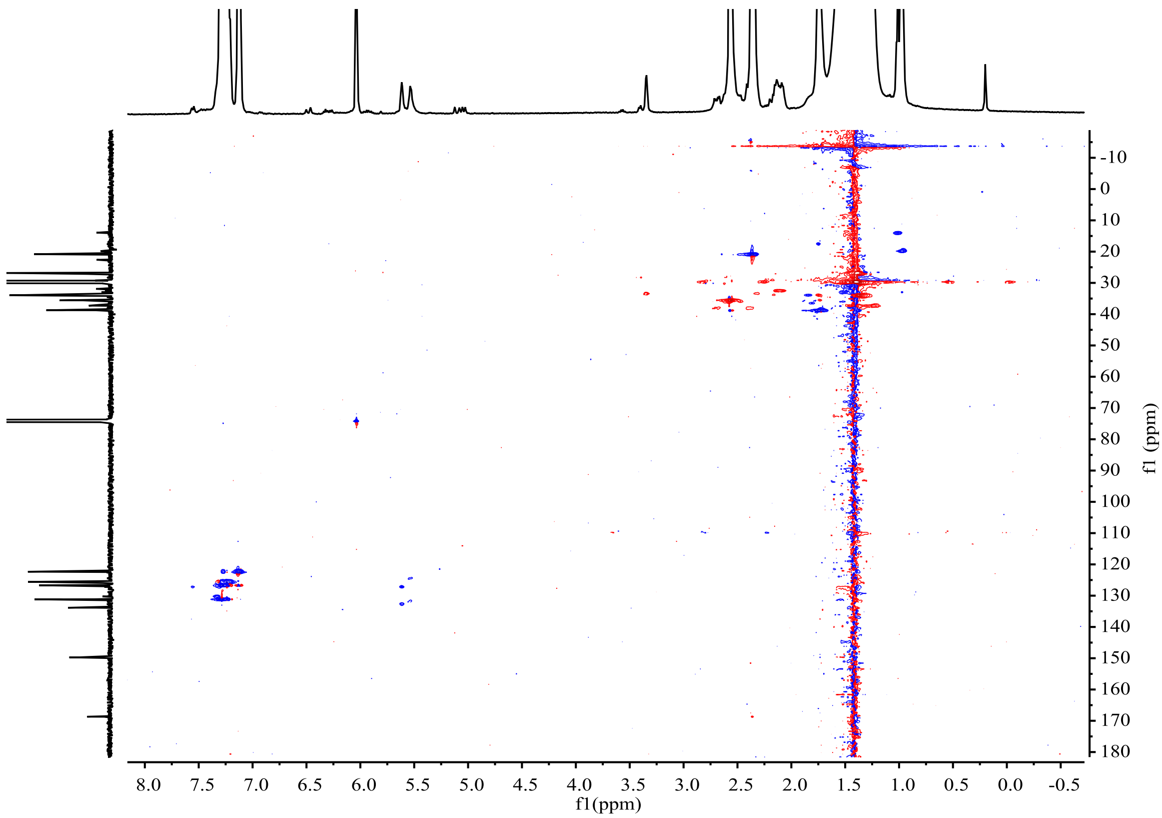


Figure S22. [1]H-[13]C HSQC NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 9.

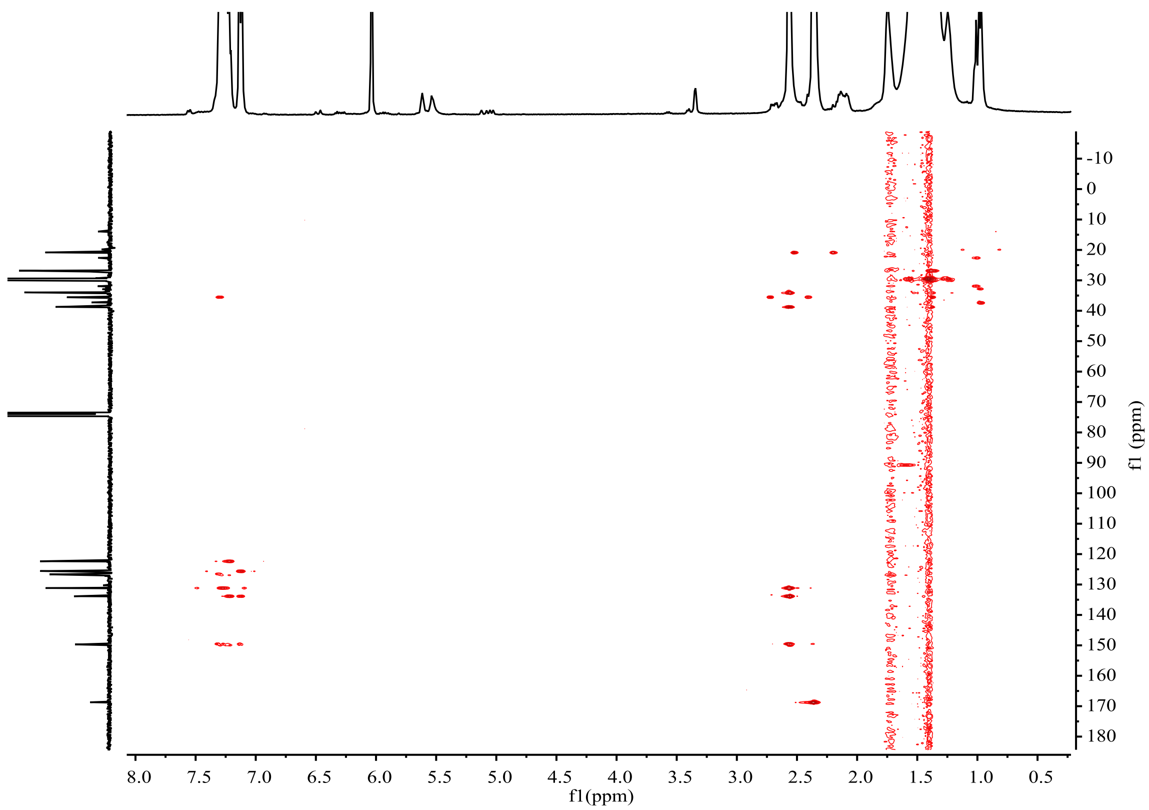


Figure S23. [1]H-[13]C HMBC NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 9.

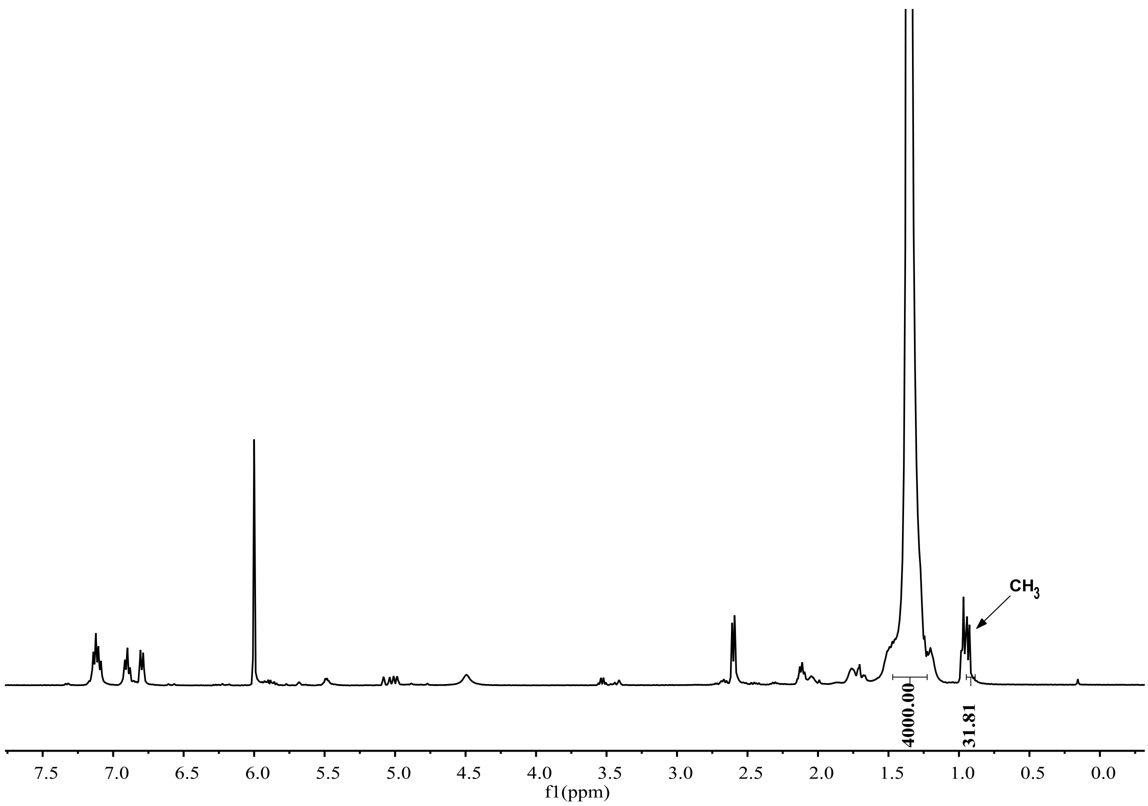


Figure S24. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 10.

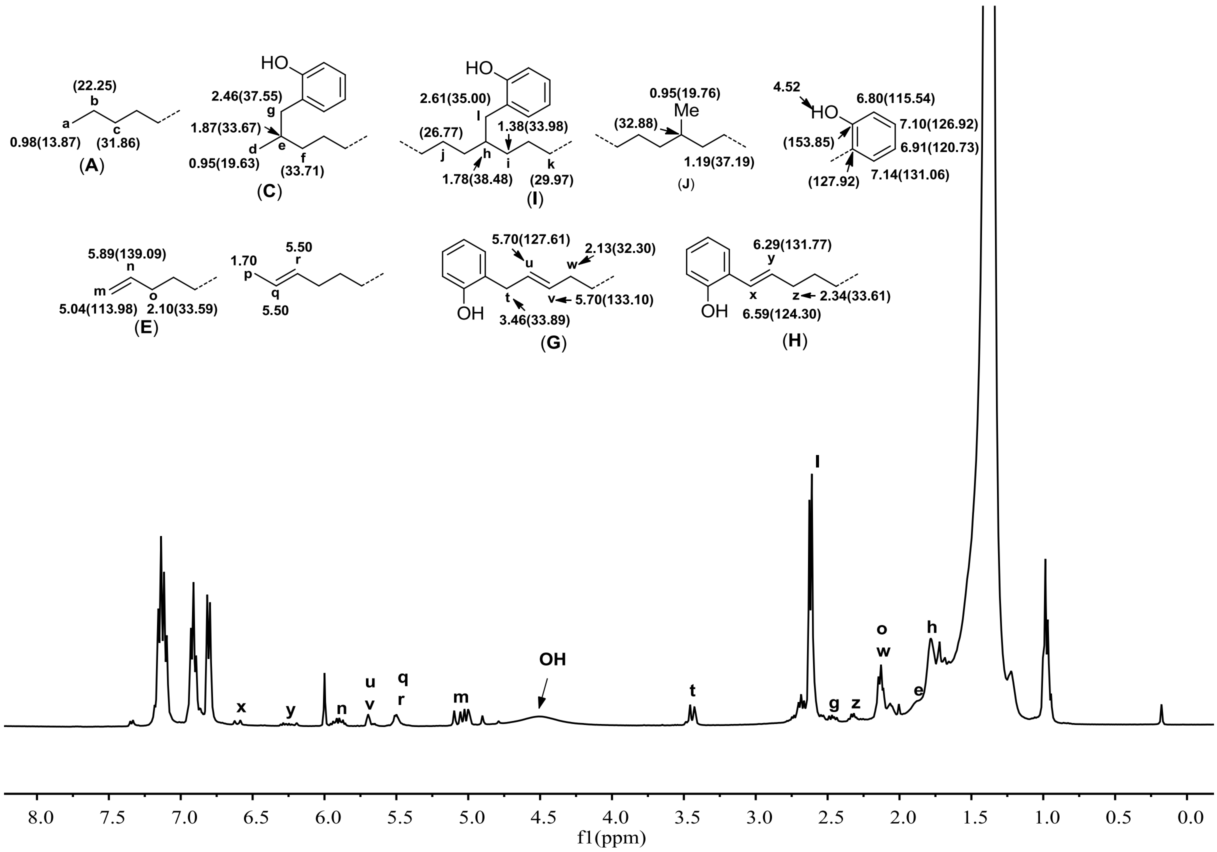


Figure S25. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 11.

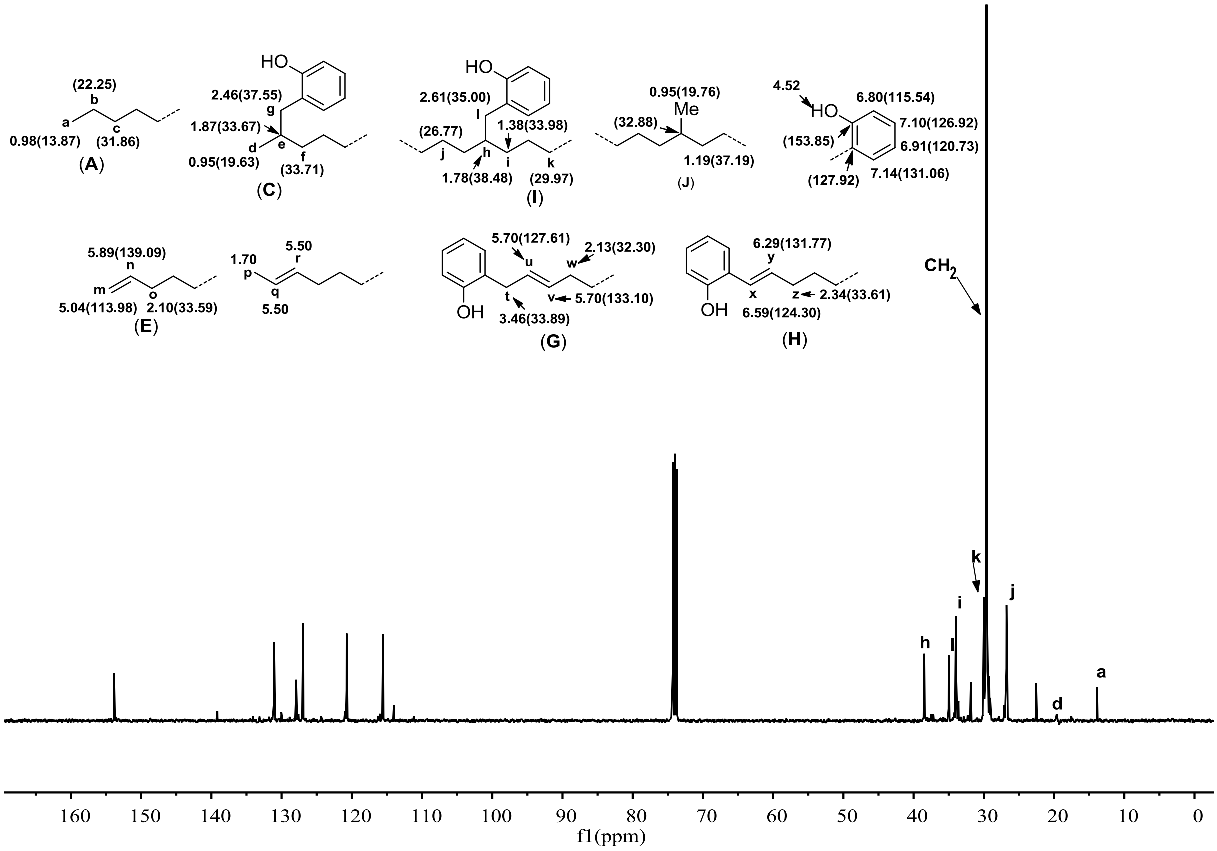


Figure S26. [13]C NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 11.

