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Supporting Information

The Influences of Electronic Effect and Isomerization of Salalen Titanium (IV) Complexes on Ethylene Polymerization in the Presence of Methylaluminoxane

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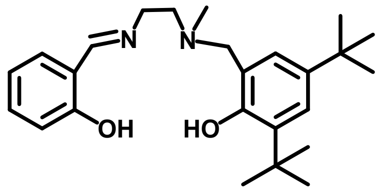
1. Characterizations of ligands and complexes



L1

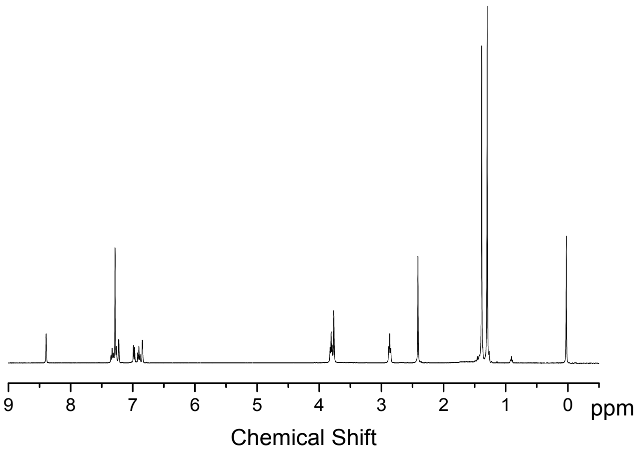


Figure S1. ^1H NMR spectrum of ligand **L1**.

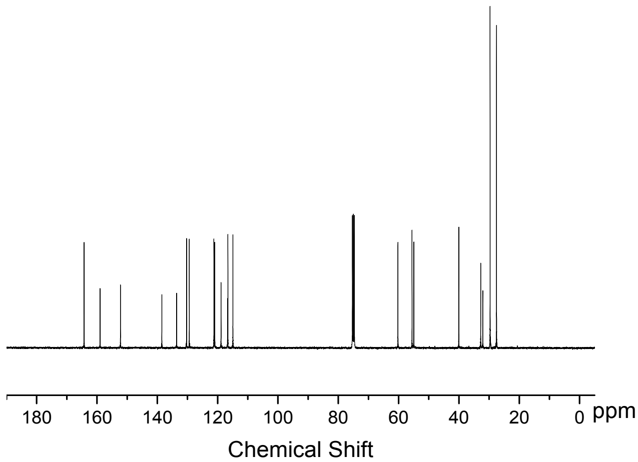
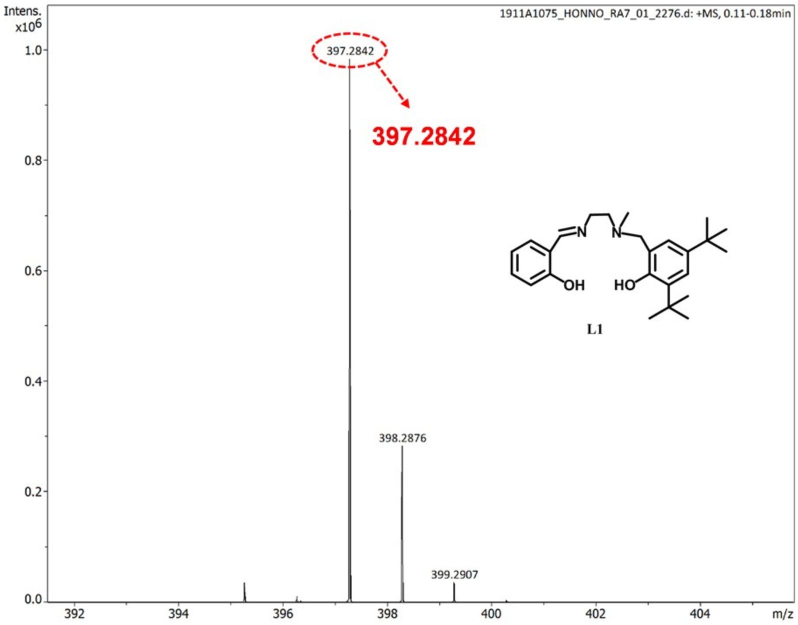
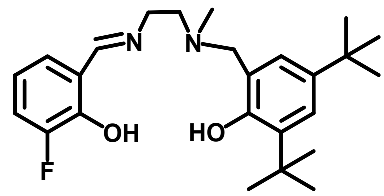


Figure S2. ^{13}C NMR spectrum of ligand **L1**.



Meas. m/z	Ion Formula	m/z	z	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
397.2842	C25H37N2O2	397.2850	1+	1.9	4.8	9.0	even	ok

Figure S3. HRMS spectrum of ligand **L1**.



L2

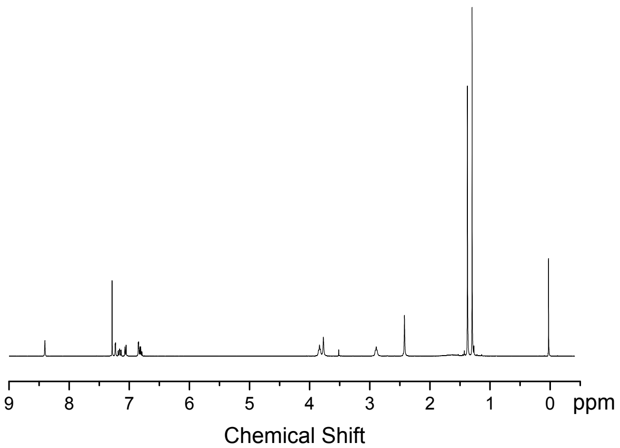


Figure S4. ^{1}H NMR spectrum of ligand **L2**.

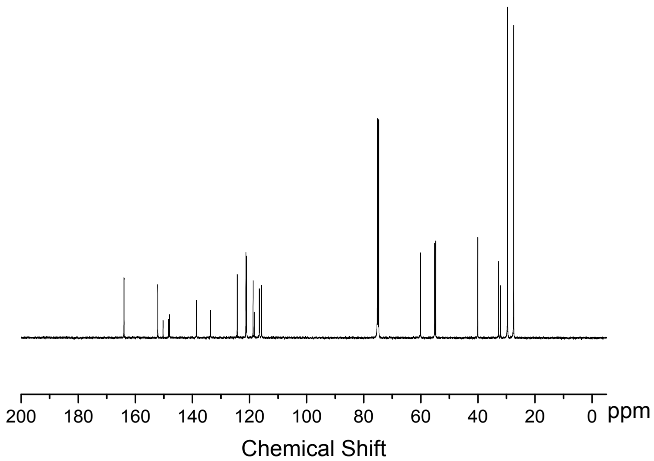


Figure S5. ^{13}C NMR spectrum of ligand **L2**.

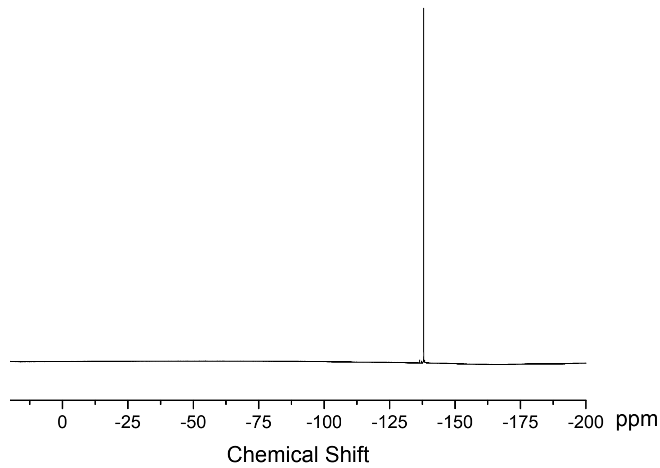


Figure S6. ^{19}F NMR spectrum of ligand **L2**.

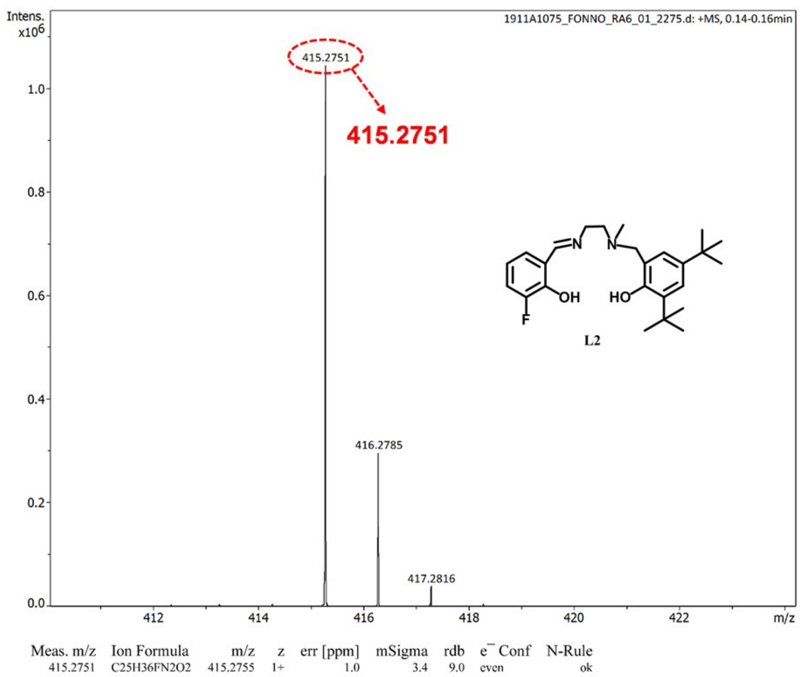
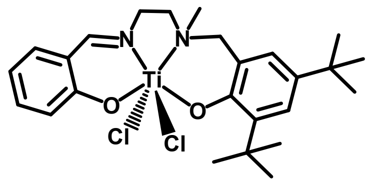


Figure S7. HRMS spectrum of ligand **L2**.



LigHTiCl$_2$

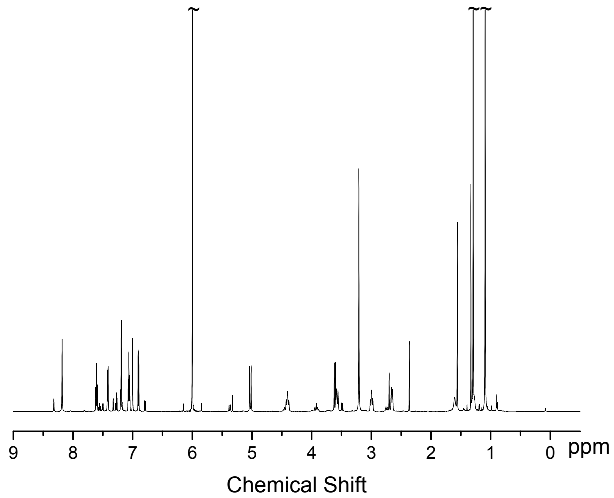


Figure S8. ^{1}H NMR spectrum of complex LigHTiCl$_2$.

