Modulating the Polyolefin Properties through the Incorporation of Nitrogen-Containing Polar Monomers

Yinna Na, Dan Zhang, Changle Chen*

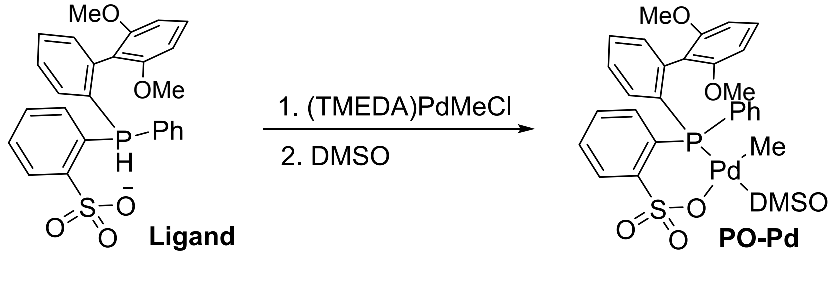
CAS Key Laboratory of Soft Matter Chemistry, iChEM (Collaborative Innovation Center of Chemistry for Energy Materials), Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, 230026, China

Table of Contents

1. Experimental Section

General Considerations. All experiments were carried out under a dry Nitrogen atmosphere using standard Schlenk techniques or in a glove-box. Deuterated solvents used for NMR were dried and distilled prior to use. ^{1}H, ^{13}C NMR spectra were recorded by a Bruker Ascend Tm 400 spectrometer at ambient temperature unless otherwise stated. The chemical shifts of the ^{1}H and ^{13}C NMR spectra were referenced to the residual solvent; Coupling constants are in Hz. Molecular weight and molecular weight distribution of the polymer were determined by gel permeation chromatography (GPC) with a PL 210 equipped with one Shodex AT-803S and two Shodex AT-806MS columns at 150 °C using o-dichlorobenzene as a solvent and calibrated with polystyrene standards. Water contact angles on polymer films were measured with Contact Angle Meter SL200B (Solon Tech. Co., Ltd.) by the dynamic sessile drop method.

Preparation of PO-Pd. The phosphine sulfonate ligand[1] (1.0 g, 2.0 mmol) was suspended in THF (16 mL). Pd(tmeda)Me_2 (550 mg, 2.1 mmol) was added at -5 °C. After stirring for 5 min, the evolution of gas stopped and the suspension turned clear. The solution was stirred overnight. The resulting white precipitate was filtered, washed with Et_2O and dried under reduced pressure to yield the tmeda-bridged dimer. The dimer was dispersed in 20 mL DMSO at room temperature. The solvent was removed under reduced pressure at 80 °C. The dimer complex is only slightly soluble in DMSO, therefore complete dissolution of the solid indicate complete conversion of the starting material. After removal of DMSO under reduced pressure, the resulting solid was dispersed in Et_2O, and isolated by filtration to yield a white solid (800 mg, 60%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.31 (s, 1H), 7.60-7.55 (m, 3H), 7.43-7.29 (m, 8H), 7.24-7.22 (m, 2H), 3.73 (s, 3H, O*Me*), 2.85 (s, 6H, DMSO), 2.70 (s, 3H, O*Me*), 0.56 (s, 3H, Pd-*Me*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.3 (s), 157.9 (s), 149.1 (d, J_{PC} = 14 Hz), 142.5 (d, J_{PC} = 18 Hz), 136.3 (s), 135.1 (d, J_{PC} = 9 Hz), 134.7(s), 133.7 (d, J_{PC} = 10 Hz), 131.8 (s), 131.1 (s), 130.5 (d, J_{PC} = 7Hz), 129.0 (br), 128.9 (br), 128.8 (br), 128.7(br), 128.5 (br), 127.1 (d, J_{PC} = 8 Hz), 118.0 (s), 104.2 (s), 103.8 (s), 56.0 (s, O*Me*), 54.6 (s, O*Me*), 41.6 (br, DMSO), 4.1 (s, Pd-*Me*). ^{31}P NMR (DMSO-d_6): δ 15.4. Anal. Calcd. for $C_{29}H_{31}O_6PPdS_2$: C, 51.44; H, 4.62. Found: C, 51.49; H, 4.60.



Procedure for copolymerization. In a typical experiment, a 350 mL glass thick-walled pressure vessel was charged with chlorobenzene, a desired amount of comonomer and a magnetic stir bar in the glovebox. The pressure vessel was connected to a high pressure line and the solution was degassed. The vessel was warmed to the desire temperature using an oil bath and allowed to equilibrate for 5 min. The metal complex in 2 mL CH_2Cl_2 was injected into the polymerization system via syringe. With rapid stirring, the reactor was pressurized, maintained at a desired of ethylene, and stirred continuously for the desired time. The pressure vessel was vented, the polymerization was quenched via the addition of MeOH (5 mL) and the polymer was precipitated using excess MeOH. After filtration, the copolymer was obtained and dried at 80 °C for 24 h under vacuum. The polar monomer incorporation (mol %) was calculated from 1H NMR analysis.

Procedure for terpolymerization. In a typical experiment, a 350 mL glass thick-walled pressure vessel was charged with chlorobenzene, a desired amount of two comonomers and a magnetic stir bar in the glovebox. The pressure vessel was connected to a high pressure line and the solution was degassed. The vessel was warmed to the desire temperature using an oil bath and allowed to equilibrate for 5 min. The metal complex in 2 mL CH_2Cl_2 was injected into the polymerization system via syringe. With rapid stirring, the reactor was pressurized, maintained at a desired of ethylene, and stirred continuously for the desired time. The pressure vessel was vented, the polymerization was quenched via the addition of MeOH (5 mL) and the polymer was precipitated using excess MeOH. After filtration, the terpolymer was obtained and dried at 80 °C for 24 h under vacuum. The polar monomer incorporation (mol %) was calculated from 1H NMR analysis.

Water contact angle measurement. Water contact angles on polymer films were measured with Contact Angle Meter SL200B (Solon Tech. Co., Ltd.) by the dynamic sessile drop method. Samples for water contact angle measurements were prepared by the evaporation of 3 to 5 % (w/w) solutions in toluene onto glass slides under ambient conditions. The solvent was evaporated on top of a glass slide for 10 minutes, and a second layer of the polymer solution was then applied in order to make the film thicker. The water contact angles of the polymer thin films were measured using a contact angle goniometer at 25 °C with an accuracy of ±3°. The reported values are the average of at least six measurements made at different positions of the film.

Mechanical properties of the polyethylene sample. Standard test method ASTM 638 was followed to measure the mechanical properties of the polyethylene sample. Polymers were melt-pressed at 30 to 35^{o}C above their melting point to obtain the test specimens. The test specimens had 28-mm gauge length, 3-mm width, and thickness of 1 mm. Stress/strain experiments were performed at 10 m/min by means of a Universal Test Machine (UTM2502) at room temperature. At least three specimens of each copolymer were tested.

Stoichiometric insertion studies. The insertion of NB-NP and NP into the Pd–Me bond of palladium complex Pd was monitored by ^{1}H NMR under pseudo first order conditions. General procedure: About 5 μmol of **PO-Pd** was dissolved in 0.5 mL of CD_2Cl_2. About 5 equivalents of monomer were added, the NMR tube was sealed. 1H NMR spectra were recorded periodically at 20 °C. The decrease of the resonances for **PO-Pd** complex and the increase of a new set of species could be clearly observed.

2. Spectra data

2.1 NMR spectra

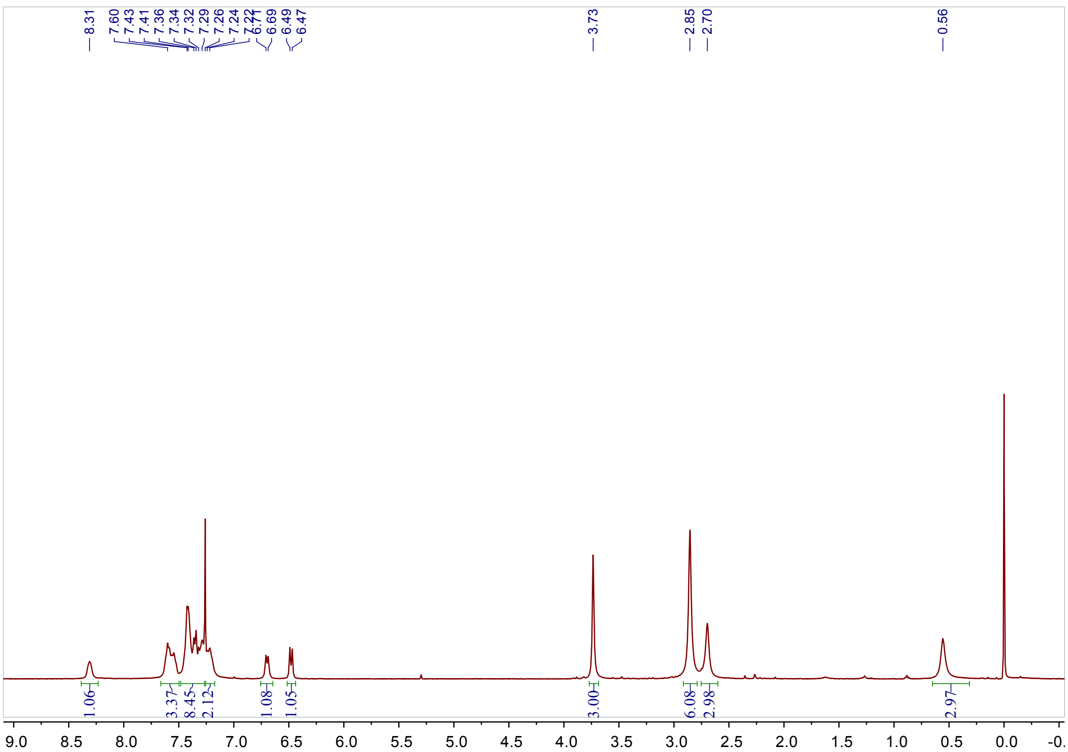


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **PO-Pd**.

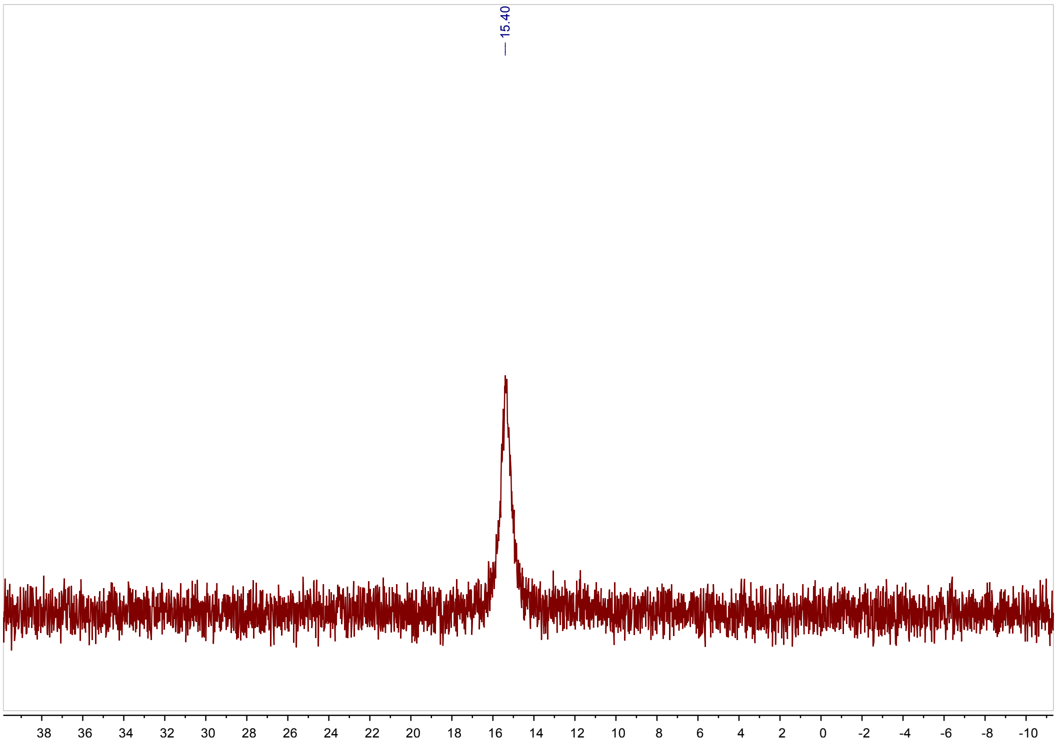


Figure S2. ^{31}P NMR spectrum (162 MHz, DMSO-d_6) of **PO-Pd**.

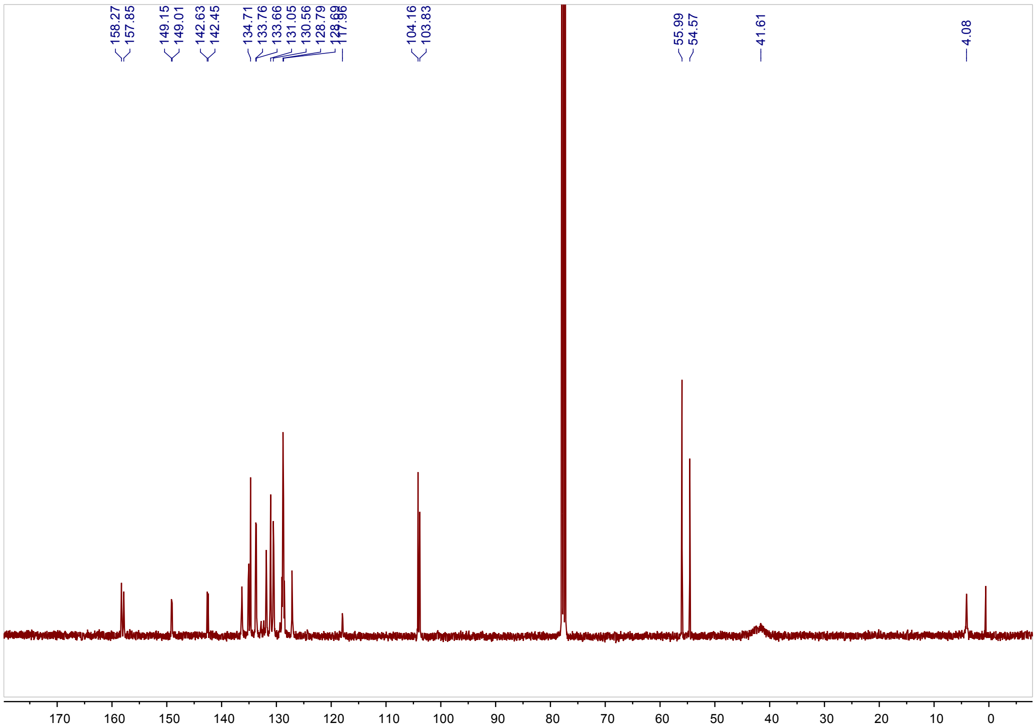


Figure S3. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **PO-Pd**.

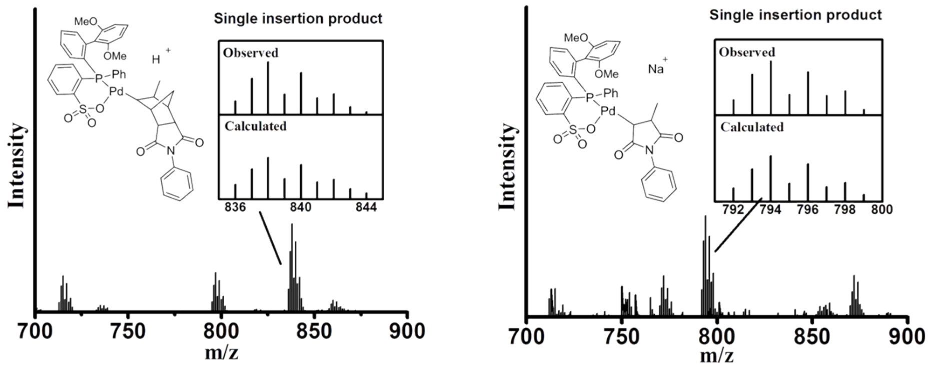


Figure S4. ESI-MS spectrum of a mixture of **PO-Pd** complex and comonomers (1:5). Inset: expanded experimental and calculated isotope patterns of single insertion product of comonomers into the Pd-allyl bond.

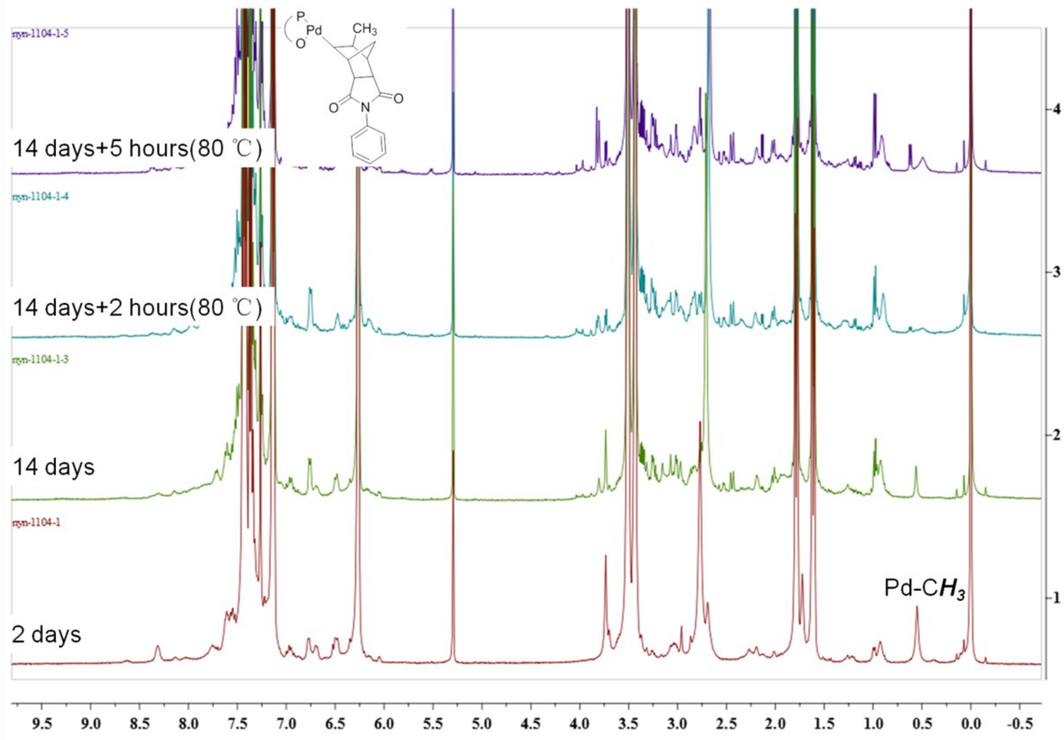


Figure S5. ^{1}H NMR ($CDCl_3$) monitoring of the reaction of PO-Pd (Pd-Me) with 5 eq of NB-NP at 25 °C.

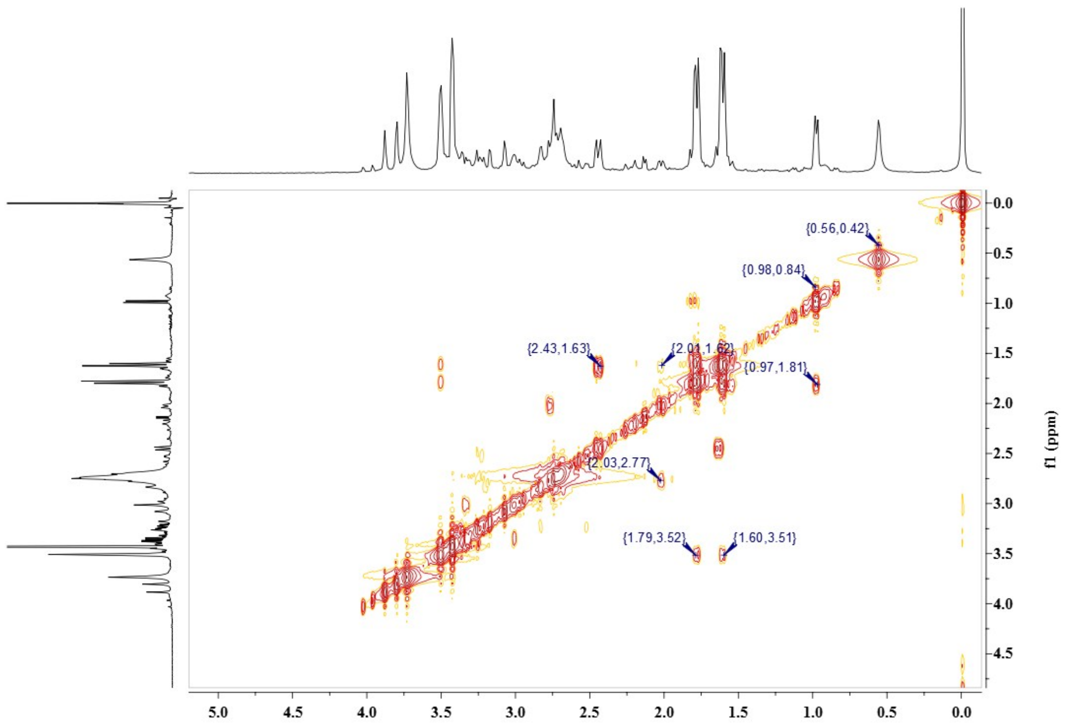


Figure S6. ^1H-^1H gCOSY 2D spectrum (25 °C, $CDCl_3$) of POPd-NBNP.

