Supplementary Materials

Copolymerization of Norbornene and Methyl Acrylate by Nickel Catalyst bearing 2-(Diarylphosphino)-N-Phenylbenzenamine Ligands

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1 Crystallographic data for ligand L2 and complexes Ni1 and Ni2

Table S1. Crystal data and structure refinement for complexes **Ni1** and **Ni2**.

Entry	Ni1	Ni2
Empirical formula	$C_{25}H_{22}Br_2Cl_2NNiP$	$C_{27}H_{24}Br_2Cl_2NNiO_2P$
Formula weight	656.839	714.876
Temperature (K)	300.0	299.0
Wavelength (Å)	1.34139	1.34139
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/n$
a (Å)	9.0465(7)	9.1088(11)
b (Å)	10.6576(8)	17.448(2)
c (Å)	14.8738(11)	18.5128(19)
α (°)	78.729(3)	90
β (°)	77.450(3)	93.780(3)
γ (°)	72.622(3)	90
Volume (Å^3)	1322.70(17)	2935.9(6)
Z	2	4
Density (calculated) (Mg/m^3)	1.326	1.385
Absorption coefficient (mm^{-1})	2.854	3.355
F(000)	652.9	1425.9
Crystal size (mm^3)	0.05 x 0.03 x 0.02	0.06 x 0.04 x 0.02
Theta range for data collection (°)	4.04 to 50.86	4.4 to 50.8
Index ranges	-10 <= h <= 10, -12 <= k <= 12,-17 <= l <= 17	-10 <= h <= 10, -21 <= k <= 21, -22 <= l <= 22
Reflections collected	66926	136841
Independent reflections	4864 [R(int) = 0.1014]	5376 [R(int) = 0.1097]
Completeness to theta = 53.594°	100%	99.9%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7508 and 0.6090	0.7508 and 0.4890
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	4864 /21 / 289	5376 / 0 / 312
Goodness-of-fit on F^2	1.058	1.058
Final R indices [I>2sigma(I)]	R1 = 0.0466, wR2 = 0.1157	R1 = 0.0503, wR2 = 0.1370
R indices (all data)	R1 = 0.0640, wR2 = 0.1277	R1 = 0.0604, wR2 = 0.1497
Extinction coefficient	n/a	n/a
Largest diff. peak and hole	1.37 and -1.04	0.86 and -0.99

(e.Å⁻³)

Table S2. Crystal data and structure refinement for ligand **L2**.

Entry	L2
Empirical formula	$C_{26}H_{24}N_1OP_1$
Formula weight	413.44
Temperature (K)	173.0
Wavelength (Å)	1.34139
Crystal system	Triclinic
Space group	P-1
a (Å)	7.3625(3)
b (Å)	11.3415(5)
c (Å)	13.1442(6)
α (°)	81.111(2)
β (°)	81.669(2)
γ (°)	83.559(2)
Volume (Å³)	1068.40(8)
Z	4
Density (calculated) (Mg/m³)	1.285
Absorption coefficient (mm⁻¹)	0.850
F(000)	436
Crystal size (mm³)	0.08 x 0.06 x 0.06
Theta range for data collection (°)	3.446 to 55.035
Index ranges	-8<=h<=8, -13<=k<=13,-16<=l<=15
Reflections collected	12523
Independent reflections	4023 [R(int) = 0.0635]
Completeness to theta = 53.594°	99.2 %
Absorption correction	Semi-empirical fromequivalents
Max. and min. transmission	0.7508 and 0.5390
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4023 / 0 / 273
Goodness-of-fit on F^2	1.039
Final R indices [I>2sigma(I)]	R1 = 0.0593, wR2 = 0.1599
R indices (all data)	R1 = 0.0681, wR2 = 0.1710
Extinction coefficient	n/a
Largest diff. peak and hole (e.Å⁻³)	0.547 and -0.675

2 Spectra data

2.1 ³¹P, ¹H and ¹³C NMR spectra of the ligands.
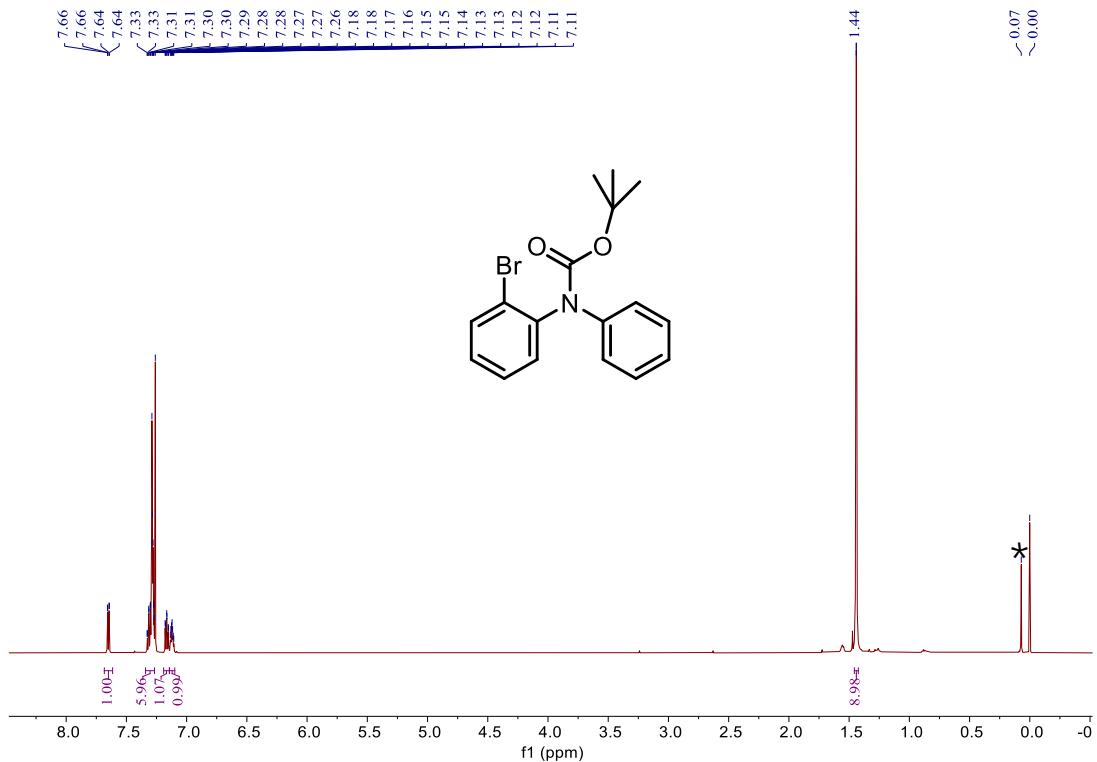
Figure S1. ³¹P NMR spectrum of *tert*-butyl N-(2-bromophenyl)-N-phenylcarbamate in CDCl₃ (*silicone grease).
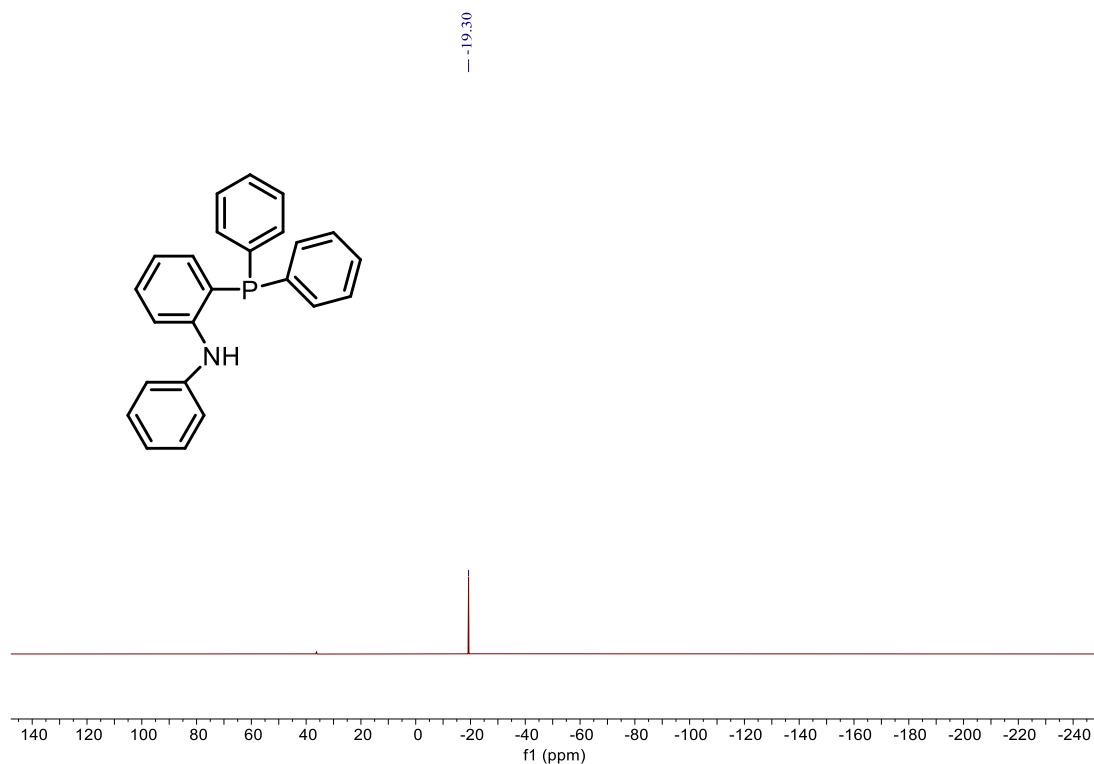
Figure S2. ^{31}P NMR spectrum of **L1** in CDCl$_3$.
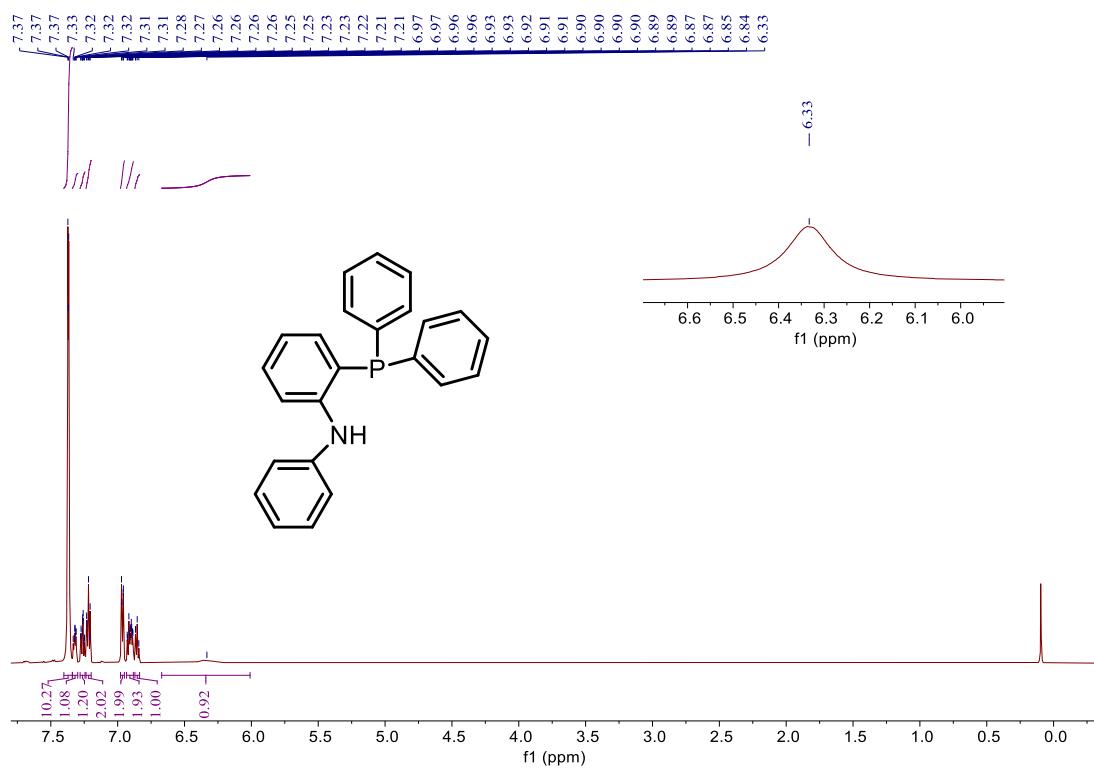

