Supporting Information:

Synthesis of Fluorinated Polyethylene of Different Topologies via Insertion Polymerization with Semifluorinated Acrylates

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1. Figures, Tables.

Table S1. Condition Optimization of Ethylene/Semifluorinated Acrylates Copolymerization with Pd Catalysts [a]

Entry	Cat.	Time (h)	[M] (mol/L)	Yield (g)	Act.[b]	X_M[c] (%)
1	**1**	2.0	0.25	1.55	15.5	1.8
2	**1**	2.0	0.5	1.33	13.3	3.5
3	**1**	2.0	1.0	1.49	14.9	6.7
4	**1**	0.5	1.0	0.38	15.2	-[d]
5	**1**	1.0	1.0	0.77	15.4	-
6	**1**	1.5	1.0	1.10	14.7	-
7	**3**	2.0	0.25	1.08	5.4	0.31
8	**3**	2.0	0.5	0.84	4.2	0.95
9	**3**	2.0	1.0	0.82	4.1	1.67
10	**3**	0.5	1.0	0.32	6.4	-
11	**3**	1.0	1.0	0.53	5.3	-
12	**3**	1.5	1.0	0.71	4.7	-

[a]Conditions: 5 μmol catalyst, total volume of toluene and **6FA**: 10 mL, 5 atm, 80 °C, 100 mg BHT for **1**. 0.010 mmol pre-catalyst, 2.0 eq. NaBAF, total volume of DCM and **6FA**: 10 mL, 2 atm, 30 °C for **3**. [b]Activity (Act.) = 10^4 g/(mol Pd·h). [c]X_M = M incorp. (mol %). [d]Not determined

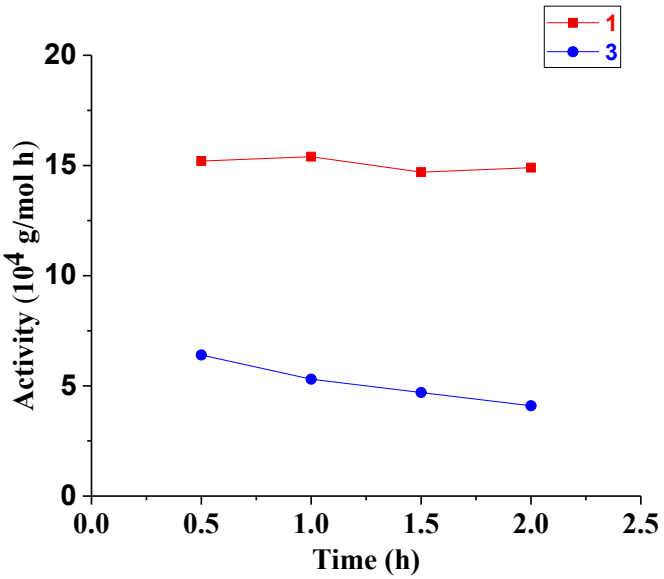


Figure S1. Plot of activity versus time for **1** (red) and **3** (blue) at optimization condition.

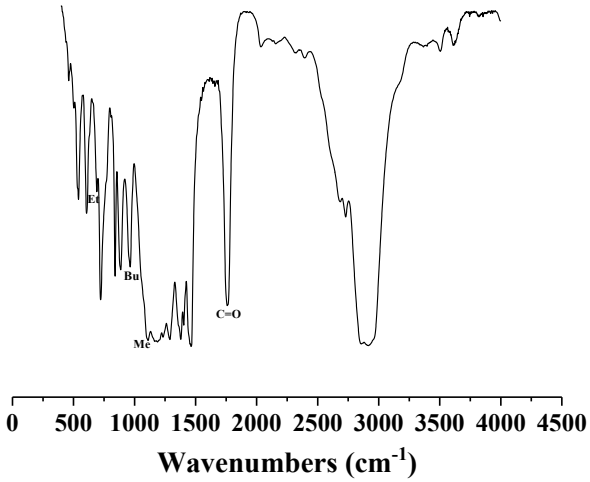


Figure S2. FTIR spectroscopy of the polymer from table 2, entry 6.

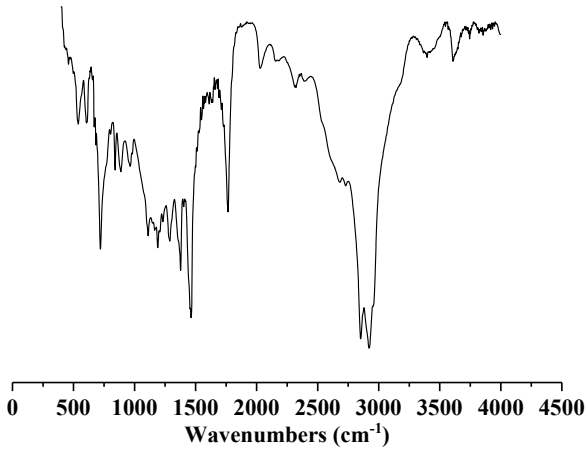


Figure S3. FTIR spectroscopy of the polymer from table 2, entry 8.

