Supporting Information for

Design and synthesis of binuclear vanadium catalysts for copolymerization of ethylene and polar monomers

Jinxin Nie, Feiyang Ren, Zhen Li, Kun Tian, Hui Zou* and Xiaohua Hou*

Department of Polymer Science and Engineering, School of Chemistry and Chemical Engineering, and Anhui Key Laboratory of Advanced Catalytic Materials and Reaction Engineering, Hefei University of Technology, 193 Tunxi Road, Hefei 230009, Anhui Province, People's Republic of China.

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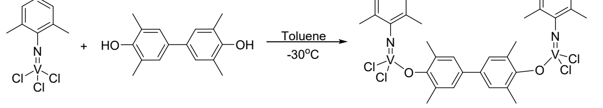
1. Materials and measurements

All experiments were carried out under a nitrogen atmosphere in a vacuum atmospheres drybox. The solvent of toluene and *n*-hexane were freshly distilled from Na/benzophenone ketyl. The solvent of dichloromethane was dried by reflux at the presence of CaH_2. The solvents were transferred into a bottle containing molecular sieves in the drybox under N_2. $AlEt_2Cl$ (n-hexane solution, 1M) was purchased from TCI. Polymerization grade ethylene (purity >99.9%) was used as received.

The ^1H and ^{13}C NMR spectra were recorded using a Bruker 600 MHz or 400 MHz {H} spectrometer operated in the Fourier Transform mode. Chemical shifts δ are reported downfield from tetramethylsilane using the residual proton solvent as an internal standard. Coupling constants are given in Hz. Elemental analyses were performed by using an Vario EL cube elemental analyzer (Elementar Inc.). Gel permeation chromatography (GPC) analyses of the molecular weight and molecular weight distribution of the (co)polymers at 150 °C were performed on a high temperature chromatograph, PL-GPC 220 instrument equipped with a triple detection array, including a differential refractive index (RI) detector, a two-angle light scattering (LS) detector, and a four-bridge capillary viscometer. Molecular weight (M_n) and polydispersity ($M_w/M_{n)}$ data are reported relative to polystyrene standards. Differential scanning calorimetric (DSC) measurements were carried on a Mettler-Toledo DSC 821e instrument. The starting material such as vanadium trichloride complex, $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_3$ was prepared from $VOCl_3$ by treatment with 2,6-dimethylphenyl isocyanate.

2. Synthesis of binuclear vanadium dichloride complexes

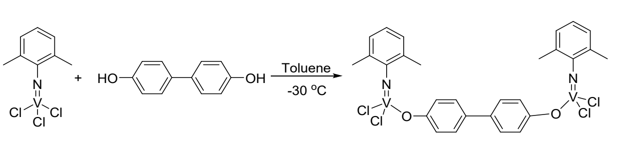
Synthesis of B1：



B1

A toluene solution (20 mL) containing $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_3$ (215 mg, 0.78 mmol) was placed at -30 °C for 2 hours. The 3,3',5,5'-tetramethylbiphenyl-4,4'-diol(94.5 mg, 0.39 mmol) was added into the solution and the reaction mixture was warmed slowly to room temperature with stirred for 12 h. The toluene was evaporated under reduced pressure. The resultant solid was dissolved in a minimum amount of CH_2Cl_2, and the solution was layered with *n*-hexane. The chilled solution placed in the freezer (−30°C) afforded black purple solid (263 mg, 93%). ^1H NMR ($CDCl_3$, 600 MHz, 25°C): δ 7.25 (s, 4H, Ar-*H*), 6.86 (br, 6H, NAr-*H*), 2.44 (s, 12H, NAr-*CH₃*), 2.37 (s, 12H, Ar-*CH₃*); ^{13}C NMR ($CDCl_3$, 101 MHz, 25°C): δ 17.1, 18.3, 126.0, 126.7, 127.4, 129.6, 137.3, 139.2, 161.8, 168.9. ^{51}V NMR ($CDCl_3$, 158 MHz) δ: 59.7 ($\Delta\nu_{1/2}$ = 540 Hz). Anal. Calcd(%) for $C_{32}H_{34}Cl_4N_2O_2V_2$: C, 53.21; H, 4.74; N, 3.88. Found (%): C, 53.49; H, 4.88; N, 3.72.

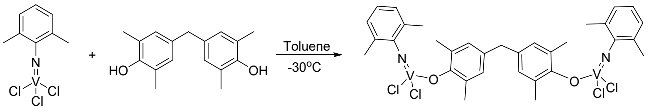
Synthesis of B2：



B2

Synthesis of **B2** was carried out by the same procedure as that in **B1** except that vanadium trichloride complex **S1** (300 mg, 1.08 mmol) and 4,4'-biphenol (101 mg, 0.54 mmol) was used. Recrystallization afforded the black brown powder (127 mg, 35%). ^1H NMR ($CDCl_3$, 600 MHz, 25°C): δ 7.48 (d, *J* = 5.2 Hz, 4H, Ar-*H*), 7.16 (d, *J* = 5.2 Hz, 4H, Ar-*H*), 6.90(s, 6H, NAr-*H*), 2.61(s, 12H, -*CH₃*). ^{13}C NMR ($CDCl_3$, 101 MHz, 25°C): δ 18.6, 116.9, 123.1, 127.5, 129.7, 139.6, 150.4, 152.5, 162.7. ^{51}V NMR ($CDCl_3$, 158 MHz) δ: 24.8 ($\Delta\nu_{1/2}$ = 552 Hz). Anal. Calcd. (%) for $C_{28}H_{26}Cl_4N_2O_2V_2$: C, 50.48; H, 3.93; N, 4.20. Found (%): C, 50.68; H, 4.16; N, 4.06.

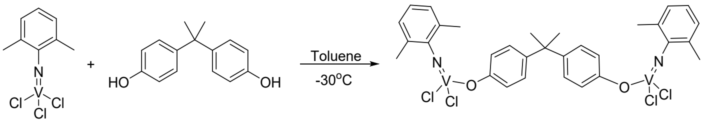
Synthesis of B3：



B3

Synthesis of **B3** was carried out by the same procedure as that in **B1** except that 4,4-methenedi(2,6-methylbiphenol) (100 mg, 0.39 mmol) in place of 3,3',5,5'-Tetramethylbiphenyl-4,4'-diol was used. Recrystallization obtained brown black solid (244 mg, 85%).^{1}H NMR ($CDCl_3$, 600 MHz, 25°C): δ 6.79 (m, 10H, Ar-*H*), 3.80(s, 2H, -CH_2-), 2.36 (s, 12H, -CH_3), 2.21 (br, 12H, -CH_3). ^{13}C NMR ($CDCl_3$, 101 MHz, 25 °C): δ 16.8, 18.1, 40.6, 125.3, 127.3, 128.6, 129.5, 138.7, 139.0, 167.7. ^{51}V NMR ($CDCl_3$, 488 MHz) δ: 53.7 ($\Delta v_{1/2}$ = 509 Hz). Anal. Calcd. (%) for $C_{33}H_{36}Cl_4N_2O_2V_2$: C, 53.83; H, 4.93; N, 3.80. Found (%): C, 54.01; H, 5.11; N, 3.66.

Synthesis of B4：



B4

Synthesis of **B4** was carried out by the same procedure as that in **B1** except that BPA (89 mg, 0.39 mmol) in placed. Recrystallization gave the formation of brown black powder. (247 mg, 89%). ^{1}H NMR ($CDCl_3$, 600 MHz, 25°C): δ 7.05 (d, *J* = 8.4 Hz, 4H, Ar-H), 6.98 (d, *J* = 8.4 Hz, 4H, Ar-H), 6.87 (br, 6H, Ar-H), 2.56 (s, 12H, CH_3), 1.60(s, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 101 MHz, 25°C): δ 18.6, 30.7, 41.4, 114.9, 126.9, 127.3, 127.5, 129.1, 137.9, 148.8, 167.5. ^{51}V NMR ($CDCl_3$, 158 MHz) δ: 18.8 ($\Delta v_{1/2}$ = 600 Hz). Anal. Calcd. (%) for $C_{31}H_{32}Cl_4N_2O_2V_2$: C, 52.57; H, 4.55; N, 3.96. Found (%): C, 52.82; H, 4.58; N, 3.91.

3. Ethylene (co)polymerization procedure.

Polymerizations were performed in a 100 mL autoclave at required temperature. The polymerization apparatus equipped with magnetically bar was vacuumed and filled by N_2 for three times. Then Al cocatalyst solution was injected into the autoclave by a dry syringe to remove the residuals water and impurity in the autoclave. Then the comonomer and complex solution was sequentially added by syringe under N_2 protection. The total volume of the polymerization medium was fixed to specified volume. The ethylene was fed rapidly to the prescribed pressure and maintained at the desired constant pressure. The solution was vigorously stirred immediately. After a specified reaction time, the solution stirring was stopped and the remaining ethylene was purged. The polymerization solution was poured into ethanol to precipitate polymer or copolymer. The polymer was collected by filtration and dried in a vacuum oven at 60 °C.

4. NMR spectra of binuclear vanadium complexes

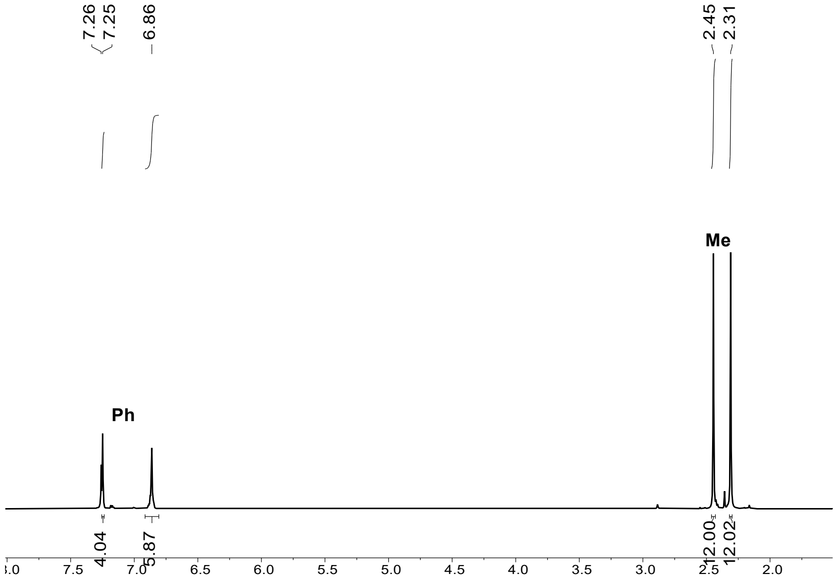


Figure S1. ^1H NMR spectrum of vanadium complex **B1** in $CDCl_3$.

