Supplementary Materials: Direct Synthesis of Branched Carboxylic Acid Functionalized Poly(1-octene) by α-Diimine Palladium Catalysts

Lihua Guo, Chen Zou, Shengyu Dai and Changle Chen

Table S1. Polymerization of 1-octene.[a]

Entry	Cat.	Yield (g)	TOF[b] (h^{-1})	M_n[c] ($\times 10^{-3}$)	PDI	B[d]	T_m[e]
1	1	0.38	113	4.2	1.43	90	oil[f]
2	2	0.47	140	53.9	1.66	97	20.9
3	3	1.02	303	93.1	1.59	95	28.1
4	4	0.53	157	66.6	1.41	64	34.3
5	5	0.43	128	53.7	1.40	55	73.5
6	6	0.29	86	36.0	1.25	60	71.0
7	7	0.05	15	14.3	1.19	79	oil[f]
8	8	0.42	125	5.2	1.34	84	oil[f]

[a] Conditions: 0.010 mmol pre-catalyst, [1-octene] = 2 mol/L; 20 °C; 1.2 eq. NaBAF; total volume of CH_2Cl_2 and monomer: 10 mL; 3 h. [b] Turnover frequency = moles of substrate converted per mole of catalyst per hour. [c] Molecular weight was determined by GPC in THF at 40 °C using polystyrene standards. [d] B = branches per 1000 carbons, branching numbers were determined using ^{1}H NMR spectroscopy. [e] Determined by differential scanning calorimetry (DSC). [f] Amorphous polymers (no T_m from –50 to 120 °C).

The 1-octene polymerization was also investigated and the results are summarized in Table S1. With this longer α-olefin monomer, more linear and less branched semicrystalline polymers were obtained through 2,1-insertion and 1,ω-enchainment. The melting temperatures of the corresponding polymers increased with the decrease of branching density. The trend of activity, polymer molecular weight, and branching density with the ligand sterics was similar with propylene polymerization. Catalyst **3** showed the highest turnover frequency (303 h^{-1}, Table S1, entry 3) and generated poly(1-octene) with the highest molecular weight (M_n = 93.1 × 10^3). Different from the propylene polymerization, catalyst **5** generated polymer product with the lowest branching density (55/1000 C) and the highest melting point (73.5 °C). Most interestingly, the microstructure analysis of poly(1-octene) samples based on ^{13}C-NMR spectroscopy showed the presence of only methyl and long chain branches (≥ hexyl) for all the catalysts (See supplementary materials, Figure S9). No ethyl, propyl, or adjacent methyl branches were detectable, indicating that the insertion occurred only into primary Pd-alkyl bonds.

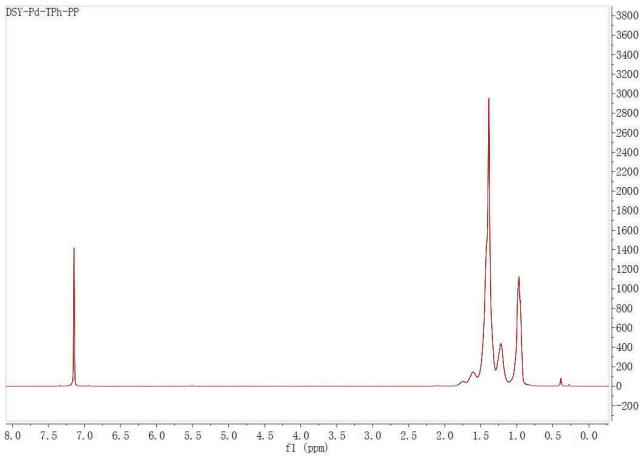


Figure S1. ^{1}H NMR spectrum of the polymer from Table 1, entry 5 (d^6-benzene).

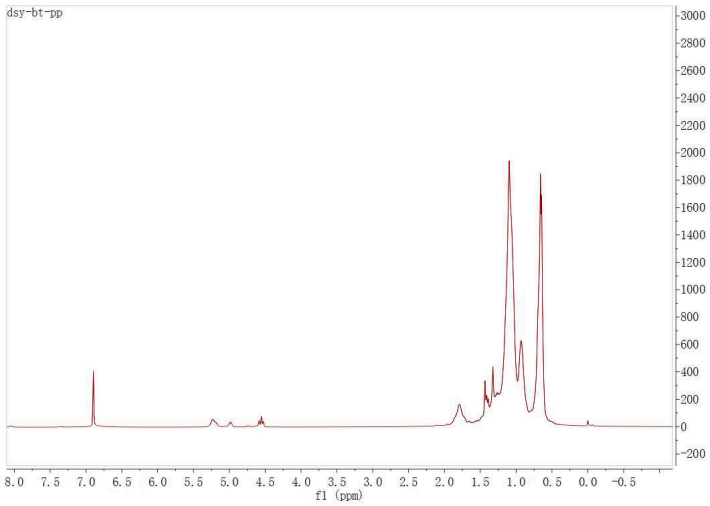


Figure S2. ^{1}H NMR spectrum of the polymer from Table 1, entry 8 (d^{6}-benzene).

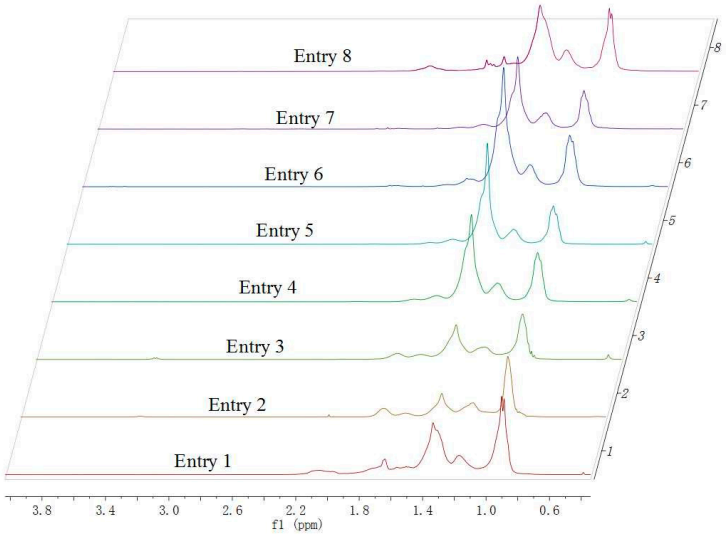


Figure S3. ^{1}H NMR spectrum of the polymer from Table 1 (d^{6}-benzene).