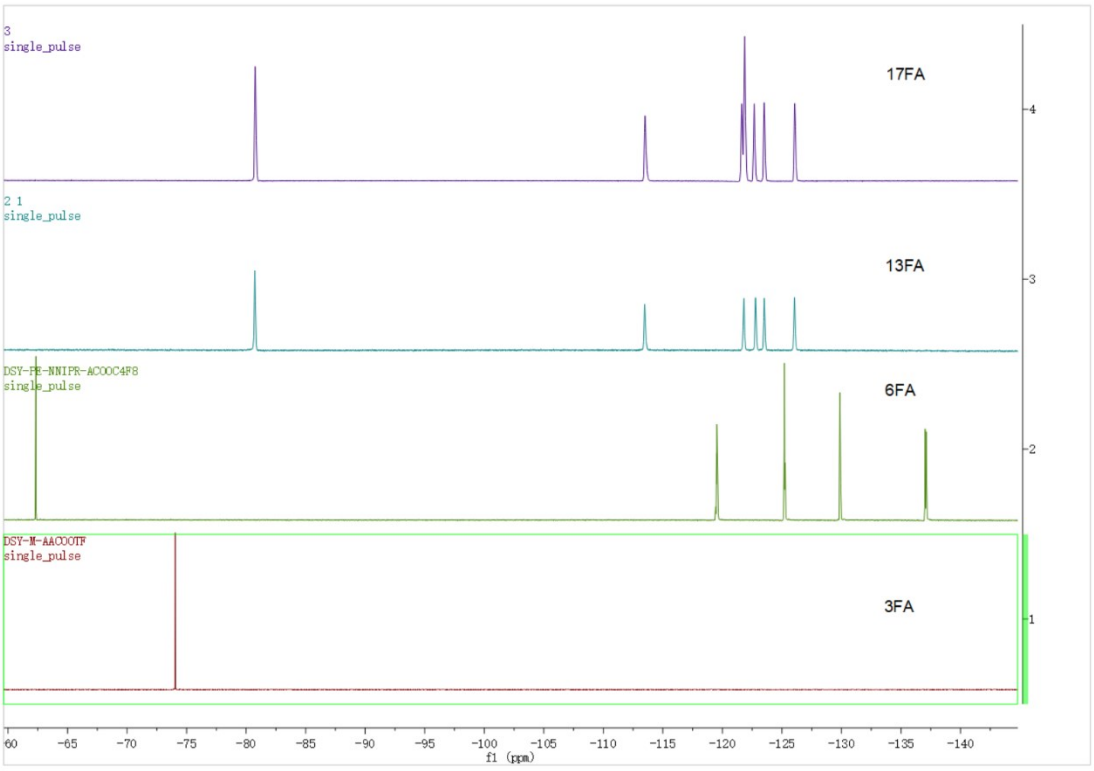


Figure S4. ^{19}F NMR spectrum of the polymers from table 1, entry 6, 10, 12, 14 ($CDCl_3$, 20 °C).

2. Spectra Data

2.1 ^{1}H NMR and ^{13}C NMR of Some Representative Polymers.

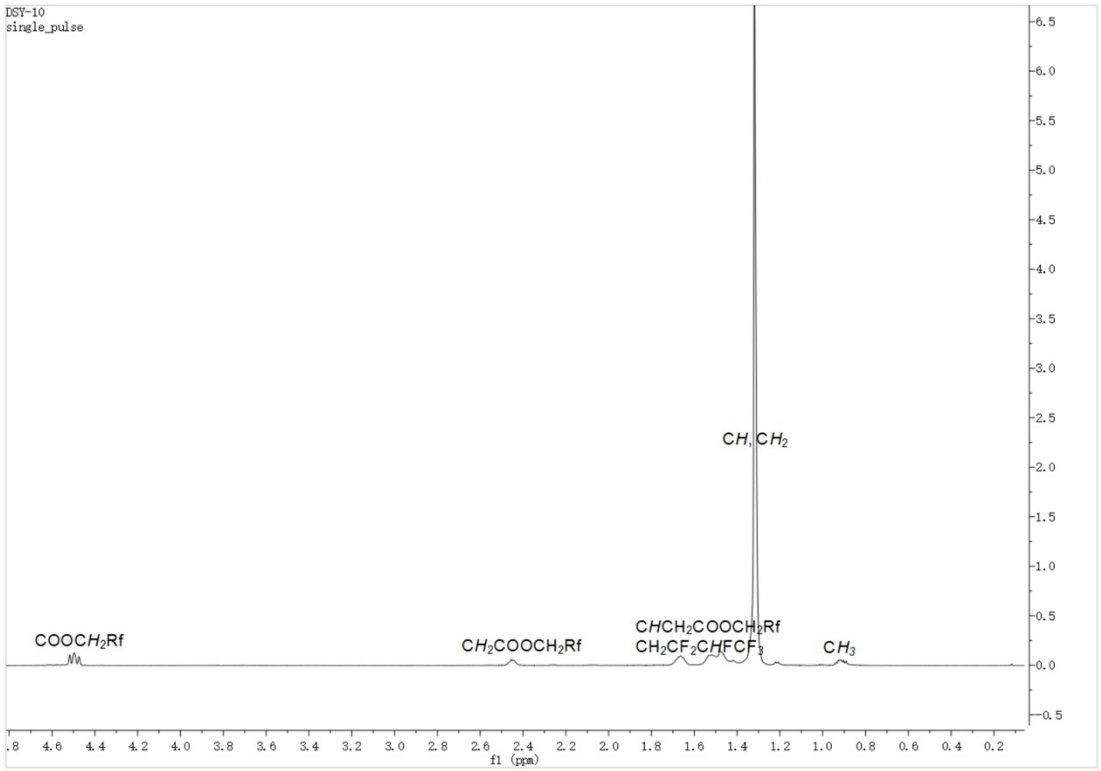


Figure S5. ^{1}H NMR spectrum of the polymer from table 1, entry 7 ($C_2D_2Cl_4$, 120 ^{o}C).