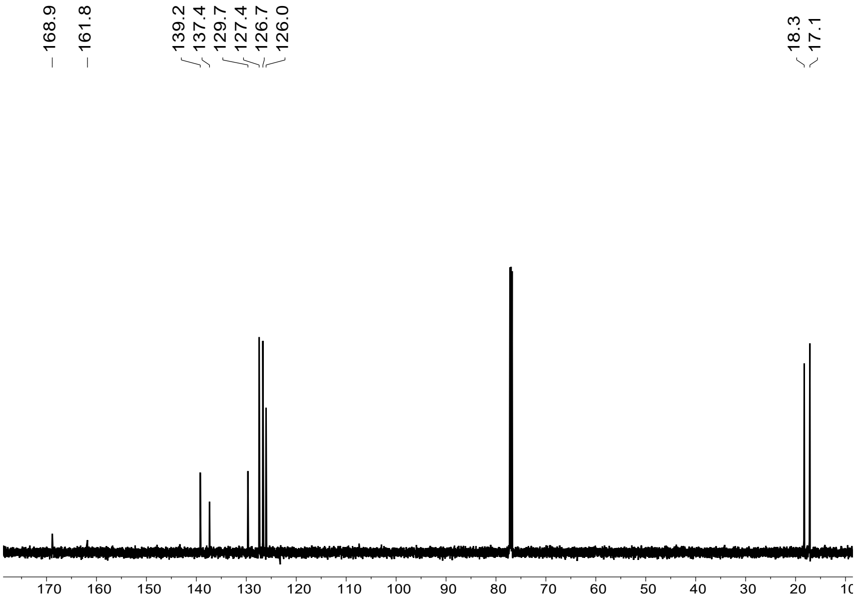


Figure S2. ^{13}C NMR spectrum of vanadium complex **B1** in $CDCl_3$.

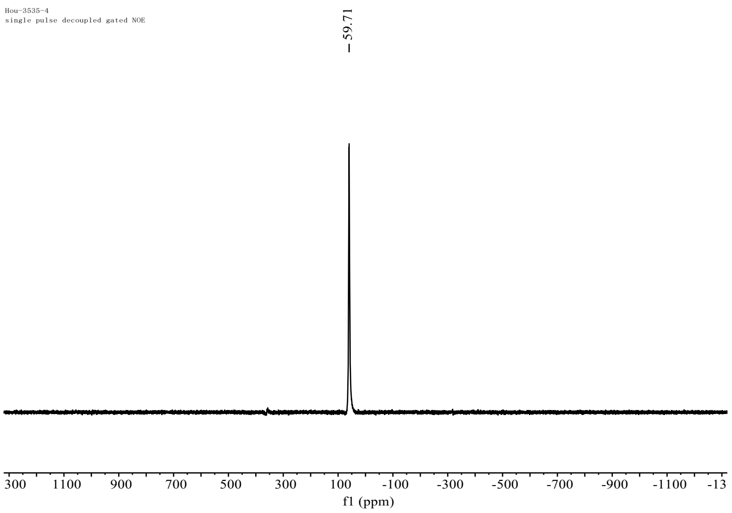


Figure S3. ^{51}V NMR spectrum of vanadium complex **B1** in $CDCl_3$.

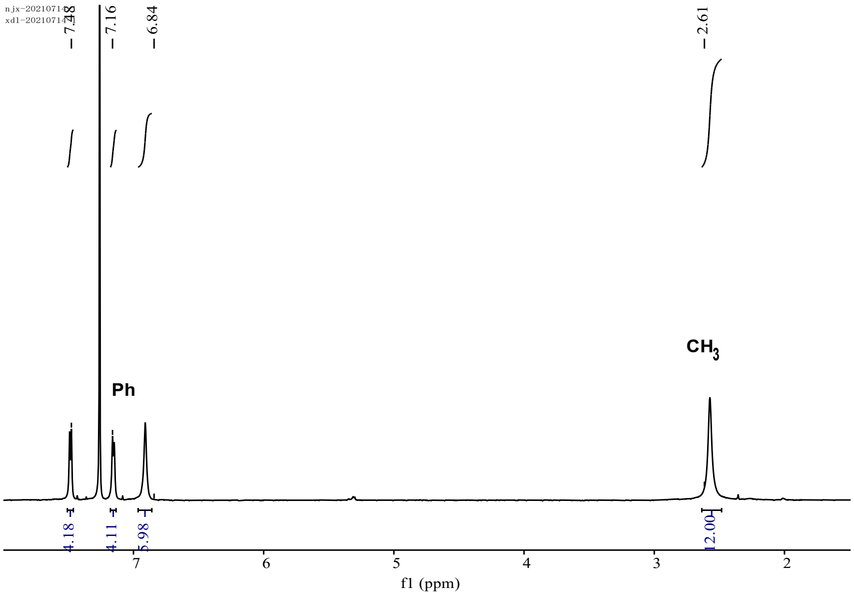


Figure S4. ^1H NMR spectrum of vanadium complex **B2** in $CDCl_3$.

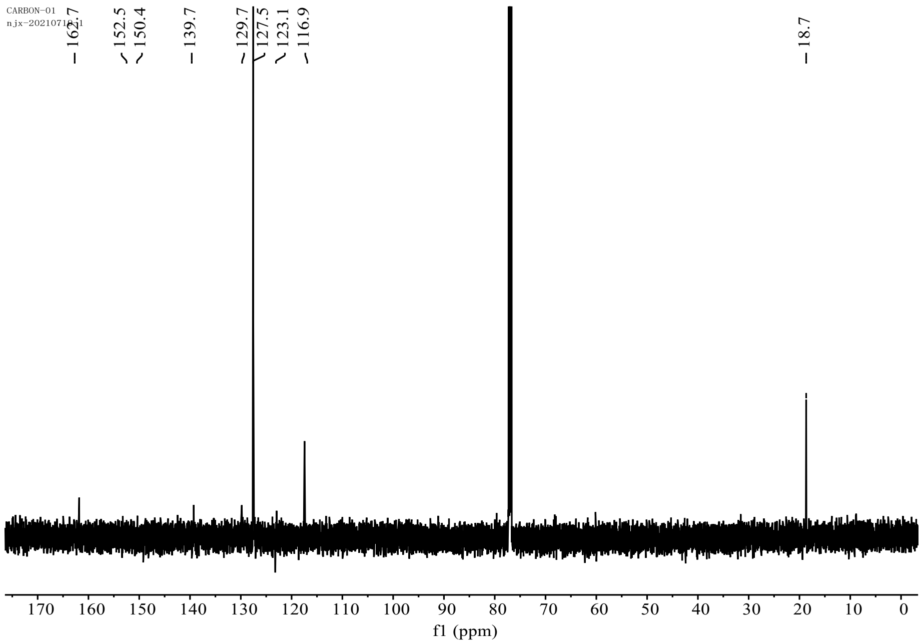


Figure S5. ^{13}C NMR spectrum of vanadium complex **B2** in $CDCl_3$.

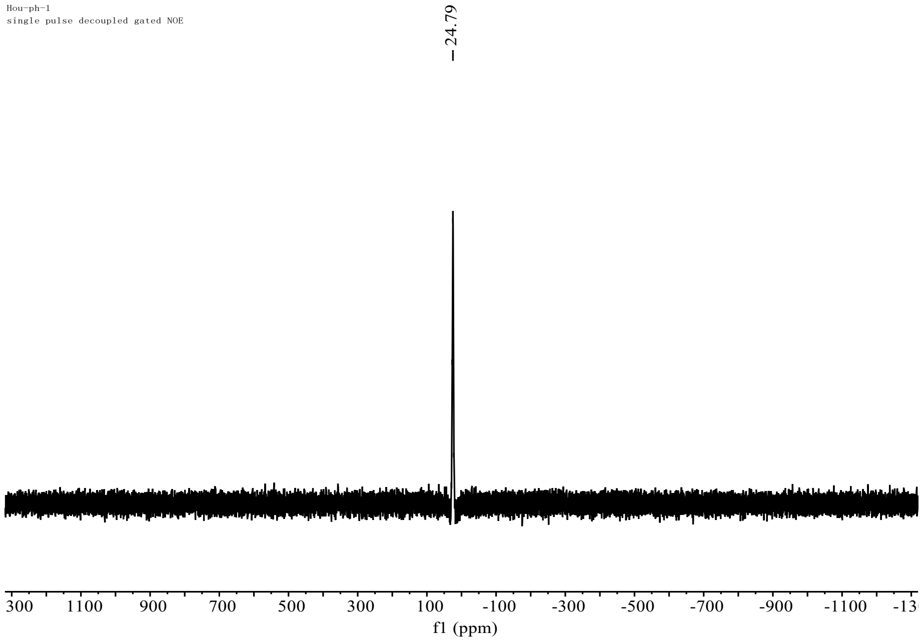


Figure S6. ^{51}V NMR spectrum of vanadium complex **B2** in $CDCl_3$.

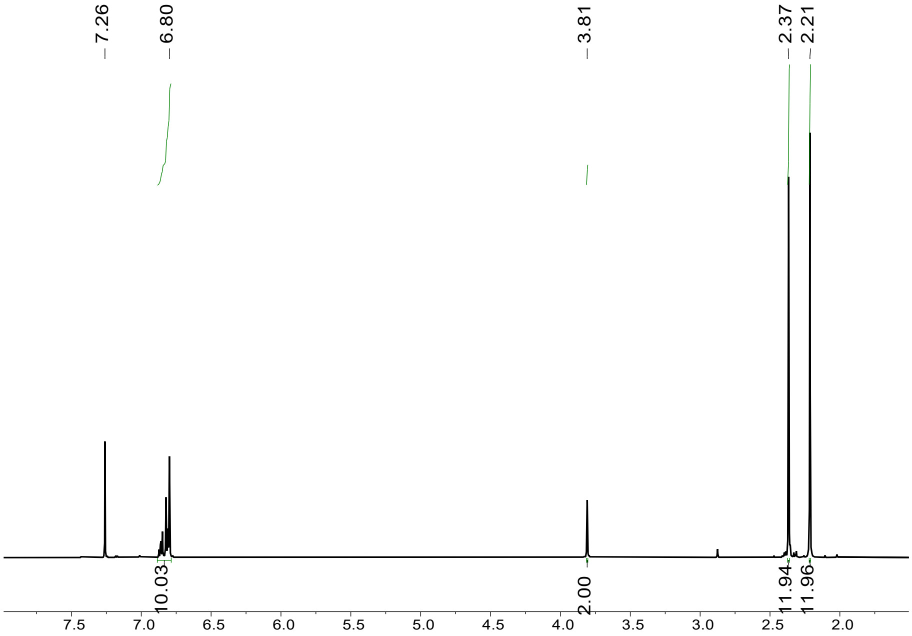


Figure S7. ^{1}H NMR spectrum of vanadium complex **B3** in CDCl$_3$.

