Supporting Information

Binuclear Ni catalyzed ethylene copolymerization with short chain alkenol monomers

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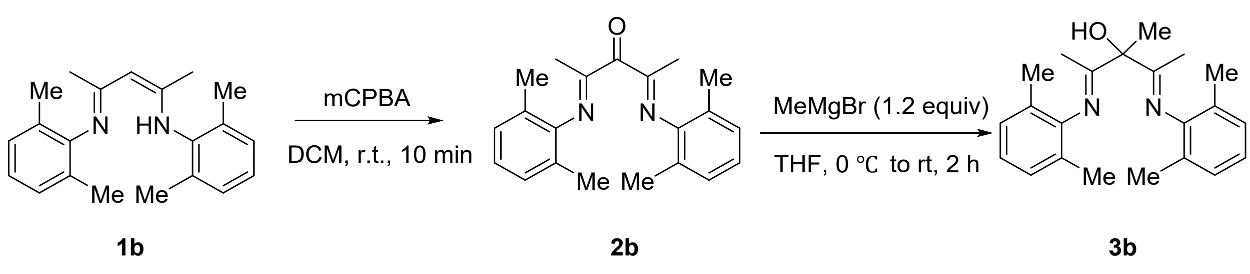
1. Materials and Methods

Toluene, *n*-hexane, dichloromethane (DCM), and tetrahydrofuran (THF) were purified by MBraun SPS-800 system. Polymerization-grade ethylene was purified through an ethylene purification system (developed by the Dalian Institute of Chemical Physics, CAS). Allyl alcohol (A-ol), 3-buten-1-ol (HAA), 4-penten-1-ol (PA), 9-decen-1-ol (DA) were dried over anhydrous $CaSO_4$ and distilled. Allyl acetate (AAc) was dried over CaH_2 and distilled. Diethylaluminum chloride (DEAC) were purchased from Jiangsu Yongjian Chemical Co., Ltd as neat liquids and diluted with toluene to 1.0 M solutions before use. Poly(E-*co*-HAA), poly(E-*co*-PA) and poly(E-*co*-DA) were acetylated before GPC measurement. **1a** [1], **1b** [1] and **2a** [2] were known and synthesized according to literature. Compounds **3a** and **4a** were reported in our previous work [3].

All air and moisture-sensitive manipulations were carried out under high purity N_2 using standard Schlenk techniques or in a glovebox. ^{1}H NMR, ^{13}C NMR, DEPT 135, COSY, HSQC and HMBC spectra were recorded on an Agilent Technologies spectrometer (400 MHz, 600 MHz) or a Varian spectrometer (400 MHz). Elemental analysis was performed by the Analytical Laboratory of the Shanghai Institute of Organic Chemistry (CAS). M_n, M_w, and dispersity index (Đ) were determined with Agilent Technologies PL-GPC 220 High temperature Gel Permeation Chromatography at 150 °C (polystyrene calibration, 1,2,4-trichlorobenzene as solvent at 150°C). X-Ray crystallographic data were collected using a Bruker AXSD8 X-ray diffractometer. Mass spectra were obtained using an HP5989A spectrometer.

2. Synthesis of compounds

(1) Synthesis of **3b** and **4b**



To a solution of compound **1b** (7.7 g, 25.0 mmol) in DCM (200 mL) was added a solution of mCPBA (10.2 g, 50.0 mmol) in DCM (200 mL). The reaction was monitored by TLC. Saturated $NaHCO_3$(aq) was added after complete conversion of the substrate (about 10 min). The organic phase was washed with saturated $NaHCO_3$(aq) two more times, dried over Na_2SO_4, filtered, concentrated under reduced pressure, and purified by flash chromatography to afford crude **2b** as an orange oil (not stable), which was used in the next step without further purification.

To a solution of the above crude **2b** in 100 mL of anhydrous THF was added a MeMgBr solution (7.7 mL, 23.1 mmol, 3.0 M in Et_2O) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 2 h being quenched with saturated NH_4Cl (aq). The organic phase was extracted with ethyl acetate three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was recrystallized from MeOH repeatedly until product **3b** was obtained as a white solid (1.4 g, 17%, two steps). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.05-7.03 (m, 4 H), 6.94-6.91 (m, 2 H), 6.16 (s, 1 H), 2.02 (s, 6 H), 1.99 (s, 6 H), 1.82 (s, 6 H), 1.80 (s, 3 H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.14, 147.39, 128.28, 128.24, 125.98, 125.66, 123.49, 80.27, 24.31, 18.21, 18.15, 15.74. **HR-MS (ESI)** $[M+Na]^+$ Calcd for $C_{22}H_{28}N_2ONa$, 359.20938; Found, 359.20999.

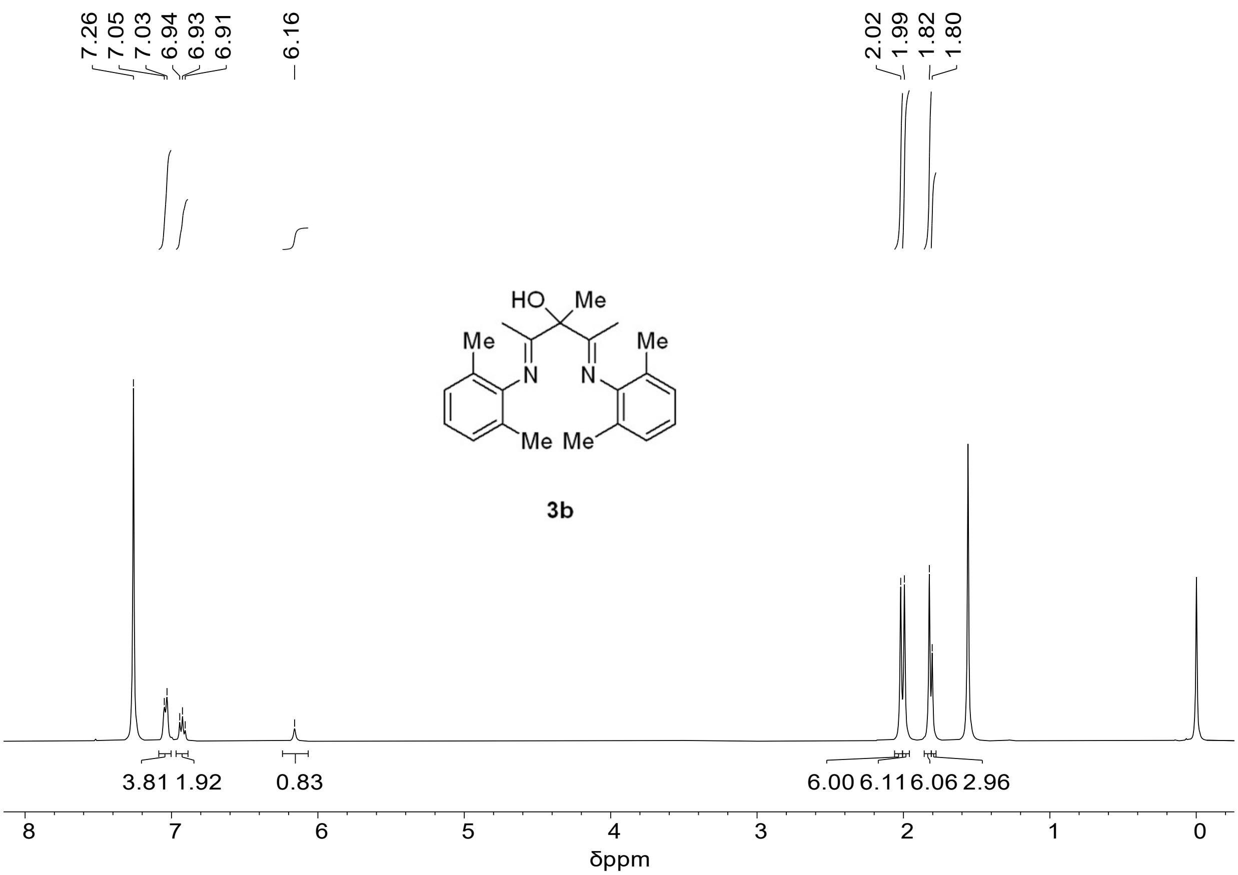


Figure S1 ^{1}H NMR spectrum (400 MHz) of **3b** in $CDCl_3$.

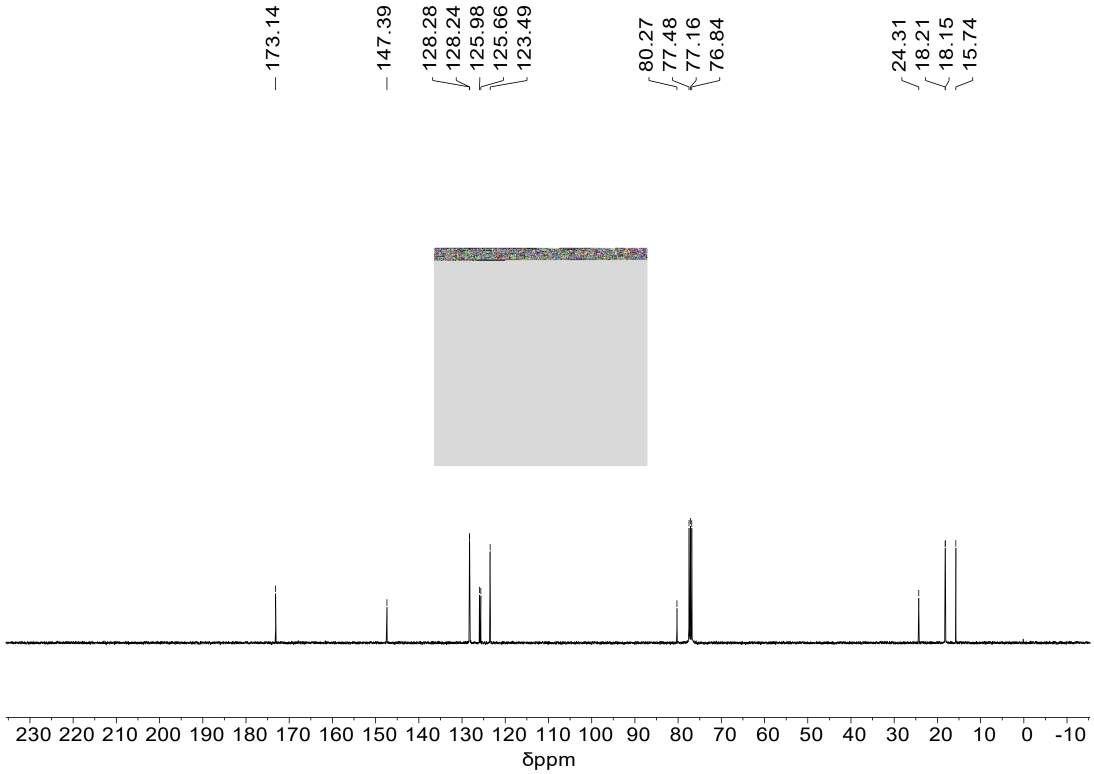
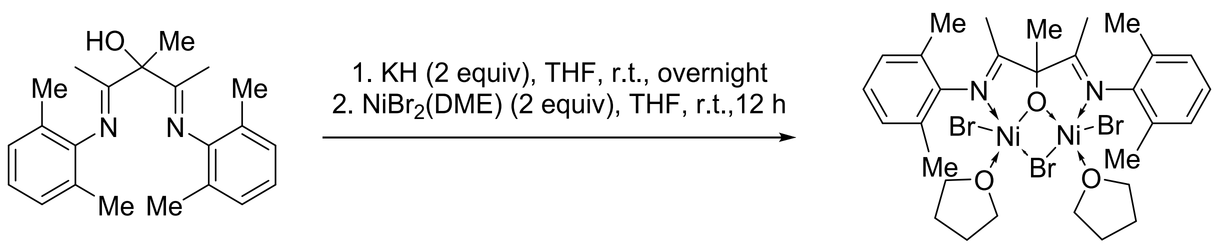


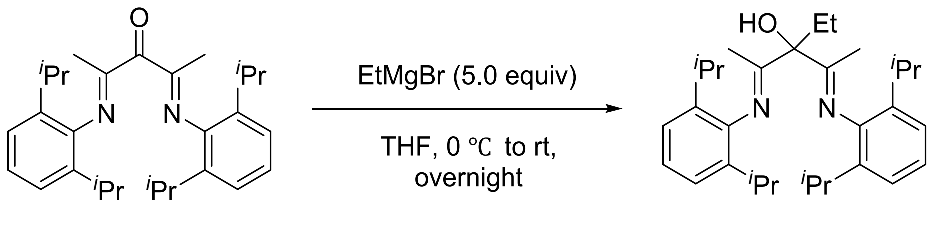
Figure S2 ^{13}C NMR spectrum (400 MHz) of **3b** in $CDCl_3$.



3b **4b**

To a suspension of potassium hydride (KH) (0.24 g, 6.0 mmol, 2.0 equiv.) in 10 mL of dry THF was added a solution of **3b** (1.0 g, 3.0 mmol) in 10 mL of THF at room temperature. The resulting suspension was stirred overnight. It was filtered into a suspension of $NiBr_2$(DME) (1.85 g, 6.0 mmol, 2.0 equiv.) in THF at room temperature, and the suspension was stirred for 12 h. The solvent was removed under reduced pressure, and the residue was dissolved in dry DCM. After filtration, the filtrate was concentrated under reduced pressure and the residue was dissolved in THF for recrystallization to afford the product **4b** (red solid, 1.83 g, 73%). Anal. Calcd. for $C_{30}H_{43}Br_3N_2Ni_2O_3$ (two THF coordination): C, 43.06; H, 5.18; N, 3.35; Found: C, 42.95; H, 5.20; N, 3.37.

(2) Synthesis of **3c** and **4c**



2a **3c**

To a solution of compound **2a** (6.5 g, 15.1 mmol) in 75 mL of anhydrous THF was added an EtMgBr solution (25.0 mL, 75.5 mmol, 3.0 M in Et_2O) at 0 °C. The reaction mixture was warmed to room temperature and stirred overnight before being quenched with saturated NH_4Cl(aq). The organic phase was extracted with ethyl acetate three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The product and unreacted substrate were isolated by flash chromatography. The recovered substrate (4.0 g, 61%) was processed in the same way as above to obtain more products. The products of two batches were combined and recrystallized from MeOH to afford the product **3c** as a white solid (1.4 g, 20% overall two batches). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16-7.14 (m, 4 H), 7.11-7.07 (m, 2H), 6.13 (s, 1 H), 2.69 (hep, *J* = 7.1 Hz, 4 H), 2.38 (q, *J* = 7.2 Hz, 2H), 1.84 (s, 6H), 1.17-1.12 (m, 24H), 1.05 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.00, 145.13, 136.28, 136.09, 124.12, 123.20, 123.16, 83.50, 29.68, 28.19, 28.16, 23.64, 23.53, 23.20, 22.78, 16.16, 7.84. **HR-MS (ESI)** $[M+H]^+$ Calcd for $C_{31}H_{47}ON_2$, 463.3683; Found, 463.3682.

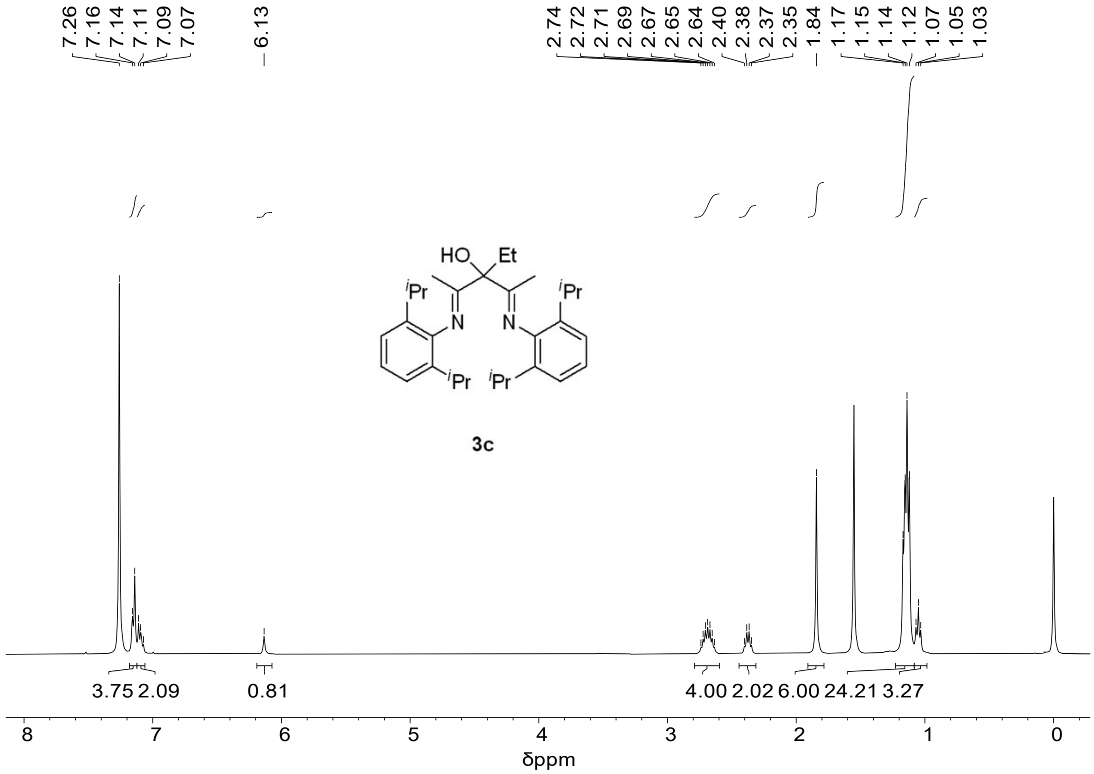


Figure S3 ^{1}H NMR spectrum (400 MHz) of **3c** in $CDCl_3$.

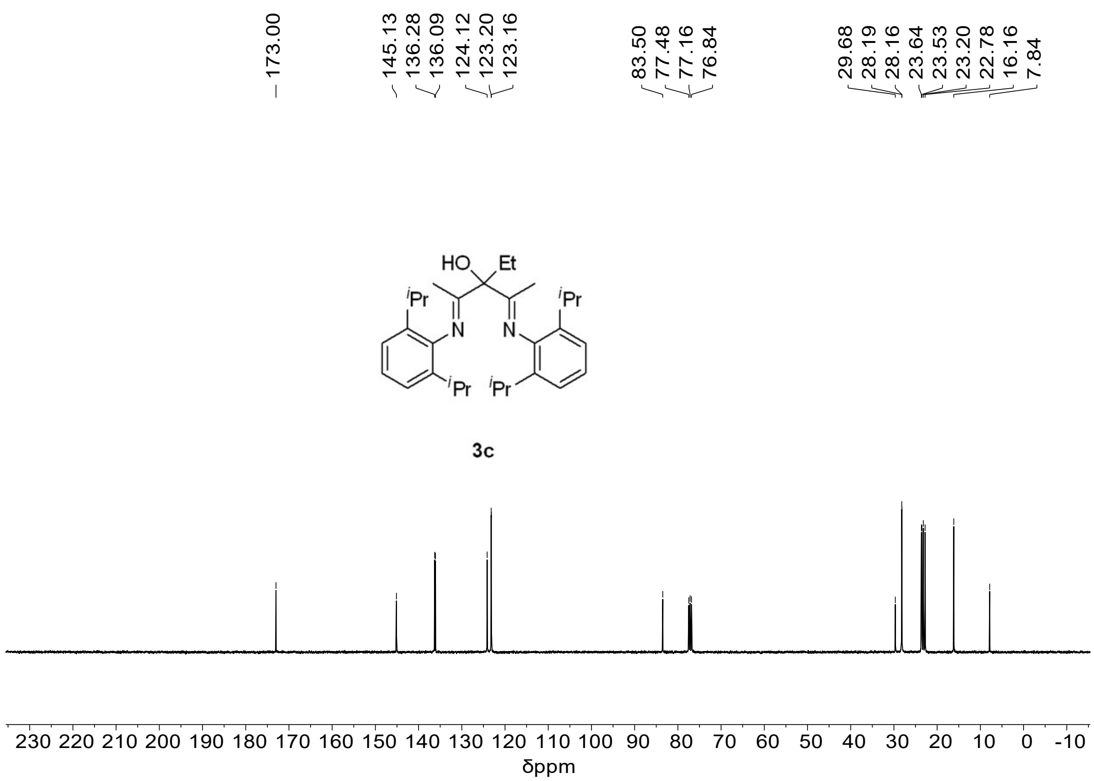
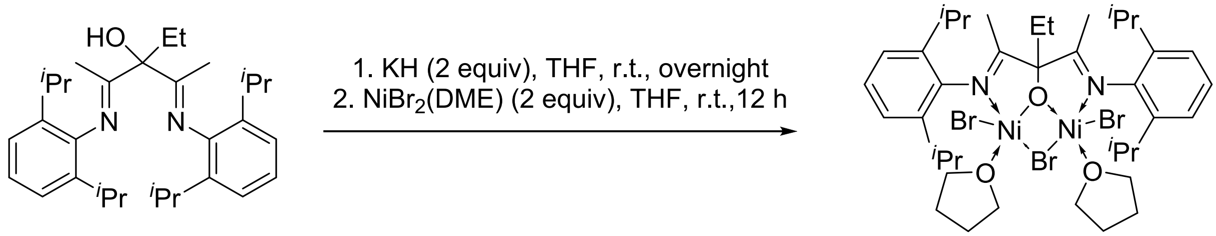


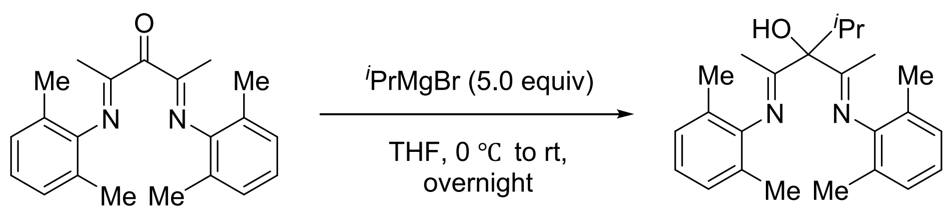
Figure S4 ^{13}C NMR spectrum (400 MHz) of **3c** in $CDCl_3$.



3c **4c**

To a suspension of potassium hydride (KH) (0.08 g, 2.0 mmol, 2.0 equiv.) in 10 mL of dry THF was added a solution of **3c** (0.46 g, 1.0 mmol) in 10 mL of THF at room temperature. The resulting suspension was stirred overnight. It was filtered into a suspension of $NiBr_2$(DME) (0.62 g, 2.0 mmol, 2.0 equiv.) in THF at room temperature, and the suspension was stirred for 12 h. The solvent was removed under reduced pressure, and the residue was dissolved in dry DCM. After filtration, the filtrate was concentrated under reduced pressure, and the residue was dissolved in THF for recrystallization to afford the product **4c** (yellow solid, 0.63 g, 65%). Anal. Calcd. for $C_{35}H_{53}Br_3N_2Ni_2O_2$ (one THF coordination): C, 47.19; H, 6.00; N, 3.14; Found: C, 47.34; H, 6.18; N, 3.15.

(3) Synthesis of **3d** and **4d**



2b **3d**

To a solution of compound **2b** (5.9 g, 18.3 mmol) in 100 mL of anhydrous THF was added an ^{i}PrMgBr solution (33.0 mL, 91.5 mmol, 2.8 M in 2-methyltetrahydrofuran) at 0 °C. The reaction mixture was warmed to room temperature and stirred overnight before being quenched with saturated NH_4Cl(aq). The organic phase was extracted with ethyl acetate three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was recrystallized from MeOH to afford the product **3b** as a white solid (1.9 g, 29%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.05-7.02 (m, 4 H), 6.94-6.91 (m, 2 H), 6.01 (s, 1 H), 3.09 (hep, J = 6.6 Hz, 1 H), 2.04 (s, 6 H), 1.99 (s, 6 H), 1.88 (s, 6 H), 1.09 (d, J = 6.6 Hz, 6 H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.81, 147.64, 128.43, 128.37, 126.14, 125.82, 123.52, 85.58, 33.28, 19.00, 18.89, 17.73, 16.64. **HR-MS (ESI)** $[M+Na]^+$ Calcd for $C_{24}H_{32}N_2ONa$, 387.24068; Found, 387.24036.

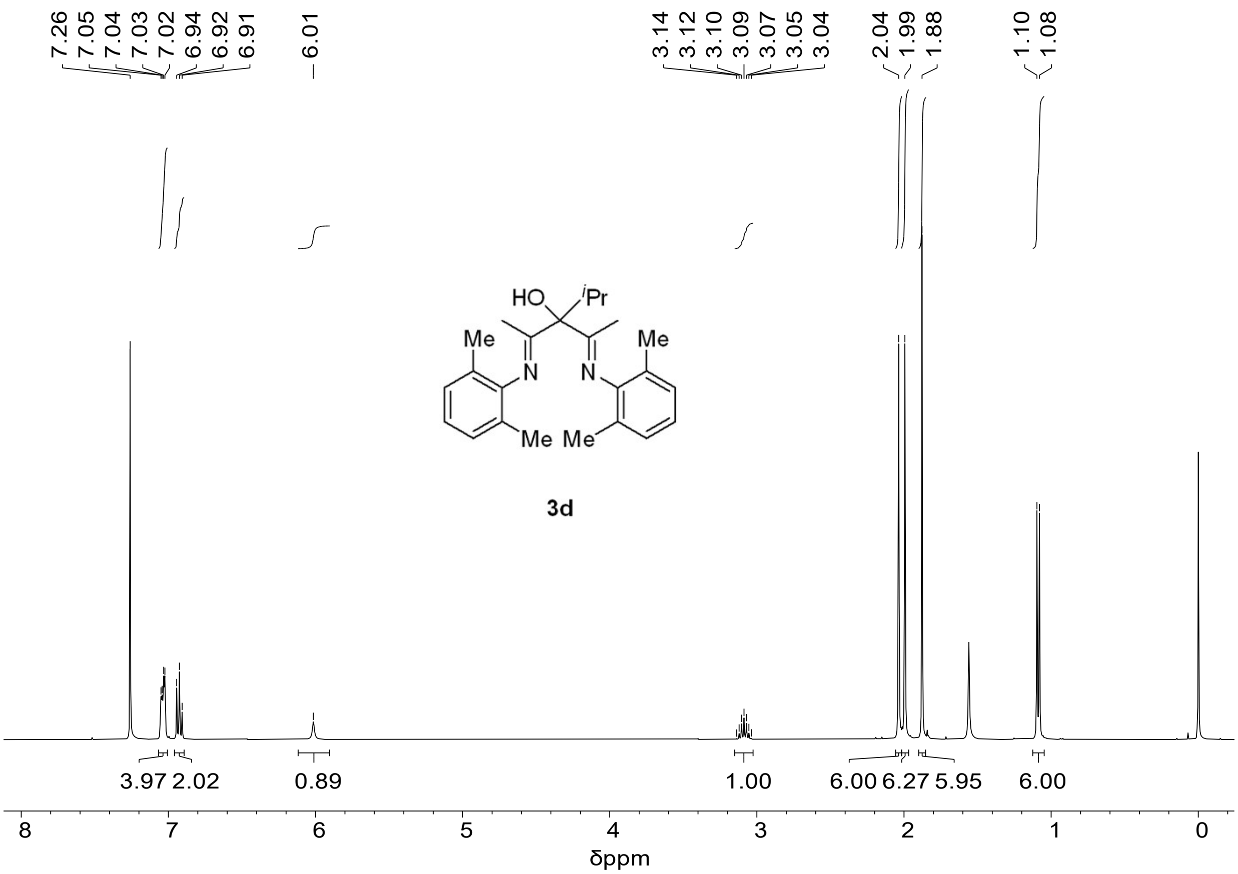


Figure S5 ^{1}H NMR spectrum (400 MHz) of **3d** in $CDCl_3$.

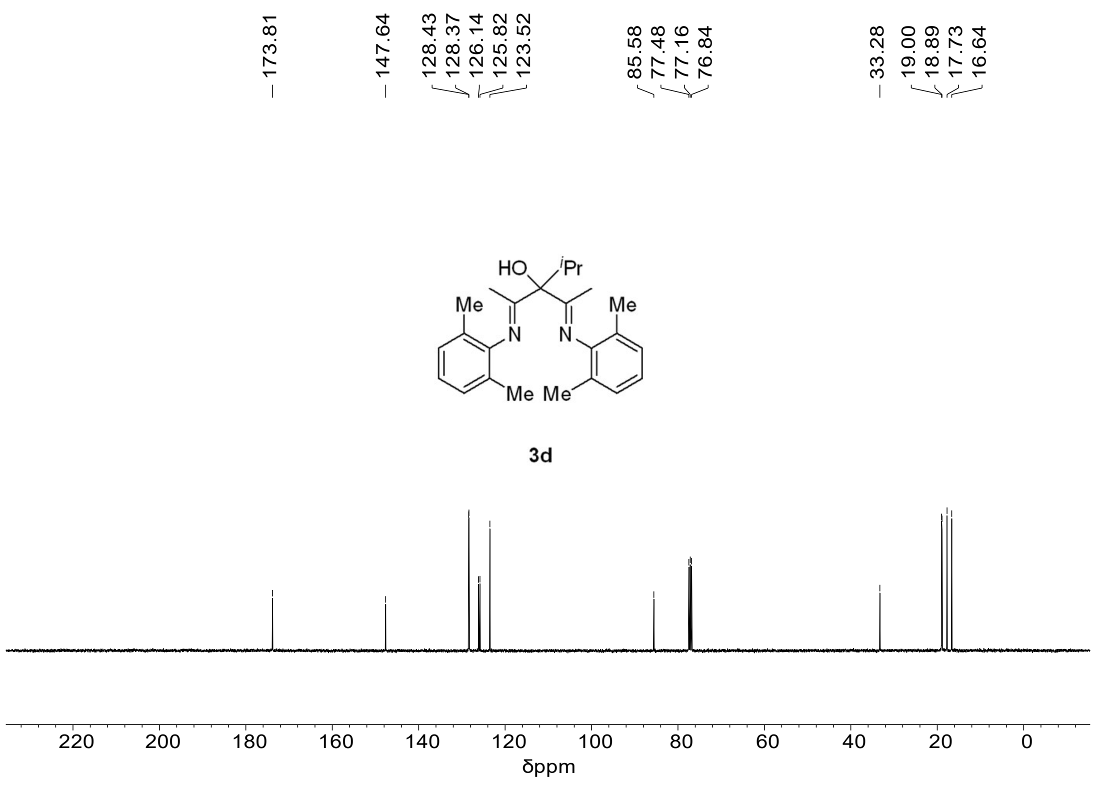
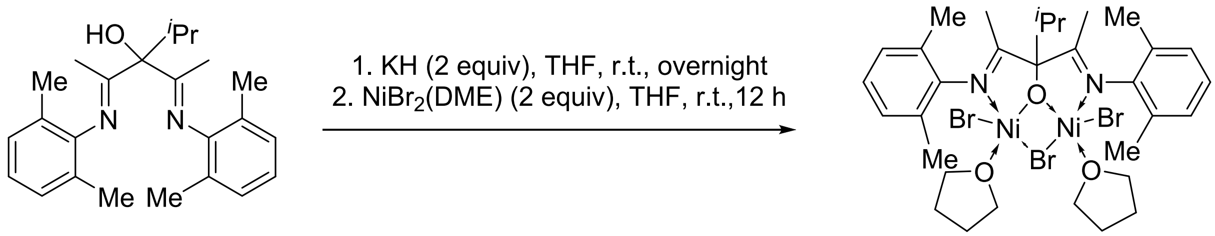


Figure S6 ^{13}C NMR spectrum (400 MHz) of **3d** in $CDCl_3$.



3d **4d**

To a suspension of potassium hydride (KH) (0.08 g, 2.0 mmol, 2.0 equiv.) in 10 mL of dry THF was added a solution of **3d** (0.36 g, 1.0 mmol) in 10 mL of THF at room temperature. The resulting suspension was stirred overnight. It was filtered into a suspension of $NiBr_2$(DME) (0.62 g, 2.0 mmol, 2.0 equiv.) in THF at room temperature, and the suspension was stirred for 12 h. The solvent was removed under reduced pressure, and the residue was dissolved in dry DCM. After filtration, the filtrate was concentrated under reduced pressure, and the residue was dissolved in THF for recrystallization to afford the product **4d** (red solid, 0.40 g, 46%). Anal. Calcd. for $C_{32}H_{47}Br_3N_2Ni_2O_3$ (two THF coordination): C, 44.44; H, 5.48; N, 3.24; Found: C, 44.43; H, 5.57; N, 3.38.