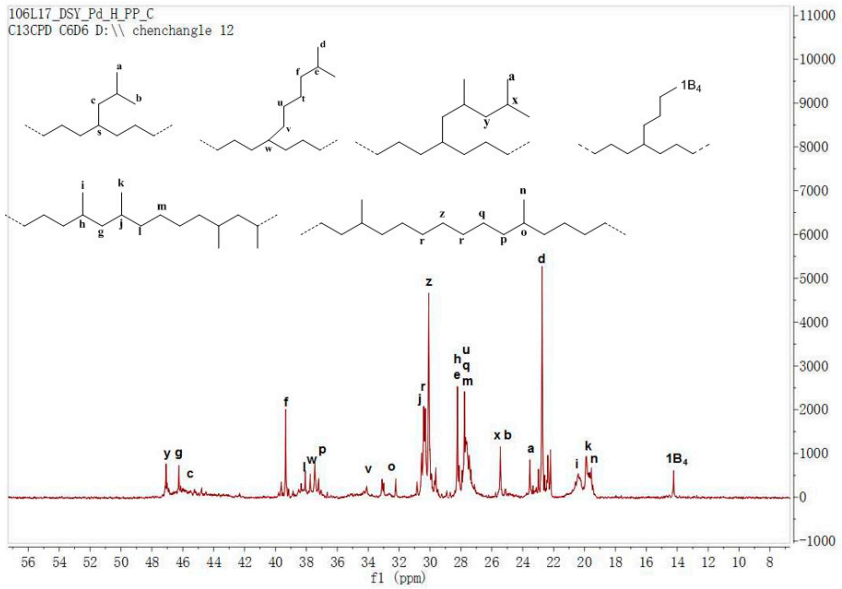


Figure S4. ^{13}C NMR spectrum of the polymer from Table 1, entry 1 (d^{6}-benzene).

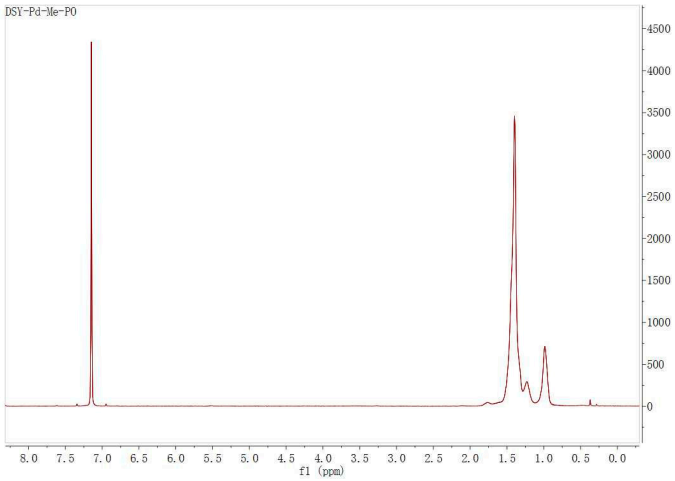


Figure S5. ^{1}H NMR spectrum of the polymer from Table S1, entry 2 (d^{6}-benzene).

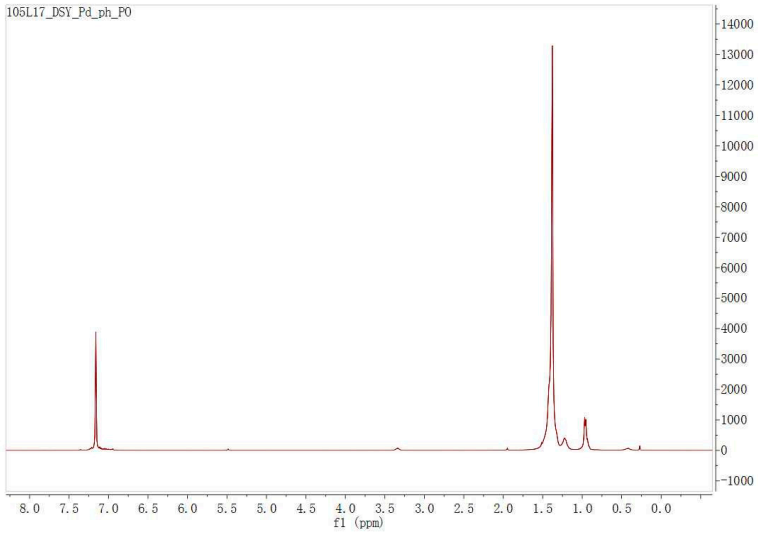


Figure S6. ^{1}H NMR spectrum of the polymer from Table S1, entry 6 (d^{6}-benzene).

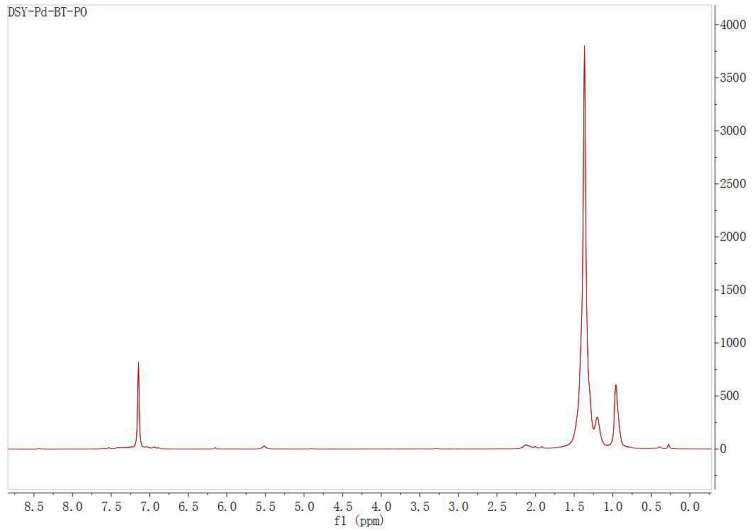


Figure S7. ^{1}H NMR spectrum of the polymer from Table S1, entry 8 (d^{6}-benzene).

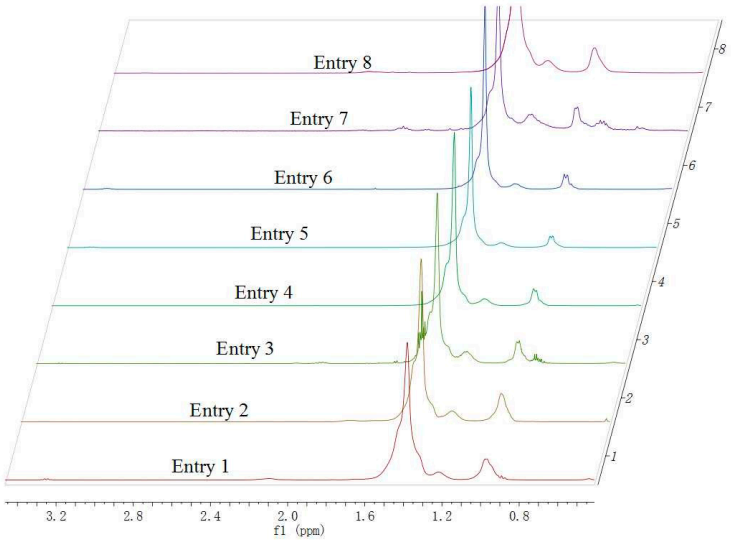


Figure S8. ^{1}H NMR spectrum of the polymer from Table S1 (d^{6}-benzene).