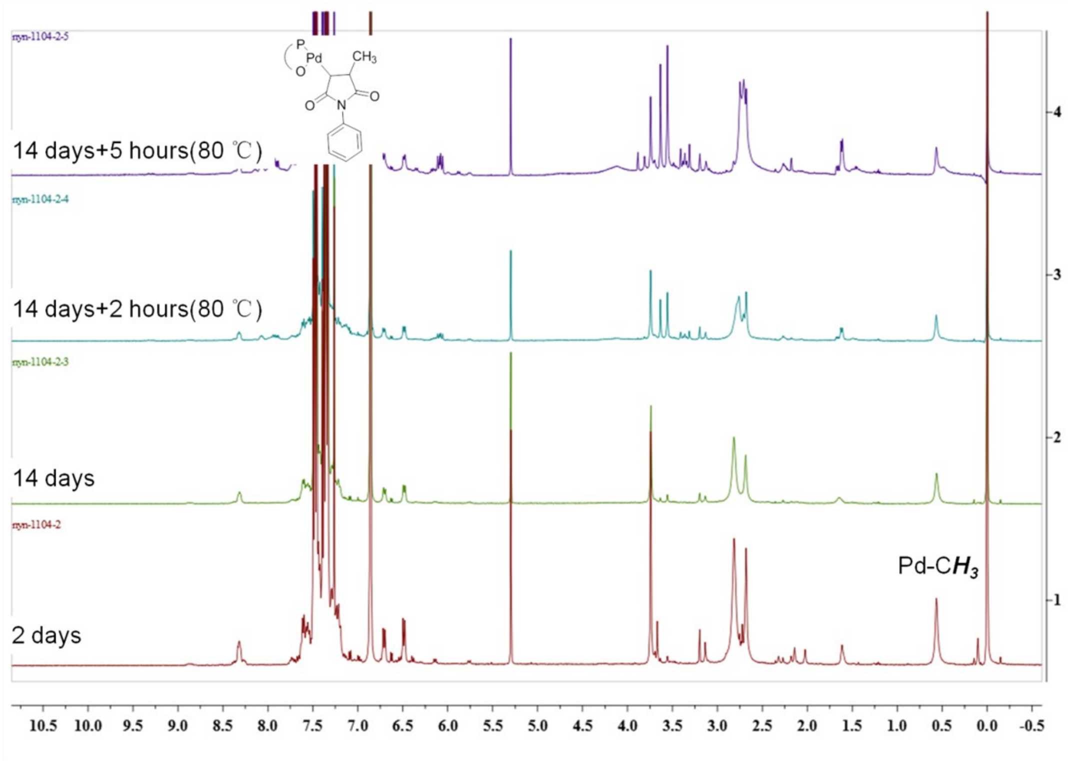


Figure S7. 1H NMR (CD_2Cl_2) monitoring of the reaction of PO-Pd (Pd-Me) with 5 eq of NP at 25 °C.

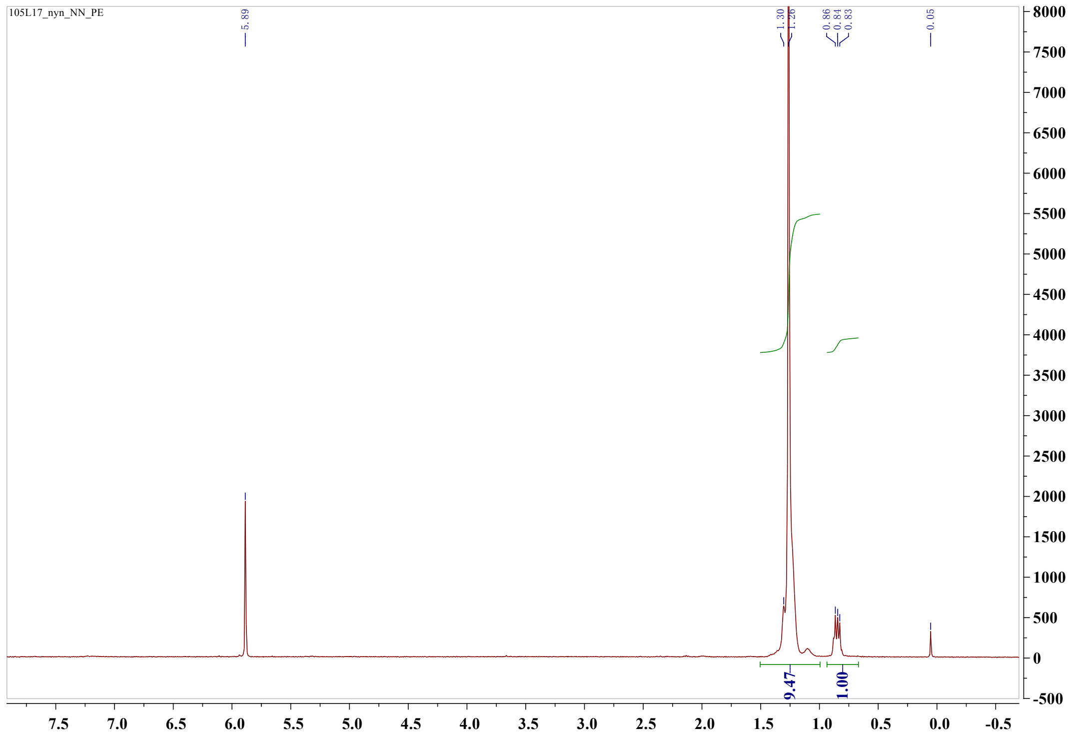


Figure S8. [1]H NMR spectrum of the polymer from table 1, entry 1. ($C_2D_2Cl_4$, 120 °C).

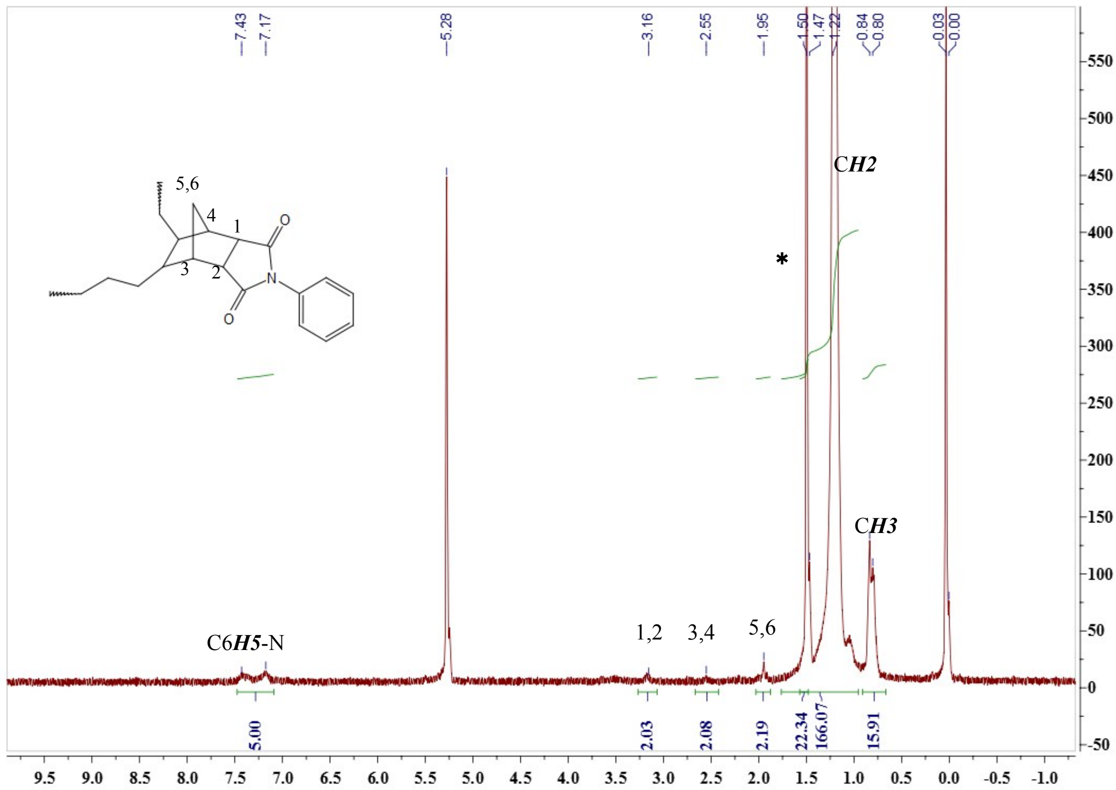


Figure S9. 1H NMR spectrum of the copolymer from table 1, entry 2. (CD_2Cl_2). ＊H_2O.

$$\text{Incorporation(\%)}=\frac{I(C6H5N)/5}{\frac{I(C6H5N)}{5}+\frac{I(CH2)+I(CH3)-2}{4}}*100\%=\frac{1}{1+39}*100\%=2.5\%$$

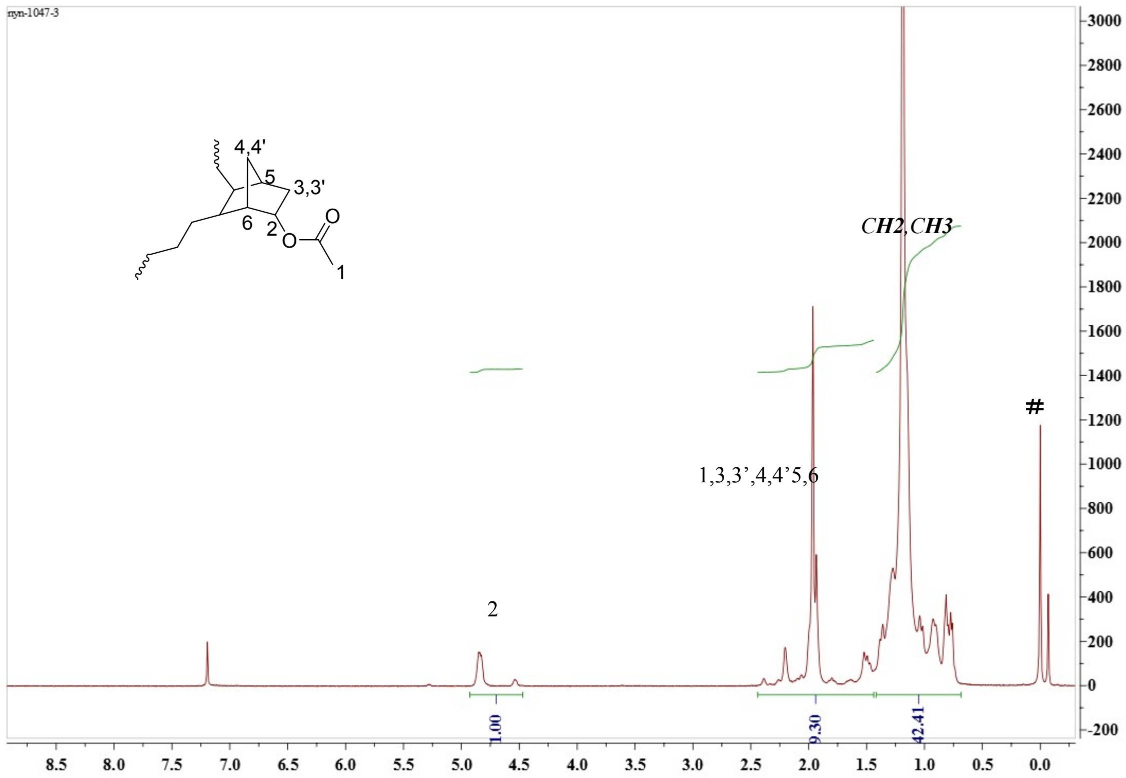


Figure S10. ^{1}H NMR spectrum of the copolymer from table 1, entry 3. ($CDCl_3$). #greese.

$$\text{Incorporation(\%)}=\frac{I(2)}{I(2)+\frac{I(CH2)+I(CH3)-2}{4}}*100\%=\frac{1}{1+10}*100\%=9.1\%$$

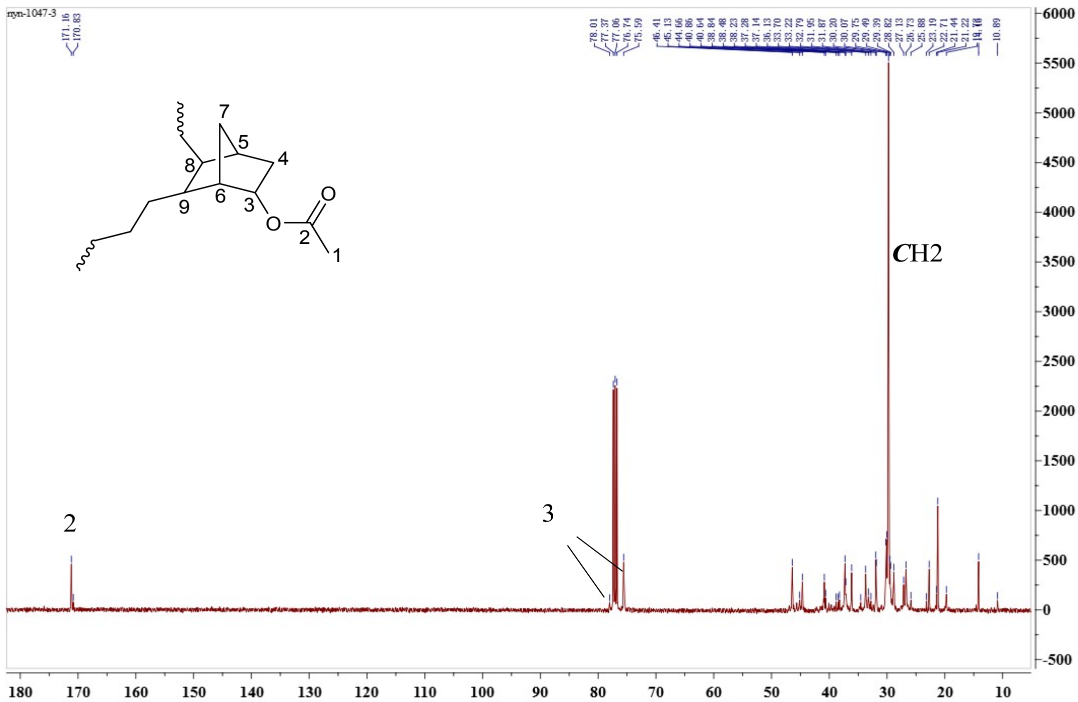


Figure S11. ^{13}C NMR spectrum of the copolymer from table 1, entry 3. ($CDCl_3$).

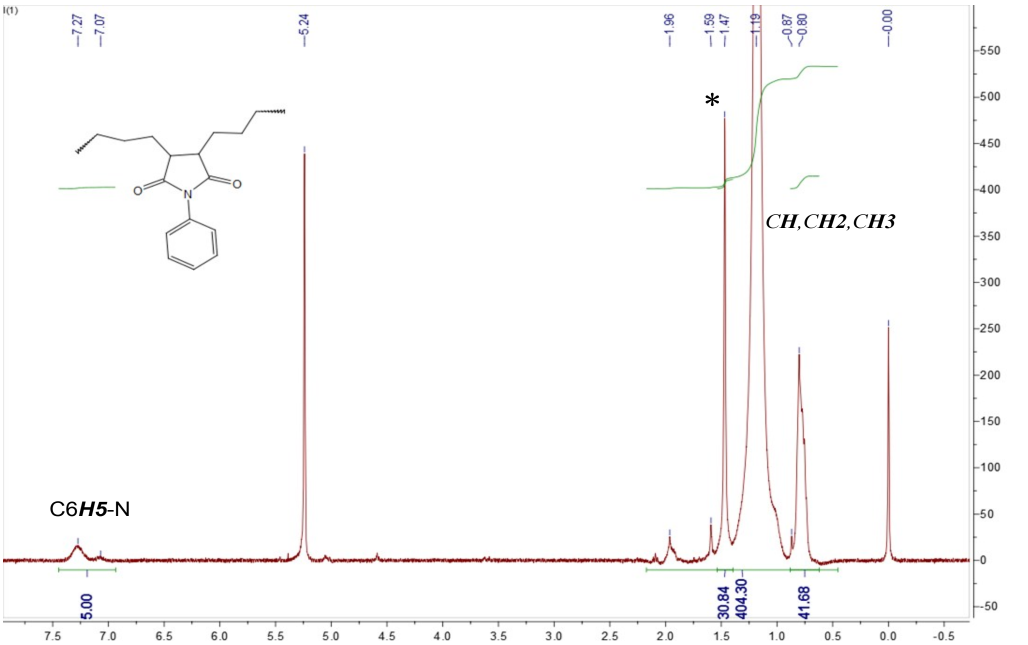


Figure S12. ^{1}H NMR spectrum of the copolymer from table 1, entry 4. (CD_2Cl_2). $\star H_2O$.

$$\text{Incorporation(\%)}=\frac{I(C6H5N)/5}{\frac{I(C6H5N)}{5}+\frac{I(CH2)+I(CH3)-2}{4}}*100\%=\frac{1}{1+93}*100\%=1.1\%$$

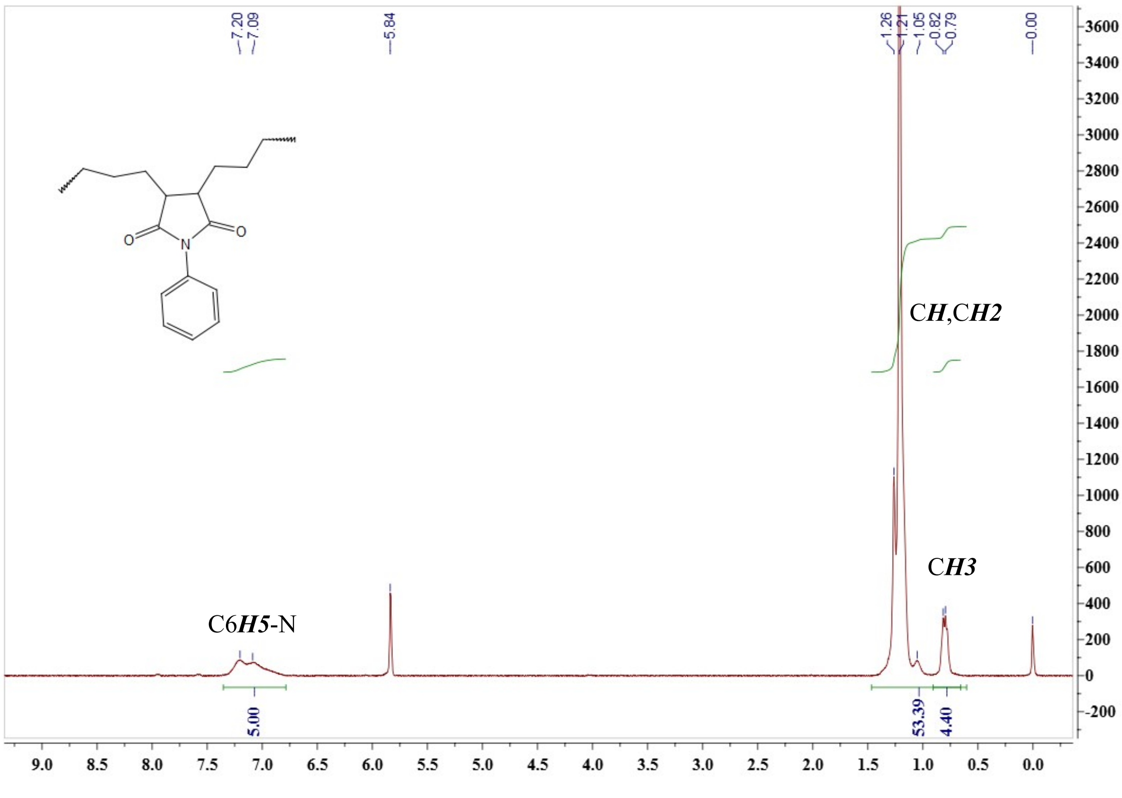


Figure S13. ^{1}H NMR spectrum of the copolymer from table 1, entry 5. (CD_2Cl_2).

$$\text{Incorporation(\%)} = \frac{I(C6H5N)/5}{\frac{I(C6H5N)}{5} + \frac{I(CH2) + I(CH3) - 2}{4}} * 100\% = \frac{1}{1+13} * 100\% = 7.1\%$$

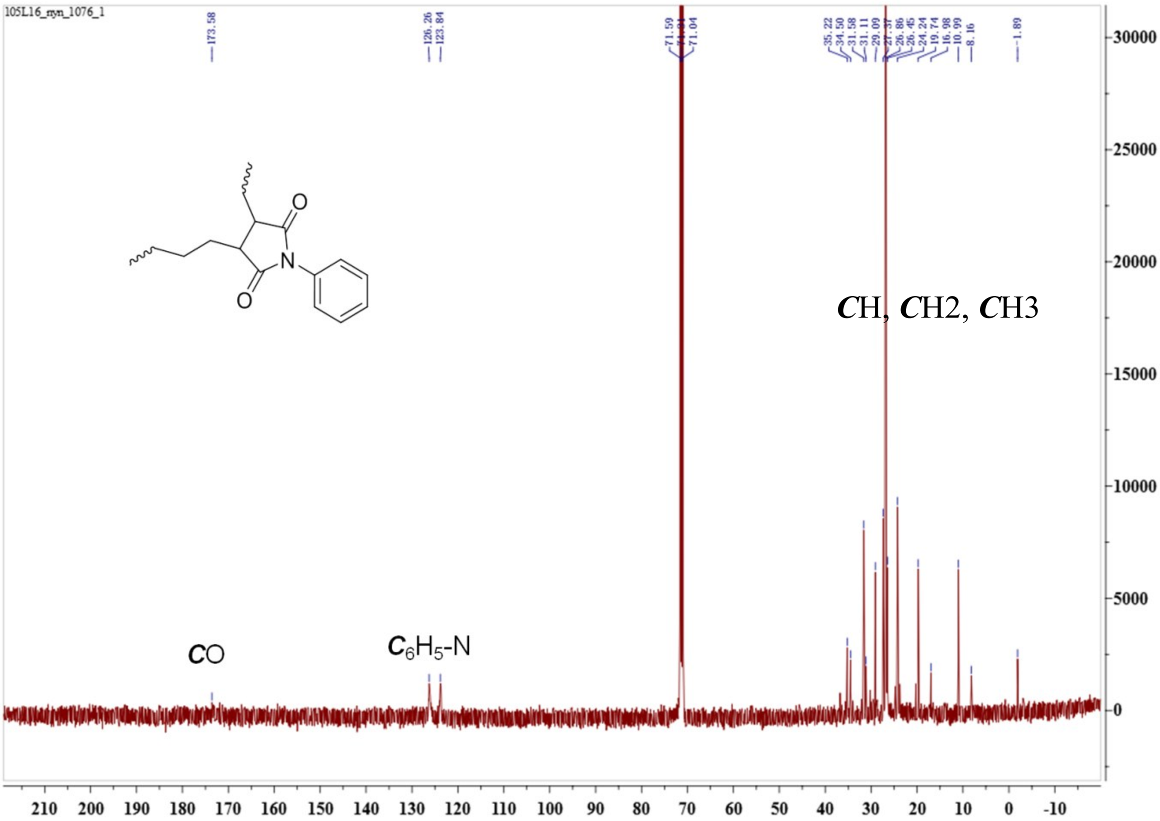


Figure S14. ^{13}C NMR spectrum of the copolymer from table 1, entry 5. (CD_2Cl_2).