3. General Procedure for Olefin Copolymerizations with Polar Monomer

Under 1 atm of ethylene, a flame-dried two-necked flask equipped with a stir bar was charged with the desired amount of toluene and DEAC solution at desired temperature. After 10 min, the polar monomer was added dropwise. The mixture was stirred for 10 min, and the desired amount of Ni catalyst in toluene was added to initiate polymerization. The reaction was quenched by pouring it into 250 mL of acidified methanol (concentrated HCl/MeOH, 1/10, v/v) and stirred at room temperature overnight. The precipitated polymer was collected, washed with methanol, and dried under vacuum at 60 °C to a constant weight.

4. Acetylation Procedure for Poly(E-*co*-Alkenol)

To a round-bottom flask equipped with a stir bar was added the poly(E-*co*-alkenol), 20 mL of 1,2-dichlorobenzene, 5 mL of glacial acetic acid, 5 drops of concentrated H_2SO_4 sequentially. A reflux condenser was installed, and the mixture was heated to 120 °C for 6 h. The hot solution was poured into 100 mL of methanol, and an additional 10 mL of acidified methanol (concentrated HCl/MeOH, 1/10, v/v) was added to precipitate the copolymer. The precipitated copolymer was filtered, washed with methanol, dried under vacuum at 60 °C to a constant weight, and further characterized by ^{1}H NMR, confirming the complete conversion of hydroxyl to acetate groups.

5. Supplementary Notes

1) NMR Assignments of Poly(E-*co*-HAA) and Comonomer Content Calculation

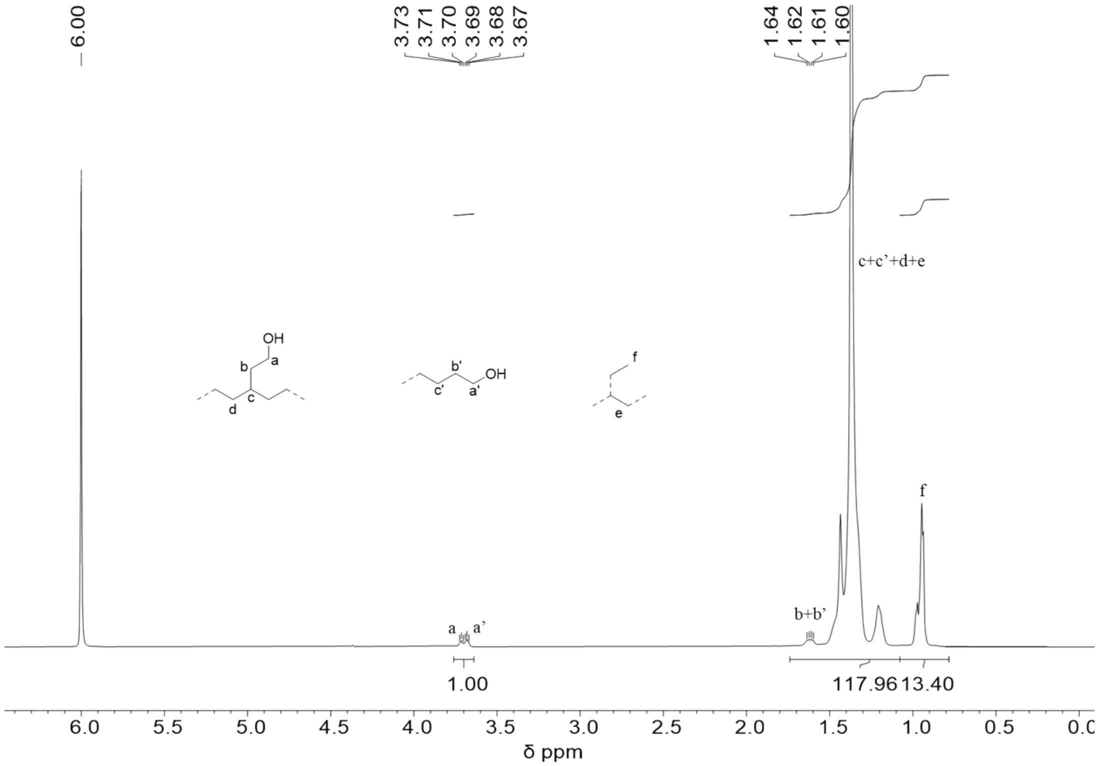


Figure S7. [1]H NMR spectrum (600 MHz) of poly(E-*co*-HAA) (Entry 8, Table 2) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

The comonomer content was calculated from quantitative [1]H NMR spectrum analysis . The mole ratios of HAA and ethylene in the copolymer are x and 1-x, respectively. The integration $I_{b+b'+c+c'+d+e+f}$ is set as n, and the integration $I_{a+a'}$ is set as 1.

$$\frac{2x}{5x+4(1-x)} = \frac{1}{n}$$

$$x = \frac{4}{2n-1} \times 100\%$$

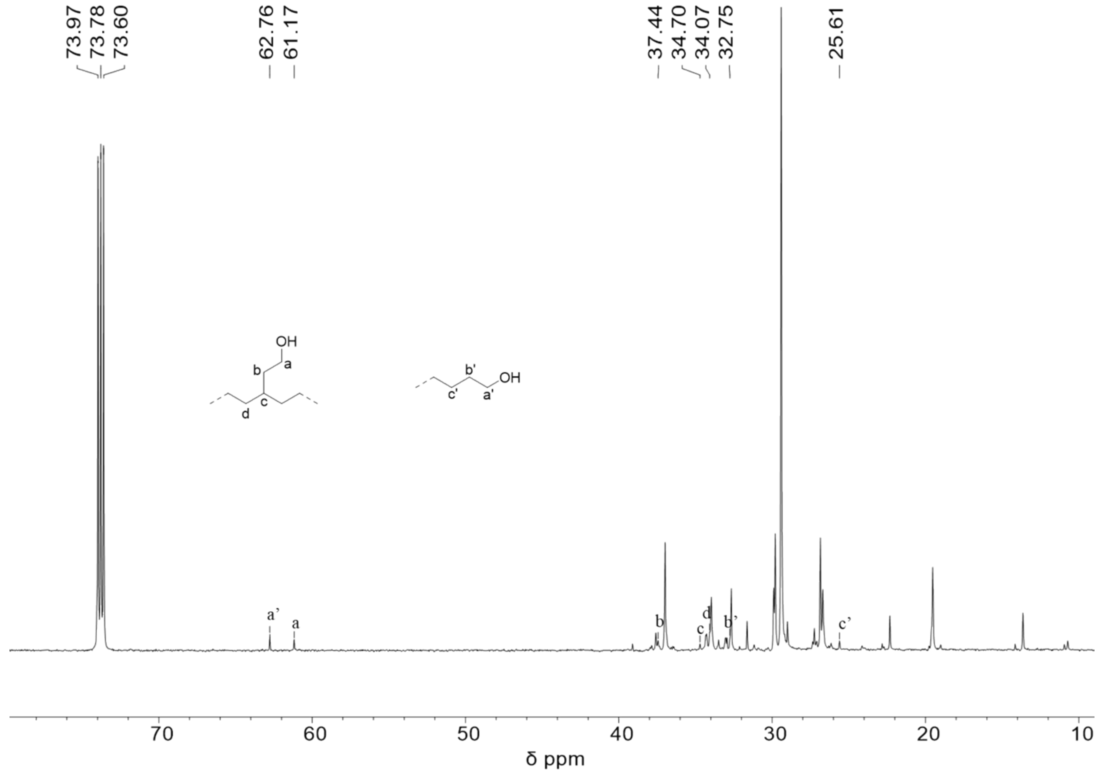


Figure S8. ^{13}C NMR spectrum (150 MHz) of poly(E-*co*-HAA) (Entry 8, Table 2) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

The signals of ^{1}H and ^{13}C NMR are assigned according to our previous work [3].

2) NMR Assignments of Poly(E-*co*-PA) and Comonomer Content Calculation

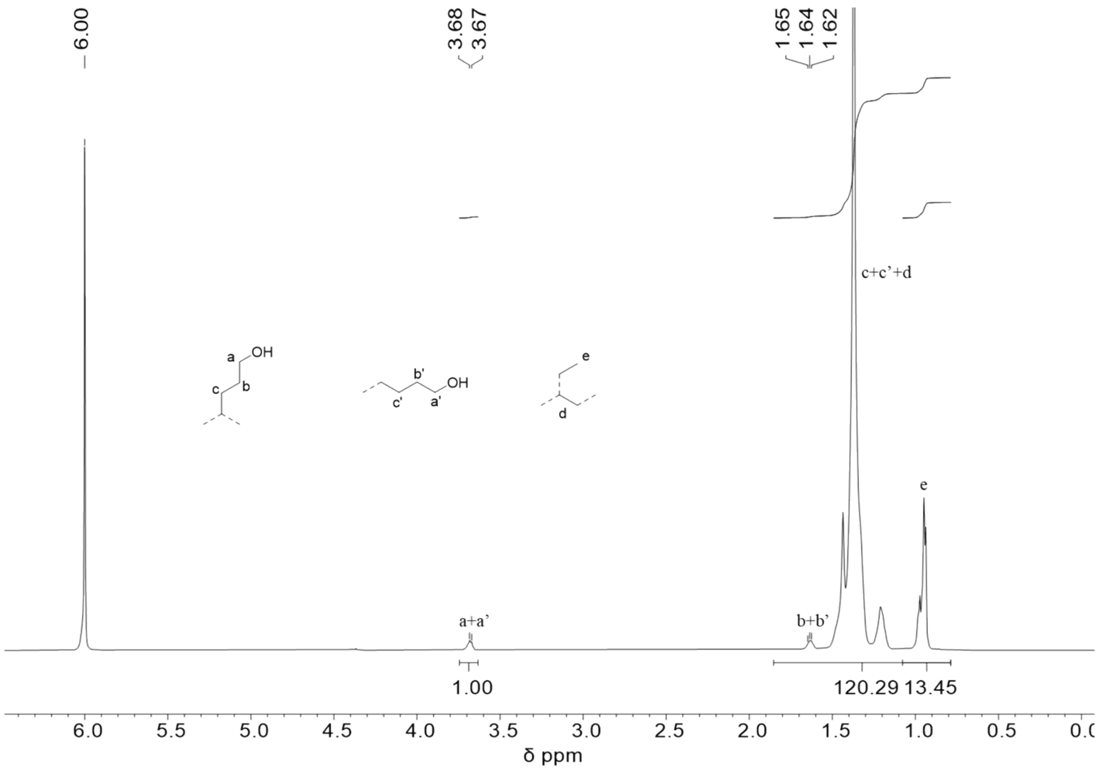


Figure S9. [1]H NMR spectrum (600 MHz) of poly(E-*co*-PA) (Entry 12, Table 2) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

The comonomer content was calculated from quantitative [1]H NMR spectrum analysis. The mole ratios of PA and ethylene in the copolymer are x and 1-x, respectively. The integration $I_{b+b'+c+c'+d+e}$ is set as n, and the integration $I_{a+a'}$ is set as 1.

$$\frac{2x}{7x+4(1-x)}=\frac{1}{n}$$

$$x=\frac{4}{2n-3}\times 100\%$$

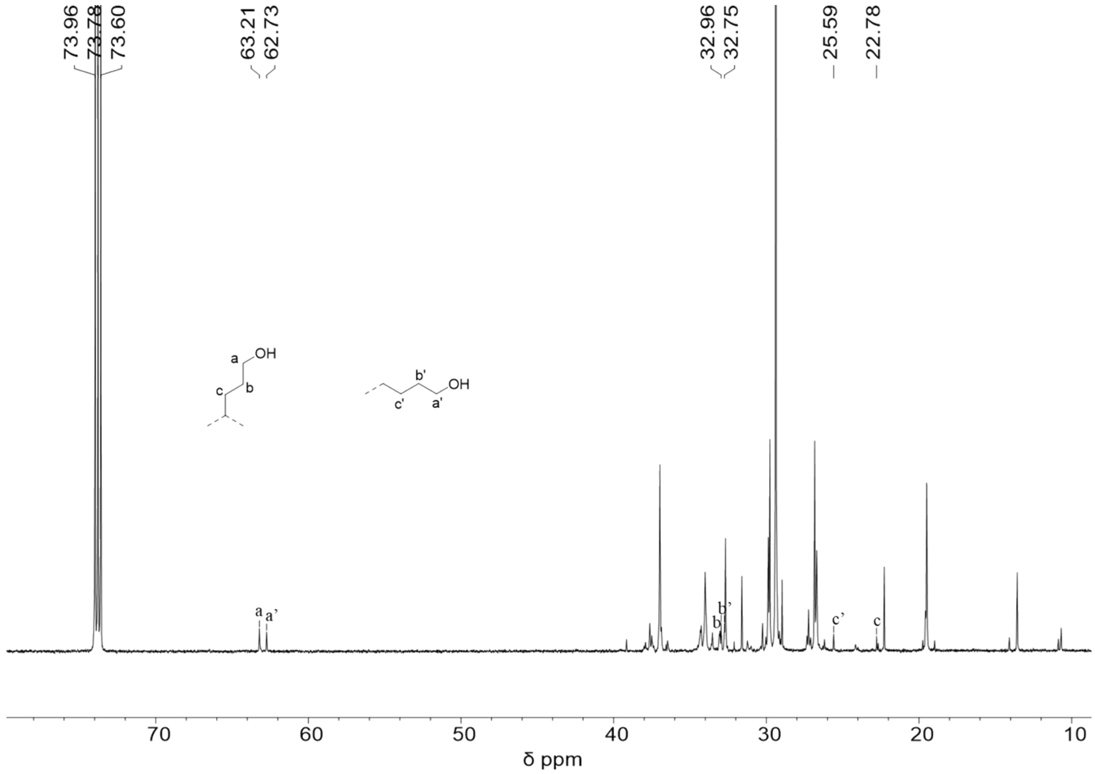


Figure S10. ^{13}C NMR spectrum (150 MHz) of poly(E-*co*-PA) (Entry 12, Table 2) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

The signals of ^{1}H and ^{13}C NMR are assigned according to our previous work [3].

3) NMR Assignments of Poly(E-*co*-DA) and Comonomer Content Calculation

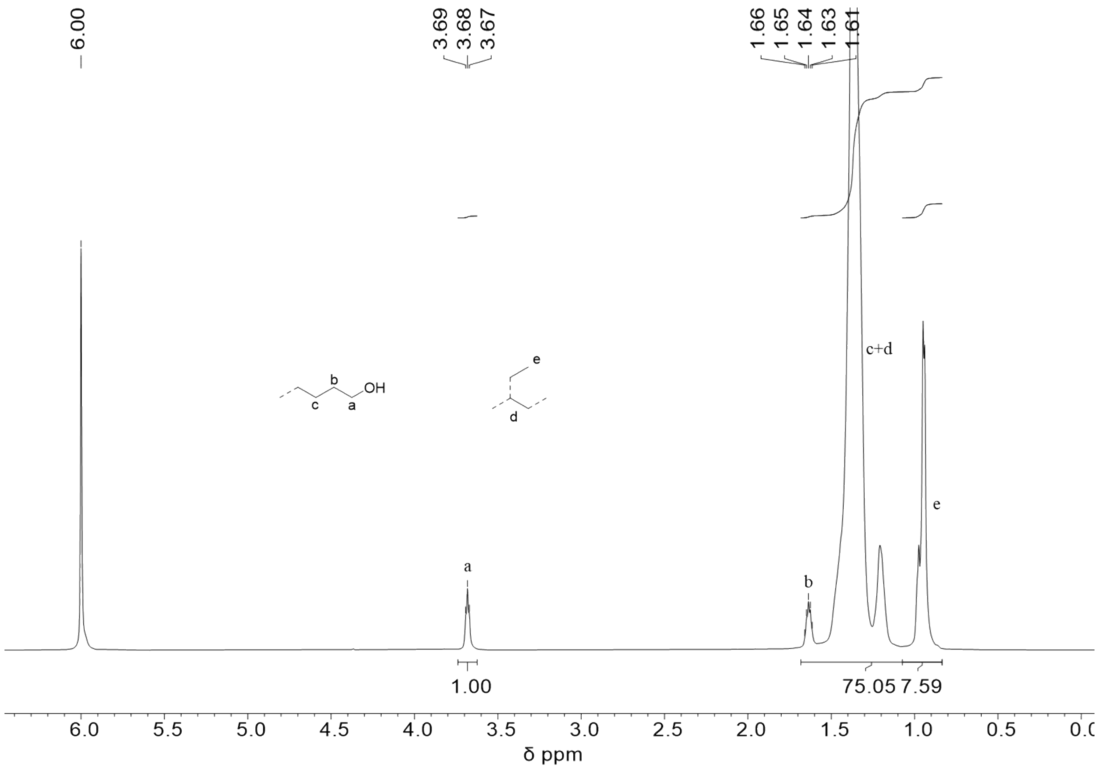


Figure S11. [1]H NMR spectrum (600 MHz) of poly(E-*co*-DA) (Entry 16, Table 2) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

The comonomer content was calculated from quantitative [1]H NMR spectrum analysis. The mole ratios of DA and ethylene in the copolymer are x and 1-x, respectively. The integration $I_{b+c+d+e}$ is set as n, and the integration I_a is set as 1.

$$\frac{2x}{17x+4(1-x)} = \frac{1}{n}$$

$$x = \frac{4}{2n-13} \times 100\%$$

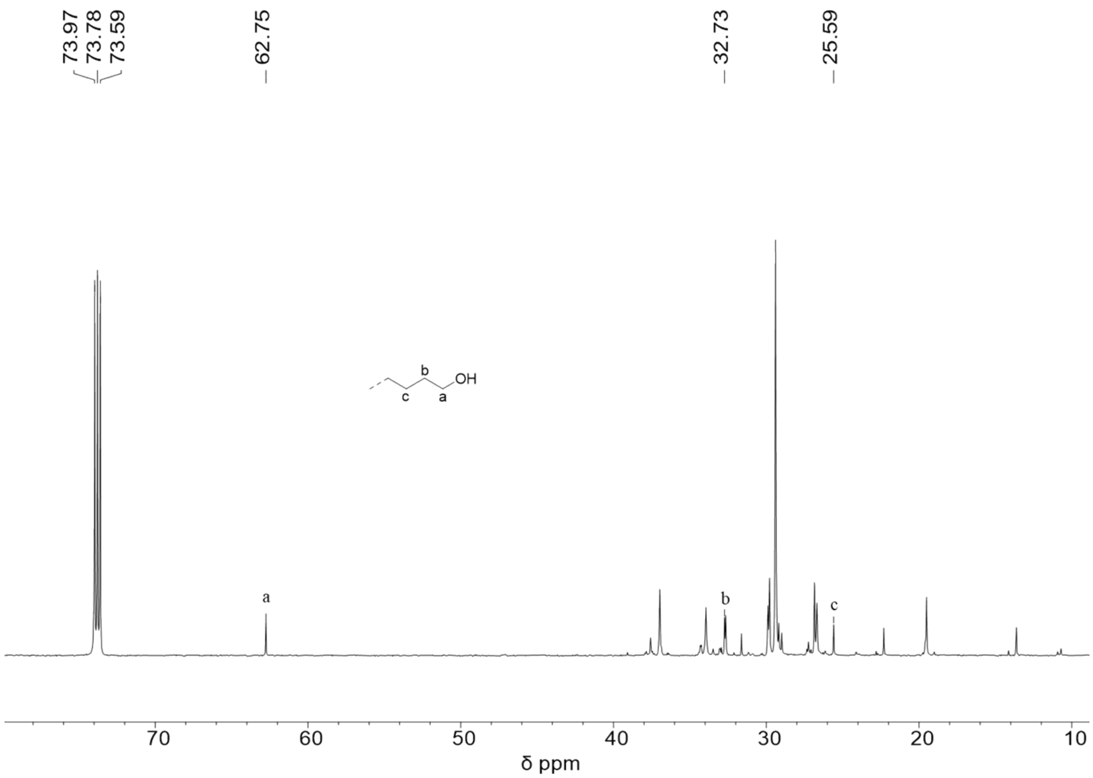
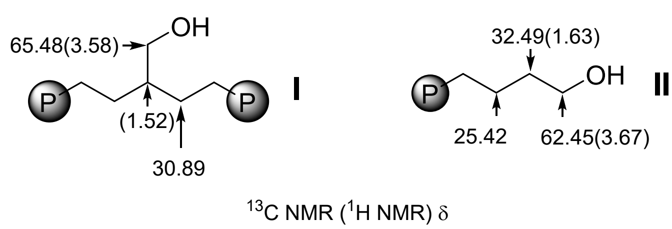


Figure S12. ^{13}C NMR spectrum (150 MHz) of poly(E-*co*-DA) (Entry 16, Table 2) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

The signals of ^{1}H and ^{13}C NMR are assigned according to our previous work [3].

4) Microstructure Analysis of Poly(E-*co*-A-ol) and Comonomer Content Calculation

According to quantitative ^{1}H, ^{13}C and 2D NMR (Figures S24-S29), as well as literature [3-6], the resulting poly(E-*co*-A-ol) exhibits microstructures as shown in the following scheme. Olefinic groups [5, 7, 8] and aromatic groups [9-12] were also detected in ^{1}H NMR, which were assigned according to literature.



Scheme S1. Microstructure of Poly(E-*co*-A-ol)

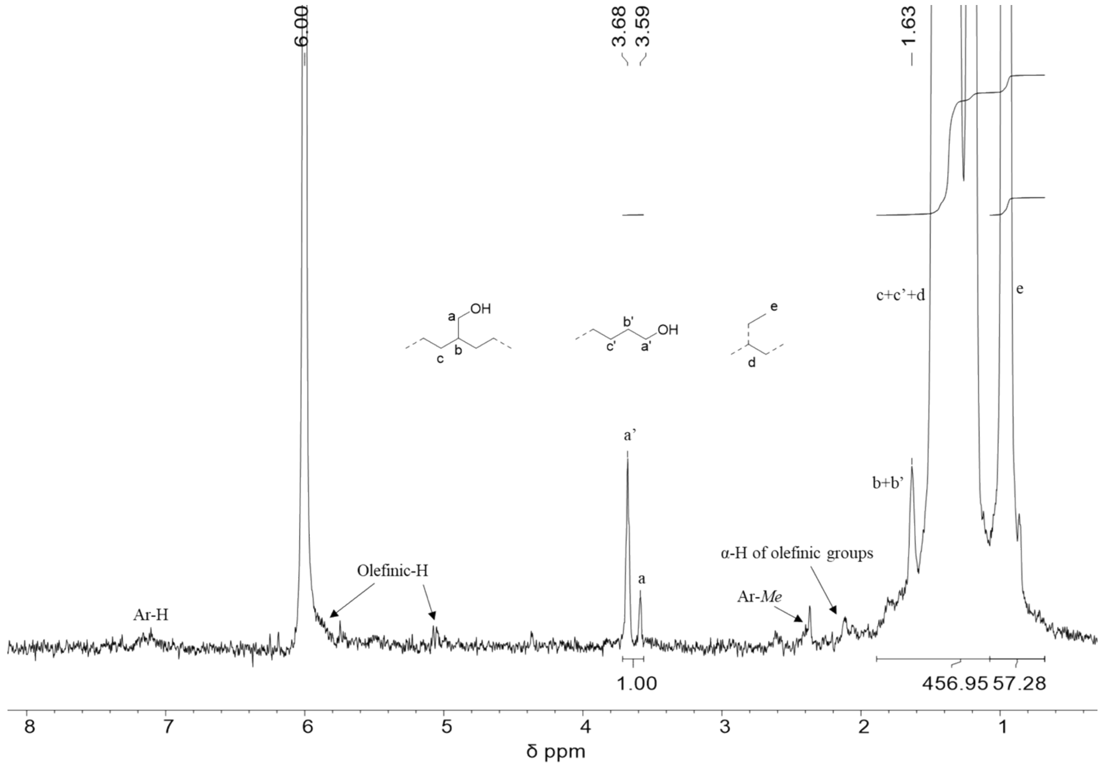


Figure S13. [1]H NMR spectrum (600 MHz) of poly(E-*co*-A-ol) (Entry 3, Table 2) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

The comonomer content was calculated from quantitative [1]H NMR spectrum analysis. The mole ratios of A-ol and ethylene in the copolymer are x and 1-x, respectively. The integration $I_{b+b'+c+c'+d+e}$ is set as n, and the integration $I_{a+a'}$ is set as 1. Note that the olefinic and aromatic groups probably from β-OAl elimination were not taken into quantitative calculation.

$$\frac{2x}{3x+4(1-x)}=\frac{1}{n}$$

$$x=\frac{4}{2n+1}\times 100\%$$

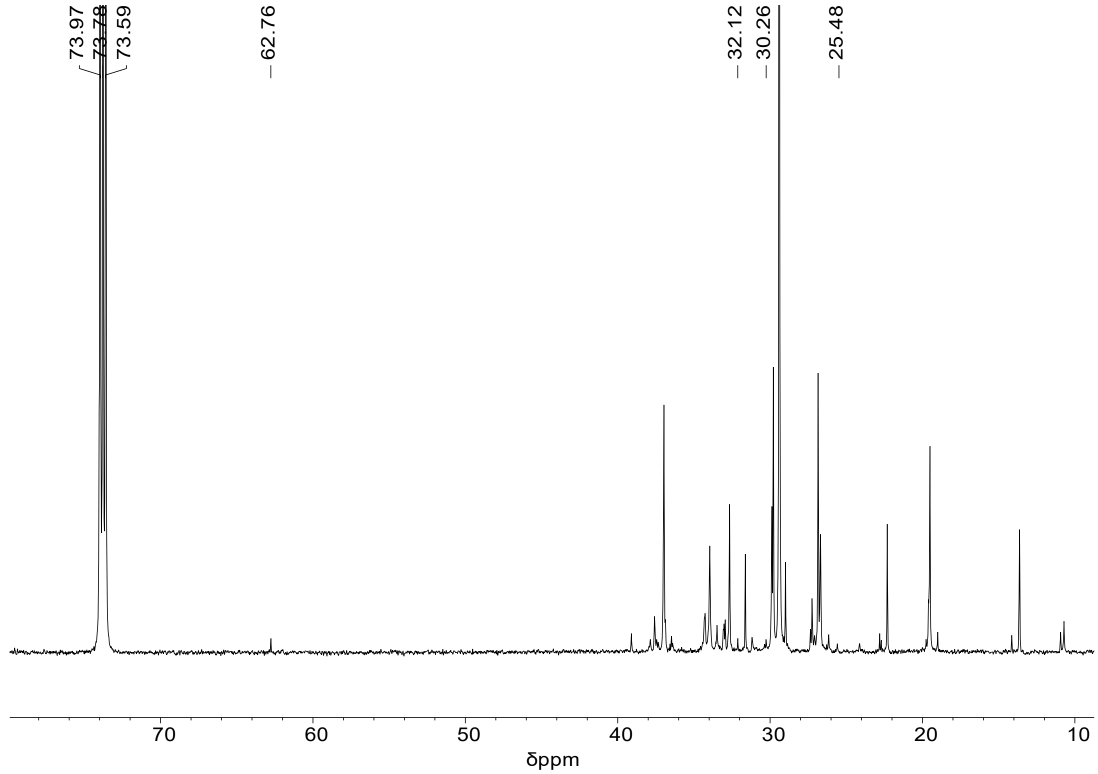


Figure S14. ^{13}C NMR spectrum (150 MHz) of poly(E-*co*-A-ol) (Entry 3, Table 2) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

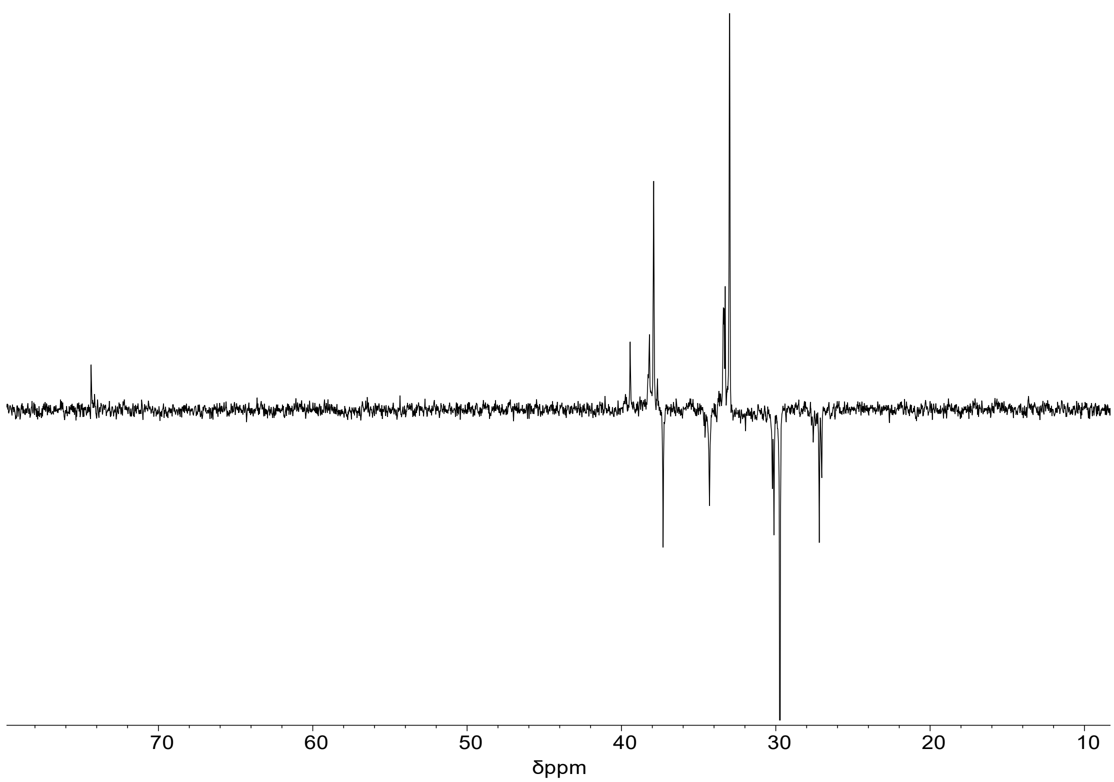


Figure S15. DEPT 135 spectrum of poly(E-*co*-A-ol) (Entry 3, Table 2) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

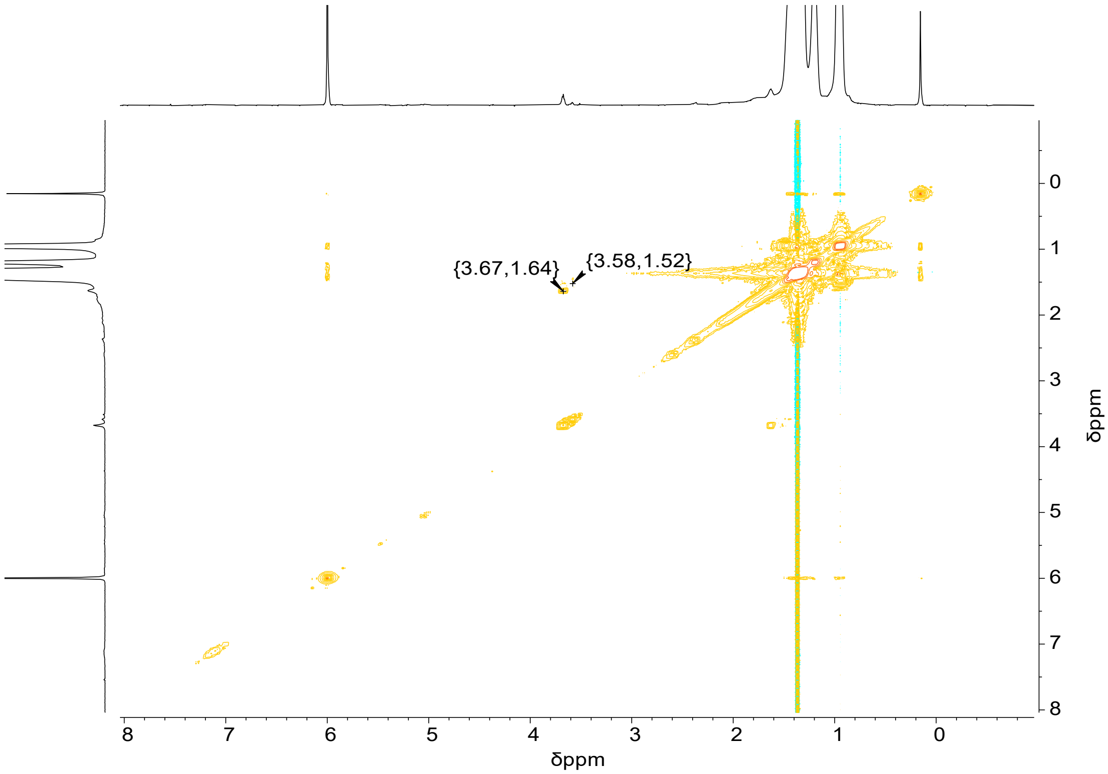


Figure S16. COSY spectrum of poly(E-*co*-A-ol) (Entry 3, Table 2) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