Figure S3. ^{1}H NMR spectrum of **L1** in CDCl$_3$.
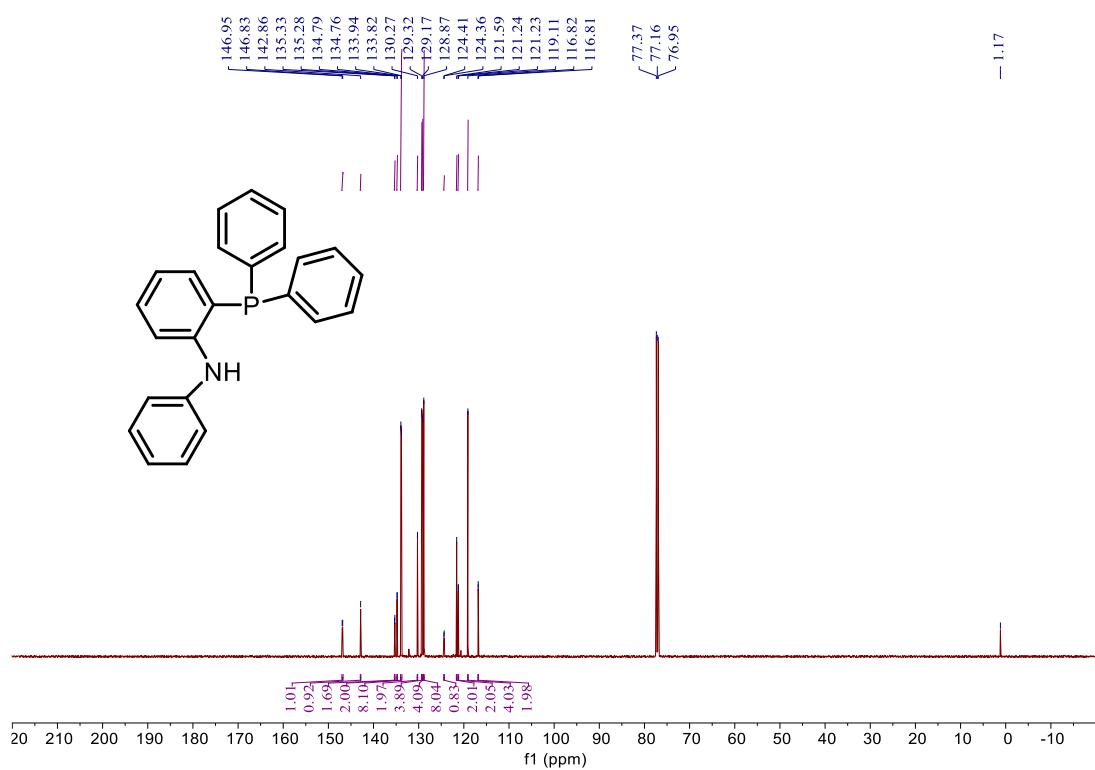
Figure S4. ^{13}C NMR spectrum of **L1** in CDCl$_3$.
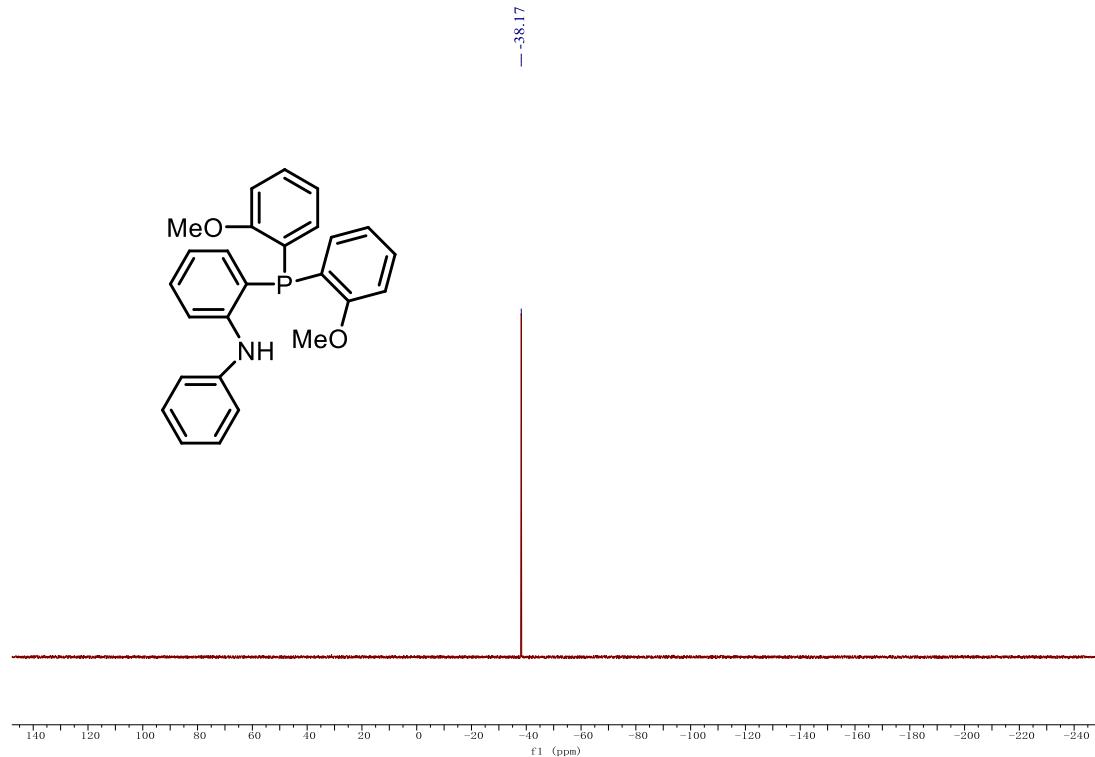
Figure S5. ^{31}P NMR spectrum of **L2** in DMSO-d_6.
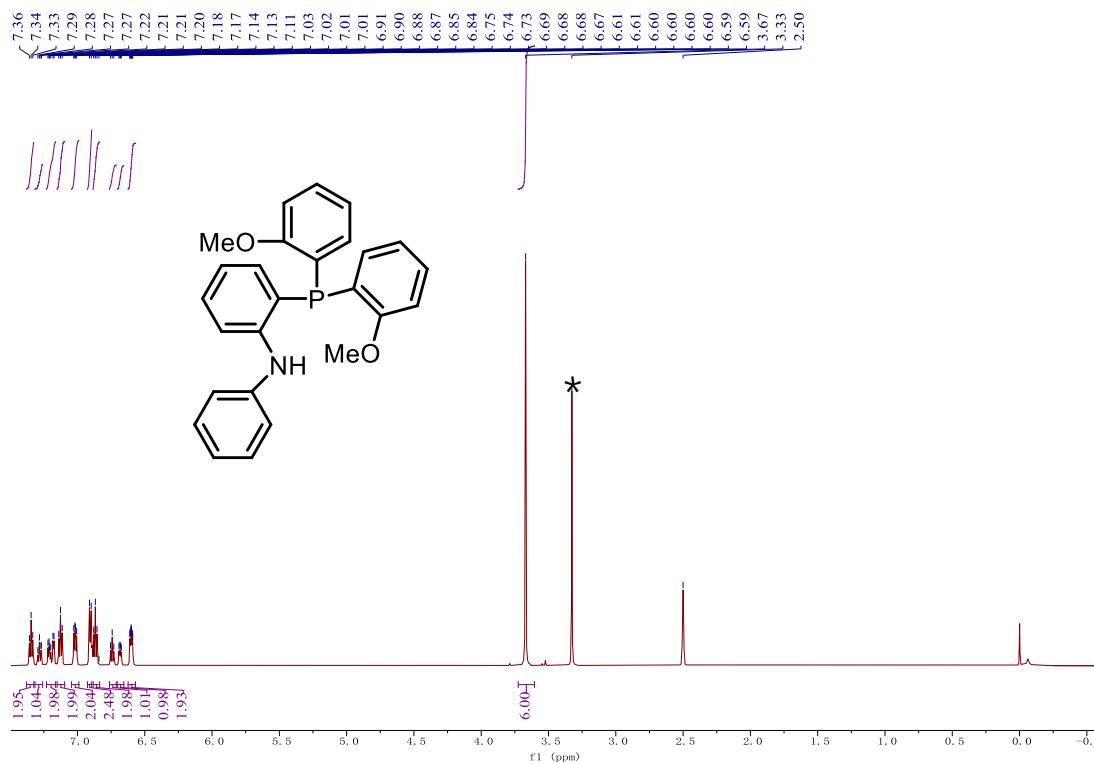
Figure S6. ^{1}H NMR spectrum of **L2** in DMSO-d_6 (*H$_2$O).
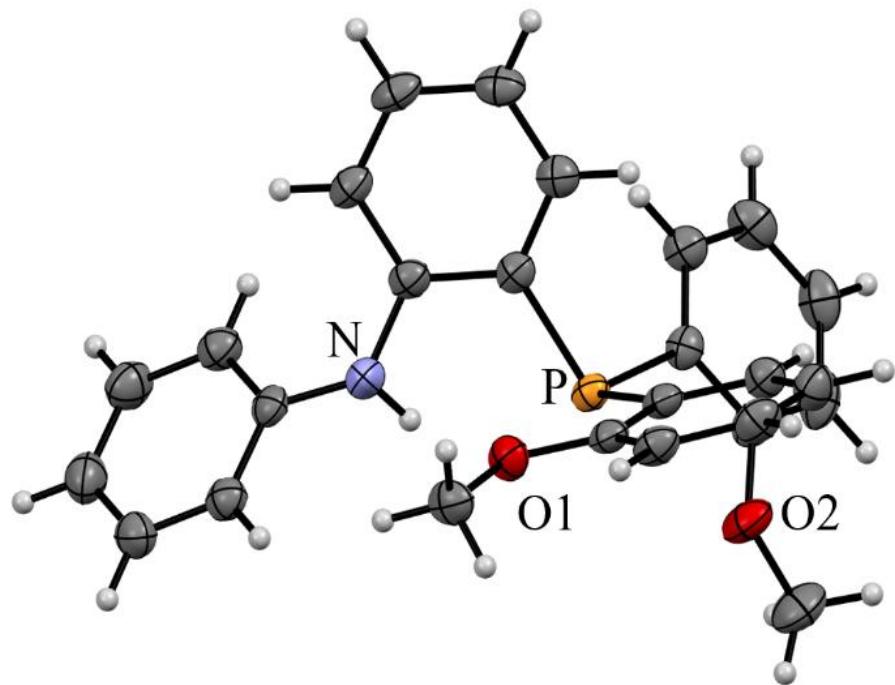
Figure S7. ORTEP representation of ligand **L2** (50% thermal ellipsoids).