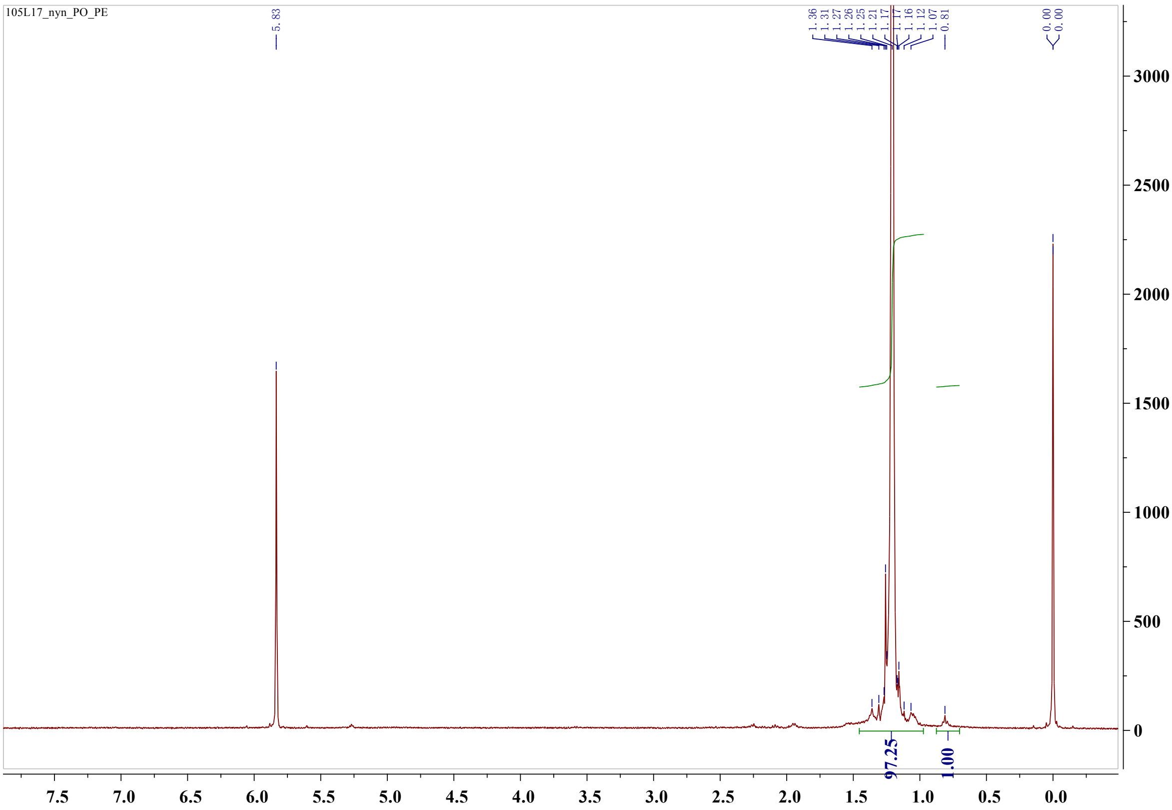


Figure S15. [1]H NMR spectrum of the polymer from table 1, entry 6. ($C_2D_2Cl_4$, 120 °C).

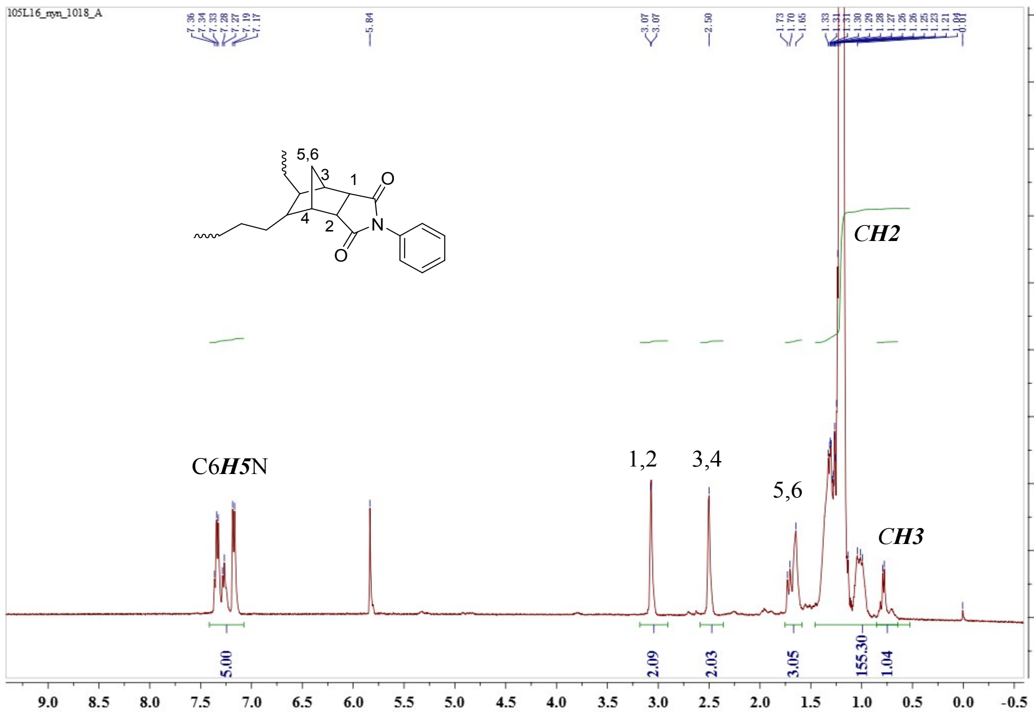


Figure S16. [1]H NMR spectrum of the copolymer from table 1, entry 7. ($C_2D_2Cl_4$, 120 °C).

$$\text{Incorporation(\%)}=\frac{I(C6H5N)/5}{\frac{I(C6H5N)}{5}+\frac{I(CH2)+I(CH3)-2}{4}}*100\%=\frac{1}{1+39}*100\%=2.5\%$$

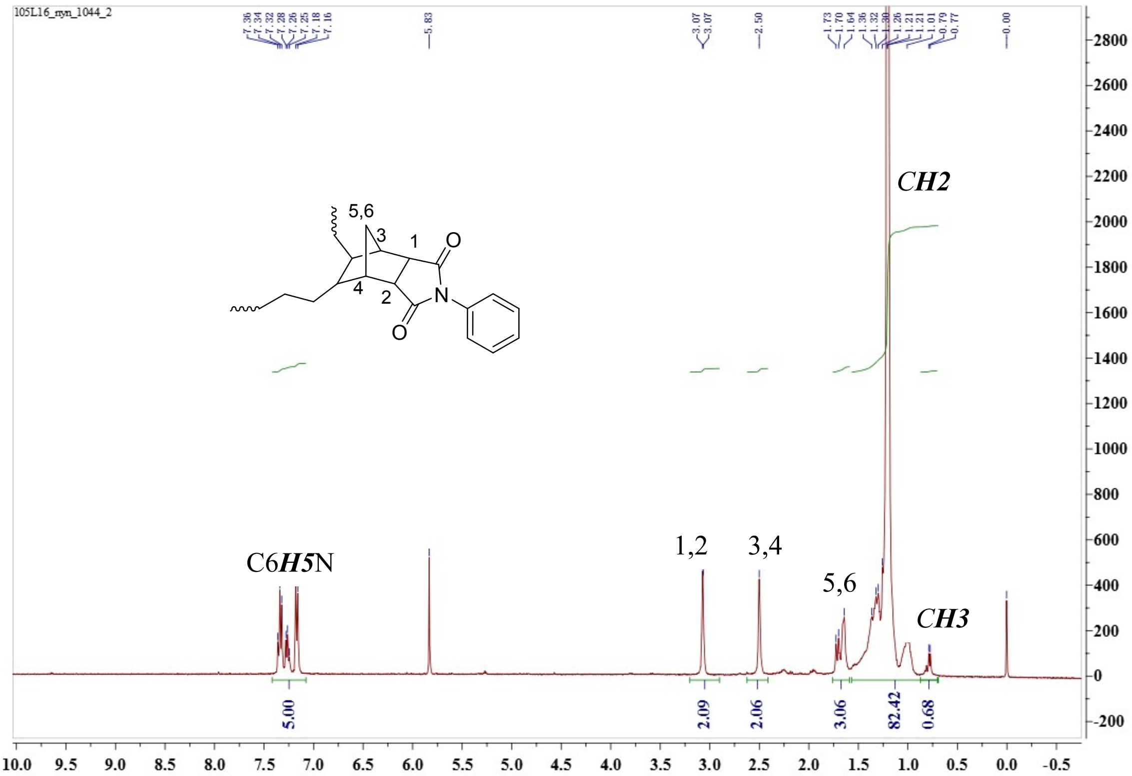


Figure S17. ^{1}H NMR spectrum of the copolymer from table 1, entry 8. ($C_2D_2Cl_4$, 120 ^{o}C).

Incorporation(%)= $$\frac{I(C6H5N)/5}{\frac{I(C6H5N)}{5}+\frac{I(CH2)+I(CH3)-2}{4}}*100\%=\frac{1}{1+20}*100\%=4.8\%$$

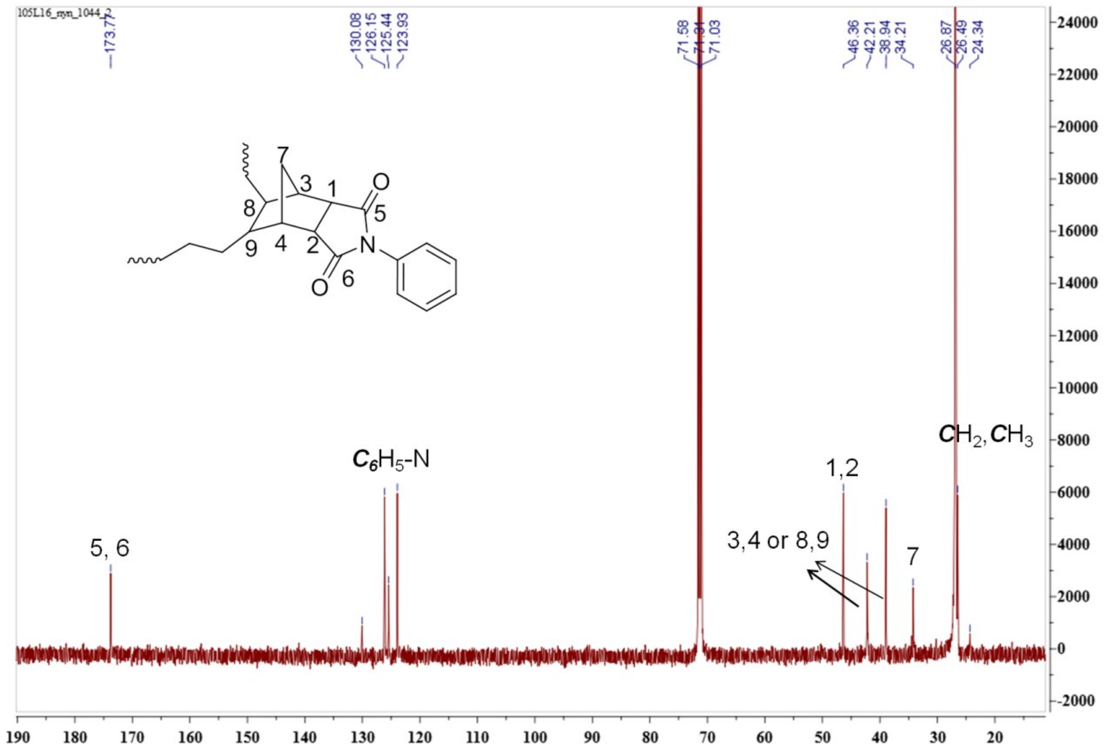


Figure S18. ^{13}C NMR spectrum of the copolymer from table 1, entry 8. ($C_2D_2Cl_4$, 120 ^{o}C).

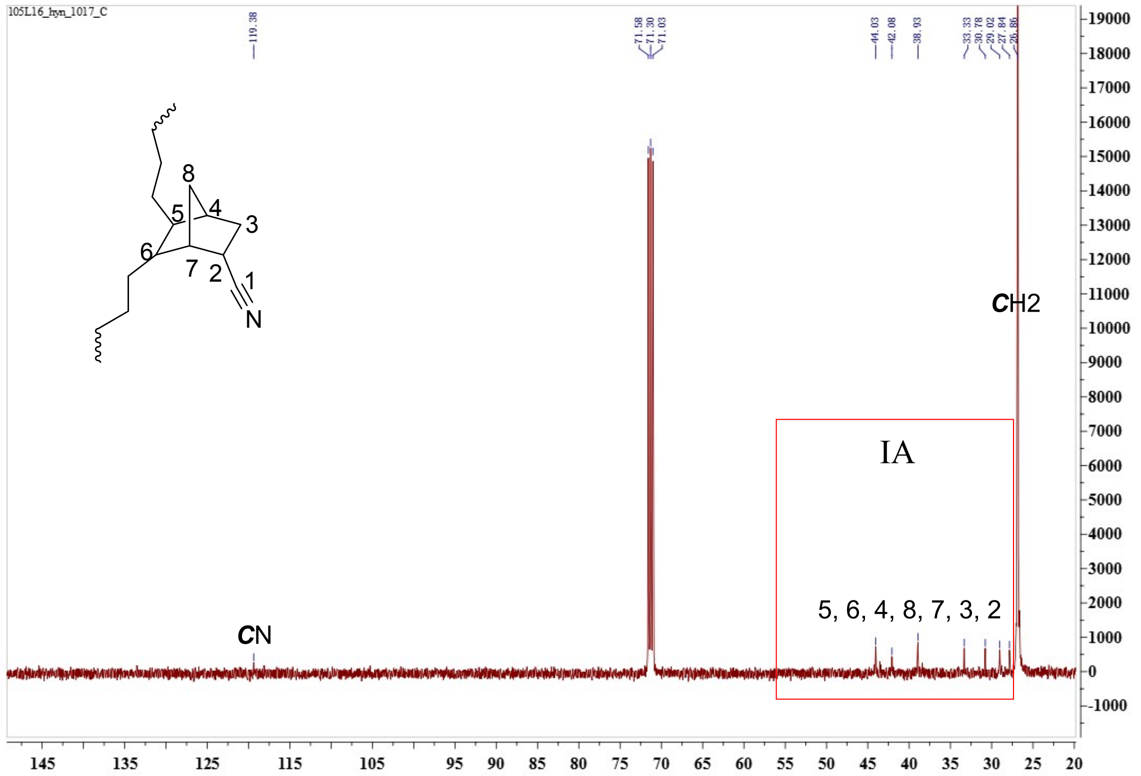


Figure S19. ^{13}C NMR spectrum of the copolymer from table 1, entry 9. ($C_2D_2Cl_4$, 120 ^{o}C).

$$\text{Incorporation}(\%) = \frac{IA/7}{IA/7 + I(CH2)} * 100\% = \frac{1}{1+60} * 100\% = 1.6\%$$

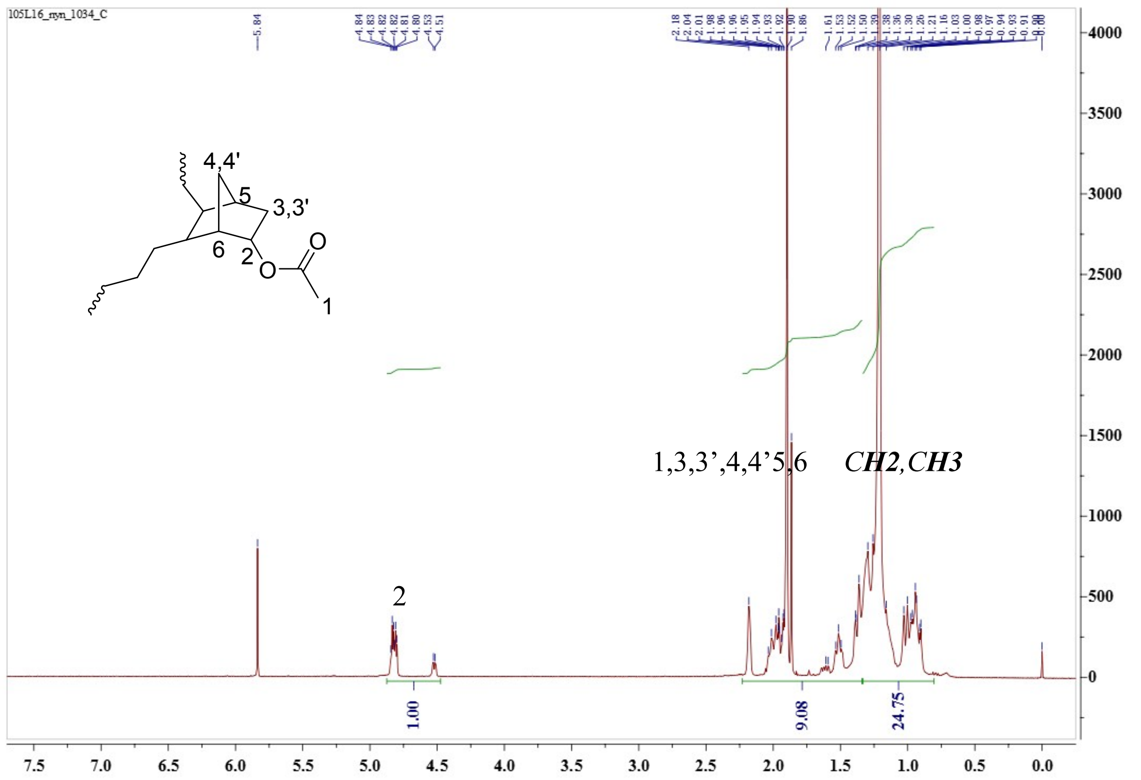


Figure S20. ^{1}H NMR spectrum of the copolymer from table 1, entry 10. ($C_2D_2Cl_4$, 120 ^{o}C).

$$\text{Incorporation(\%)} = \frac{I(1)}{I(1) + \frac{I(CH2) + I(CH3) - 2}{4}} * 100\% = \frac{1}{1+6} * 100\% = 14.3\%$$

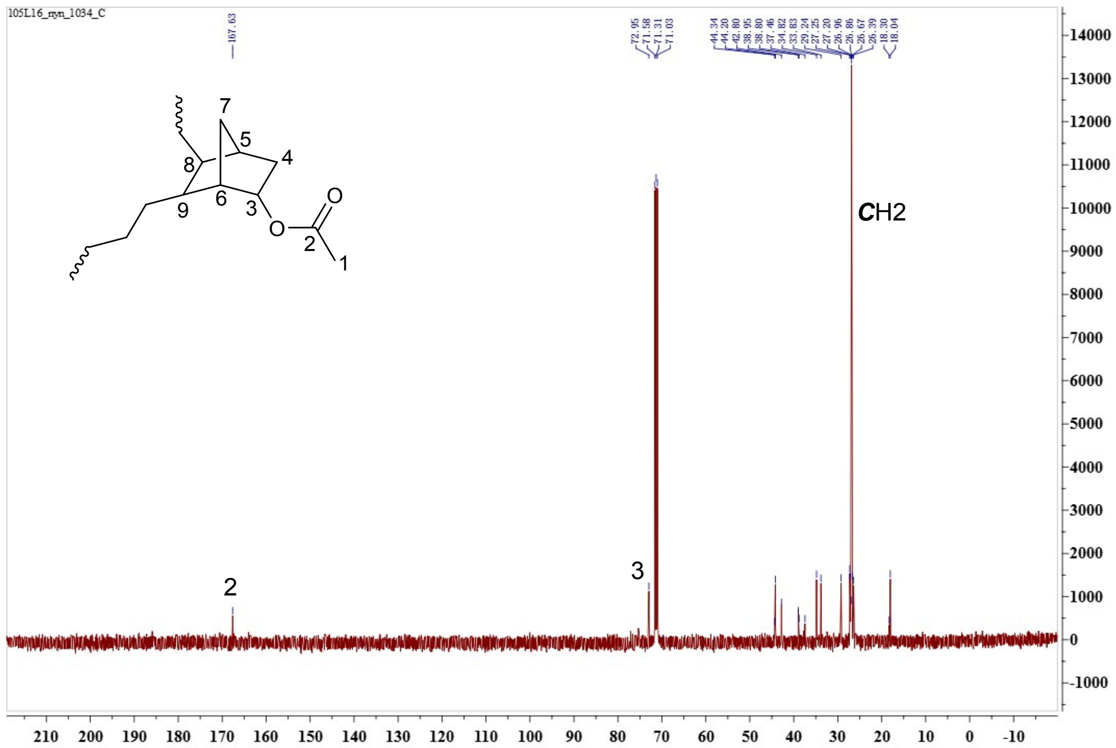


Figure S21. ^{13}C NMR spectrum of the copolymer from table 1, entry 10. ($C_2D_2Cl_4$, 120 ^{o}C).