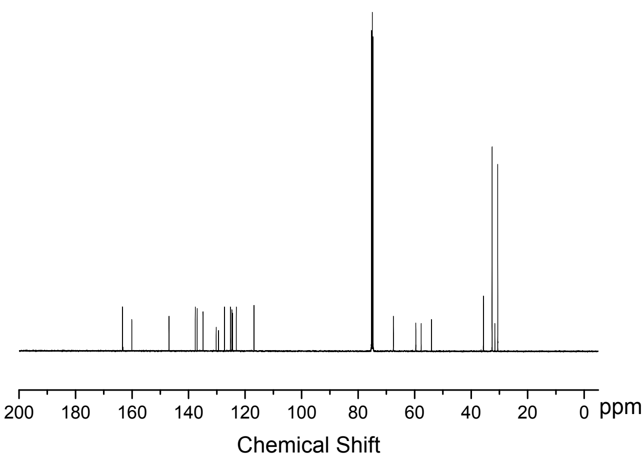
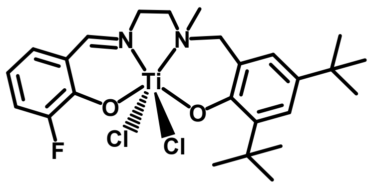


Figure S9. ^{13}C NMR spectrum of complex LigHTiCl$_2$.



LigFTiCl$_2$

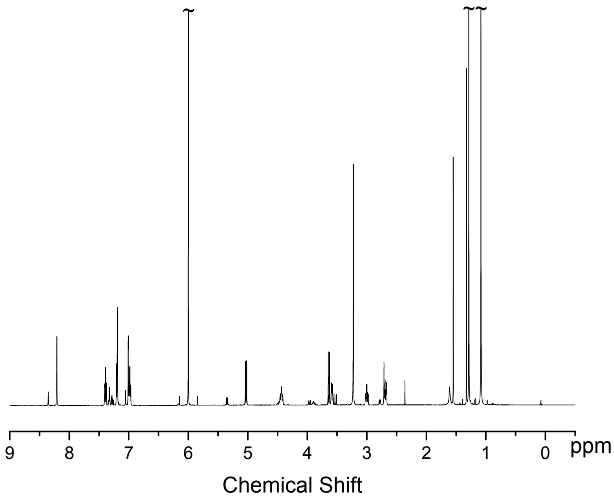


Figure S10. ^{1}H NMR spectrum of complex LigFTiCl$_2$.

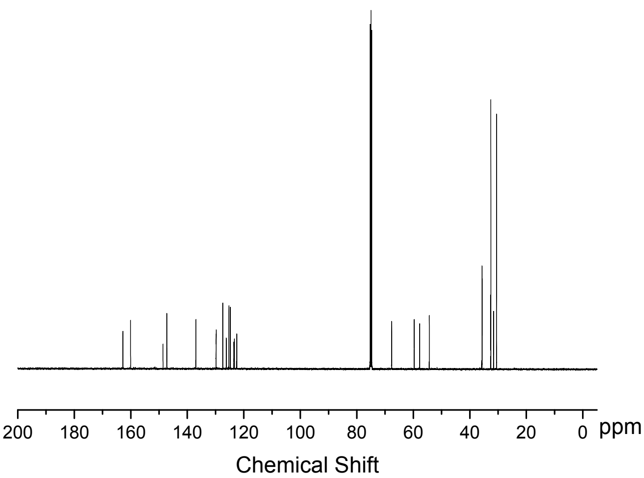


Figure S11. ^{13}C NMR spectrum of complex LigFTiCl$_2$.

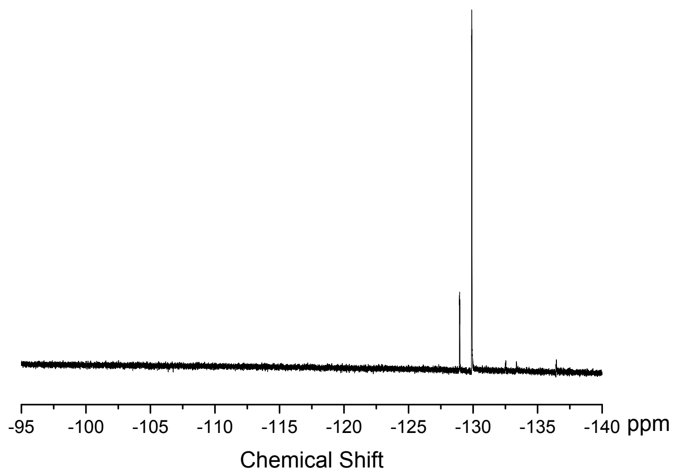


Figure S12. ^{19}F NMR spectrum of complex $LigFTiCl_2$.

2. NMR of Polyethylene

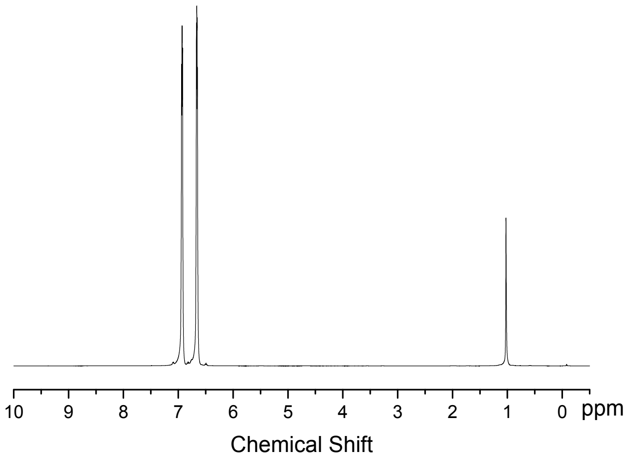


Figure S13: High temperature (120 °C) ^{1}H NMR spectrum of the polyethylene entry 7 (500 MHz, in C6D_4Cl2 + C6H_4Cl2 (1:1) solution).

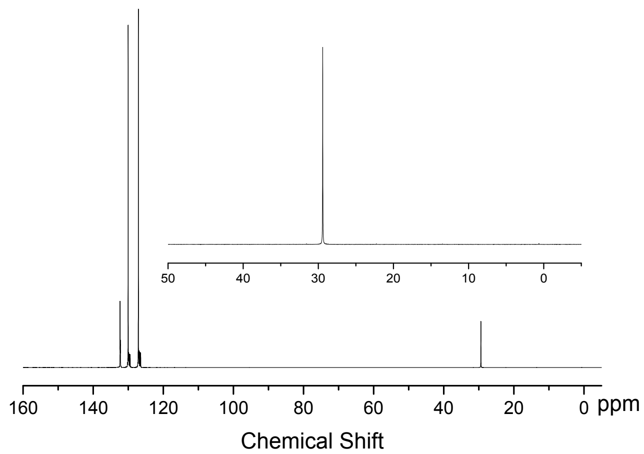
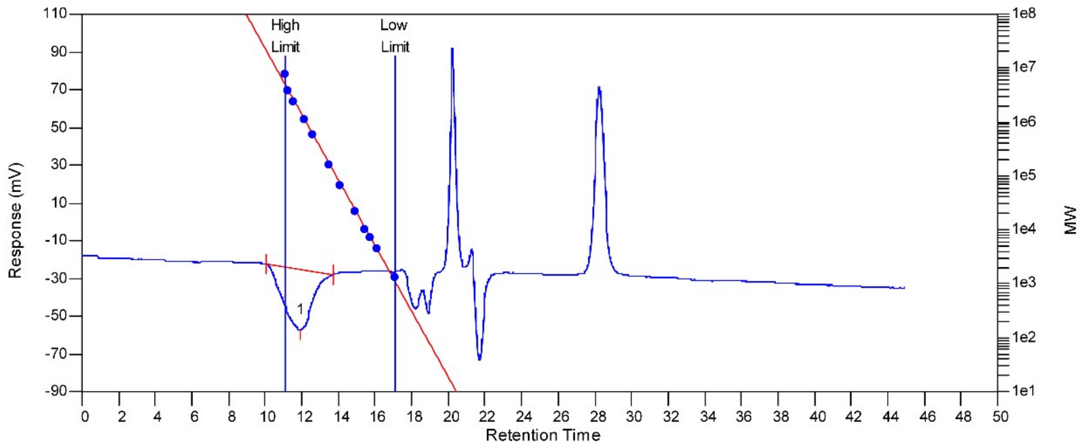
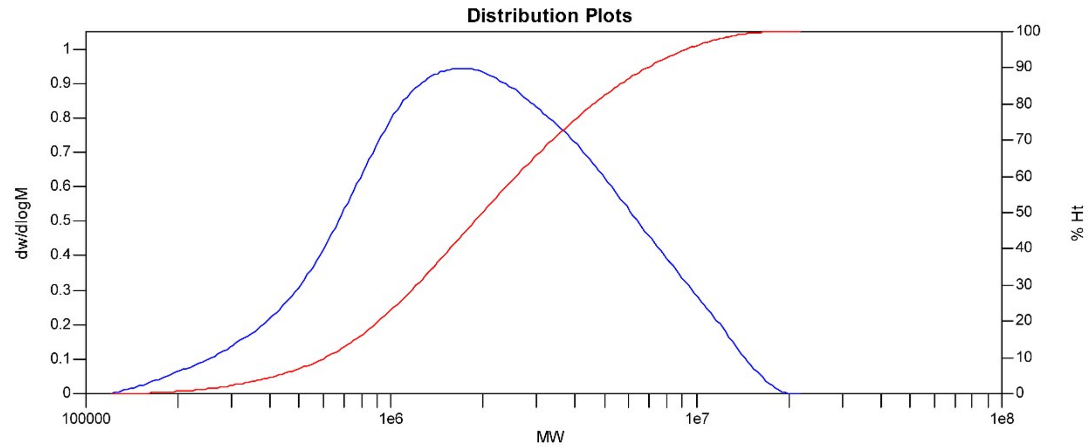


Figure S14: High temperature (120 °C) ^{13}C NMR spectrum of the polyethylene entry 7 (500 MHz, in C6D_4Cl2 + C6H_4Cl2 (1:1) solution).