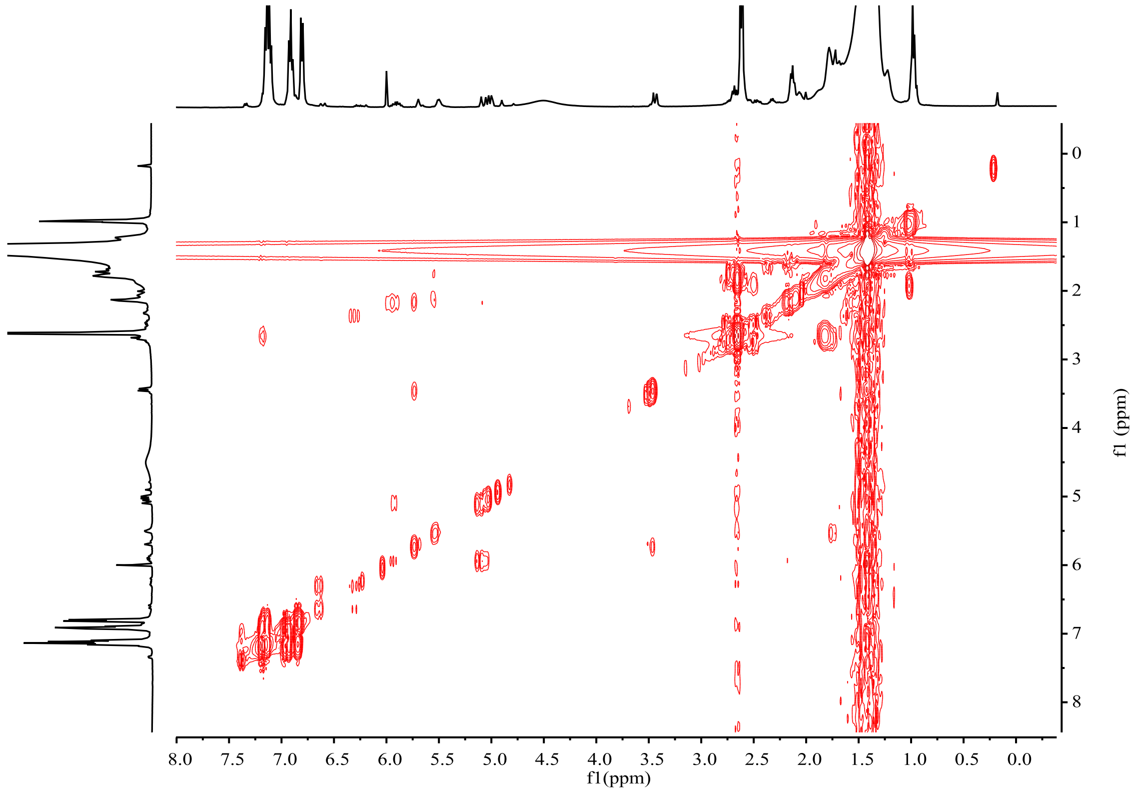


Figure S27. [1]H-[1]H COSY NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 11.

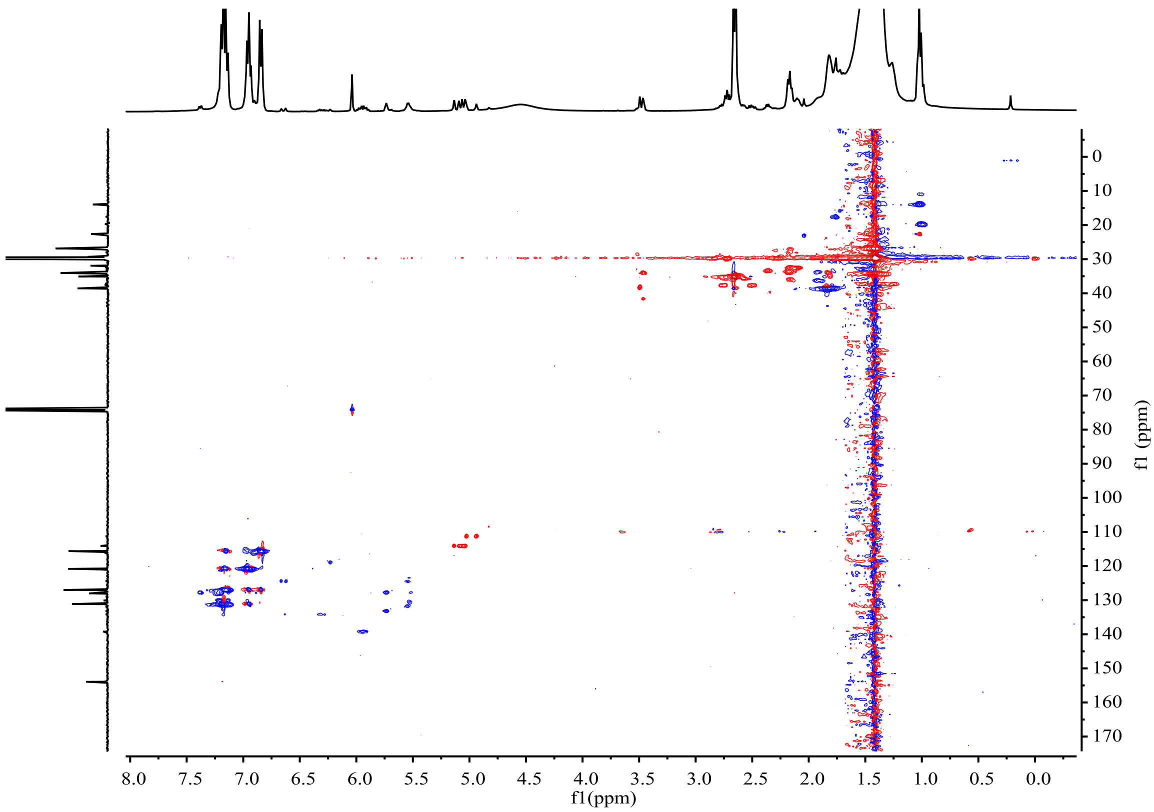


Figure S28. ^{1}H-^{13}C HSQC NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 11.

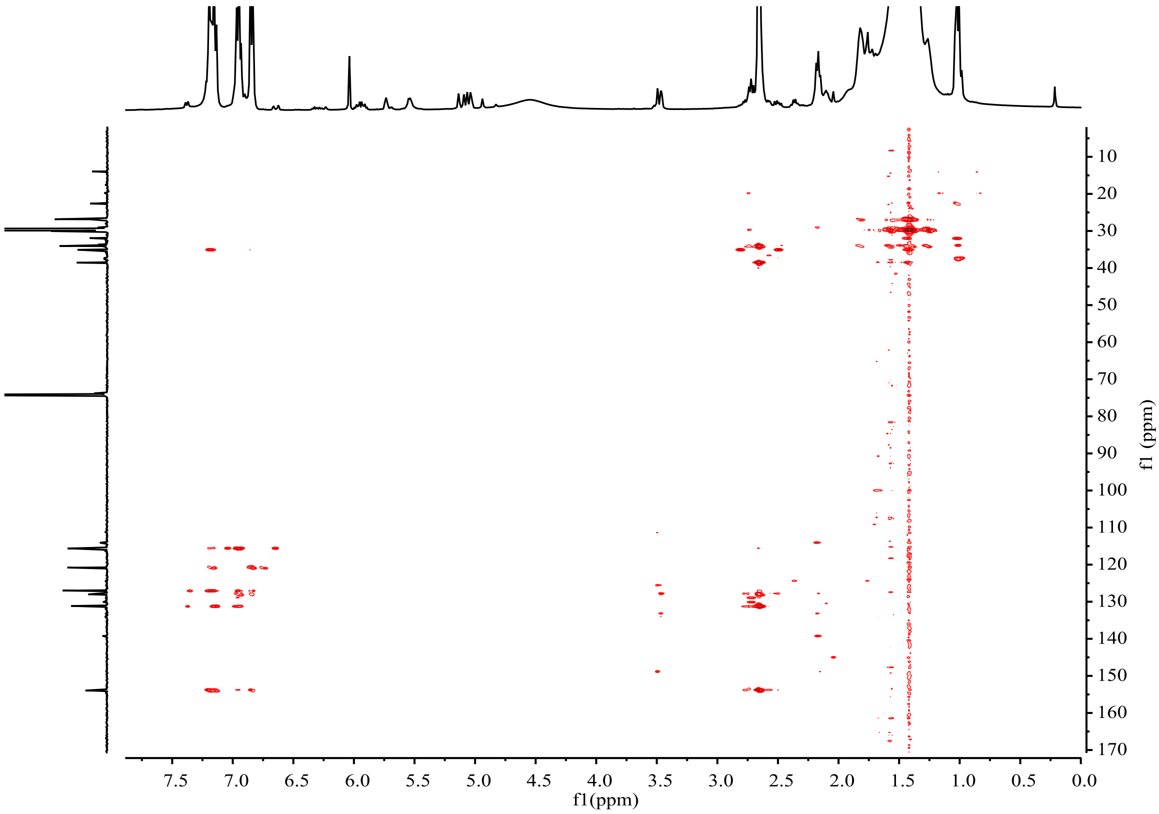


Figure S29. ^{1}H-^{13}C HMBC NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 11.

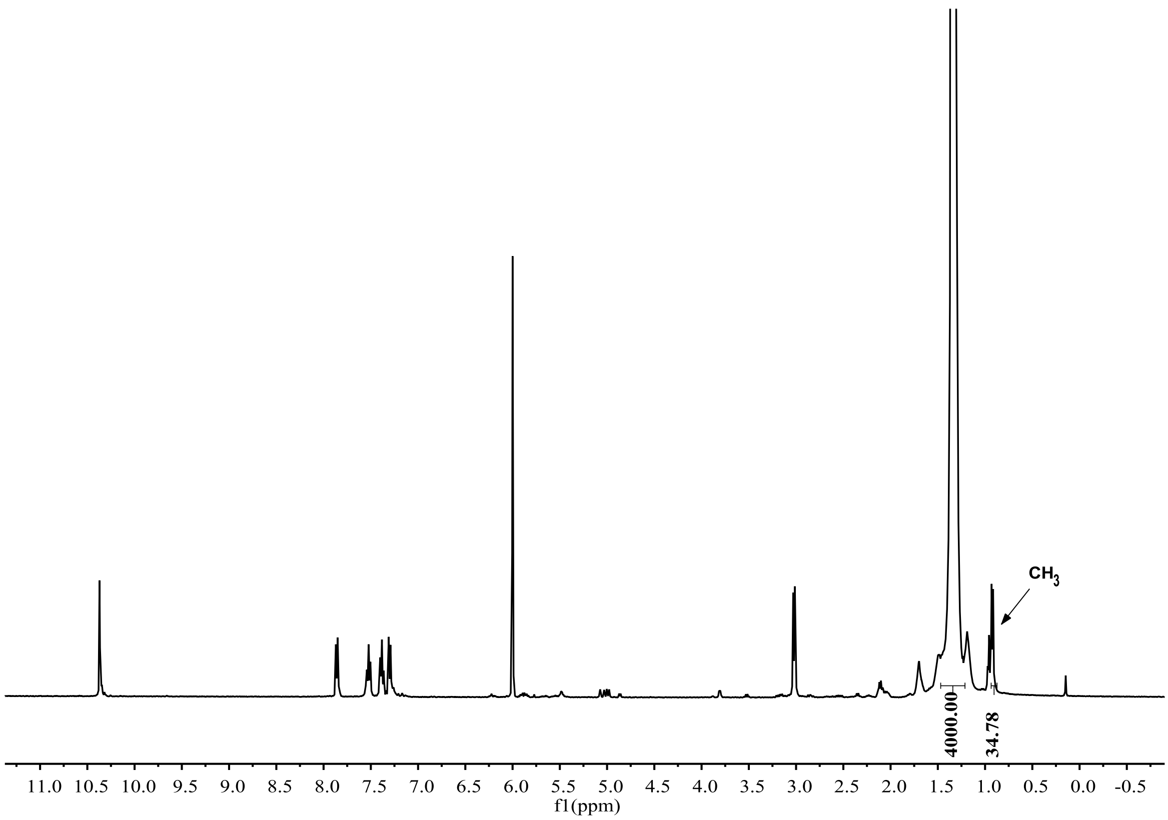


Figure S30. [1]H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 12.