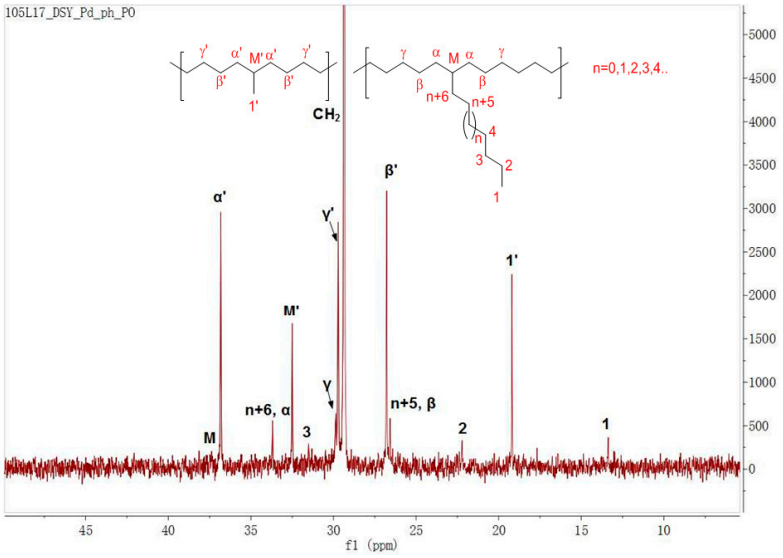


Figure S9. ^{13}C NMR spectrum of the polymer from Table S1, entry 6 (d^{6}-benzene, 60°C).

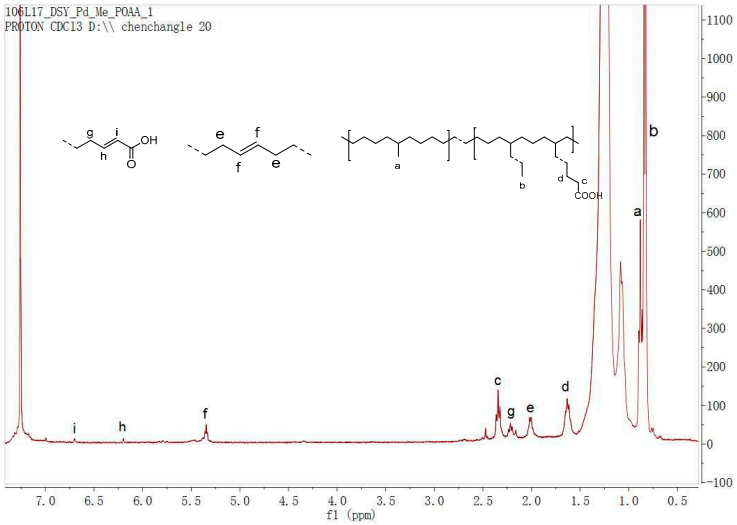


Figure S10. ^{1}H NMR spectrum of the polymer from Table 2, entry 9 (CDCl$_3$).

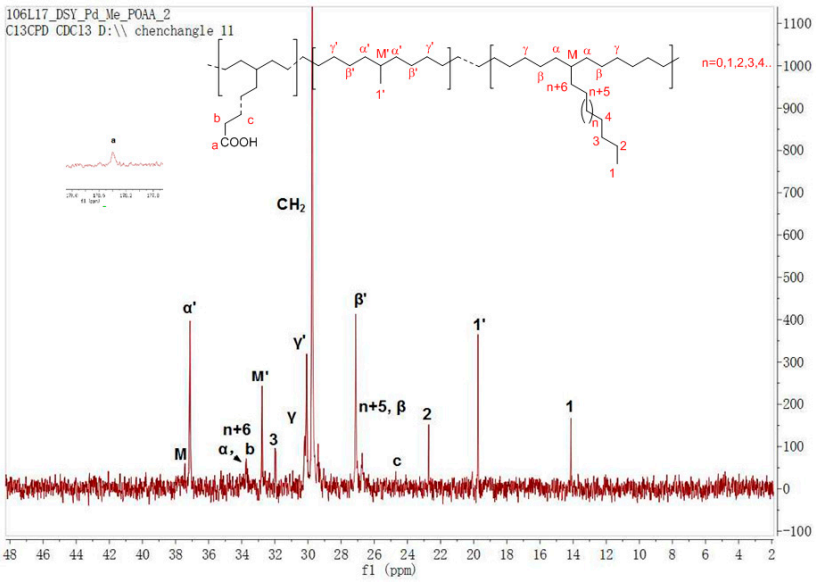


Figure S11. ^{13}C NMR spectrum of the polymer from Table 2, entry 9 ($CDCl_3$).

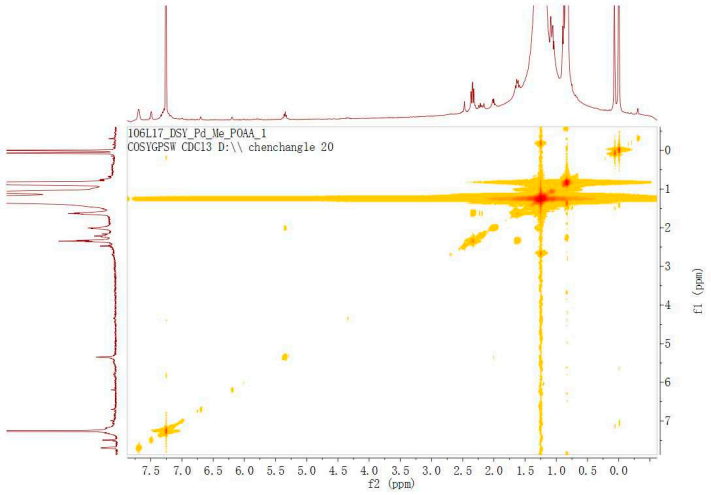


Figure S12. H-H COSY-NMR spectrum of the polymer from Table 2, entry 9 ($CDCl_3$).

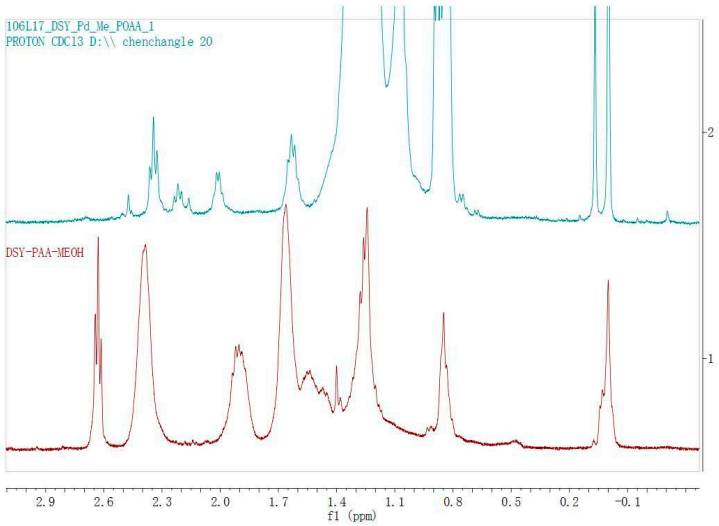


Figure S13. Top: ^{1}H NMR spectrum of the polymer from tTable 2, entry 9 ($CDCl_3$). **Bottom**: ^{1}H NMR spectrum of poly(acrylic acid) (CD_3OD).