2. GPC of polymer





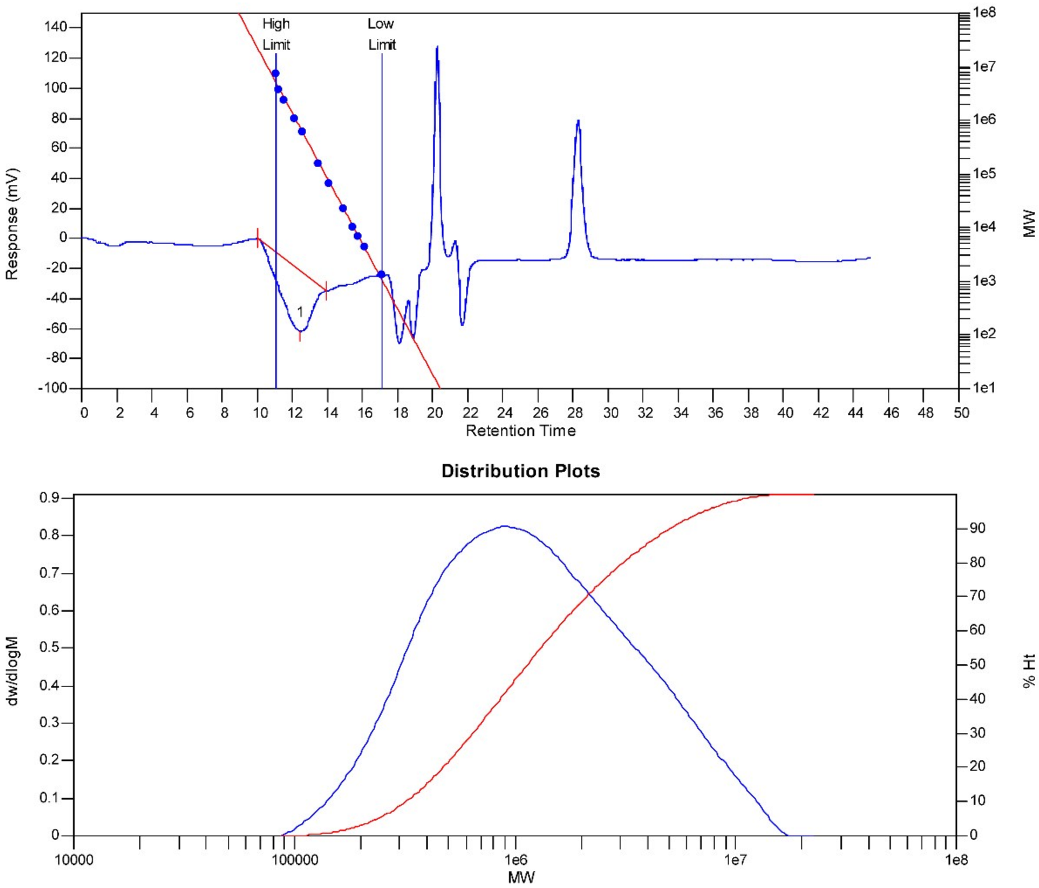
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1750788	1291182	2958438	5642315	8329460	2639732	2.29126

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.03	11.90	13.73	-32.2197	100	3367.35	100

Figure S15. GPC of the polymer from table 1, entry 1.



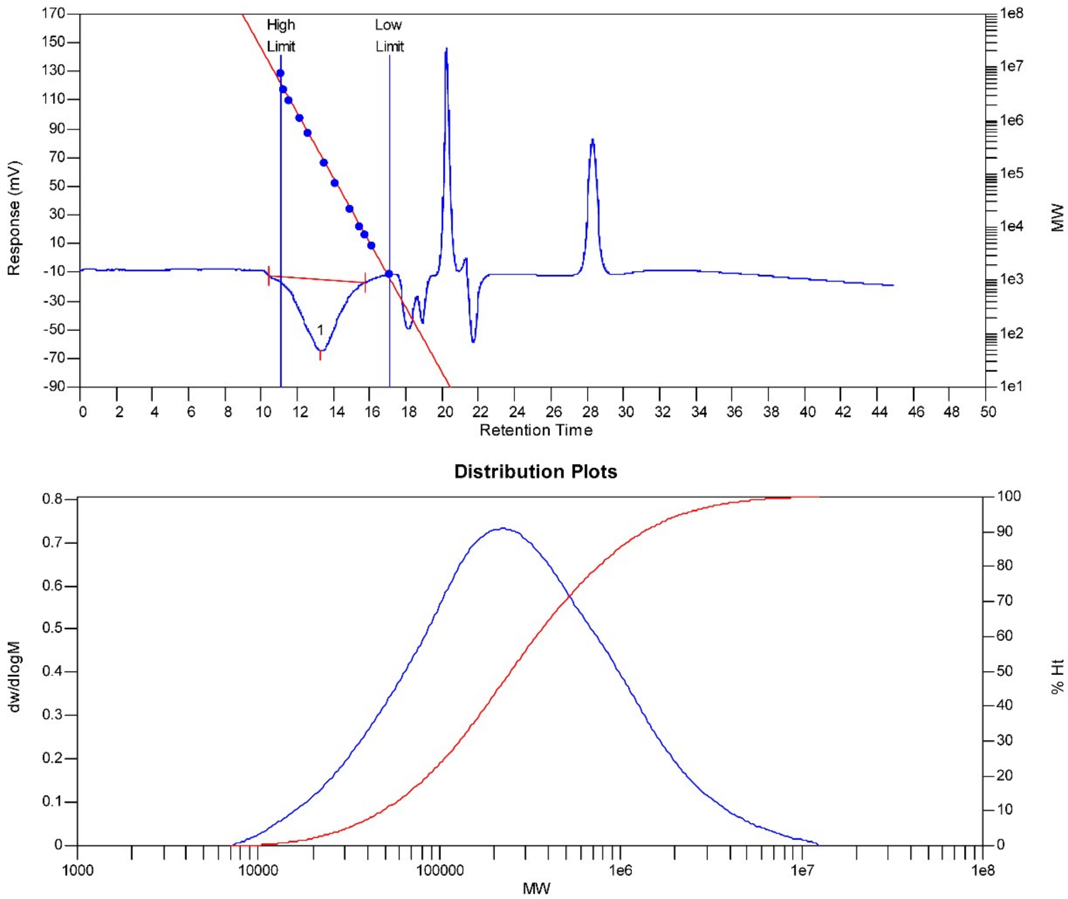
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	888815	731752	2010609	4697171	7414059	1725455	2.74766

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.02	12.47	13.97	-40.1469	100	4900.14	100

Figure S16. GPC of the polymer from table 1, entry 2.



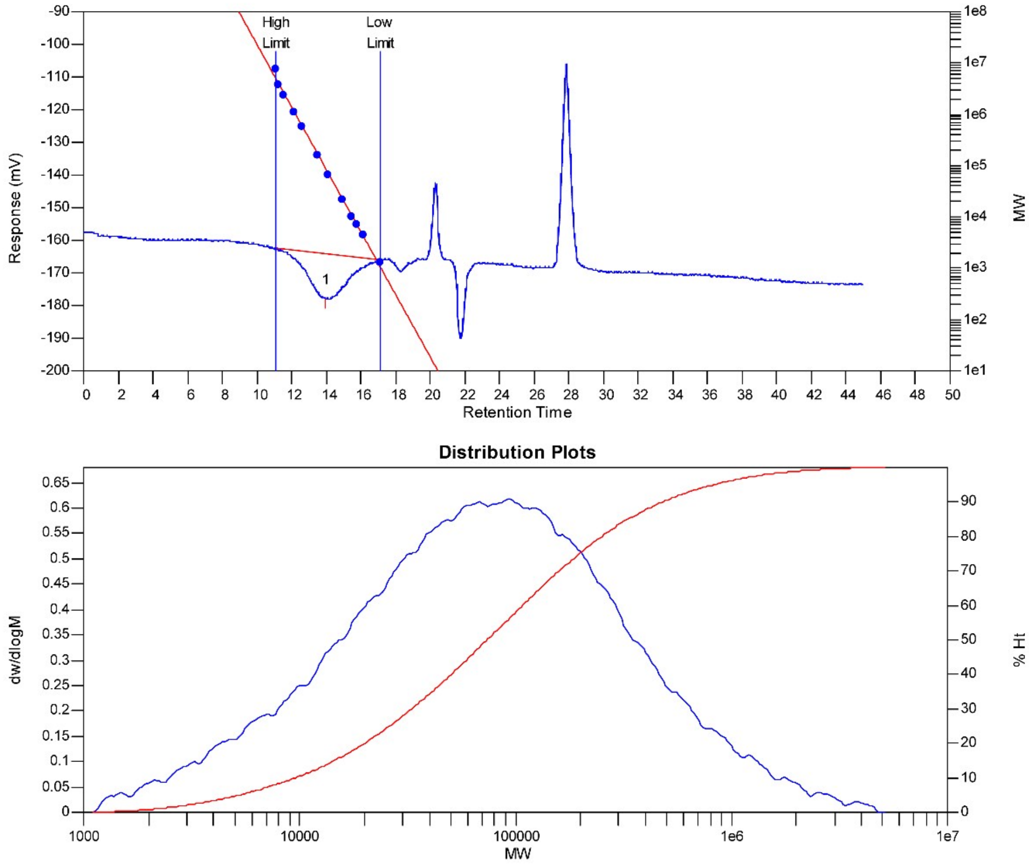
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	229070	116955	562147	2225331	4797613	443022	4.80652

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.43	13.30	15.77	-49.5697	100	6668.62	100

Figure S17. GPC of the polymer from table 1, entry 3.