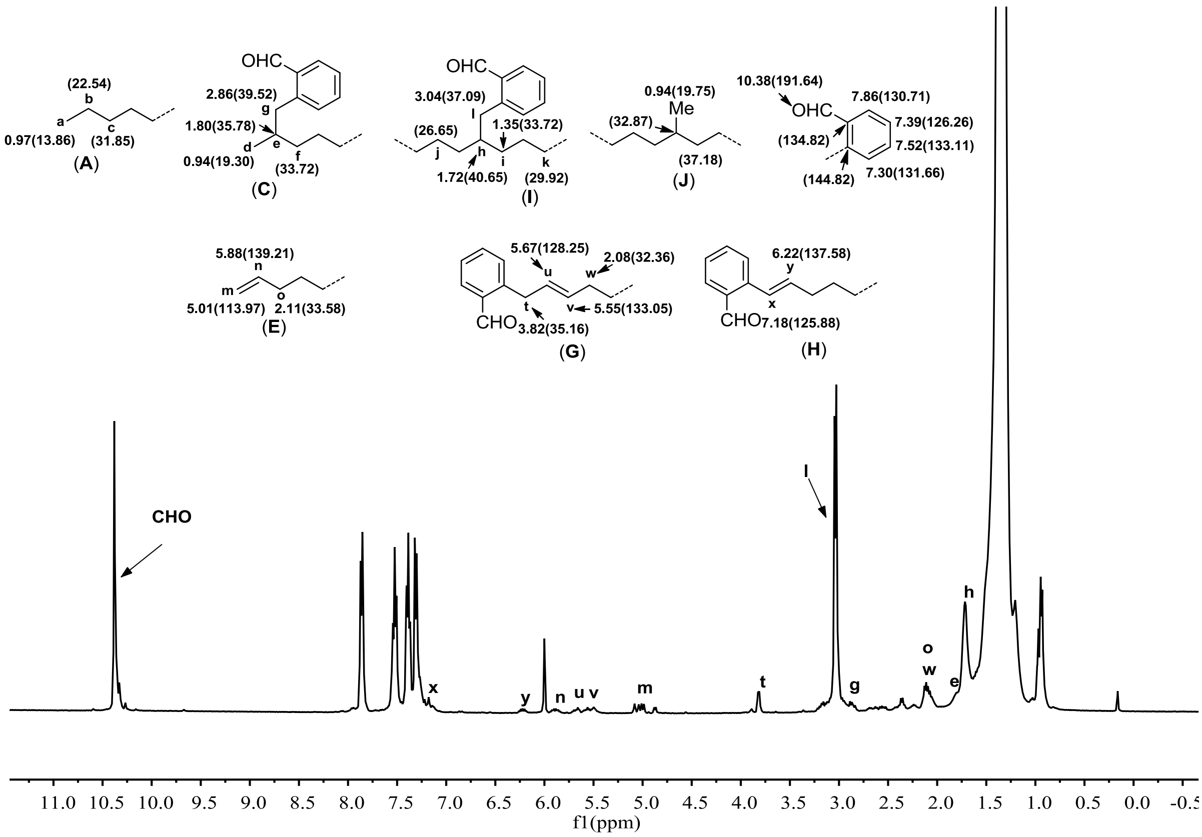


Figure S31. [1]H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 13.

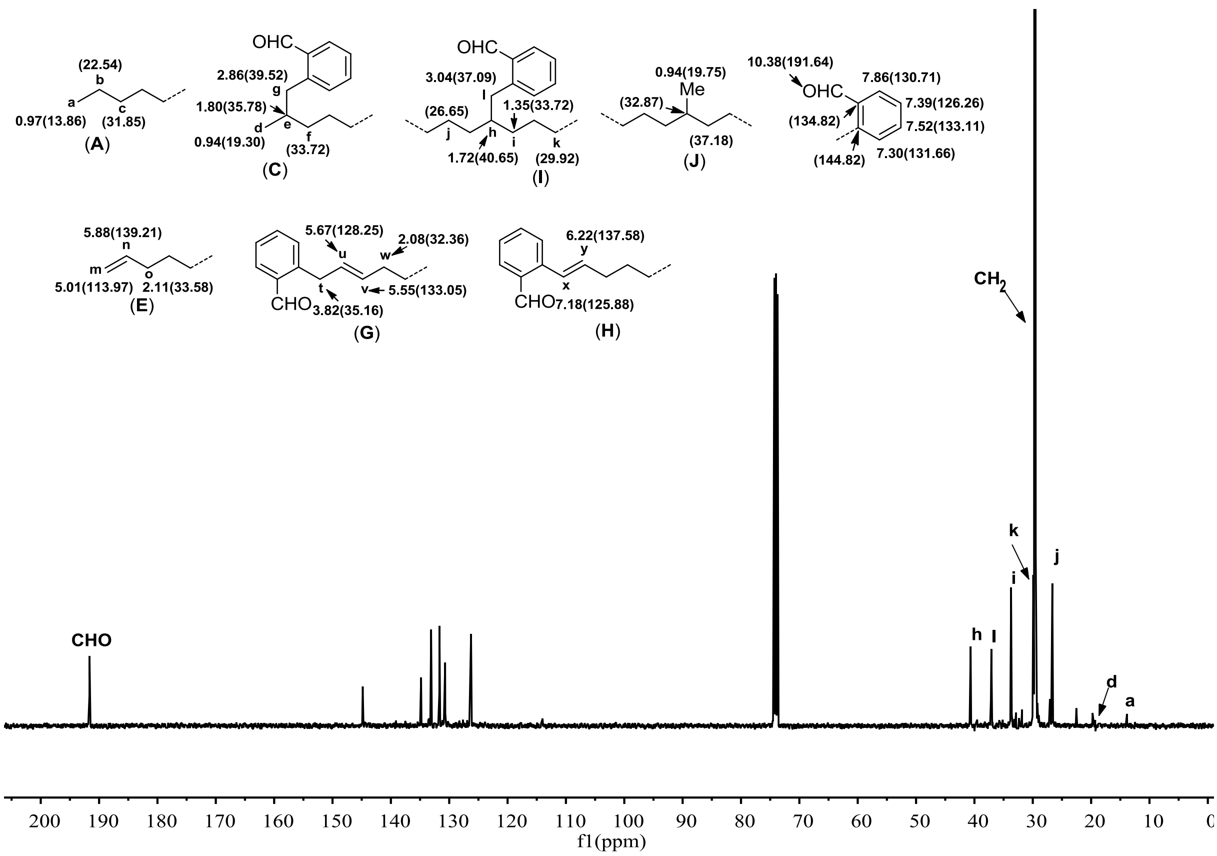


Figure S32. ^{13}C NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 13.

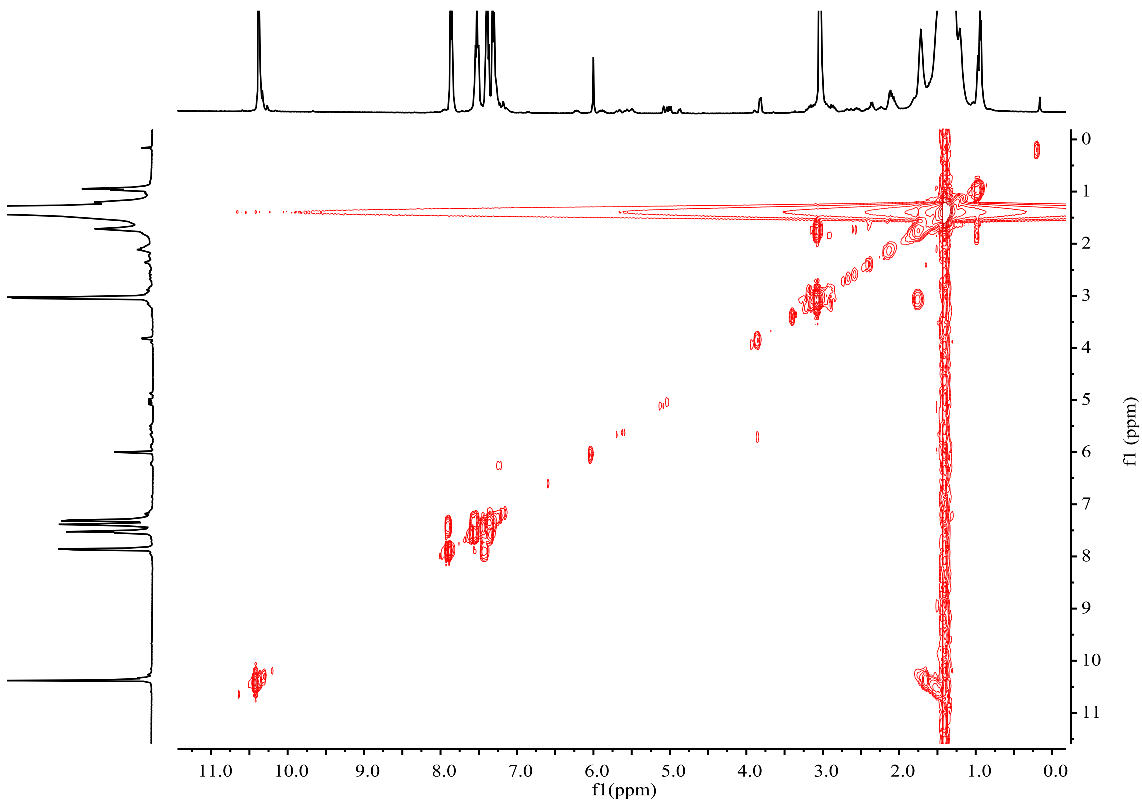


Figure S33. ^{1}H-^{1}H COSY NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 13.

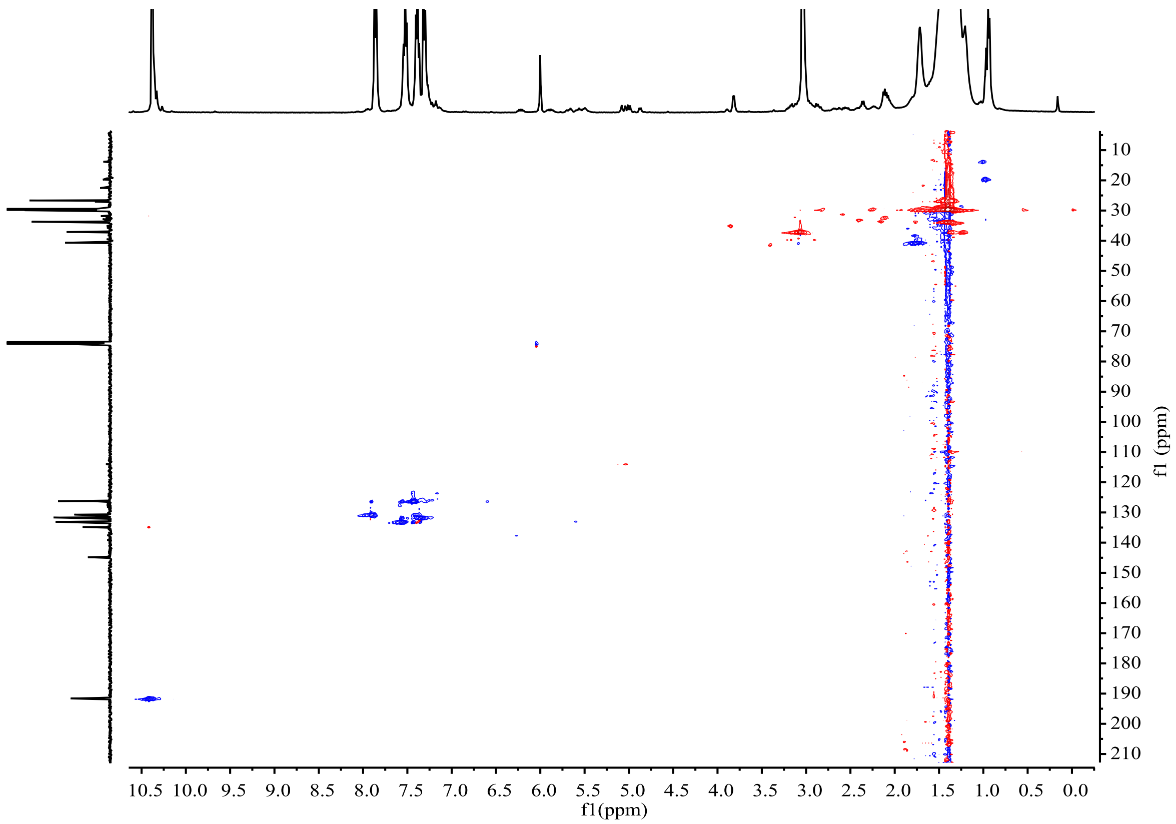


Figure S34. ^{1}H-^{13}C HSQC NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 13.

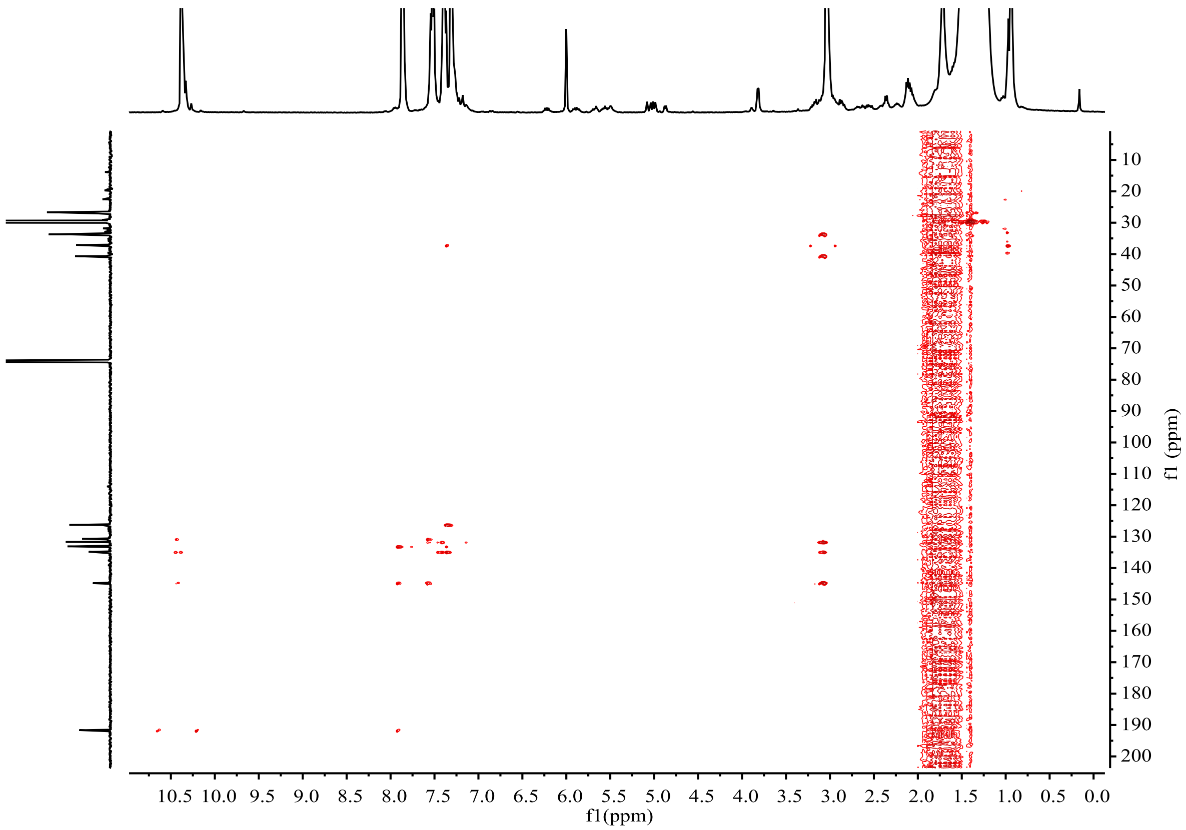


Figure S35. ^{1}H-^{13}C HMBC NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 13.