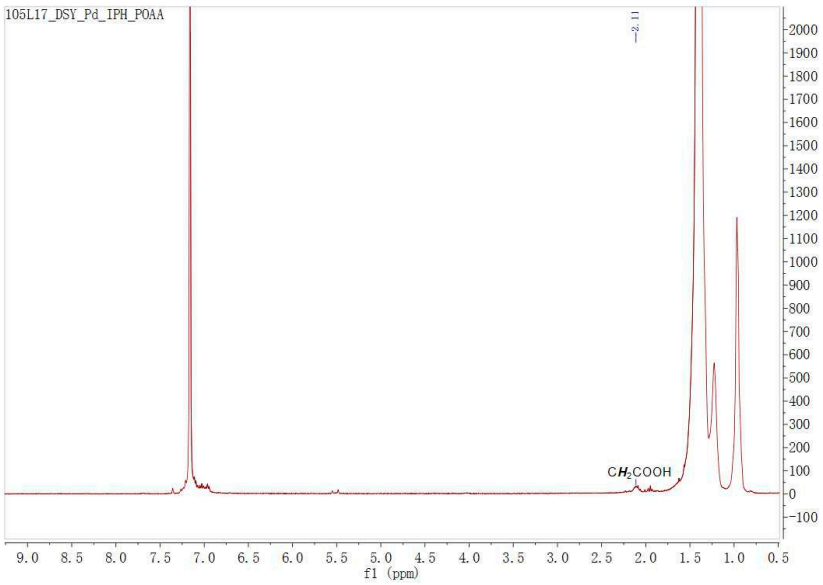


Figure S14. ^{1}H NMR spectrum of the polymer from Table 2, entry 4 (d^{6}-benzene, 60 °C).

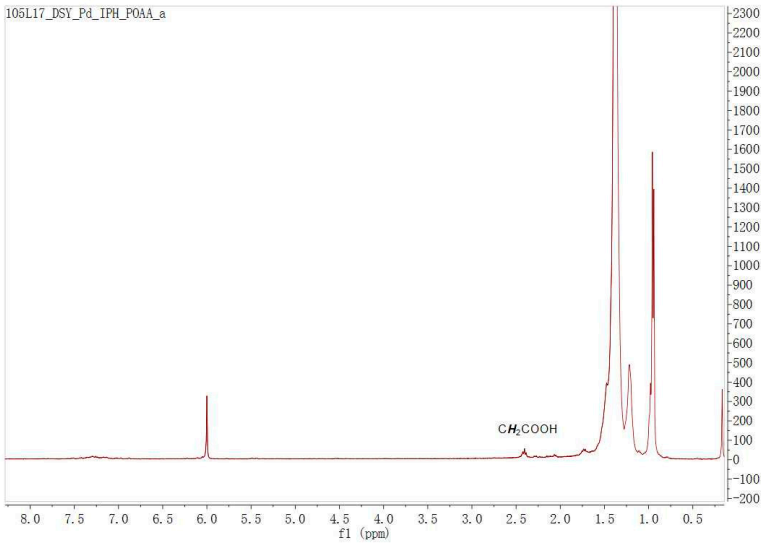


Figure S15. ^{1}H NMR spectrum of the polymer from Table 2, entry 4 ($CDCl_2CDCl_2$, 120 °C).

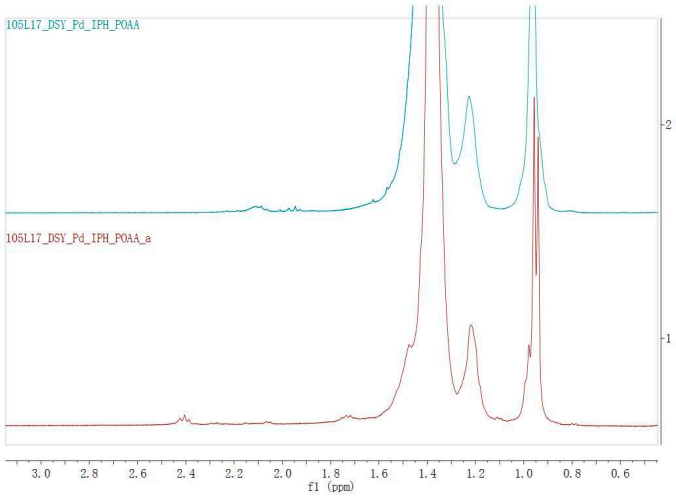


Figure S16. Top: ^{1}H NMR spectrum of the polymer from Table 2, entry 4 (d^{6}-benzene, 60 °C). **Bottom**: ^{1}H NMR spectrum of the polymer from Table 2, entry 4 ($C_2D_2Cl_4$, 120 °C).

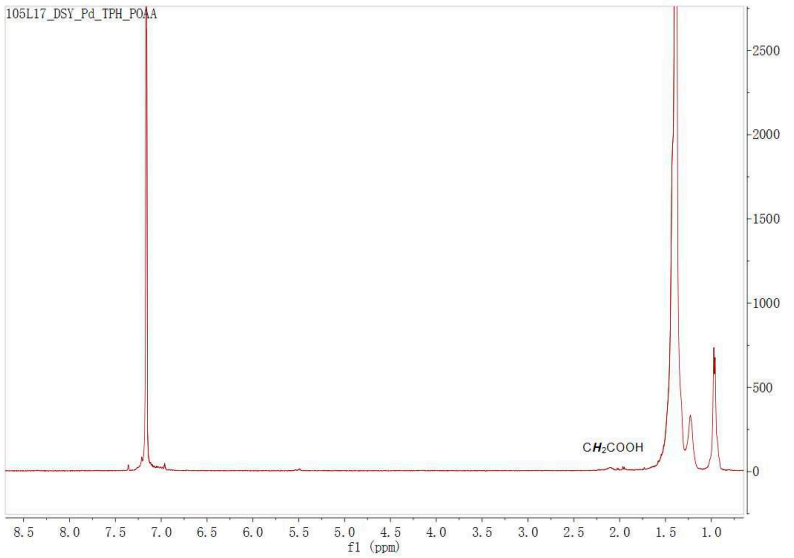


Figure S17. ^{1}H NMR spectrum of the polymer from Table 2, entry 5 (d^{6}-benzene, 60 °C).

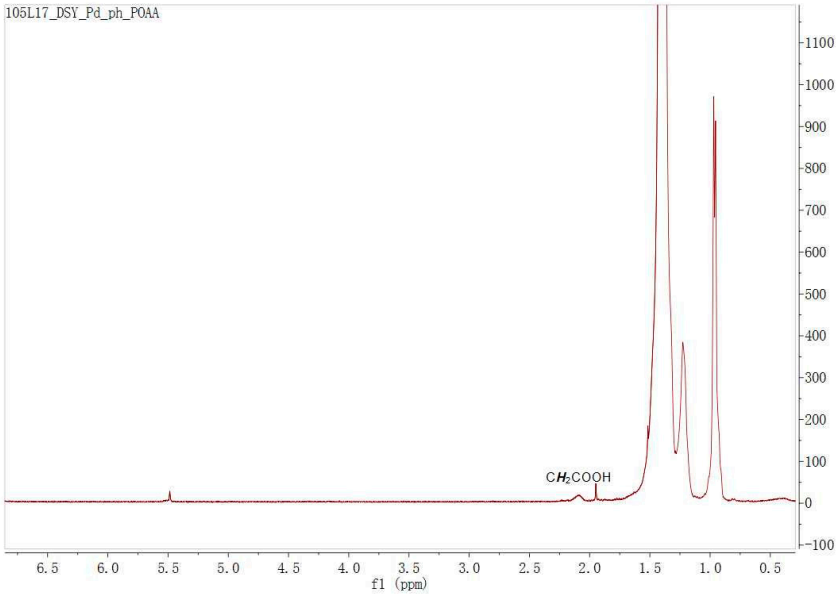


Figure S18. ^{1}H NMR spectrum of the polymer from Table 2, entry 6 (d^{6}-benzene, 60 °C).