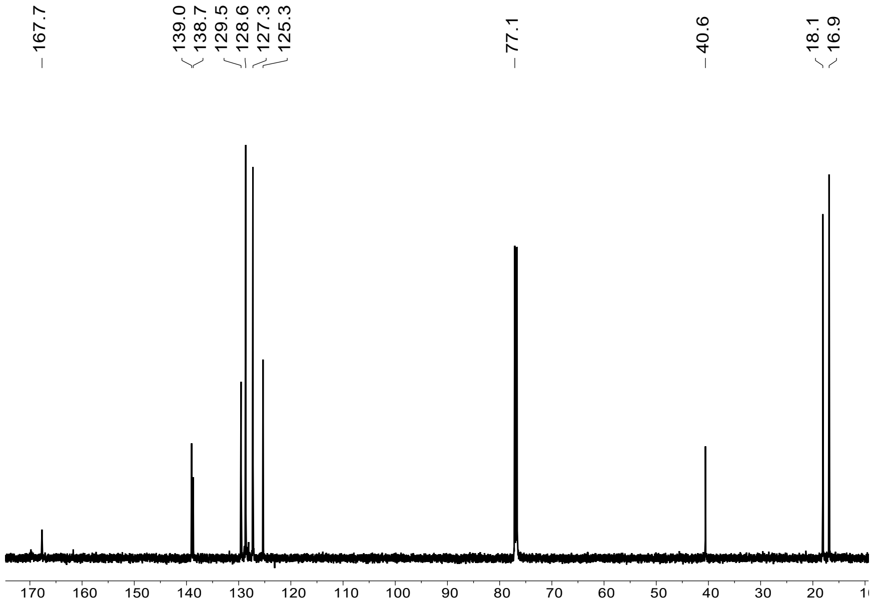


Figure S8. ^{13}C NMR spectrum of vanadium complex **B3** in CDCl$_3$.

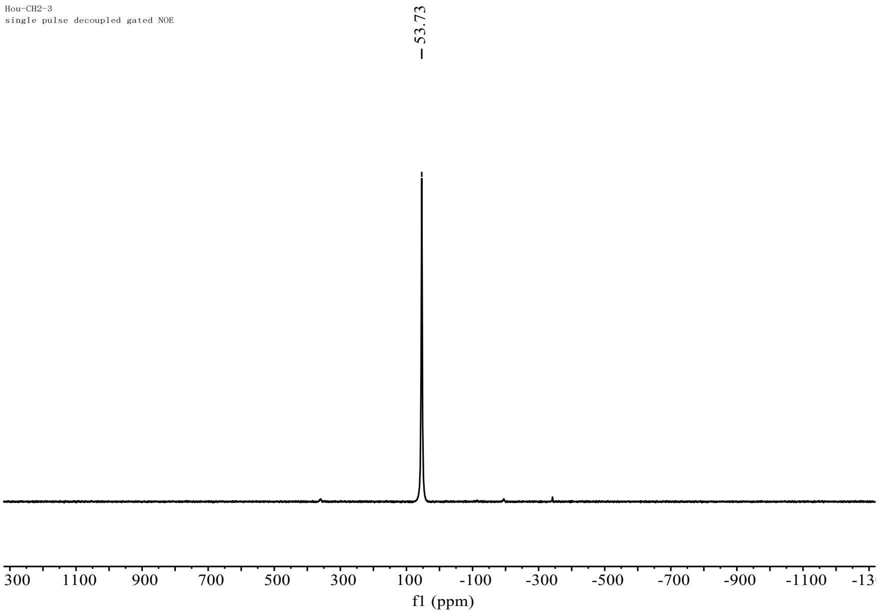


Figure S9. ^{51}V NMR spectrum of vanadium complex **B3** in $CDCl_3$.

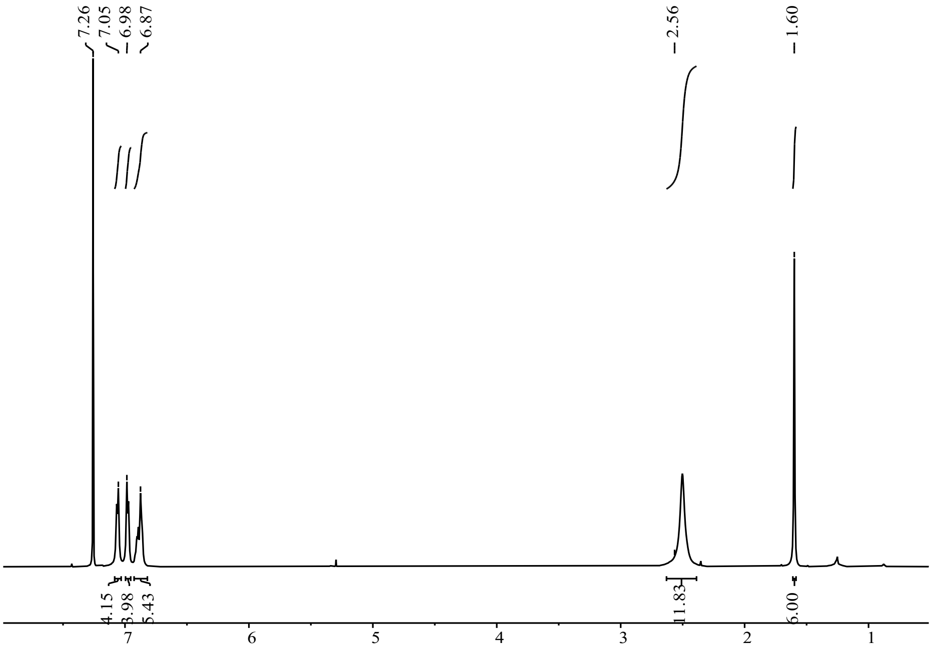


Figure S10. ^{1}H NMR spectrum of vanadium complex **B4** in $CDCl_3$.

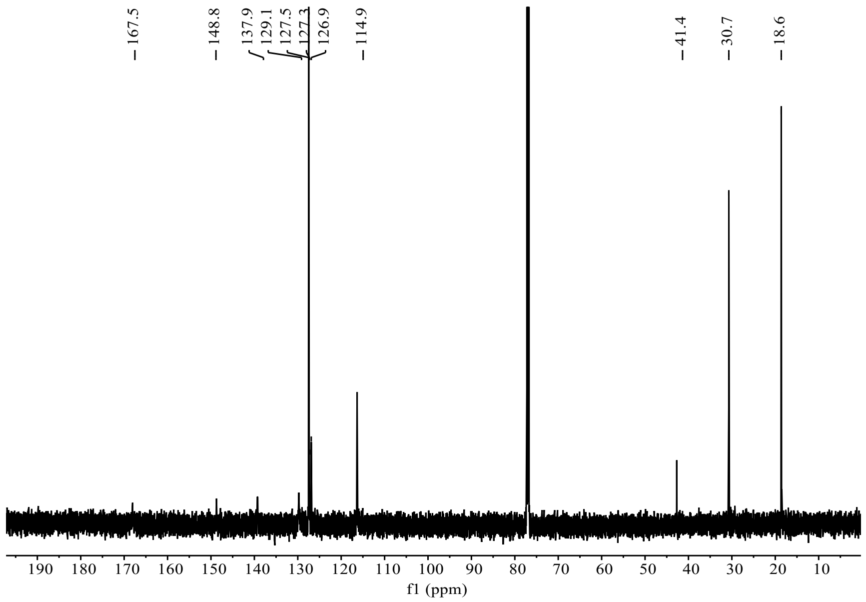


Figure S11. ^{13}C NMR spectrum of vanadium complex **B4** in $CDCl_3$.

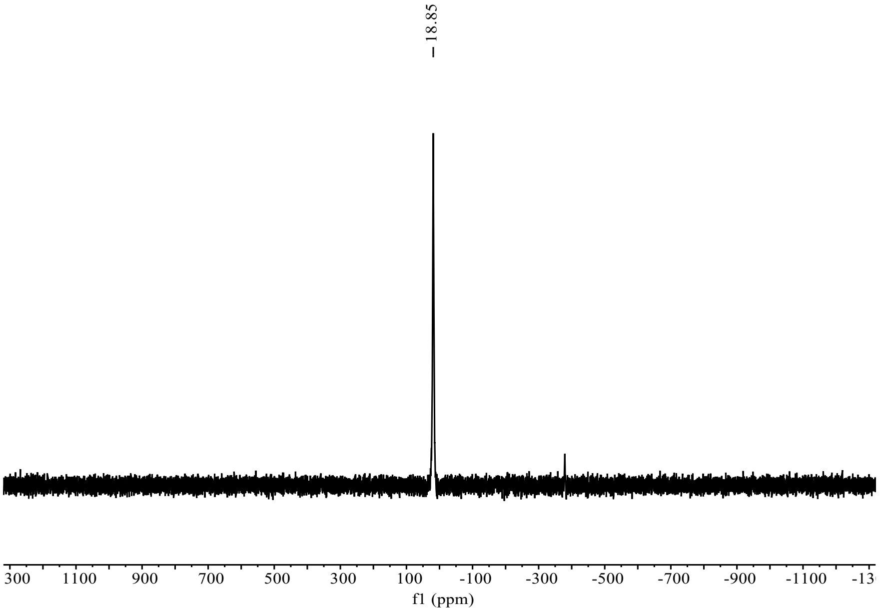


Figure S12. ^{51}V NMR spectrum of vanadium complex **B4** in $CDCl_3$.

5. NMR spectra of ethylene copolymer with various polar monomers

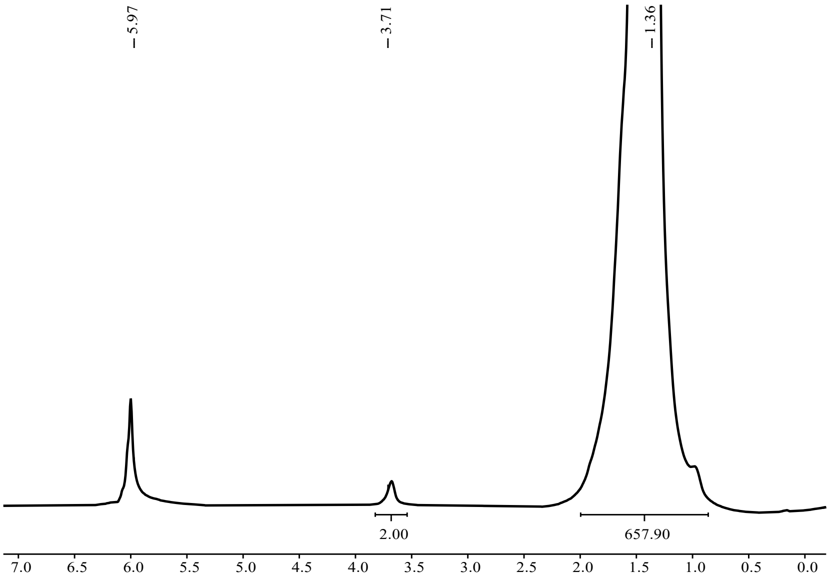


Figure S13. ^{1}H NMR spectrum of E/UOH copolymer by **B1** in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