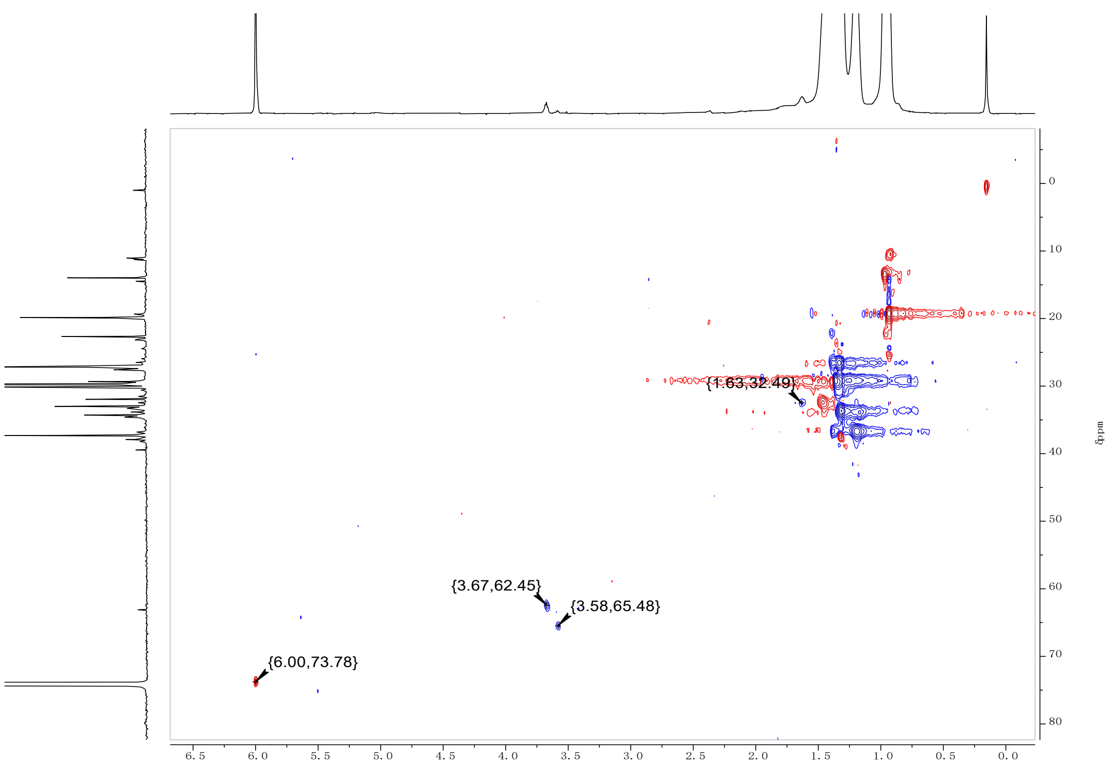


Figure S17. HSQC spectrum of poly(E-*co*-A-ol) (Entry 3, Table 2) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

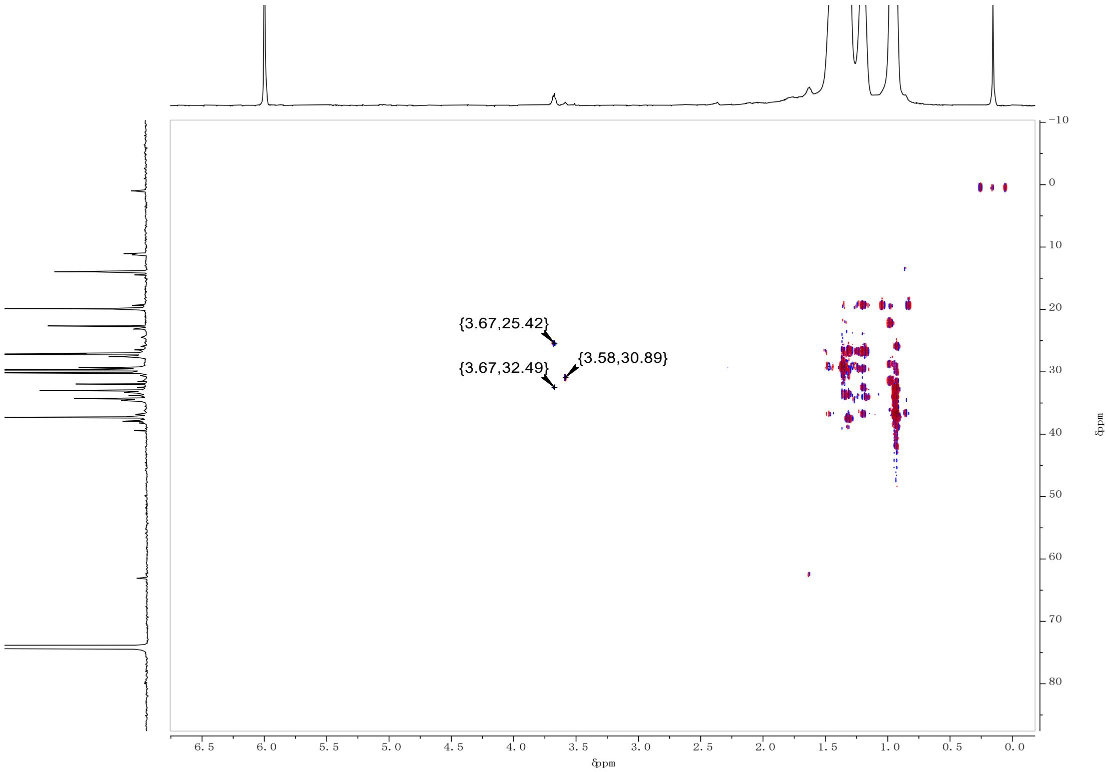


Figure S18. HMBC spectrum of poly(E-*co*-A-ol) (Entry 3, Table 2) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

5) NMR Assignments of Poly(E-*co*-AAc) and Double Bond Content Calculation

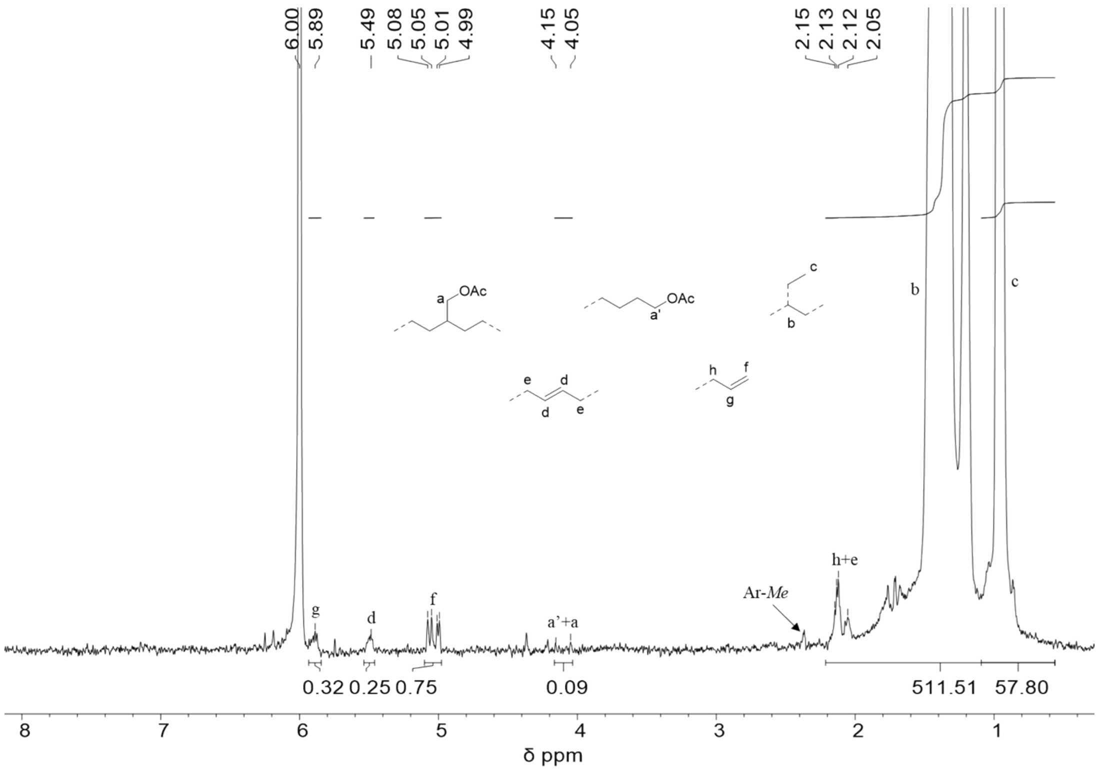


Figure S19. [1]H NMR spectrum (600 MHz) of poly(E-*co*-AAc) (Entry 2, Table 4) (little -OAc content but double bond detected) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

Negligible peaks assigned to the -OAc group were observed in the [1]H NMR spectra of the poly(E-*co*-AAc) samples. The double bond content was calculated from quantitative [1]H NMR spectrum analysis. The mole ratios of double bond and ethylene in the copolymer are x and 1-x, respectively. The integration $I_{b+c+e+h}$ is set as n; the integration I_{d+f} is set as 1, and the integration I_f is set as m.

$$\frac{2x}{5x+4(1-x)} = \frac{1}{n+1+m/2}$$

$$x = \frac{4}{2n+m+1} \times 100\%$$

Note that the aromatic groups were also detected in [1]H NMR but were not taken into quantitative calculation. The double bond content calculated based on the equation above in Table 4 ranged from 0.2~0.5 mol%, which could be expressed as trace content, so their quantitative analysis was not pursued either.

6) Branching Analysis from [1]H NMR

The amount of methyl groups ($N_{Me\ groups/1000C}$) based on [1]H NMR spectra were analyzed according to literature [7, 8].

N_{Me} groups/1000C = $2 \times I_{Me}/(3 \times I_{tot}) \times 1000$

6. Polymer Characterizations

1) NMR Spectra of Poly(E-*co*-HAA)

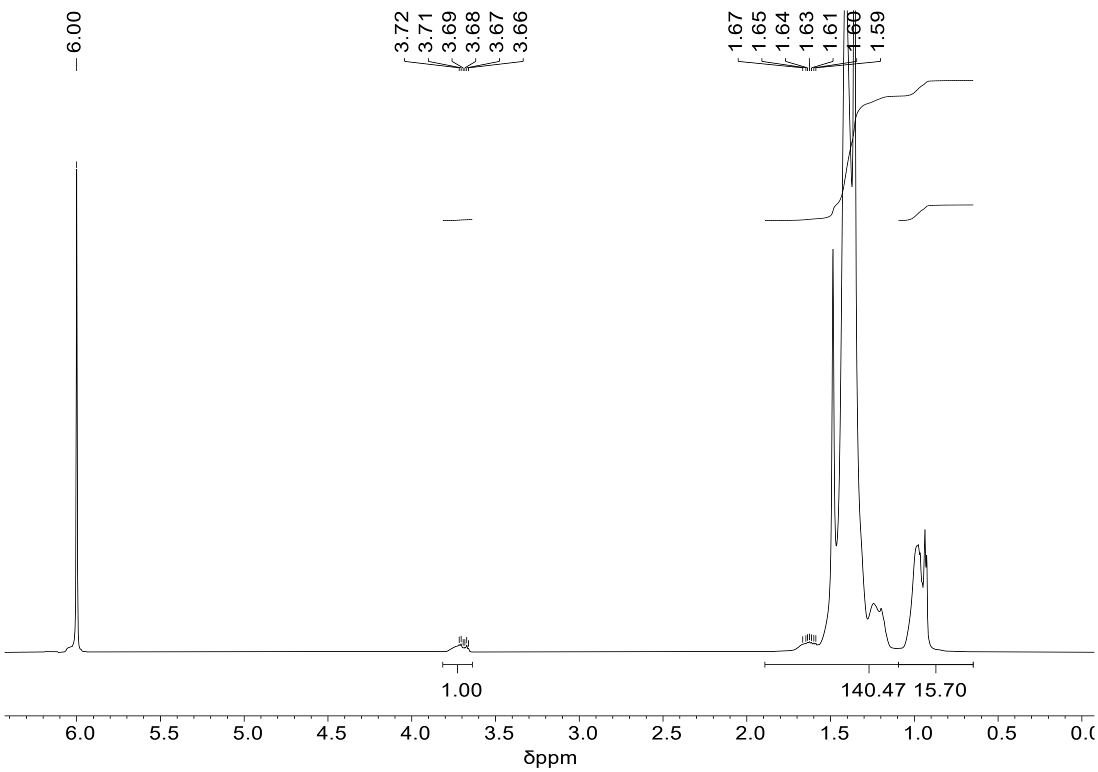


Figure S20. [1]H NMR spectrum (600 MHz) of poly(E-*co*-HAA) (Entry 2, Table 1) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

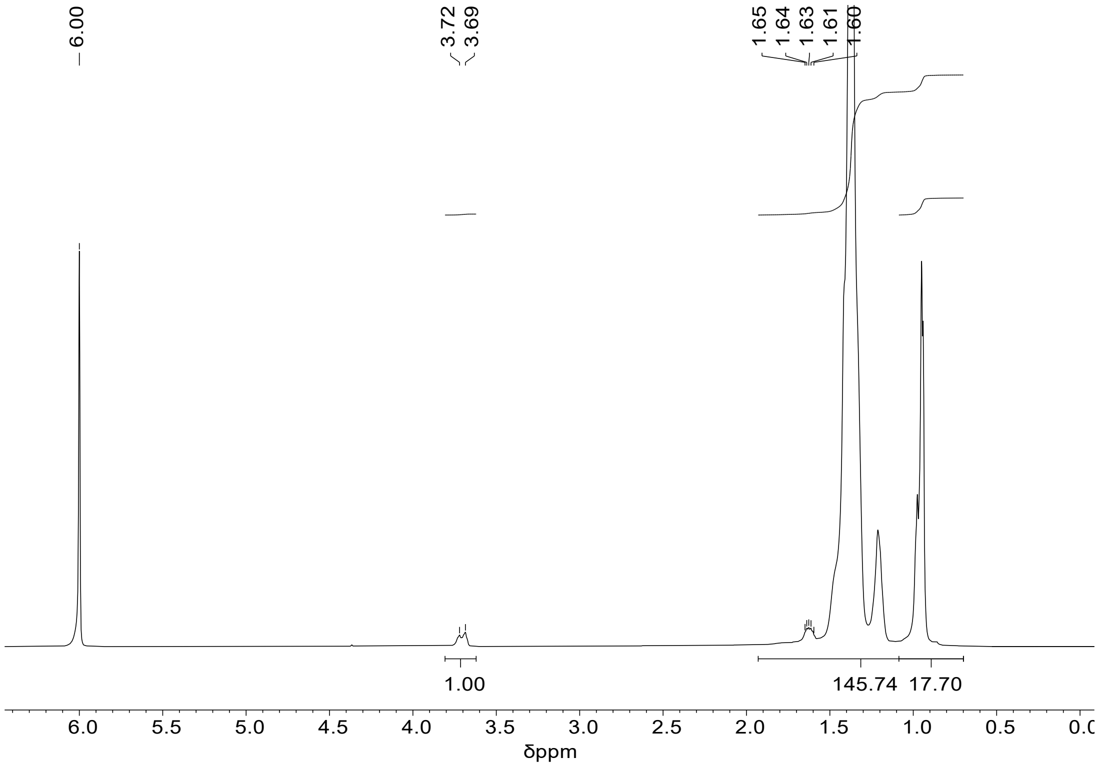


Figure S21. [1]H NMR spectrum (600 MHz) of poly(E-*co*-HAA) (Entry 3, Table 1) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

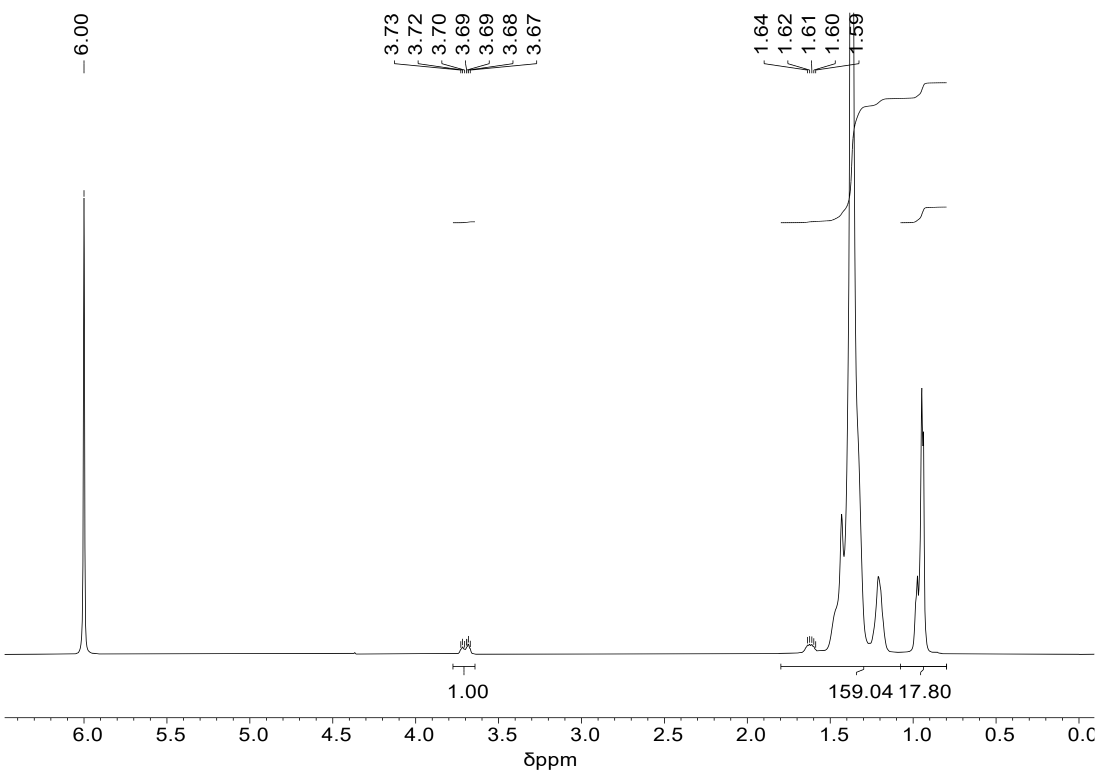


Figure S22. [1]H NMR spectrum (600 MHz) of poly(E-*co*-HAA) (Entry 4, Table 1 & Entry 6, Table 2) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

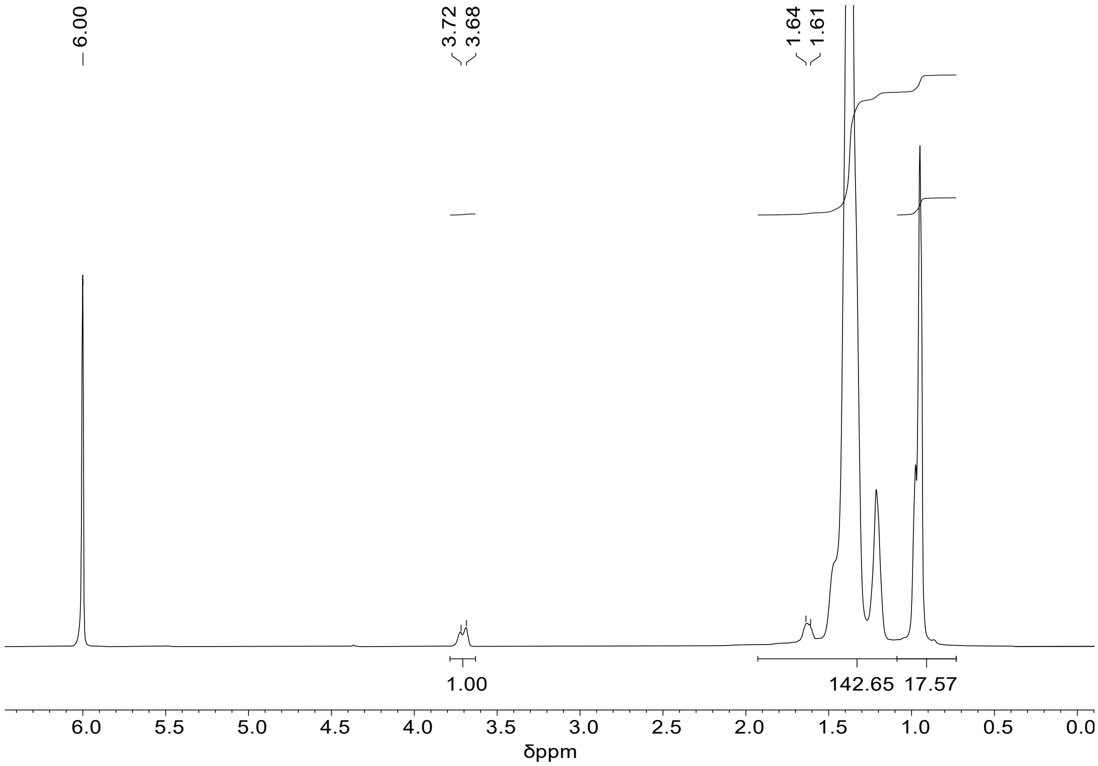


Figure S23. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-HAA) (Entry 5, Table 1) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

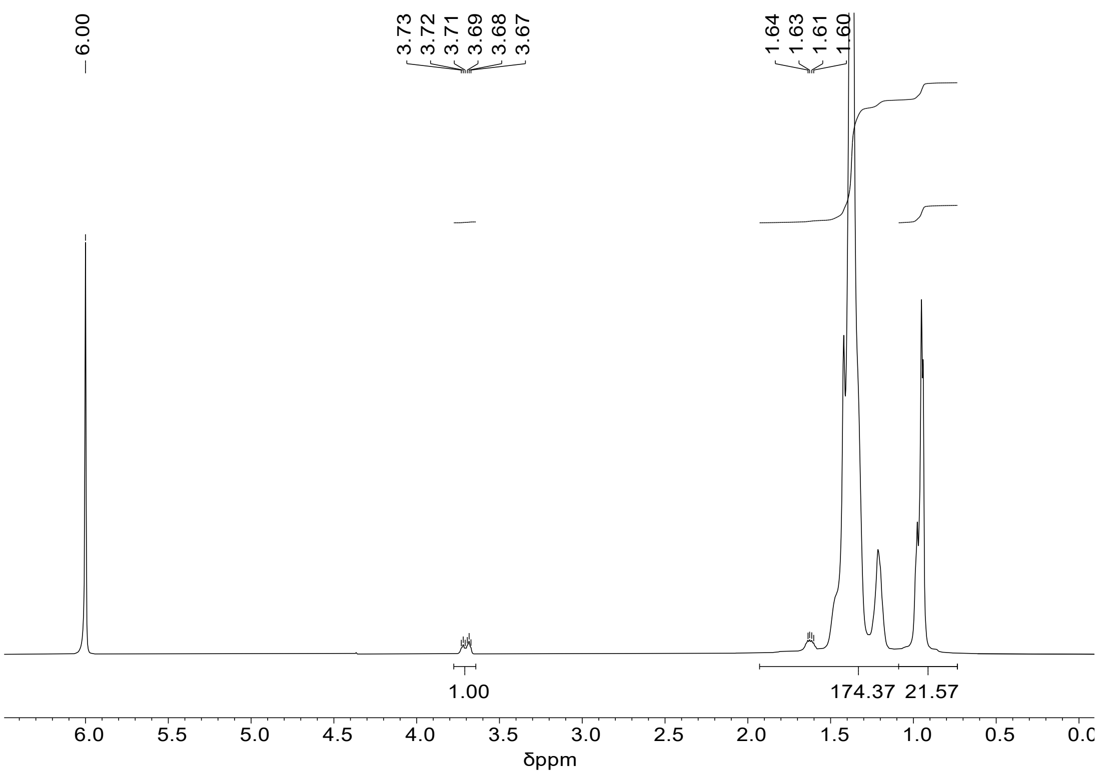


Figure S24. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-HAA) (Entry 6, Table 1) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

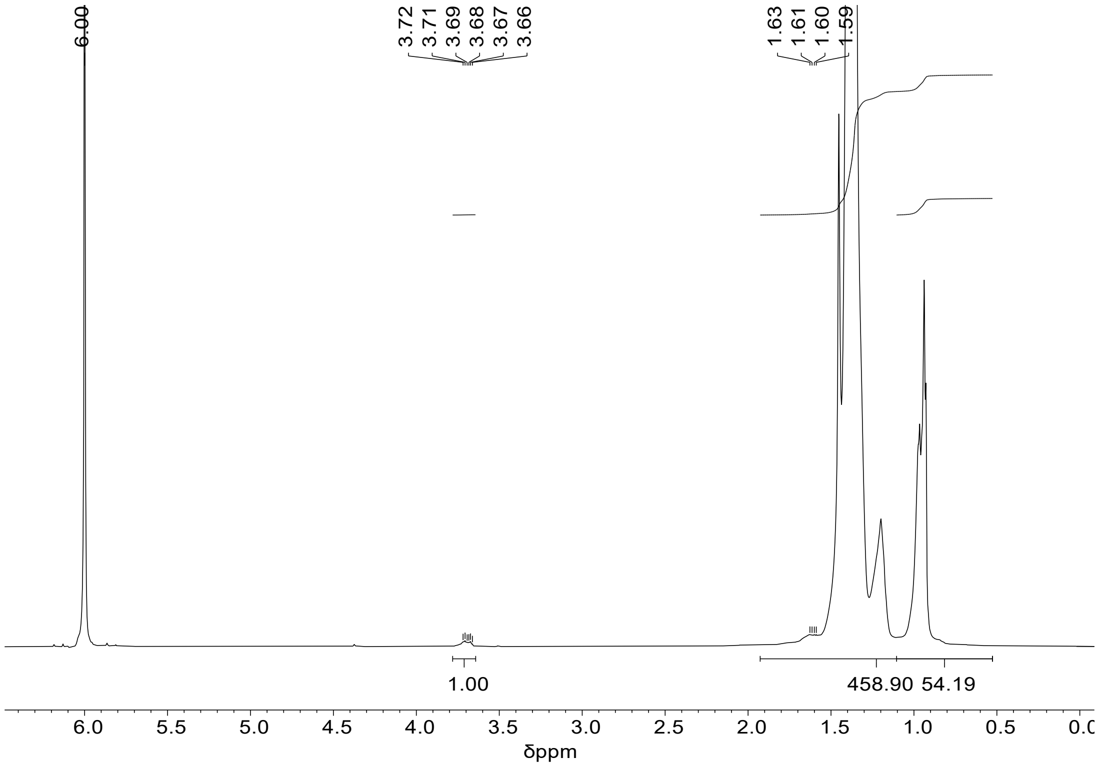


Figure S25. [1]H NMR spectrum (600 MHz) of poly(E-*co*-HAA) (Entry 7, Table 1) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

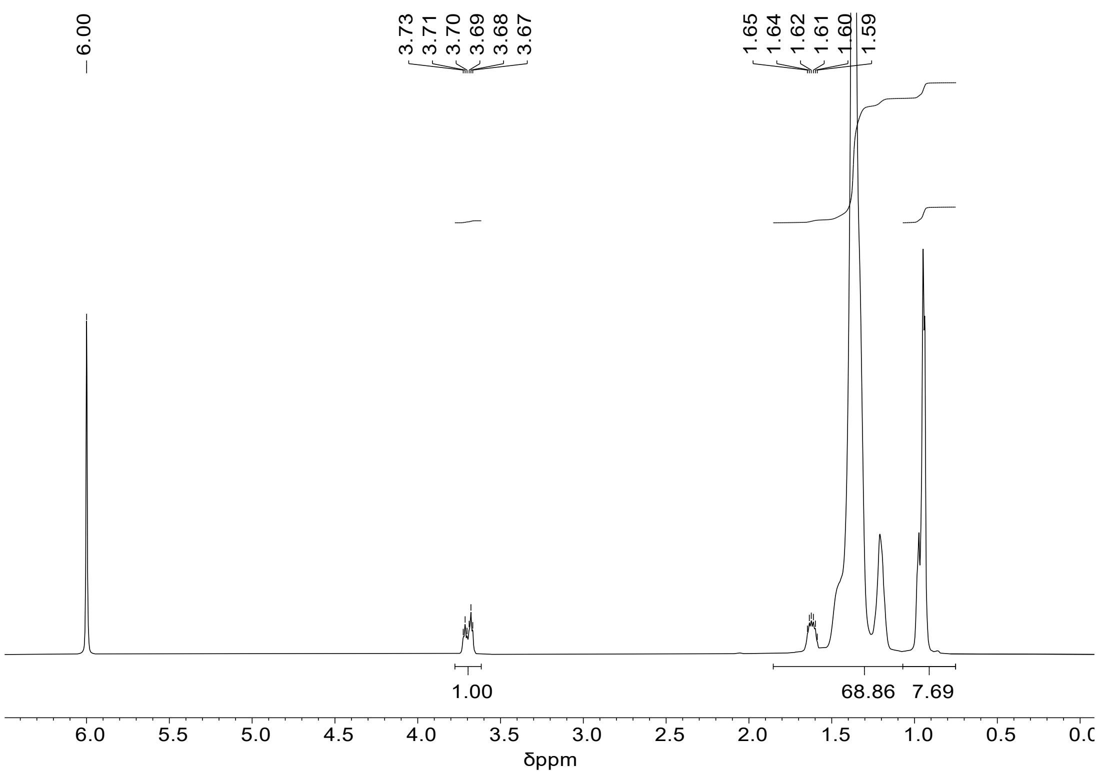


Figure S26. [1]H NMR spectrum (600 MHz) of poly(E-*co*-HAA) (Entry 8, Table 1) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

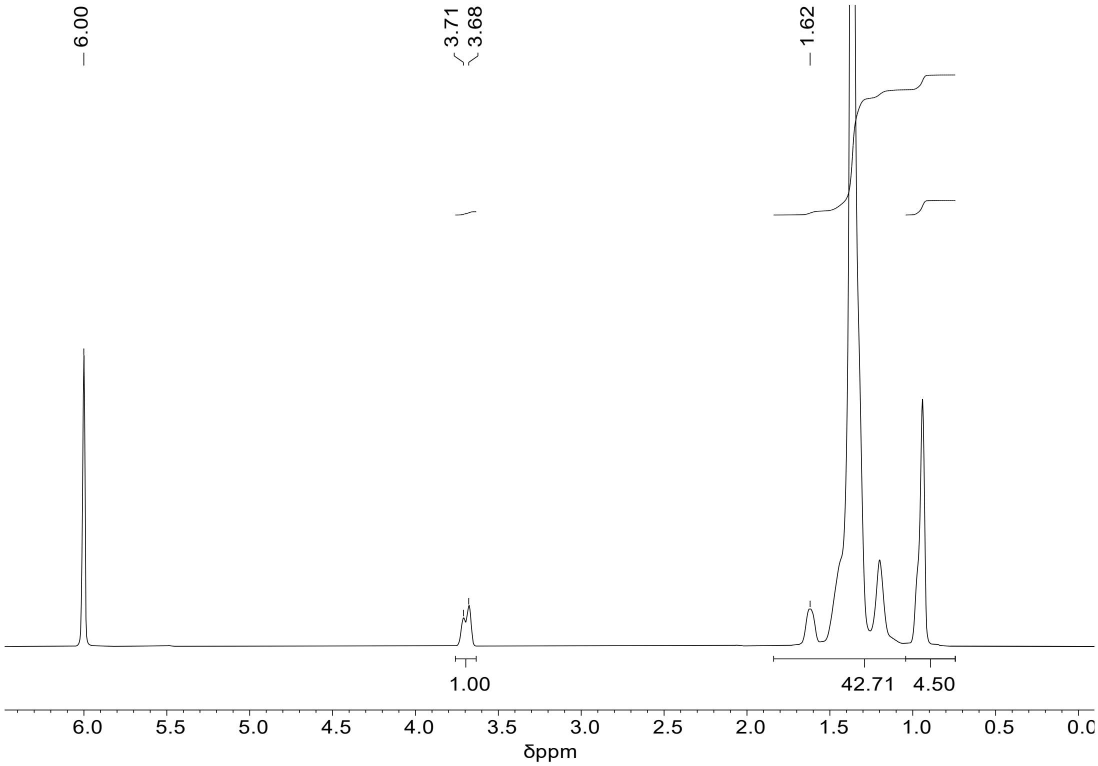


Figure S27. [1]H NMR spectrum (600 MHz) of poly(E-*co*-HAA) (Entry 9, Table 1) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