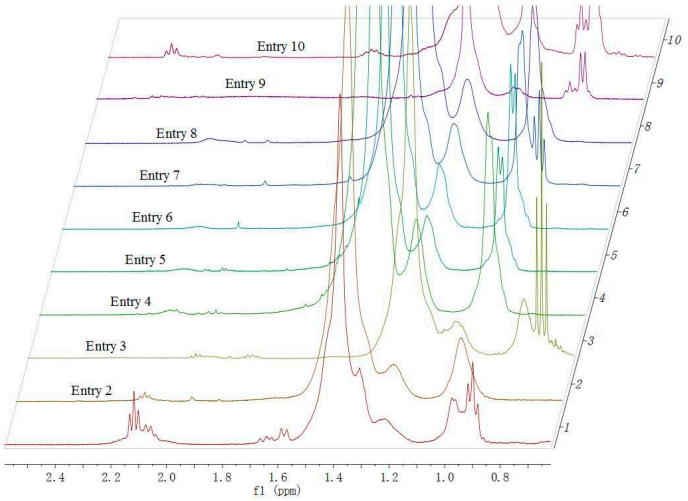


Figure S19. ^{1}H NMR spectrum of the polymer from Table 2 (entry 1–8, d^{6}-benzene), (entry 9–10, $CDCl_3$).

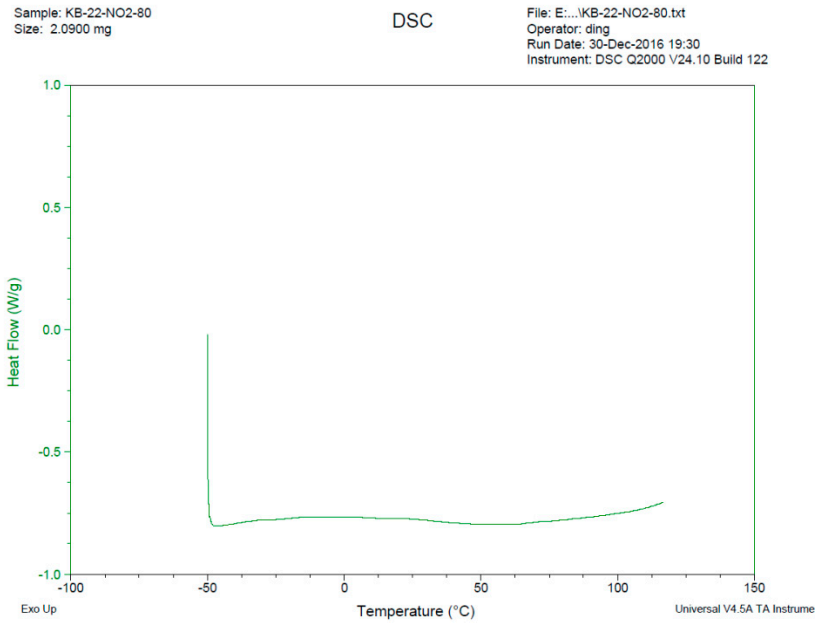


Figure S20. DSC of the polymer from Table 1, entry 3.

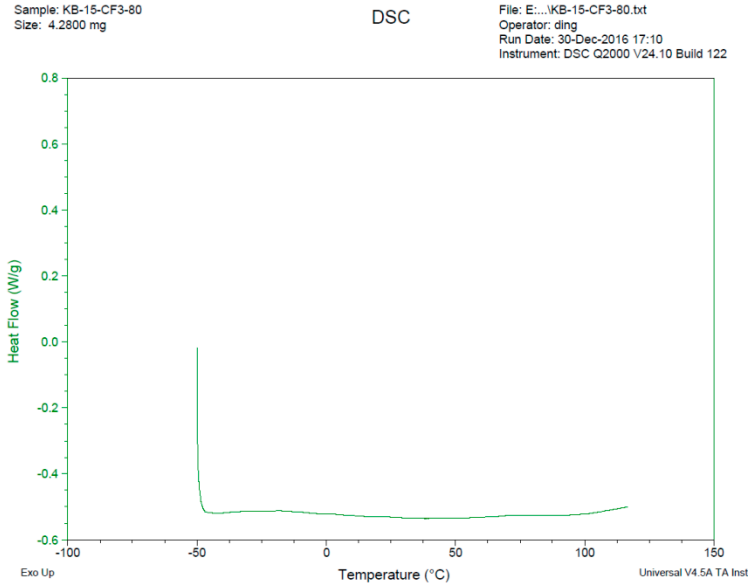


Figure S21. DSC of the polymer from Table S1, entry 1.

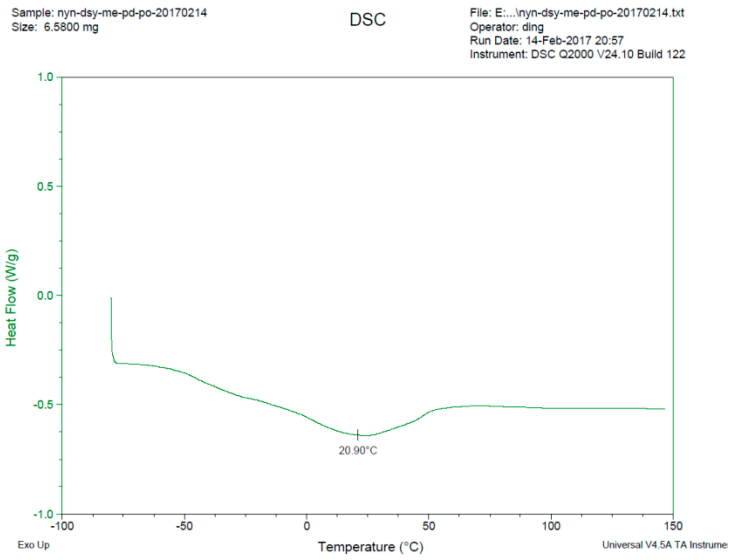


Figure S22. DSC of the polymer from Table S1, entry 2.