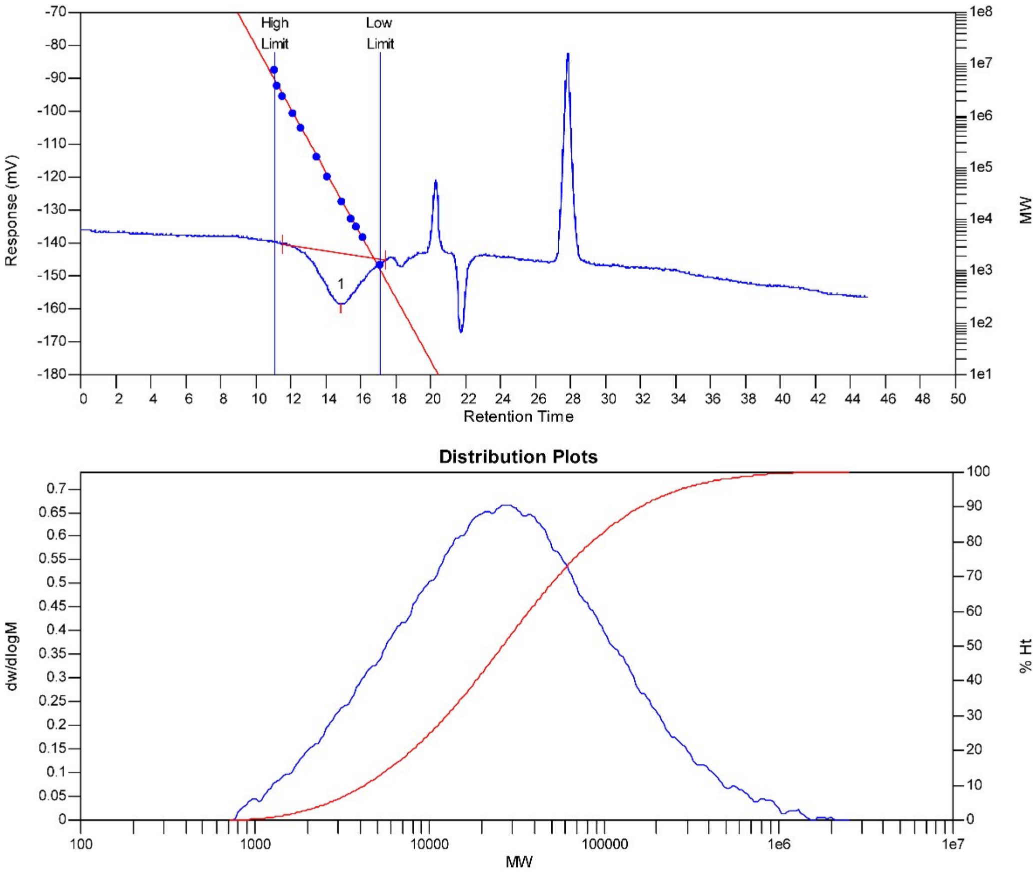
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	92049	23243	198117	950367	2037037	148157	8.52373

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.07	13.93	17.08	-13.8322	100	2204.78	100

Figure S18. GPC of the polymer from table 1, entry 4.



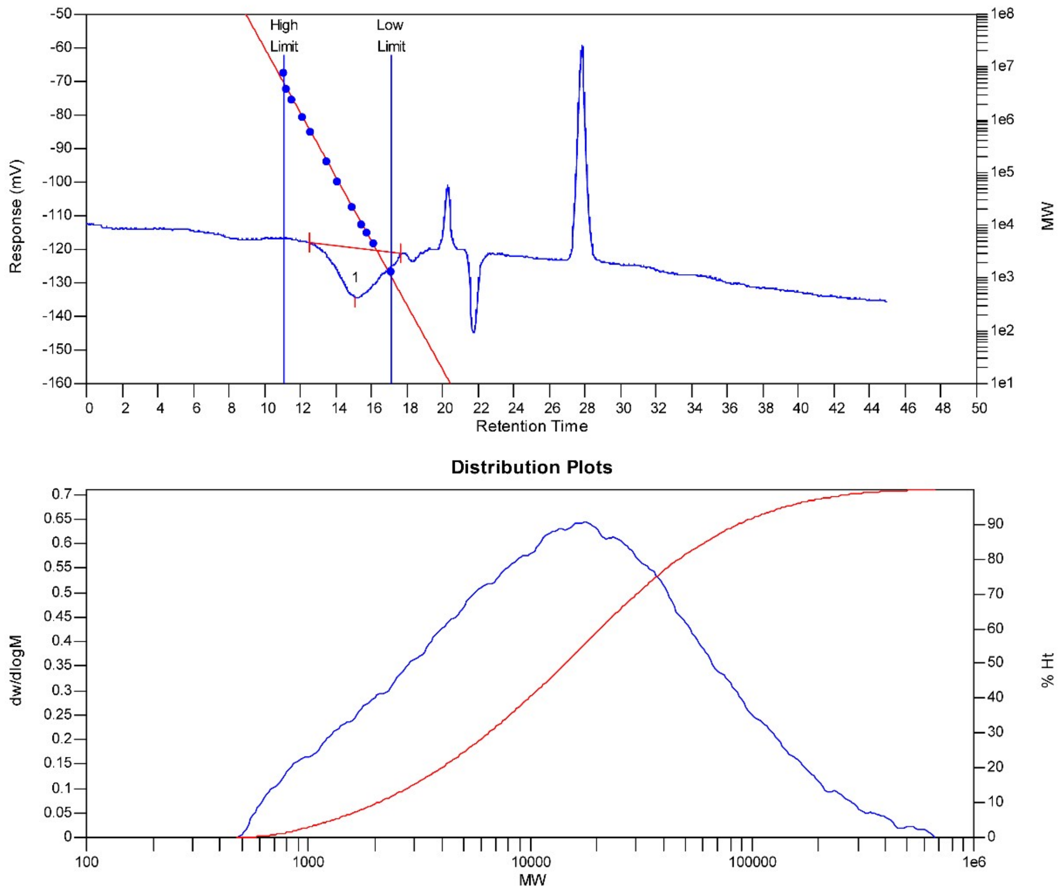
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	27941	10797	67462	322006	733986	51103	6.24822

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	14.83	17.40	-15.5493	100	2303.68	100

Figure S19. GPC of the polymer from table 1, entry 5.



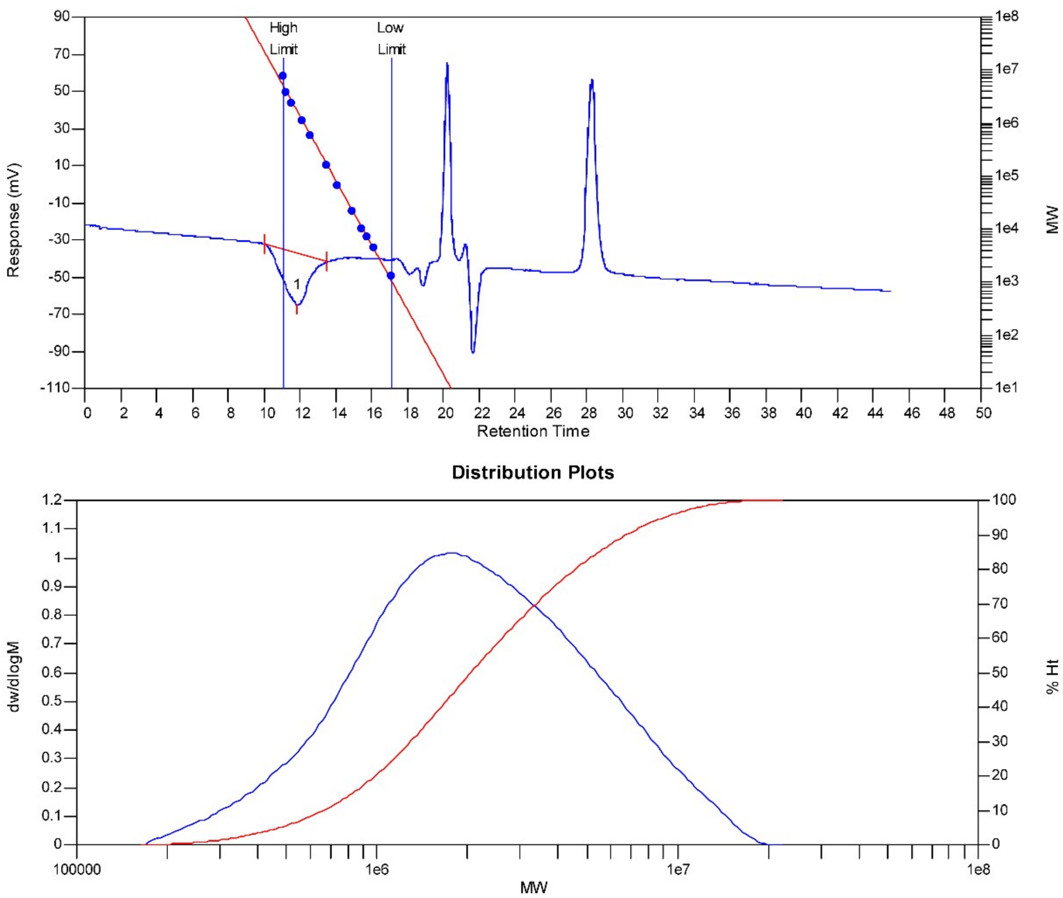
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	17506	5573	34445	135628	271065	26668	6.18069

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.52	15.12	17.68	-14.8659	100	2274.33	100

Figure S20. GPC of the polymer from table 1, entry 6.



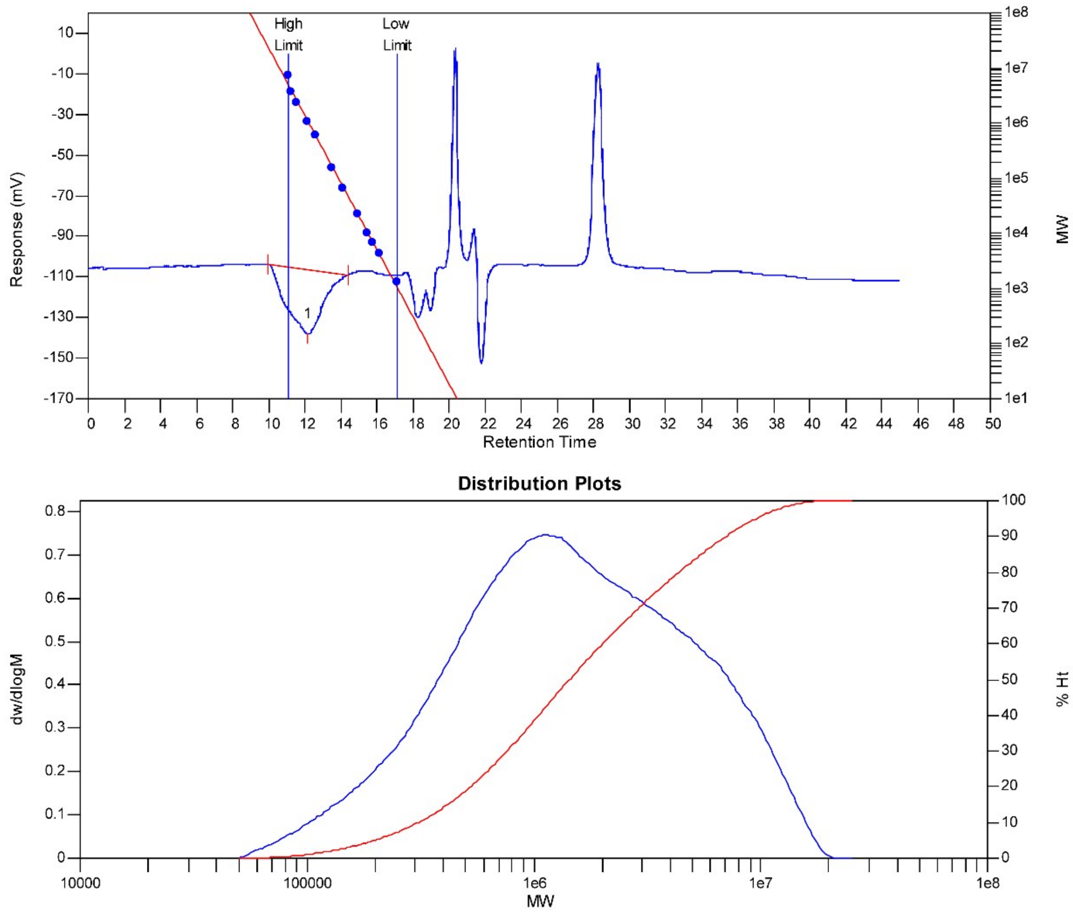
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1792198	1401202	2977009	5530749	8215922	2675921	2.12461

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.02	11.87	13.52	-27.5941	0	2682.99	100

Figure S21. GPC of the polymer from table 1, entry 7.