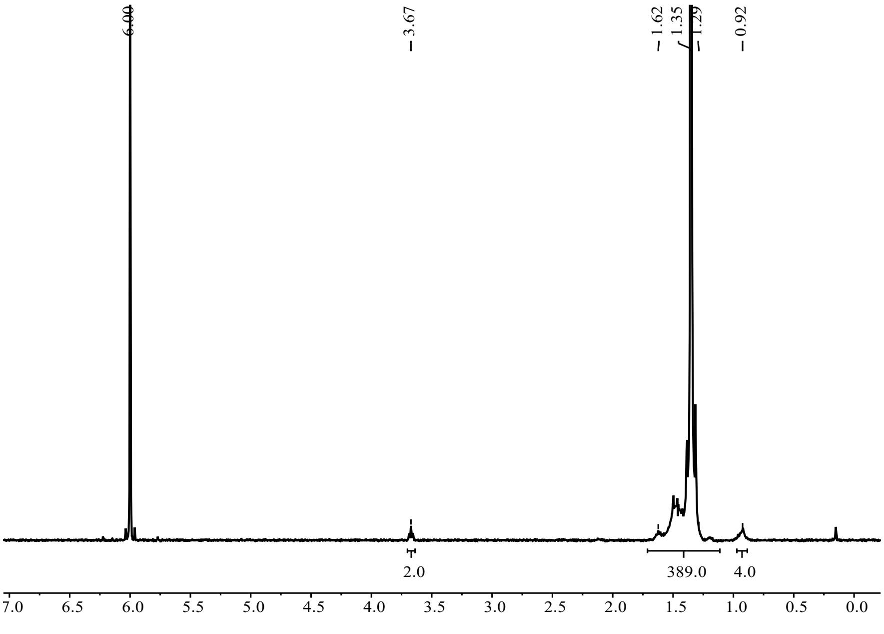


Figure S14. ^{1}H NMR spectrum of E/UOH copolymer by **B2** in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

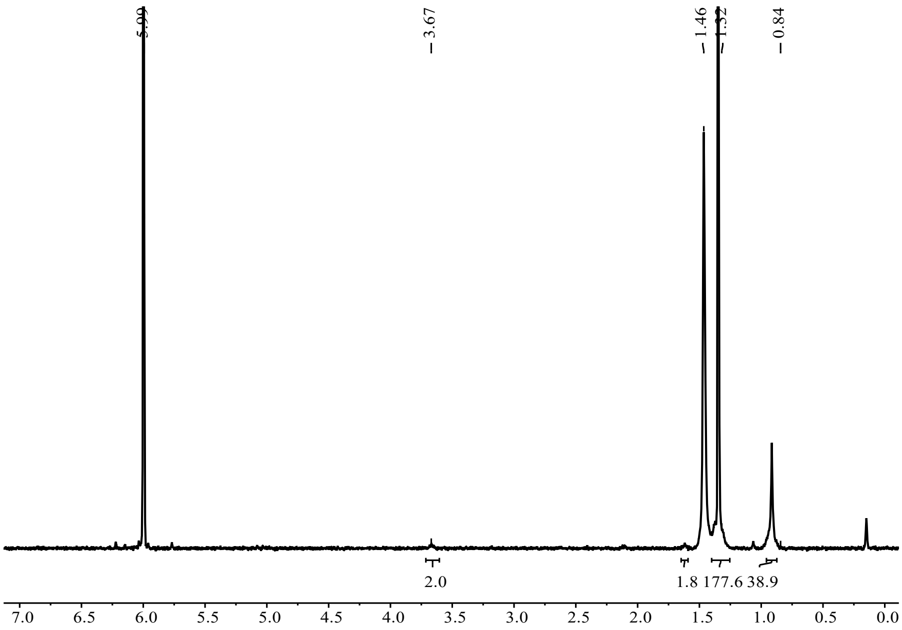


Figure S15. ^{1}H NMR spectrum of E/UOH copolymer by **B3** in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

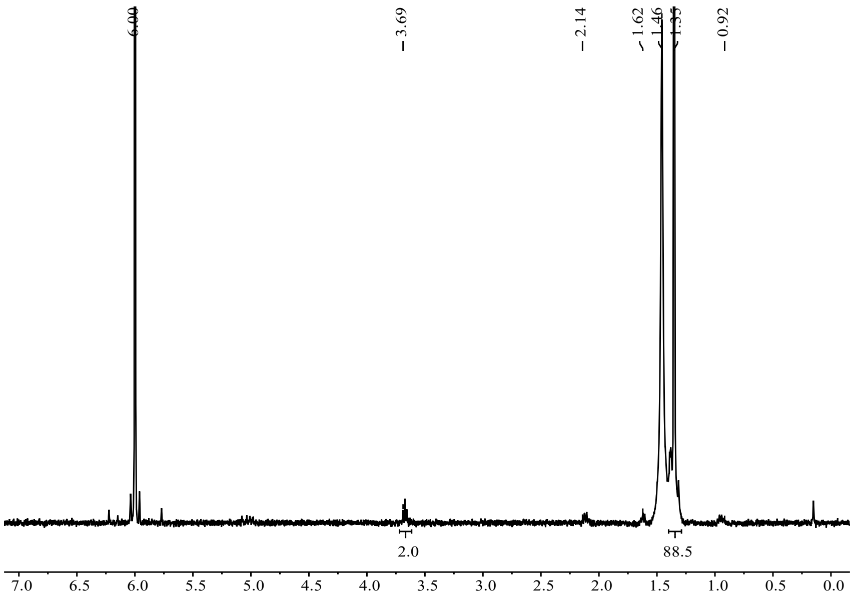


Figure S16. ^{1}H NMR spectrum of E/UOH copolymer by **B4** in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

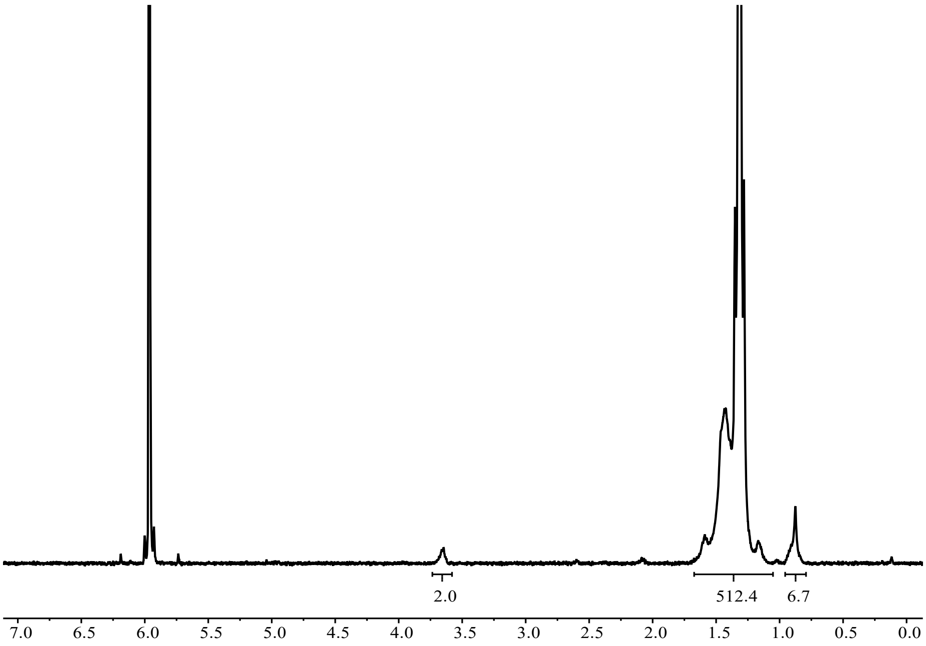


Figure S17. ^{1}H NMR spectrum of E/UOH copolymer by **M2** in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

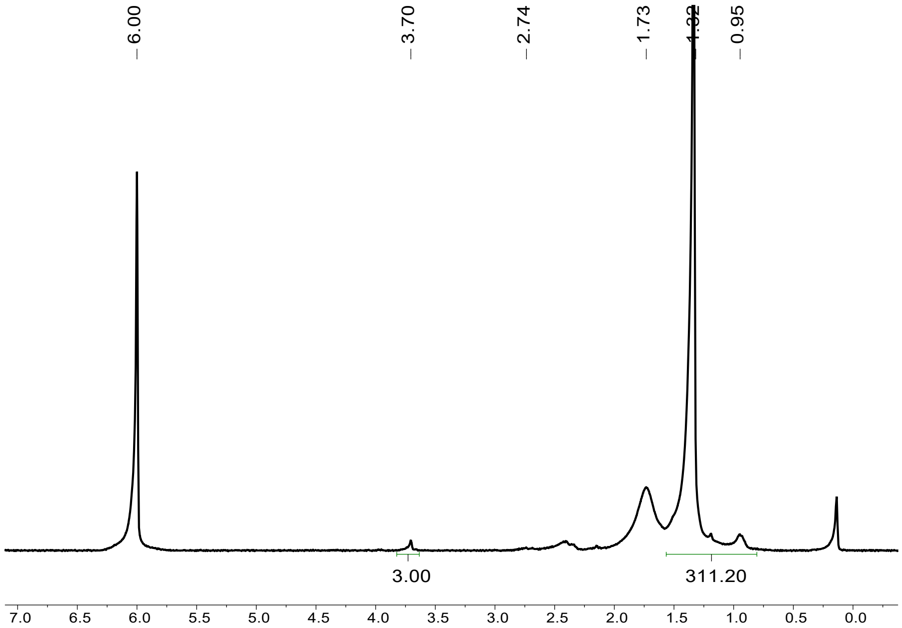


Figure S18. ^{1}H NMR spectrum of E/UA copolymer by **B1** in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

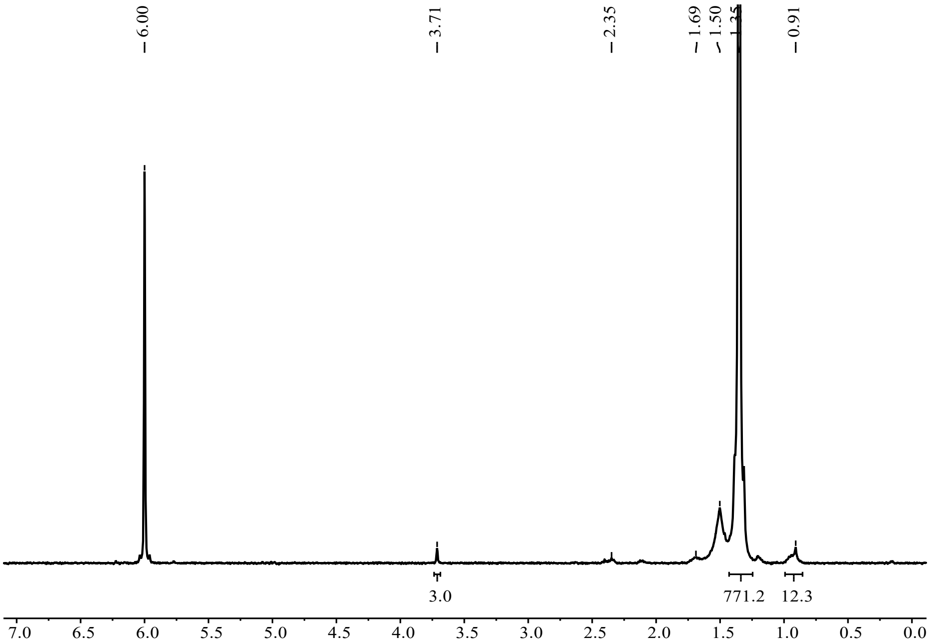


Figure S19. ^{1}H NMR spectrum of E/UA copolymer by **B2** in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