2.1 MALDI-TOF-MS spectrometry of ligands and complexes.
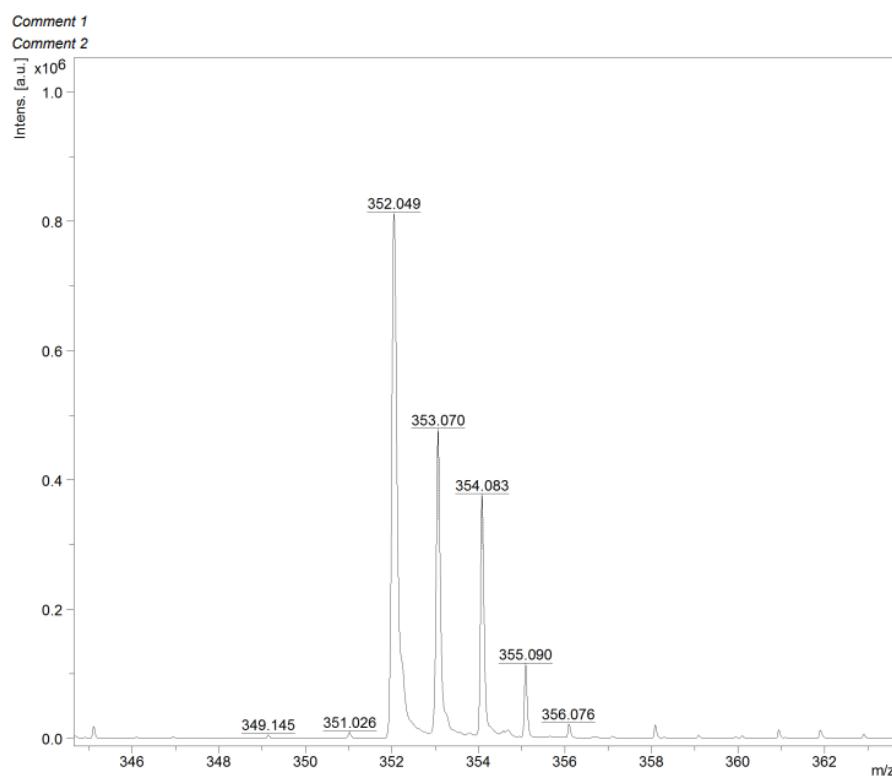
Figure S8. MALDI-TOF-MS spectrum of **L1**.
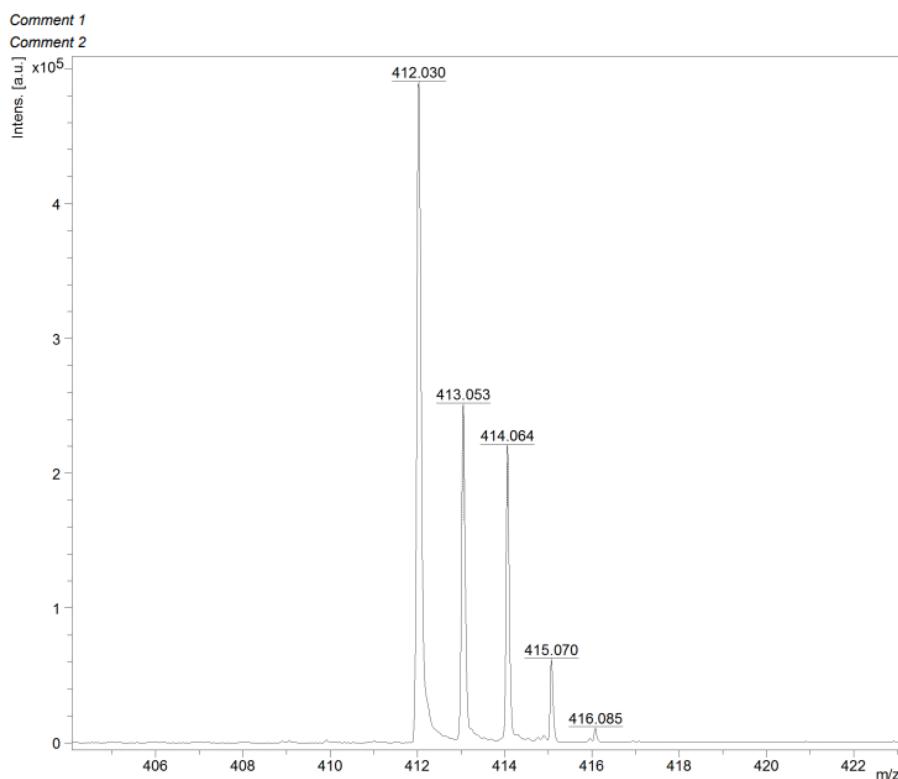
Figure S9. MALDI-TOF-MS spectrum of **L2**.
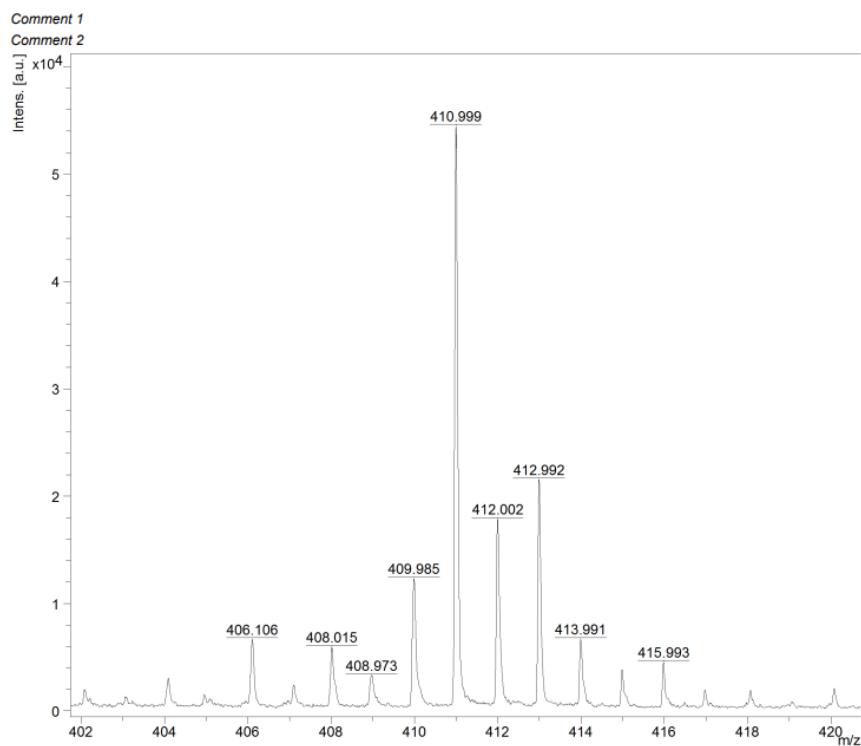
Figure S10. MALDI-TOF-MS spectrum of **Ni1**.
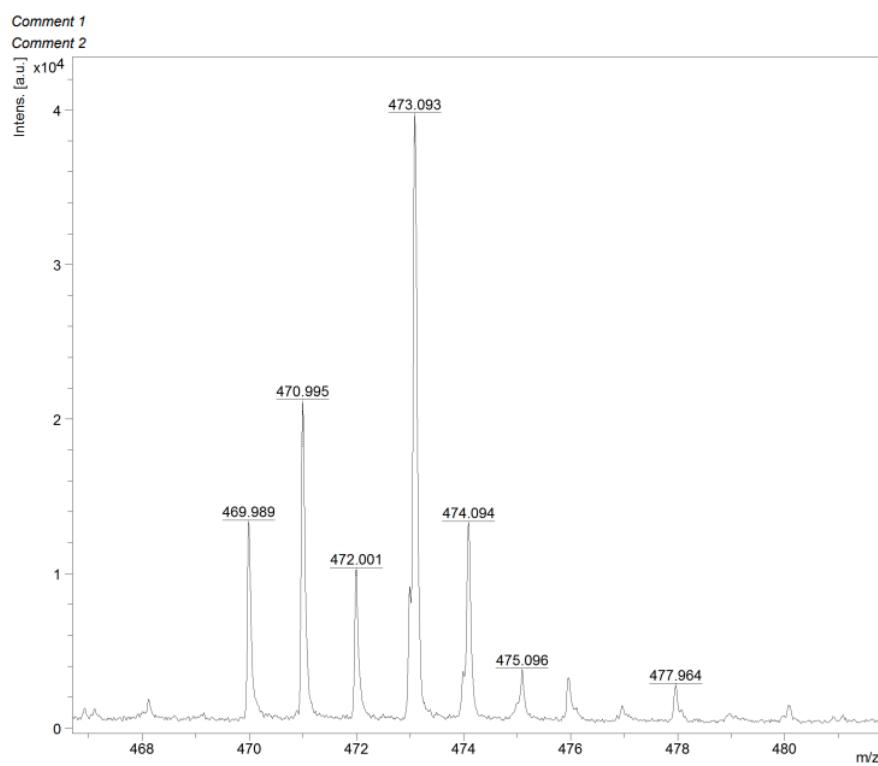
Figure S11. MALDI-TOF-MS spectrum of **Ni2**.