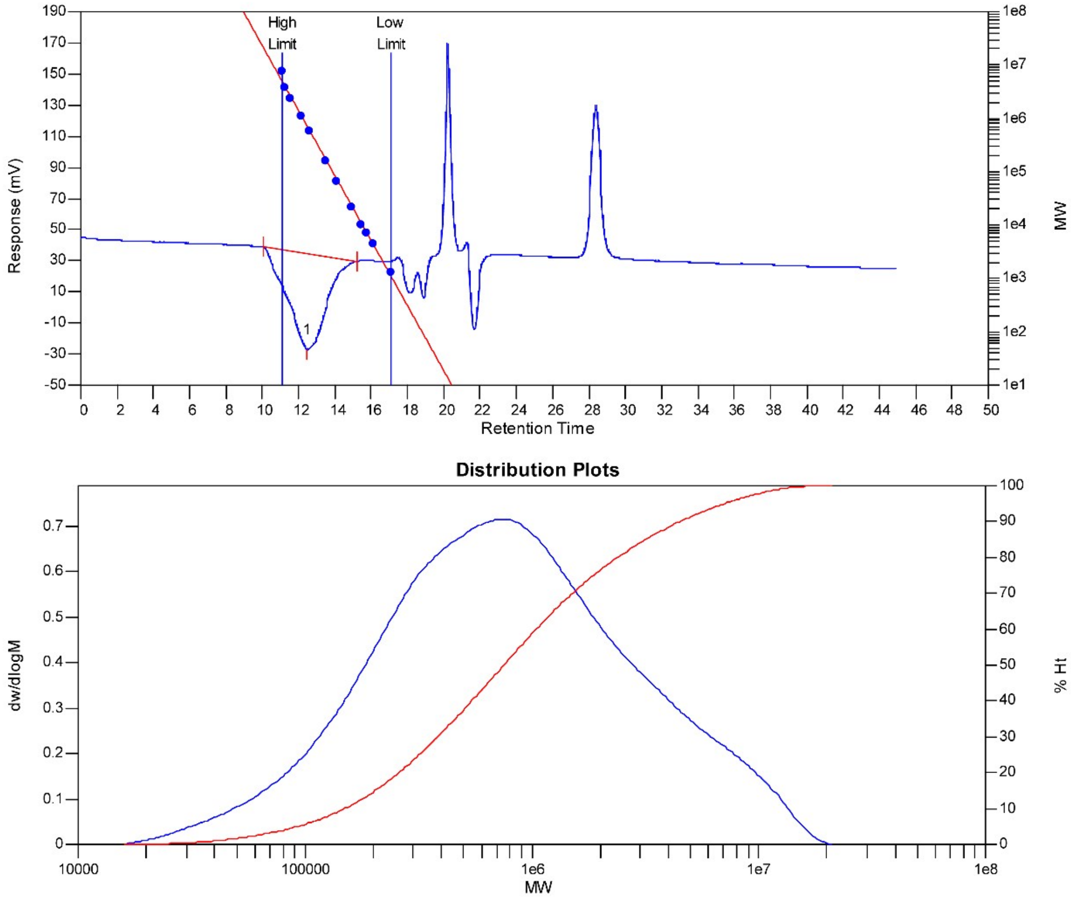
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1122888	1096715	2647788	6151744	9128415	2243906	2.41429

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		9.93	12.17	14.37	-31.6111	100	4166.16	100

Figure S22. GPC of the polymer from table 1, entry 8.



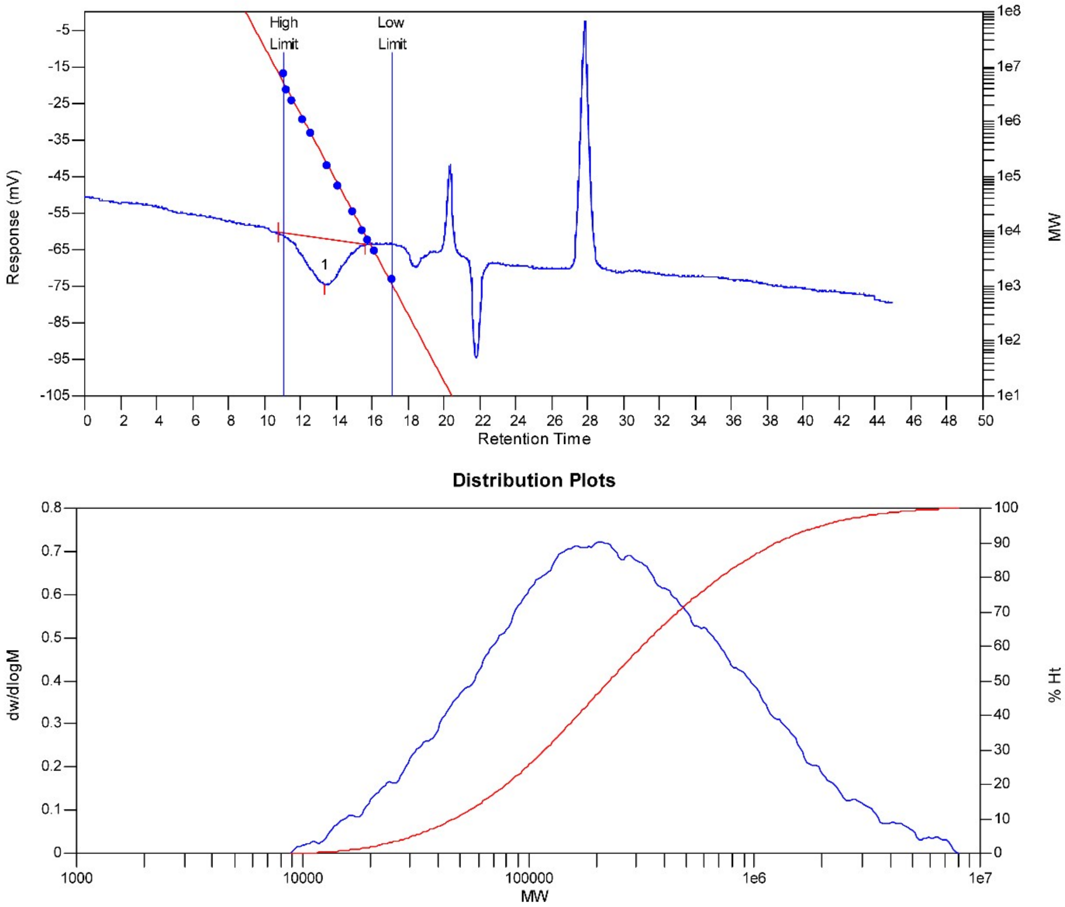
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1509353	437932	1632044	3396502	5365770	1420158	3.7267

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.07	12.47	15.18	-61.397	100	8439.45	100

Figure S23. GPC of the polymer from table 1, entry 9.



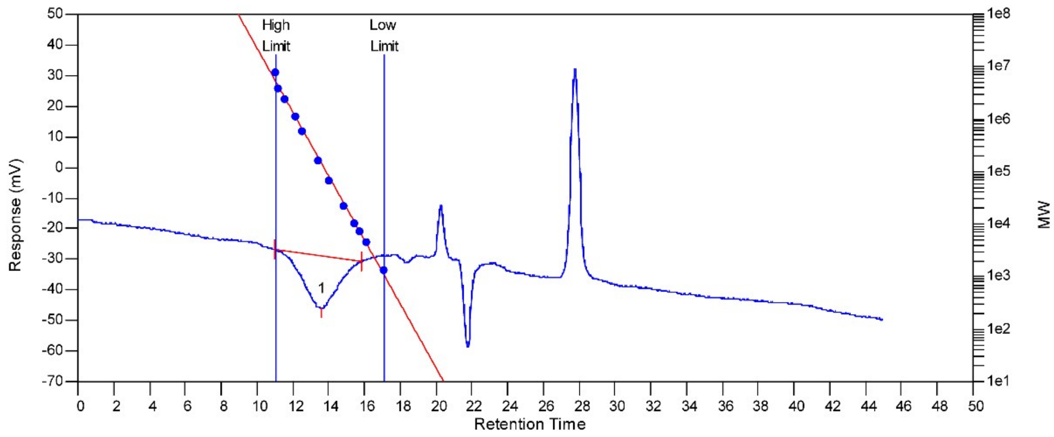
MW Averages

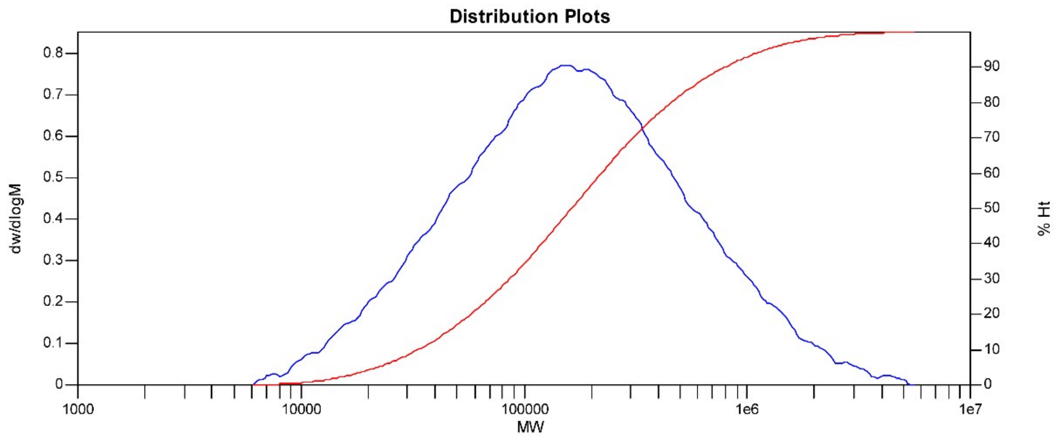
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	208621	114525	511168	1800683	3482317	407734	4.46337

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.75	13.37	15.60	-12.5413	100	1713.52	100

Figure S24. GPC of the polymer from table 1, entry 10.