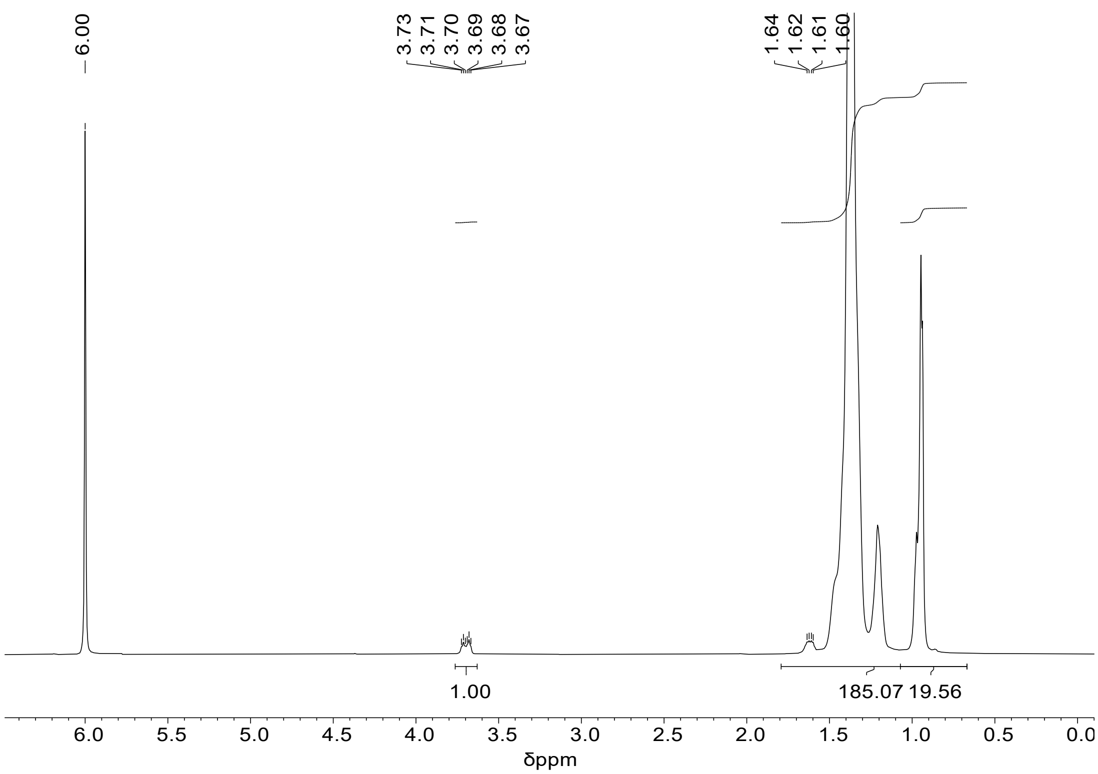


Figure S28. [1]H NMR spectrum (600 MHz) of poly(E-*co*-HAA) (Entry 10, Table 1) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

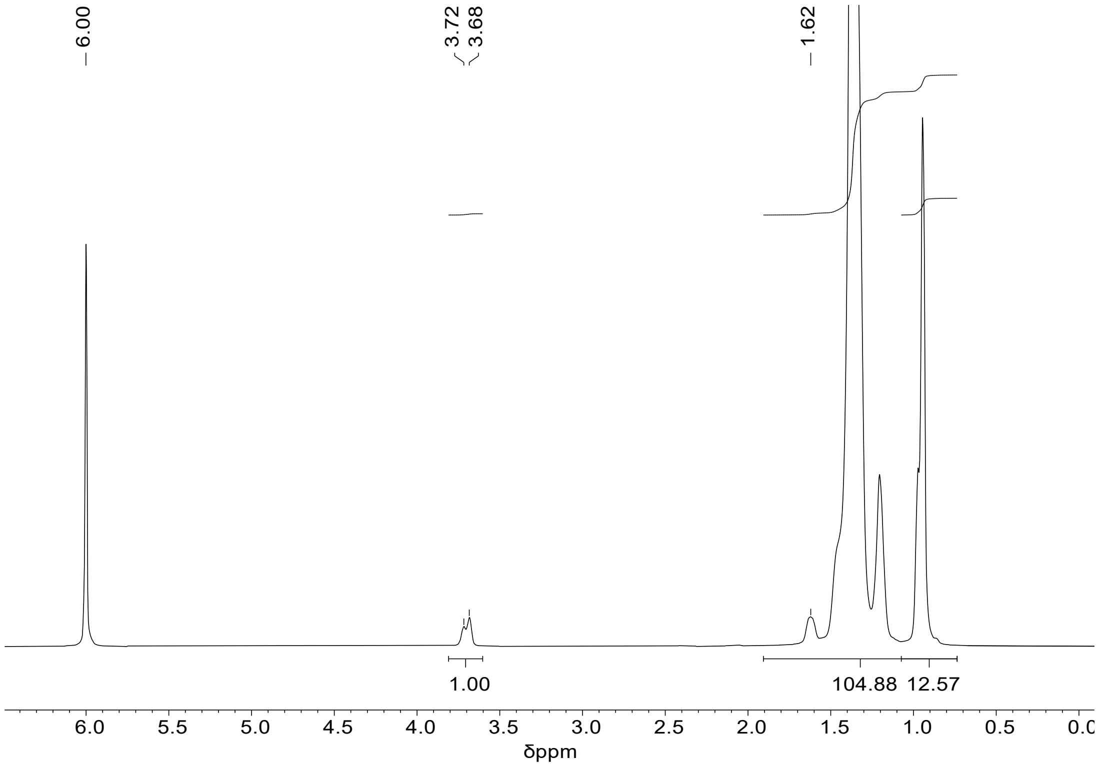


Figure S29. [1]H NMR spectrum (600 MHz) of poly(E-*co*-HAA) (Entry 11, Table 1) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

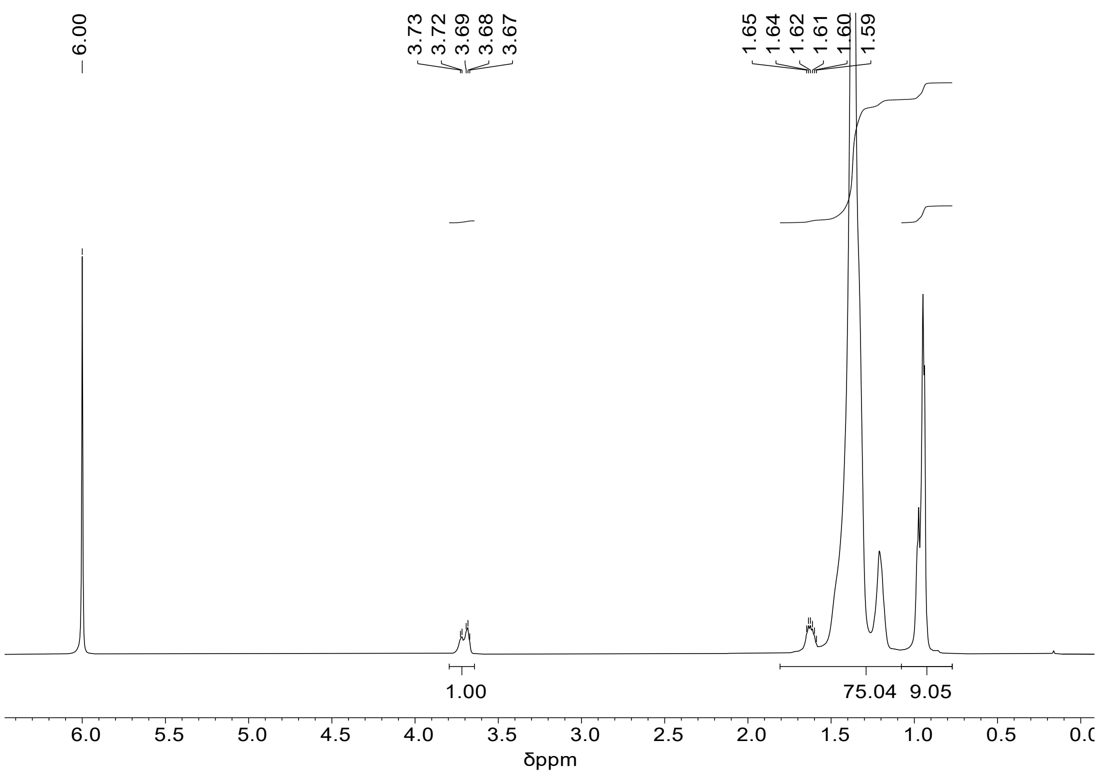


Figure S30. [1]H NMR spectrum (600 MHz) of poly(E-*co*-HAA) (Entry 12, Table 1) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

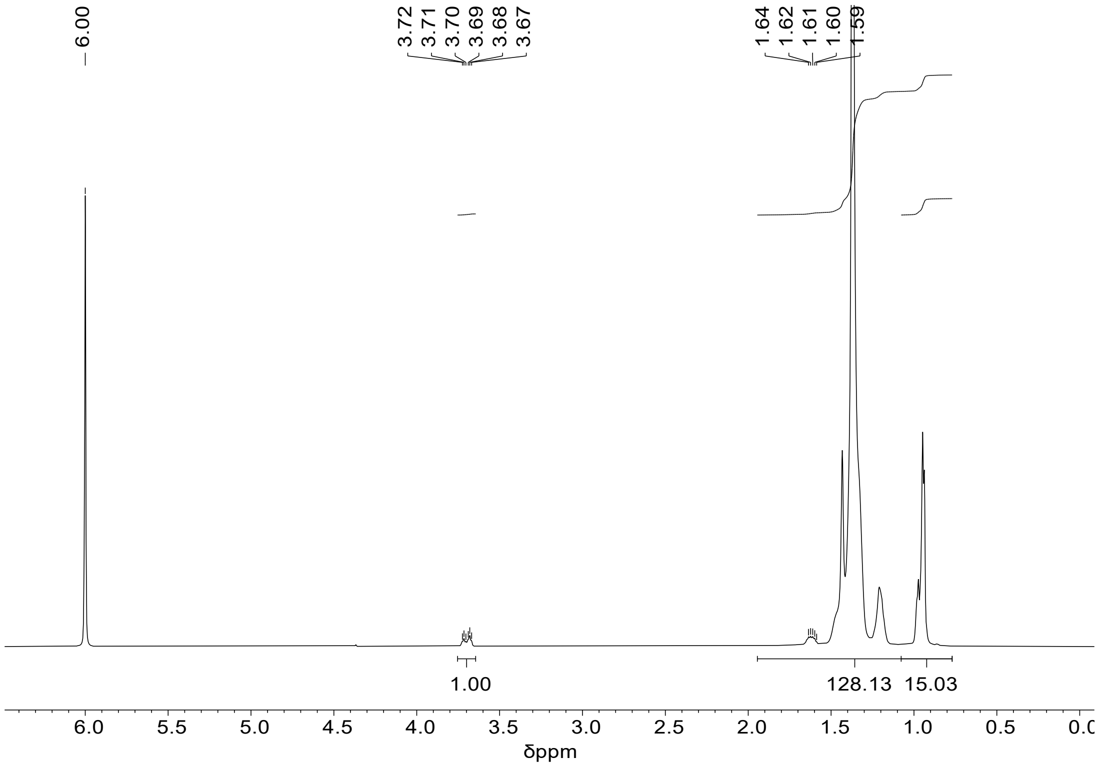


Figure S31. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-HAA) (Entry 13, Table 1) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

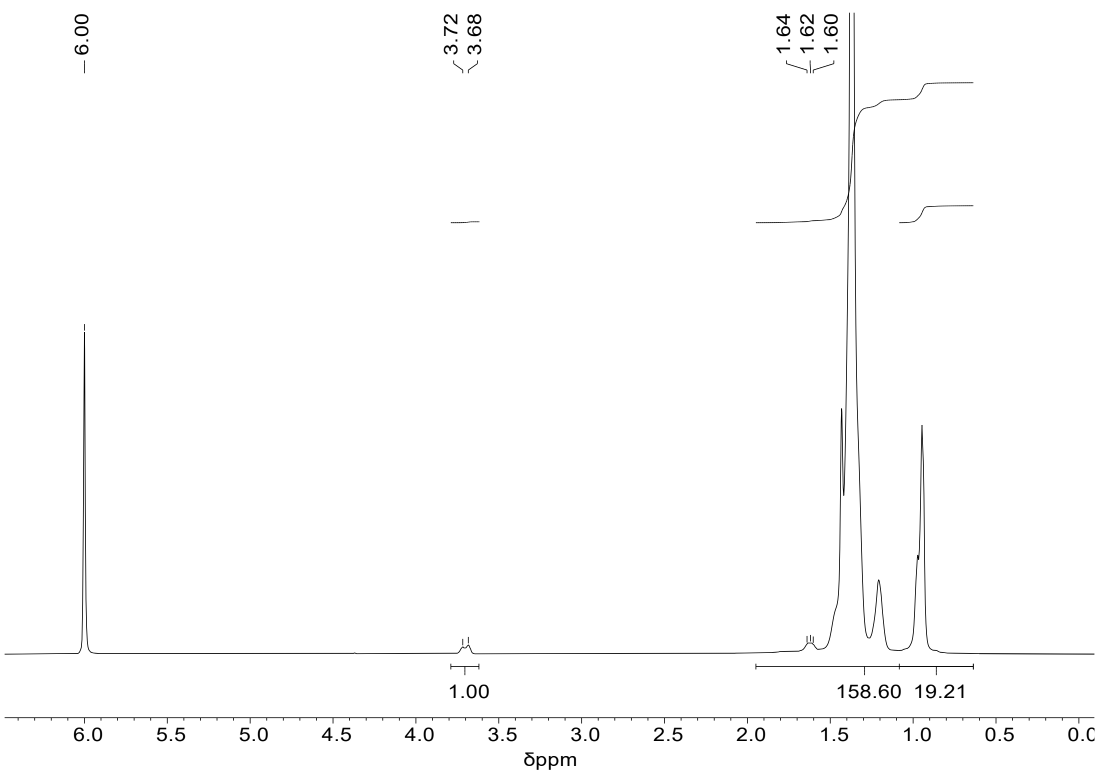


Figure S32. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-HAA) (Entry 14, Table 1) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

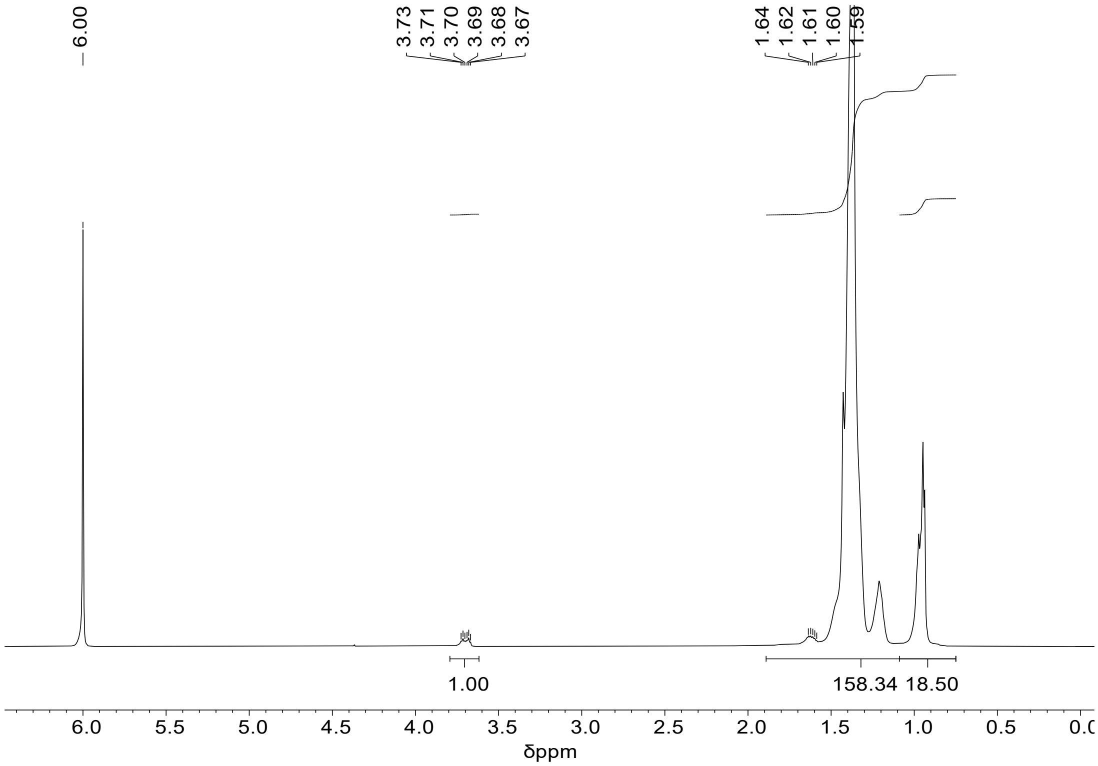


Figure S33. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-HAA) (Entry 15, Table 1) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

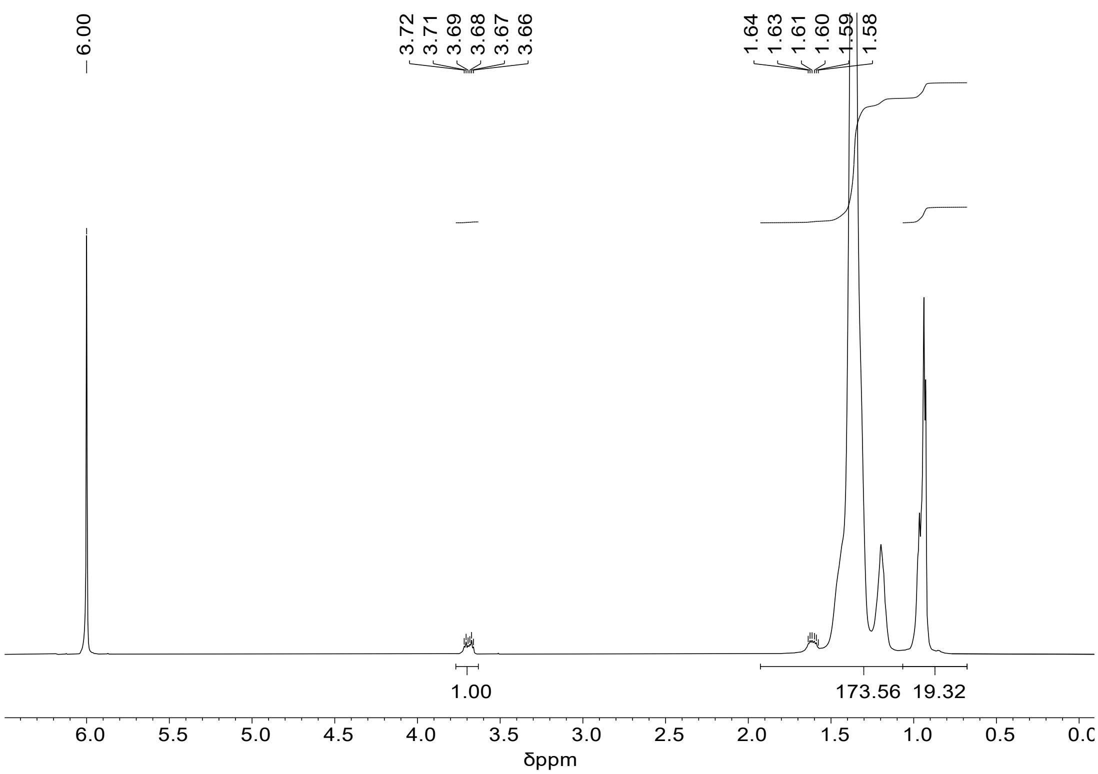


Figure S34. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-HAA) (Entry 16, Table 1) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

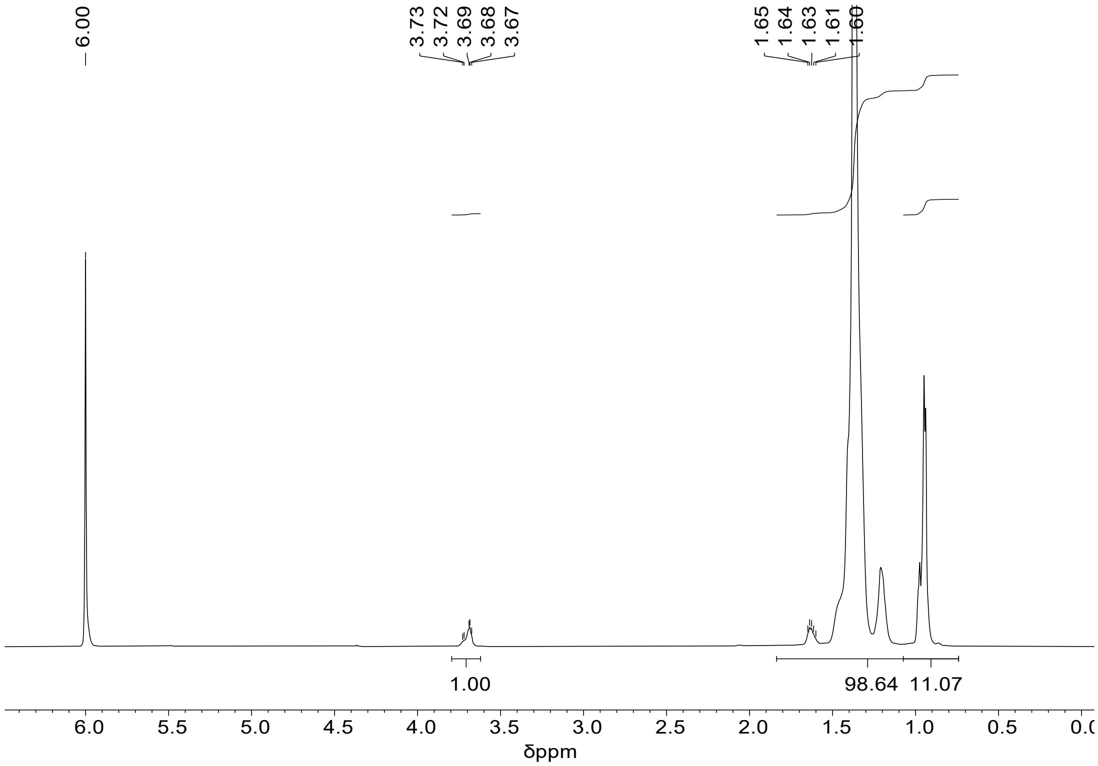


Figure S35. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-HAA) (Entry 7, Table 2) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

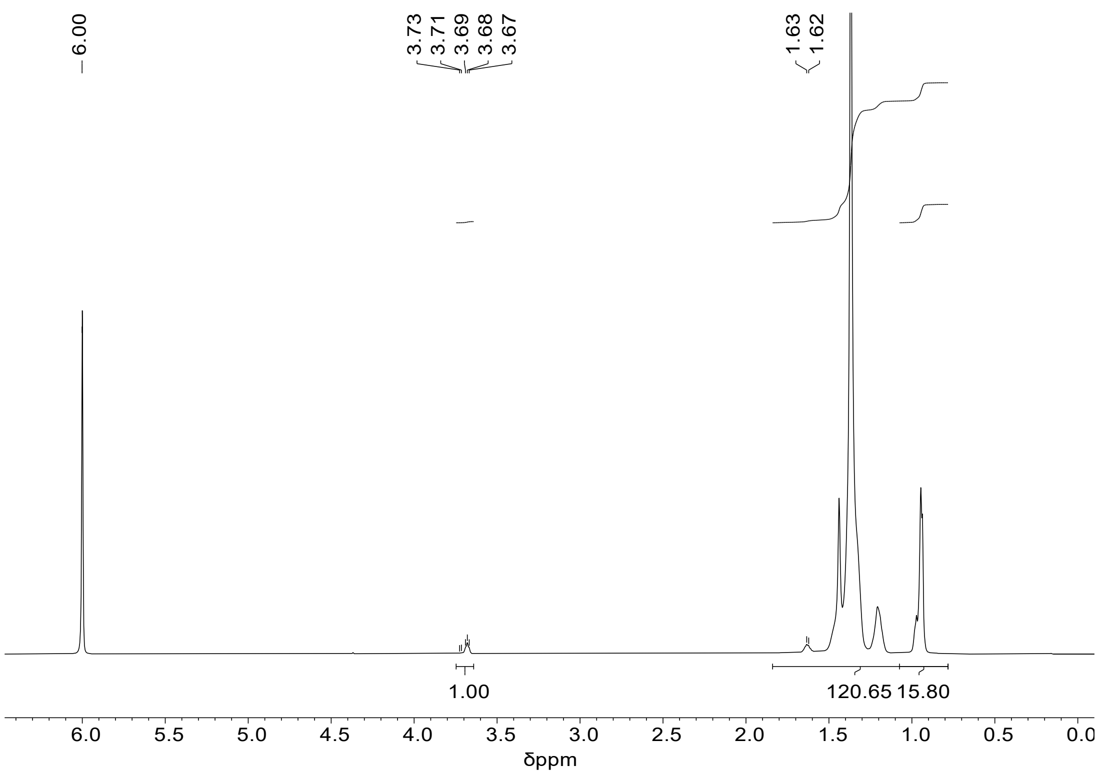


Figure S36. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-HAA) (Entry 9, Table 2) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

2) NMR Spectra of Poly(E-*co*-PA)

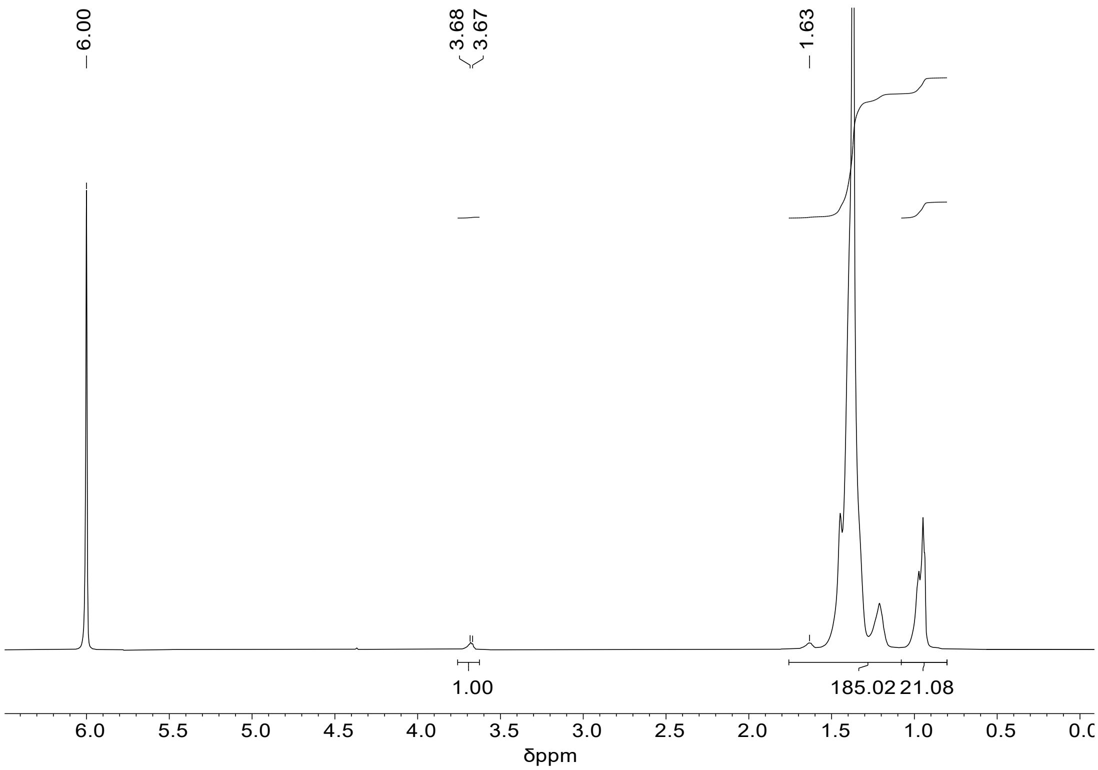


Figure S37. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-PA) (Entry 10, Table 2) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

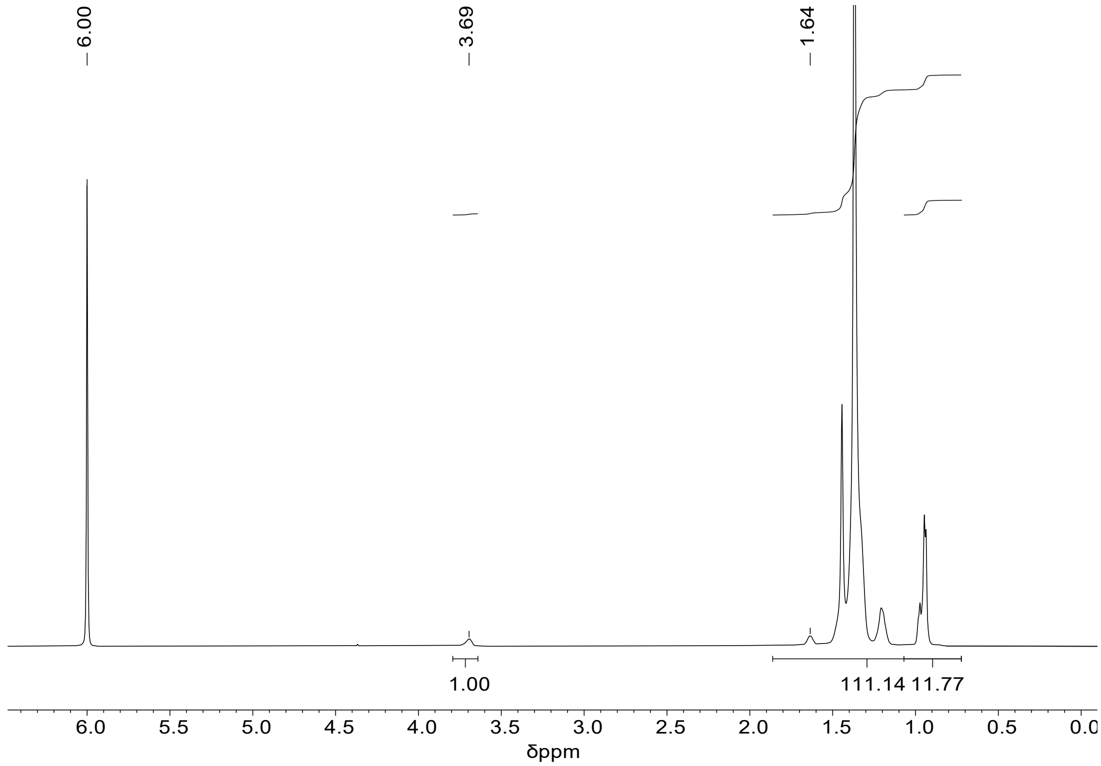


Figure S38. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-PA) (Entry 11, Table 2) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