2.3 ¹H and ¹³C NMR spectra of copolymers
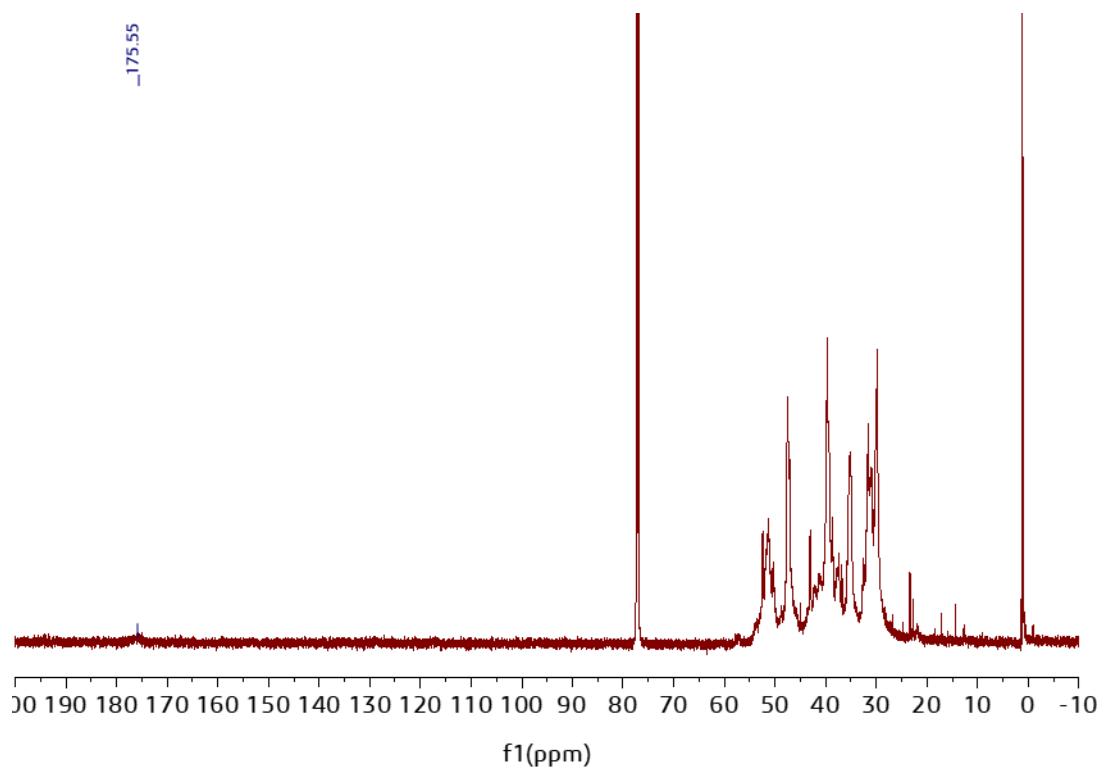
Figure S12. ¹³C NMR spectrum of copolymer from Table 2, entry 3.
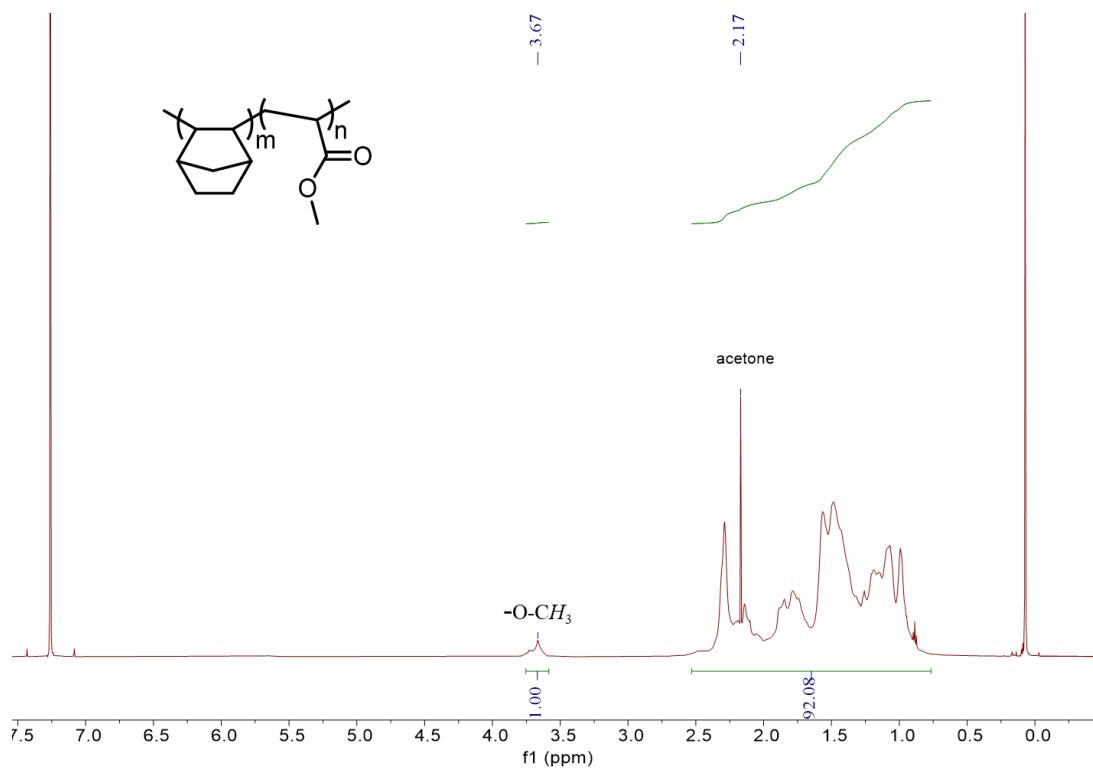
Figure S13. ¹H NMR spectrum of copolymer from Table 2, entry 1.
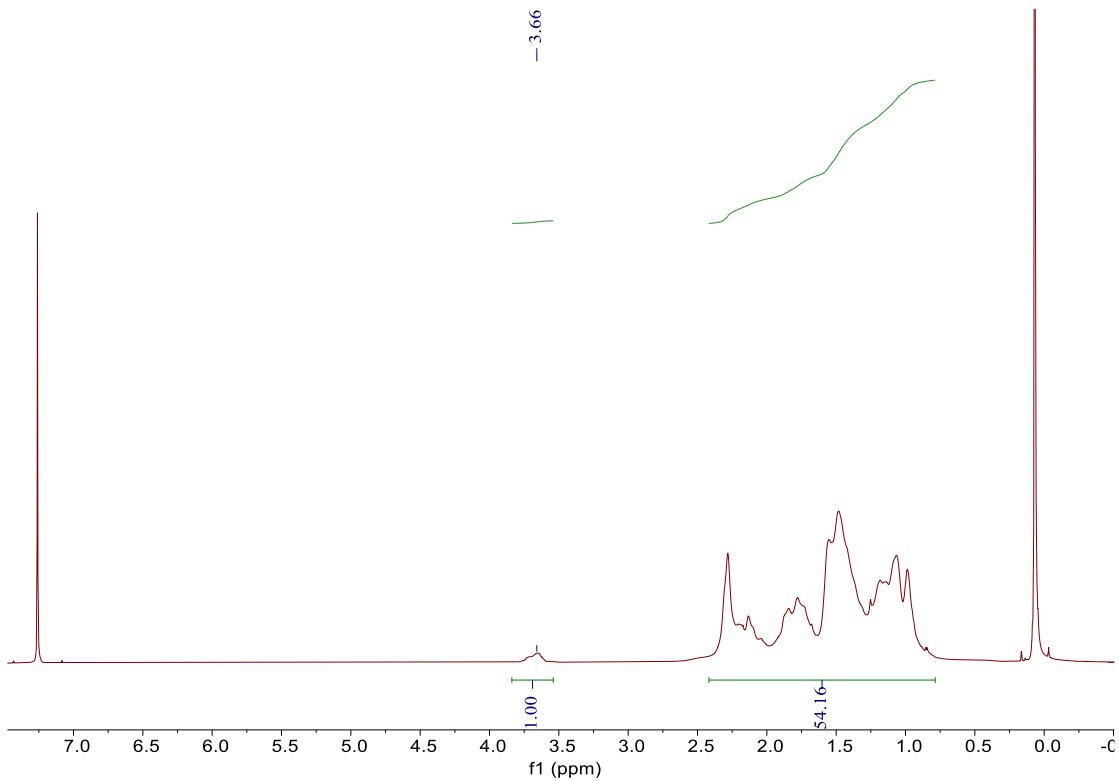
**Figure S14.** ^{1}H NMR spectrum of copolymer from Table 2, entry 2.
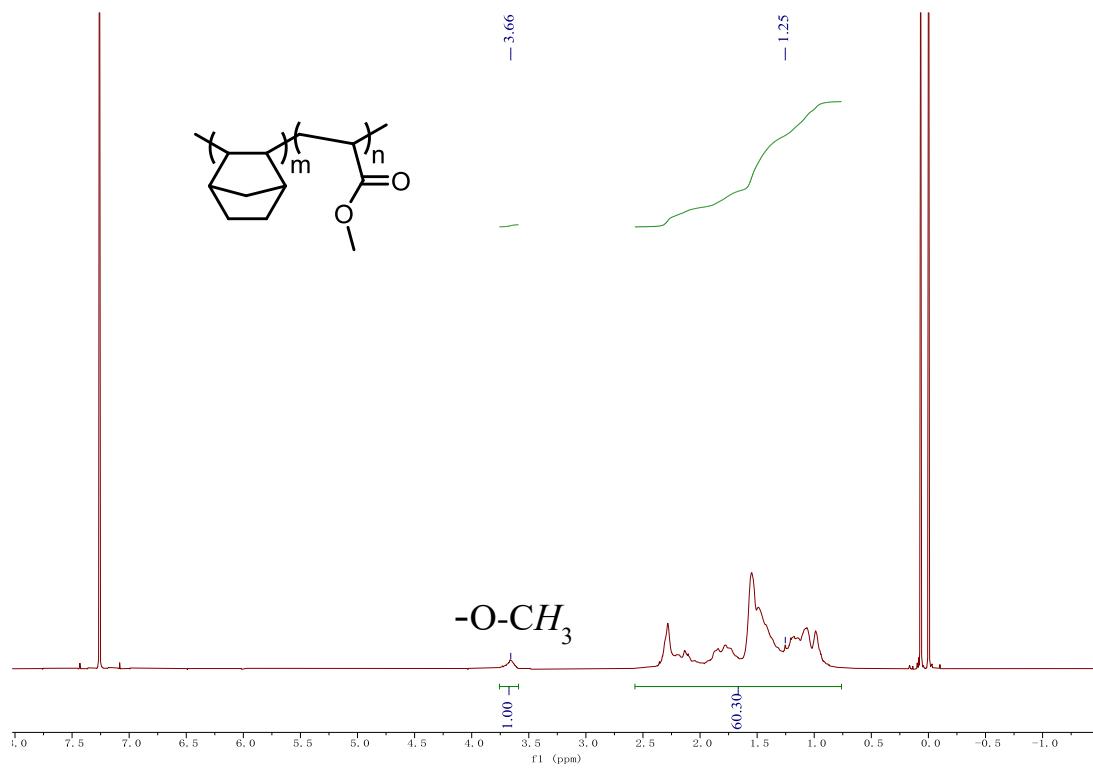
Figure S15. ^{1}H NMR spectrum of copolymer from Table 2, entry 3.
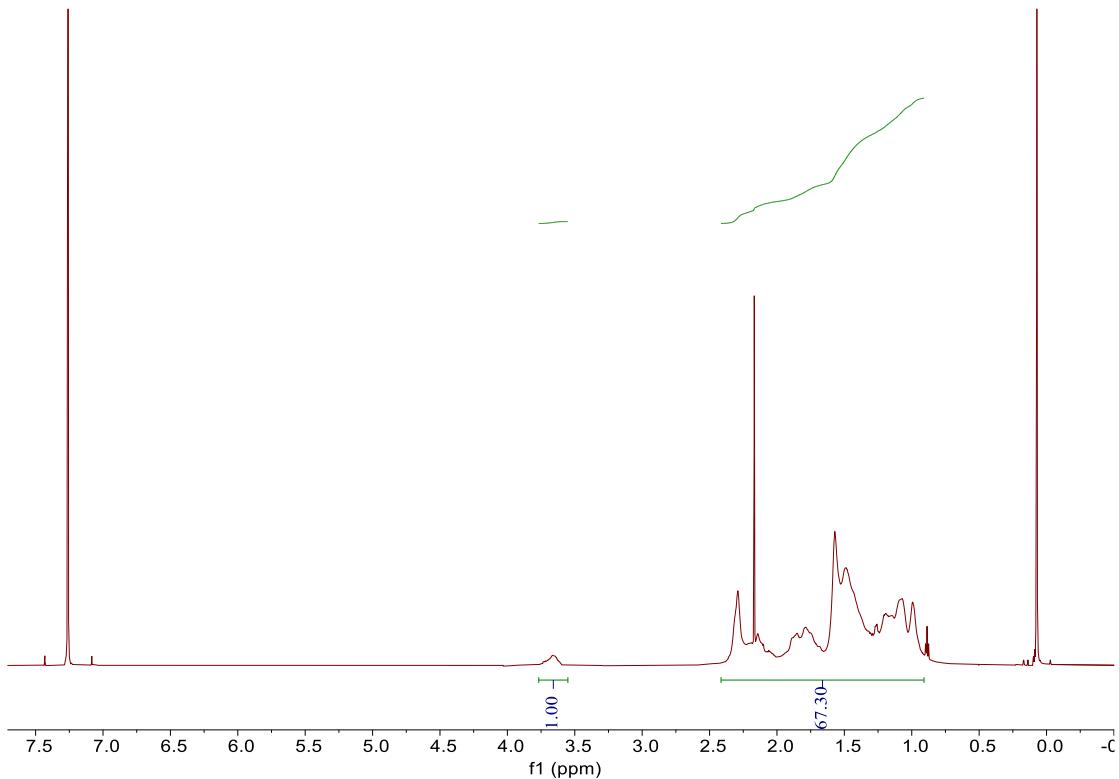
Figure S16. ¹H NMR spectrum of copolymer from Table 2, entry 4.
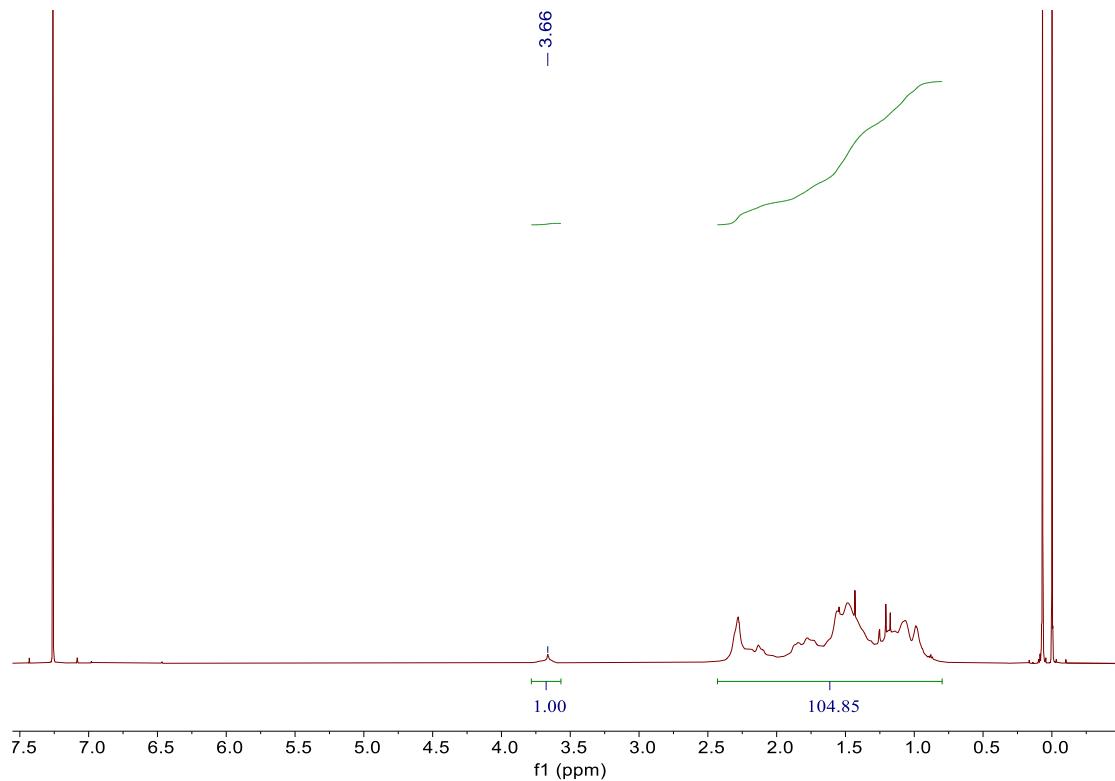
**Figure S17.** ¹H NMR spectrum of copolymer from Table 2, entry 5.
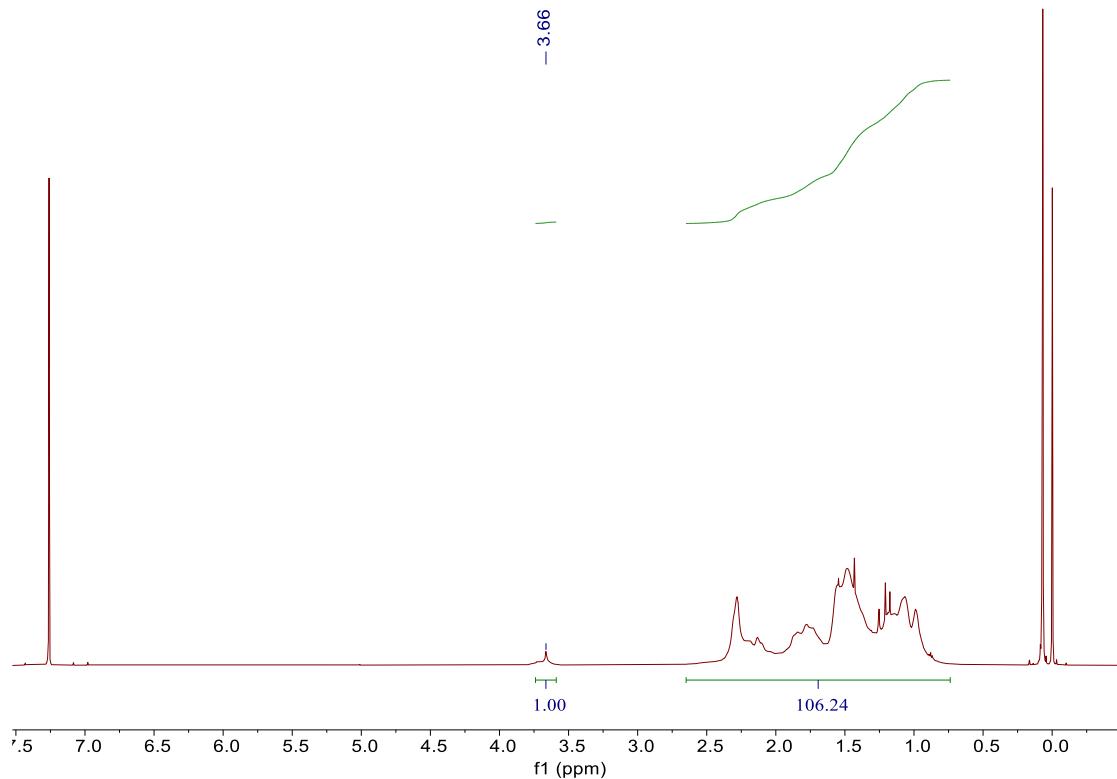
Figure S18. ^{1}H NMR spectrum of copolymer from Table 2, entry 6.