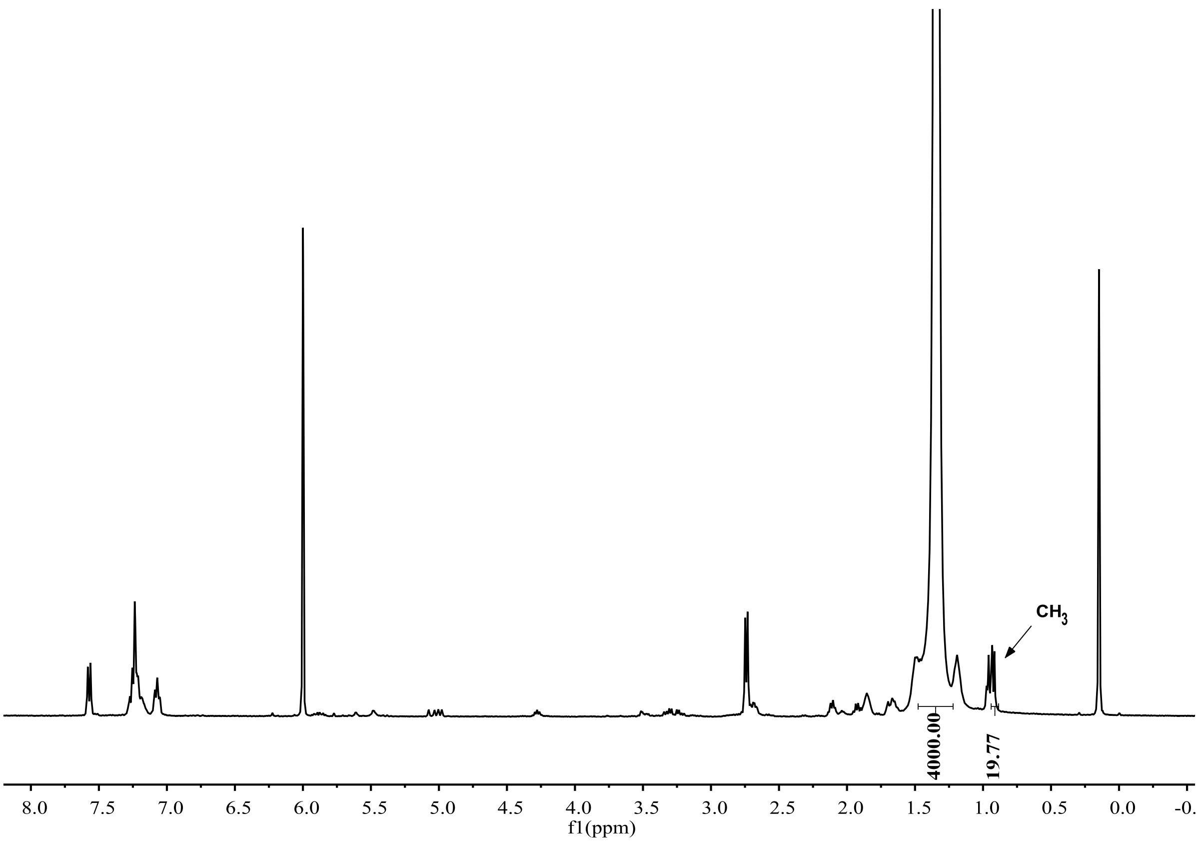


Figure S36. [1]H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 14.

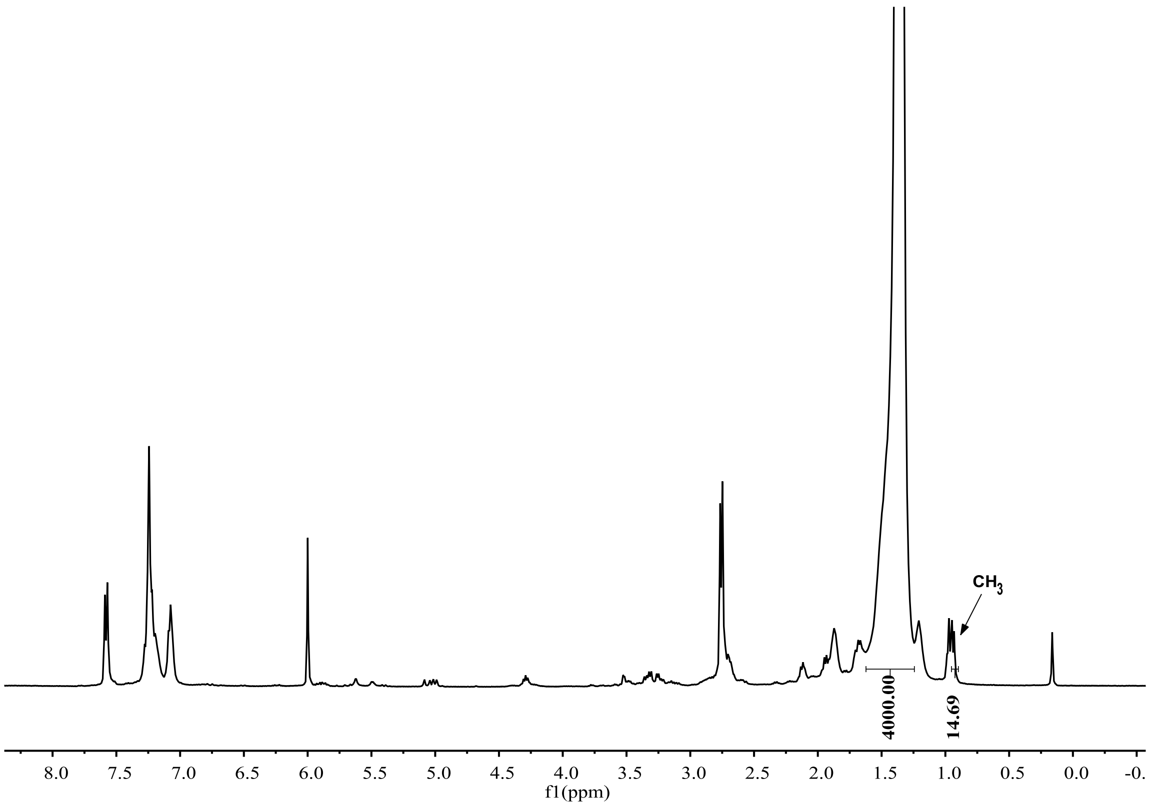


Figure S37. [1]H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 15.

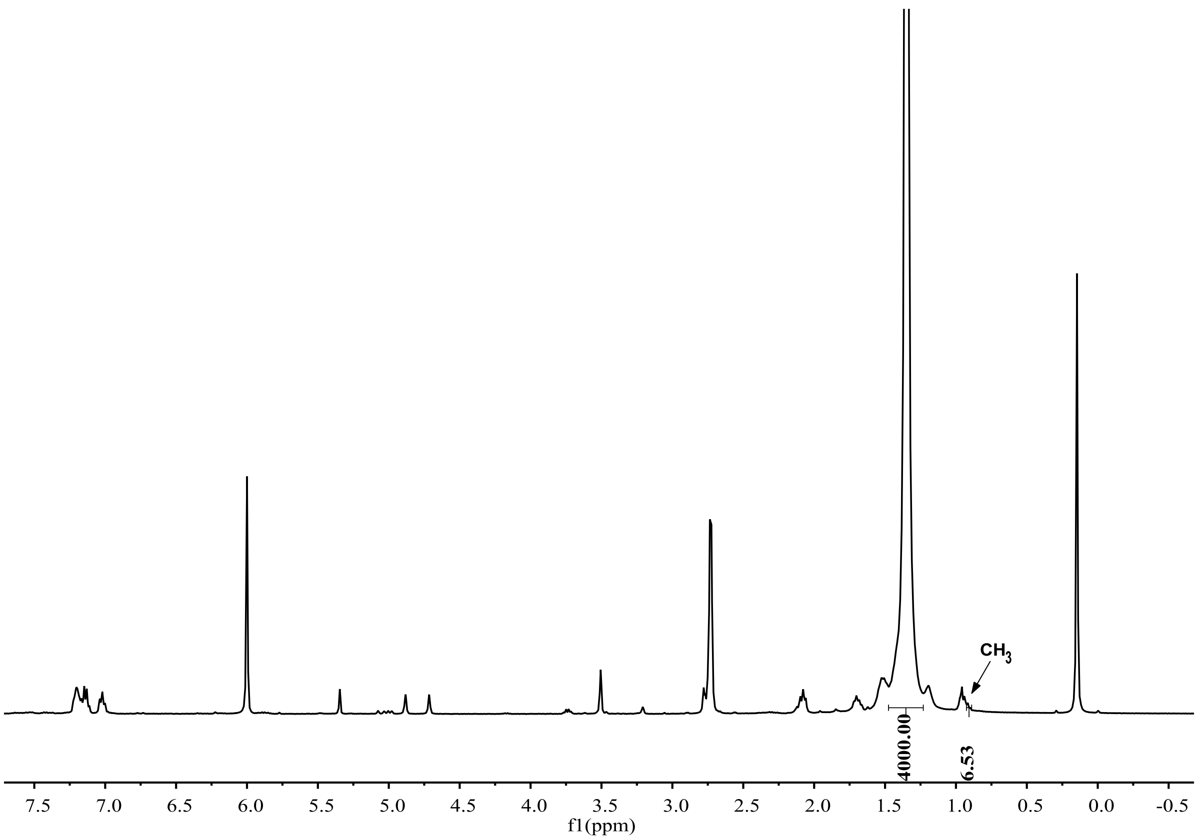


Figure S38. ^{1}H NMR spectrum (400 MHz, $C_2D_2Cl_4$, 110 ℃) of the copolymer from table 1, entry 17.

MW Averages

Mp: 4307	Mn: 1965	Mv: 6055	Mw: 7023
Mz: 16635	Mz+1: 26803	PD: 3.5740	

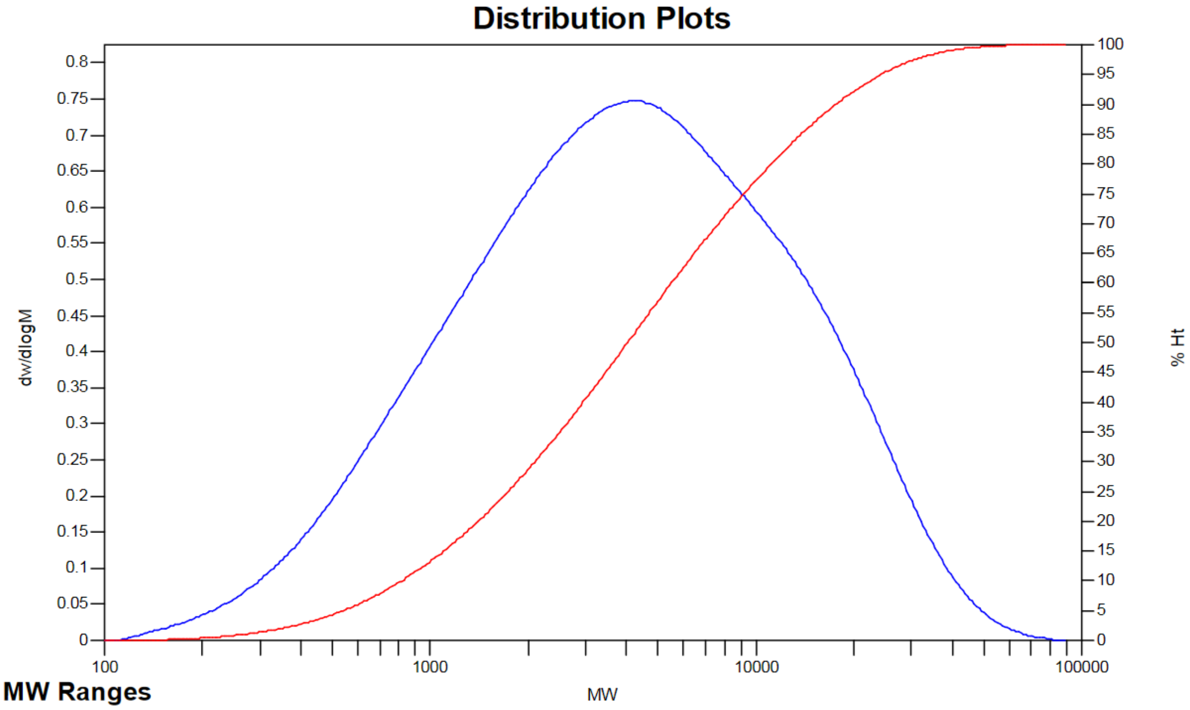


Figure S39. GPC trace of the copolymer from table 1, entry 4.