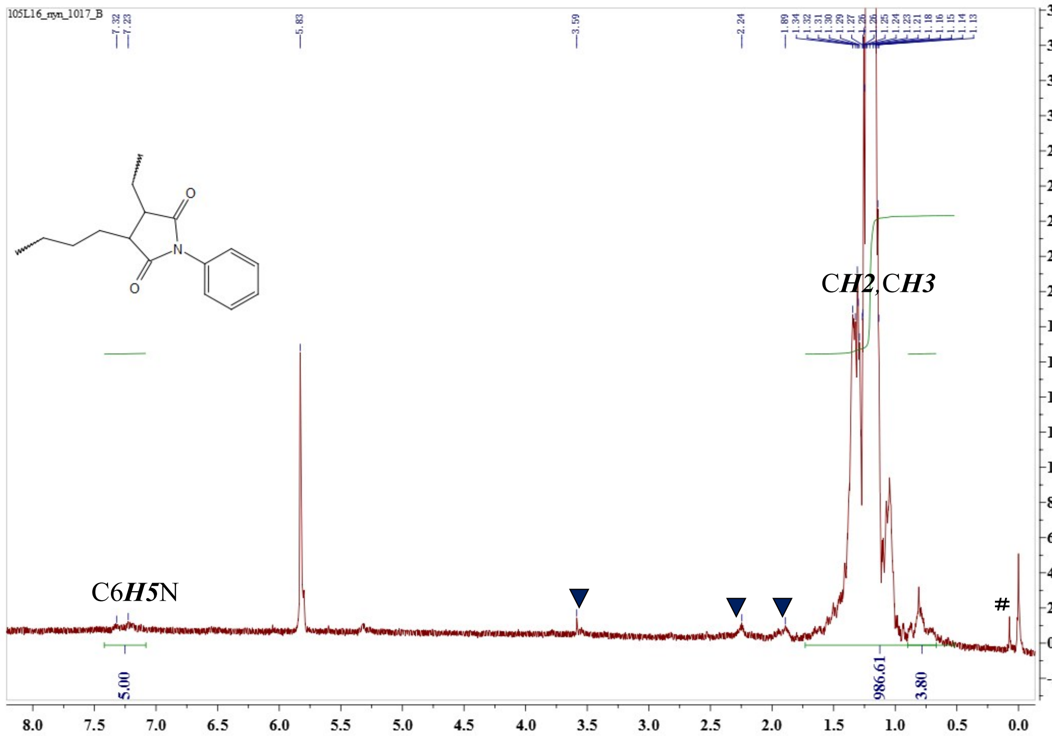


Figure S22. ^{1}H NMR spectrum of the copolymer from table 1, entry 11. ($C_2D_2Cl_4$, 120 ^{o}C). ▼Solvent inpurity.

$$\text{Incorporation(\%)}=\frac{I(C6H5N)/5}{\frac{I(C6H5N)}{5}+\frac{I(CH2)+I(CH3)-2}{4}}*100\%=\frac{1}{1+246}*100\%=0.4\%$$

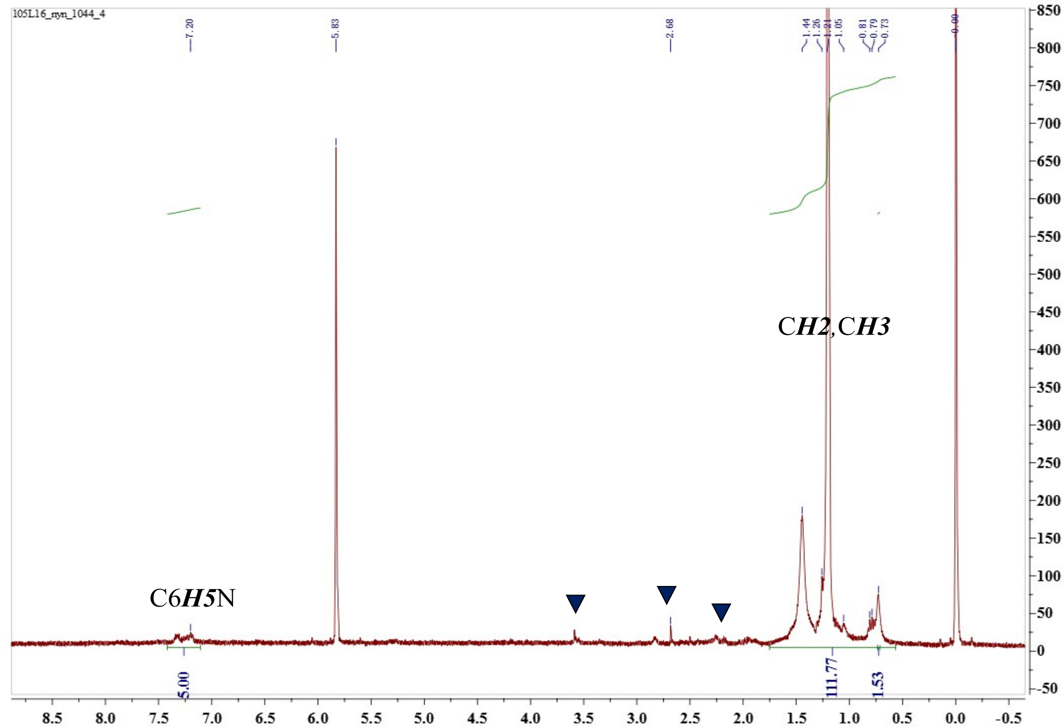


Figure S23. [1]H NMR spectrum of the copolymer from table 1, entry 12. ($C_2D_2Cl_4$, 120 ^oC).

$$\text{Incorporation(\%)}=\frac{I(C6H5N)/5}{\frac{I(C6H5N)}{5}+\frac{I(CH2)+I(CH3)-2}{4}}*100\%=\frac{1}{1+27}*100\%=3.6\%$$

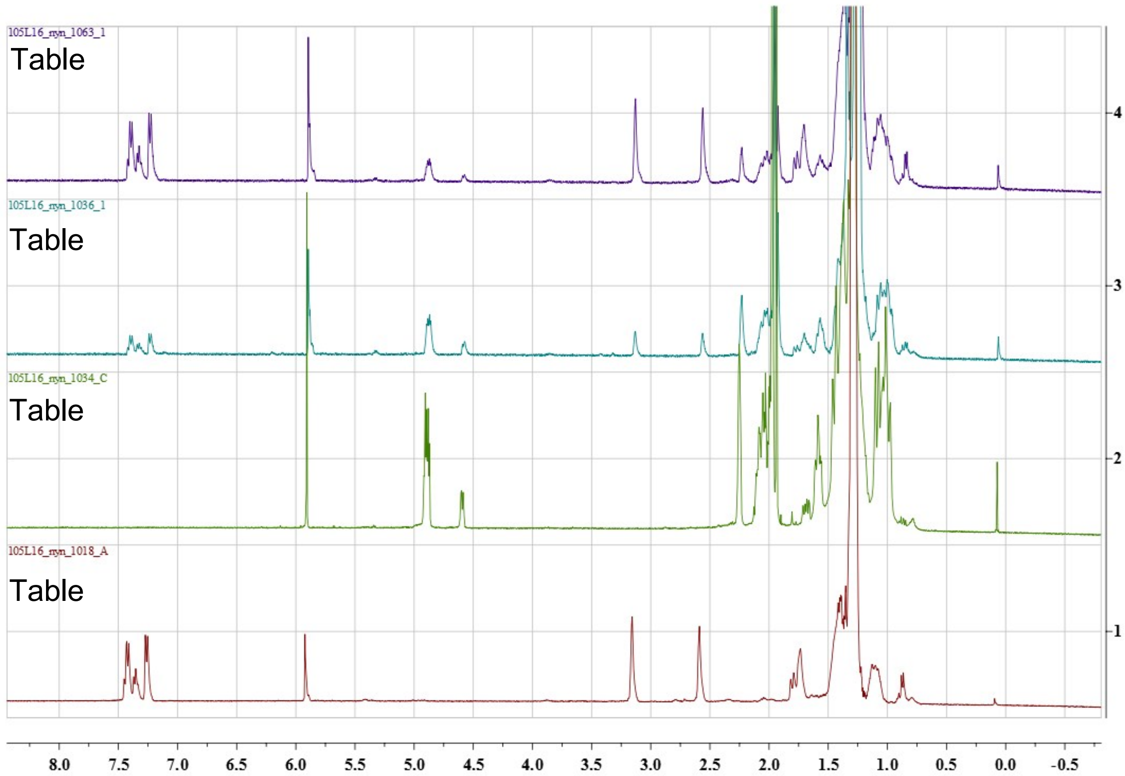


Figure S24. ^{1}H NMR spectrum comparison of the terpolymers (ethylene/NB-NP/NB-OAc) and copolymers (ethylene/NB-NP and ethylene/NB-OAc).

The terpolymers showed peaks that are not shifted from those of their constituent copolymers.

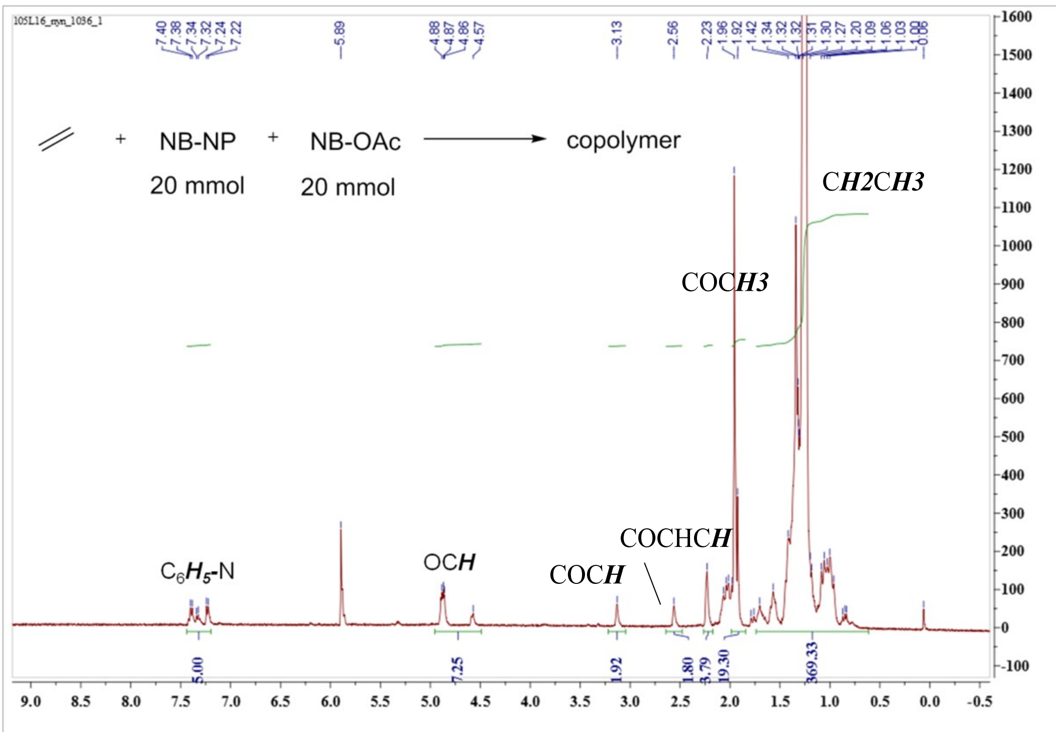


Figure S25. ^{1}H NMR spectrum of the copolymer from table 2, entry 1. ($C_2D_2Cl_4$, 120 ^{o}C).

Incorporation(%) of NB-NP=
$$\frac{I(C6H5N)/5}{\frac{I(C6H5N)}{5}+\frac{I(CH2)+I(CH3)\text{ - }2}{4}}*100\%=\frac{1}{1+92}*100\%=1.1\%$$

Incorporation(%) of NB-OAc=7.25*1.1%=8.0%

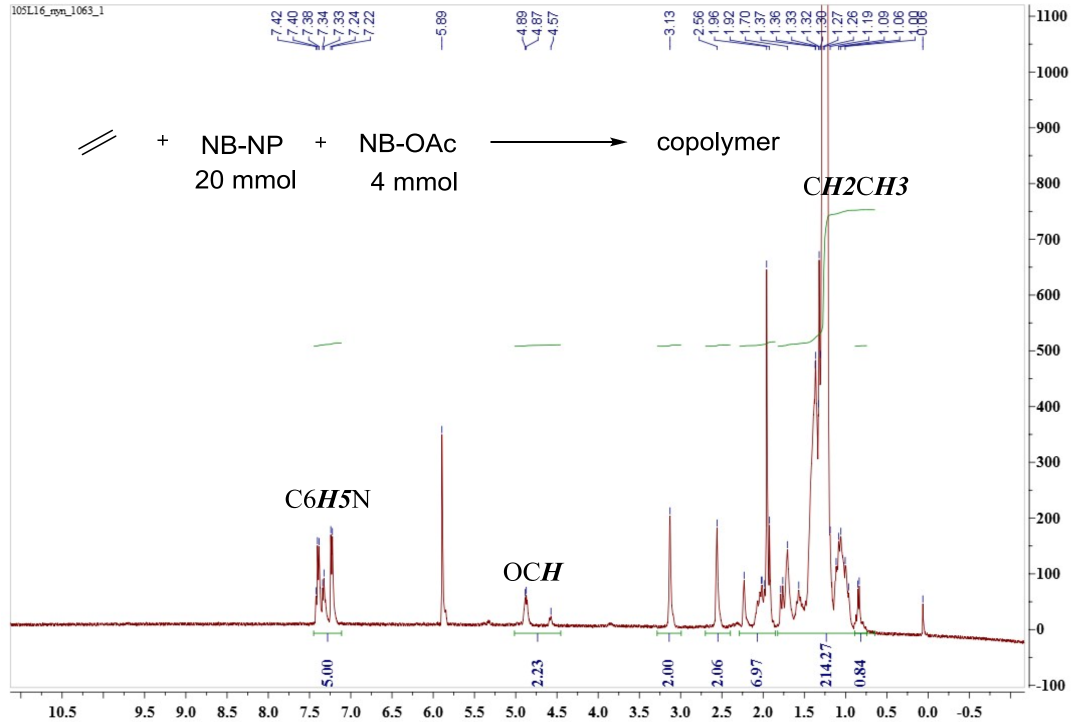


Figure S26. 1H NMR spectrum of the copolymer from table 2, entry 2. ($C_2D_2Cl_4$, 120 ^oC).

Incorporation(%) of NB-NP=
$$\frac{I(C6H5N)/5}{\frac{I(C6H5N)}{5}+\frac{I(CH2)+I(CH3)-2}{4}}*100\%=\frac{1}{1+53}*100\%=1.9\%$$

Incorporation(%) of NB-OAc=2.23*1.9%=4.2%

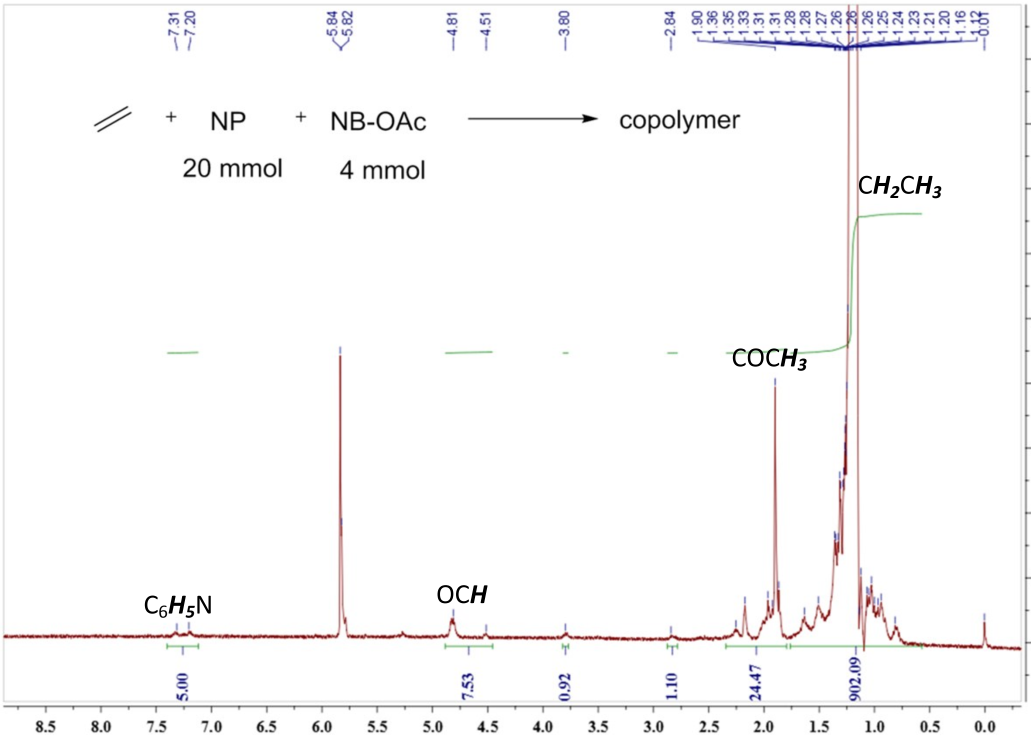


Figure S27. 1H NMR spectrum of the copolymer from table 2, entry 3. ($C_2D_2Cl_4$, 120 °C).

$$\text{Incorporation(\%) of NB-NP} = \frac{I(C6H5N)/5}{\frac{I(C6H5N)}{5} + \frac{I(CH2)+I(CH3)-2}{4}} * 100\% = \frac{1}{1+225} * 100\% = 0.4\%$$

Incorporation(%) of NB-OAc=7.53*0.4%=3.0%

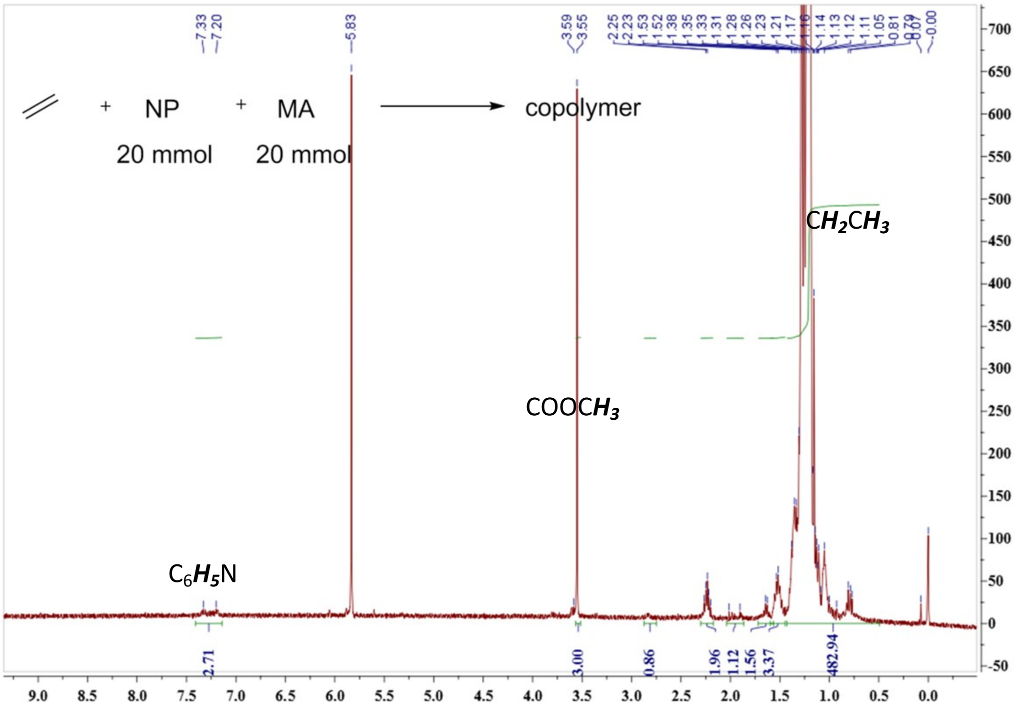


Figure S28. 1H NMR spectrum of the copolymer from table 2, entry 4. ($C_2D_2Cl_4$, 120 °C).

Incorporation(%) of MA= $\frac{I(COOCH3)/3}{\frac{I(COOCH3)}{3}+\frac{I(CH2)+I(CH3)}{4}} * 100\% = \frac{1}{1+120} * 100\% = 0.8\%$

Incorporation(%) of NP=2.71/5*0.8%=0.4%

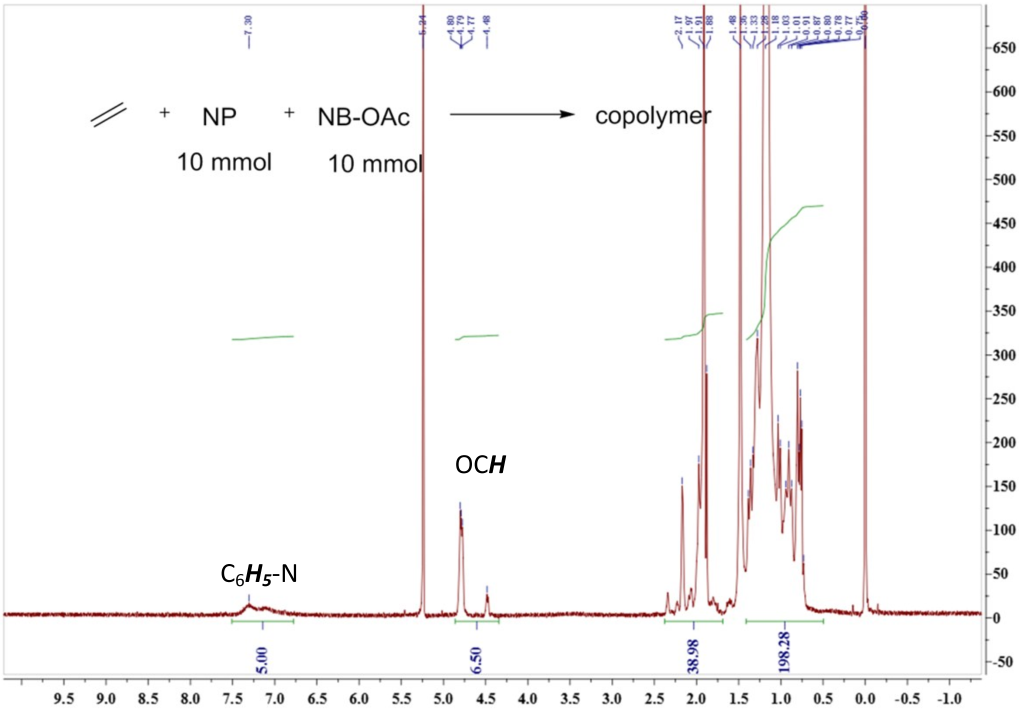


Figure S29. 1H NMR spectrum of the copolymer from table 2, entry 5. (CD_2Cl_2). ⋆ H_2O.