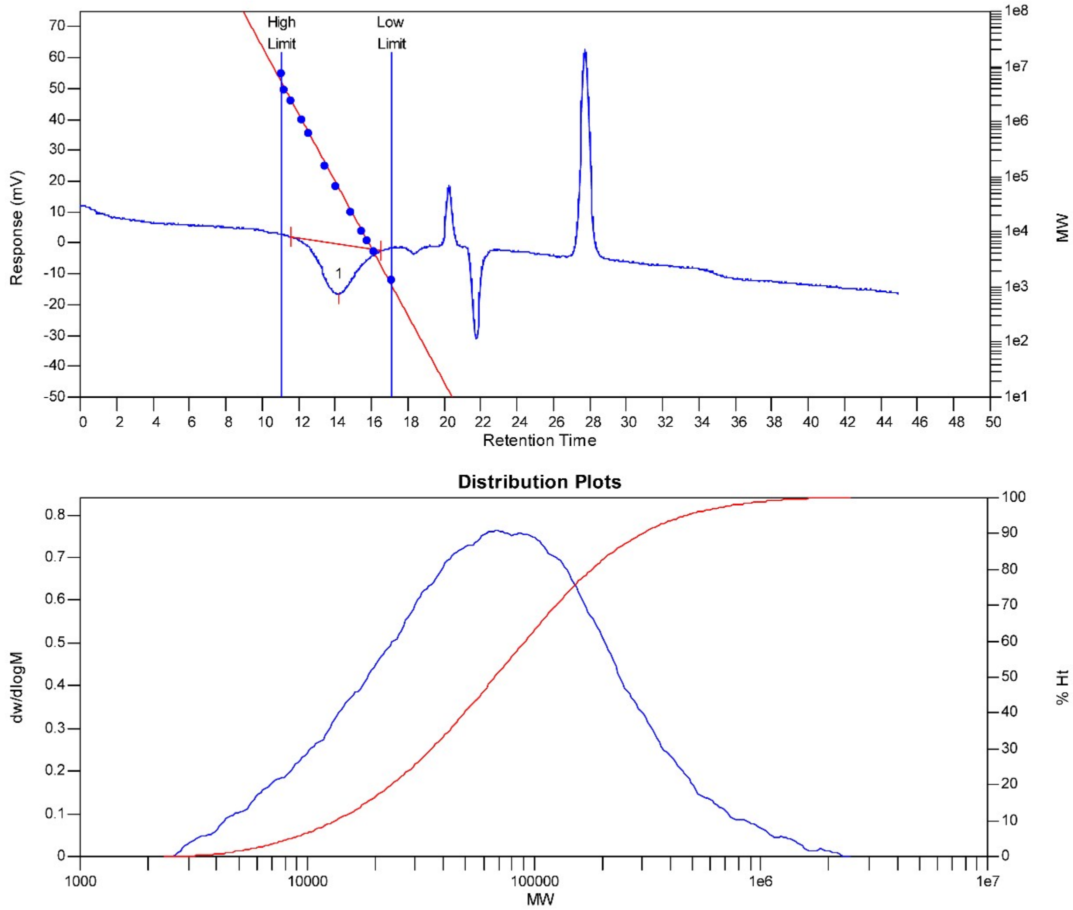
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	150391	81533	325262	1042283	2067630	265528	3.98933

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.00	13.58	15.87	-17.2296	100	2201.34	100

Figure S25. GPC of the polymer from table 1, entry 11.



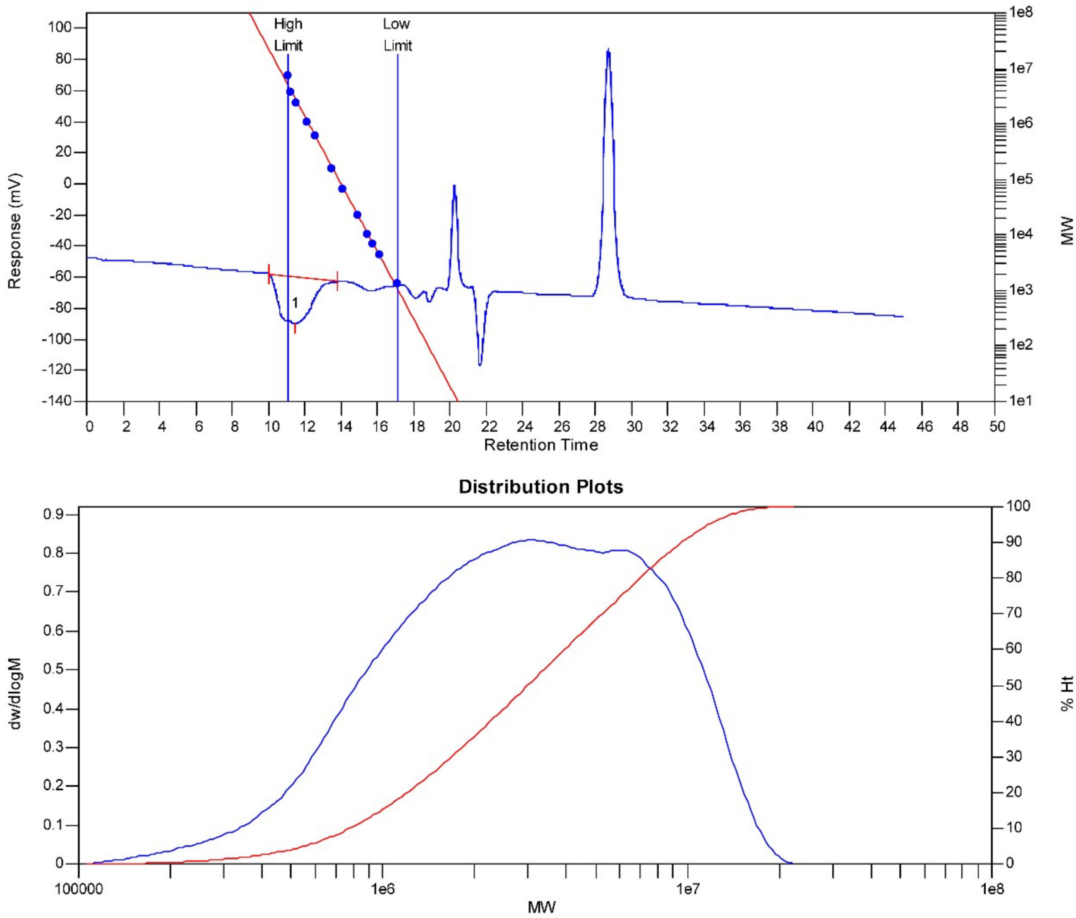
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	69533	32504	129178	418268	863222	105824	3.97422

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	14.18	16.55	-16.1343	0	2087.79	100

Figure S26. GPC of the polymer from table 1, entry 12.



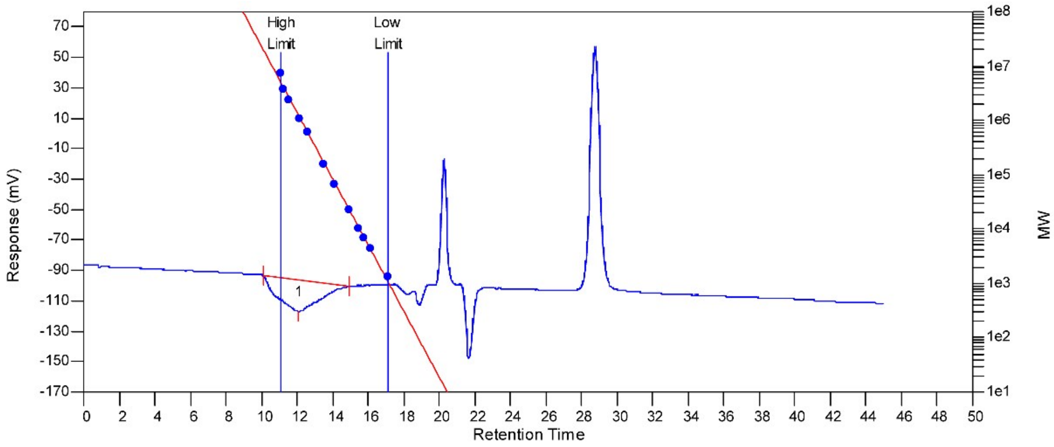
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	3068266	1118529	2702390	7219734	9672829	3734931	2.41602

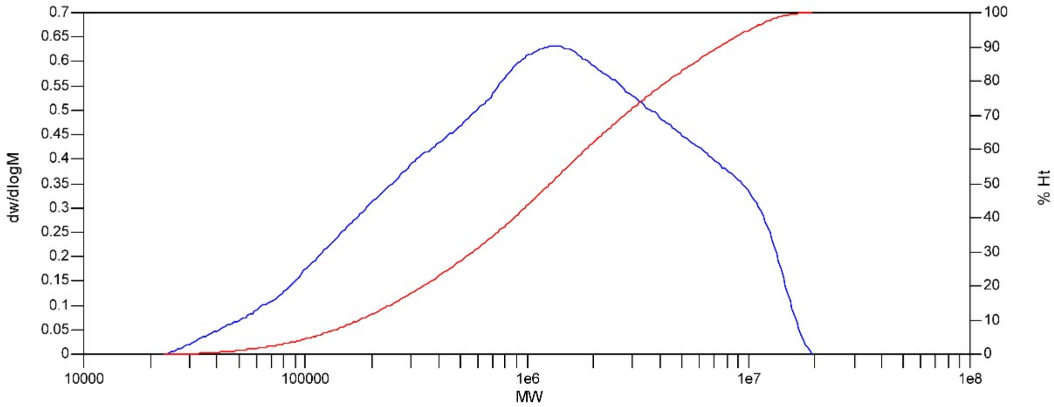
Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.02	11.43	13.83	-30.068	0	3545.05	100

Figure S27. GPC of the polymer from table 1, entry 13.