MW Averages

Mp: 3310	Mn: 1670	Mv: 4620	Mw: 5301
Mz: 11919	Mz+1: 18786	PD: 3.1743	

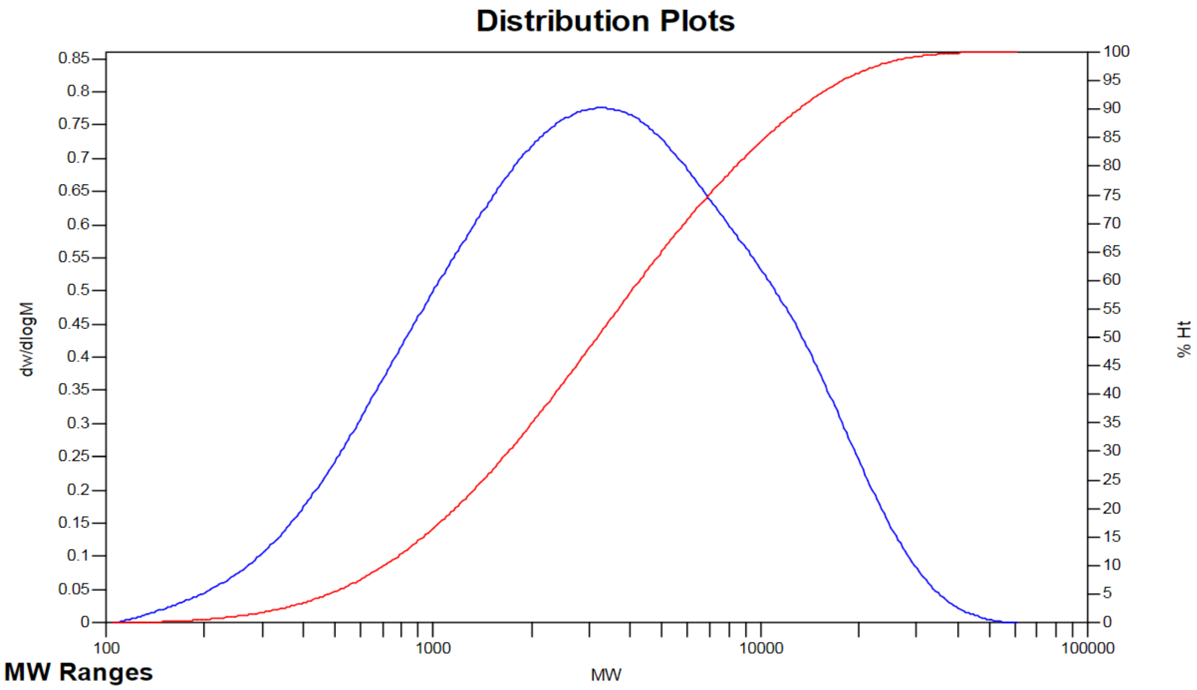


Figure S40. GPC trace of the copolymer from table 1, entry 5.

MW Averages

Mp: 8459	Mn: 2987	Mv: 7823	Mw: 8713
Mz: 16470	Mz+1: 24621	PD: 2.9170	

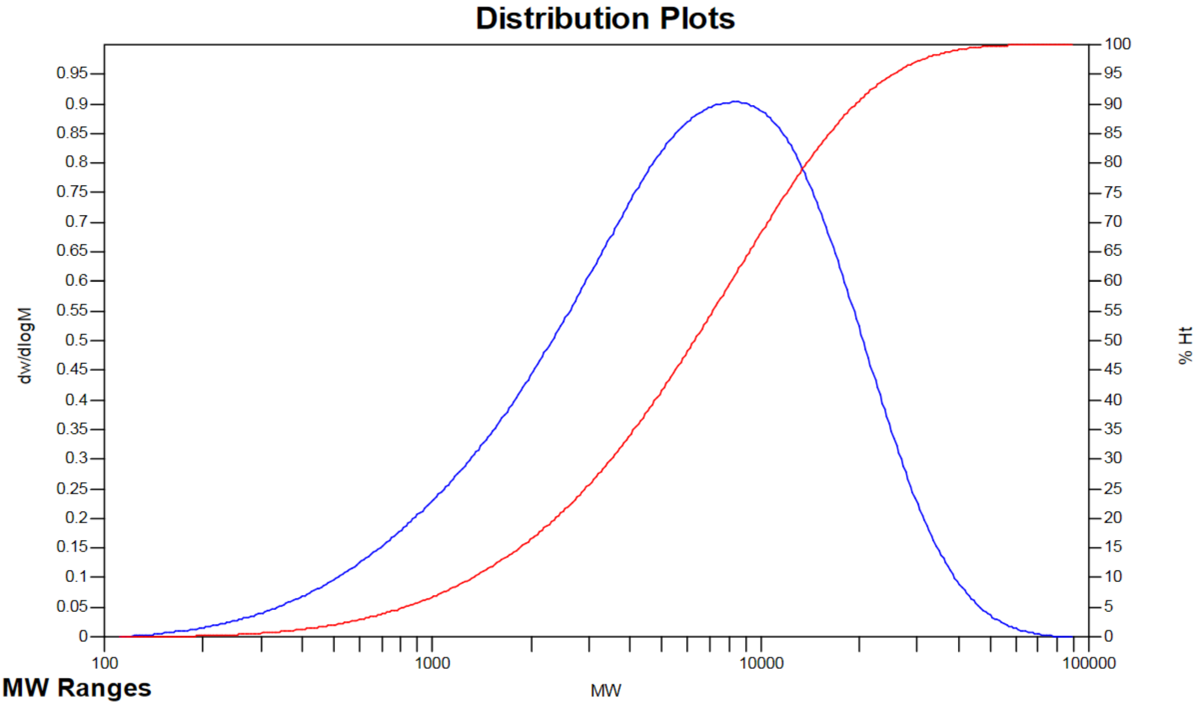


Figure S41. GPC trace of the copolymer from table 1, entry 6.

MW Averages

Mp: 6290	Mn: 2559	Mv: 6485	Mw: 7237
Mz: 13927	Mz+1: 21126	PD: 2.8281	

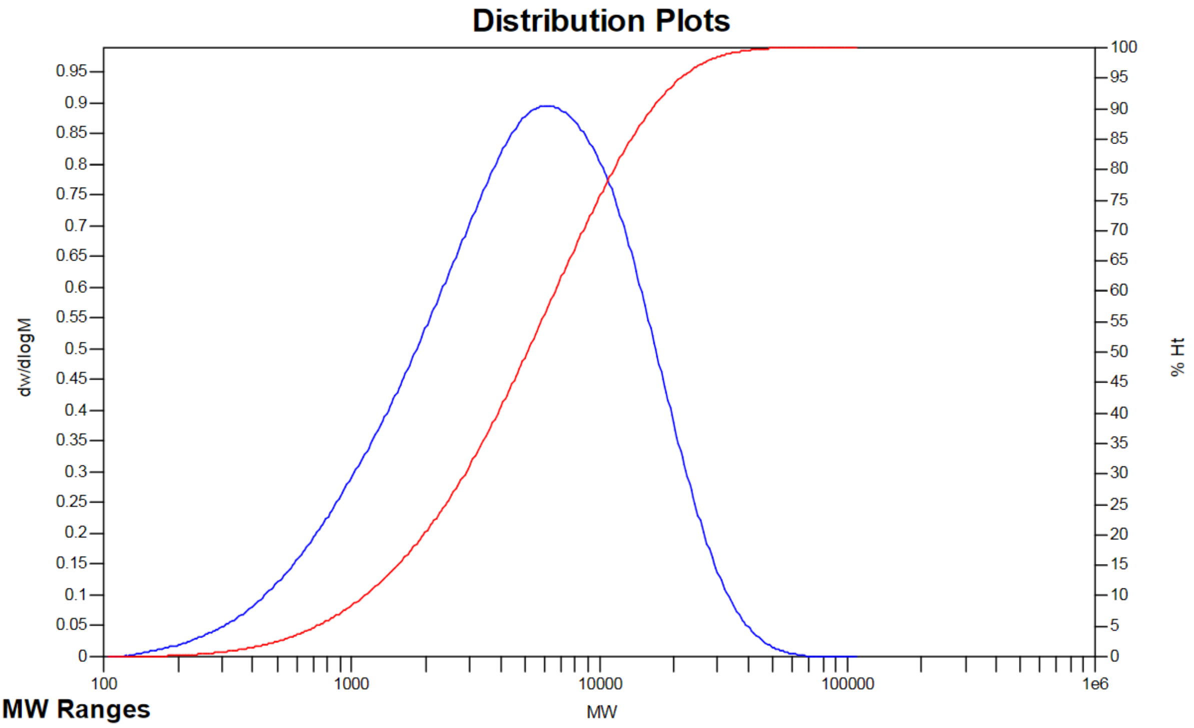
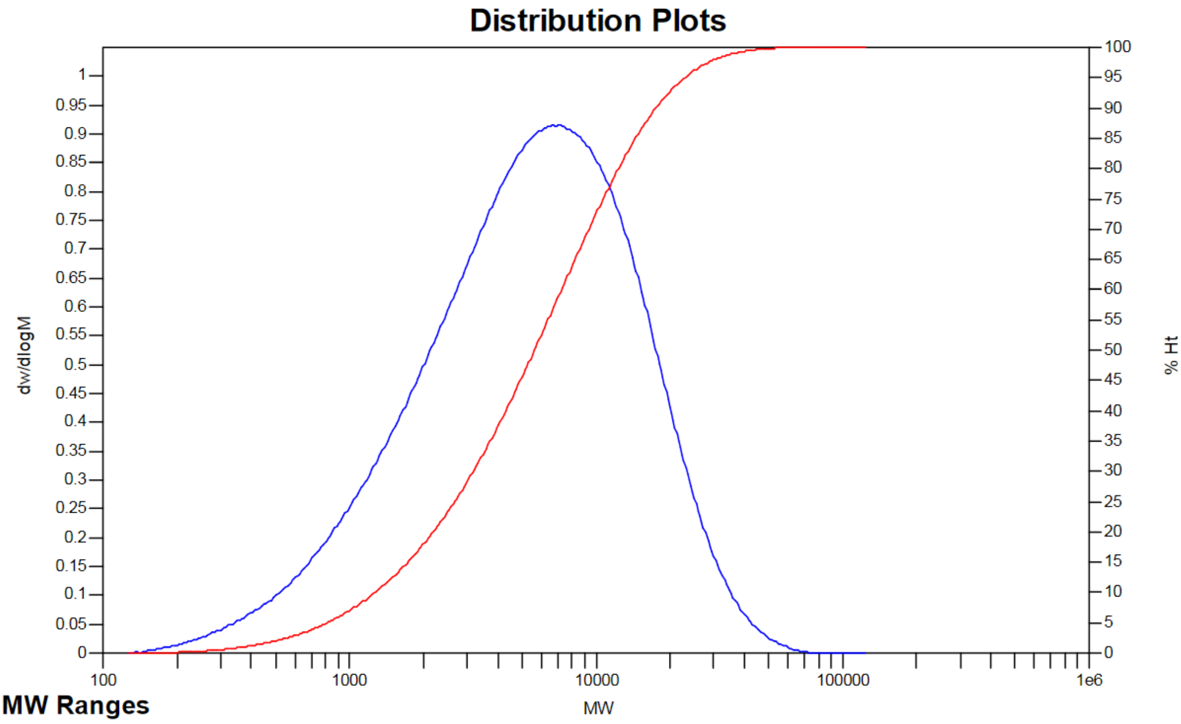


Figure S42. GPC trace of the copolymer from table 1, entry 7.