2.4 GPC data of polymer and copolymer

MW Averages

| Mp: 2493666 | Mn: 1114700 | Mv: 2370487 | Mw: 2633822 |
| Mz: 4780318 | Mz+1: 7250507 | PD: 2.3628 | |
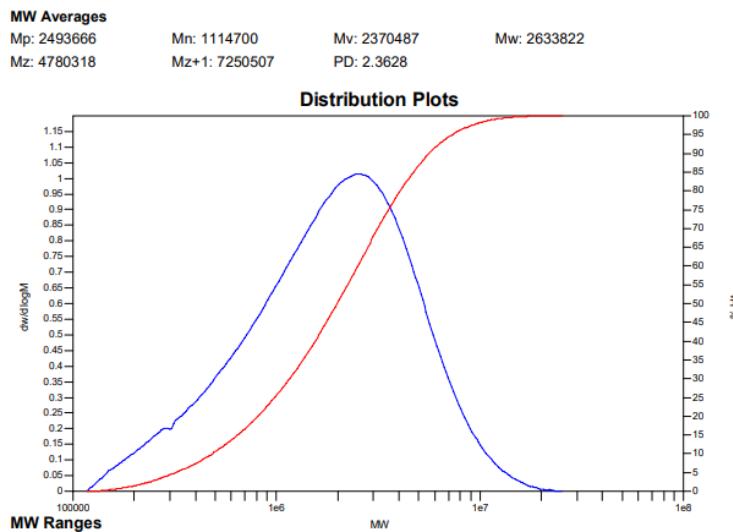
Figure S19. GPC data of the polymer from Table 1, entry 1.

MW Averages

Mp: 2598251   Mn: 1055123   Mv: 2283320   Mw: 2532709

Mz: 4483517   Mz+1: 6531876   PD: 2.4004
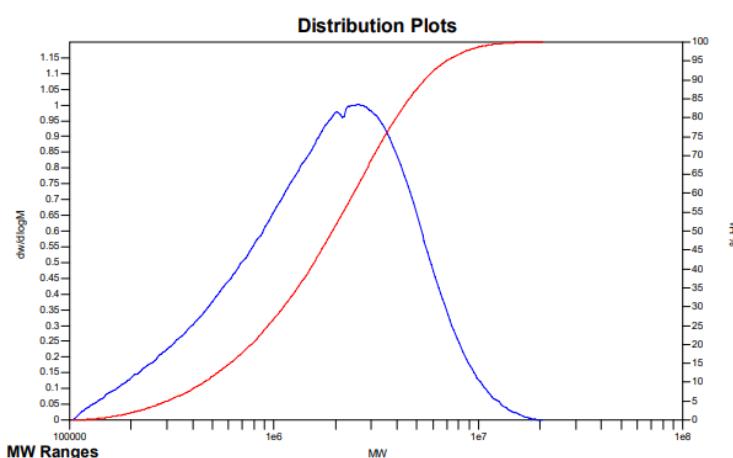
Figure S20. GPC data of the polymer from Table 1, entry 2.

MW Averages

Mp: 3999724   Mn: 1947133   Mv: 3922610   Mw: 4310371

Mz: 7366350   Mz+1: 10801220   PD: 2.2137
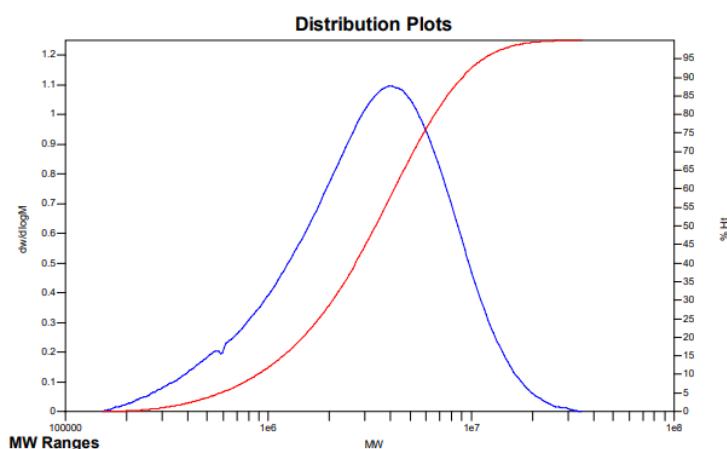
Figure S21. GPC data of the polymer from Table 1, entry 3.