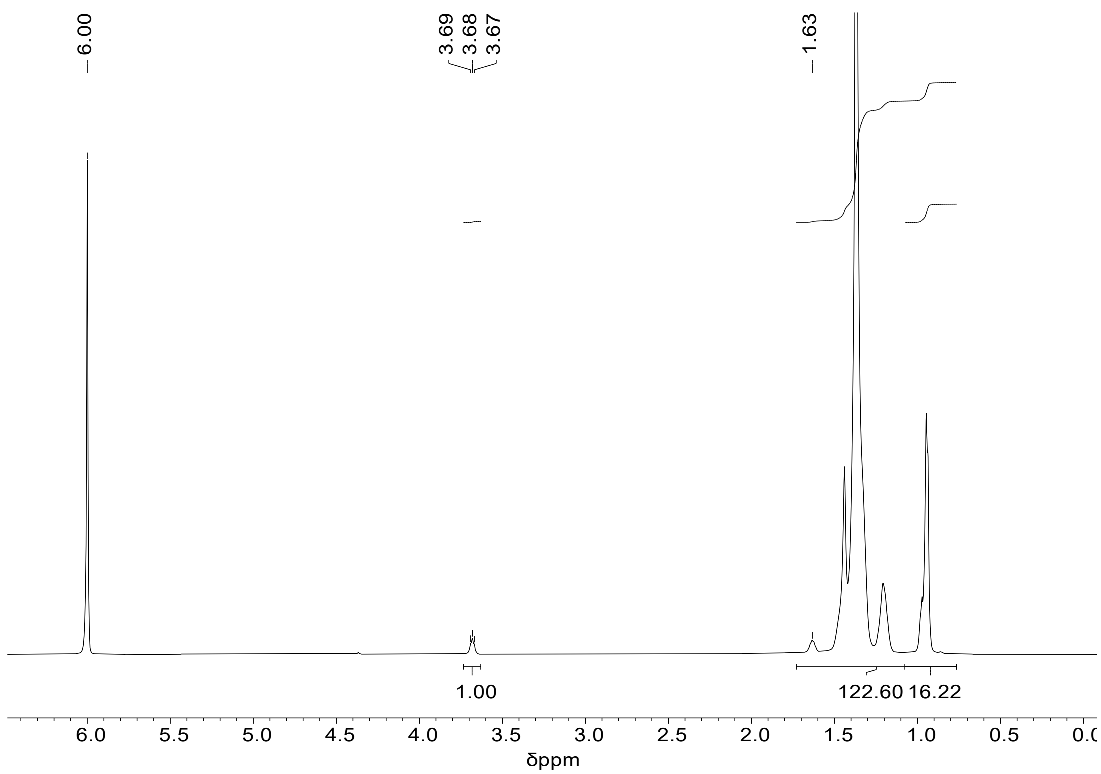


Figure S39. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-PA) (Entry 13, Table 2) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

3) NMR Spectra of Poly(E-*co*-DA)

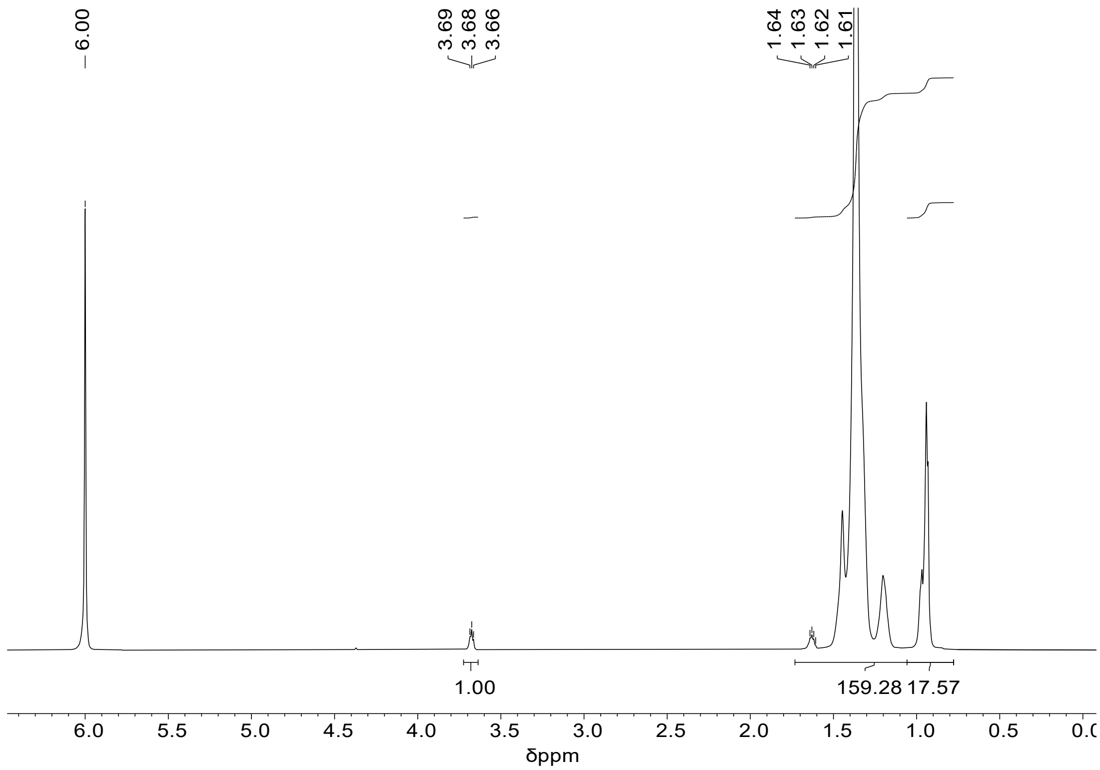


Figure S40. [1]H NMR spectrum (600 MHz) of poly(E-*co*-DA) (Entry 14, Table 2) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

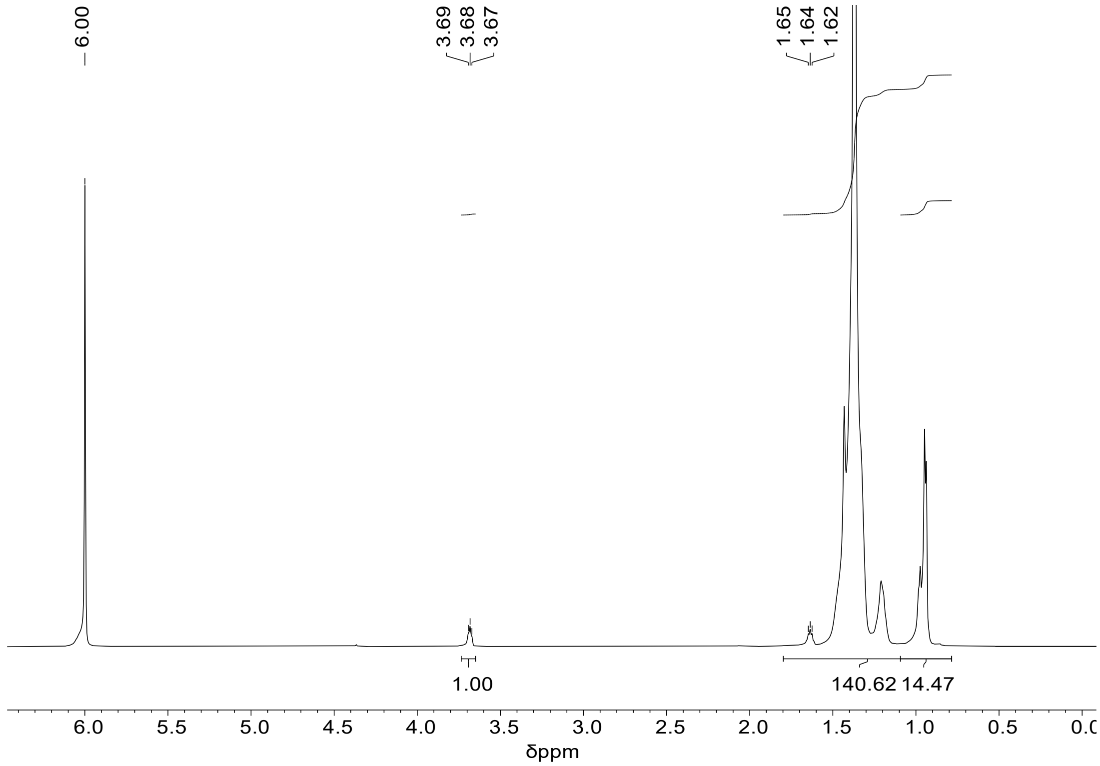


Figure S41. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-DA) (Entry 15, Table 2) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

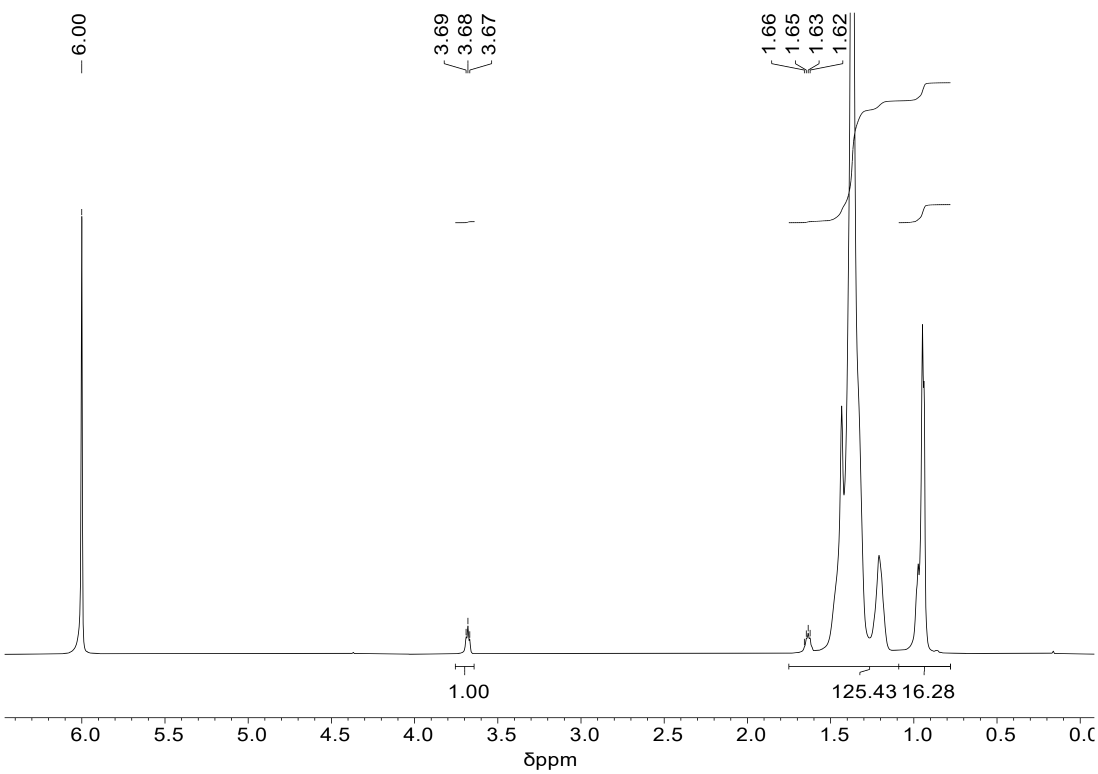


Figure S42. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-DA) (Entry 17, Table 2) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

4) NMR Spectra of Poly(E-*co*-A-ol)

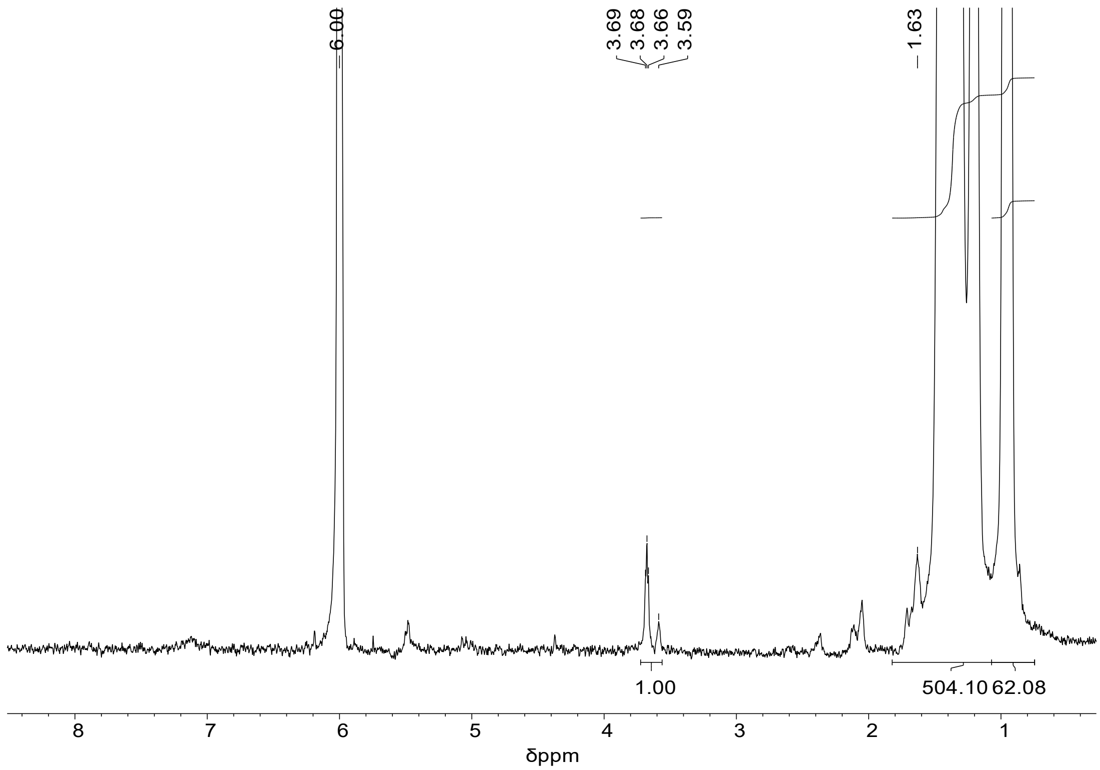


Figure S43. [1]H NMR spectrum (600 MHz) of poly(E-*co*-A-ol) (Entry 1, Table 2) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

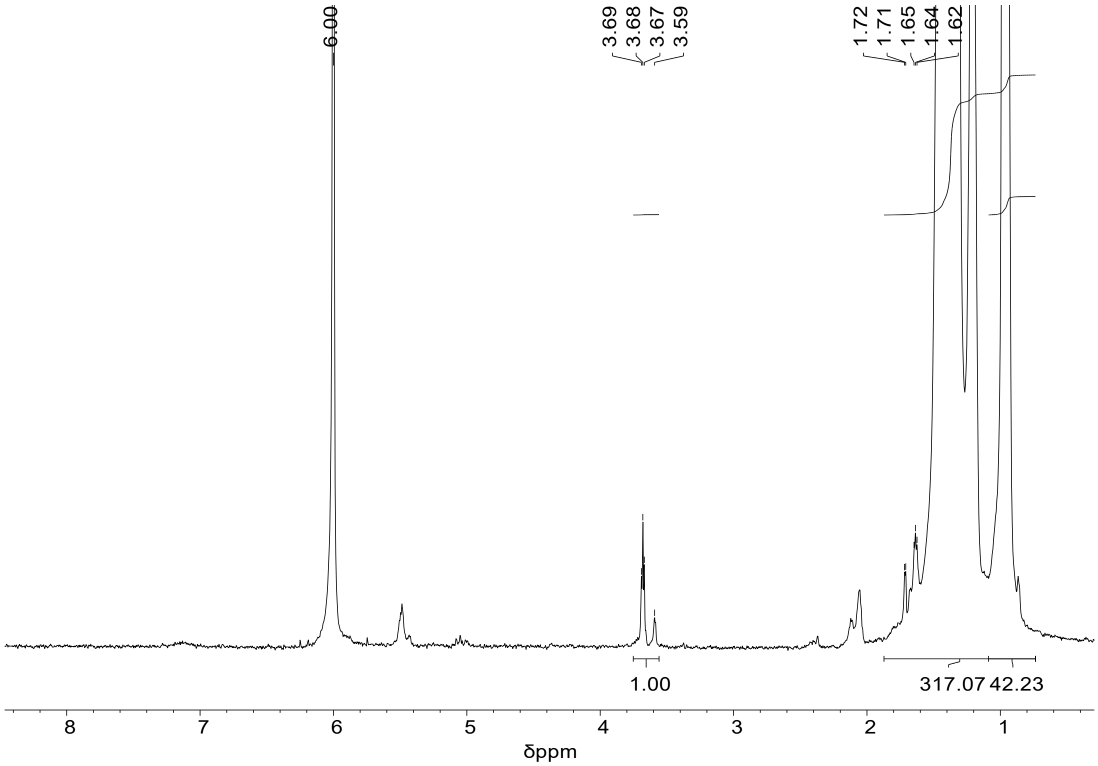


Figure S44. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-A-ol) (Entry 2, Table 2) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

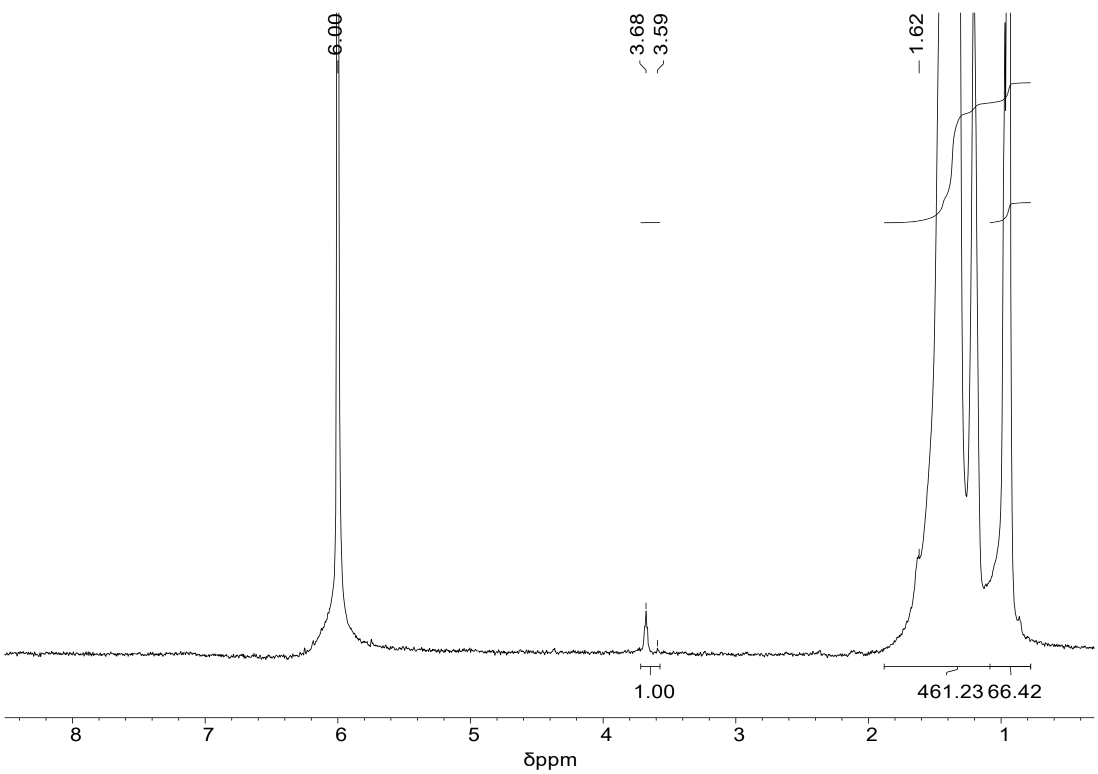


Figure S45. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-A-ol) (Entry 4, Table 2) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

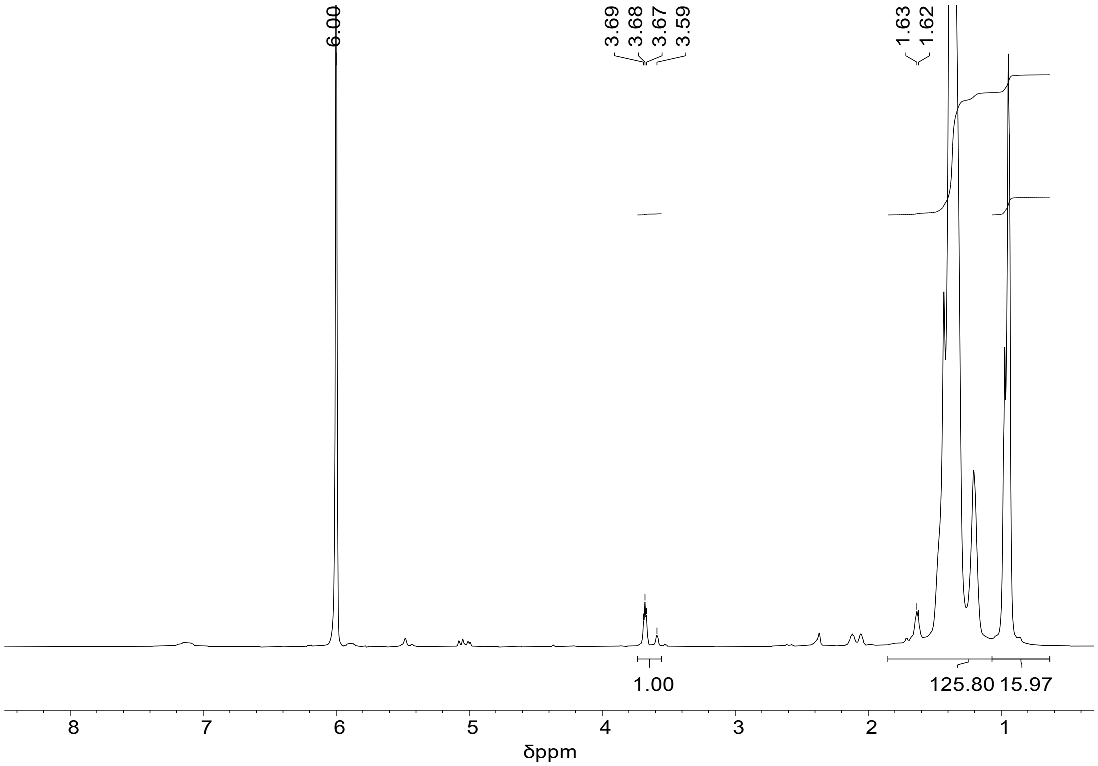


Figure S46. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-A-ol) (Entry 5, Table 2) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

5) NMR Spectra of Poly(E-*co*-AAc)

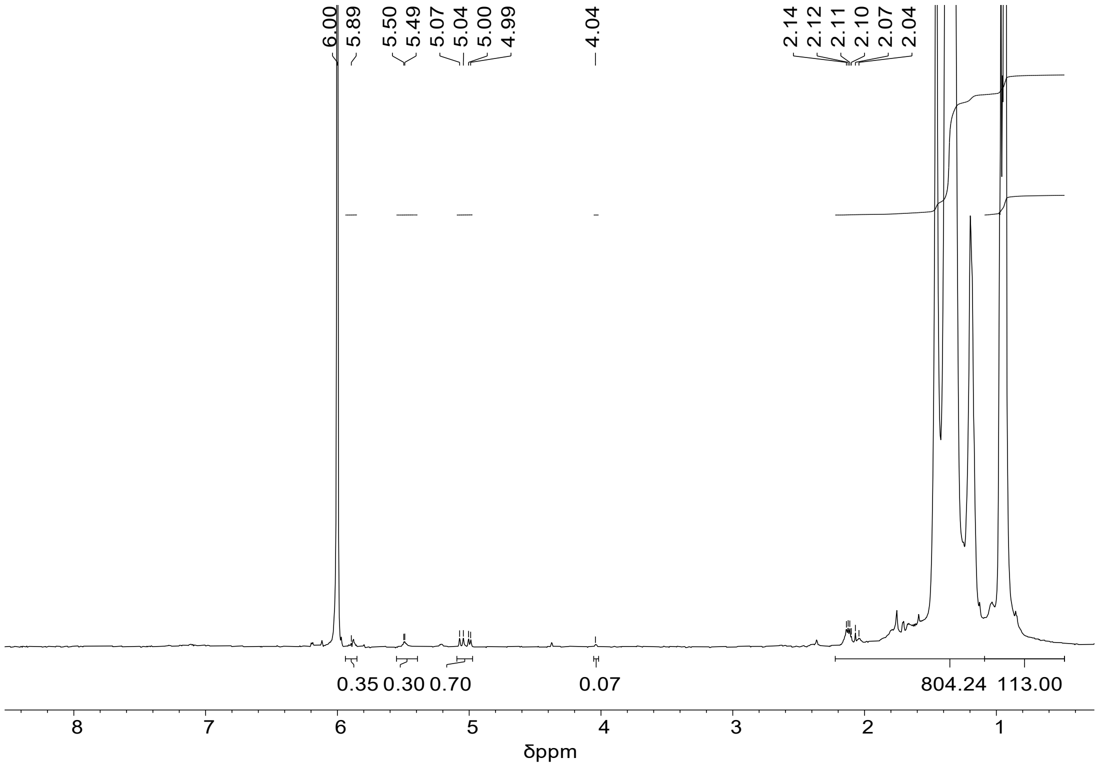


Figure S47. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-AAc) (Entry 1, Table 4) (little -OAc content but double bond detected) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

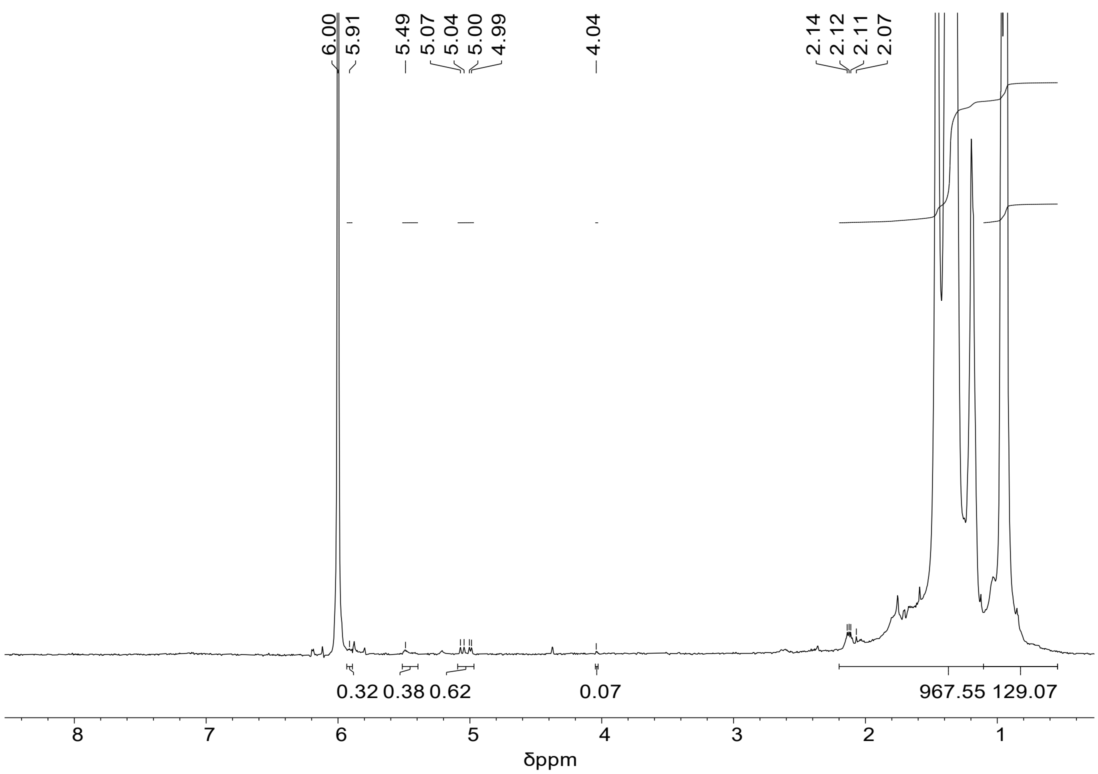


Figure S48. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-AAc) (Entry 3, Table 4) (no -OAc incorporation but double bond detected) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

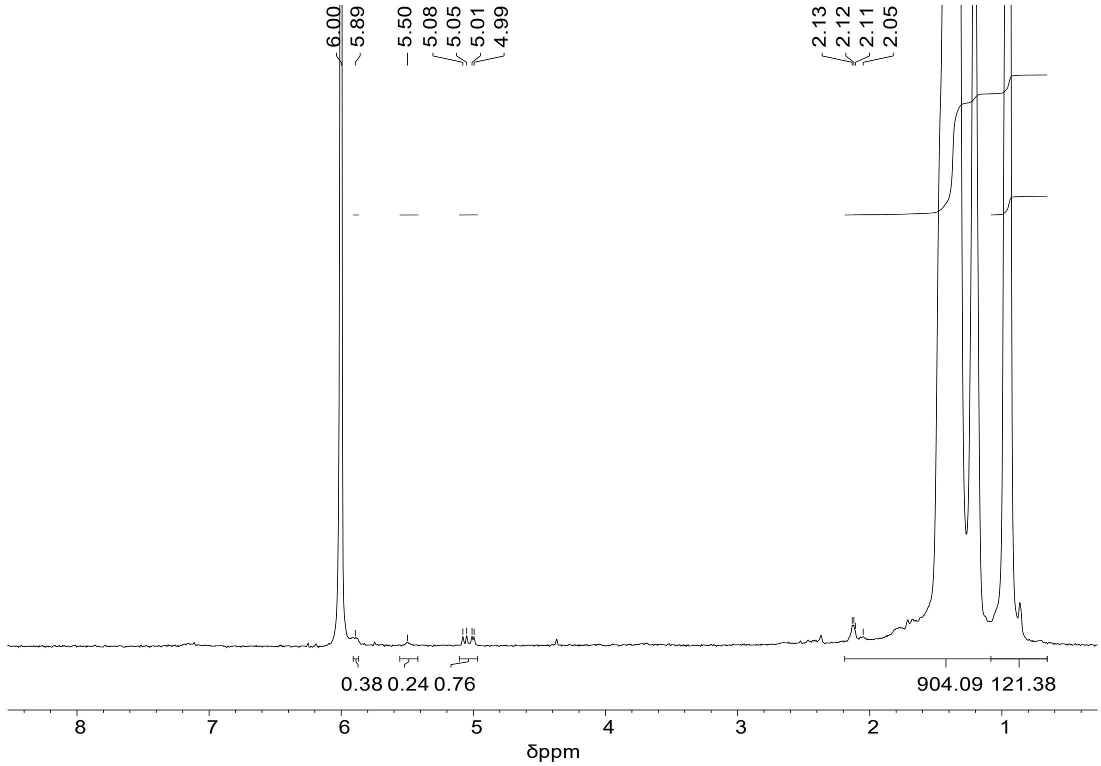


Figure S49. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-AAc) (Entry 4, Table 4) (no -OAc incorporation but double bond detected) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

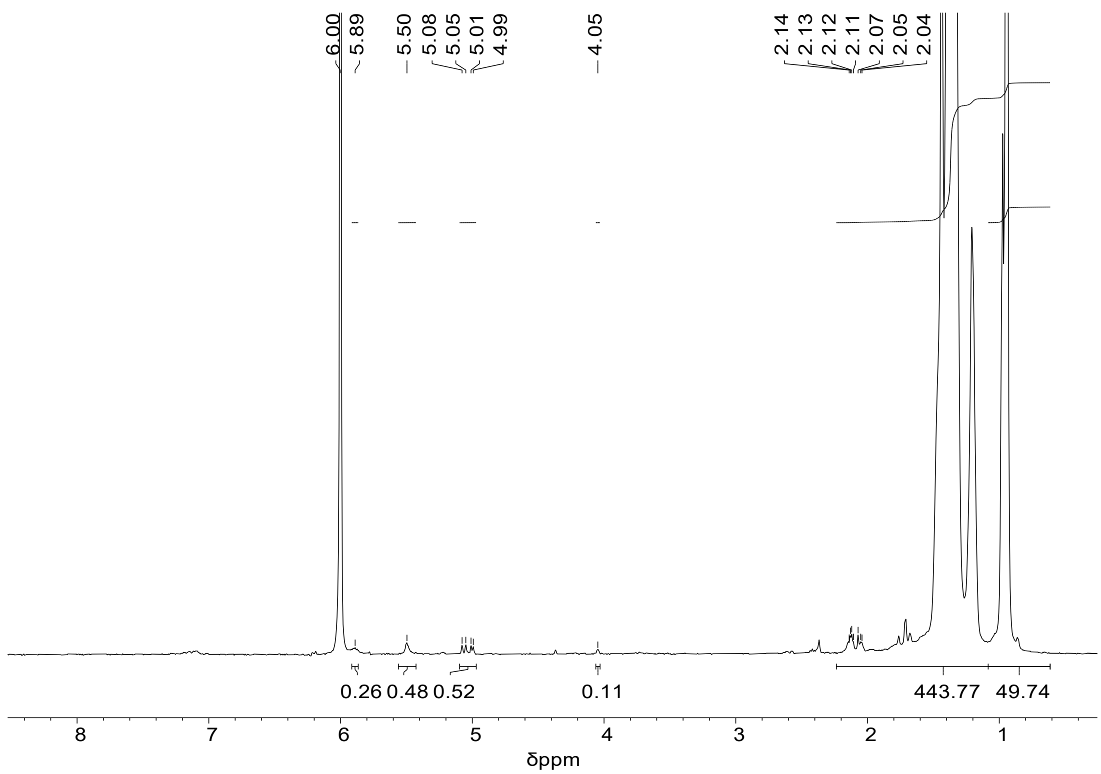


Figure S50. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-AAc) (Entry 5, Table 4) (no -OAc incorporation but double bond detected) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