Incorporation(%) of NP= $\frac{I(C6H5N)/5}{\frac{I(C6H5N)}{5}+\frac{I(CH2)+I(CH3)-2}{4}} * 100\% = \frac{1}{1+49} * 100\% = 2.0\%$

Incorporation(%) of NB-OAc=6.5*2.0%=13.0%

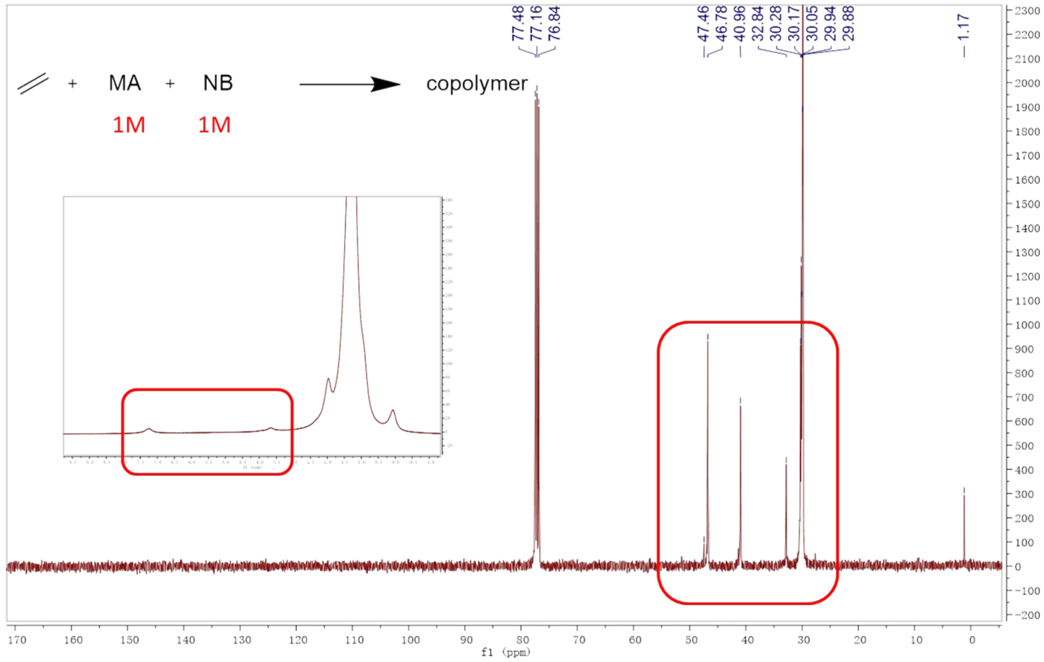


Figure S30. ^{13}C NMR spectrum of the attempted E-MA-**NB** MA 1 mol/L, **NB** 1 mol/L) terpolymerization product. The characteristic peaks between δ 30 and 50 ppm are from **NB** comonomer.

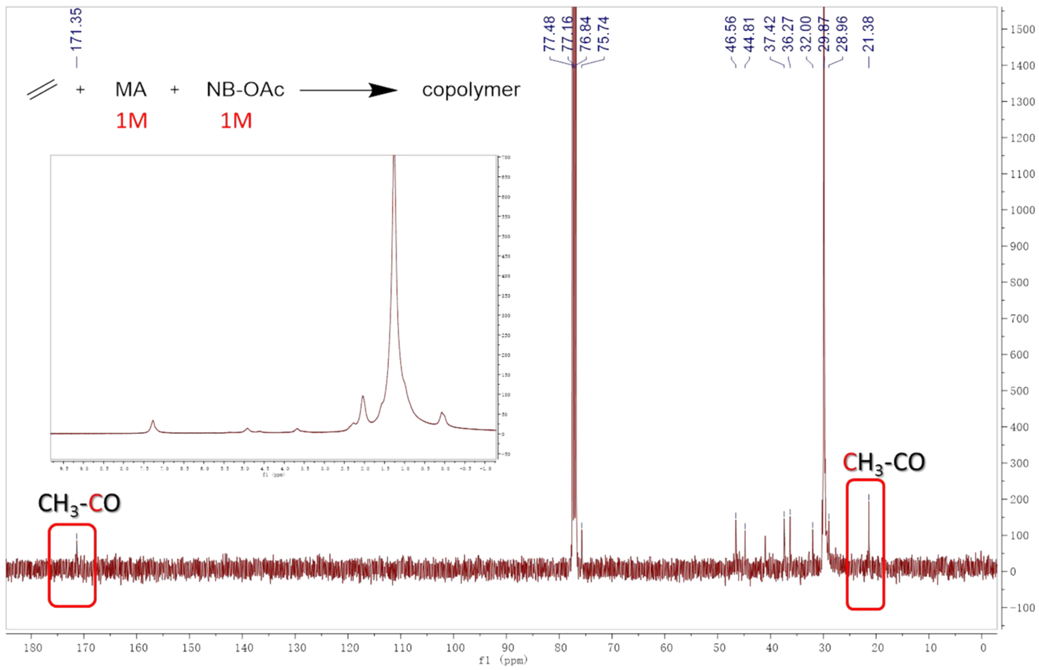


Figure S31. ^{13}C NMR spectrum of the attempted E-MA-**NB-OAc** (MA 1 mol/L, **NB-OAc** 1 mol/L) terpolymerization product. Only the characteristic peaks from **NB-OAc** comonomer were observed.

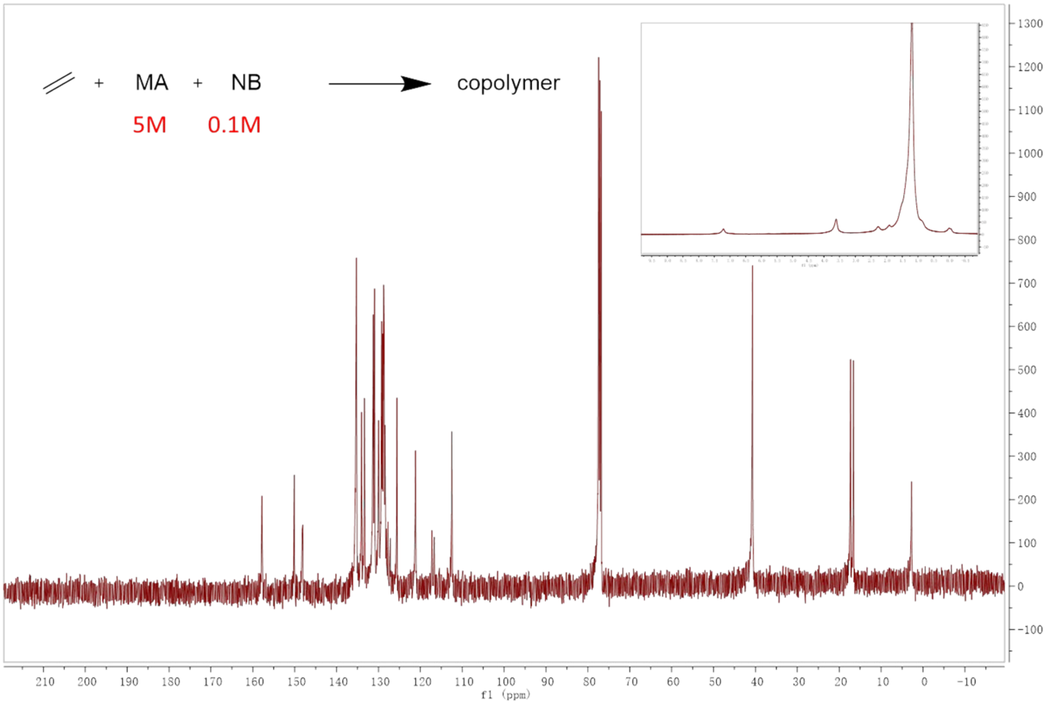


Figure S32. ^{13}C NMR spectrum of the attempted E-MA-**NB** (MA 5 mol/L, NB 0.1 mol/L) terpolymerization product. Only the characteristic peaks from **MA** comonomer were observed (the peaks between δ 110 and 160 ppm are from the catalyst residue).

2.2 DSC, GPC of copolymer.

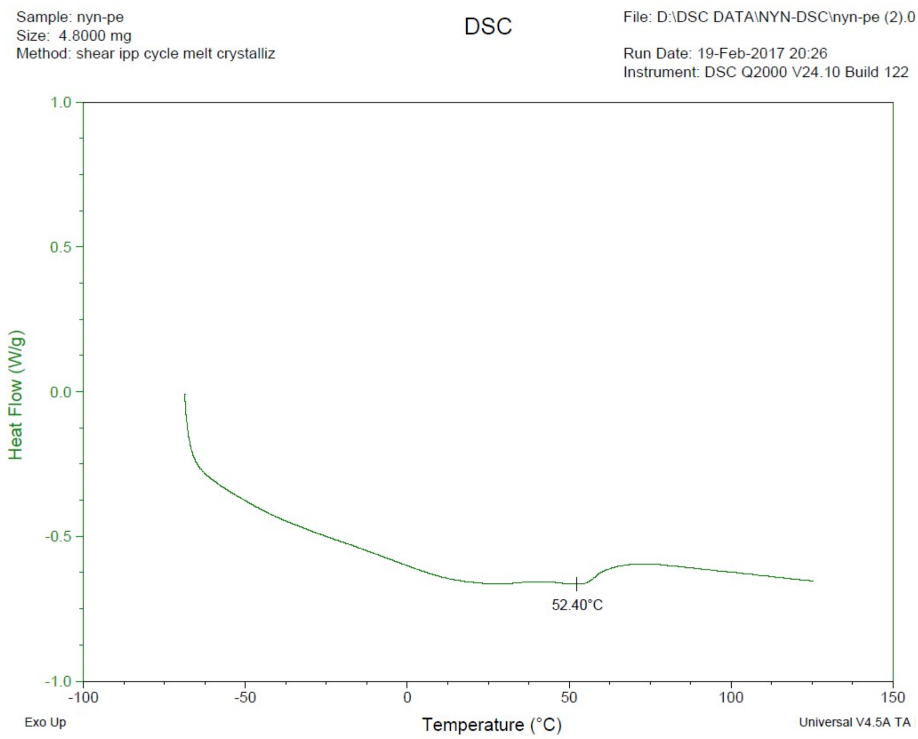


Figure S33. DSC of the copolymer from table 1, entry 1.

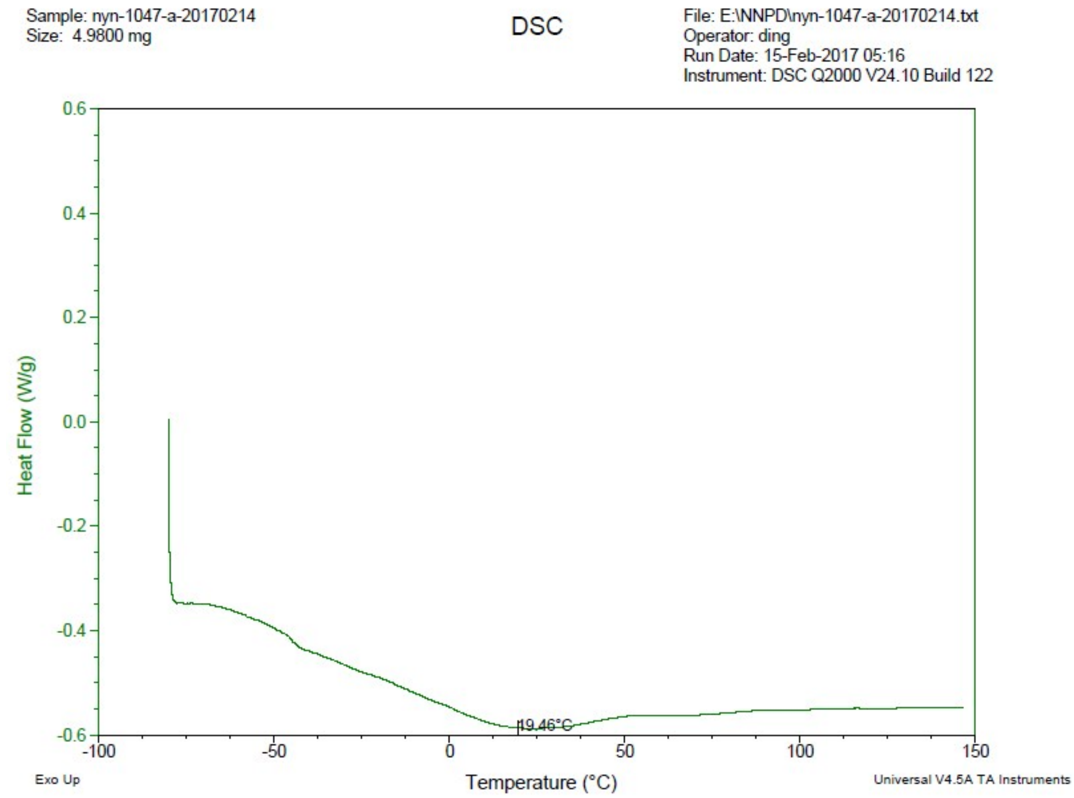


Figure S34. DSC of the copolymer from table 1, entry 2.

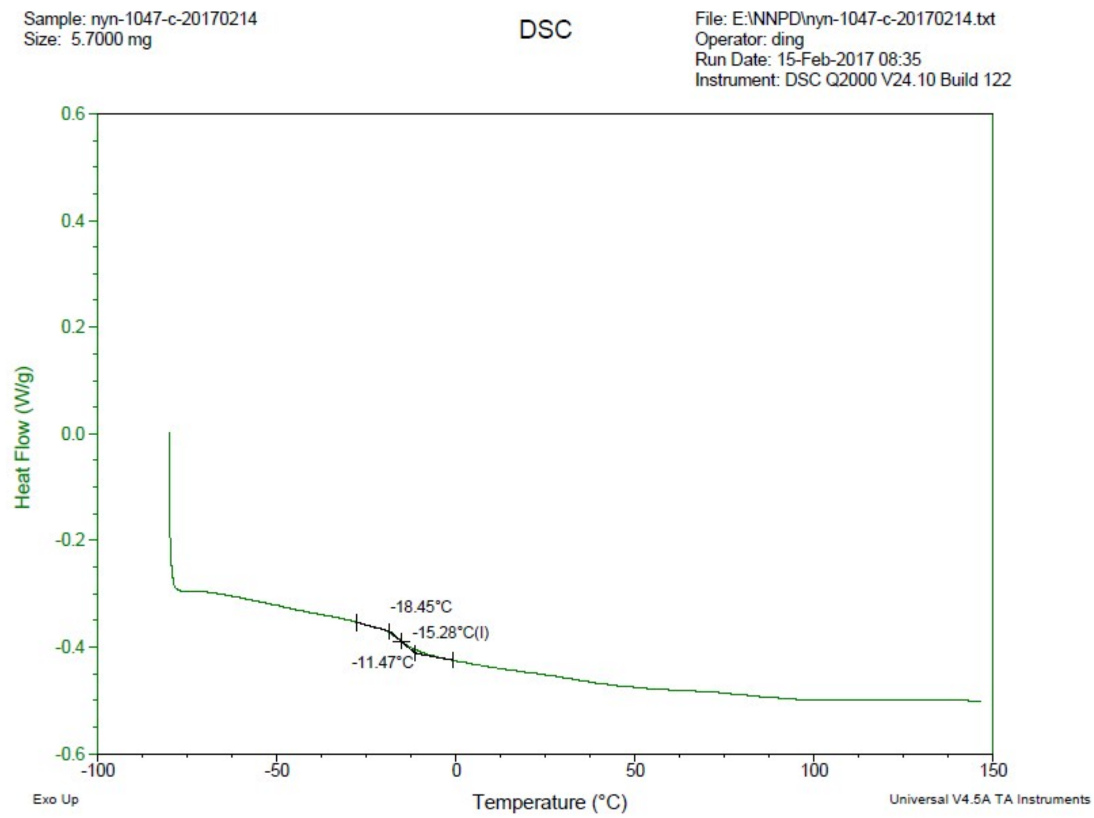


Figure S35. DSC of the copolymer from table 1, entry 3.

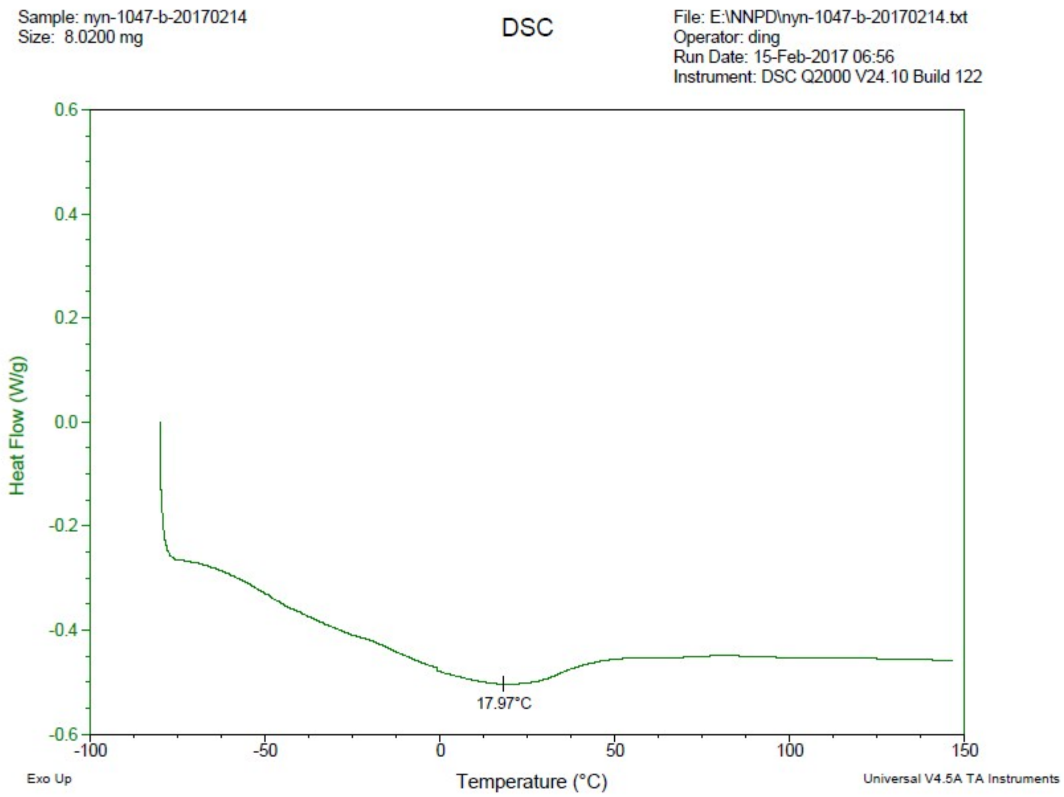


Figure S36. DSC of the copolymer from table 1, entry 4.

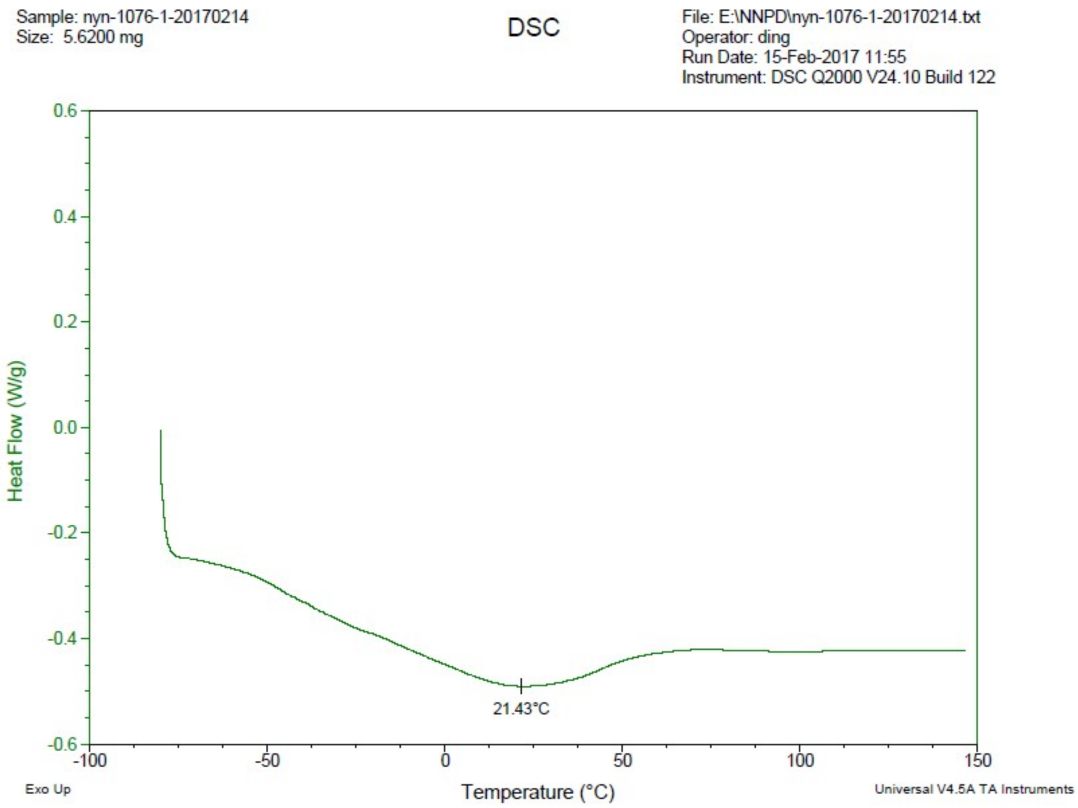


Figure S37. DSC of the copolymer from table 1, entry 5.