Distribution Plots



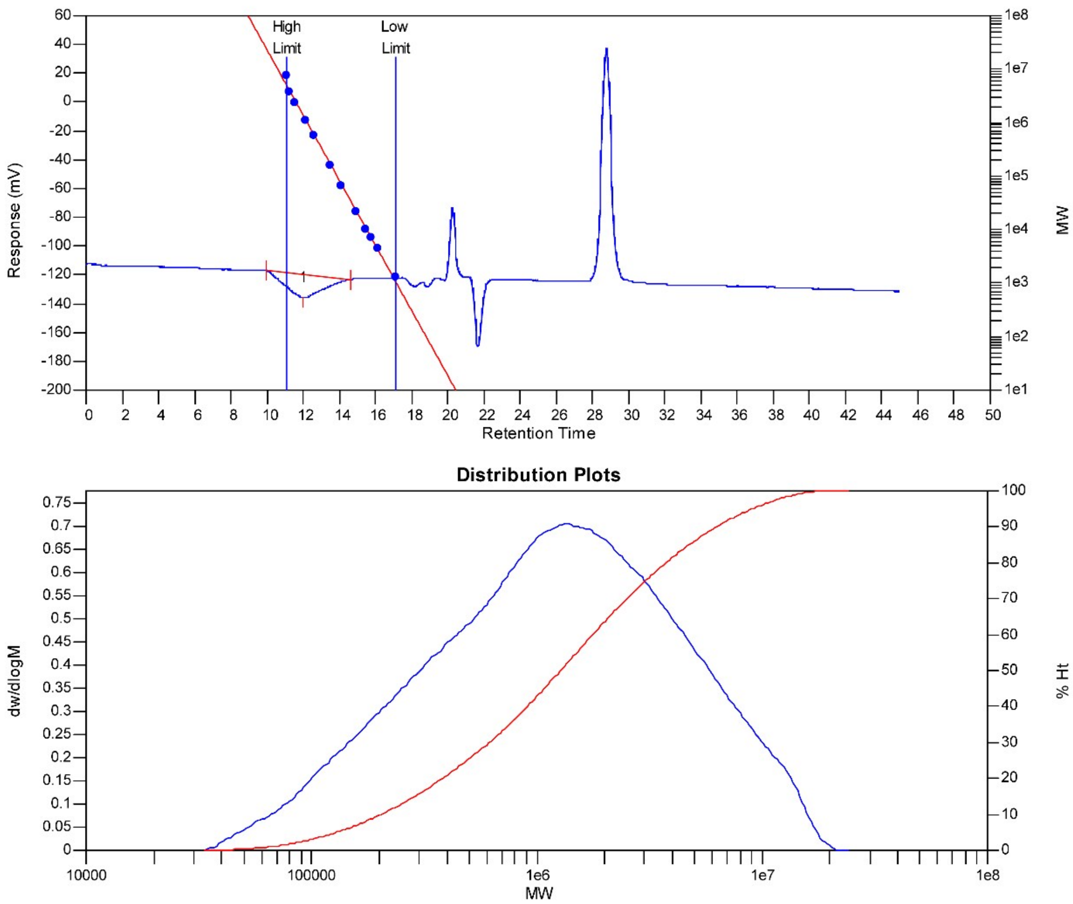
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1353805	450579	2582325	6551861	9452740	2117206	5.73113

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.12	12.07	14.92	-20.3372	0	3177.7	100

Figure S28. GPC of the polymer from table 1, entry 14.



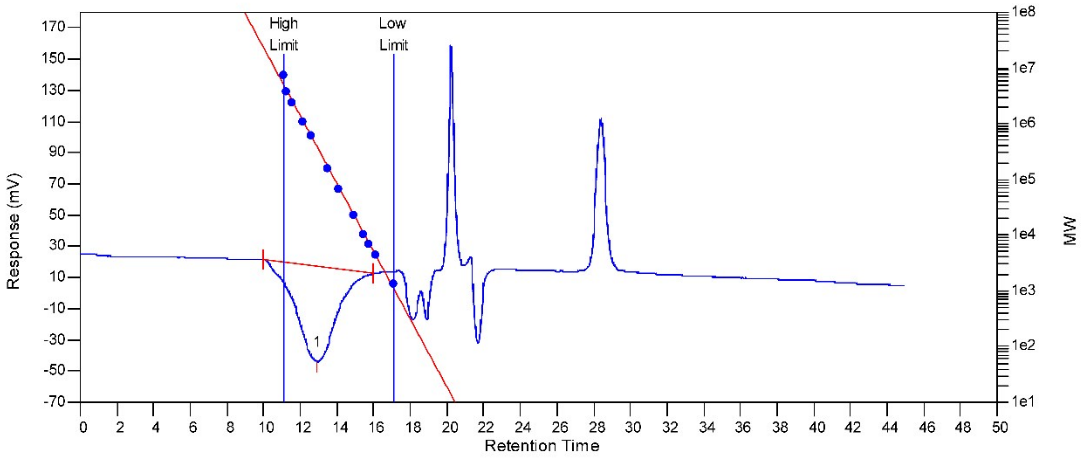
MW Averages

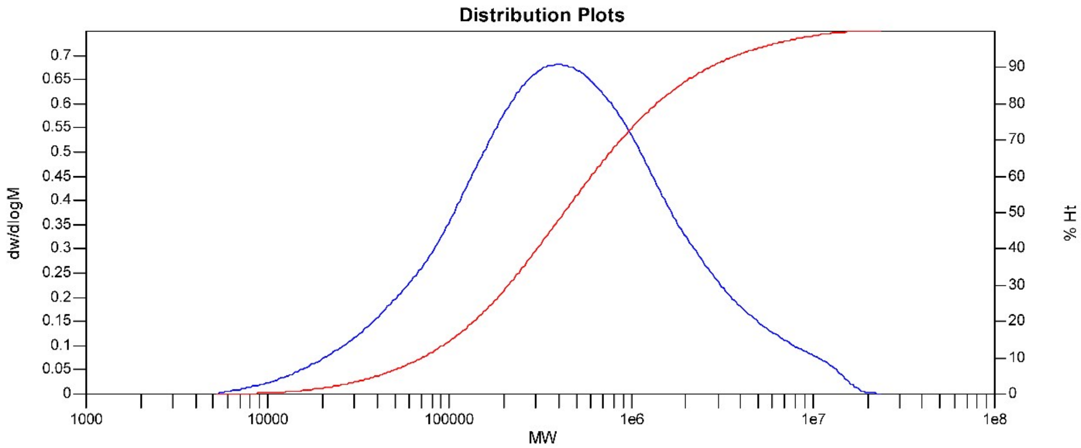
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1353805	522498	2377357	6026624	9291649	1976025	4.54998

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		9.97	12.02	14.65	-16.032	100	2240.52	100

Figure S29. GPC of the polymer from table 1, entry 15.





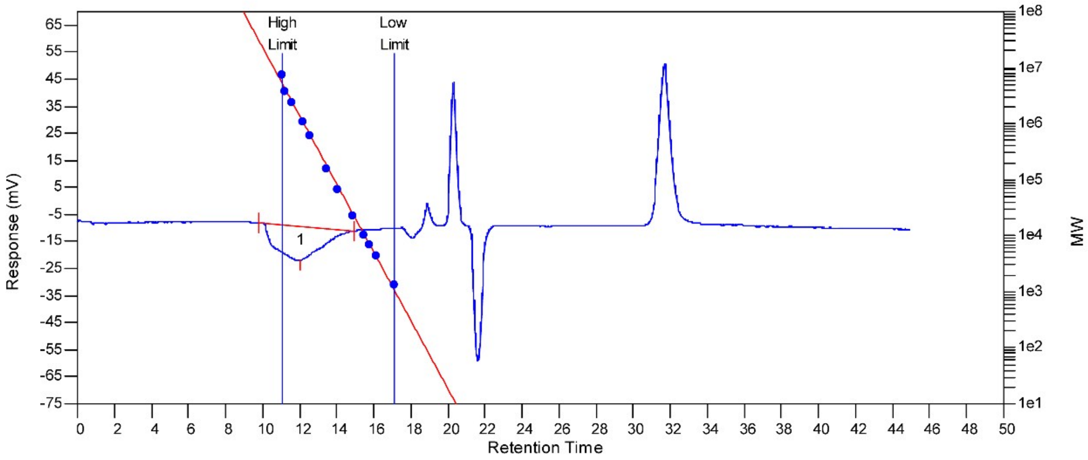
MW Averages

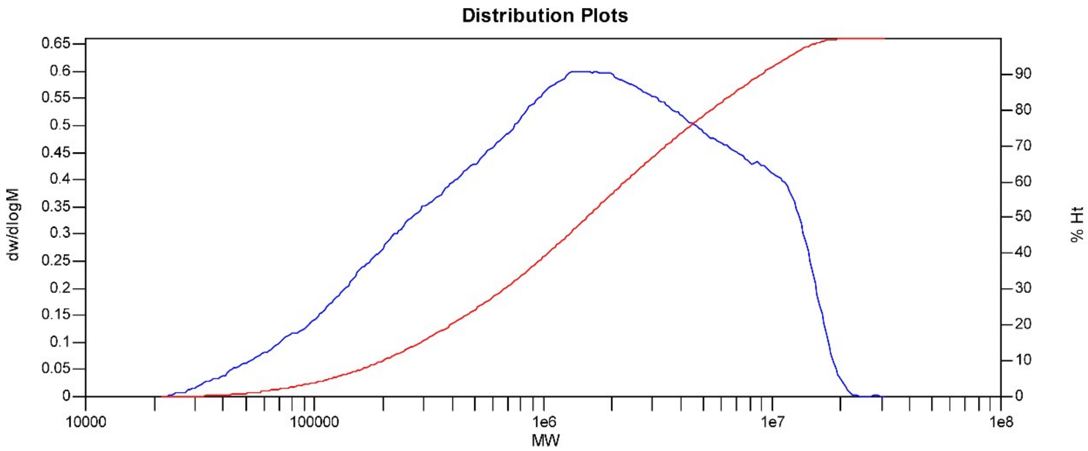
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	953387	449008	1109577	2292176	3495735	974130	2.47117

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.73	12.62	14.12	-9.54527	100	1180.39	100

Figure S30. GPC of the polymer from table 1, entry 16.