MW Averages

Mp: 4911835   Mn: 2232385   Mv: 5145984   Mw: 5738706

Mz: 10578315   Mz+1: 16044205   PD: 2.5707
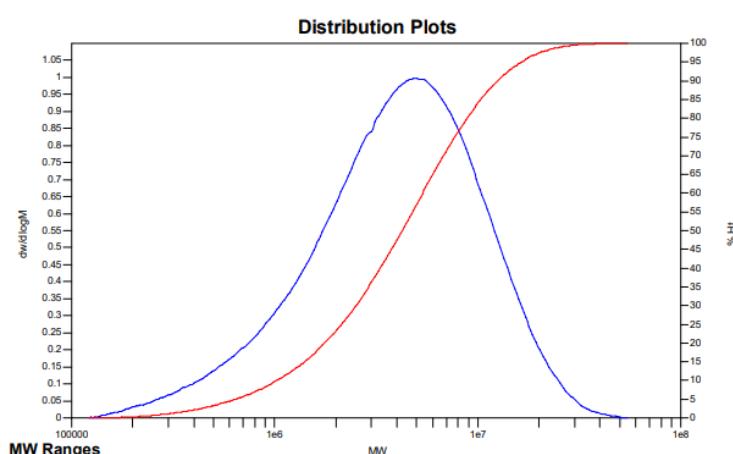
Figure S22. GPC data of the polymer from Table 1, entry 4.

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MW Averages

Mp: 5332481   Mn: 2743683   Mv: 5564762   Mw: 6131354
Mz: 10611977   Mz+1: 15438445   PD: 2.2347
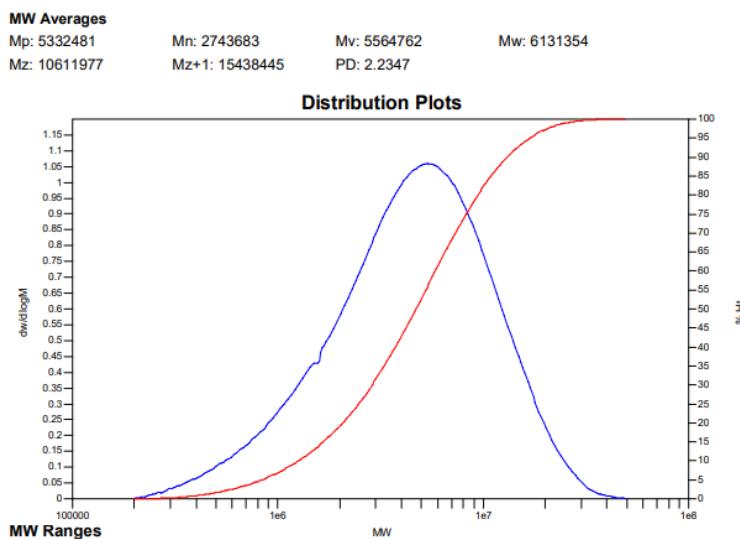
Figure S23. GPC data of the polymer from Table 1, entry 5.

MW Averages

Mp: 3535914   Mn: 1364875   Mv: 3399330   Mw: 3811780
Mz: 7181173   Mz+1: 11027160   PD: 2.7928
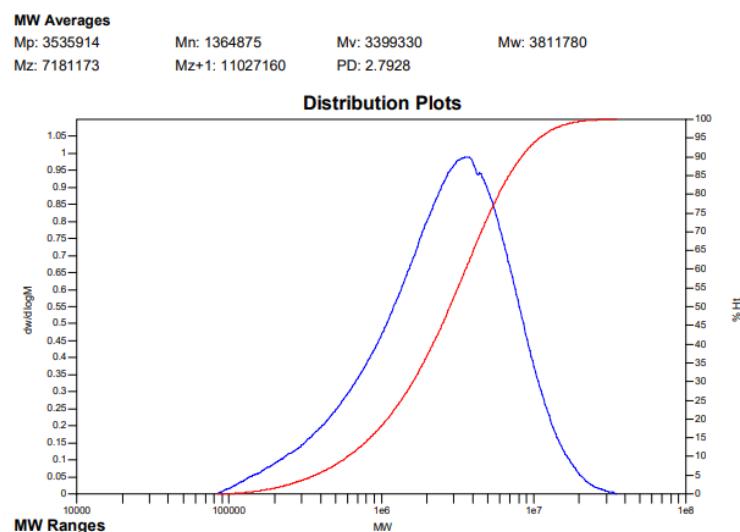
Figure S24. GPC data of the polymer from Table 1, entry 6.

MW Averages

Mp: 3464020   Mn: 1374080   Mv: 3285797   Mw: 3677346
Mz: 6806121   Mz+1: 10127961   PD: 2.6762
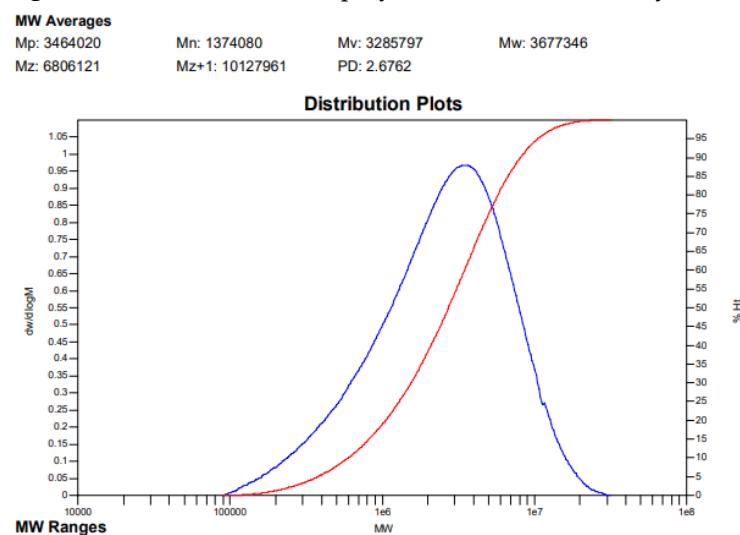
Figure S25. GPC data of the polymer from Table 1, entry 7.

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MW Averages

Mp: 2707222   Mn: 1057687   Mv: 2446778   Mw: 2729397
Mz: 4963096   Mz+1: 7313067   PD: 2.5805
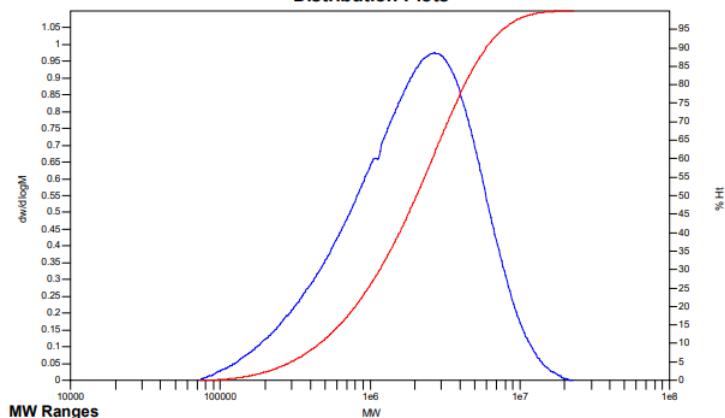
Figure S26. GPC data of the polymer from Table 1, entry 8.

MW Averages

Mp: 2393291   Mn: 926606   Mv: 2085413   Mw: 2307345
Mz: 4014098   Mz+1: 5817539   PD: 2.4901
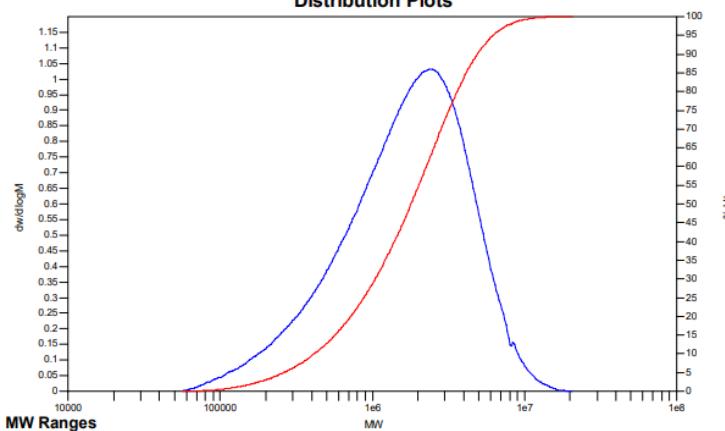
Figure S27. GPC data of the polymer from Table 1, entry 9.

MW Averages

Mp: 4167473   Mn: 1742976   Mv: 3912747   Mw: 4363069
Mz: 7937286   Mz+1: 11742152   PD: 2.5032
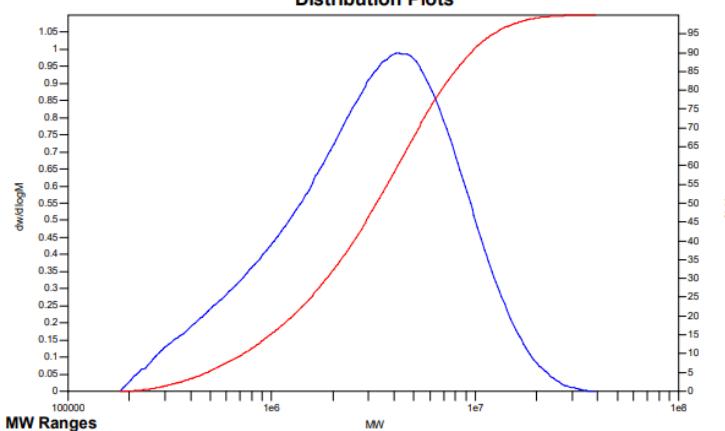
Figure S28. GPC data of the polymer from Table 1, entry 10.

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MW Averages
Mp: 3062331   Mn: 987997   Mv: 2614708   Mw: 2956992
Mz: 5725453   Mz+1: 8703246   PD: 2.9929

Distribution Plots


MW Ranges
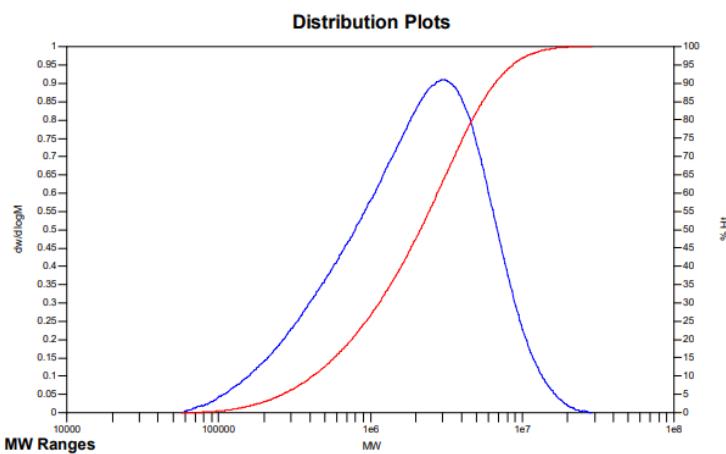
Figure S29. GPC data of the polymer from Table 1, entry 11.

MW Averages
Mp: 2820763   Mn: 940319   Mv: 2434581   Mw: 2745464
Mz: 5253549   Mz+1: 8008309   PD: 2.9197

Distribution Plots

MW Ranges
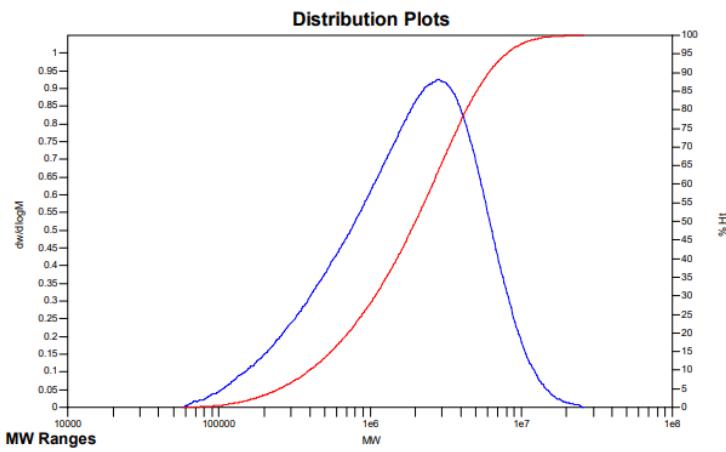
Figure S30. GPC data of the polymer from Table 1, entry 12.