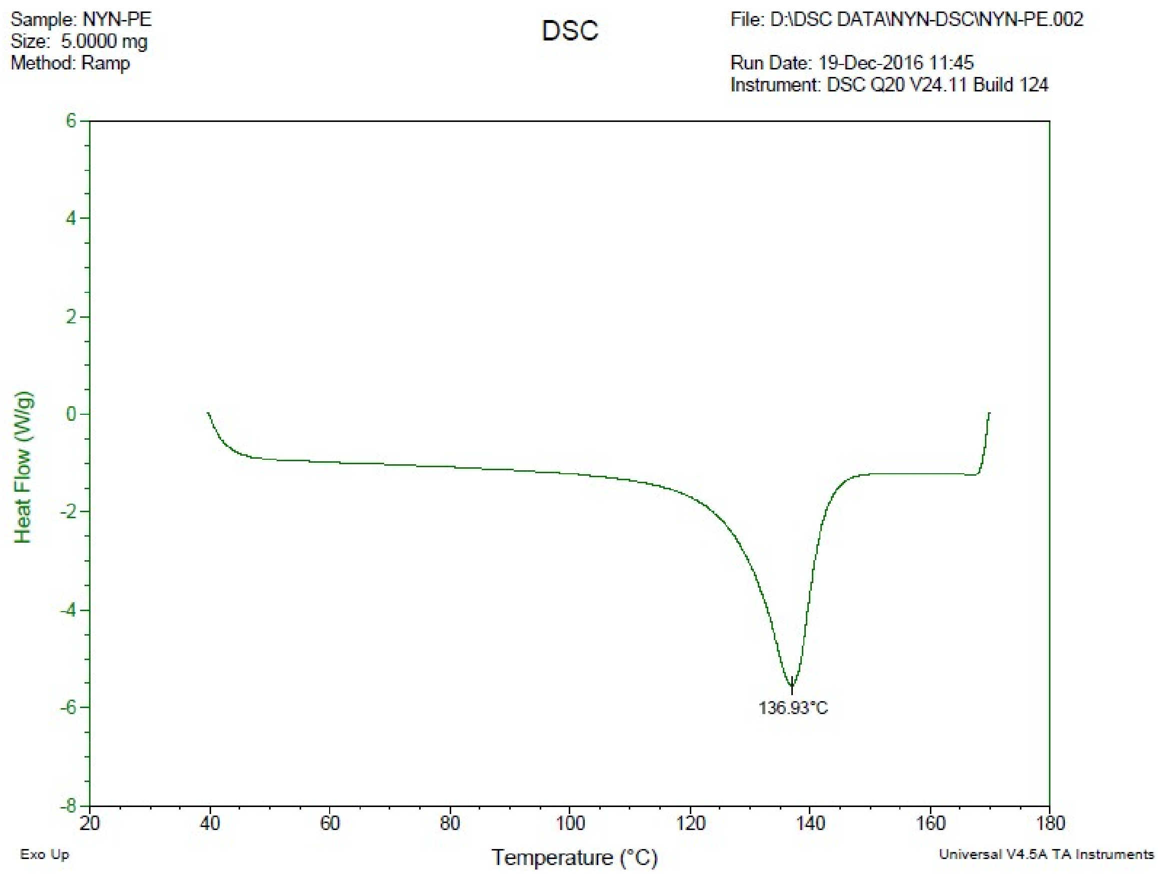


Figure S38. DSC of the copolymer from table 1, entry 6.

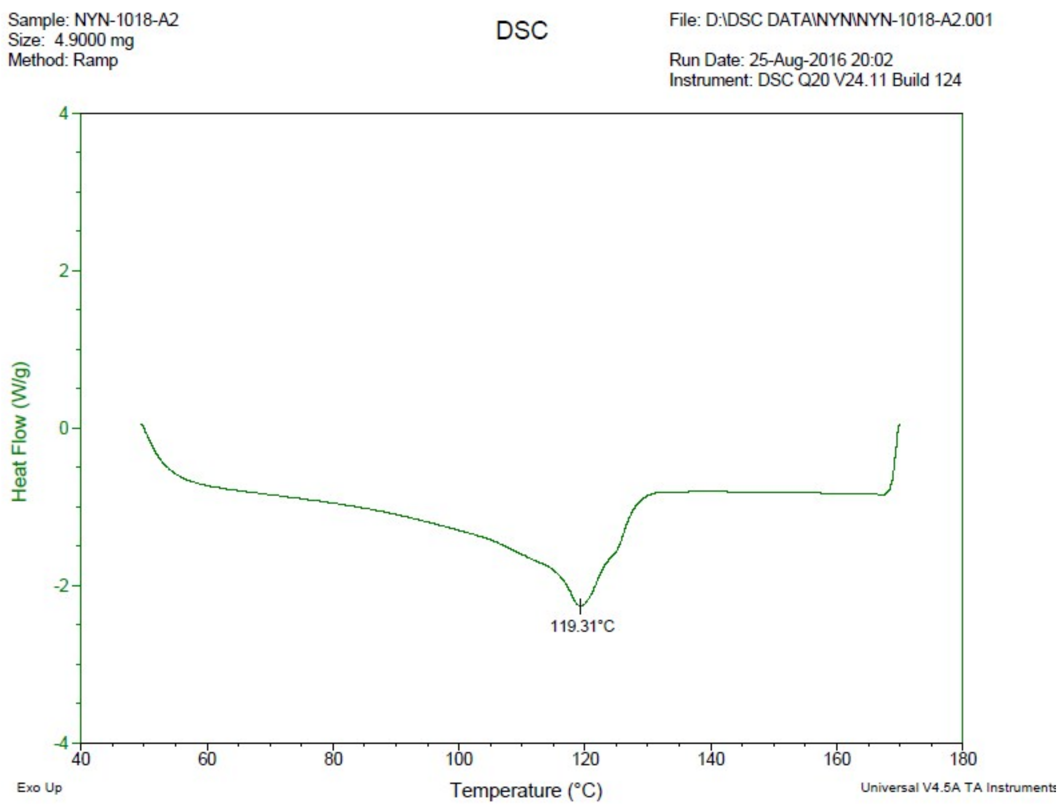


Figure S39. DSC of the copolymer from table 1, entry 7.

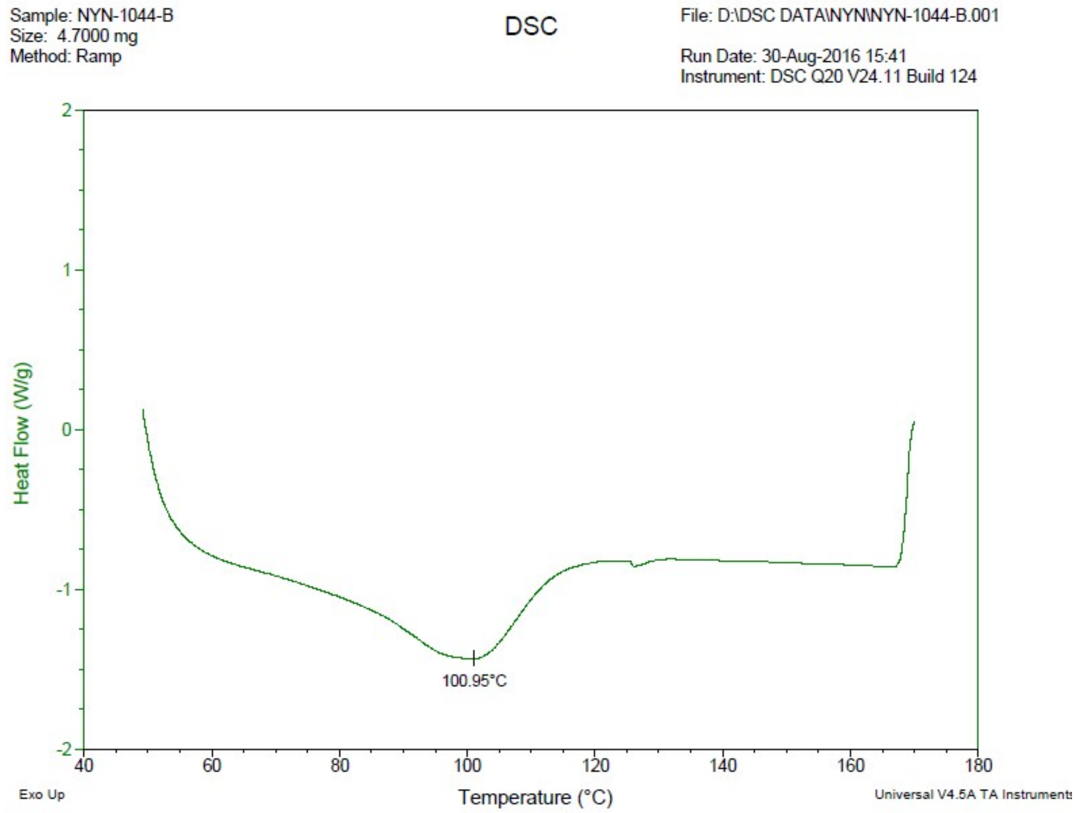


Figure S40. DSC of the copolymer from table 1, entry 8.

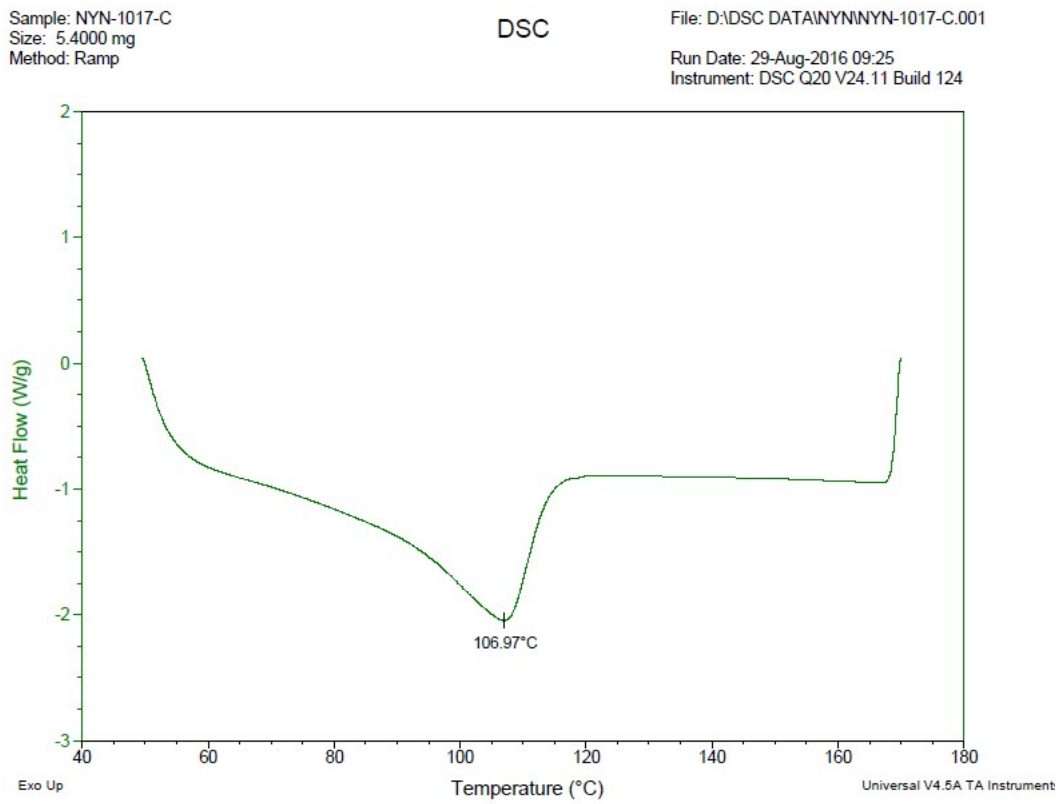


Figure S41. DSC of the copolymer from table 1, entry 9.

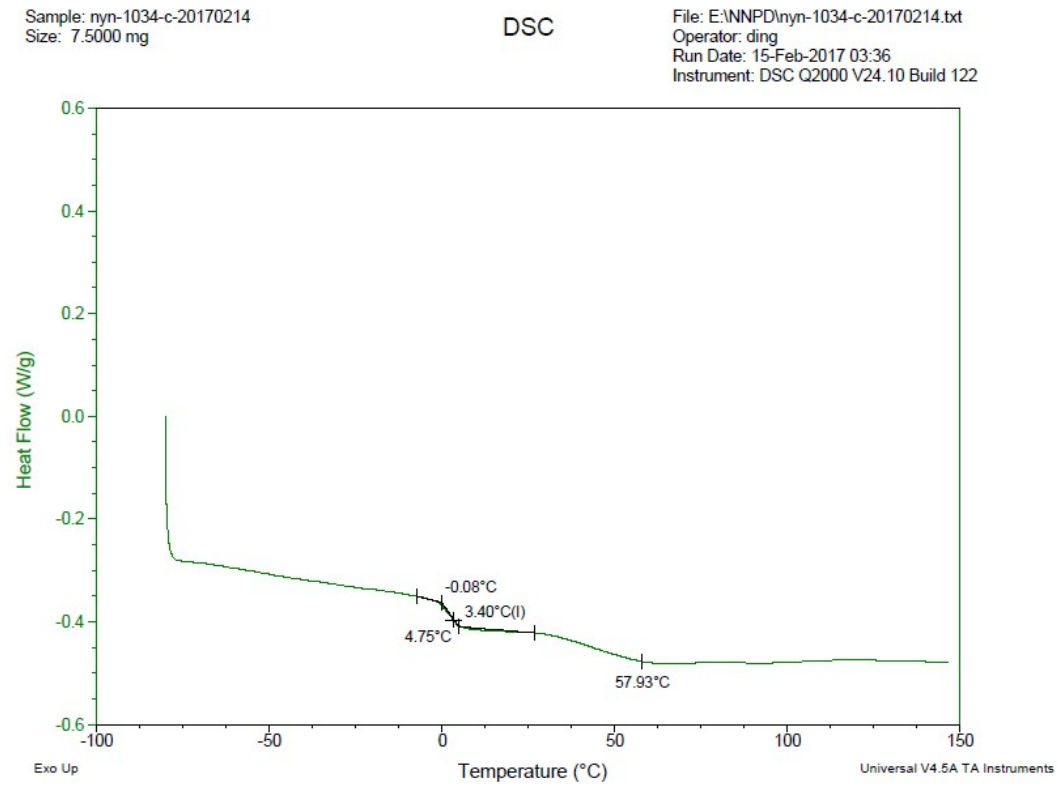


Figure S42. DSC of the copolymer from table 1, entry 10.

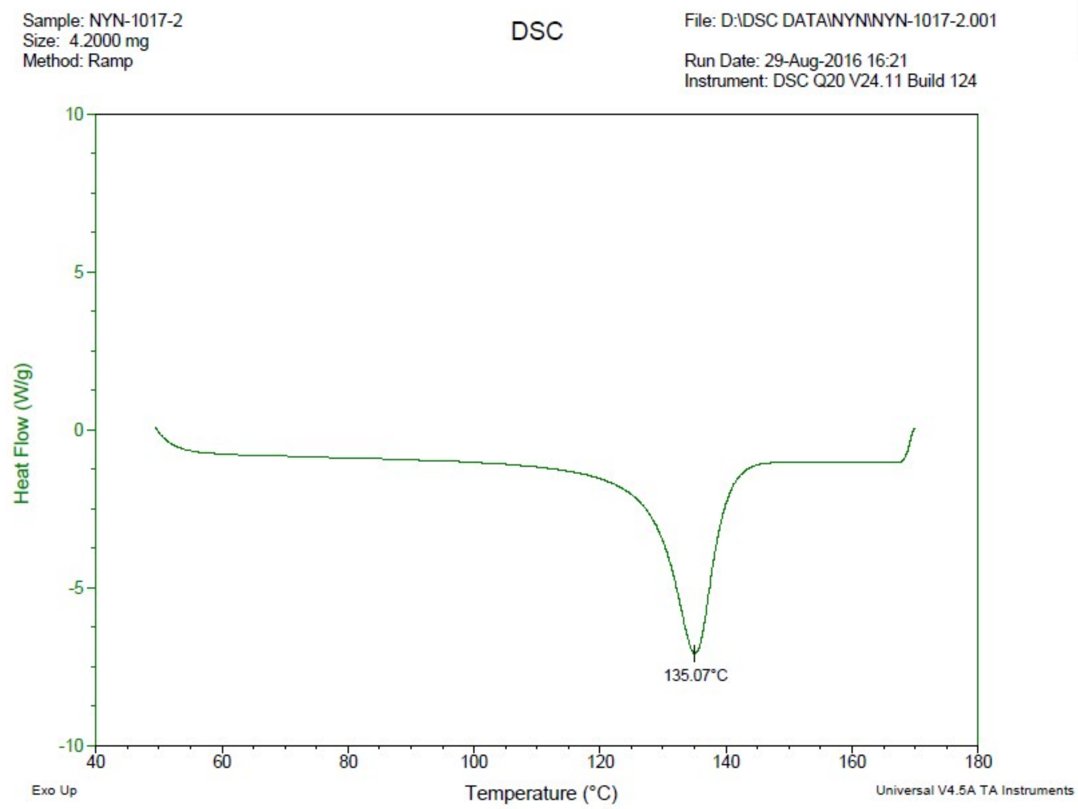


Figure S43. DSC of the copolymer from table 1, entry 11.

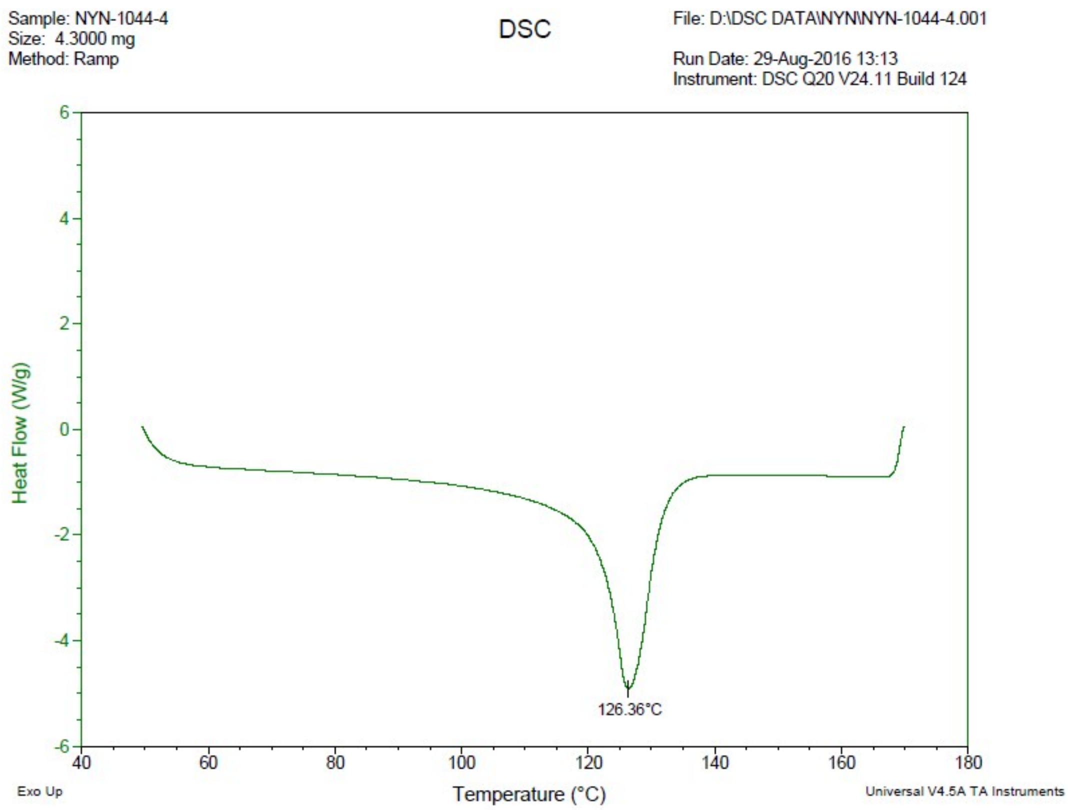


Figure S44. DSC of the copolymer from table 1, entry12.