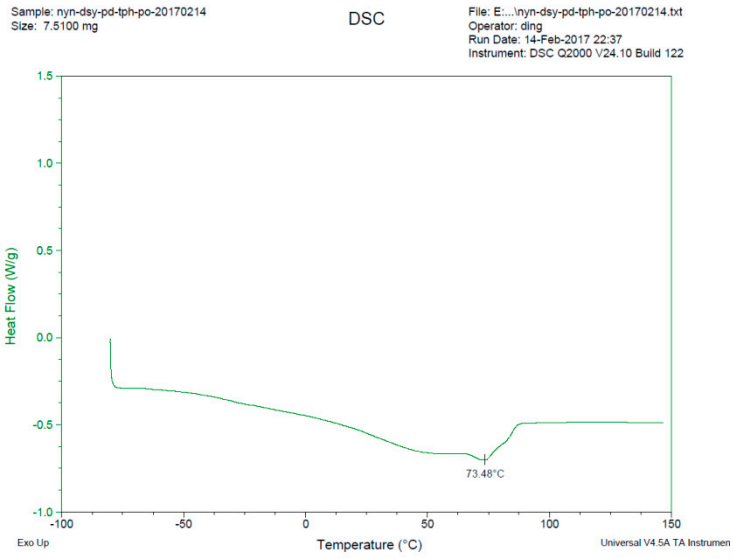


Figure S23. DSC of the polymer from Table S1, entry 5.

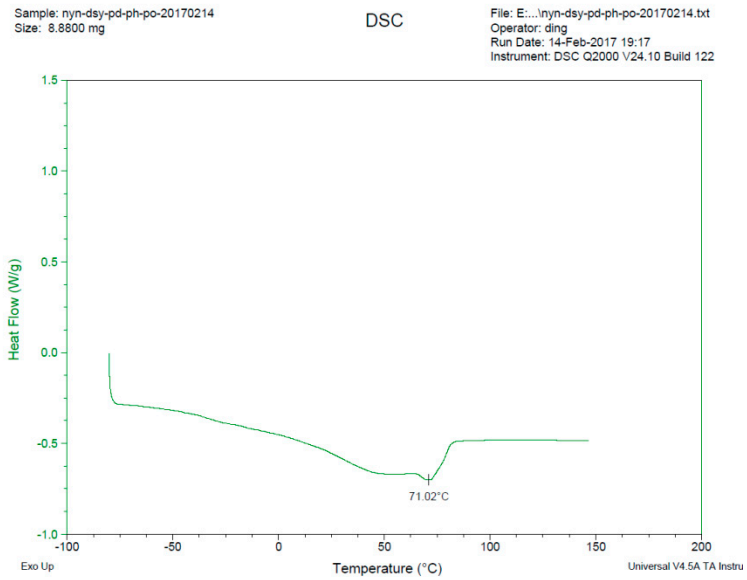


Figure S24. DSC of the polymer from Table S1, entry 6.

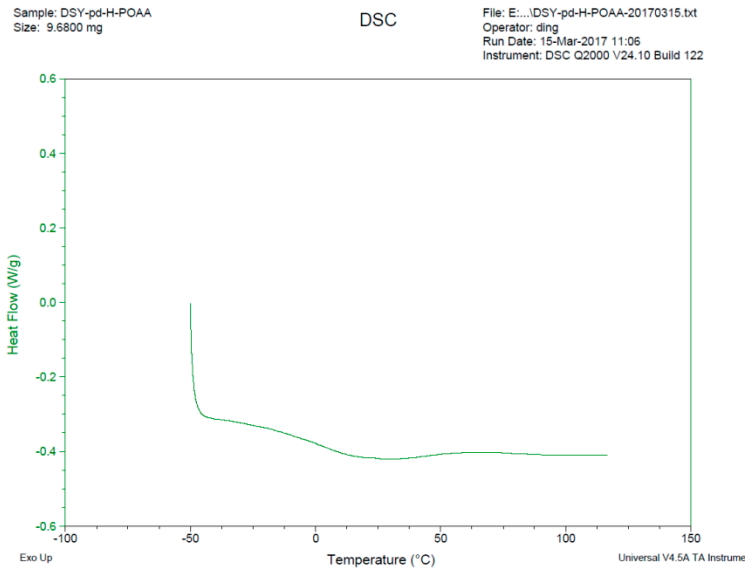


Figure S25. DSC of the polymer from Table 2, entry 1.

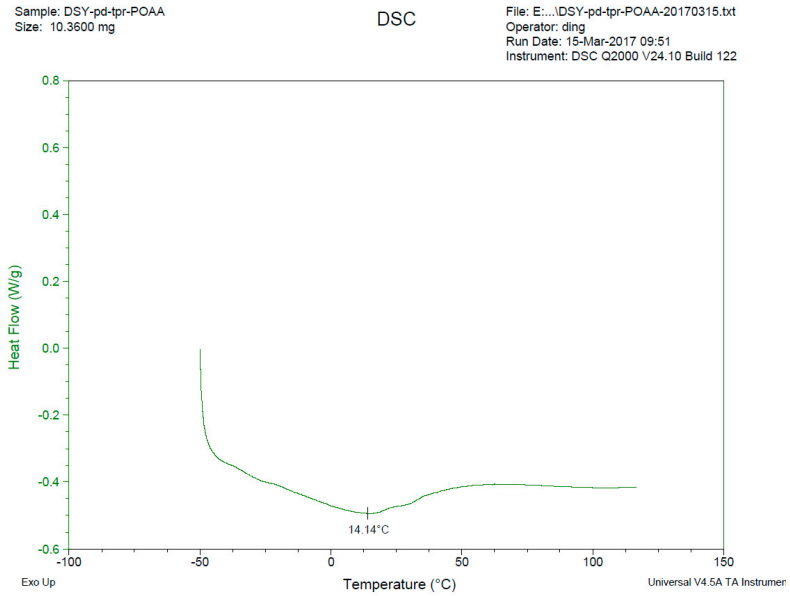


Figure S26. DSC of the polymer from Table 2, entry 3.

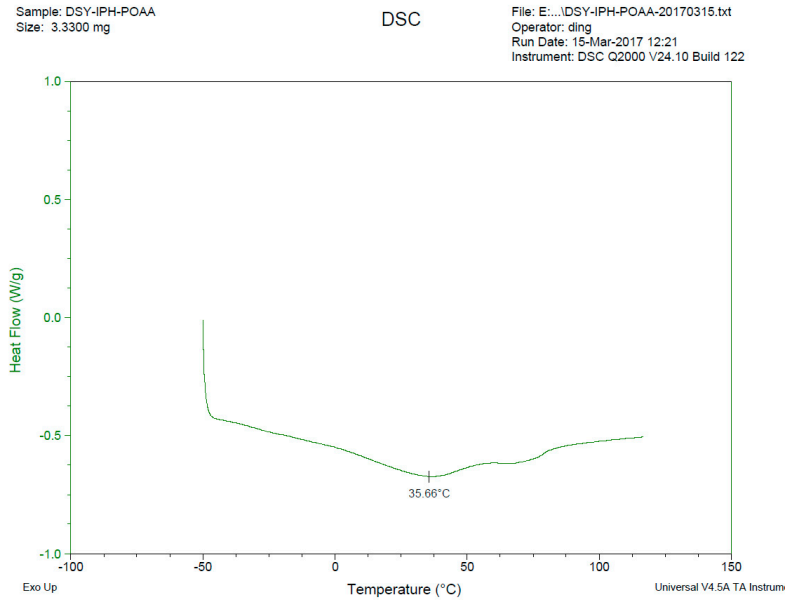


Figure S27. DSC of the polymer from Table 2, entry 4.