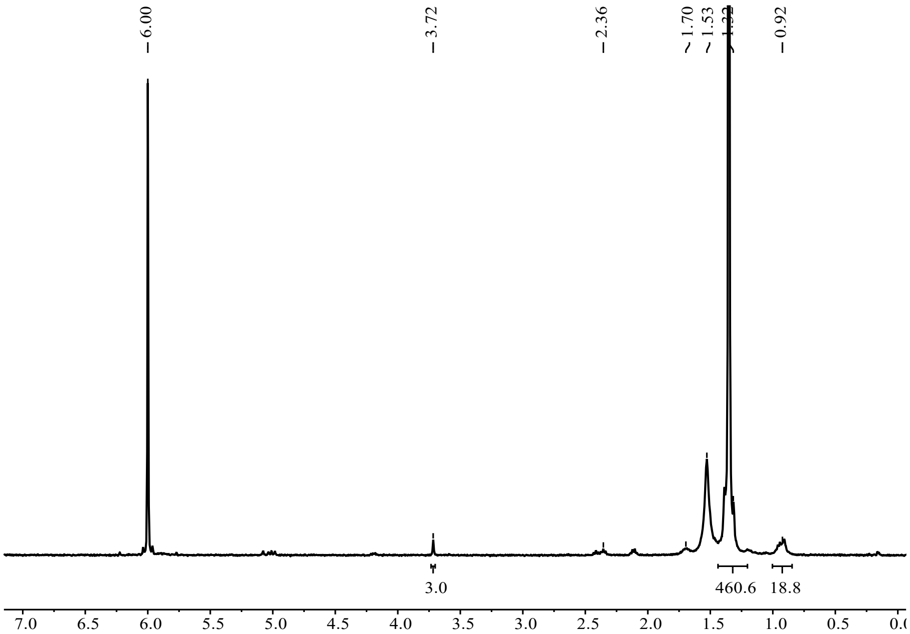


Figure S20. ^{1}H NMR spectrum of E/UA copolymer by **B3** in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

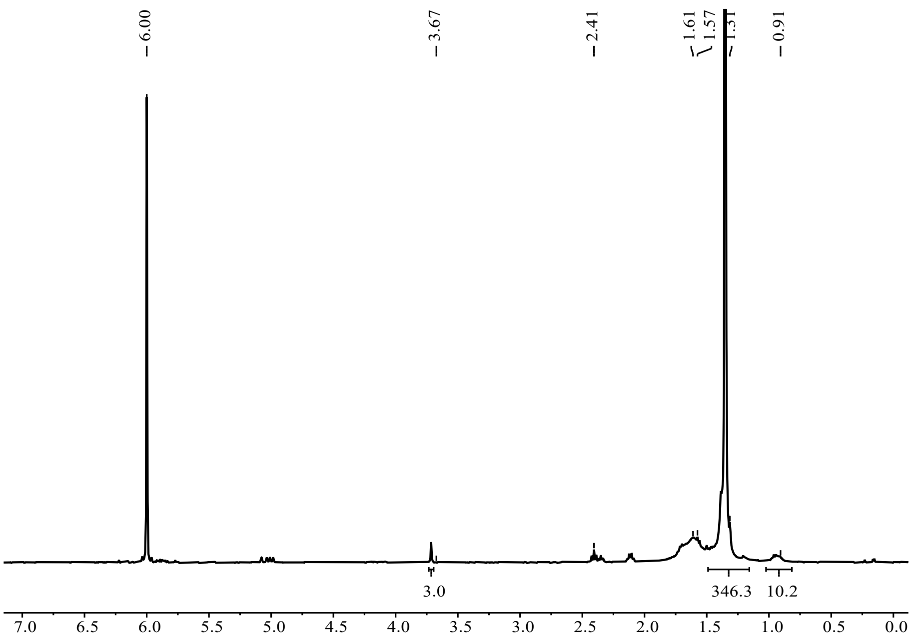


Figure S21. ^{1}H NMR spectrum of E/UA copolymer by **B4** in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

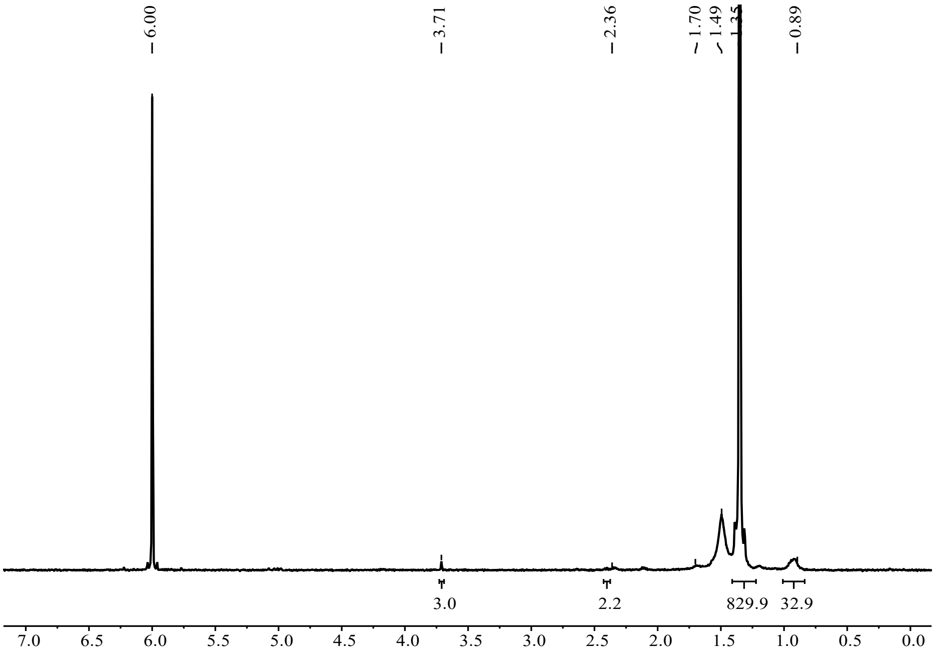


Figure S22. ^{1}H NMR spectrum of E/UA copolymer by **M2** in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

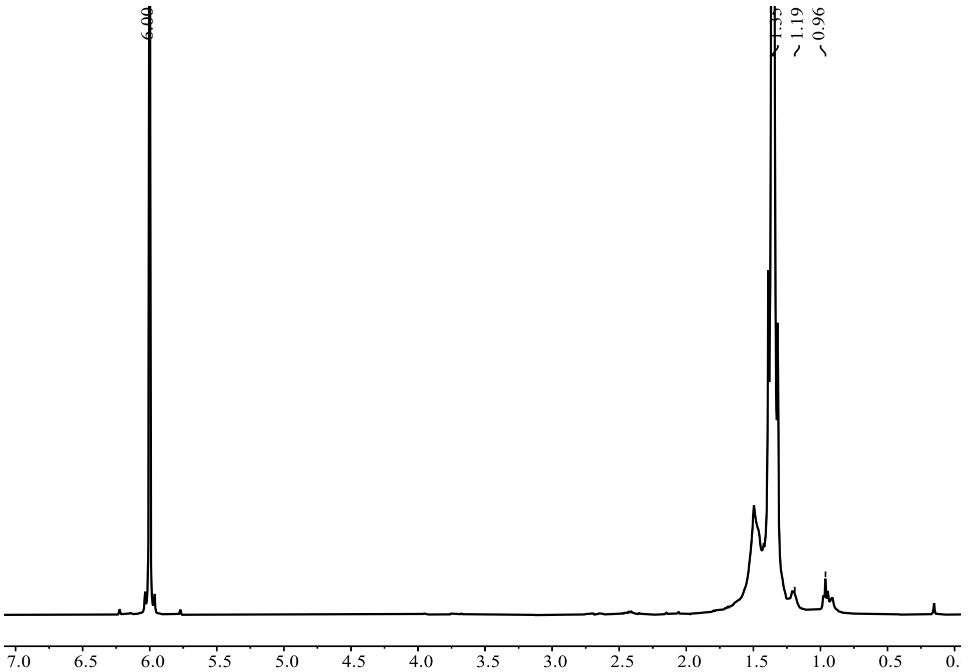


Figure S23. ^{1}H NMR spectrum of E/MA polymer by **B1** in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

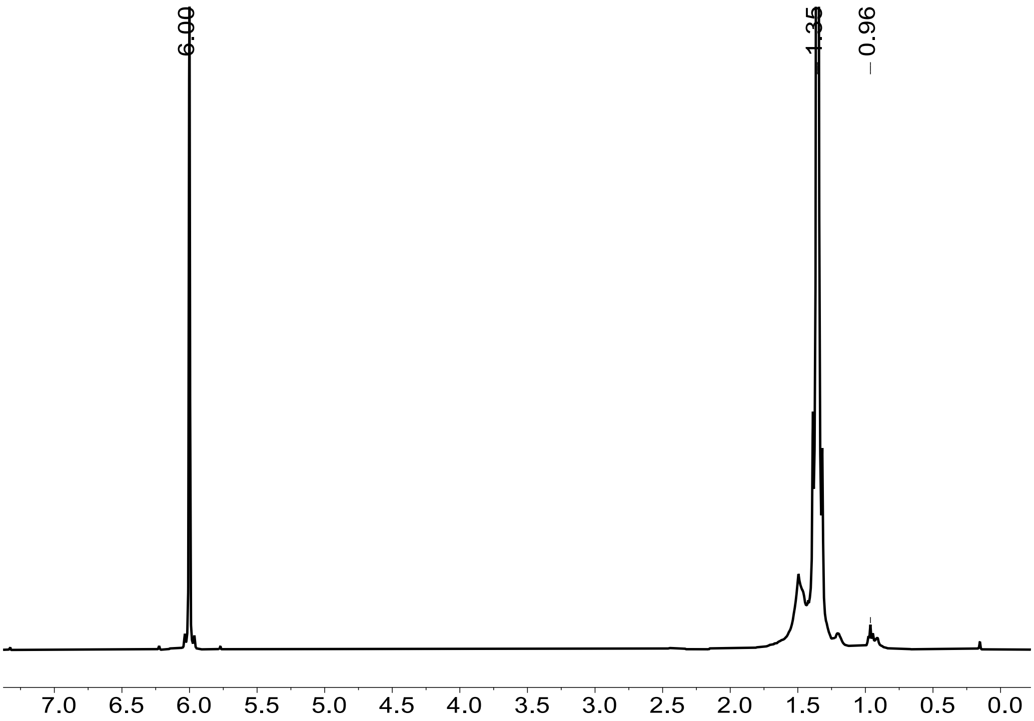
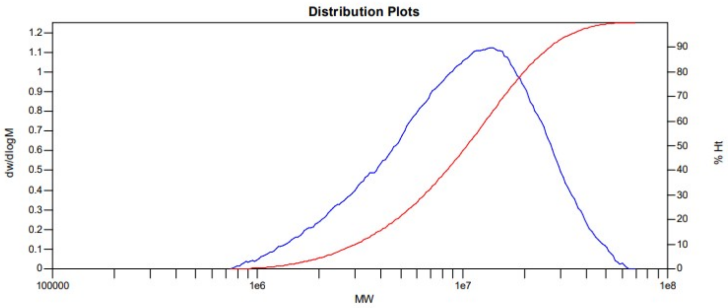


Figure S24. ^{1}H NMR spectrum of E/MMA polymer by **B1** in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

6. GPC curves of polymers



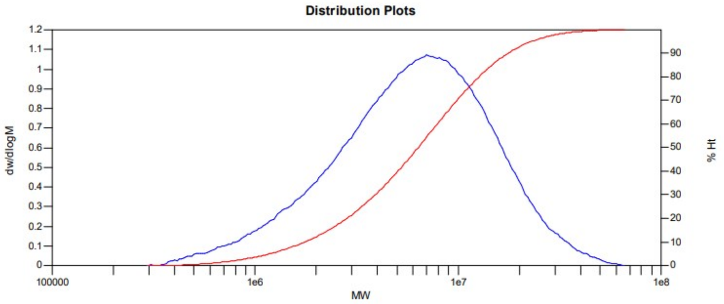
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	13841315	6572154	12872847	20327980	27327556	11823728	1.9587

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		9.27	10.37	12.37	-3.23008	0	271.221	100

Figure S25. GPC chart of polyethylene obtained by **B1** (Table 1, run 2).