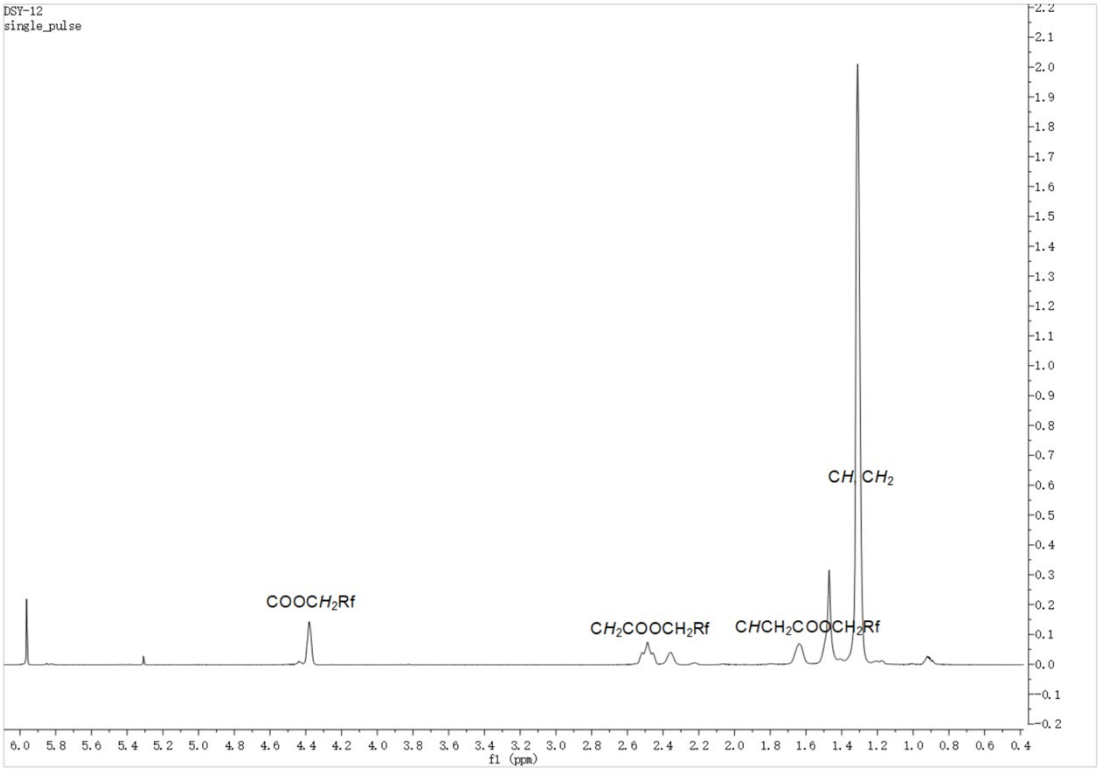


Figure S6. ^{1}H NMR spectrum of the polymer from table 1, entry 13 ($C_2D_2Cl_4$, 120 ^{o}C).

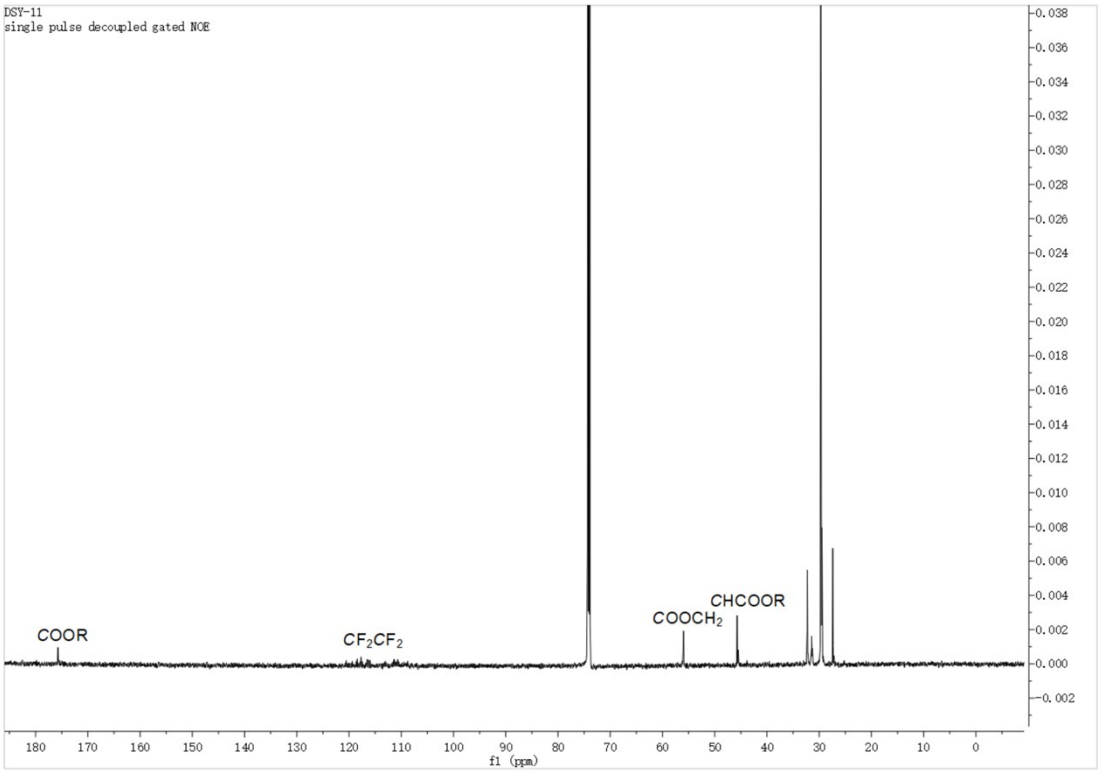


Figure S7. ^{13}C NMR spectrum of the polymer from table 1, entry 13 ($C_2D_2Cl_4$, 120 ^oC).