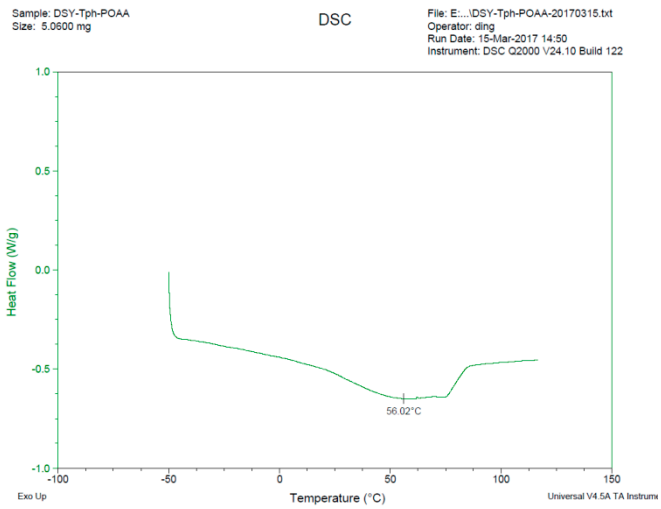


Figure S28. DSC of the polymer from Table 2, entry 5.

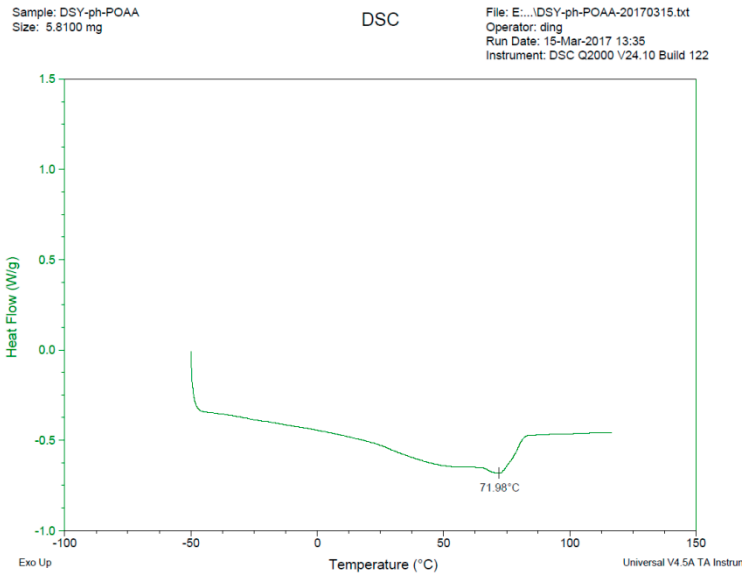
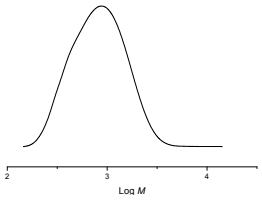


Figure S29. DSC of the polymer from Table 2, entry 6.

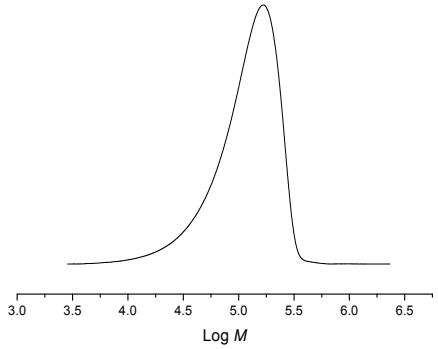


Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]	M_n	681
Peak start	8.610	0.971	14,232	M_w	976
Peak top	10.508	164.293	870	M_z	1,403
Peak end	11.728	1.209	144	M_{z+1}	2,112
				M_v	976
Height [mV]		163.177		M_p	871
Area [mV·s]		10952.759		M_z/M_w	1.437
Area% [%]		100.000		M_w/M_n	1.434
[eta]		976.21958		M_{z+1}/M_w	2.163

Figure S30. GPC of the polymer from Table 1, entry 1.

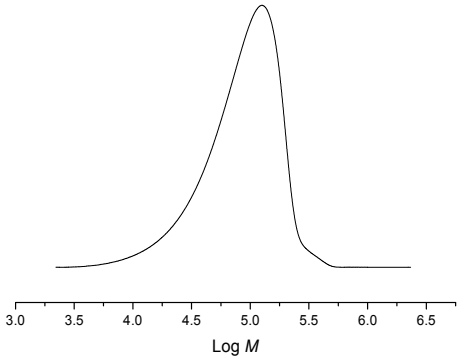


Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]	M_n	85,967
Peak start	5.147	-0.038	2,327,316	M_w	136,692
Peak top	6.940	239.341	166,206	M_z	175,768
Peak end	9.703	1.057	2847	M_{z+1}	220,024
				M_v	136,692
Height [mV]		238.948		M_p	166,206
Area [mV·s]		13,034.455		M_z/M_w	1.286
Area% [%]		100.000		M_w/M_n	1.590
[eta]		136,692.15043		M_{z+1}/M_w	1.610

Figure S31. GPC of the polymer from Table 1, entry 3.

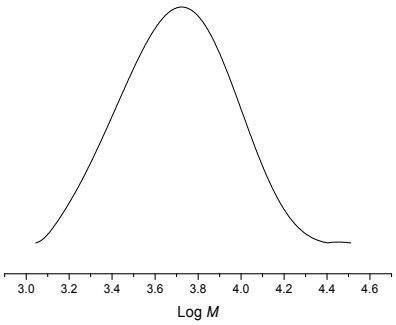


Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]	M_n	59,322
Peak start	5.640	–0.036	1,126,008	M_w	103,258
Peak top	7.123	203.261	126,902	M_z	142,813
Peak end	9.878	1.635	2200	M_{z+1}	183,348
				M_v	103,258
Height [mV]		202.712		M_p	126,902
Area [mV·s]		12,789.272		M_z/M_w	1.383
Area% [%]		100.000		M_w/M_n	1.741
[eta]		103,257.99615		M_{z+1}/M_w	1.776

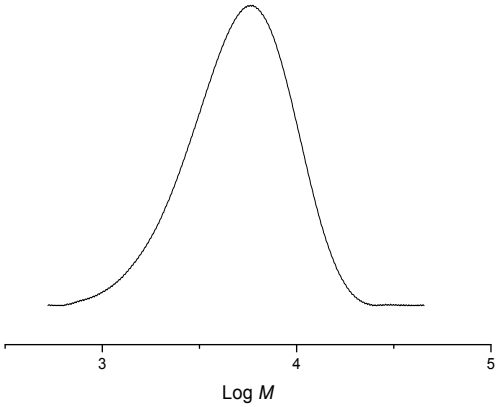
Figure S32. GPC of the polymer from Table 1, entry 4.