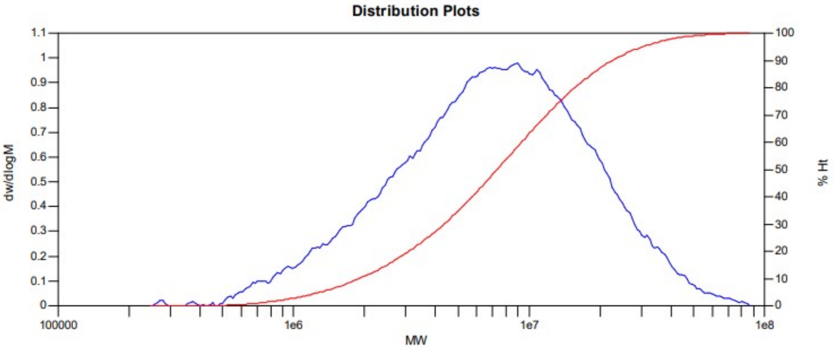
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	6986824	3798490	8324637	14713665	22135715	7520563	2.19156

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		9.30	10.83	13.00	-5.58735	0	491.171	100

Figure S26. GPC chart of polyethylene obtained by **B1** (Table 1, run 4).



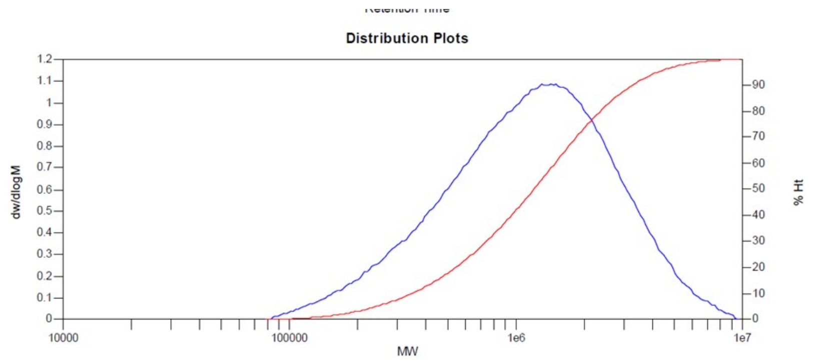
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	8918969	4264514	10280207	19836947	31224501	9138648	2.41064

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		9.12	10.67	13.12	-1.80715	0	174.298	100

Figure S27. GPC chart of E/Cl-Hex copolymer obtained by **B1** (Table 2, run 3)



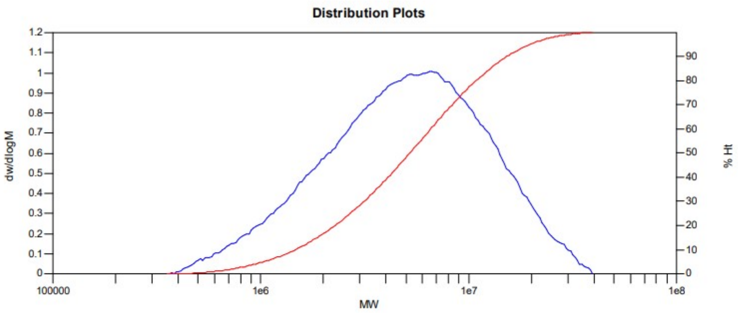
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1499471	756139	1543869	2611592	3753978	1404533	2.04178

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.22	11.65	13.65	-2.85041	0	258.546	100

Figure S28. GPC chart of polyethylene obtained by **M2** (Table 2, run 4).



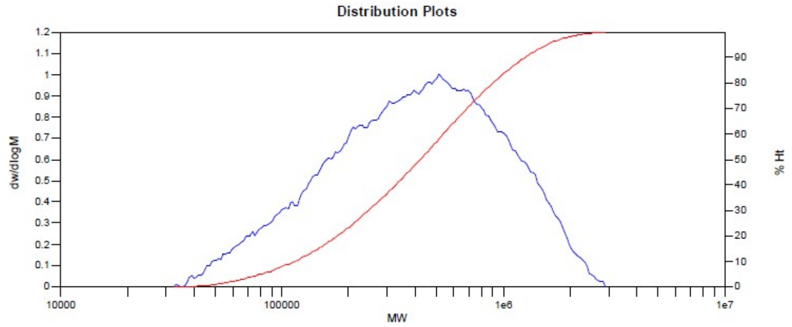
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	6493358	3248917	6951263	12087798	17176922	6278091	2.13956

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		9.65	10.88	12.87	-2.34438	0	219.077	100

Figure S29. GPC chart of E/UOH copolymer obtained by **B1** (Table 2, run 6)



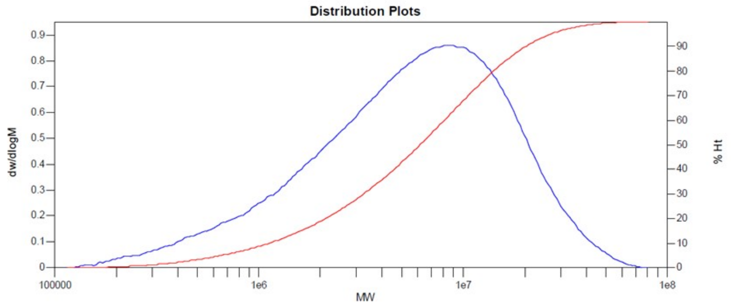
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	511464	260529	560361	953576	1302861	506533	2.15086

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		11.08	12.32	14.28	-1.16453	0	114.547	100

Figure S30. GPC chart of E/UOH copolymer obtained by **M2** (Table 2, run 11)



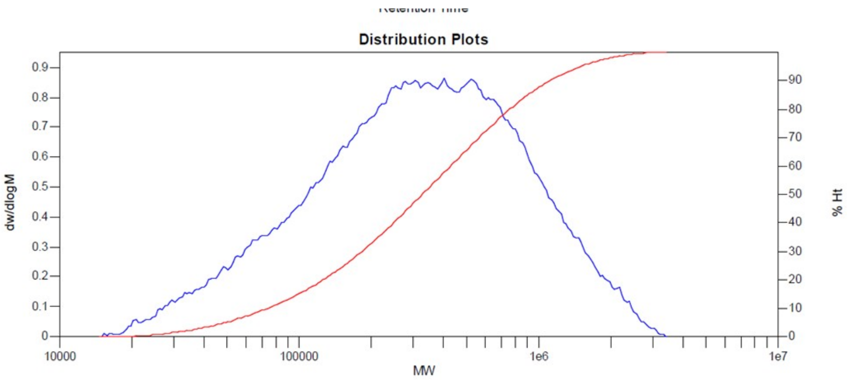
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	8703845	2583943	8796330	17524548	26427013	7681533	3.40423

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		9.17	10.68	13.63	-6.56634	0	718.764	100

Figure S31. GPC chart of E/UA copolymer obtained by **B1** (Table 2, run 12)



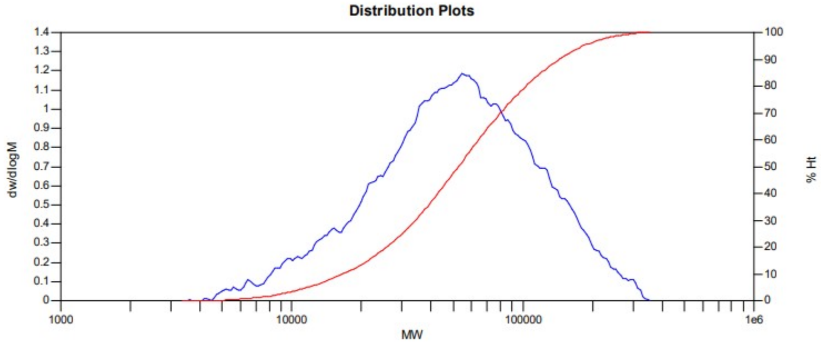
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	404824	175123	479765	944968	1402433	421450	2.73959

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.97	12.68	14.85	-1.22916	0	141.263	100

Figure S32. GPC chart of E/UA copolymer obtained by **M2** (Table 2, run 17).



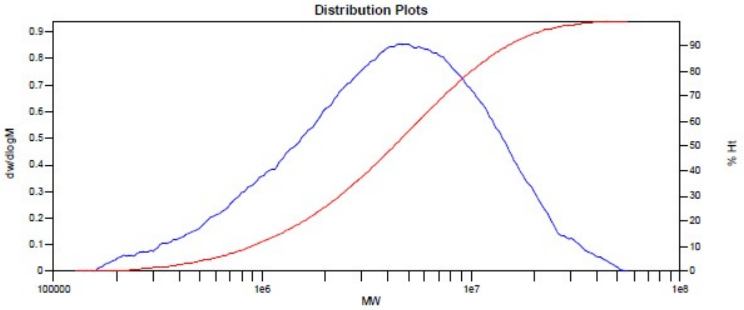
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	54223	35229	67819	111174	155334	62082	1.92509

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		12.87	14.15	16.05	-1.31874	0	104.93	100

Figure S33. GPC chart of polymer obtained by **B1** at the presence of MA (Table 3, run 1).



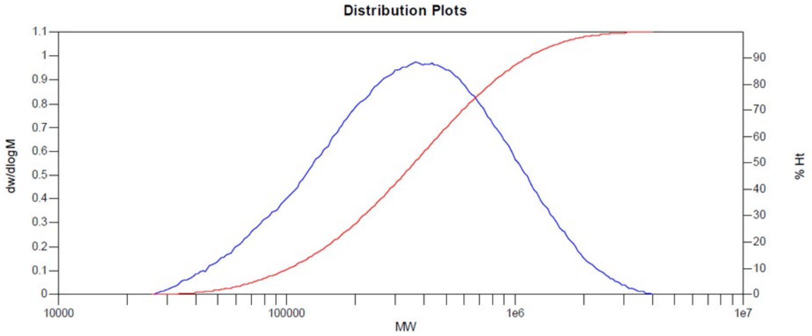
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	4613394	2081121	6394577	13392540	21051869	5559358	3.07266

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		9.42	11.12	13.57	-3.9586	0	436.61	100

Figure S34. GPC chart of polymer obtained by **M2** at the presence of MA (Table 3, run 7).