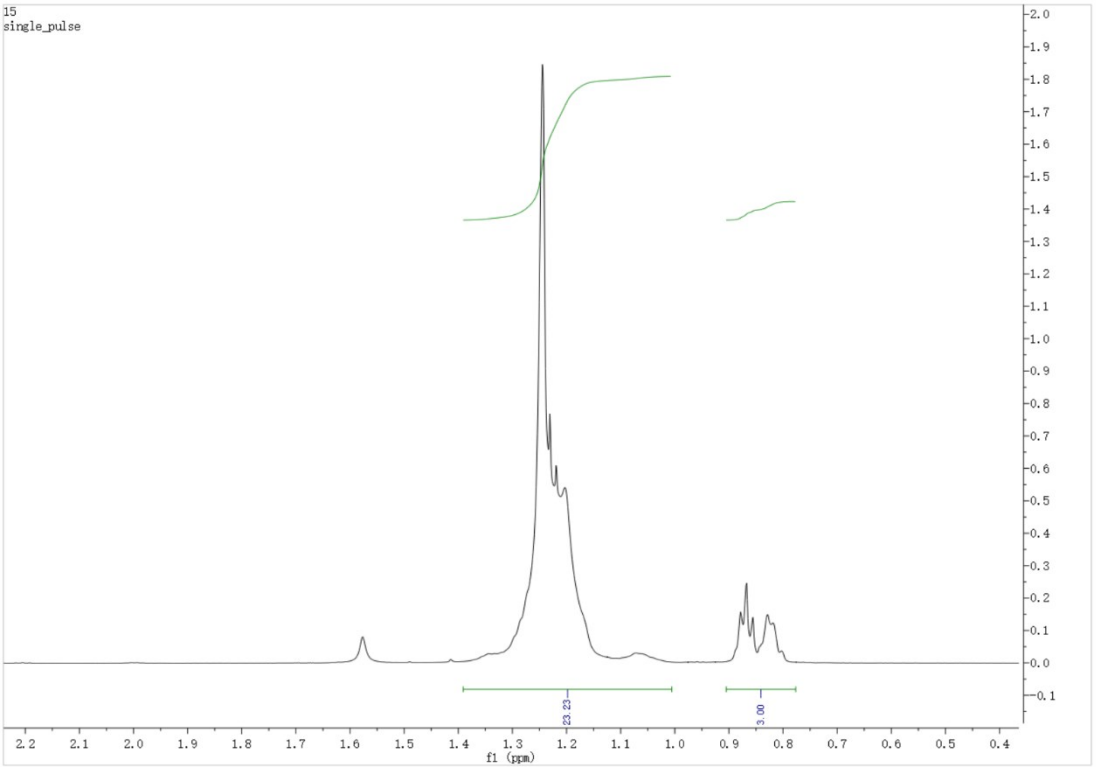


Figure S8. ^1H NMR spectrum of the polymer from table 2, entry 2 ($CDCl_3$, 20 ^oC).

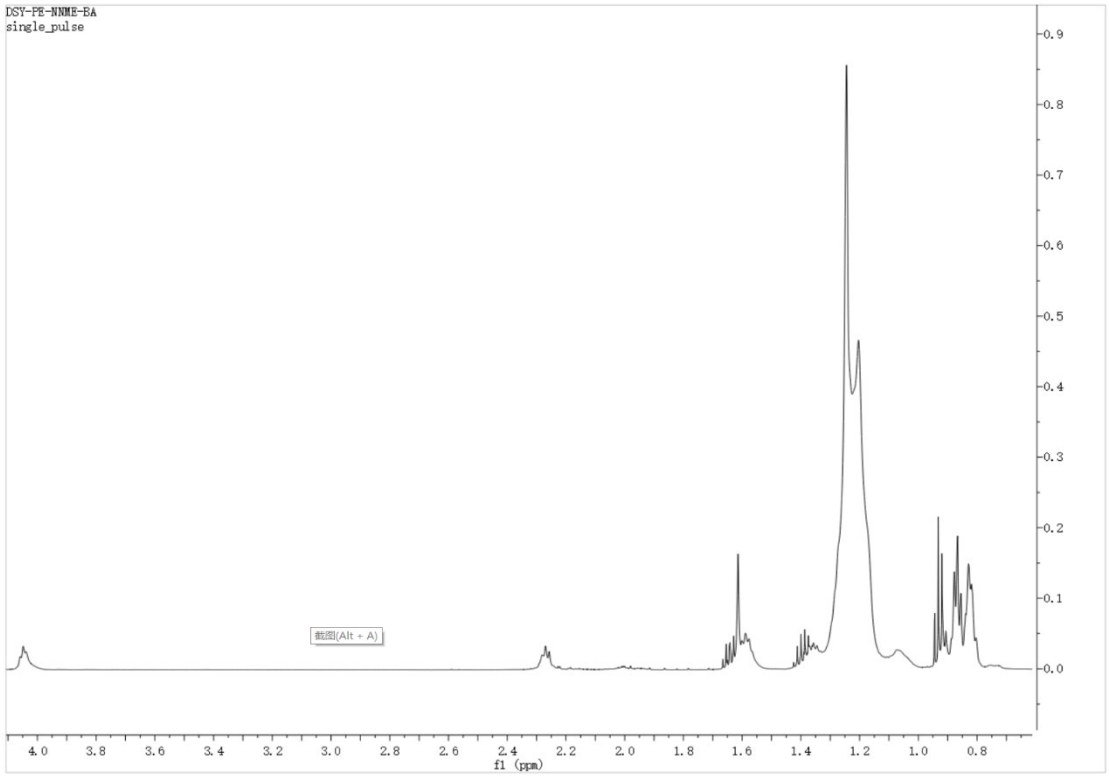


Figure S9. ^{1}H NMR spectrum of the polymer from table 2, entry 3 ($CDCl_3$, 20 ^{o}C).