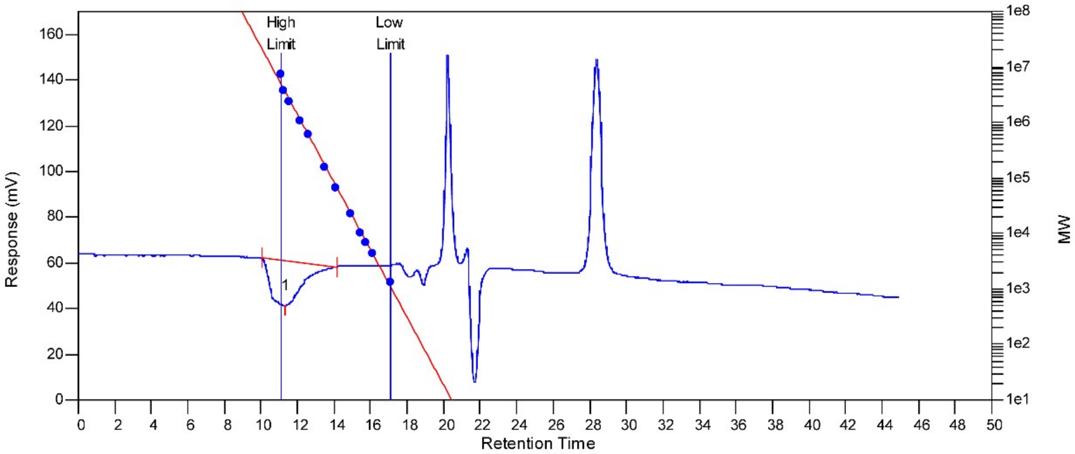
MW Averages

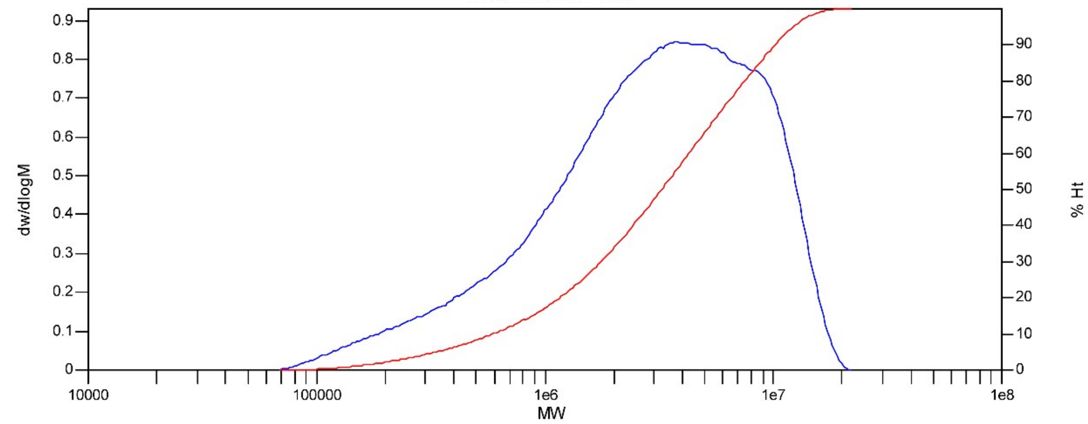
Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1670816	1151059	3492746	7097233	9703091	3030055	3.03438

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.18	12.02	13.62	-9.48544	100	1285.36	100

Figure S31. GPC of the polymer from table 1, entry 17.





MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	3699242	1353233	4364436	7588163	9916564	3897603	3.22519

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.03	11.30	14.13	-19.554	100	2278.76	100

Figure S32. GPC of the polymer from table 1, entry 18.

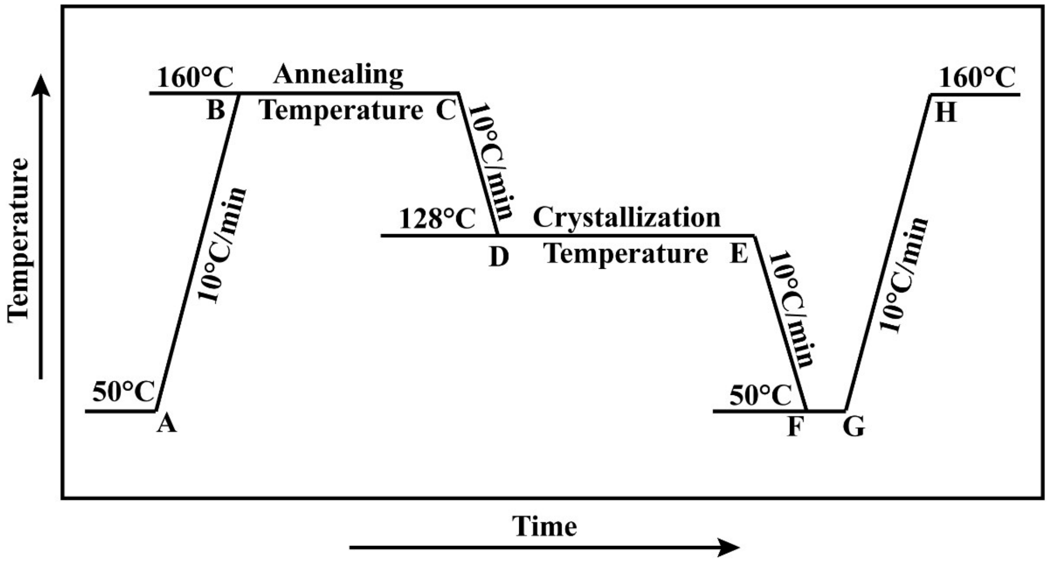
3. Crystallographic data for titanium complexes

Table S1. Crystallographic data for the titanium complexes [LigHTiCl_2] and [LigFTiCl_2].

	LigHTiCl_2·PhMe	**LigFTiCl_2**
Empirical formula	$C_{25}H_{34}Cl_2N_2O_2Ti \cdot C_7H_8$	$C_{25}H_{33}Cl_2FN_2O_2Ti$
Formula weight	605.47	521.33
Crystal color	Red	Red
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (Å)	10.2955(4)	20.5893(9)
b (Å)	30.4590(9)	9.7299(4)
c (Å)	10.5847(3)	12.9904(6)
α (deg)	90	90
β (deg)	111.381(4)	96.974(4)
γ (deg)	90	90
Volume (Å^3)	3090.82(19)	2583.1(2)
Z	4	4
ρ_{calc} (g/cm^3)	1.301	1.366
F (000)	1280.0	1112.0
Absorp. Coeff. (mm^{-1})	4.172	0.570
Crystal size (mm^3)	0.1 × 0.1 × 0.1	0.3 × 0.25 × 0.2
Radiation source [λ, Å]	CuKα [1.54178]	MoKα [0.71073]
θ range (deg)	9.432 to 144.03	3.41 to 27.00
Index ranges	$-12 \leq h \leq 10$ $-20 \leq k \leq 36$ $-12 \leq l \leq 13$	$-26 \leq h \leq 26$ $-12 \leq k \leq 11$ $-16 \leq l \leq 16$
Reflections Collected	9595	25808
Data completeness	0.966	0.998
Data / restraints / parameters	5877 / 0 /360	5636 / 0 / 305
Goodness-of-fit on F^2	1.118	1.026
R1; wR2 (I > 2σ (I))	0.0856; 0.2418	0.0387; 0.0892
R1; wR2 (all data)	0.1189; 0.2670	0.0488; 0.0955
ρ_{max} / ρ_{min} (e / Å^3)	1.19 / - 0.50	0.33 / -0.34

4. Thermal Analysis Protocol

Scheme S1. Thermal analysis protocol.



Thermal protocol[1]: method: Ramp 1: 50 °C to 160 °C (A-B) at 10 °C/min. hold at 160 °C for 5/15/30/60/360 mins. (B-C). Ramp 2: Cooling to 128 °C at 10 °C/min. (C-D) and hold at 128 °C for 180 min. (D-E). Ramp 3: Cooling to 50 °C at 10 °C/min. (E-F) and hold at 50 °C for 3 min. (F-G). Ramp 4: Heating from 50 °C to 160 °C at 10 °C/min. (G-H). The DSC plots shown (Fig. 5) were obtained during ramp 4 (G-H).

5. XPS Analysis

XPS Measurements: XPS measurements were carried out using Thermo Fisher Scientific X-ray Photoelectron Spectrometer (XPS) System. As the catalyst is air/moisture sensitive, a vacuum transfer module was used to transfer samples from a glove box environment into the test unit without exposure to air. The peak fitting was carried out using Avantage software with Shirley type background.

Synthesis of MAO treated catalyst [Al/Ti] = 100: In a round bottom Schlenk flask 26.2 mg (49.3 μmol) of LigFTiCl_2 and 3.28 mL (493 μmol, 1.5 M, 100 equivalent) of MAO were added and stirred for about an hour at room temperature. The solvent was removed in *vacuo*, and the residual solid was washed three times with *n*-hexane and dried in *vacuo* to give an orange powder.

Ti 2p XPS spectra are shown in Figure S33, and a quantitative distribution of Ti valence states is listed in Table S2. Two distinct peaks corresponding to the spin-orbit split of 2p centered around 458.8 and 464.5 eV are discernible from the Ti 2p core-level spectrum, the binding energy values are in line with the reported values.[2] Before addition of MAO, we could only fit one type of Ti species, i.e., Ti^{4+} [BE = 458.8 eV], thus, the complex before addition of MAO gave a strong indication to be a pure Ti (IV) complex. After addition of MAO at [Al]/[Ti] ratio = 100, the we still could only fit on type of Ti species, i.e., Ti^{4+} [BE = 458.8 eV]. This strongly indicated that the MAO has no influence on oxidation state of Ti in this type of complex.

Table S2. XPS Data of the LigFTiCl_2 at the Ti $2p_{3/2}$ Level.

Al/Ti	Ti $2p_{3/2}$	peak B.E. (eV)	atomic (%)
before addition of MAO	Ti^{4+}	458.8	>99
100	Ti^{4+}	458.6	>99

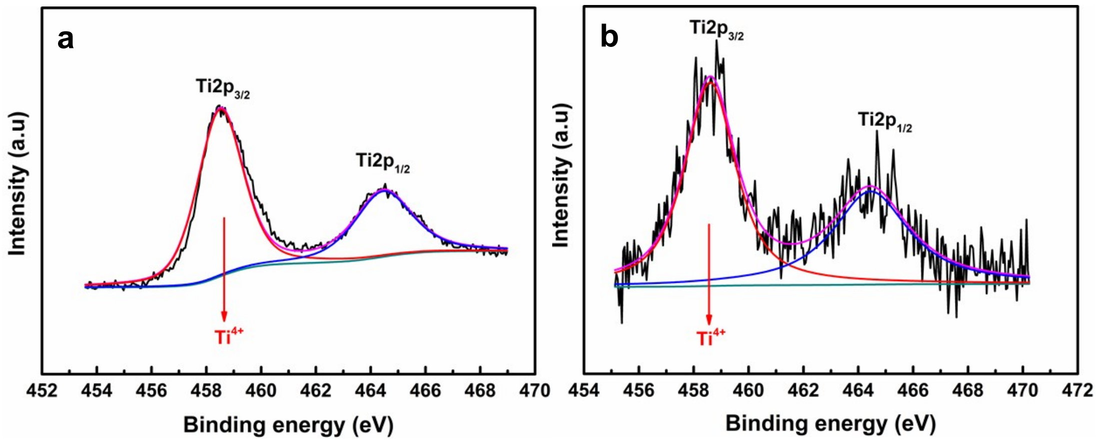


Figure S33. (a) Ti 2p XPS spectra of catalyst LigFTiCl_2 before addition of MAO, (b) after addition of MAO [Al]/[Ti] = 100.

6. References

1. K. Liu, E. L. de Boer, Y. Yao, D. Romano, S. Ronca and S. Rastogi, *Macromolecules*, 2016, **49**, 7497-7509.
2. G. Lu, S. L. Bernasek and J. Schwartz, *Surf. Sci.*, 2000, **458**, 80-90.