MW Averages
Mp: 2879307   Mn: 1037706   Mv: 2444665   Mw: 2720880
Mz: 4905366   Mz+1: 7407379   PD: 2.6220

Distribution Plots

MW Ranges
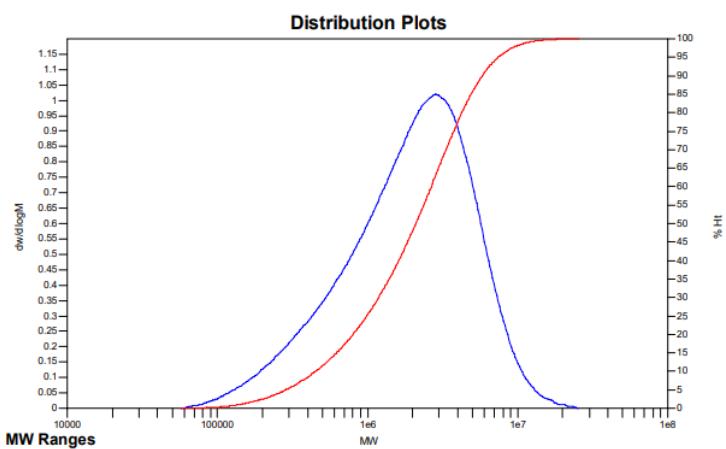
**Figure S31.** GPC data of the polymer from Table 1, entry 13.

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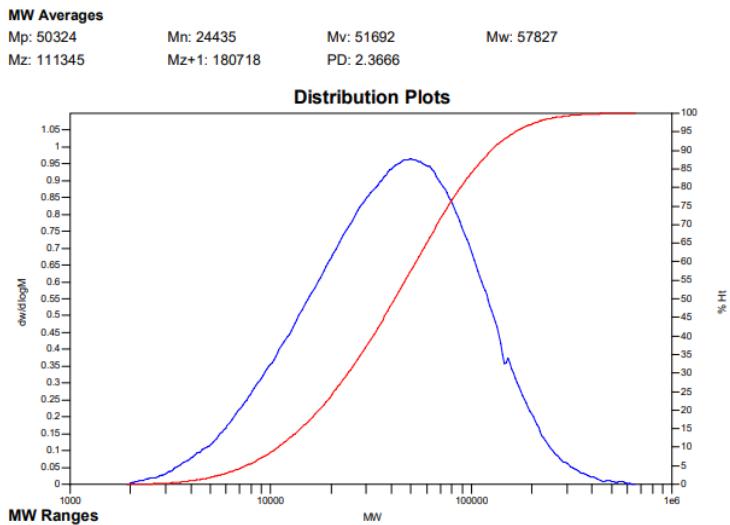
**Figure S32.** GPC data of the polymer from Table 2, entry 1.
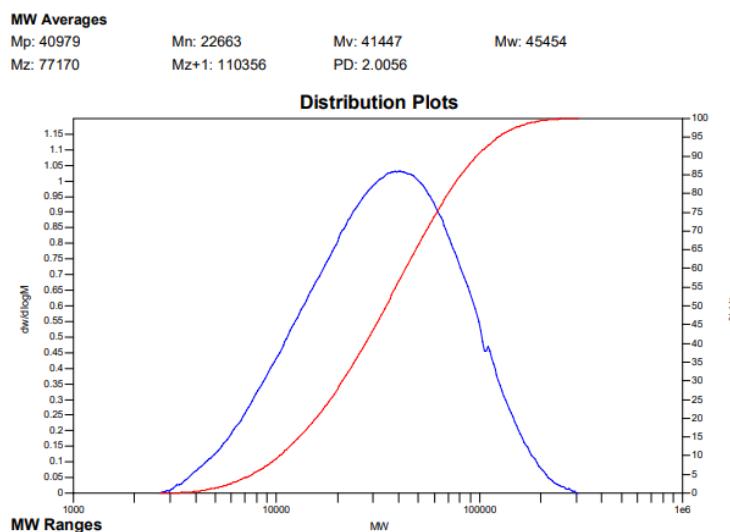
Figure S33. GPC data of the polymer from Table 2, entry 2.
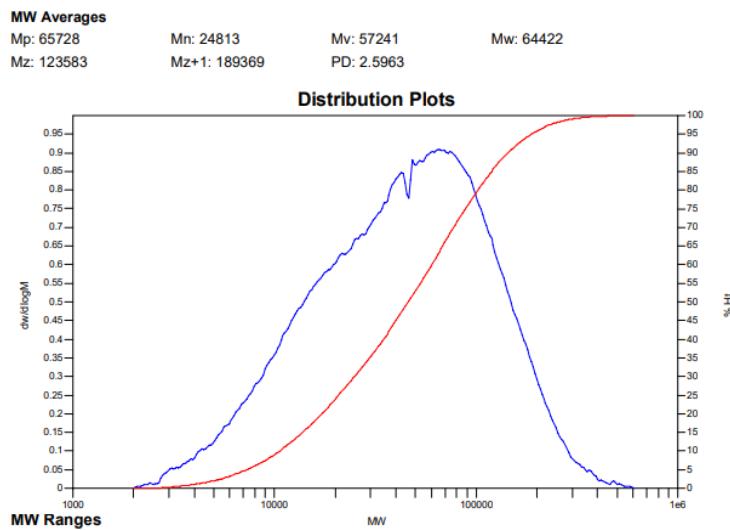
**Figure S34.** GPC data of the polymer from Table 2, entry 3.

MW Averages

Mp: 132154   Mn: 62000   Mv: 137195   Mw: 151893

Mz: 272272   Mz+1: 419437   PD: 2.4499
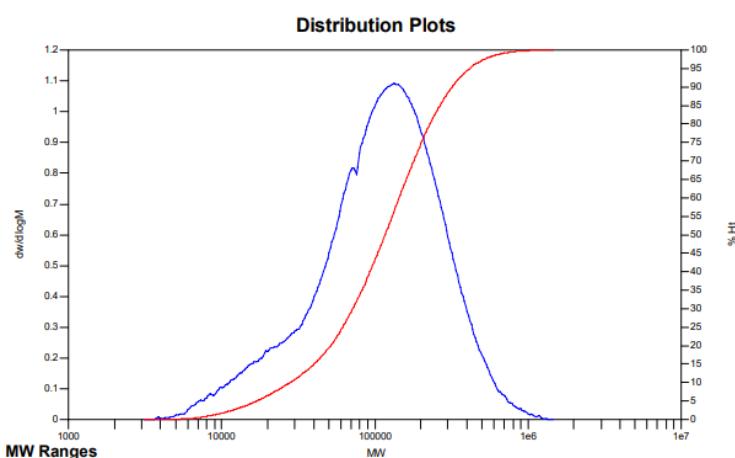
Figure S35. GPC data of the polymer from Table 2, entry 4.

MW Averages

Mp: 34768   Mn: 28778   Mv: 108014   Mw: 133767

Mz: 392033   Mz+1: 671547   PD: 4.6482
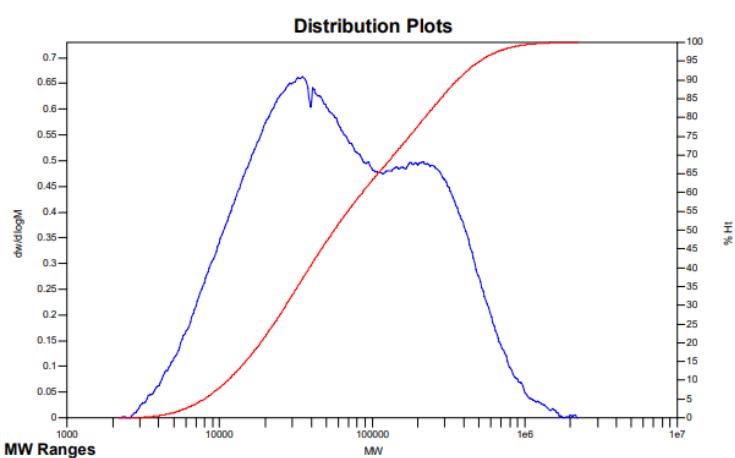
**Figure S36.** GPC data of the polymer from Table 2, entry 6.

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2.5 DSC data of copolymer
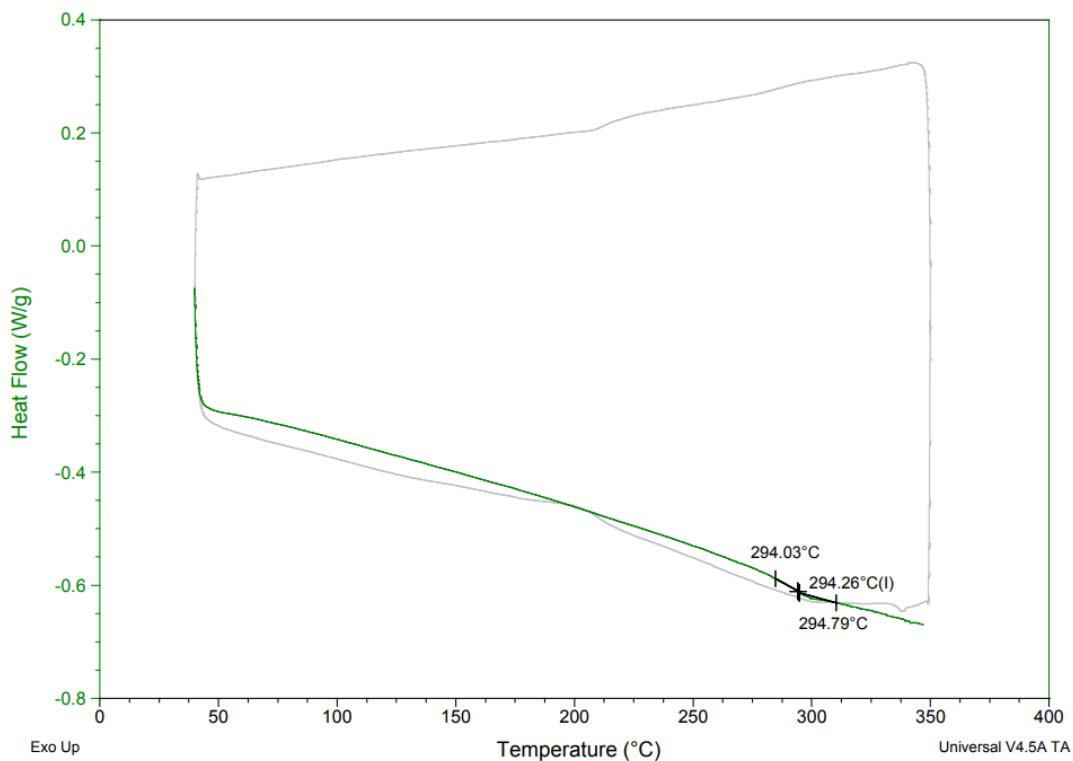
Figure S37. DSC curves of the polymer from Table 2, entry 1
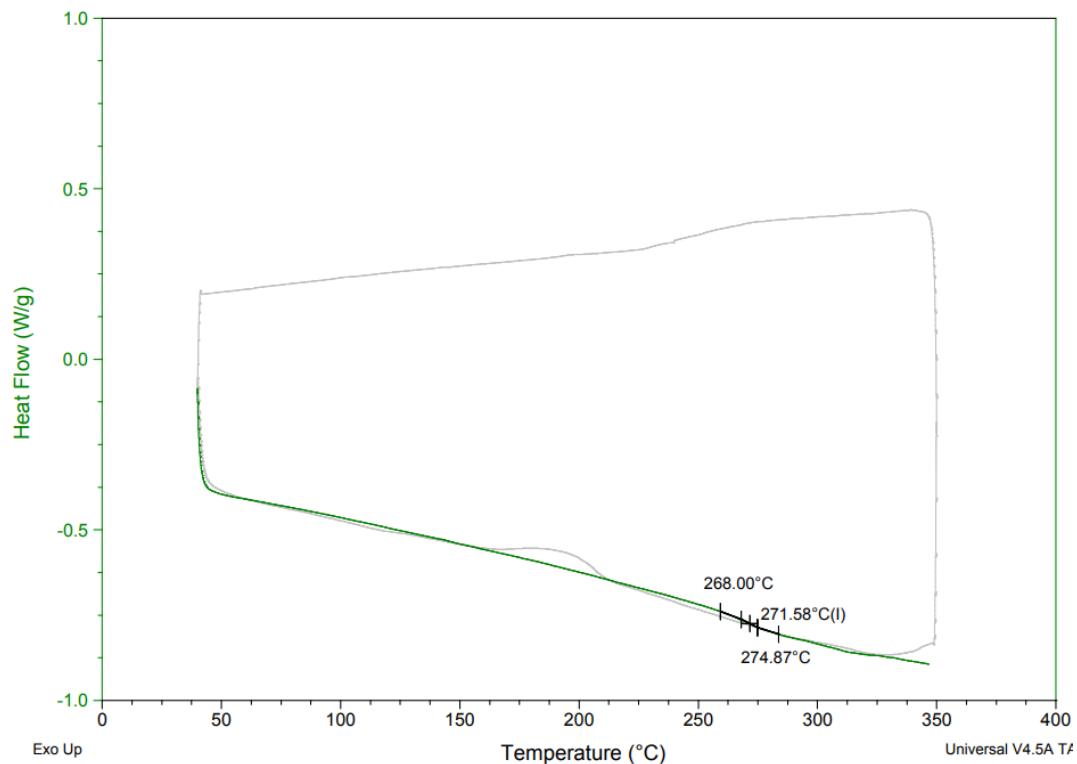