Result of molecular weight calculation (RI)
Peak 1 Base Peak

	[min]	**[mV]**	**[mol]**	M_n	**4304**
Peak start	8.052	0.803	32,368	M_w	5883
Peak top	9.278	169.785	5322	M_z	7850
Peak end	10.347	41.304	1104	M_{z+1}	9996
				M_v	5883
Height [mV]		147.334		M_p	5322
Area [mV·s]		9080.087		M_z/M_w	1.334
Area% [%]		100.000		M_w/M_n	1.367
[eta]		5883.28126		M_{z+1}/M_w	1.699

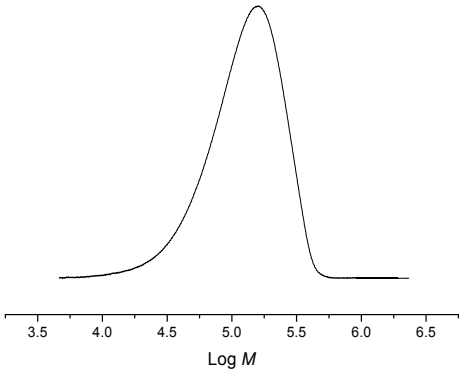
Figure S33. GPC of the polymer from Table 1, entry 8.



Result of molecular weight calculation (RI)
Peak 1 Base Peak

	[min]	**[mV]**	**[mol]**	M_n	**4180**
Peak start	7.825	0.086	45,185	M_w	5963
Peak top	9.202	22.526	5958	M_z	7968
Peak end	10.853	2.030	524	M_{z+1}	10,204
				M_v	5,963
Height [mV]		21.556		M_p	5,958
Area [mV·s]		1310.241		M_z/M_w	1.336
Area% [%]		100.000		M_w/M_n	1.427
[eta]		5963.05904		M_{z+1}/M_w	1.711

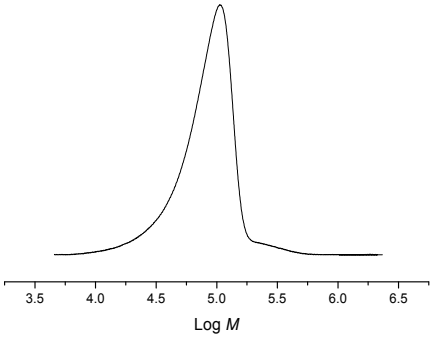
Figure S34. GPC of the polymer from Table S1, entry 1.



Result of molecular weight calculation (RI)
Peak 1 Base Peak

	[min]	[mV]	[mol]	M_n	93,091
Peak start	5.277	0.142	1,922,055	M_w	147,876
Peak top	6.973	22.523	158,249	M_z	201,638
Peak end	9.373	0.181	4,627	M_{z+1}	281,567
				M_v	147,876
Height [mV]		22.365		M_p	158,249
Area [mV·s]		1396.348		M_z/M_w	1.364
Area% [%]		100.000		M_w/M_n	1.589
[eta]		147,876.17847		M_{z+1}/M_w	1.904

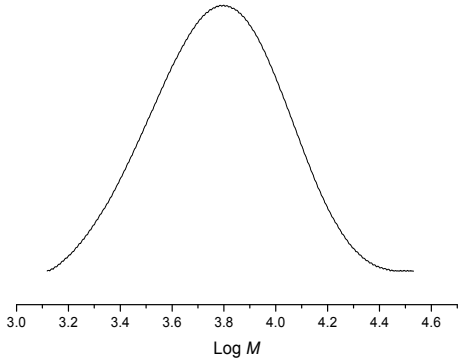
Figure S35. GPC of the polymer from Table S1, entry 3.



Result of molecular weight calculation (RI)
Peak 1 Base Peak

	[min]	[mV]	[mol]	M_n	66,591
Peak start	5.208	0.025	2,125,402	M_w	93,554
Peak top	7.247	29.457	105,837	M_z	140,184
Peak end	9.383	0.234	4560	M_{z+1}	380,096
				M_v	93,554
Height [mV]		29.330		M_p	105,838
Area [mV·s]		1186.394		M_z/M_w	1.498
Area% [%]		100.000		M_w/M_n	1.405
[eta]		93,554.14342		M_{z+1}/M_w	4.063

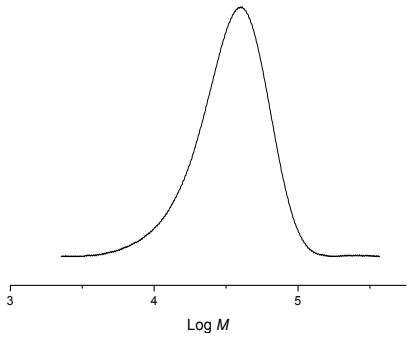
Figure S36. GPC of the polymer from Table S1, entry 4.



Result of molecular weight calculation (RI)
Peak 1 Base Peak

	[min]	**[mV]**	**[mol]**	M_n	**5,157**
Peak start	8.018	0.259	33,996	M_w	6912
Peak top	9.165	19.152	6288	M_z	9038
Peak end	10.232	2.418	1308	M_{z+1}	11,314
				M_v	6912
Height [mV]		17.774		M_p	6288
Area [mV·s]		1050.988		M_z/M_w	1.308
Area% [%]		100.000		M_w/M_n	1.340
[eta]		6912.11954		M_{z+1}/M_w	1.637

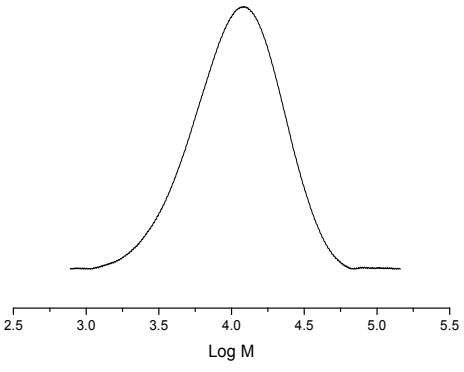
Figure S37. GPC of the polymer from Table S1, entry 8.



Result of molecular weight calculation (RI)
Peak 1 Base Peak

	[min]	**[mV]**	**[mol]**	M_n	**28,246**
Peak start	6.397	0.540	369,758	M_w	39,710
Peak top	7.912	16.877	39,774	M_z	52,718
Peak end	9.863	0.998	2250	M_{z+1}	73,785
				M_v	39,710
Height [mV]		16.137		M_p	39,775
Area [mV·s]		866.880		M_z/M_w	1.328
Area% [%]		100.000		M_w/M_n	1.406
[eta]		39,709.66949		M_{z+1}/M_w	1.858

Figure S38. GPC of the polymer from Table 2, entry 5.



Result of molecular weight calculation (RI)
Peak 1 Base Peak

	[min]	**[mV]**	**[mol]**	M_n	**8,492**
Peak start	7.032	-0.062	145,230	M_w	13,495
Peak top	8.715	17.607	12,194	M_z	20,226
Peak end	10.588	1.122	774	M_{z+1}	30,047
				M_v	13,495
Height [mV]		17.109		M_p	12,194
Area [mV·sec]		1192.169		M_z/M_w	1.499
Area% [%]		100.000		M_w/M_n	1.589
[eta]		13,494.91892		M_{z+1}/M_w	2.227

Figure S39. GPC of the polymer from Table 2, entry 8.