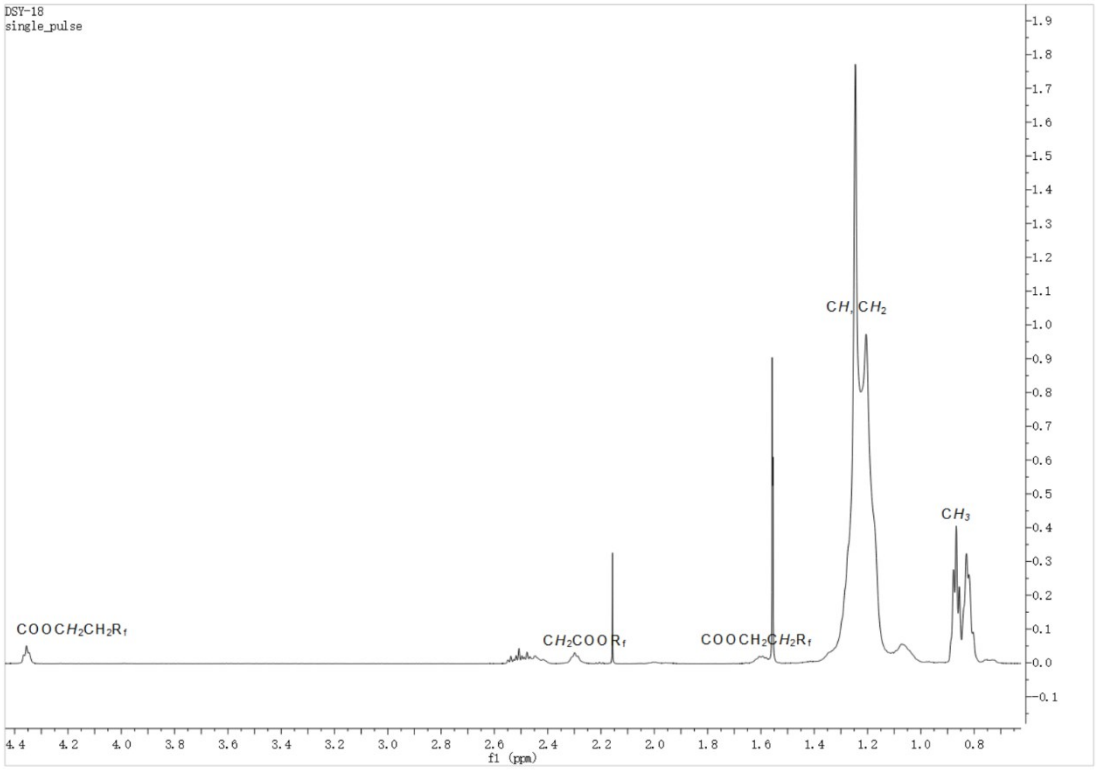


Figure S10. ^{1}H NMR spectrum of the polymer from table 2, entry 11 ($CDCl_3$, 20 ^{o}C).

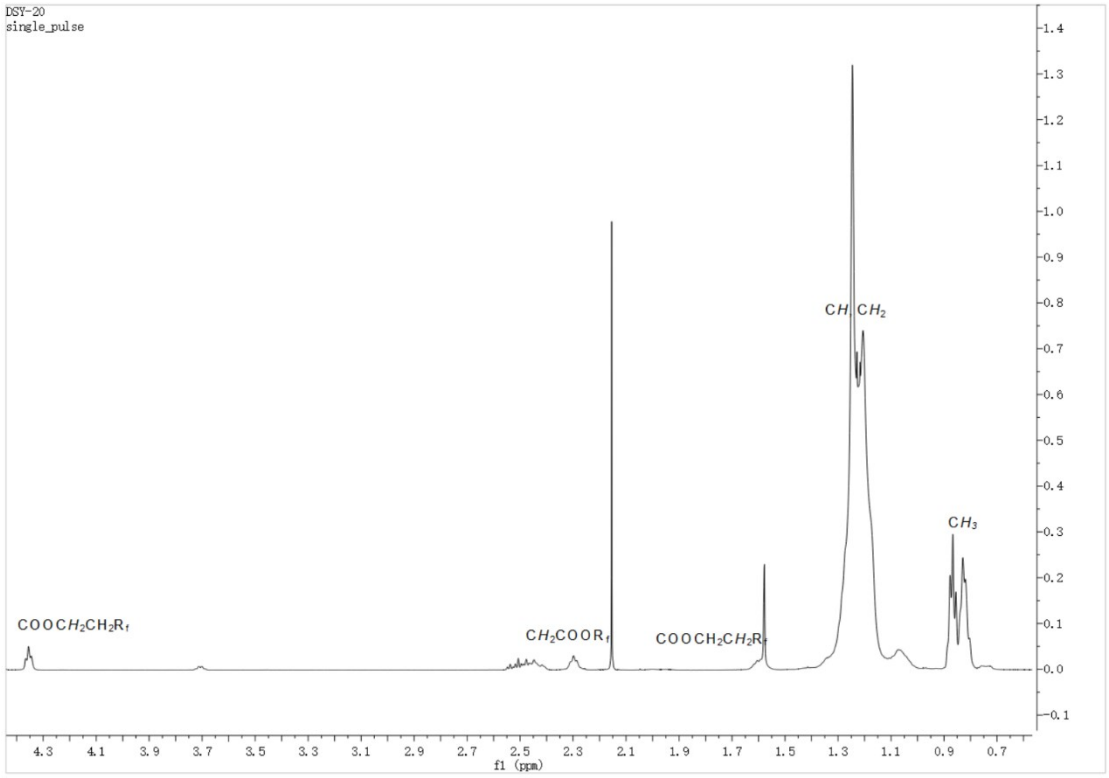


Figure S11. ^{1}H NMR spectrum of the polymer from table 2, entry 13 ($CDCl_3$, 20 ^{o}C).