MW Averages

Mp: 6718 Mn: 2845 Mv: 7065 Mw: 7867

Mz: 15049 Mz+1: 23021 PD: 2.7652



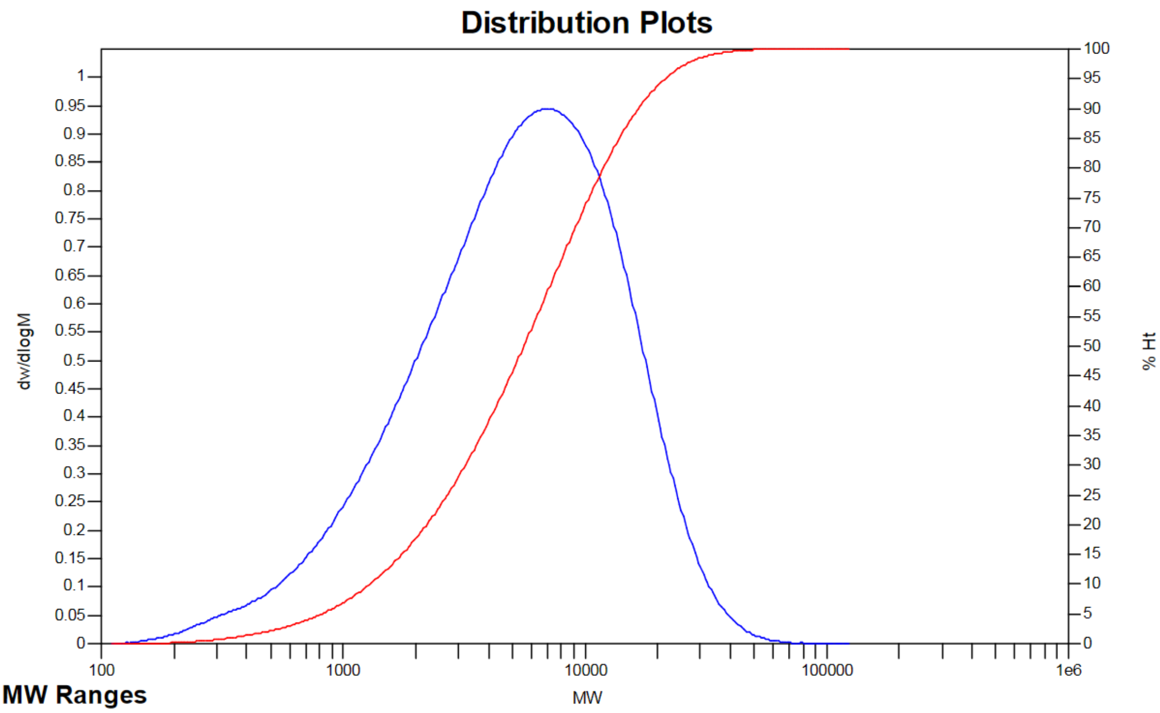
MW Ranges

Figure S43. GPC trace of the copolymer from table 1, entry 8

MW Averages

Mp: 6943 Mn: 2818 Mv: 6858 Mw: 7592

Mz: 14065 Mz+1: 21600 PD: 2.6941

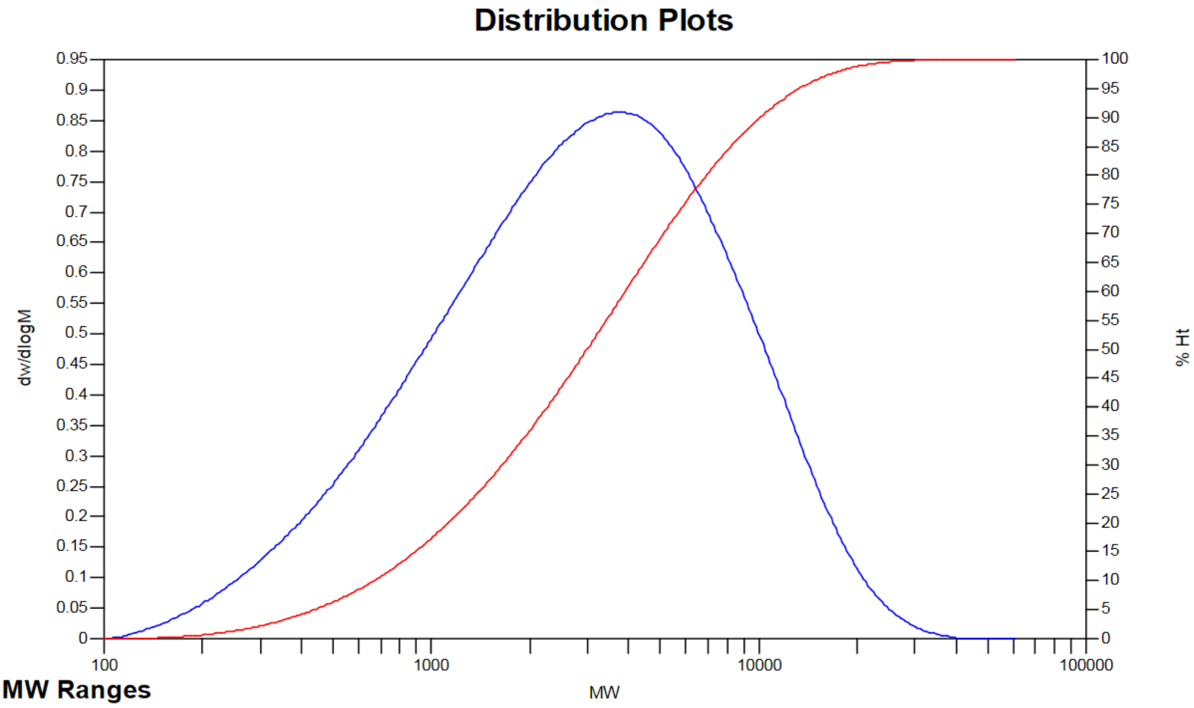


MW Ranges

Figure S44. GPC trace of the copolymer from table 1, entry 9

MW Averages

Mp: 3714	Mn: 1558	Mv: 3899	Mw: 4375
Mz: 8701	Mz+1: 13294	PD: 2.8081	

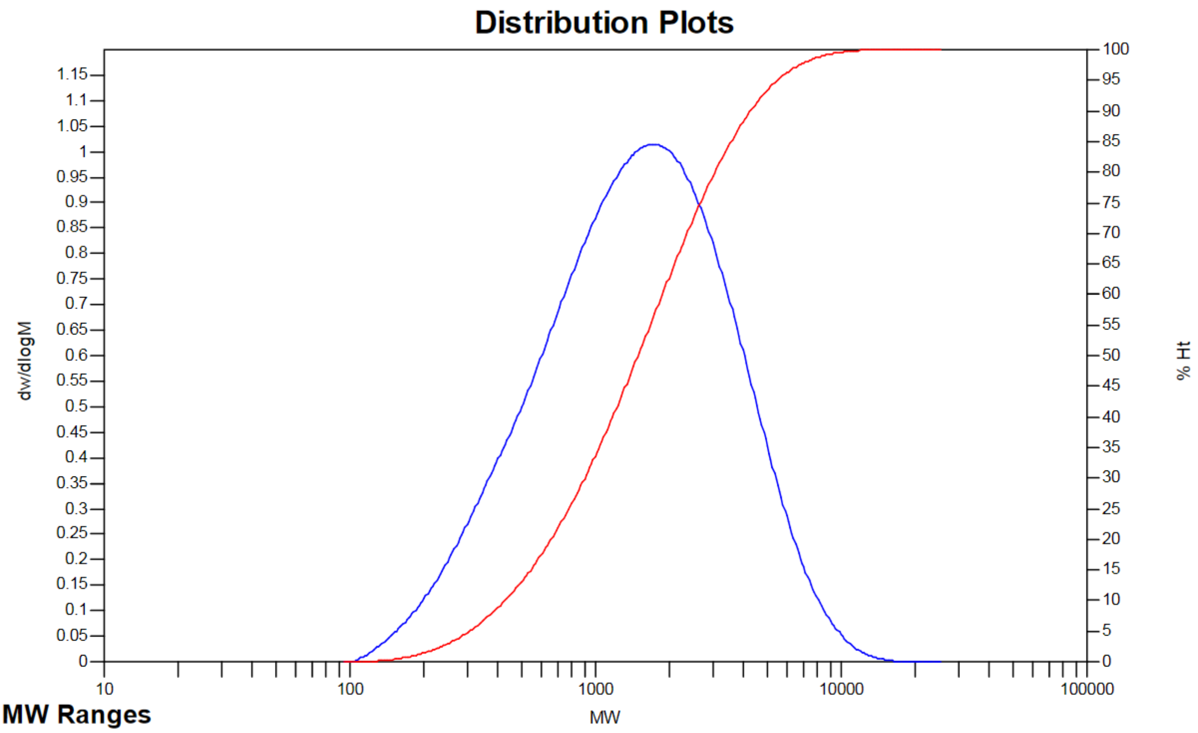


MW Ranges

Figure S45. GPC trace of the copolymer from table 1, entry 10

MW Averages

Mp: 1741	Mn: 948	Mv: 1821	Mw: 1991
Mz: 3504	Mz+1: 5191	PD: 2.1002	



MW Ranges

Figure S46. GPC trace of the copolymer from table 1, entry 11

MW Averages

Mp: 8321	Mn: 3007	Mv: 8292	Mw: 9303
Mz: 18413	Mz+1: 28651	PD: 3.0938	

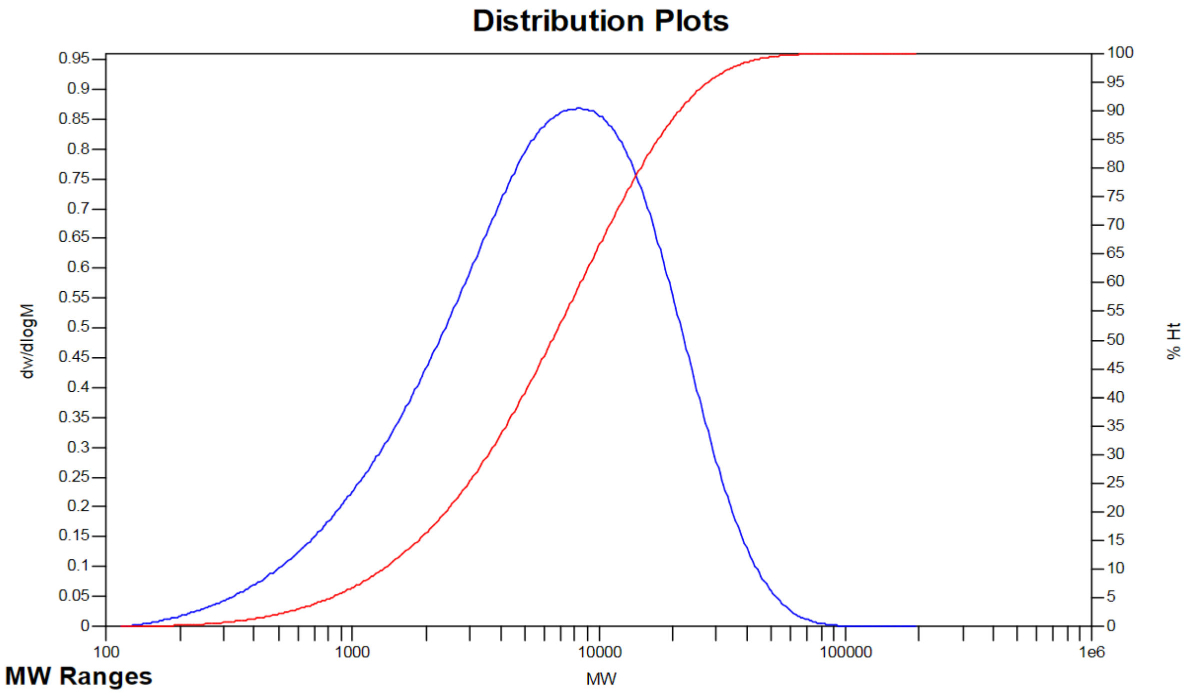