**Figure S38.** DSC data of the polymer from Table 2, entry 2

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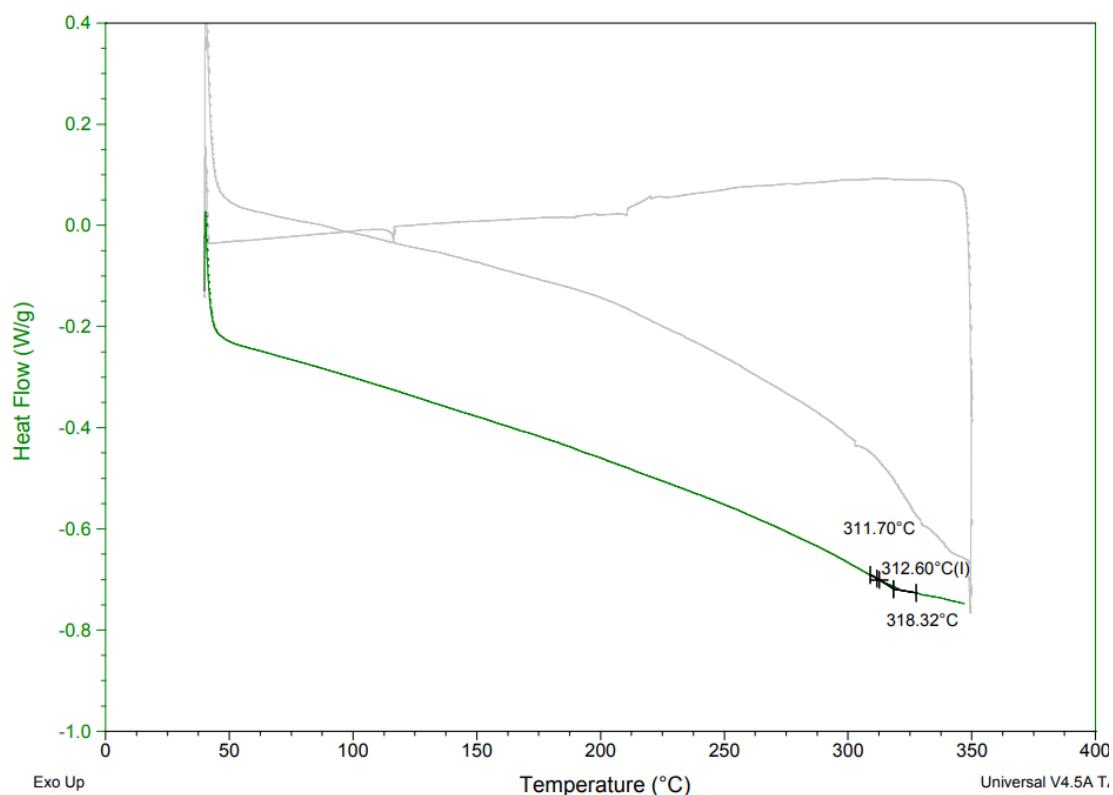
**Figure S39.** DSC data of the polymer from Table 2, entry 3
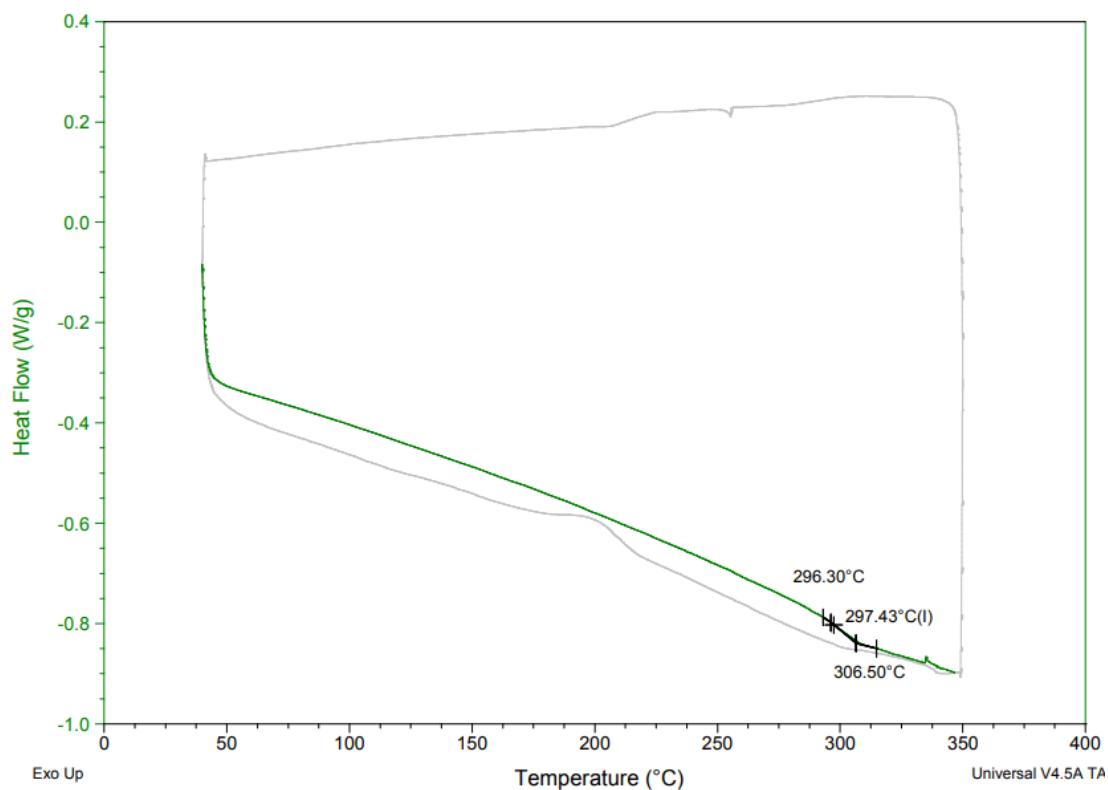
**Figure S40.** DSC data of the polymer from Table 2, entry 5

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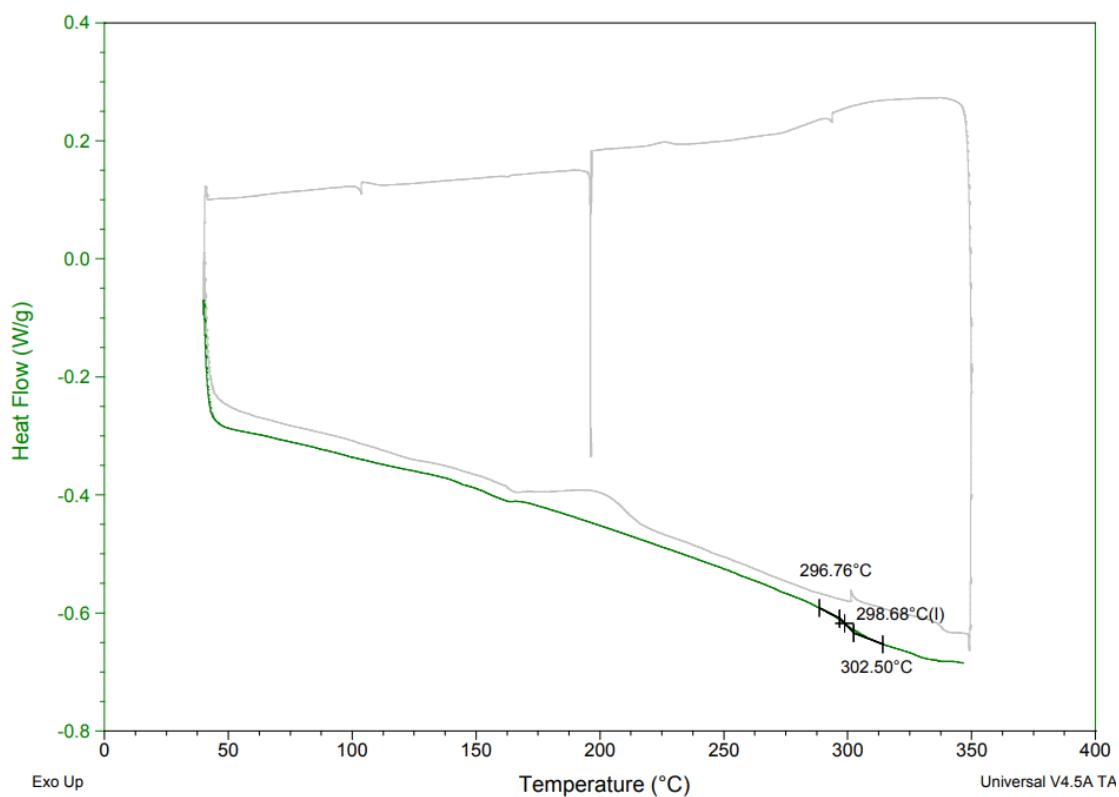
Figure S41. DSC data of the polymer from Table 2, entry 6