2.2 DSC, GPC of Some Representative Polymers.

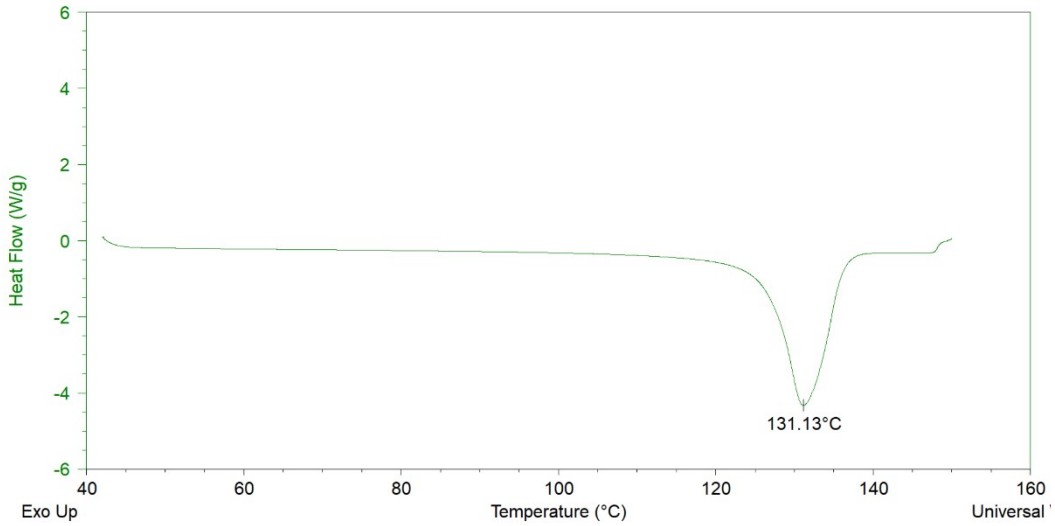


Figure S12. DSC of the polymer from table 1, entry 1.

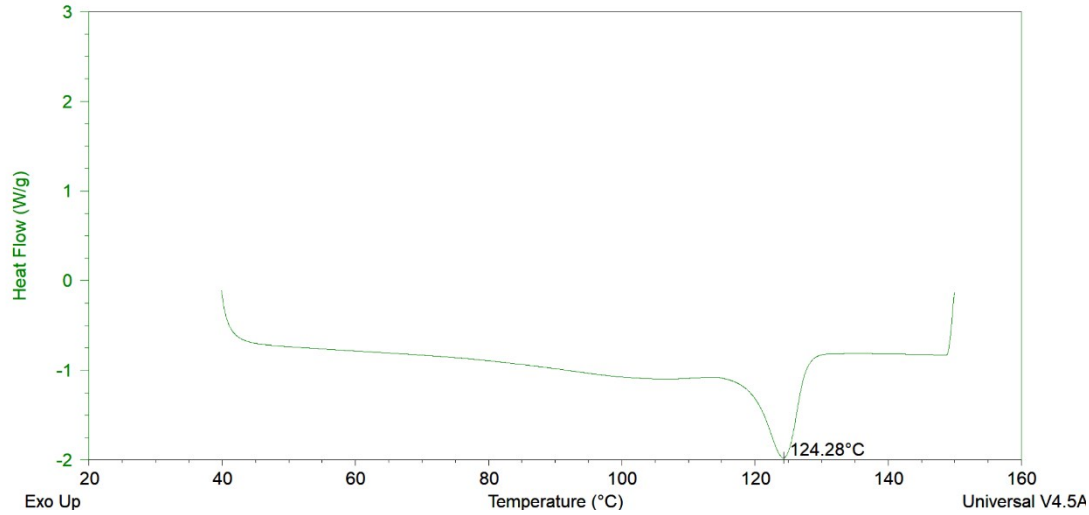


Figure S13. DSC of the polymer from table 1, entry 2.

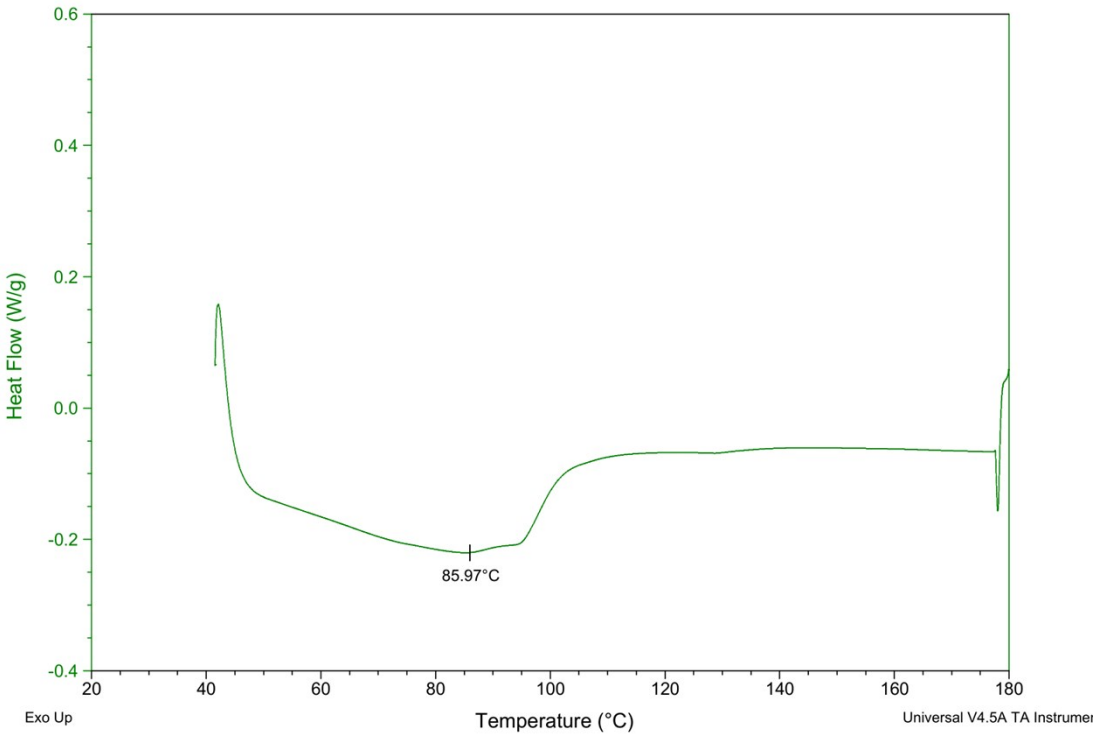


Figure S14. DSC of the polymer from table 1, entry 5.