Figure S47. GPC trace of the copolymer from table 1, entry 12

MW Averages

Mp: 5605	Mn: 2377	Mv: 5909	Mw: 6592
Mz: 12622	Mz+1: 18909	PD: 2.7732	

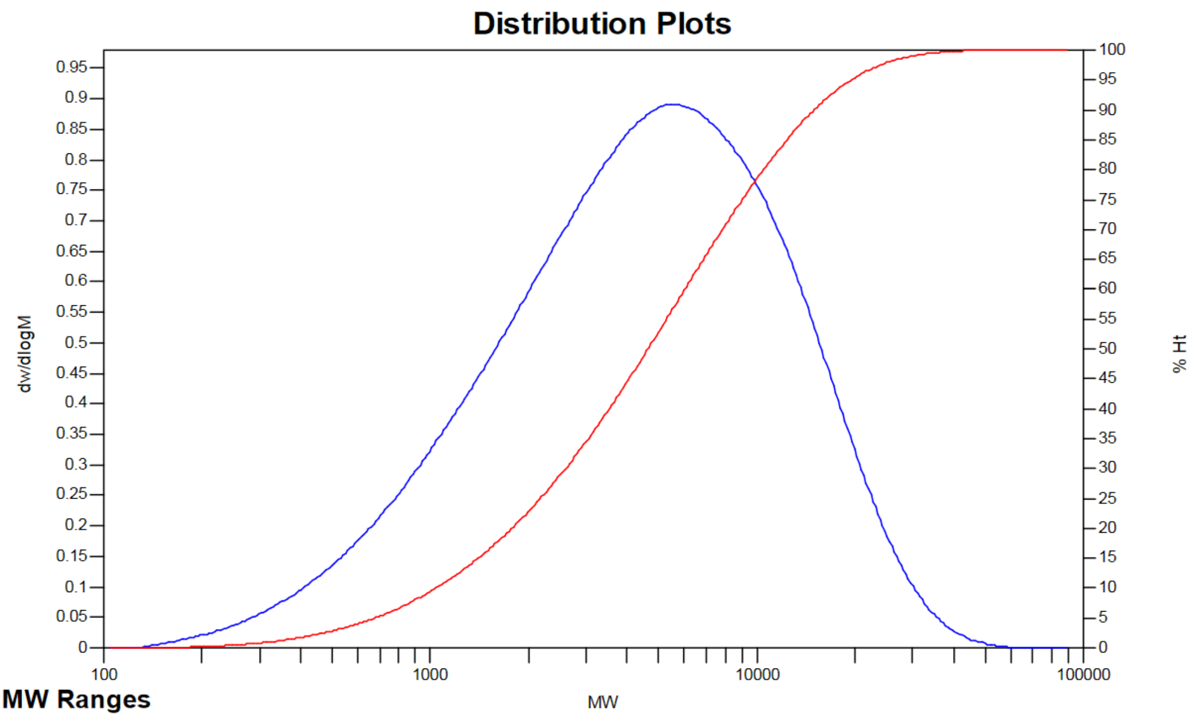


Figure S48. GPC trace of the copolymer from table 1, entry 13

MW Averages

Mp: 11953 Mn: 4154 Mv: 10228 Mw: 11248

Mz: 19693 Mz+1: 28175 PD: 2.7078

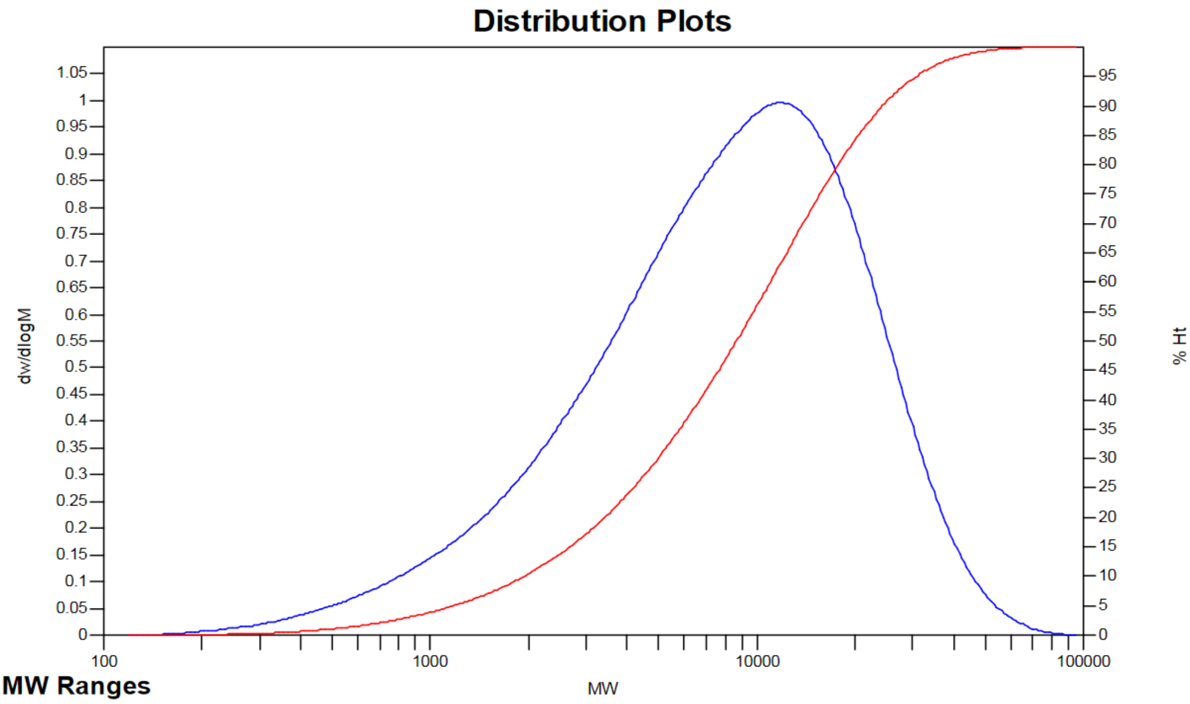


Figure S49. GPC trace of the copolymer from table 1, entry 14

MW Averages

Mp: 7920 Mn: 3064 Mv: 7182 Mw: 7900

Mz: 14026 Mz+1: 20990 PD: 2.5783

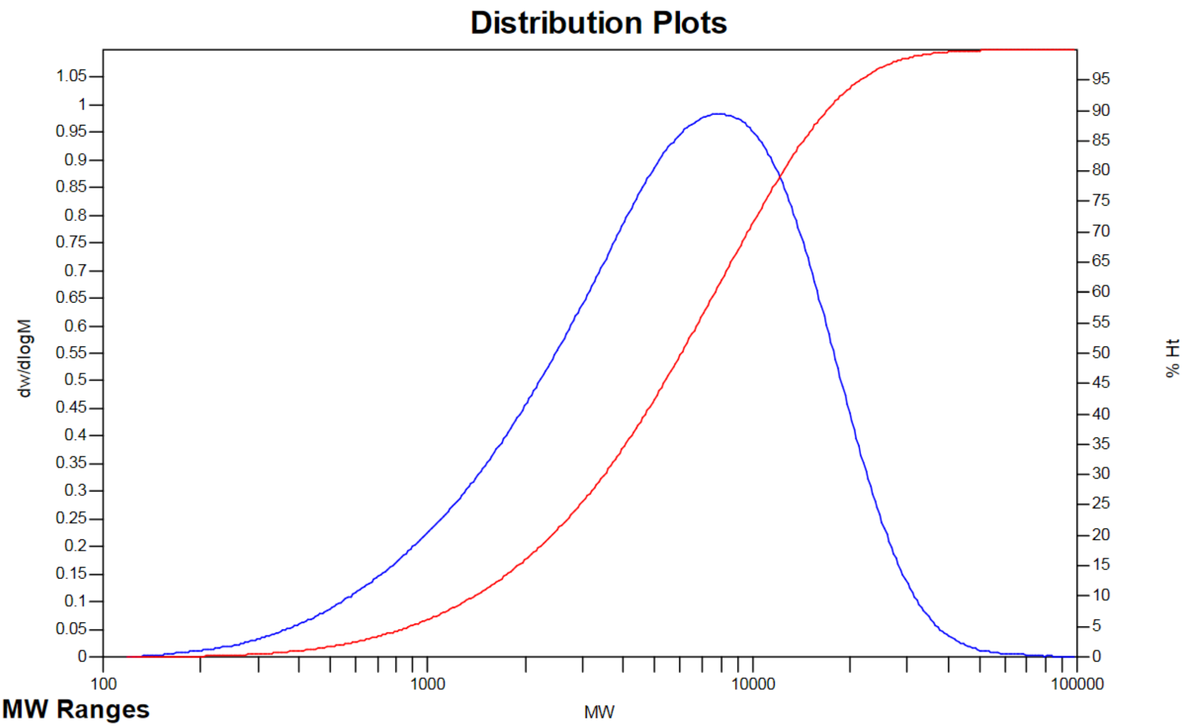


Figure S50. GPC trace of the copolymer from table 1, entry 15

MW Averages

Mp: 5078	Mn: 2029	Mv: 4702	Mw: 5180
Mz: 9150	Mz+1: 12968	PD: 2.5530	

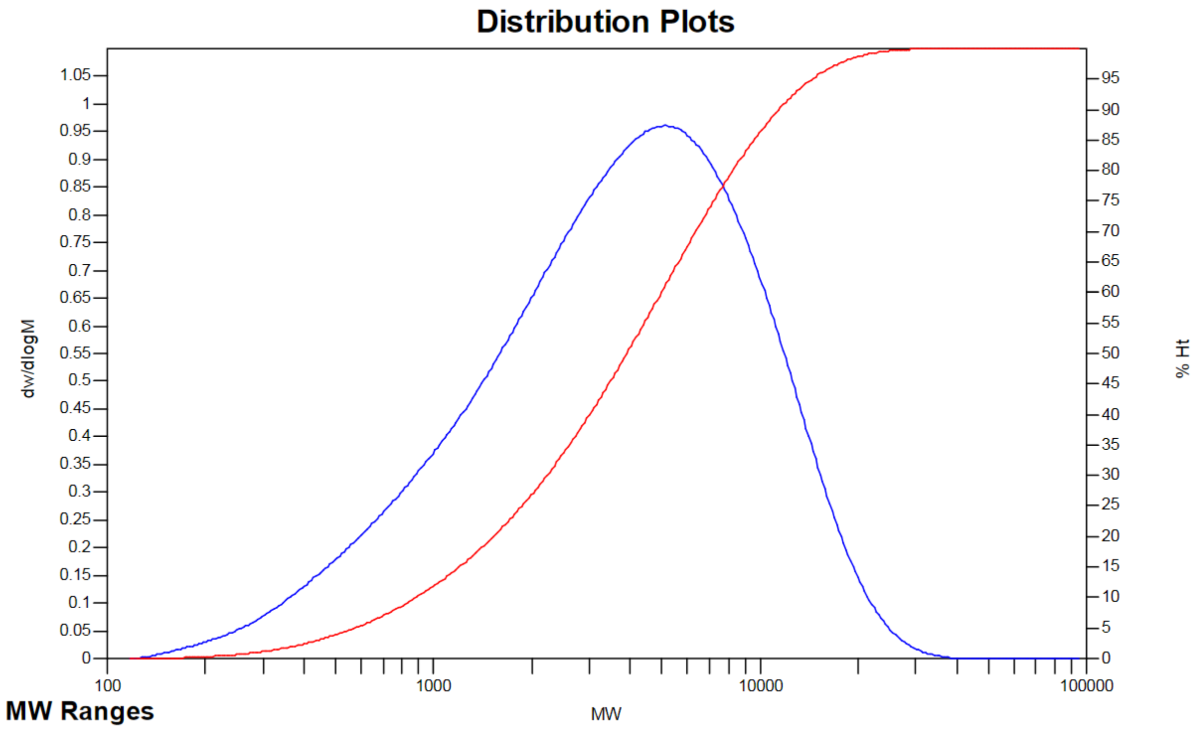


Figure S51. GPC trace of the copolymer from table 1, entry 17

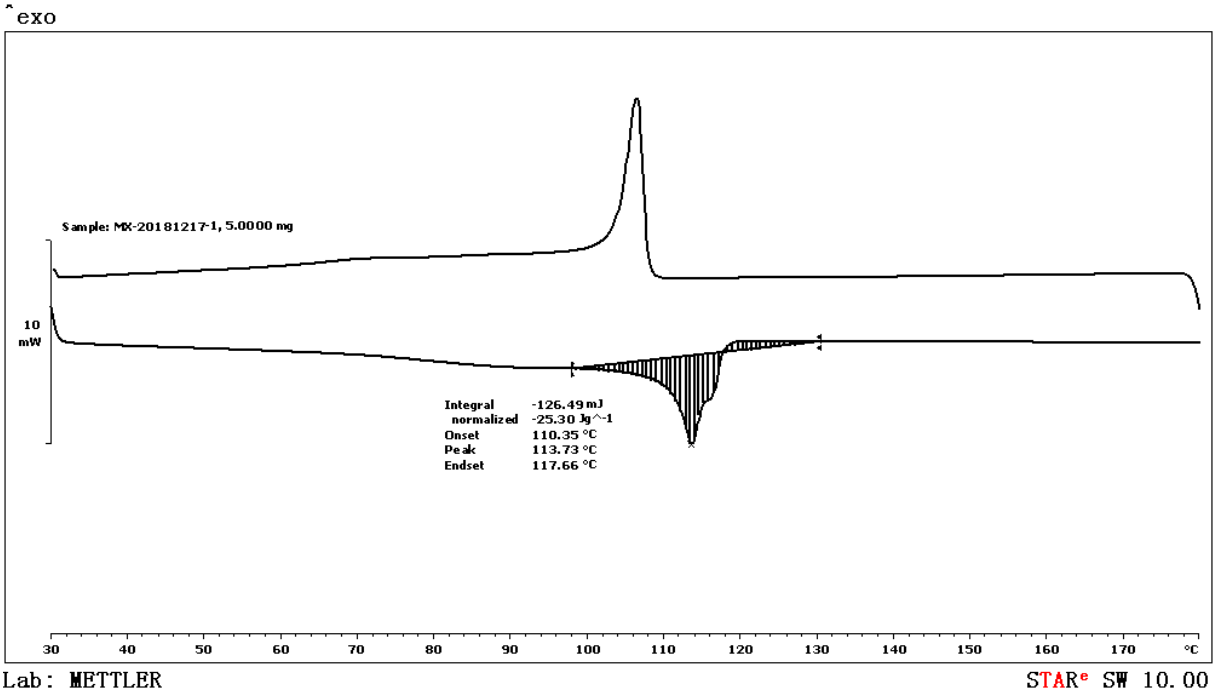


Figure S52. DSC data of the polymer from table 1, entry 4.