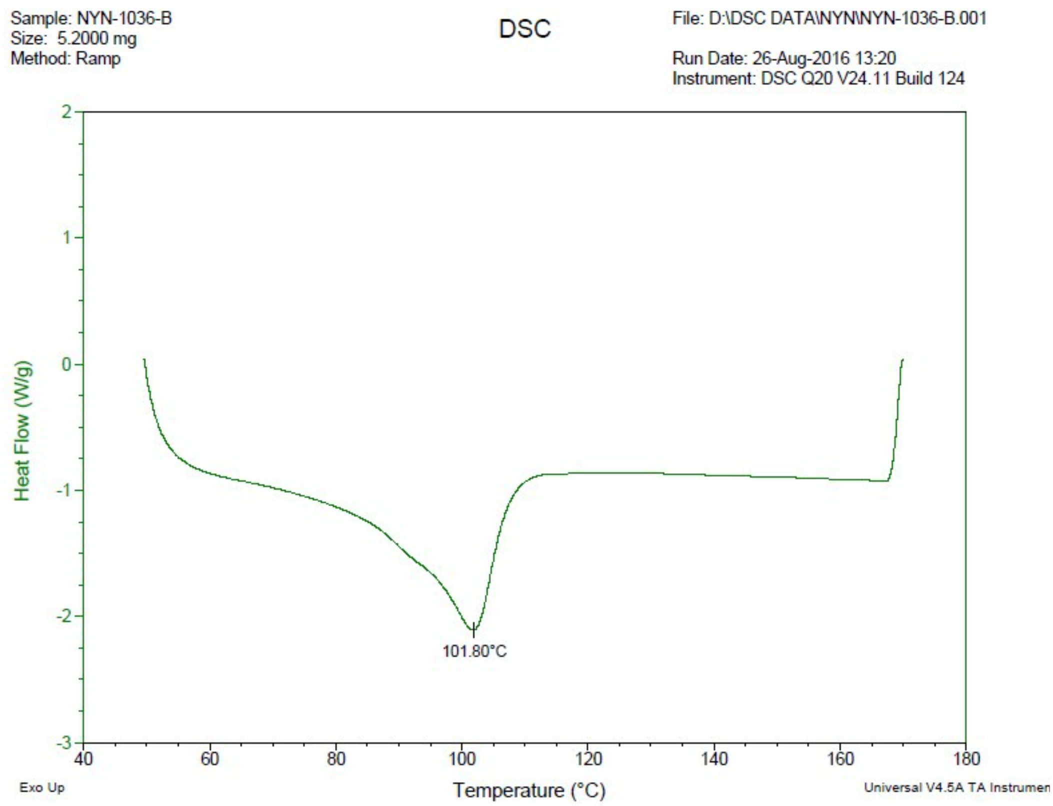


Figure S45. DSC of the copolymer from table 2, entry1.

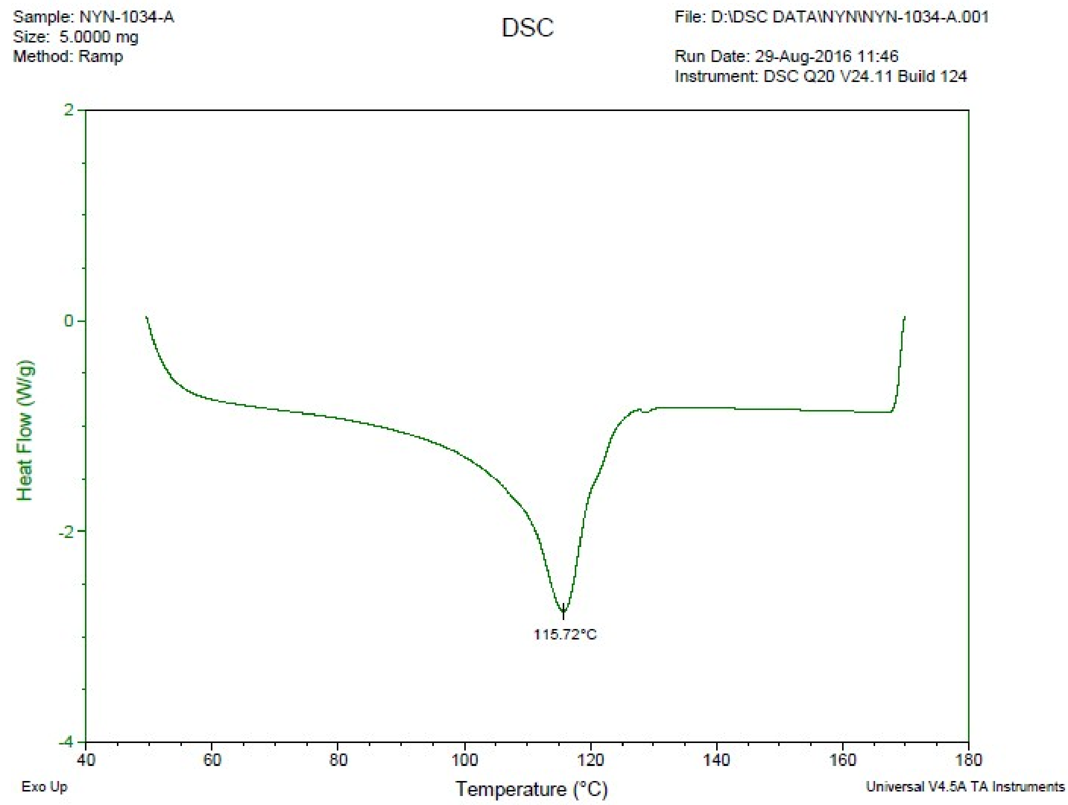


Figure S46. DSC of the copolymer from table 2, entry 2.

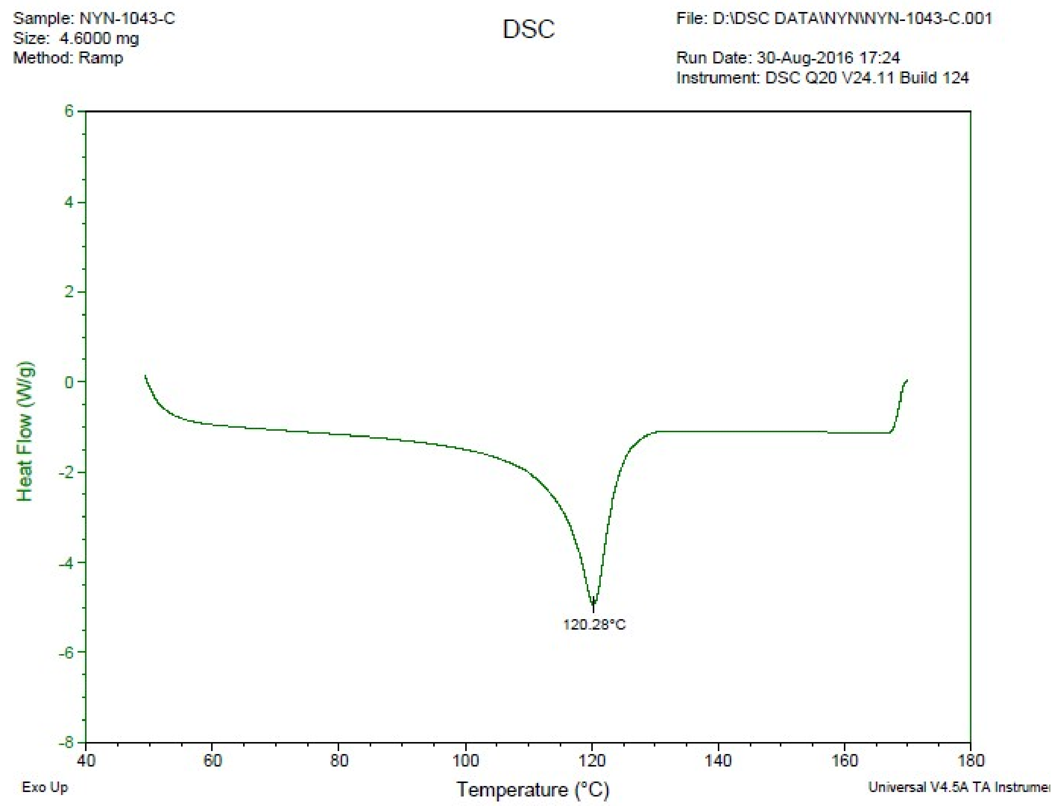


Figure S47. DSC of the copolymer from table 2, entry 3.

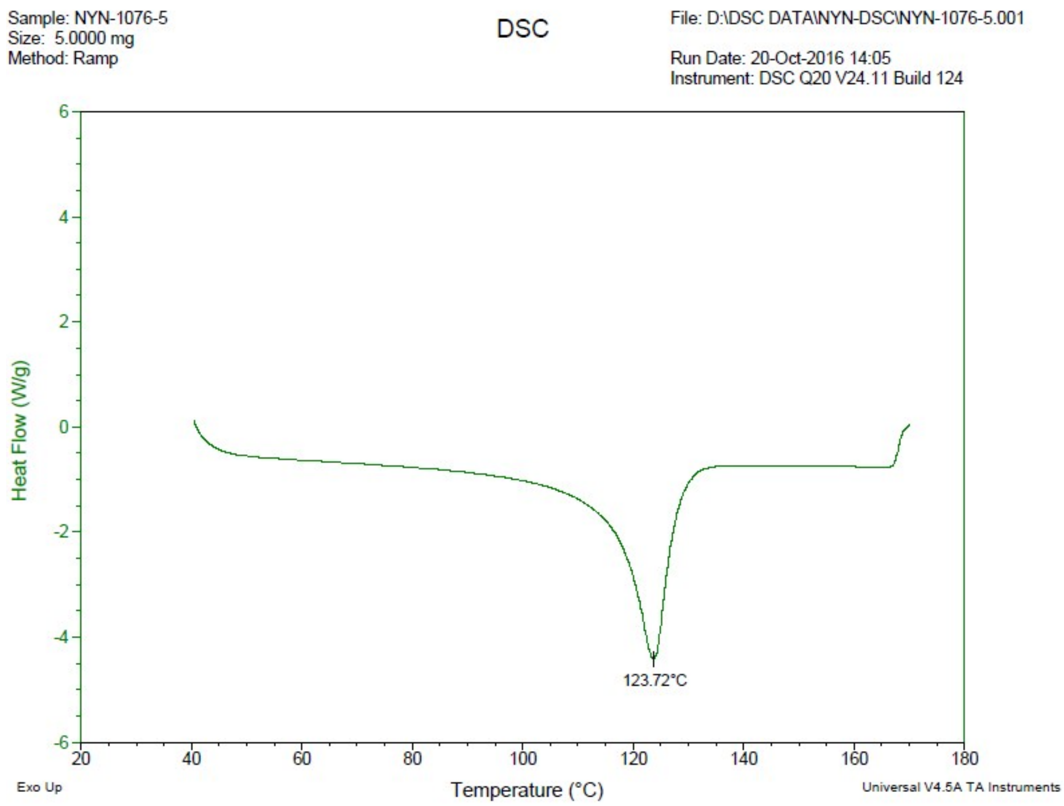


Figure S48. DSC of the copolymer from table 2, entry 4.

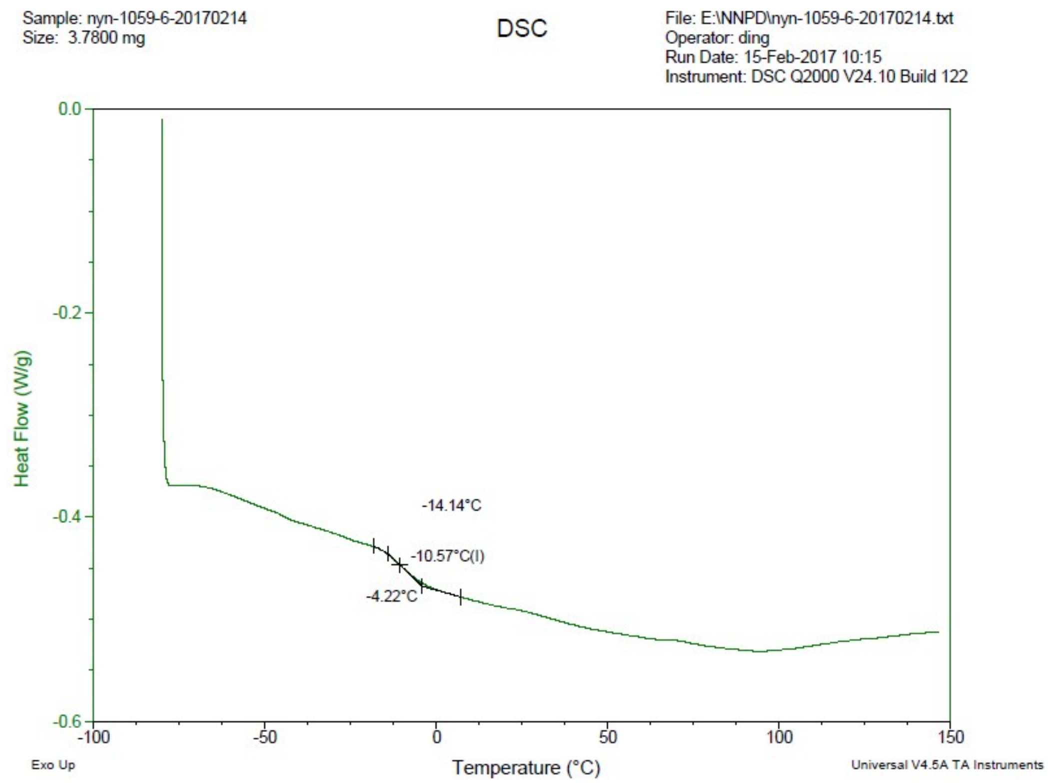
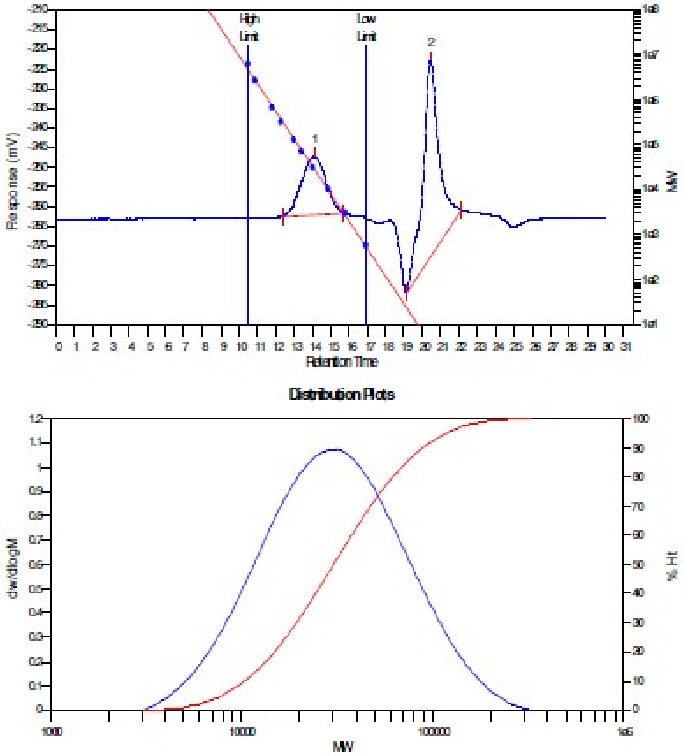


Figure S49. DSC of the copolymer from table 2, entry 5.



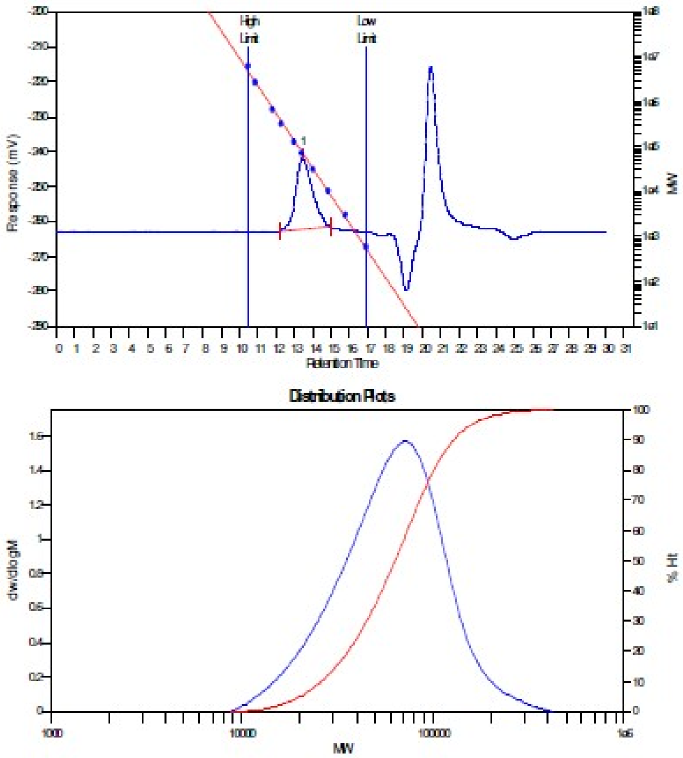
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	28765	21699	41697	74961	115217	37872	1.92161
2	3	2	4	6	9	4	2

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.37	14.10	15.68	14.7904	22.85	1350.13	30.8293
2		19.15	20.43	22.12	49.9378	77.15	3029.24	69.1707

Figure S50. GPC of the copolymer from table 1, entry 2.



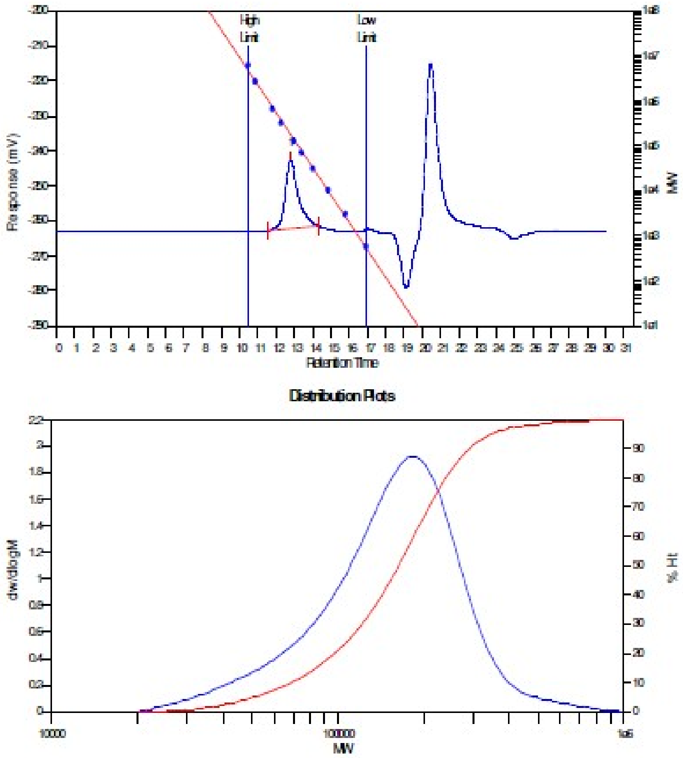
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	70268	49005	72088	101829	139719	68293	1.47103

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.18	13.47	14.95	20.2101	0	1266.1	100

Figure S51. GPC of the copolymer from table 1, entry 3.



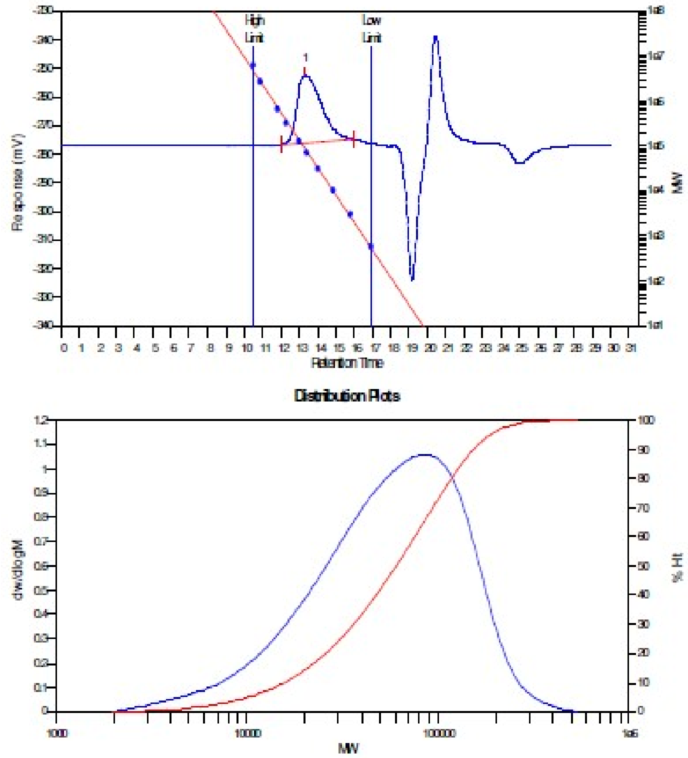
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	184194	125242	175107	231389	305124	167618	1.39815

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.58	12.78	14.35	19.731	0	1004.8	100

Figure S52. GPC of the copolymer from table 1, entry 4.



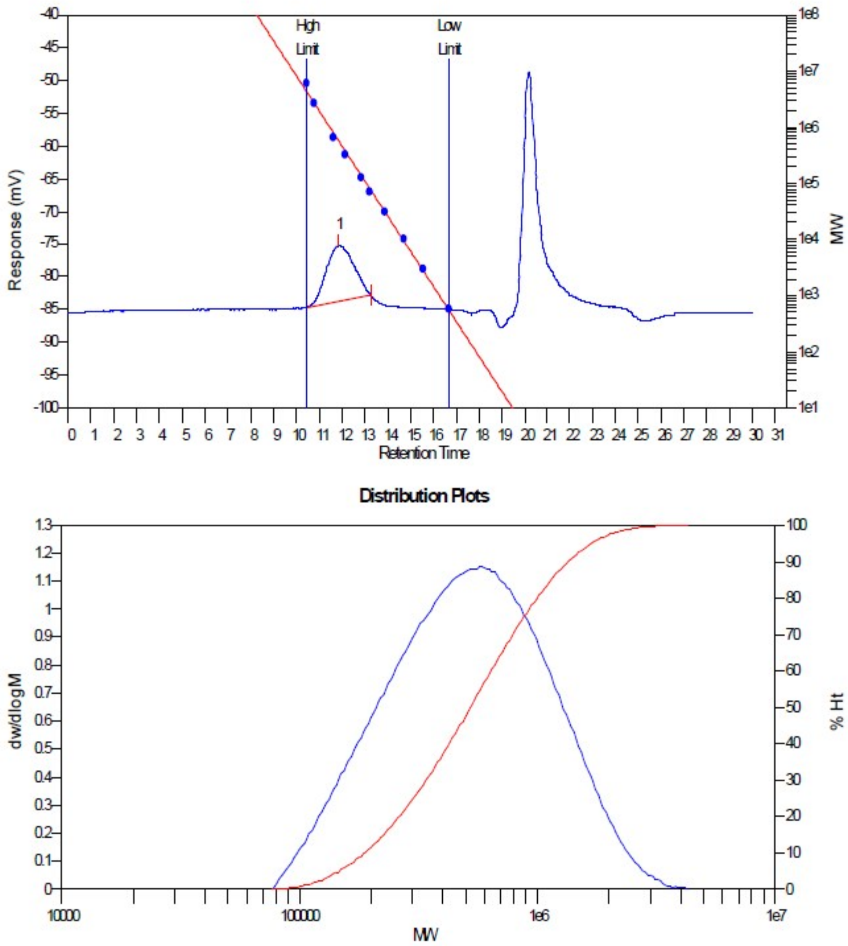
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	86822	33213	74870	122070	169604	68468	2.25424

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.03	13.32	16.00	23.6304	100	2191.93	100

Figure S53. GPC of the copolymer from table 1, entry 5.