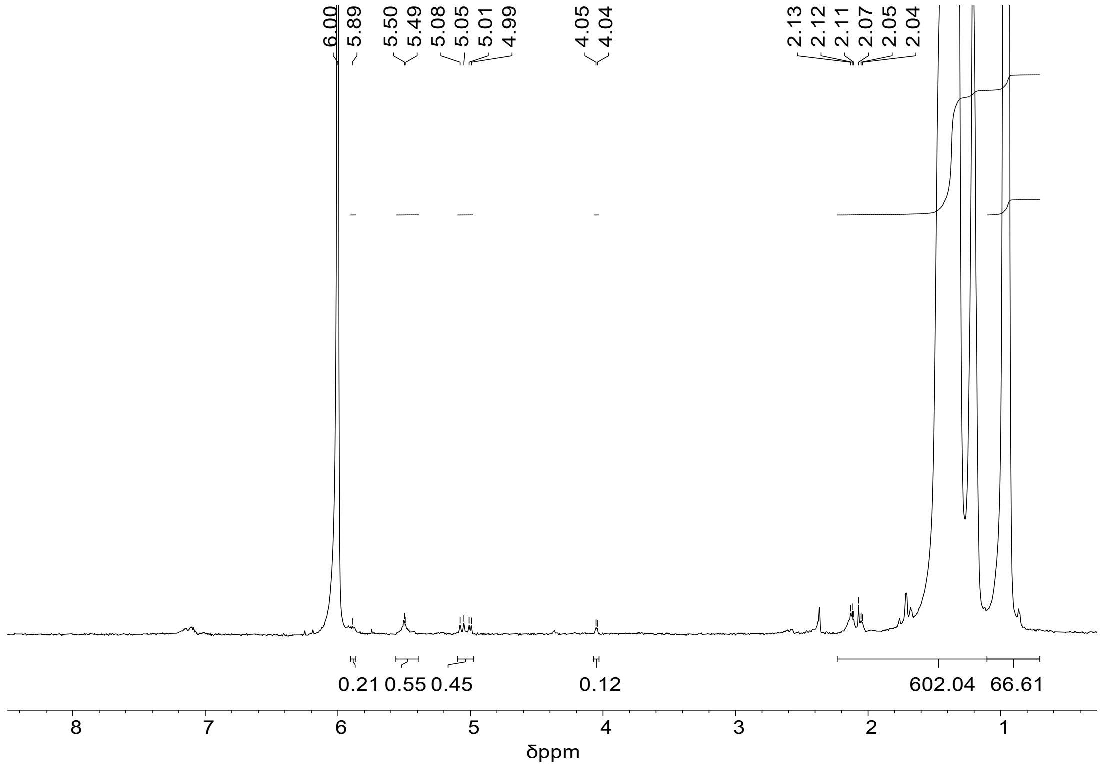


Figure S51. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-AAc) (Entry 6, Table 4) (no -OAc incorporation but double bond detected) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

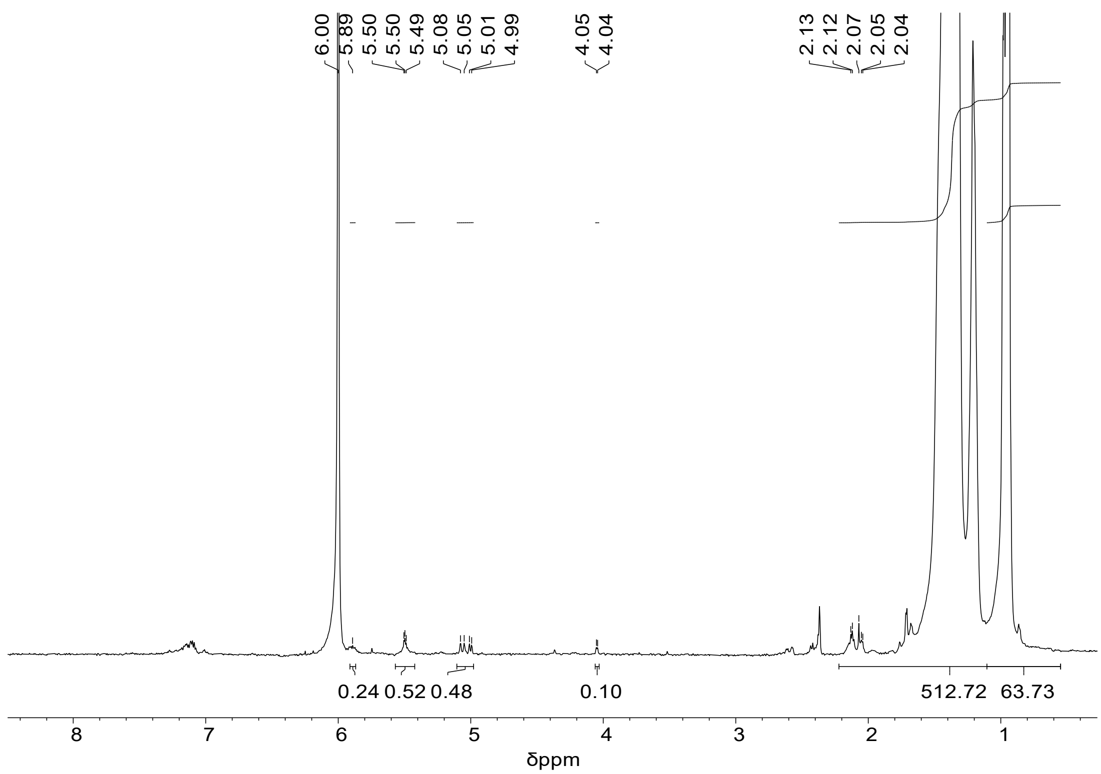


Figure S52. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-AAc) (Entry 7, Table 4) (no -OAc incorporation but double bond detected) in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

6) Representative NMR Spectra of Poly(E-*co*-Alkenol) after Acetylation

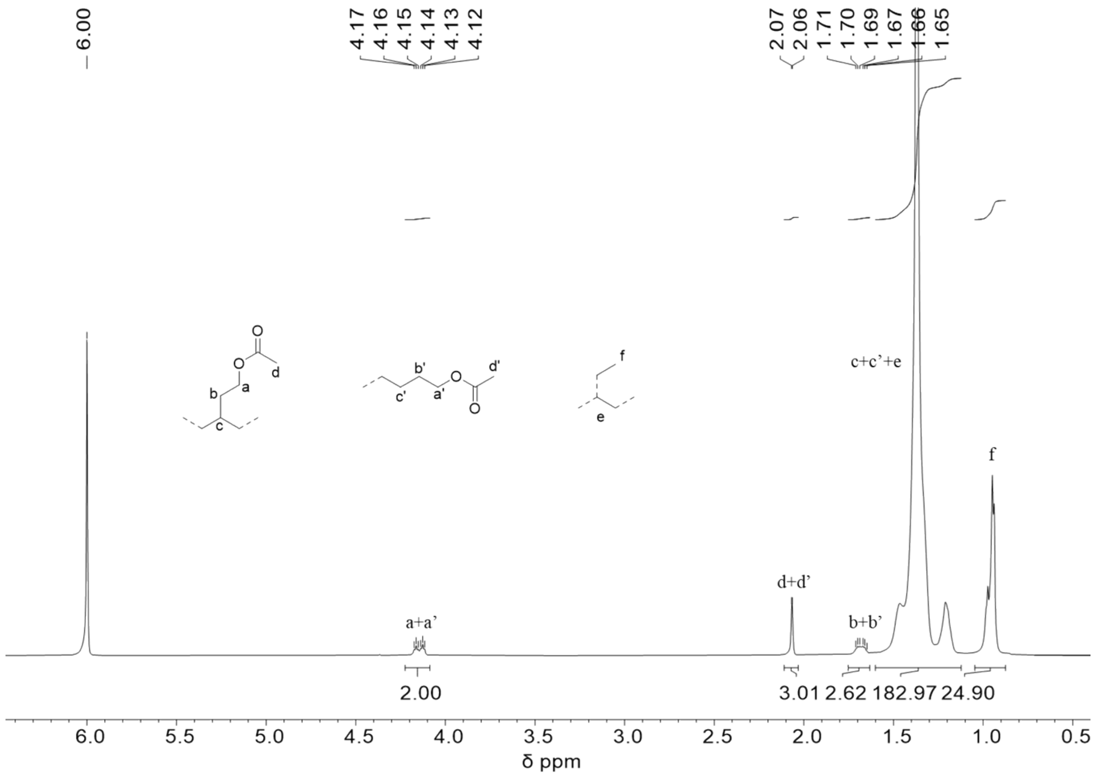


Figure S53. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-HAA) (Entry 8, Table 2) after acetylation in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

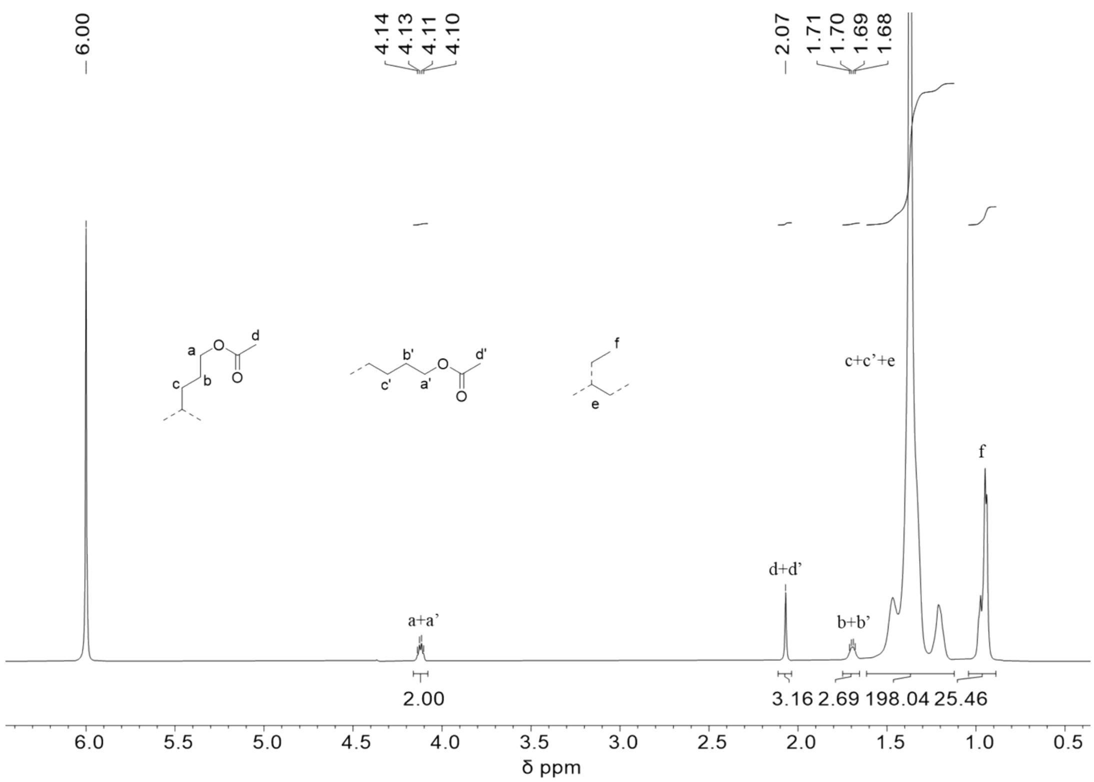


Figure S54. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-PA) (Entry 12, Table 2) after acetylation in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

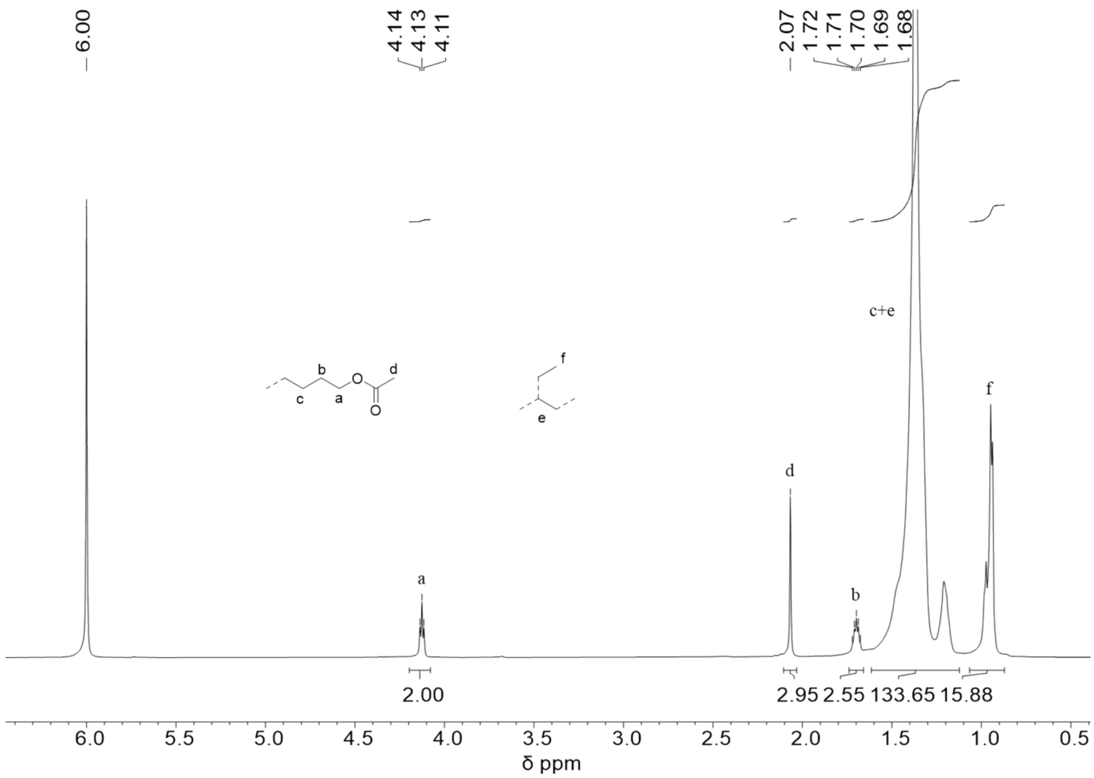
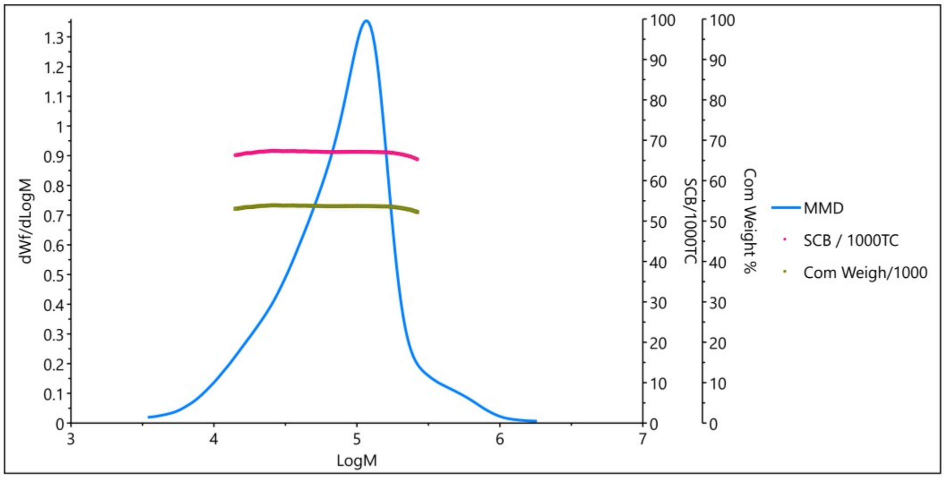


Figure S55. ^{1}H NMR spectrum (600 MHz) of poly(E-*co*-DA) (Entry 16, Table 2) after acetylation in 1,1,2,2-tetrachloroethane-d_2 at 120 °C.

7) GPC Traces of Polymer Samples



Results

Mw	111511	g/mol
Mn	46251	g/mol
Mw / Mn	2.41	
Mz	259276	g/mol
Mp	116137	g/mol
Mv	99874	g/mol
IVmwd	1.86	dL/g
Bulk CH3 / 1000C	67.21	
Bulk SCB / 1000C	66.58	
Bulk Comonomer Wt%	53.26	%
Pump Flow Rate	1.00	ml / min
Columns Temp	150	ºC
Detectors Temp	150	ºC
Nominal MHa	0.725	
Nominal MHK	0.00044	

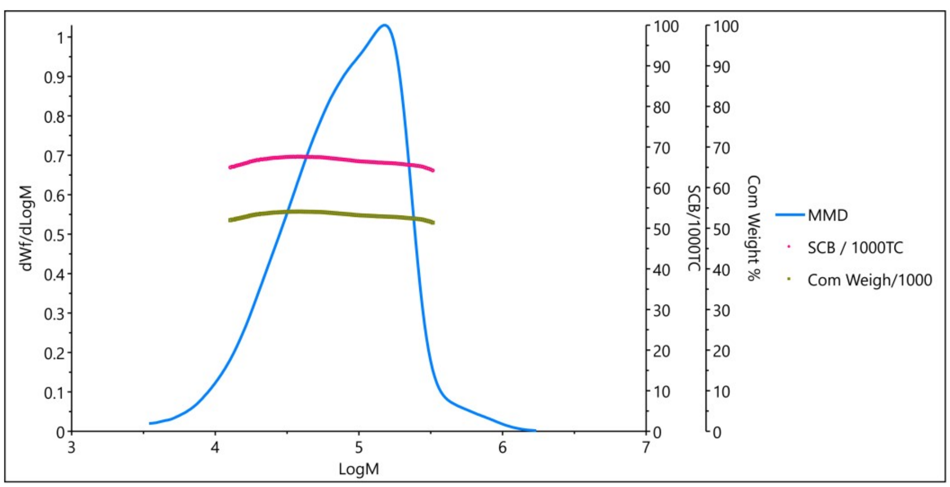
Calibrations

Flow Marker	28.32	mL
Mass constant	0.45	mL·V/mg

Performance

Flow Marker	28.60	mL
Mass recovery	88	%
Plate Count	1671	

Figure S56. GPC trace of poly(E-*co*-HAA) (Entry 2, Table 1) after acetylation.



Results

Mw	111504	g/mol
Mn	46664	g/mol
Mw / Mn	2.39	
Mz	225330	g/mol
Mp	149748	g/mol
Mv	100835	g/mol
IVmwd	1.87	dL/g
Bulk CH3 / 1000C	66.75	
Bulk SCB / 1000C	66.12	
Bulk Comonomer Wt%	52.89	%
Pump Flow Rate	1.00	ml / min
Columns Temp	150	ºC
Detectors Temp	150	ºC
Nominal MHa	0.725	
Nominal MHK	0.00044	

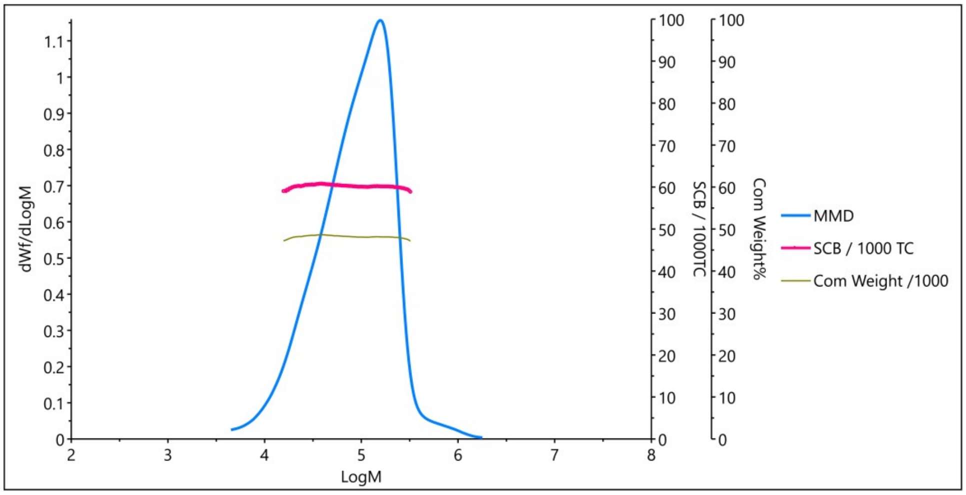
Calibrations

Flow Marker	28.32	mL
Mass constant	0.45	mL·V/mg

Performance

Flow Marker	28.28	mL
Mass recovery	90	%
Plate Count	3964	

Figure S57. GPC trace of poly(E-*co*-HAA) (Entry 3, Table 1) after acetylation.



Results

Mw	119936	g/mol
Mn	53905	g/mol
Mw / Mn	2.22	
Mz	235724	g/mol
Mp	156314	g/mol
Mv	108182	g/mol
IVmwd	1.5404	dL/g
Bulk CH3 / 1000C	60.331	
Corrected Bulk CH3 / 1000C	59.8	CH3/1000TC corr

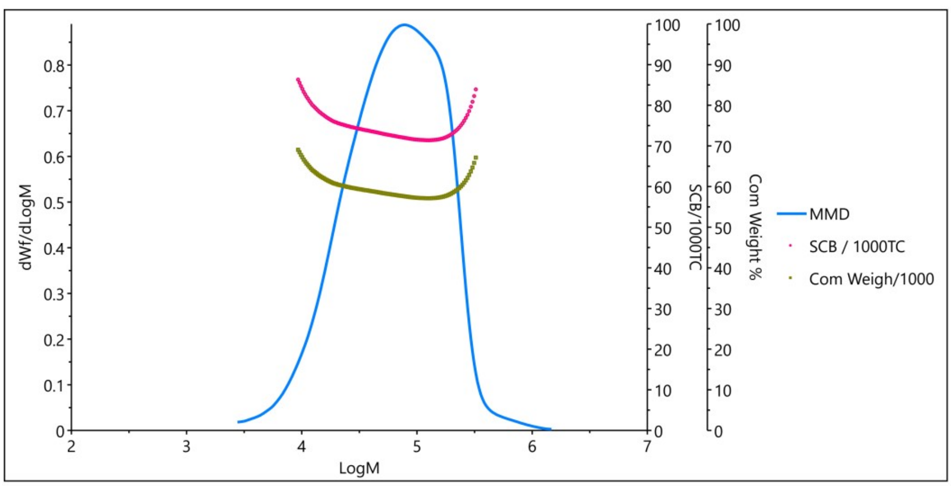
Calibrations

Calib Flow Marker	28.02	mL
Calib Mass constant	0.28	mL·V/mg

Performance

Flow Marker	27.94	mL
Mass recovery	79	%
Plate Count	18640	

Figure S58. GPC trace of poly(E-*co*-HAA) (Entry 4, Table 1; Entry 6, Table 2) after acetylation.



Results

Mw	93575	g/mol
Mn	38265	g/mol
Mw / Mn	2.45	
Mz	188205	g/mol
Mp	78061	g/mol
Mv	84339	g/mol
IVmwd	1.65	dL/g
Bulk CH3 / 1000C	78.03	
Bulk SCB / 1000C	77.26	
Bulk Comonomer Wt%	61.81	%
Pump Flow Rate	1.00	ml / min
Columns Temp	150	ºC
Detectors Temp	150	ºC
Nominal MHa	0.725	
Nominal MHK	0.00044	

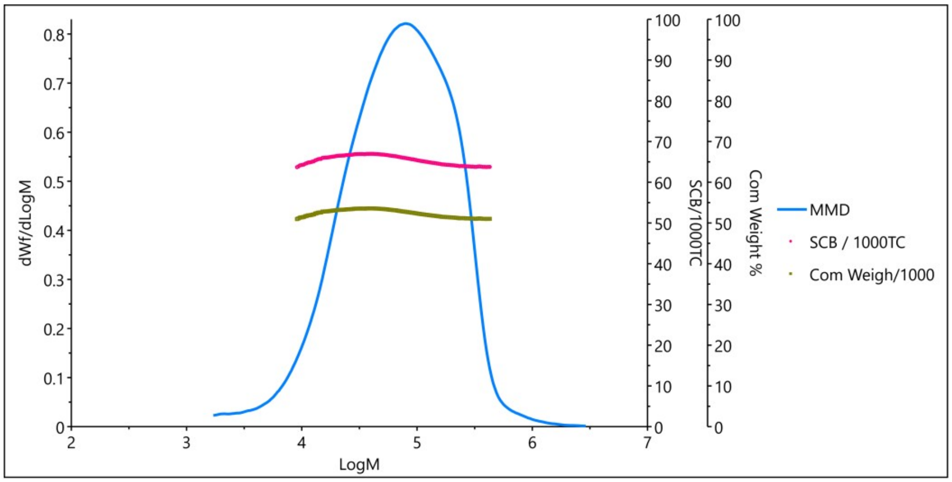
Calibrations

Flow Marker	28.32	mL
Mass constant	0.45	mL·V/mg

Performance

Flow Marker	28.27	mL
Mass recovery	90	%
Plate Count	3924	

Figure S59. GPC trace of poly(E-*co*-HAA) (Entry 5, Table 1) after acetylation.



Results

Mw	110132	g/mol
Mn	35528	g/mol
Mw / Mn	3.10	
Mz	262586	g/mol
Mp	80034	g/mol
Mv	97088	g/mol
IVmwd	1.82	dL/g
Bulk CH3 / 1000C	66.22	
Bulk SCB / 1000C	65.38	
Bulk Comonomer Wt%	52.31	%
Pump Flow Rate	1.00	ml / min
Columns Temp	150	ºC
Detectors Temp	150	ºC
Nominal MHa	0.725	
Nominal MHK	0.00044	

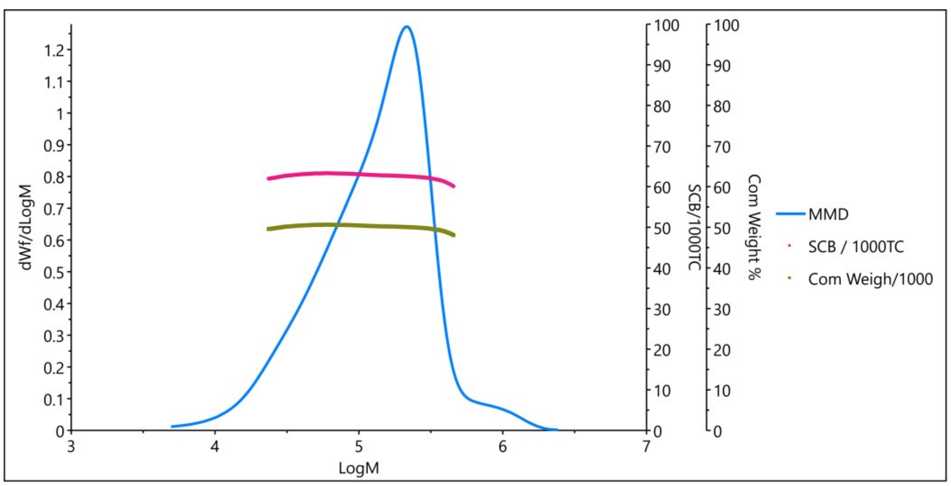
Calibrations

Flow Marker	28.32	mL
Mass constant	0.45	mL·V/mg

Performance

Flow Marker	28.28	mL
Mass recovery	85	%
Plate Count	2474	

Figure S60. GPC trace of poly(E-*co*-HAA) (Entry 6, Table 1) after acetylation.



Results

Mw	181121	g/mol
Mn	78973	g/mol
Mw / Mn	2.29	
Mz	359538	g/mol
Mp	214299	g/mol
Mv	164635	g/mol
IVmwd	2.67	dL/g
Bulk CH3 / 1000C	62.41	
Bulk SCB / 1000C	62.04	
Bulk Comonomer Wt%	49.63	%
Pump Flow Rate	1.00	ml / min
Columns Temp	150	ºC
Detectors Temp	150	ºC
Nominal MHa	0.725	
Nominal MHK	0.00044	

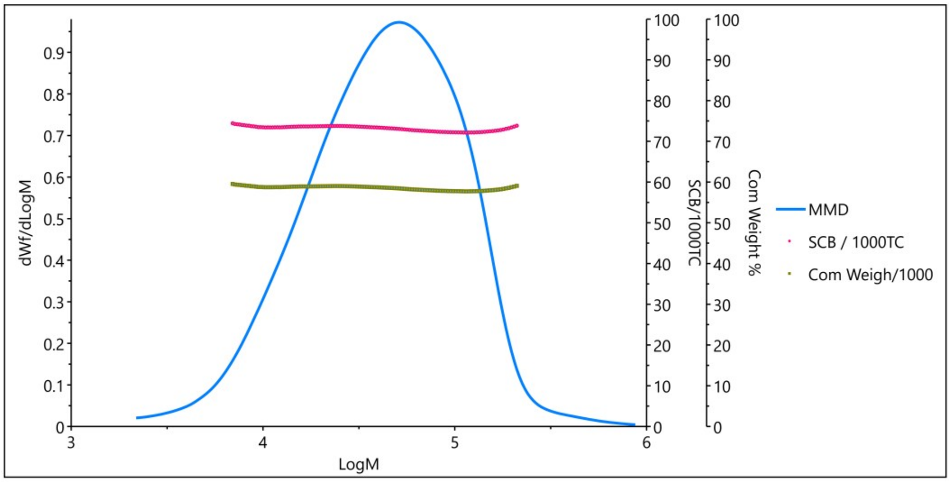
Calibrations

Flow Marker	28.16	mL
Mass constant	0.45	mL·V/mg

Performance

Flow Marker	28.11	mL
Mass recovery	88	%
Plate Count	12524	

Figure S61. GPC trace of poly(E-*co*-HAA) (Entry 7, Table 1) after acetylation.



Results

Mw	61221	g/mol
Mn	27007	g/mol
Mw / Mn	2.27	
Mz	120944	g/mol
Mp	51253	g/mol
Mv	55476	g/mol
IVmwd	1.21	dL/g
Bulk CH3 / 1000C	74.71	
Bulk SCB / 1000C	73.63	
Bulk Comonomer Wt%	58.90	%
Pump Flow Rate	1.00	ml / min
Columns Temp	150	ºC
Detectors Temp	150	ºC
Nominal MHa	0.725	
Nominal MHK	0.00044	

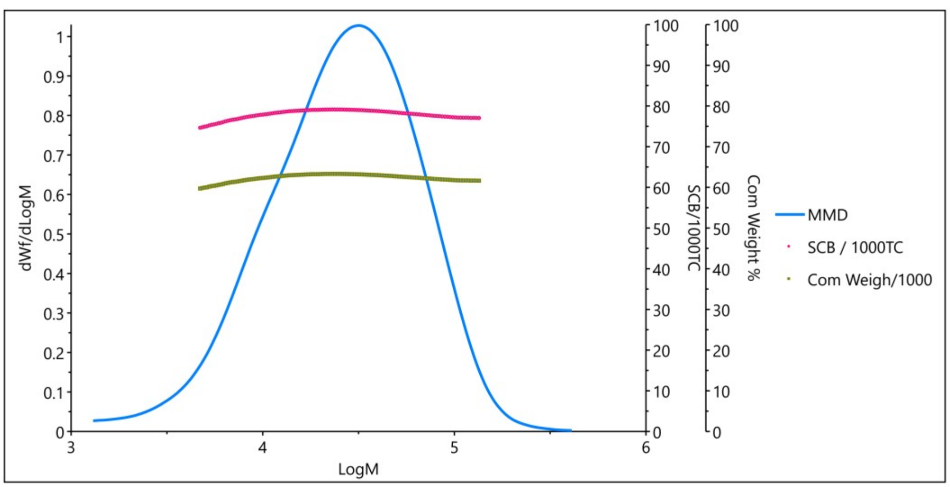
Calibrations

Flow Marker	28.16	mL
Mass constant	0.45	mL·V/mg

Performance

Flow Marker	28.16	mL
Mass recovery	86	%
Plate Count	14312	

Figure S62. GPC trace of poly(E-*co*-HAA) (Entry 8, Table 1) after acetylation.