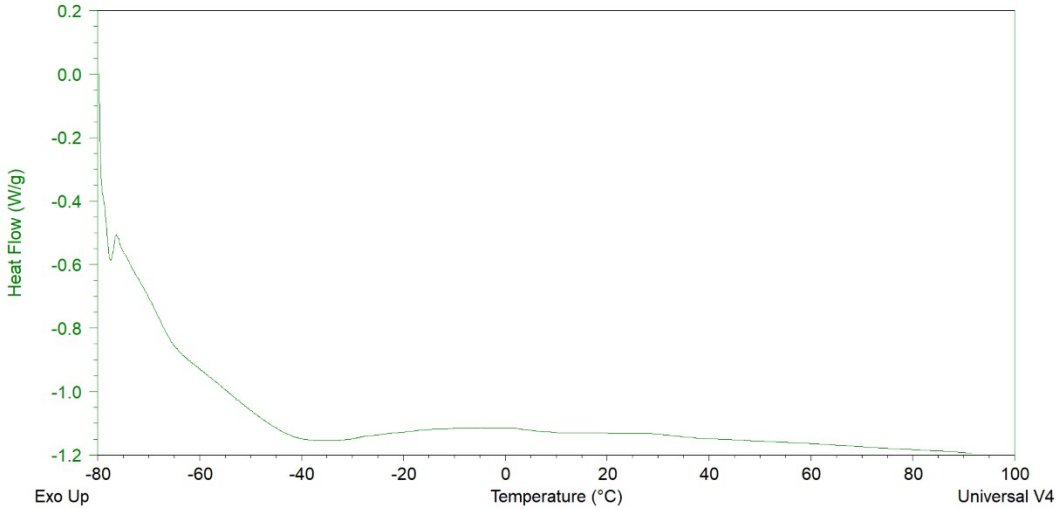
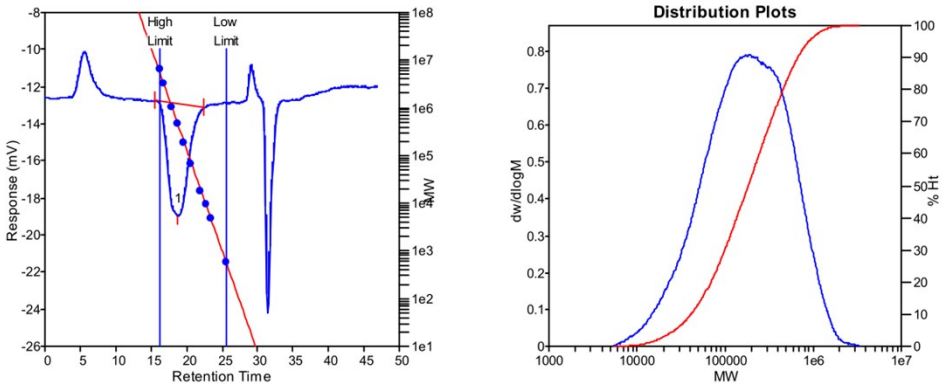


Figure S15. DSC of the polymer from table 2, entry 6.



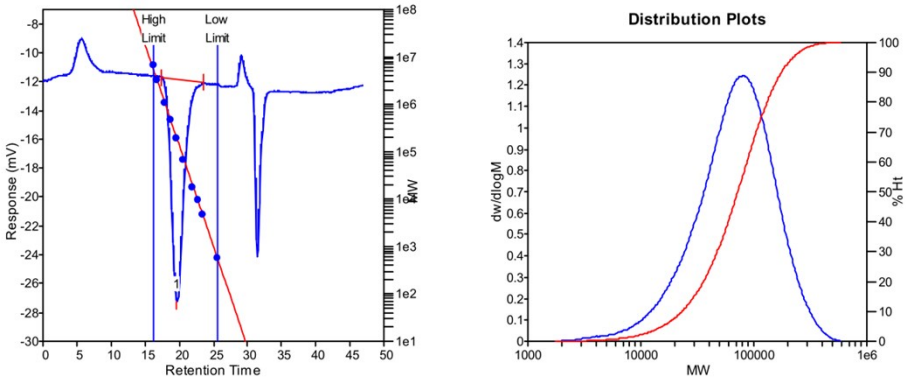
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	189526	93942	285260	604454	965919	251588	3.03655

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		15.58	18.75	22.38	-6.08277	100	1125.1	100

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



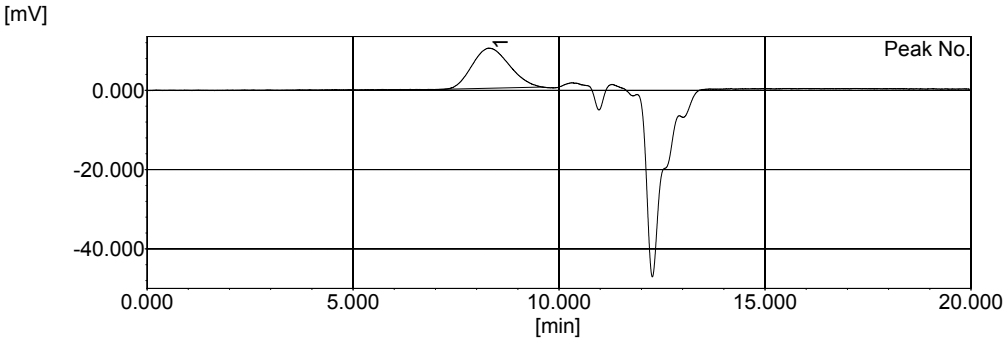
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	80871	44791	88487	139929	197402	82365	1.97555

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		17.43	19.53	23.58	-15.376	100	1802.33	100

Figure S17. GPC of the polymer from table 1, entry 7.