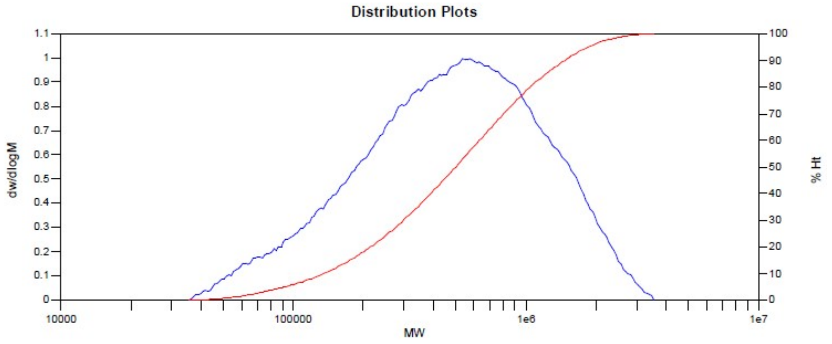
MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	368678	228969	506699	945078	1435367	453199	2.21296

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.85	12.55	14.45	-3.28538	0	332.128	100

Figure S35. GPC chart of polymer obtained by **M2** at the presence of MMA (Table 3, run 8).



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	574896	304741	663260	1132000	1562698	599646	2.17647

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		10.93	12.23	14.22	-1.81617	0	179.455	100

Figure S36. GPC chart of polymer obtained by **M2** at the presence of MMA (Table 3, run 9).

7. DSC Charts of Polymers

Differential scanning calorimetric (DSC) analysis was performed using a DSC Q2000 (TA Instruments). The temperature and heat flow of the apparatus were calibrated with an indium standard. Polymer samples were first equilibrated at 25 °C, followed by heating from -50 °C to 200 °C at a rate of 10 °C/min under N_2 flow (50 mL/min). This temperature was maintained for 5 min then samples were cooled to -50 °C at a rate of 10 °C/min. This temperature was maintained for 5 min then samples were reheated to 200 °C at a rate of 10 °C/min. The melting temperature (T_m) was determined from the second heating scan. The percent crystallinity was calculated from ΔH_f (J/g)/ΔH_{std} (J/g), where ΔH_{std} is the heat of fusion for a perfectly crystalline polyethylene; this equals to 293.0 J/g

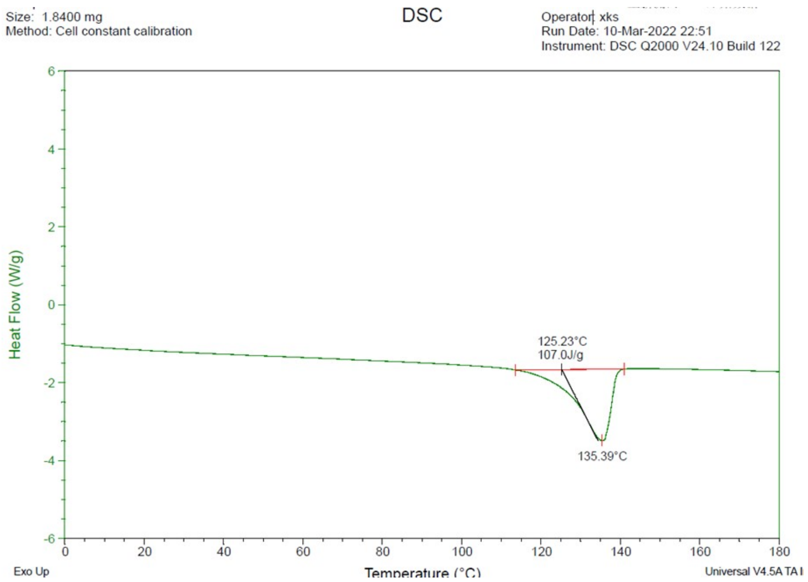


Figure S37. DSC chart of polyethylene obtained by **B1**.

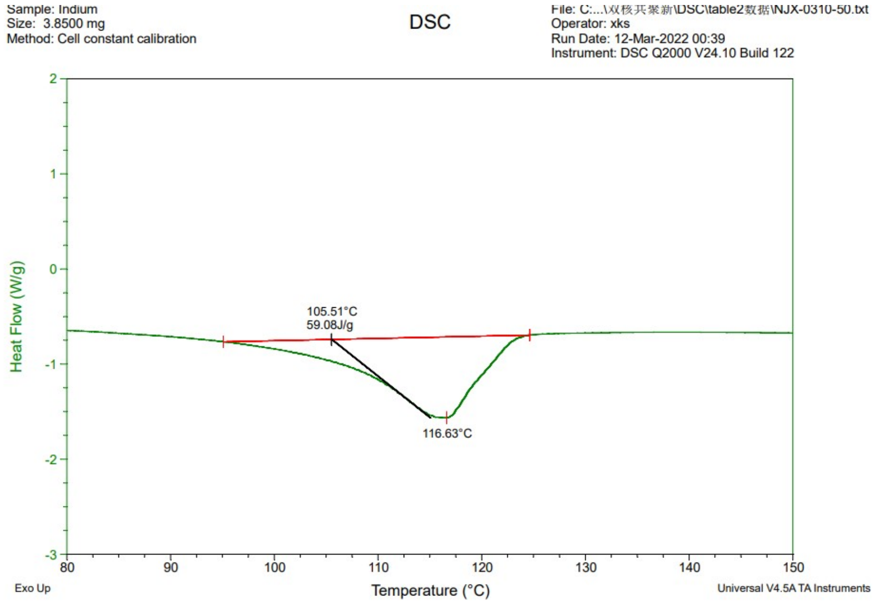


Figure S38. DSC chart of E/Cl-Hex copolymer obtained by **B1** (Table 2, run 3)

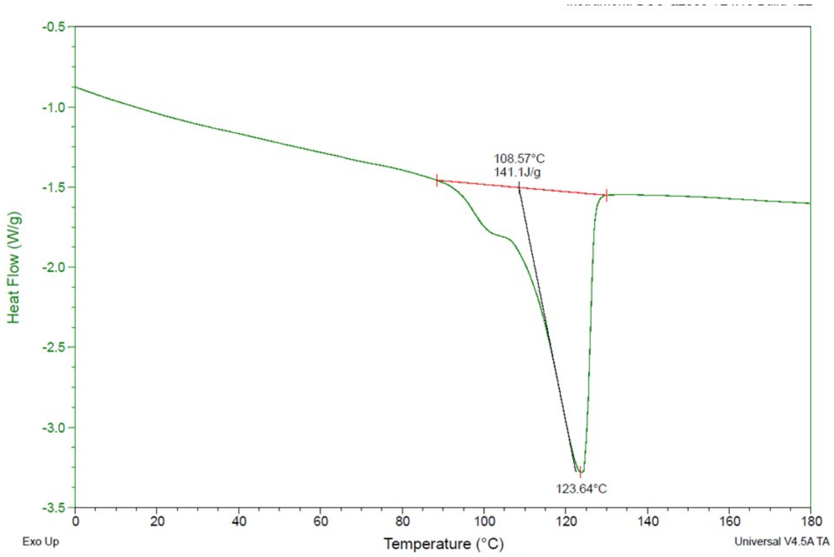


Figure S39. DSC chart of E/UOH copolymer obtained by **B1** (Table 2, run 6)

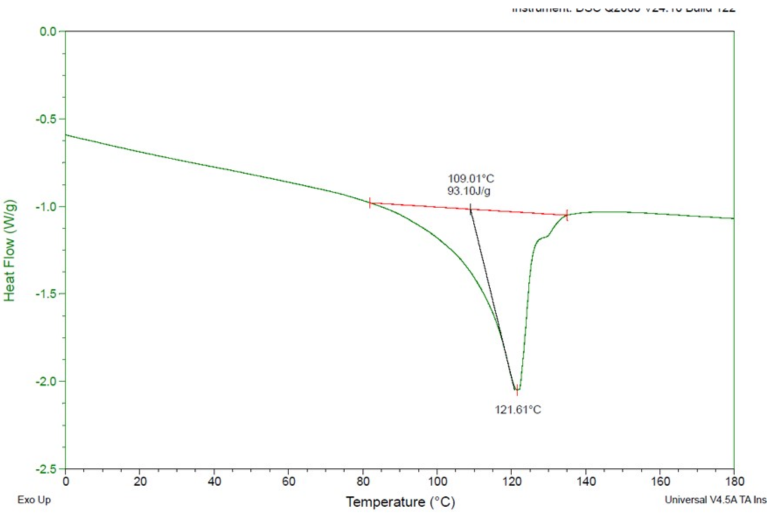


Figure S40. DSC chart of E/UOH copolymer obtained by **B2** (Table 2, run 8)

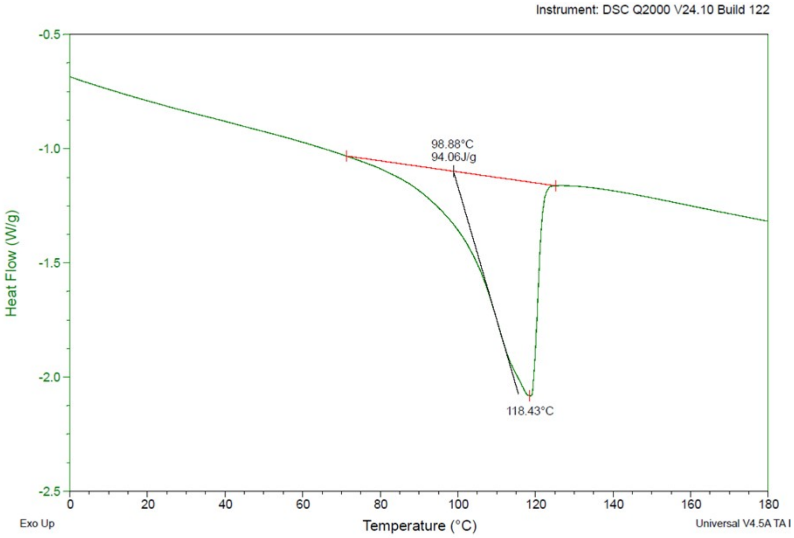


Figure S41. DSC chart of E/UOH copolymer obtained by **B3** (Table 2, run 9)

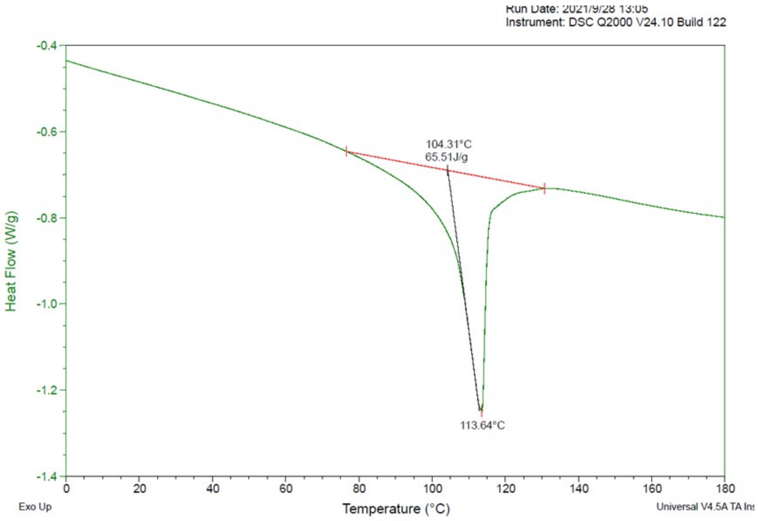


Figure S42. DSC chart of E/UOH copolymer obtained by **B4** (Table 2, run 10)