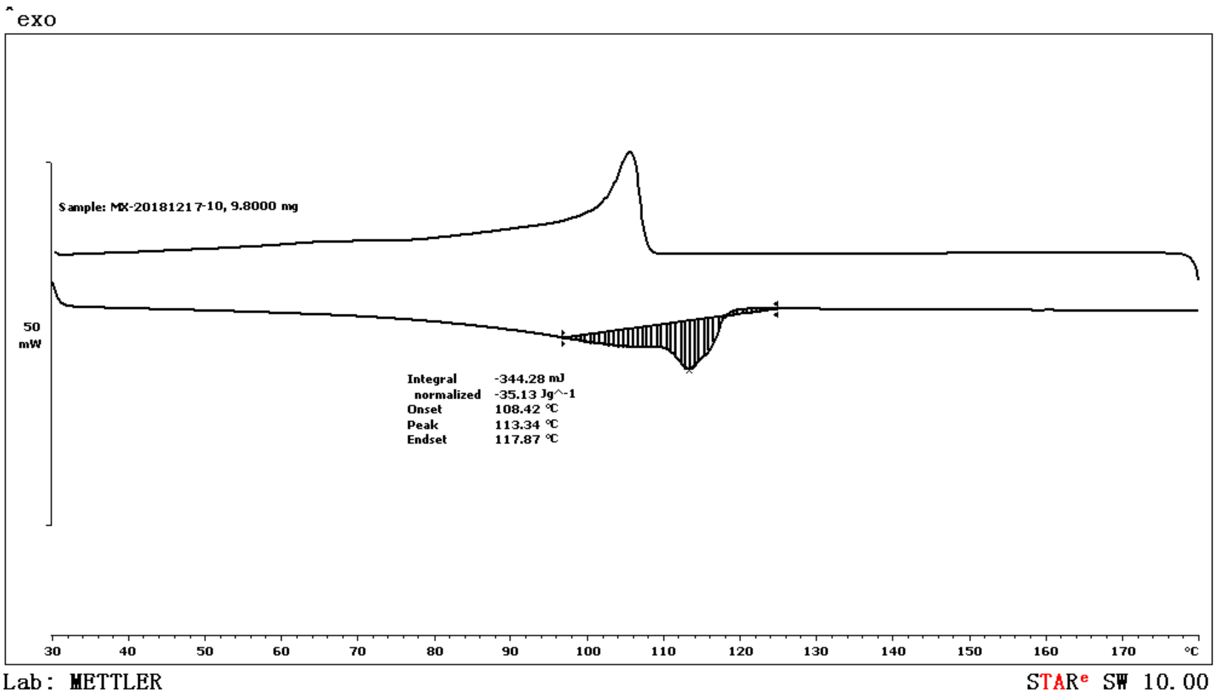


Figure S53. DSC data of the polymer from table 1, entry 8

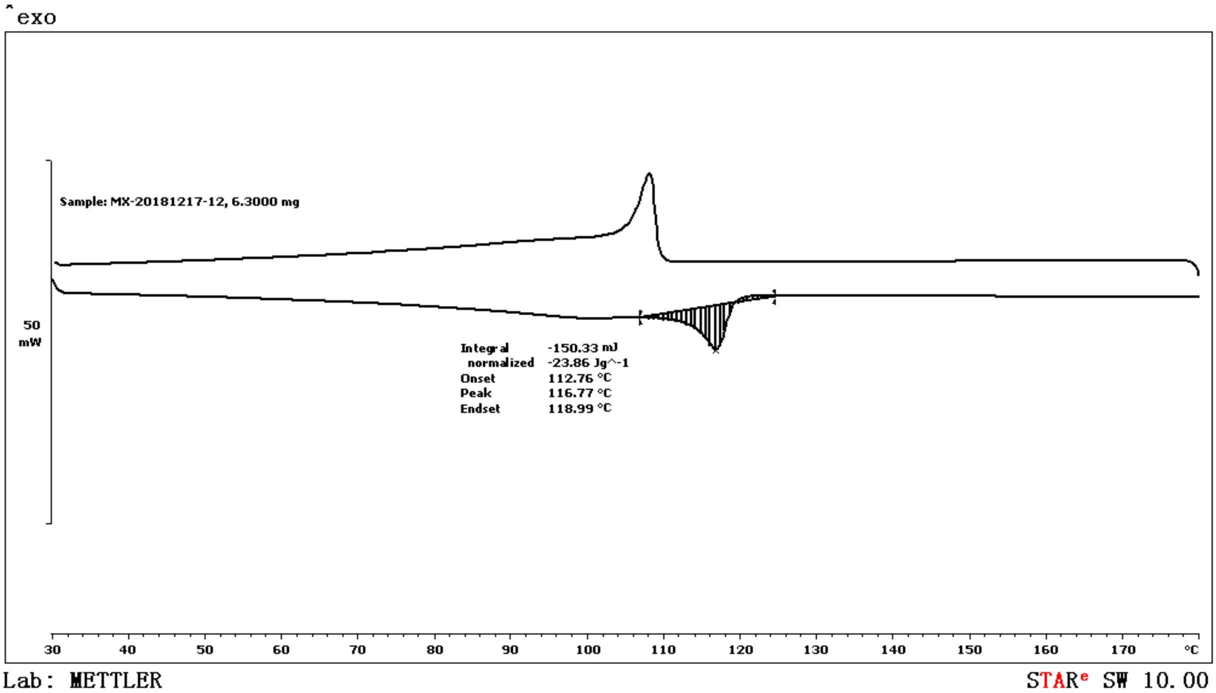


Figure S54. DSC data of the polymer from table 1, entry 10

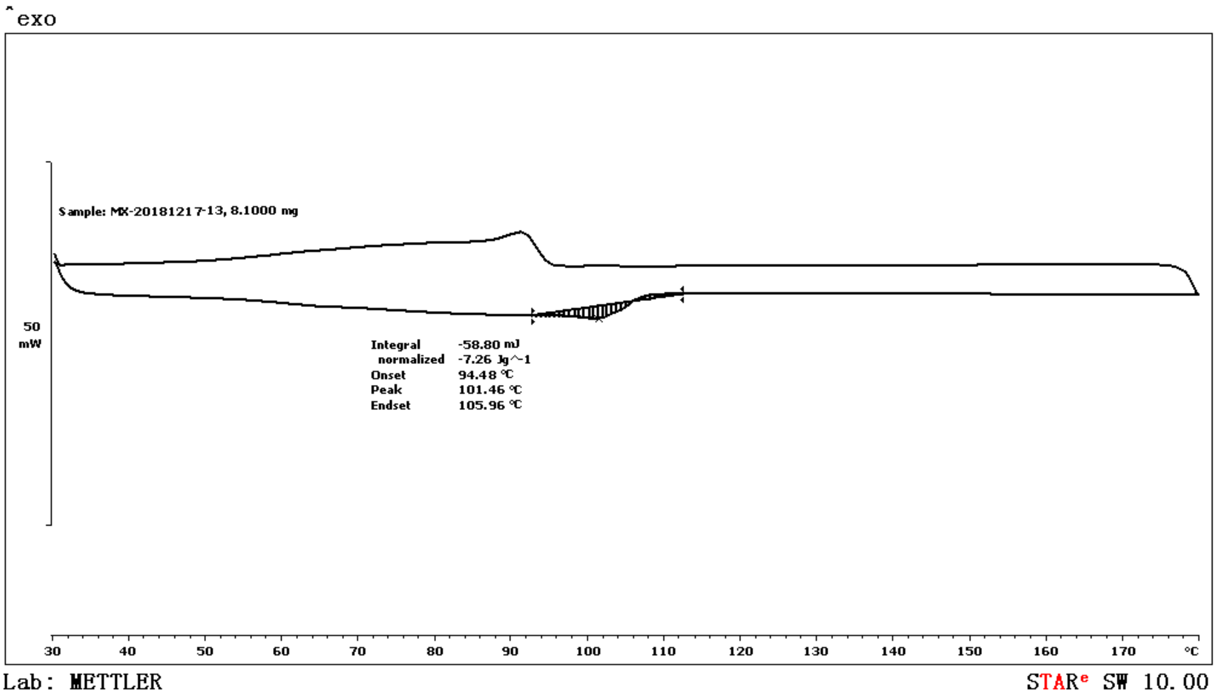


Figure S55. DSC data of the polymer from table 1, entry 11

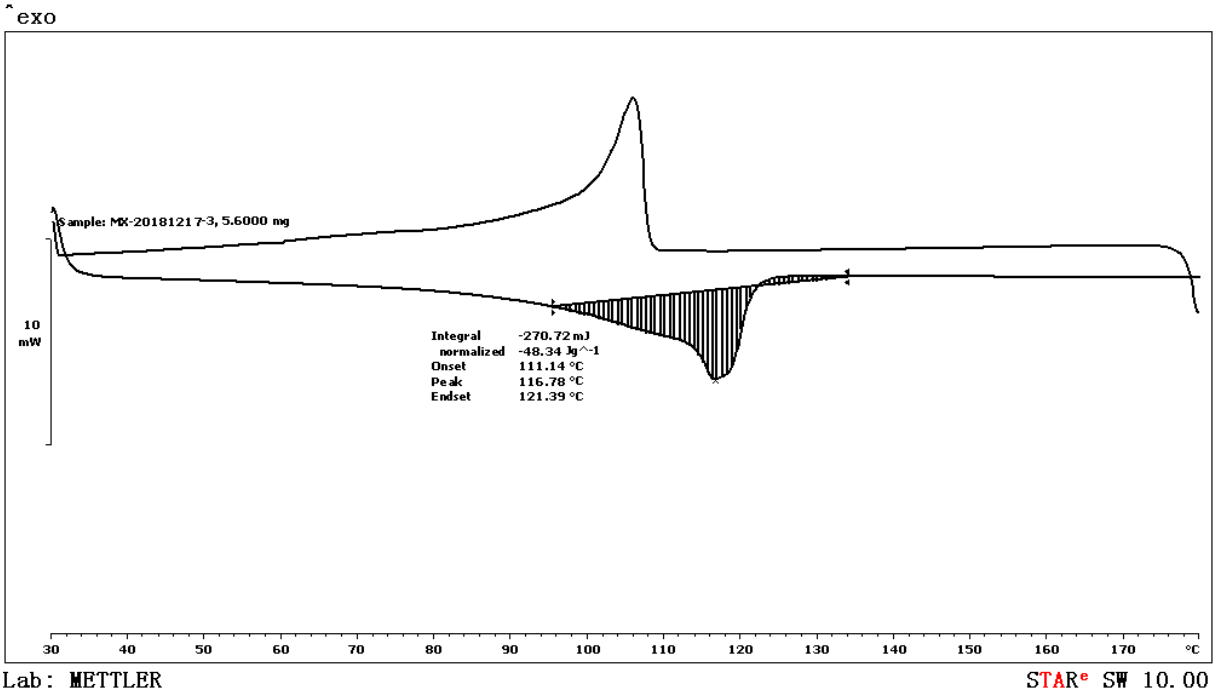


Figure S56. DSC data of the polymer from table 1, entry 12

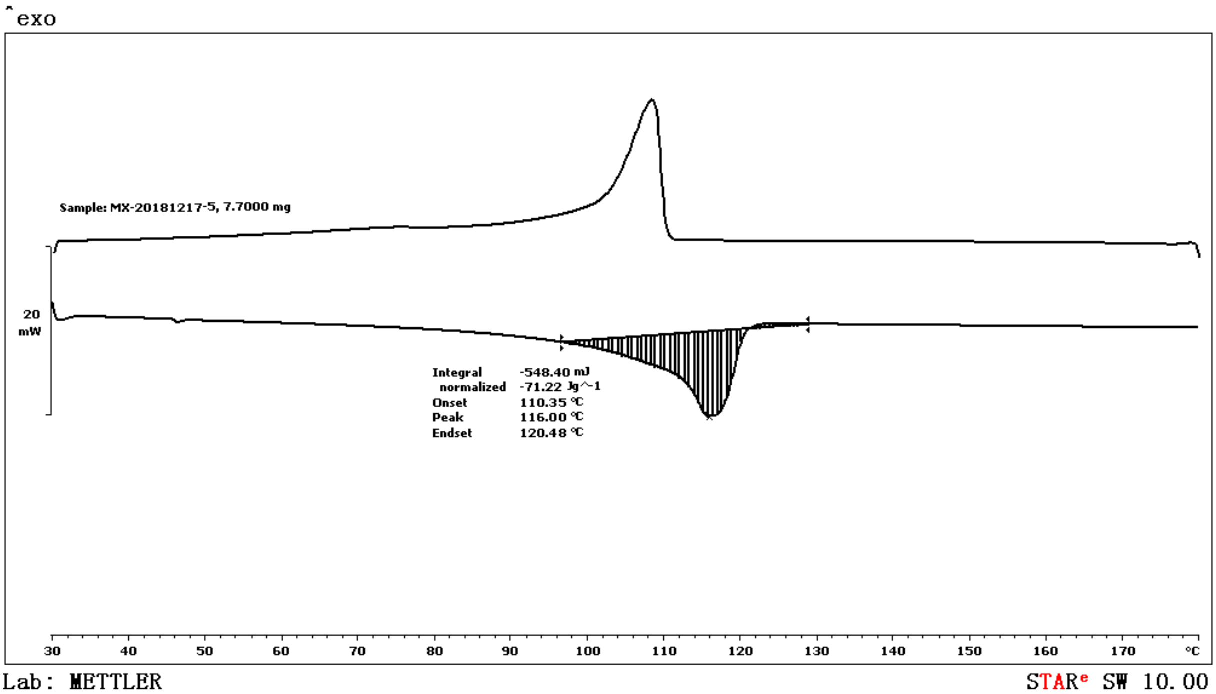


Figure S57. DSC data of the polymer from table 1, entry 14

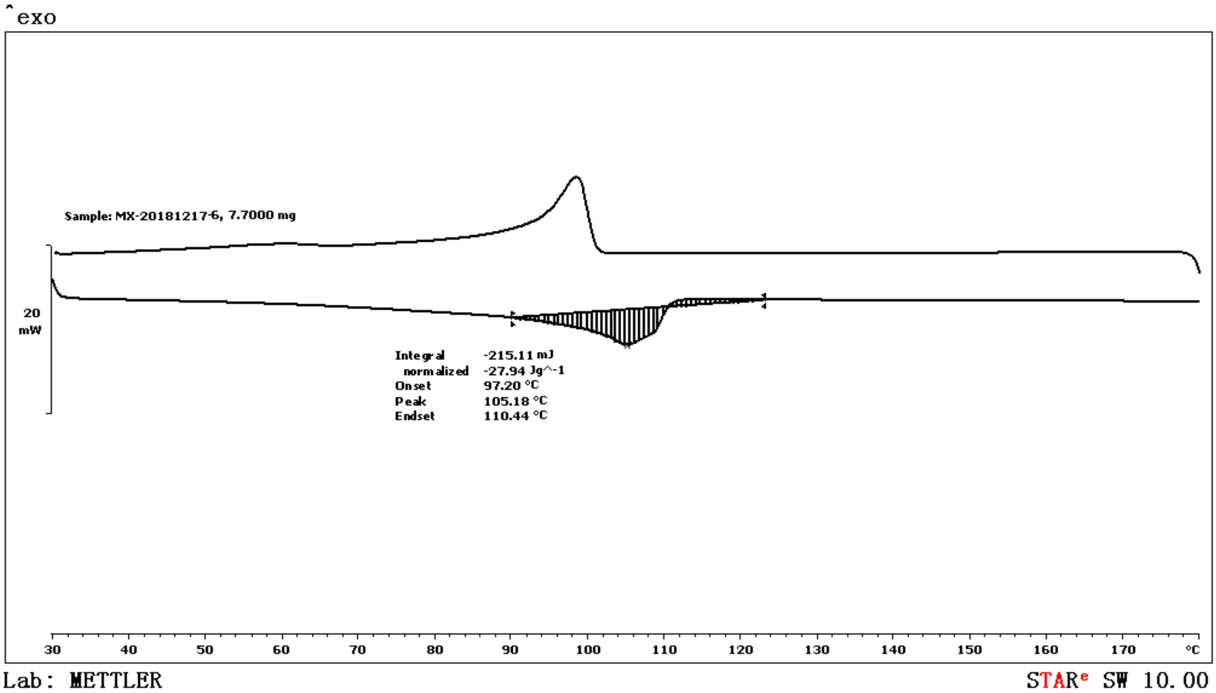


Figure S58. DSC data of the polymer from table 1, entry 15

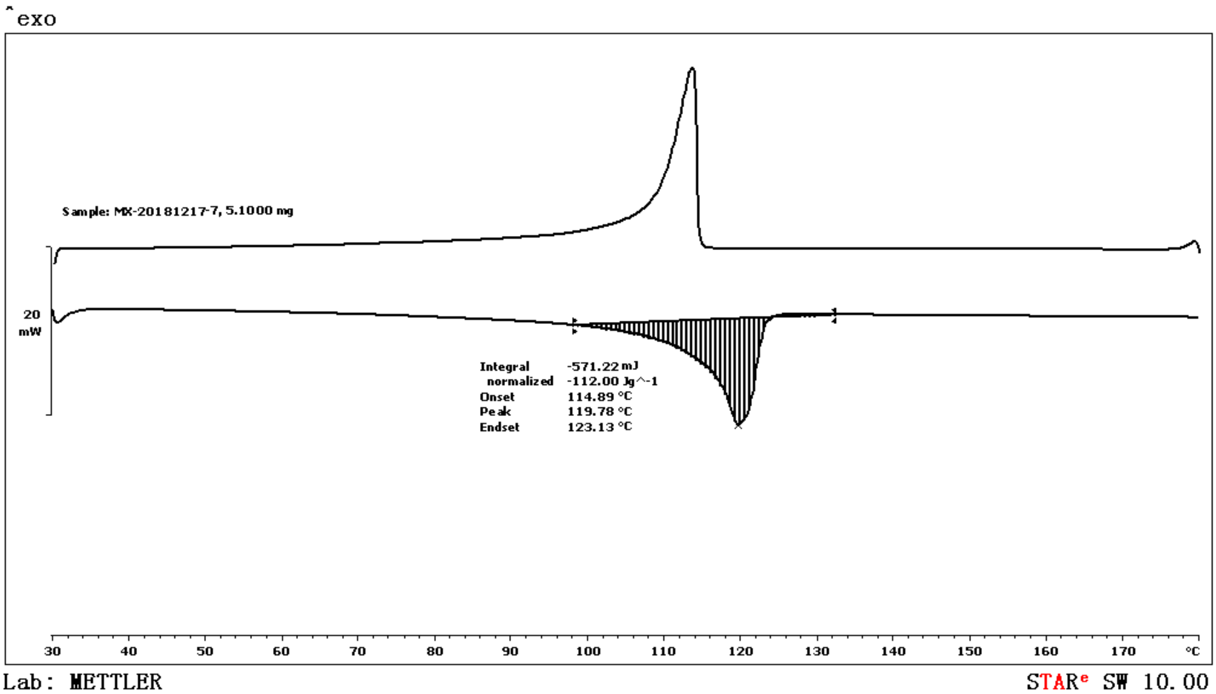


Figure S59. DSC data of the polymer from table 1, entry 17

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