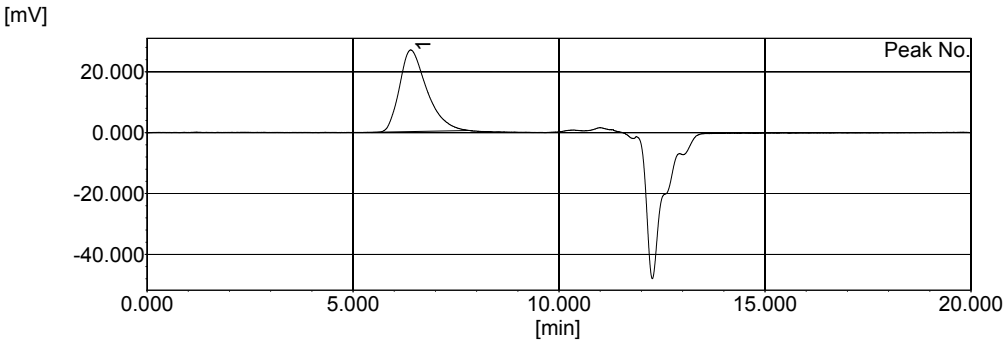


Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	6.957	0.221	164,208	Mn	16,809
Peak top	8.283	10.655	22,955	Mw	24,061
Peak end	9.595	0.831	3,281	Mz	32,910
				Mz+1	43,039
				Mv	24,061
Height [mV]			10.127	Mp	22,955
Area [mV*sec]			636.556	Mz/Mw	1.368
Area% [%]			100.000	Mw/Mn	1.431
[eta]			24060.90892	Mz+1/Mw	1.789

Figure S18. GPC of the polymer from table 1, entry 5.

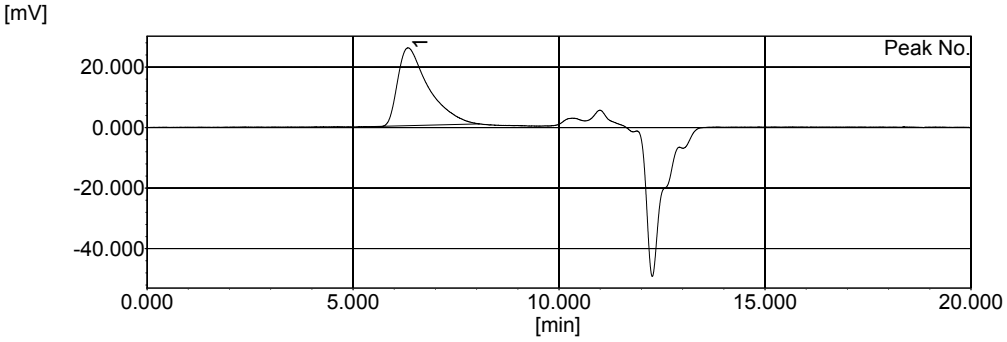


Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	5.213	0.054	2,179,172	Mn	276,265
Peak top	6.407	27.204	371,240	Mw	354,597
Peak end	7.808	0.724	46,433	Mz	429,810
				Mz+1	505,334
				Mv	354,597
Height [mV]			26.842	Mp	371,241
Area [mV*sec]			1237.622	Mz/Mw	1.212
Area% [%]			100.000	Mw/Mn	1.284
[eta]			354596.61347	Mz+1/Mw	1.425

Figure S19. GPC of the polymer from table 2, entry 7.

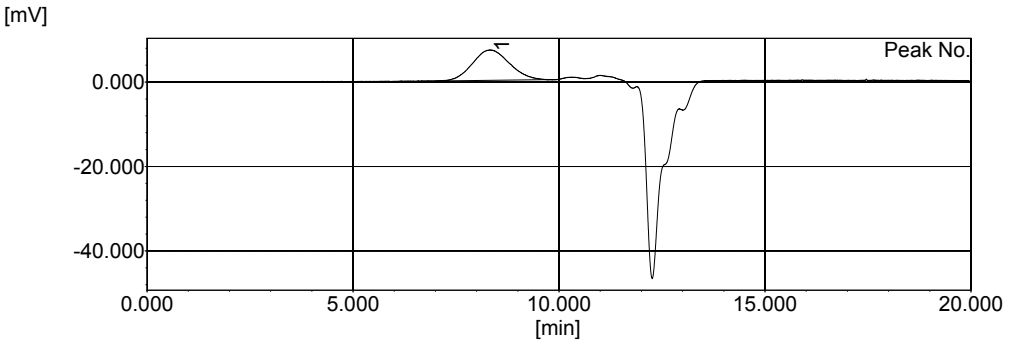


Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	5.298	0.290	1,921,066	Mn	239,643
Peak top	6.330	26.380	415,946	Mw	343,651
Peak end	8.043	1.230	32,769	Mz	433,808
				Mz+1	515,406
				Mv	343,651
Height [mV]			25.737	Mp	415,947
Area [mV*sec]			1333.399	Mz/Mw	1.262
Area% [%]			100.000	Mw/Mn	1.434
[eta]			343650.76479	Mz+1/Mw	1.500

Figure S20. GPC of the polymer from table 2, entry 8.



Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	6.660	0.228	254,965	Mn	16,785
Peak top	8.312	7.623	22,010	Mw	24,462
Peak end	9.723	0.584	2,712	Mz	35,529
				Mz+1	54,914
				Mv	24,462
Height [mV]			7.203	Mp	22,010
Area [mV*sec]			447.840	Mz/Mw	1.452
Area% [%]			100.000	Mw/Mn	1.457
[eta]			24462.02343	Mz+1/Mw	2.245

Figure S21. GPC of the polymer from table 2, entry 11.