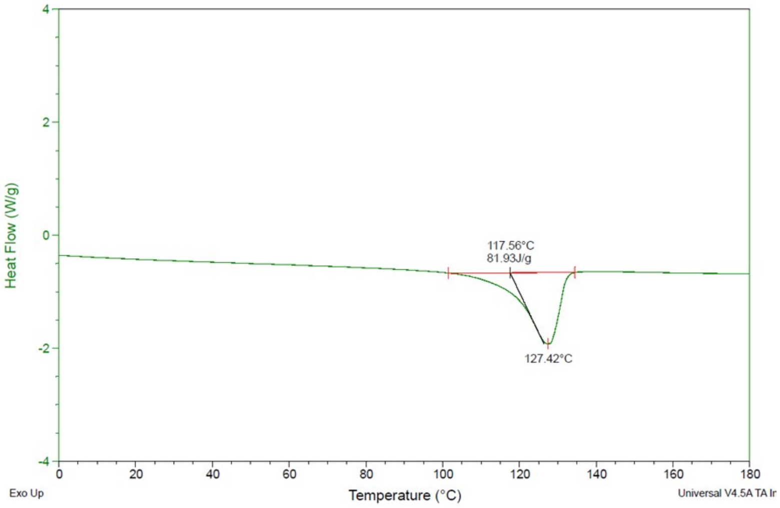


Figure S43. DSC chart of E/UA copolymer obtained by **B1** (Table 2, run12)

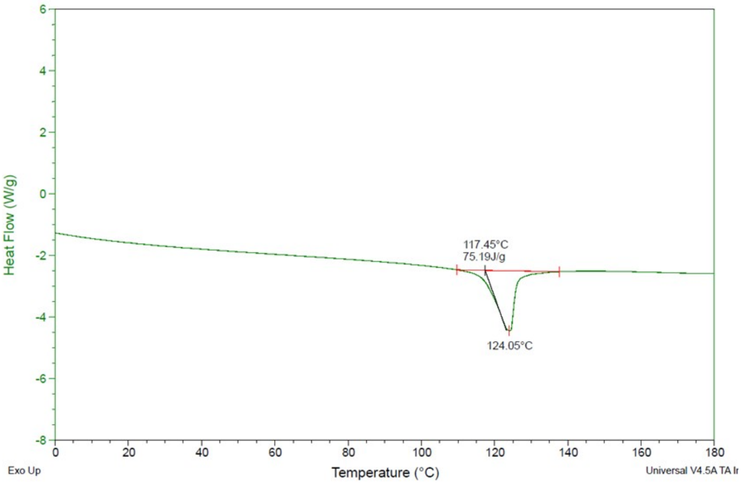


Figure S44. DSC chart of E/UA copolymer obtained by **B1** (Table 2, run 13)

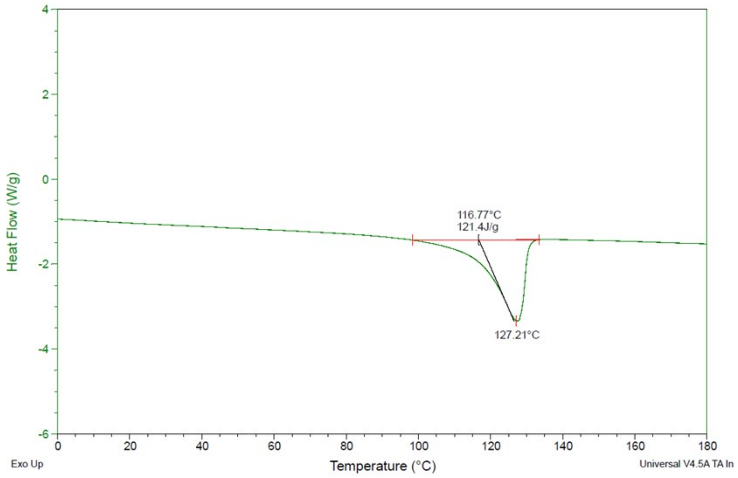


Figure S45. DSC chart of E/UA copolymer obtained by **B2** (Table 2, run 14)

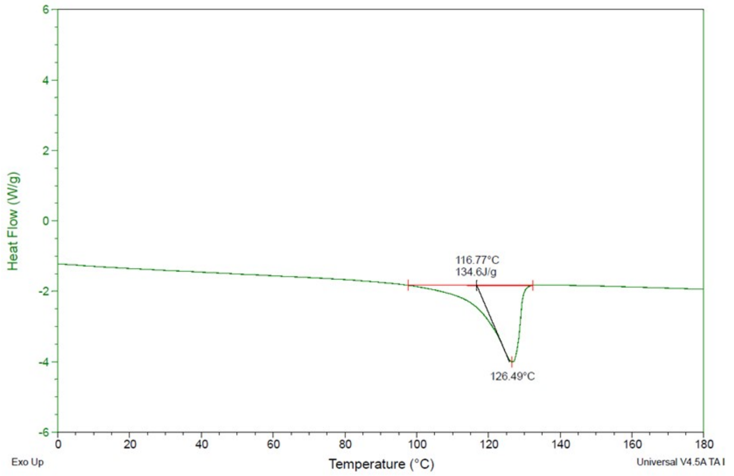


Figure S46 DSC traces of E/UA copolymer obtained by **B3** (Table 2, run 15)

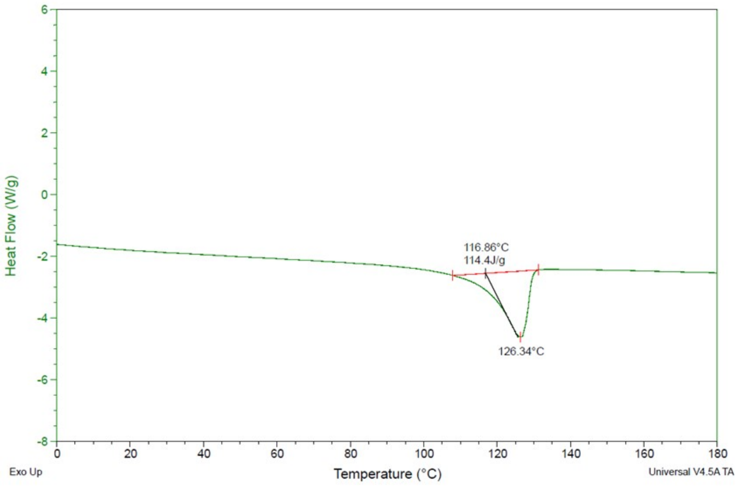


Figure S47 DSC traces of E/UA copolymer obtained by **B4** (Table 2, run 16)

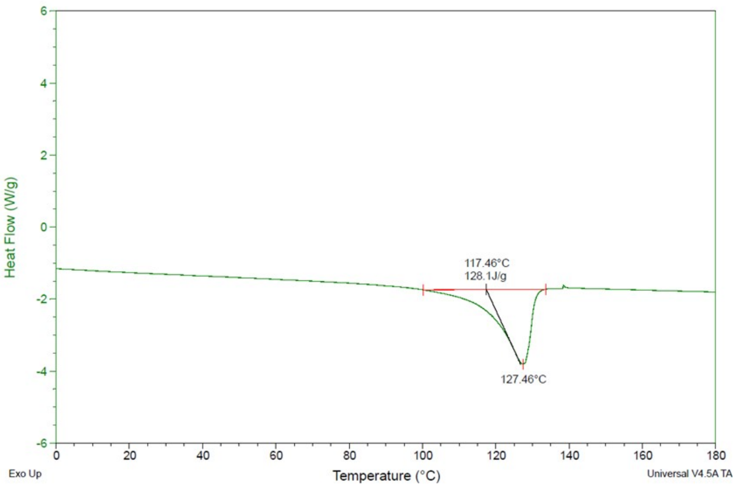


Figure S48 DSC traces of E/UA copolymer obtained by **M2** (Table 2, run 17)

8. FTIR spectra of polymers

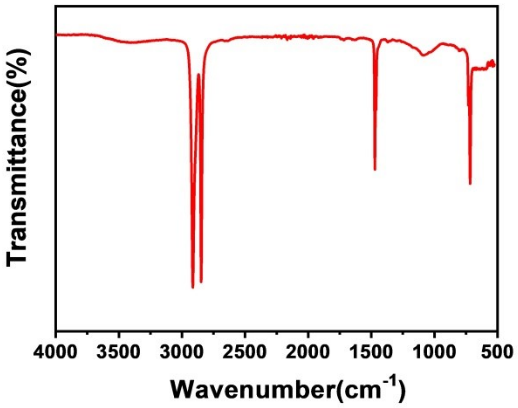


Figure S49. FTIR spectra of polyethylene obtained by **B1.**

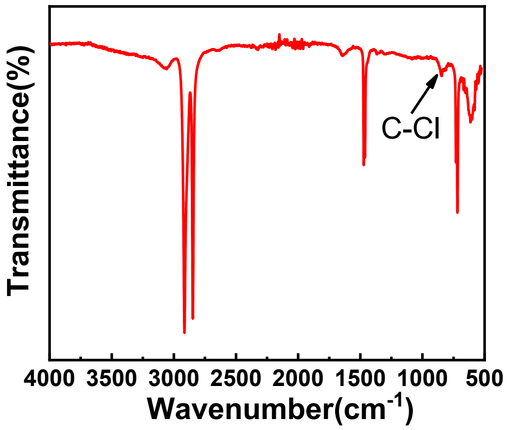


Figure S50. FTIR spectra of E/Cl-Hex copolymer obtained by **B1.**

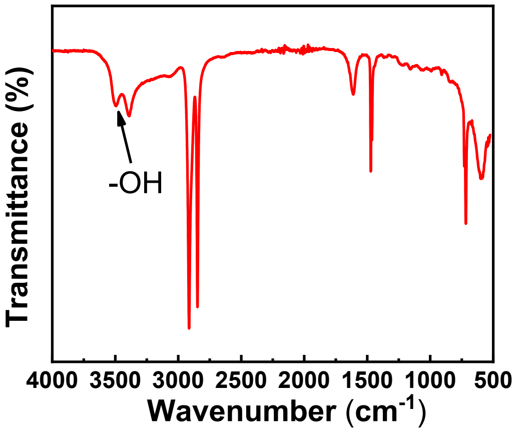


Figure S51. FTIR spectra of E/UOH copolymer obtained by **B1.**

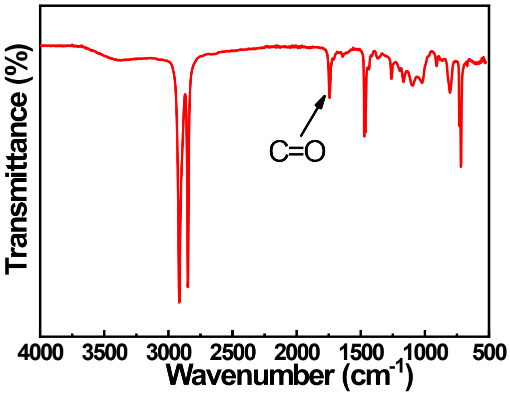


Figure S52. FTIR spectra of E/UA copolymer obtained by **B1.**