Results

Mw	36923	g/mol
Mn	16714	g/mol
Mw / Mn	2.21	
Mz	66079	g/mol
Mp	31627	g/mol
Mv	33726	g/mol
IVmwd	0.85	dL/g
Bulk CH3 / 1000C	79.70	
Bulk SCB / 1000C	77.97	
Bulk Comonomer Wt%	62.38	%
Pump Flow Rate	1.00	ml / min
Columns Temp	150	ºC
Detectors Temp	150	ºC
Nominal MHa	0.725	
Nominal MHK	0.00044	

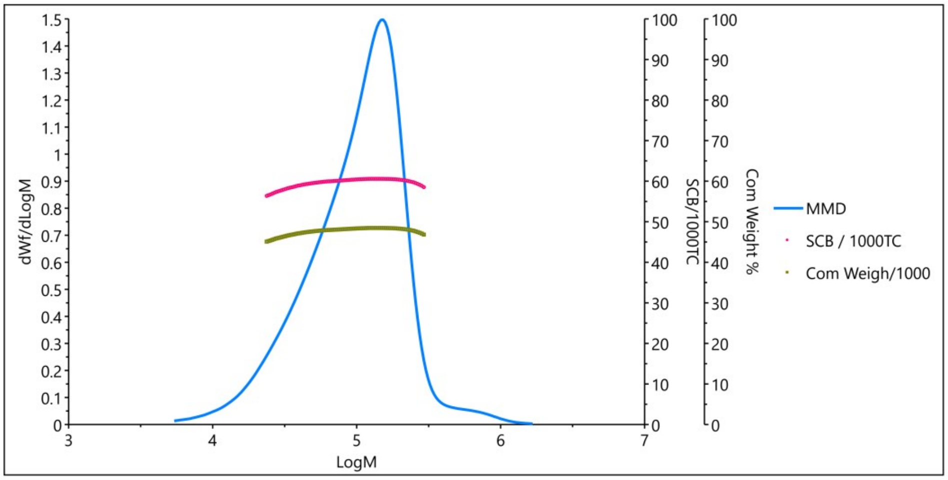
Calibrations

Flow Marker	28.16	mL
Mass constant	0.45	mL·V/mg

Performance

Flow Marker	28.16	mL
Mass recovery	83	%
Plate Count	14515	

Figure S63. GPC trace of poly(E-*co*-HAA) (Entry 9, Table 1) after acetylation.

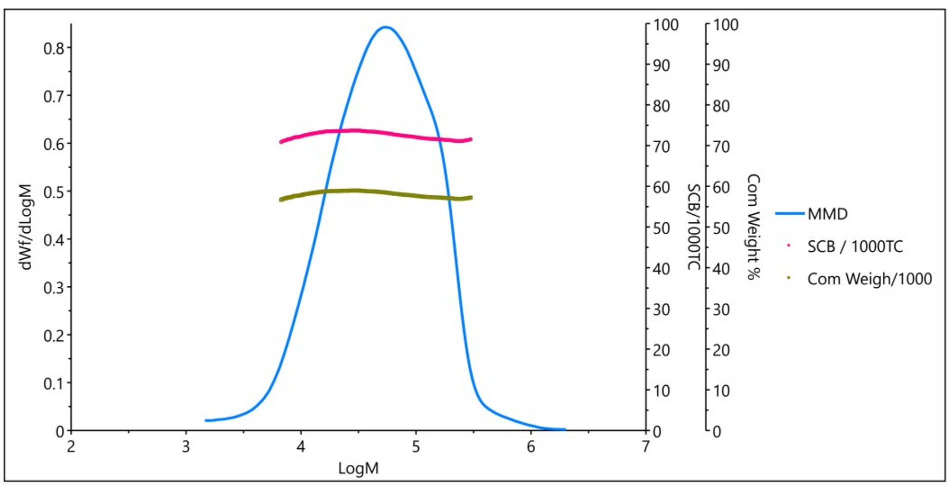


Results		
Mw	128294	g/mol
Mn	68062	g/mol
Mw / Mn	1.88	
Mz	225782	g/mol
Mp	149988	g/mol
Mv	119131	g/mol
IVmwd	2.11	dL/g
Bulk CH3 / 1000C	59.03	
Bulk SCB / 1000C	58.60	
Bulk Comonomer Wt%	46.88	%
Pump Flow Rate	1.00	ml / min
Columns Temp	150	ºC
Detectors Temp	150	ºC
Nominal MHa	0.725	
Nominal MHK	0.00044	

Calibrations		
Flow Marker	28.16	mL
Mass constant	0.45	mL·V/mg

Performance		
Flow Marker	28.16	mL
Mass recovery	88	%
Plate Count	14419	

Figure S64. GPC trace of poly(E-*co*-HAA) (Entry 10, Table 1) after acetylation.

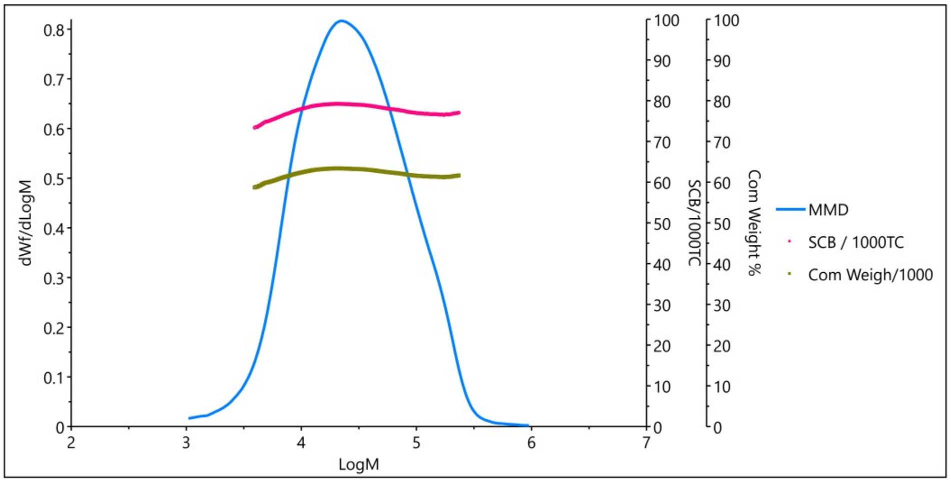


Results		
Mw	79530	g/mol
Mn	27245	g/mol
Mw / Mn	2.92	
Mz	199686	g/mol
Mp	54679	g/mol
Mv	69893	g/mol
IVmwd	1.44	dL/g
Bulk CH3 / 1000C	73.74	
Bulk SCB / 1000C	72.65	
Bulk Comonomer Wt%	58.12	%
Pump Flow Rate	1.00	ml / min
Columns Temp	150	ºC
Detectors Temp	150	ºC
Nominal MHa	0.725	
Nominal MHK	0.00044	

Calibrations		
Flow Marker	28.32	mL
Mass constant	0.45	mL·V/mg

Performance		
Flow Marker	28.24	mL
Mass recovery	86	%
Plate Count	4672	

Figure S65. GPC trace of poly(E-*co*-HAA) (Entry 11, Table 1) after acetylation.



Results

Mw	46250	g/mol
Mn	15913	g/mol
Mw / Mn	2.91	
Mz	113746	g/mol
Mp	22537	g/mol
Mv	40227	g/mol
IVmwd	0.96	dL/g
Bulk CH3 / 1000C	79.60	
Bulk SCB / 1000C	77.77	
Bulk Comonomer Wt%	62.21	%
Pump Flow Rate	1.00	ml / min
Columns Temp	150	ºC
Detectors Temp	150	ºC
Nominal MHa	0.725	
Nominal MHK	0.00044	

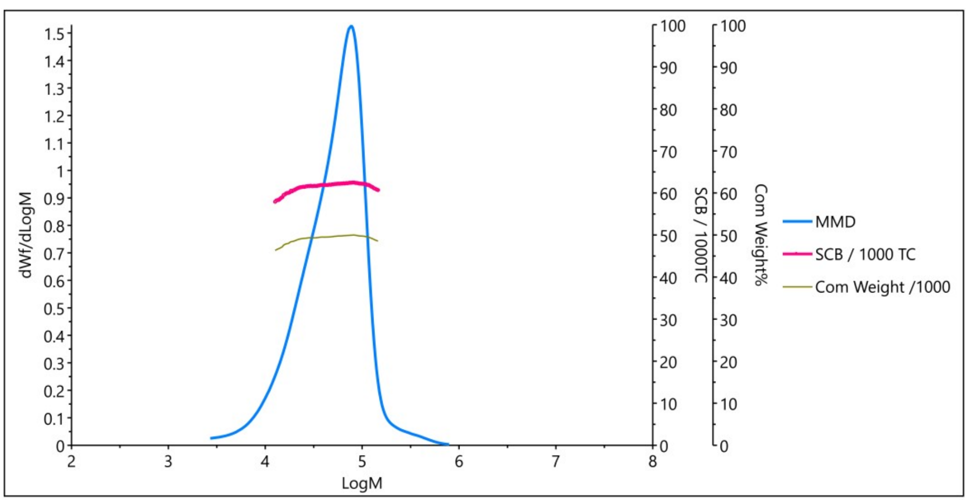
Calibrations

Flow Marker	28.32	mL
Mass constant	0.45	mL·V/mg

Performance

Flow Marker	28.27	mL
Mass recovery	91	%
Plate Count	4546	

Figure S66. GPC trace of poly(E-*co*-HAA) (Entry 12, Table 1) after acetylation.



Results

Mw	63805	g/mol
Mn	34026	g/mol
Mw / Mn	1.88	
Mz	108490	g/mol
Mp	76476	g/mol
Mv	58970	g/mol
IVmwd	1.0116	dL/g
Bulk CH3 / 1000C	61.675	
Corrected Bulk CH3 / 1000C	60.8	CH3/1000TC corr

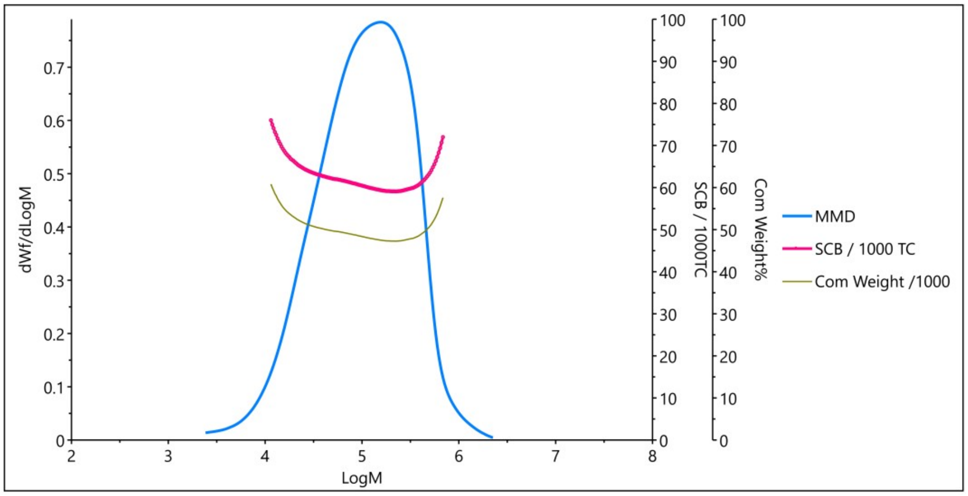
Calibrations

Calib Flow Marker	28.02	mL
Calib Mass constant	0.28	mL·V/mg

Performance

Flow Marker	28.11	mL
Mass recovery	82	%
Plate Count	17076	

Figure S67. GPC trace of poly(E-*co*-HAA) (Entry 13, Table 1) after acetylation.



Results

Mw	170245	g/mol
Mn	52710	g/mol
Mw / Mn	3.23	
Mz	380527	g/mol
Mp	155739	g/mol
Mv	147404	g/mol
IVmwd	1.9087	dL/g
Bulk CH3 / 1000C	65.282	
Corrected Bulk CH3 / 1000C	64.7	CH3/1000TC corr

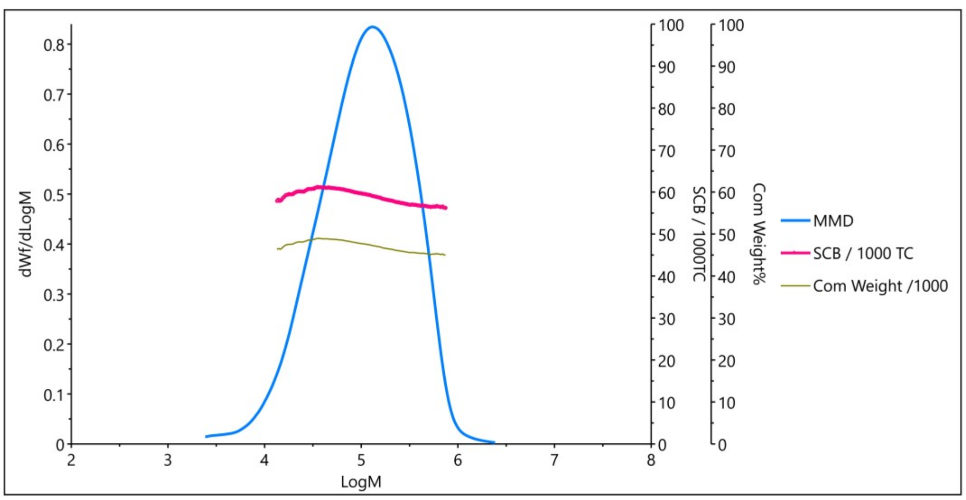
Calibrations

Calib Flow Marker	27.97	mL
Calib Mass constant	0.28	mL·V/mg

Performance

Flow Marker	27.80	mL
Mass recovery	82	%
Plate Count	22055	

Figure S68. GPC trace of poly(E-*co*-HAA) (Entry 14, Table 1) after acetylation.



Results

Mw	173059	g/mol
Mn	56342	g/mol
Mw / Mn	3.07	
Mz	359738	g/mol
Mp	131137	g/mol
Mv	151325	g/mol
IVmwd	1.9438	dL/g
Bulk CH3 / 1000C	59.264	
Corrected Bulk CH3 / 1000C	58.7	CH3/1000TC corr

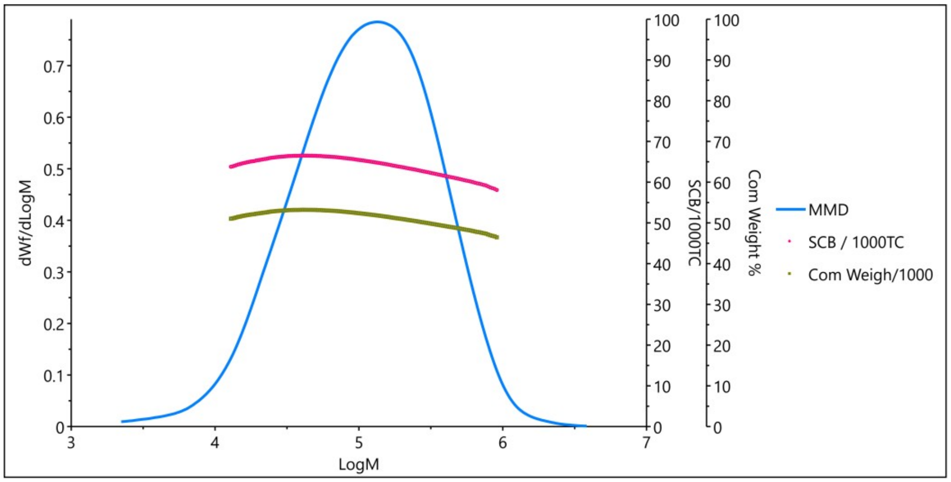
Calibrations

Calib Flow Marker	28.02	mL
Calib Mass constant	0.28	mL·V/mg

Performance

Flow Marker	28.08	mL
Mass recovery	86	%
Plate Count	17815	

Figure S69. GPC trace of poly(E-*co*-HAA) (Entry 15, Table 1) after acetylation.

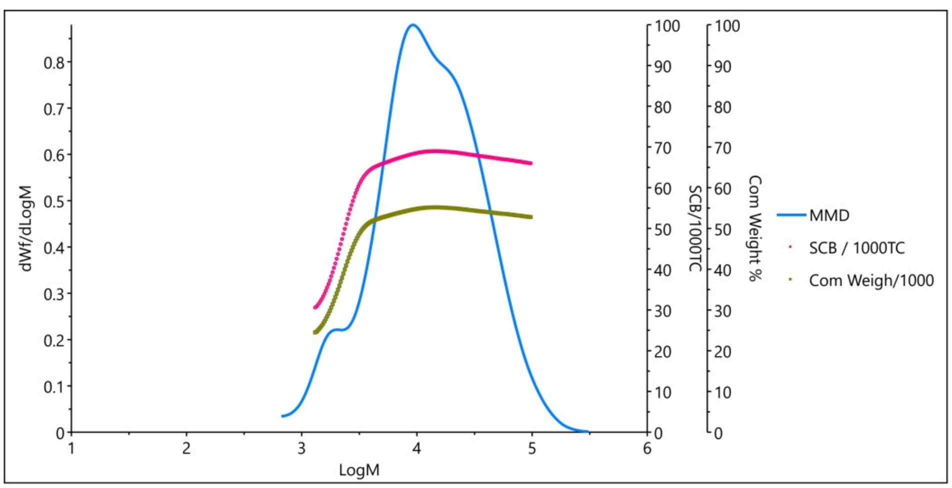


Results		
Mw	187684	g/mol
Mn	56261	g/mol
Mw / Mn	3.34	
Mz	452934	g/mol
Mp	134826	g/mol
Mv	163396	g/mol
IVmwd	2.66	dL/g
Bulk CH3 / 1000C	64.50	
Bulk SCB / 1000C	63.97	
Bulk Comonomer Wt%	51.17	%
Pump Flow Rate	1.00	ml / min
Columns Temp	150	ºC
Detectors Temp	150	ºC
Nominal MHa	0.725	
Nominal MHK	0.00044	

Calibrations		
Flow Marker	28.16	mL
Mass constant	0.45	mL·V/mg

Performance		
Flow Marker	28.11	mL
Mass recovery	85	%
Plate Count	12546	

Figure S70. GPC trace of poly(E-*co*-HAA) (Entry 16, Table 1) after acetylation.

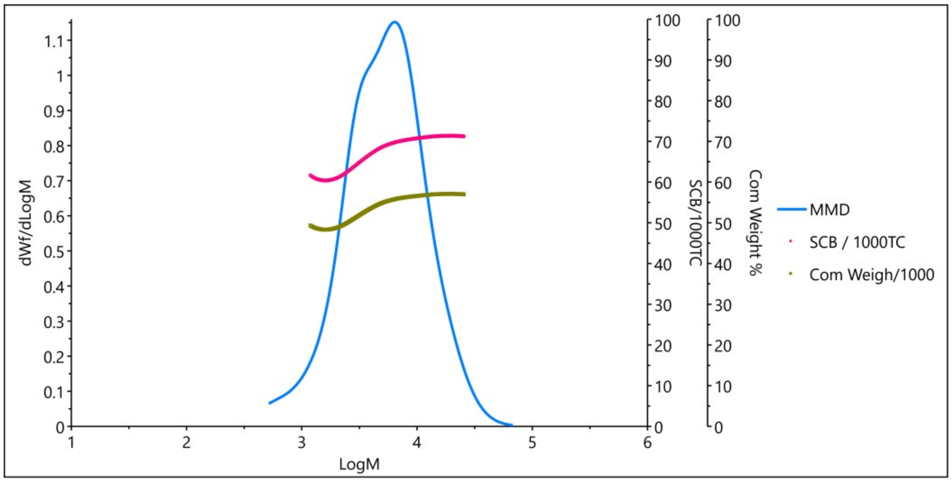


Results		
Mw	20628	g/mol
Mn	7085	g/mol
Mw / Mn	2.91	
Mz	47802	g/mol
Mp	9262	g/mol
Mv	18076	g/mol
IVmwd	0.54	dL/g
Bulk CH3 / 1000C	69.11	
Bulk SCB / 1000C	65.03	
Bulk Comonomer Wt%	52.03	%
Pump Flow Rate	1.00	ml / min
Columns Temp	150	ºC
Detectors Temp	150	ºC
Nominal MHa	0.725	
Nominal MHK	0.00044	

Calibrations		
Flow Marker	28.32	mL
Mass constant	0.45	mL·V/mg

Performance		
Flow Marker	28.37	mL
Mass recovery	96	%
Plate Count	736	

Figure S71. GPC trace of poly(E-*co*-A-ol) (Entry 1, Table 2).

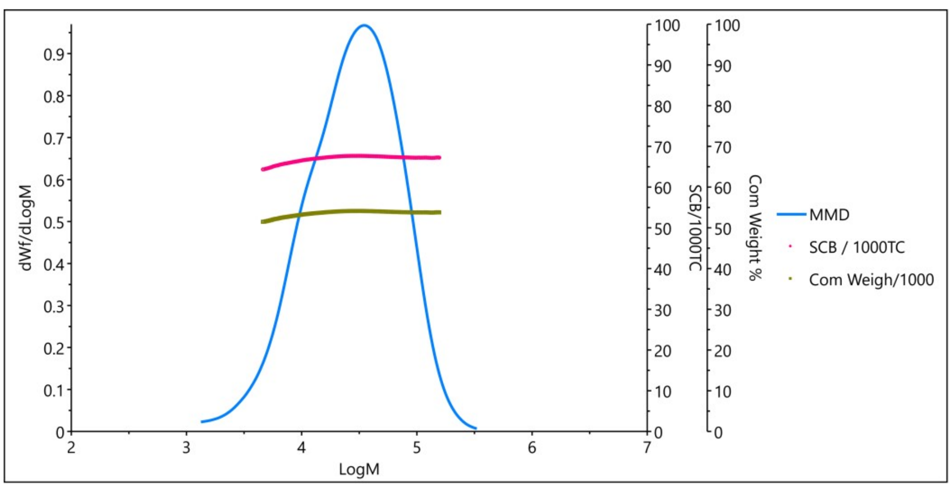


Results		
Mw	7138	g/mol
Mn	3770	g/mol
Mw / Mn	1.89	
Mz	12531	g/mol
Mp	6389	g/mol
Mv	6575	g/mol
IVmwd	0.26	dL/g
Bulk CH3 / 1000C	75.17	
Bulk SCB / 1000C	67.65	
Bulk Comonomer Wt%	54.12	%
Pump Flow Rate	1.00	ml / min
Columns Temp	150	ºC
Detectors Temp	150	ºC
Nominal MHa	0.725	
Nominal MHK	0.00044	

Calibrations		
Flow Marker	28.32	mL
Mass constant	0.45	mL·V/mg

Performance		
Flow Marker	28.43	mL
Mass recovery	95	%
Plate Count	10976	

Figure S72. GPC trace of poly(E-*co*-A-ol) (Entry 2, Table 2).

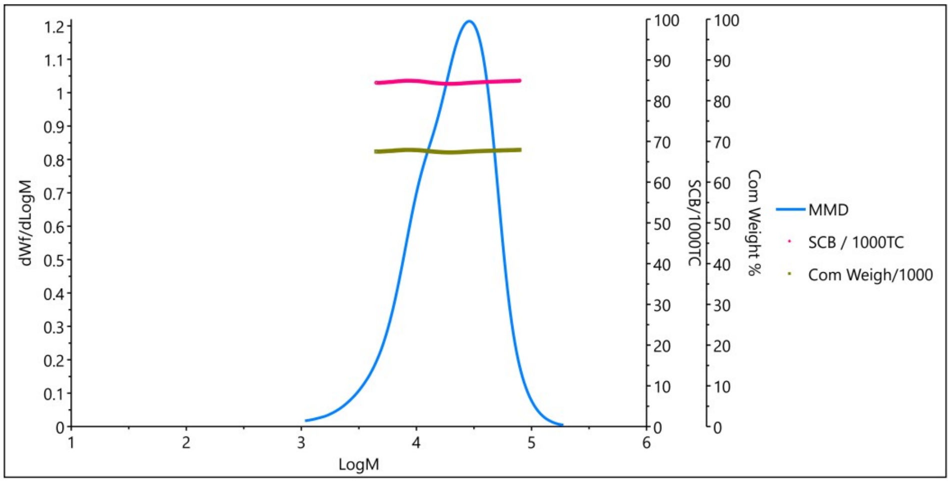


Results		
Mw	40113	g/mol
Mn	17210	g/mol
Mw / Mn	2.33	
Mz	73294	g/mol
Mp	34877	g/mol
Mv	36420	g/mol
IVmwd	0.90	dL/g
Bulk CH3 / 1000C	68.71	
Bulk SCB / 1000C	67.02	
Bulk Comonomer Wt%	53.61	%
Pump Flow Rate	1.00	ml / min
Columns Temp	150	ºC
Detectors Temp	150	ºC
Nominal MHa	0.725	
Nominal MHK	0.00044	

Calibrations		
Flow Marker	28.32	mL
Mass constant	0.45	mL·V/mg

Performance		
Flow Marker	28.48	mL
Mass recovery	94	%
Plate Count	8720	

Figure S73. GPC trace of poly(E-*co*-A-ol) (Entry 3, Table 2).

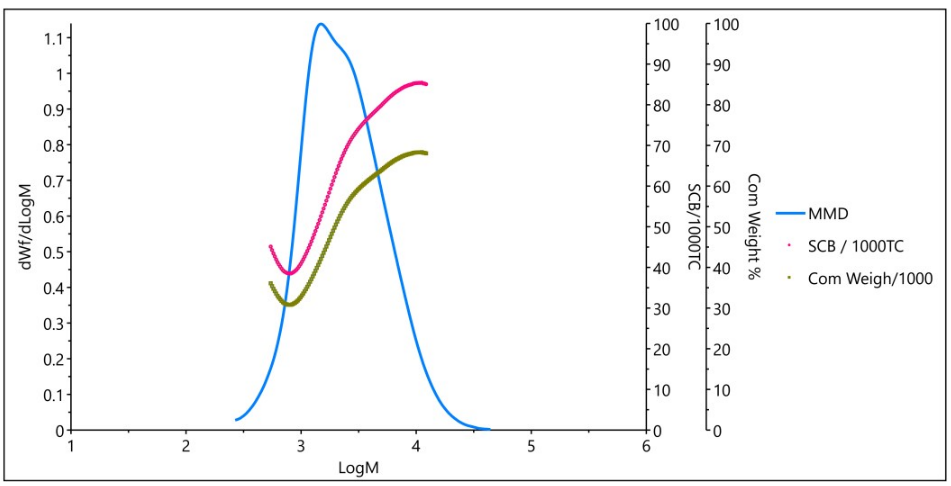


Results		
Mw	26246	g/mol
Mn	13851	g/mol
Mw / Mn	1.89	
Mz	40665	g/mol
Mp	28776	g/mol
Mv	24499	g/mol
IVmwd	0.67	dL/g
Bulk CH3 / 1000C	86.59	
Bulk SCB / 1000C	84.51	
Bulk Comonomer Wt%	67.61	%
Pump Flow Rate	1.00	ml / min
Columns Temp	150	ºC
Detectors Temp	150	ºC
Nominal MHa	0.725	
Nominal MHK	0.00044	

Calibrations		
Flow Marker	28.32	mL
Mass constant	0.45	mL·V/mg

Performance		
Flow Marker	28.48	mL
Mass recovery	96	%
Plate Count	14017	

Figure S74. GPC trace of poly(E-*co*-A-ol) (Entry 4, Table 2).

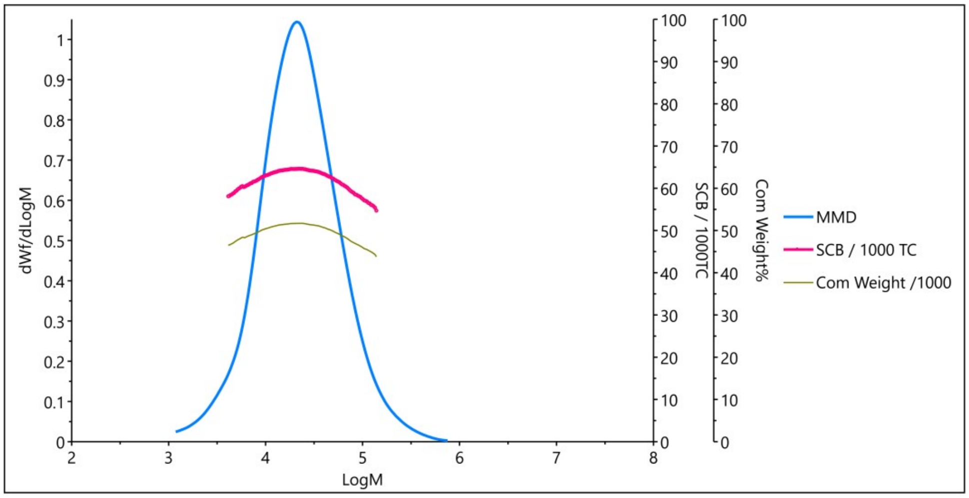


Results		
Mw	3273	g/mol
Mn	1745	g/mol
Mw / Mn	1.88	
Mz	6479	g/mol
Mp	1497	g/mol
Mv	2978	g/mol
IVmwd	0.15	dL/g
Bulk CH3 / 1000C	80.09	
Bulk SCB / 1000C	63.94	
Bulk Comonomer Wt%	51.15	%
Pump Flow Rate	1.00	ml / min
Columns Temp	150	ºC
Detectors Temp	150	ºC
Nominal MHa	0.725	
Nominal MHK	0.00044	

Calibrations		
Flow Marker	28.16	mL
Mass constant	0.45	mL·V/mg

Performance		
Flow Marker	28.16	mL
Mass recovery	81	%
Plate Count	14595	

Figure S75. GPC trace of poly(E-*co*-A-ol) (Entry 5, Table 2).



Results

Mw	35771	g/mol
Mn	14128	g/mol
Mw / Mn	2.53	
Mz	98855	g/mol
Mp	21061	g/mol
Mv	30767	g/mol
IVmwd	0.6445	dL/g
Bulk CH3 / 1000C	63.878	
Corrected Bulk CH3 / 1000C	61.8	CH3/1000TC corr

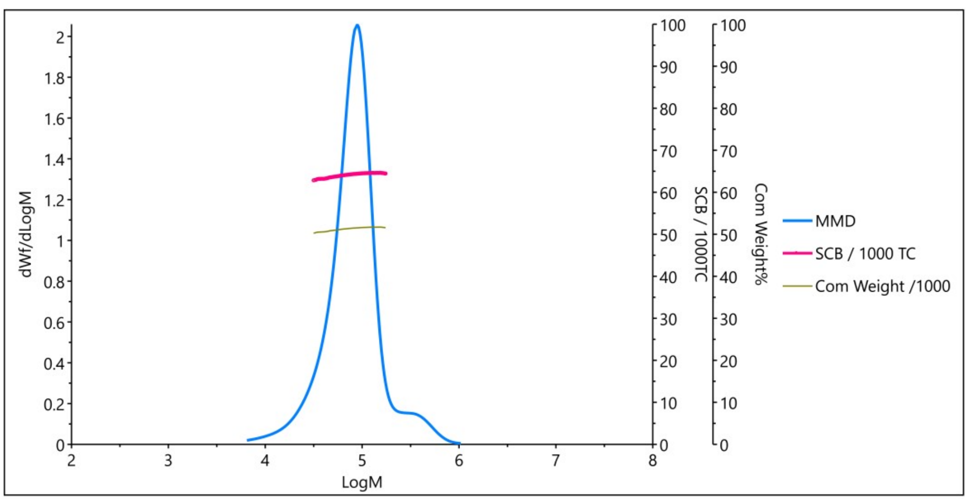
Calibrations

Calib Flow Marker	28.02	mL
Calib Mass constant	0.28	mL·V/mg

Performance

Flow Marker	28.03	mL
Mass recovery	92	%
Plate Count	18093	

Figure S76. GPC trace of poly(E-*co*-HAA) (Entry 7, Table 2) after acetylation.