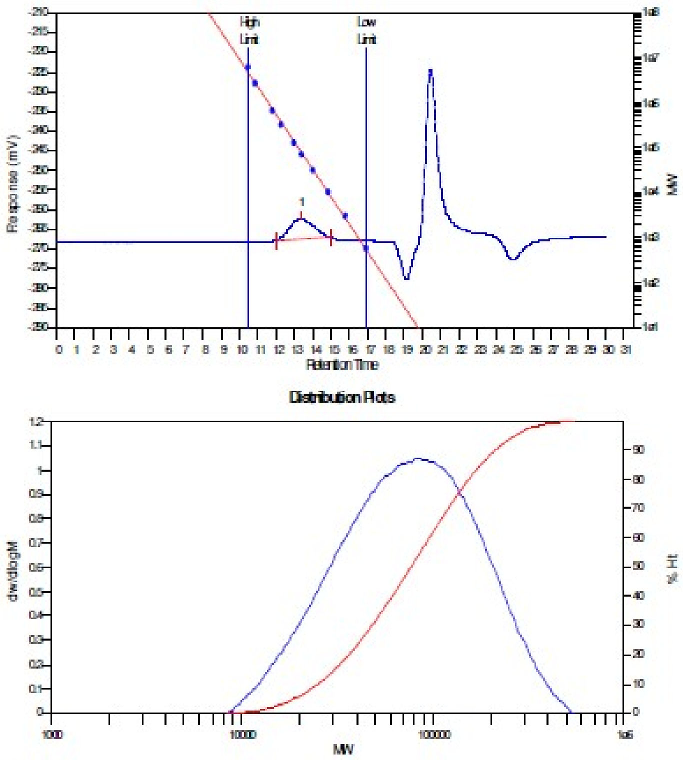
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	586216	387756	662312	1047450	1466420	613565	1.70806

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.45	11.85	13.25	8.5807	100	717.15	100

Figure S54. GPC of the copolymer from table 1, entry 6.



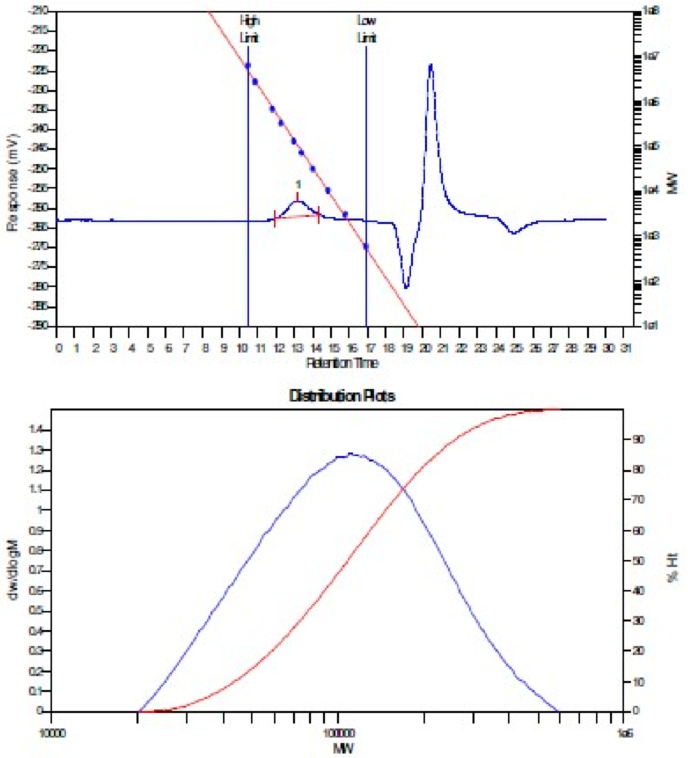
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	80911	53447	99646	163199	226445	91478	1.86439

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.02	13.37	14.97	4.83274	0	452.006	100

Figure S55. GPC of the copolymer from table 1, entry 7.



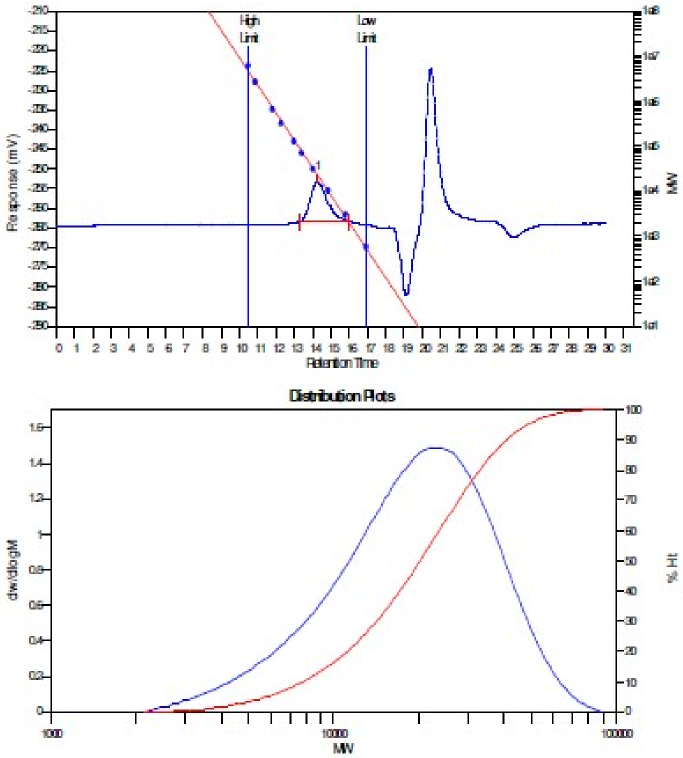
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	109826	85570	131501	192378	255985	123540	1.53677

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.95	13.15	14.35	3.94218	0	301.524	100

Figure S56. GPC of the copolymer from table 1, entry 8.



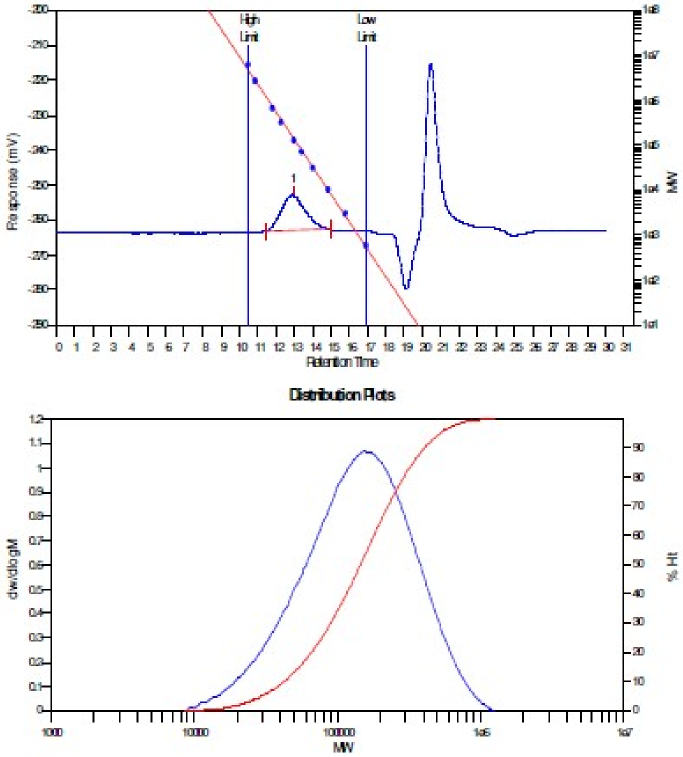
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	23280	14918	22464	30194	37407	21346	1.50583

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		13.30	14.25	15.93	9.98112	0	657.906	100

Figure S57. GPC of the copolymer from table 1, entry 9.



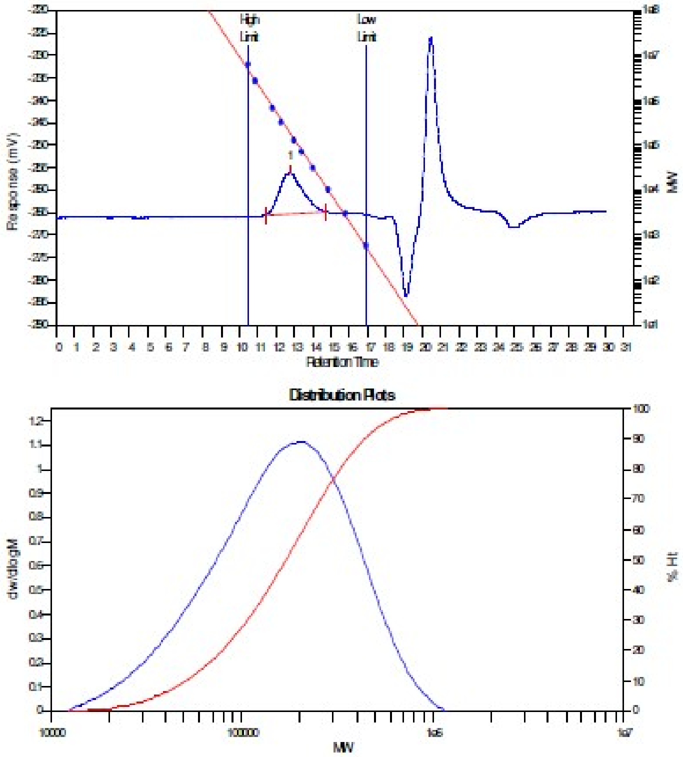
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	152621	91276	189657	325006	468168	172660	2.07784

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.43	12.92	14.95	10.1055	0	927.895	100

Figure S58. GPC of the copolymer from table 1, entry 10.



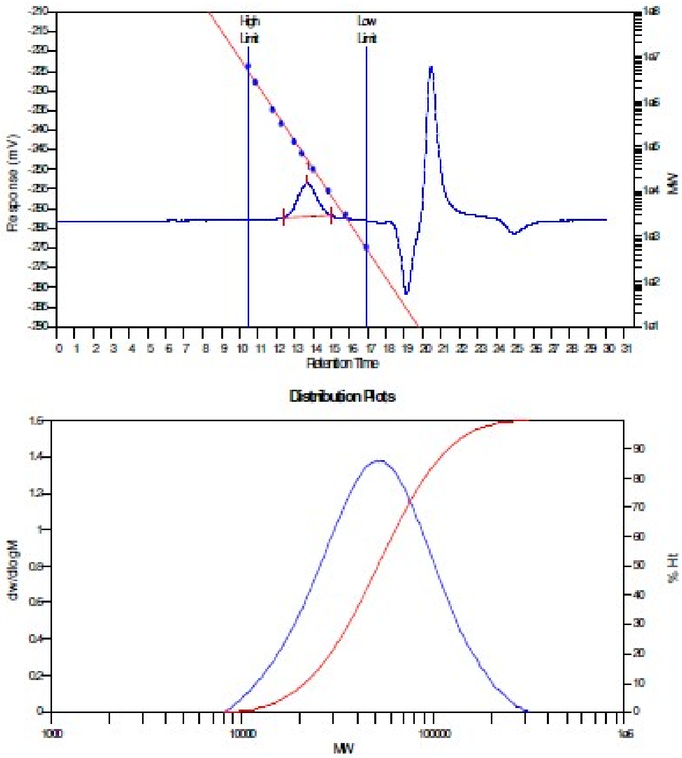
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	202352	109629	211996	338894	463722	195134	1.93376

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.47	12.73	14.70	9.04033	0	796.653	100

Figure S59. GPC of the copolymer from table 1, entry 11.



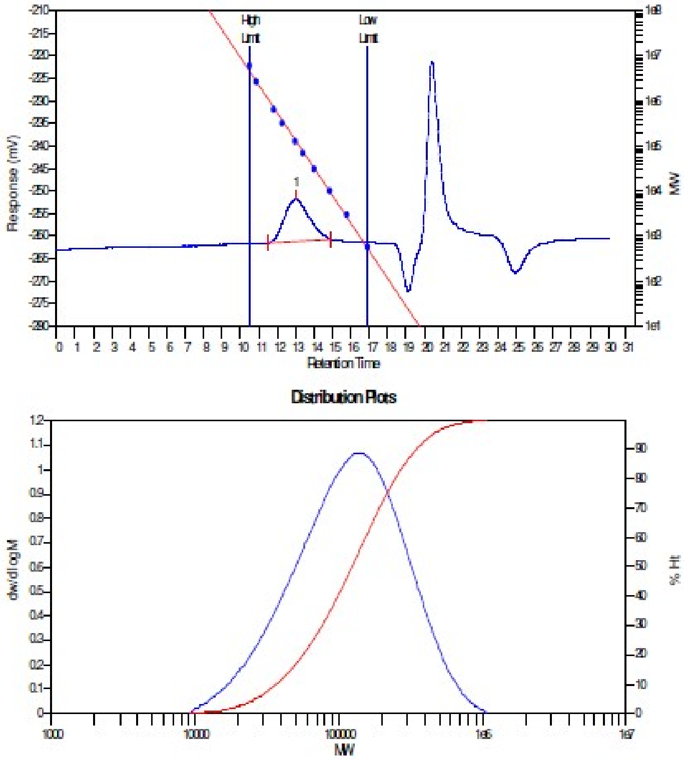
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	50565	40655	61977	90973	123800	58282	1.52446

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.40	13.70	15.00	8.41446	0	597.934	100

Figure S60. GPC of the copolymer from table 1, entry 12.



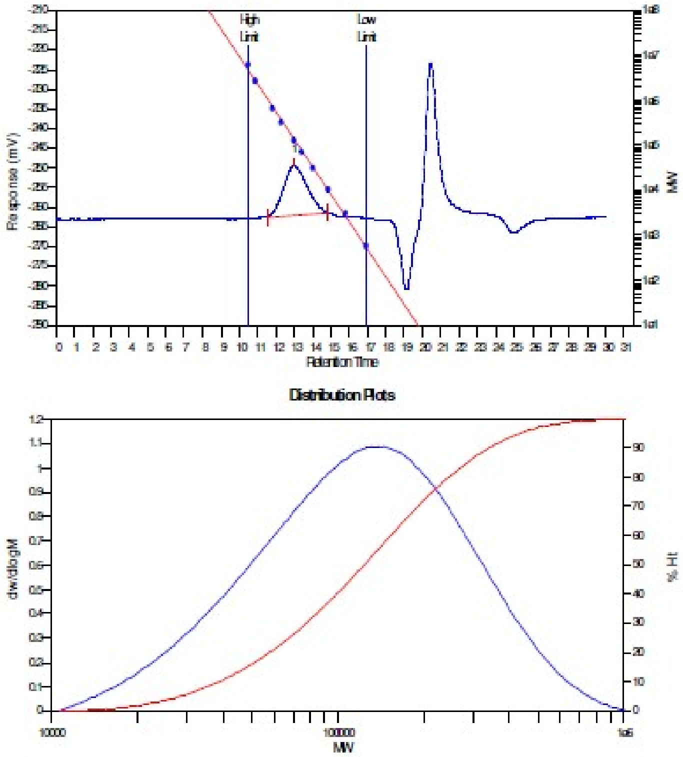
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	138926	79779	161264	276165	400500	146963	2.02138

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.53	13.00	14.92	9.34034	0	858.342	100

Figure S61. GPC of the copolymer from table 2, entry 1.



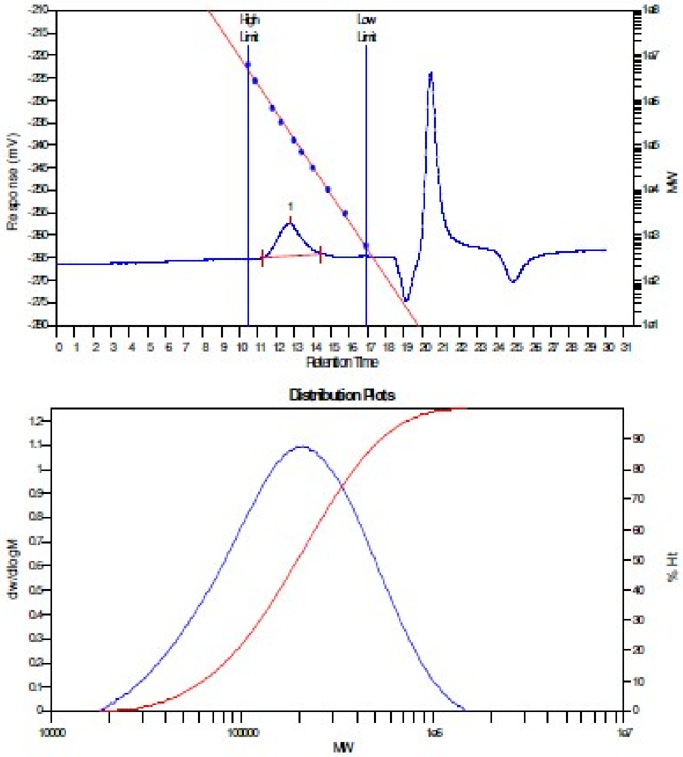
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	135699	82706	160282	268305	383513	146695	1.93797

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.57	13.00	14.80	12.5774	0	1133.03	100

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



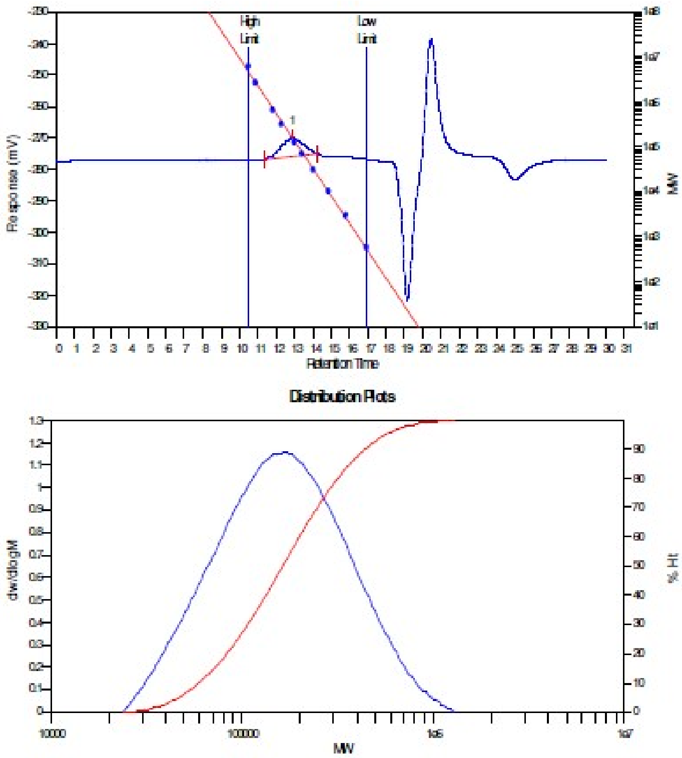
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	193060	133490	254051	421688	596768	232870	1.90315

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.30	12.75	14.43	7.05893	0	632.549	100

Figure S63. GPC of the copolymer from table 2, entry 3.



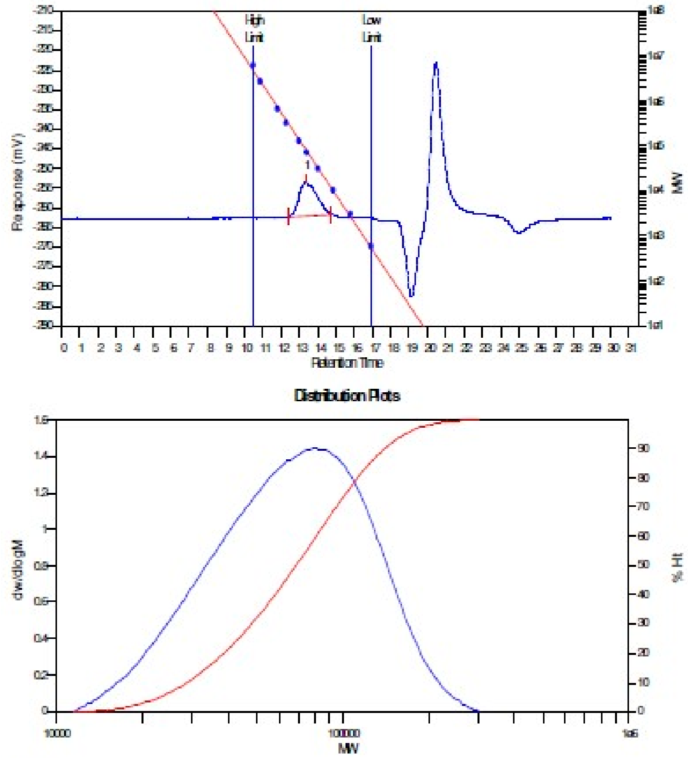
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	163771	122186	211674	346554	499375	195231	1.73239

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.40	12.87	14.23	5.86276	100	495.543	100

Figure S64. GPC of the copolymer from table 2, entry 4.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	79031	54112	77145	102856	127590	73513	1.42565

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.43	13.38	14.75	8.30125	0	564.394	100

Figure S65. GPC of the copolymer from table 2, entry 5.

3. References

P. Perrotin, J. S. J. McCahill, G. Wu and S. L. Scott, *Chem. Commun.***,** 2011, **47**, 6948.