Results

Mw	101776	g/mol
Mn	64161	g/mol
Mw / Mn	1.59	
Mz	179467	g/mol
Mp	88492	g/mol
Mv	94442	g/mol
IVmwd	1.4020	dL/g
Bulk CH3 / 1000C	64.156	
Corrected Bulk CH3 / 1000C	63.7	CH3/1000TC corr

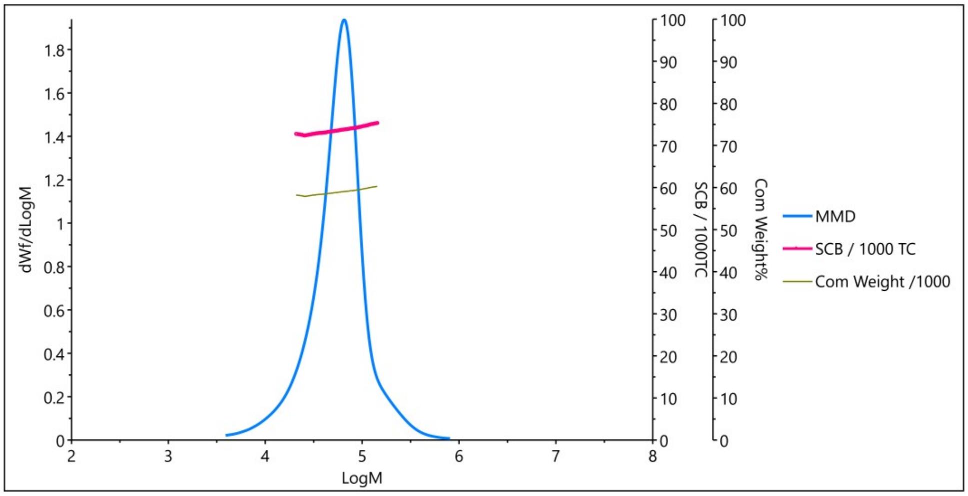
Calibrations

Calib Flow Marker	28.02	mL
Calib Mass constant	0.28	mL·V/mg

Performance

Flow Marker	28.04	mL
Mass recovery	85	%
Plate Count	18211	

Figure S77. GPC trace of poly(E-*co*-HAA) (Entry 8, Table 2) after acetylation.



Results

Mw	70718	g/mol
Mn	42941	g/mol
Mw / Mn	1.65	
Mz	120354	g/mol
Mp	65152	g/mol
Mv	65821	g/mol
IVmwd	1.0917	dL/g
Bulk CH3 / 1000C	74.106	
Corrected Bulk CH3 / 1000C	73.4	CH3/1000TC corr

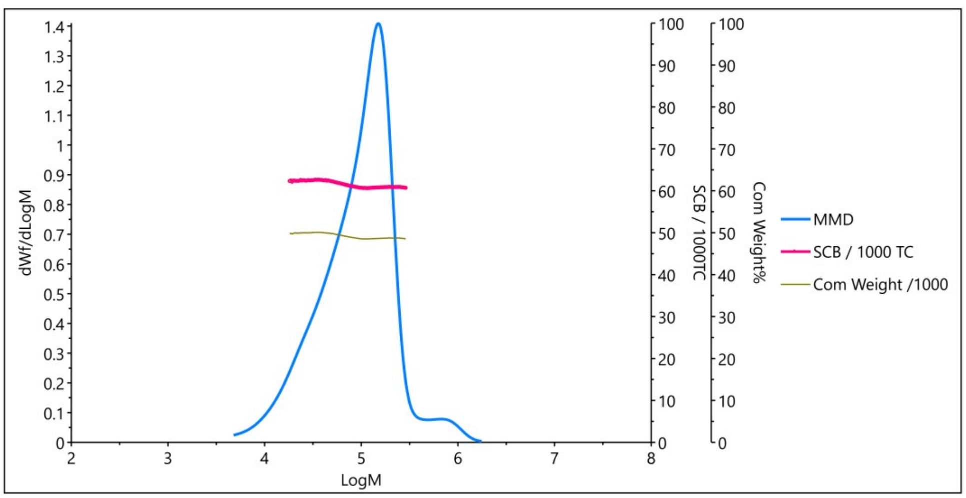
Calibrations

Calib Flow Marker	28.02	mL
Calib Mass constant	0.28	mL·V/mg

Performance

Flow Marker	28.03	mL
Mass recovery	80	%
Plate Count	18048	

Figure S78. GPC trace of poly(E-*co*-HAA) (Entry 9, Table 2) after acetylation.



Results

Mw	130735	g/mol
Mn	57031	g/mol
Mw / Mn	2.29	
Mz	285773	g/mol
Mp	149658	g/mol
Mv	116662	g/mol
IVmwd	1.6231	dL/g
Bulk CH3 / 1000C	61.398	
Corrected Bulk CH3 / 1000C	60.9	CH3/1000TC corr

Calibrations

Calib Flow Marker	28.02	mL
Calib Mass constant	0.28	mL·V/mg

Performance

Flow Marker	28.04	mL
Mass recovery	86	%
Plate Count	17935	

Figure S79. GPC trace of poly(E-*co*-PA) (Entry 10, Table 2) after acetylation.

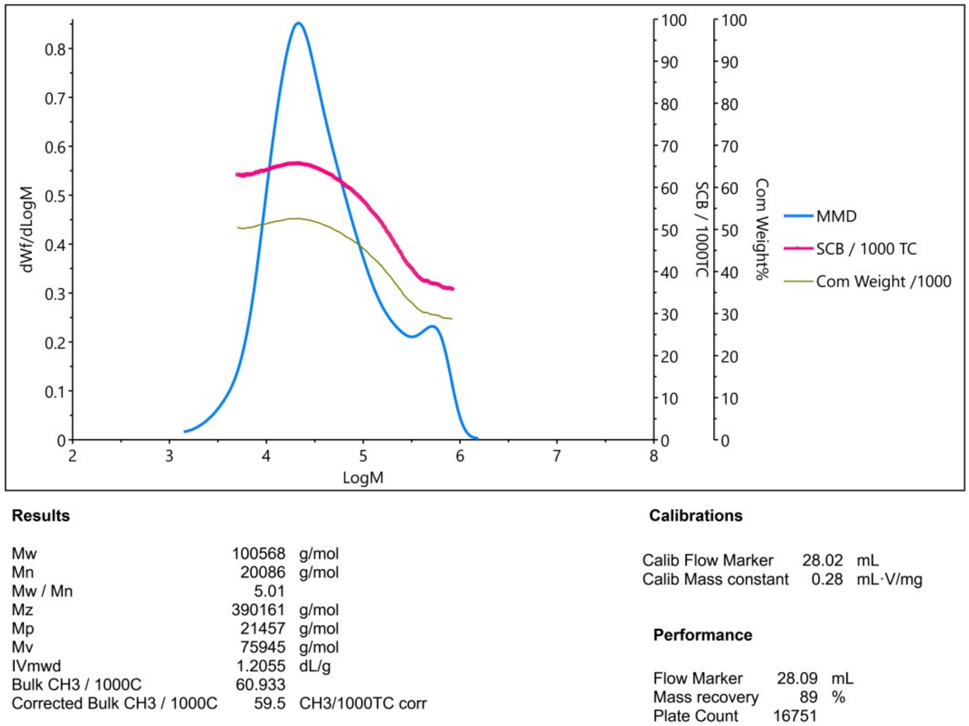


Figure S80(a). GPC trace of poly(E-*co*-PA) (Entry 11, Table 2) after acetylation.

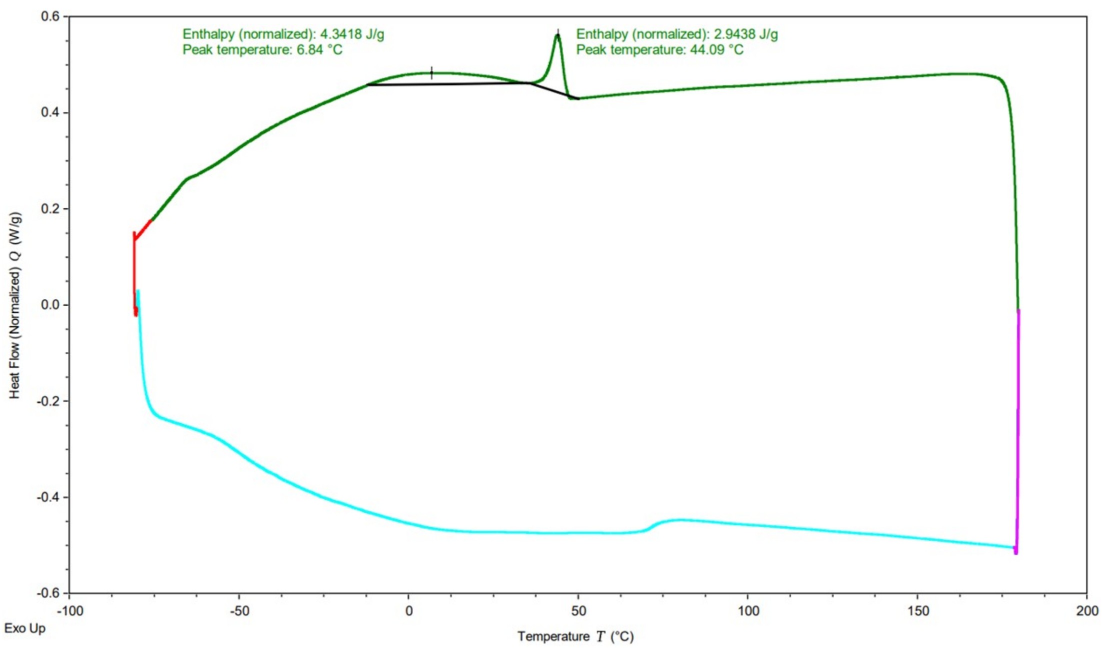
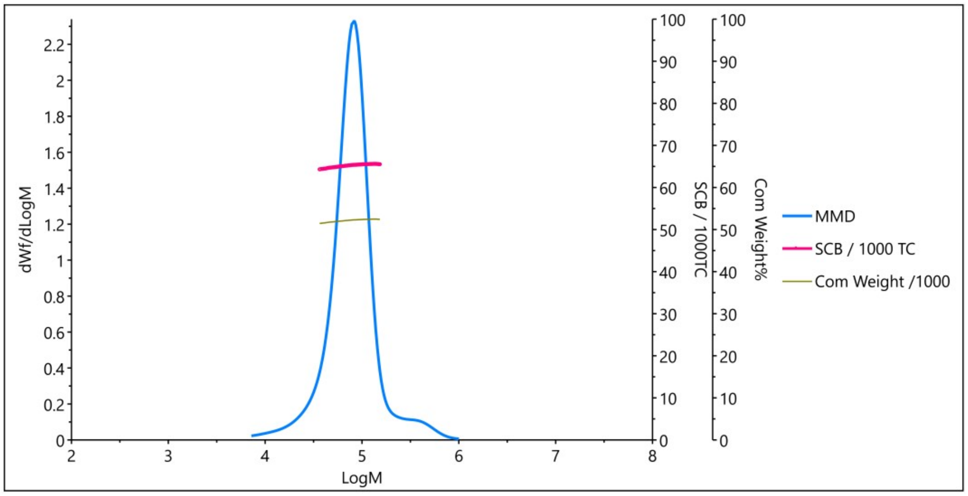


Figure S80(b). DSC trace of poly(E-*co*-PA) (Entry 11, Table 2)



Results

Mw	95771	g/mol
Mn	65187	g/mol
Mw / Mn	1.47	
Mz	164677	g/mol
Mp	82020	g/mol
Mv	89666	g/mol
IVmwd	1.3525	dL/g
Bulk CH3 / 1000C	65.266	
Corrected Bulk CH3 / 1000C	64.8	CH3/1000TC corr

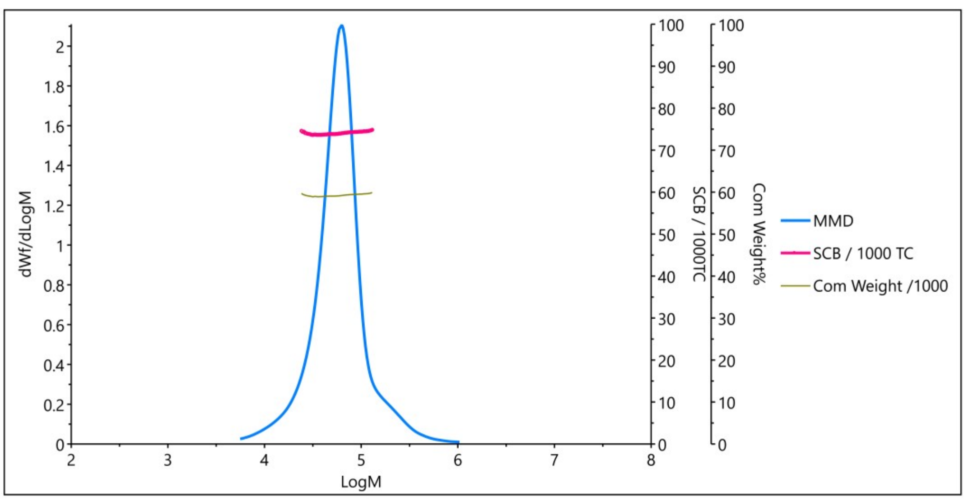
Calibrations

Calib Flow Marker	28.02	mL
Calib Mass constant	0.28	mL·V/mg

Performance

Flow Marker	28.03	mL
Mass recovery	86	%
Plate Count	18041	

Figure S81. GPC trace of poly(E-*co*-PA) (Entry 12, Table 2) after acetylation.



Results

Mw	74878	g/mol
Mn	47062	g/mol
Mw / Mn	1.59	
Mz	146441	g/mol
Mp	62256	g/mol
Mv	69068	g/mol
IVmwd	1.1287	dL/g
Bulk CH3 / 1000C	74.984	
Corrected Bulk CH3 / 1000C	74.4	CH3/1000TC corr

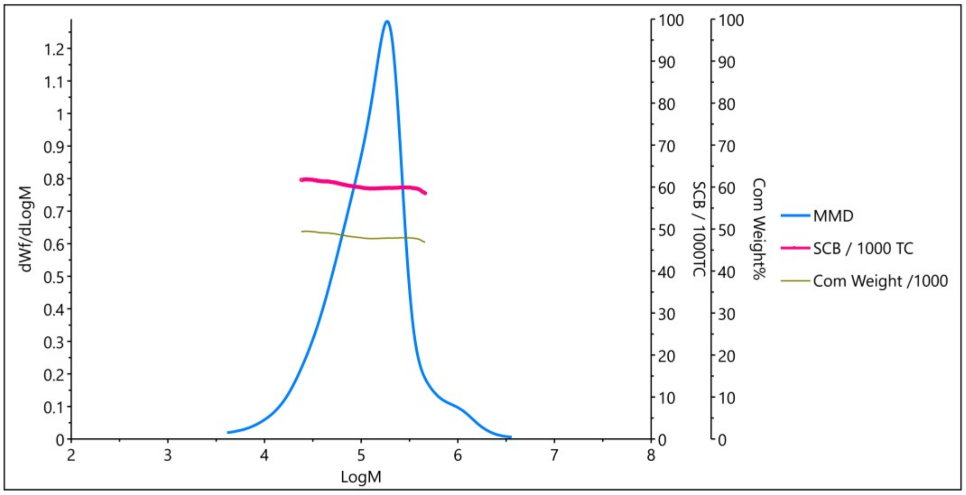
Calibrations

Calib Flow Marker	28.02	mL
Calib Mass constant	0.28	mL·V/mg

Performance

Flow Marker	28.03	mL
Mass recovery	86	%
Plate Count	18089	

Figure S82. GPC trace of poly(E-*co*-PA) (Entry 13, Table 2) after acetylation.



Results

Mw	193221	g/mol
Mn	71031	g/mol
Mw / Mn	2.72	
Mz	539926	g/mol
Mp	184987	g/mol
Mv	166760	g/mol
IVmwd	2.0791	dL/g
Bulk CH3 / 1000C	60.200	
Corrected Bulk CH3 / 1000C	59.8	CH3/1000TC corr

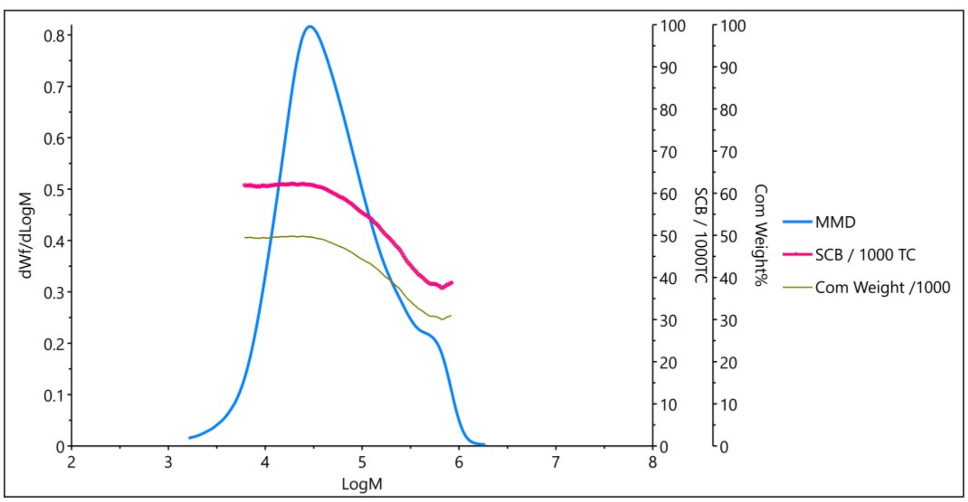
Calibrations

Calib Flow Marker	28.02	mL
Calib Mass constant	0.28	mL·V/mg

Performance

Flow Marker	28.02	mL
Mass recovery	87	%
Plate Count	17750	

Figure S83. GPC trace of poly(E-*co*-DA) (Entry 14, Table 2) after acetylation.



Results

Mw	110118	g/mol
Mn	25727	g/mol
Mw / Mn	4.28	
Mz	376230	g/mol
Mp	29050	g/mol
Mv	86737	g/mol
IVmwd	1.3217	dL/g
Bulk CH3 / 1000C	58.103	
Corrected Bulk CH3 / 1000C	57.0	CH3/1000TC corr

Calibrations

Calib Flow Marker	28.02	mL
Calib Mass constant	0.28	mL·V/mg

Performance

Flow Marker	28.09	mL
Mass recovery	92	%
Plate Count	16976	

Figure S84(a). GPC trace of poly(E-*co*-DA) (Entry 15, Table 2) after acetylation.

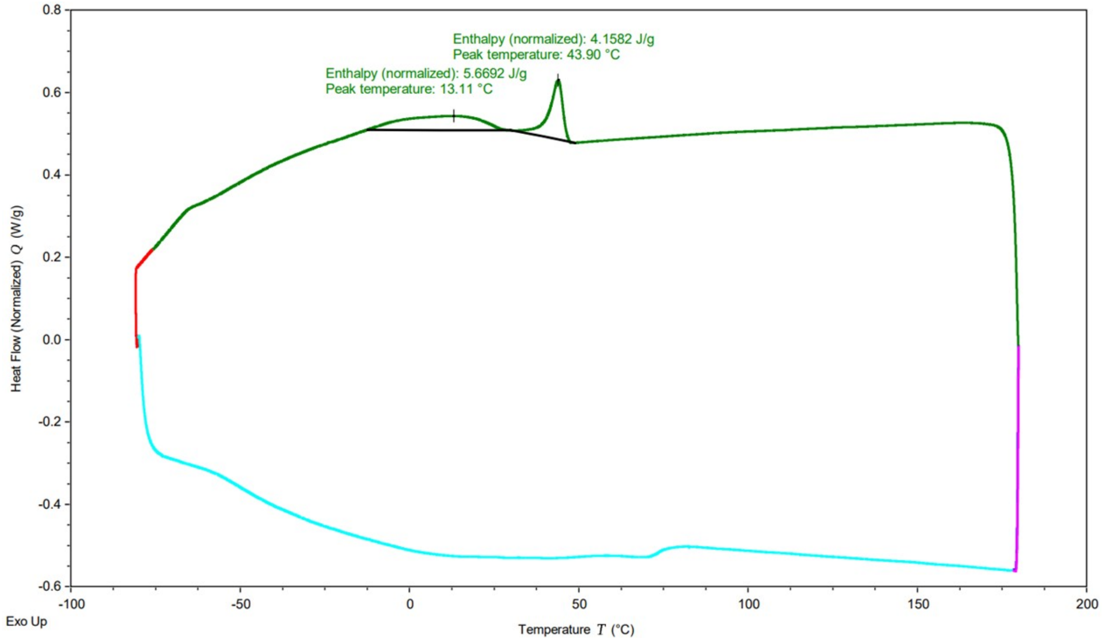


Figure S84(b). DSC trace of poly(E-*co*-DA) (Entry 15, Table 2)

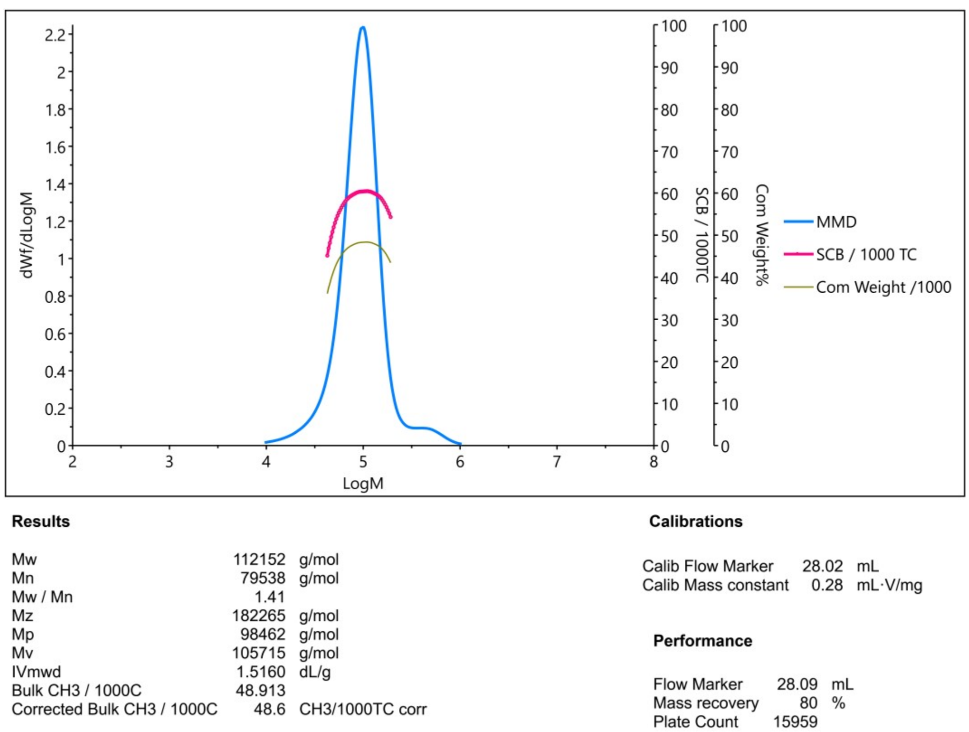
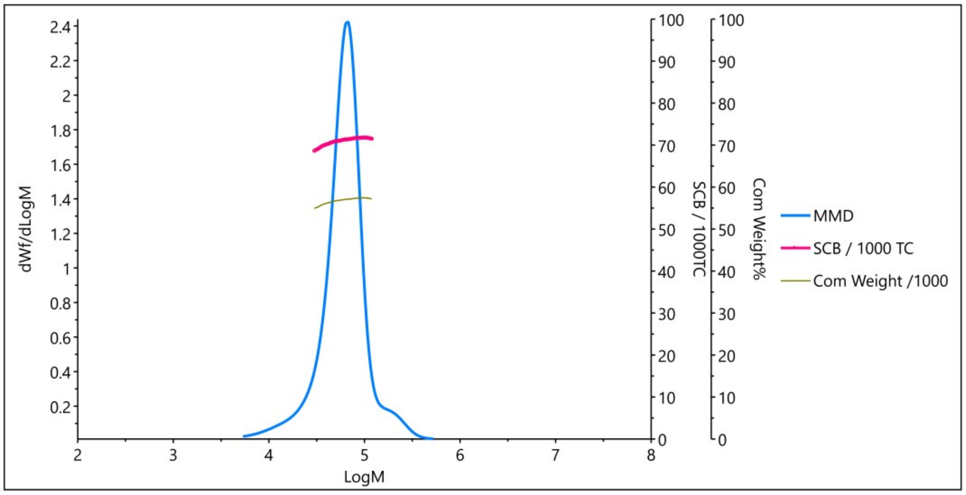


Figure S85. GPC trace of poly(E-*co*-DA) (Entry 16, Table 2) after acetylation.



Results

Mw	70764	g/mol
Mn	49704	g/mol
Mw / Mn	1.42	
Mz	101335	g/mol
Mp	65957	g/mol
Mv	67355	g/mol
IVmwd	1.1093	dL/g
Bulk CH3 / 1000C	70.434	
Corrected Bulk CH3 / 1000C	69.9	CH3/1000TC corr

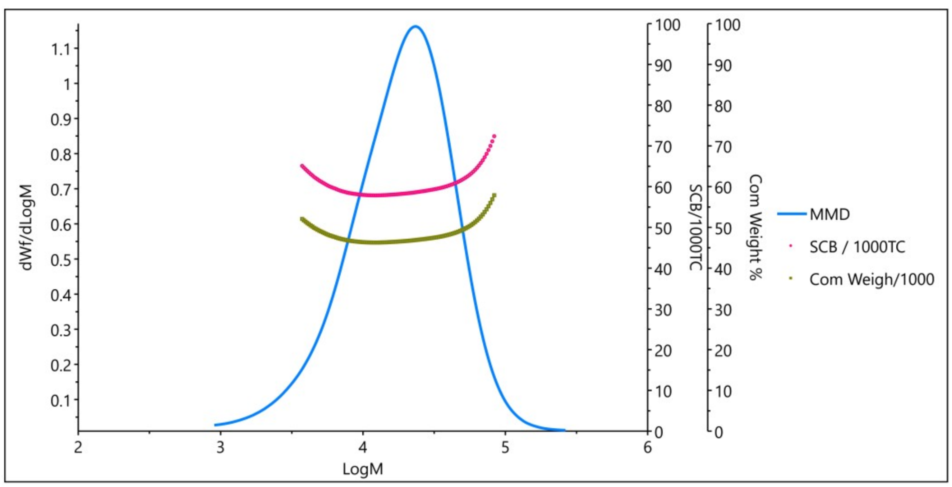
Calibrations

Calib Flow Marker	28.02	mL
Calib Mass constant	0.28	mL·V/mg

Performance

Flow Marker	28.10	mL
Mass recovery	82	%
Plate Count	17138	

Figure S86. GPC trace of poly(E-*co*-DA) (Entry 17, Table 2) after acetylation.



Results

Mw	25468	g/mol
Mn	11881	g/mol
Mw / Mn	2.14	
Mz	46256	g/mol
Mp	23359	g/mol
Mv	23358	g/mol
IVmwd	0.65	dL/g
Bulk CH3 / 1000C	64.23	
Bulk SCB / 1000C	61.80	
Bulk Comonomer Wt%	49.44	%
Pump Flow Rate	1.00	ml / min
Columns Temp	150	ºC
Detectors Temp	150	ºC
Nominal MHa	0.725	
Nominal MHK	0.00044	

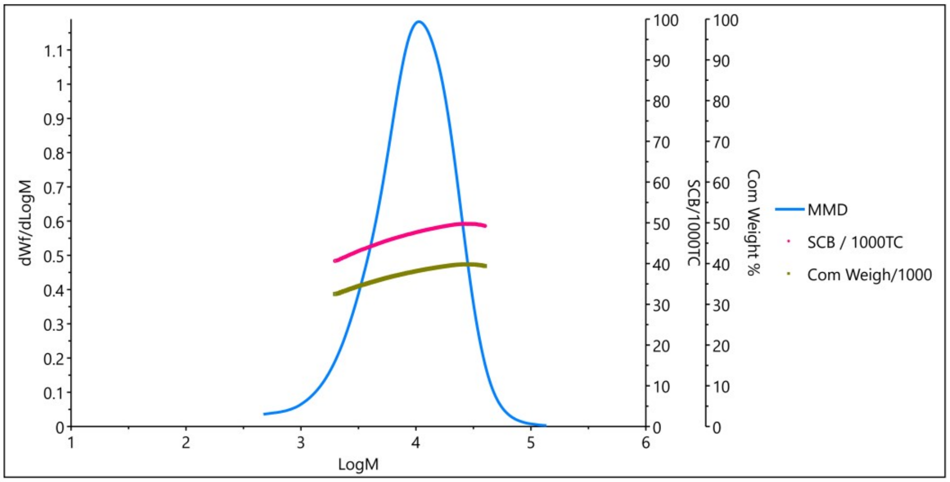
Calibrations

Flow Marker	28.16	mL
Mass constant	0.45	mL·V/mg

Performance

Flow Marker	28.10	mL
Mass recovery	99	%
Plate Count	3411	

Figure S87. GPC trace of poly(E-*co*-AAc) (Entry 1, Table 4).



Results

Mw	12569	g/mol
Mn	6070	g/mol
Mw / Mn	2.07	
Mz	21227	g/mol
Mp	10649	g/mol
Mv	11617	g/mol
IVmwd	0.39	dL/g
Bulk CH3 / 1000C	51.68	
Bulk SCB / 1000C	46.98	
Bulk Comonomer Wt%	37.58	%
Pump Flow Rate	1.00	ml / min
Columns Temp	150	ºC
Detectors Temp	150	ºC
Nominal MHa	0.725	
Nominal MHK	0.00044	

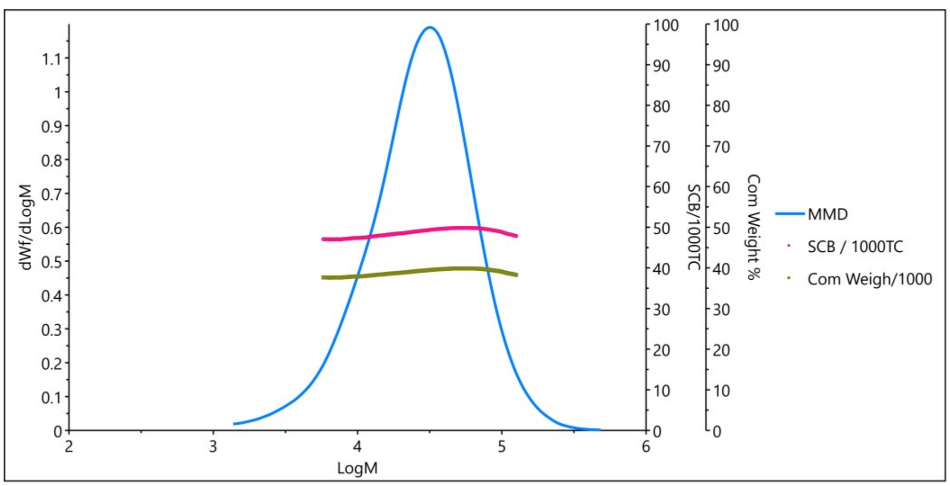
Calibrations

Flow Marker	28.32	mL
Mass constant	0.45	mL·V/mg

Performance

Flow Marker	28.30	mL
Mass recovery	95	%
Plate Count	3140	

Figure S88. GPC trace of poly(E-*co*-AAc) (Entry 2, Table 4).



Results

Mw	37401	g/mol
Mn	18158	g/mol
Mw / Mn	2.06	
Mz	67002	g/mol
Mp	31760	g/mol
Mv	34364	g/mol
IVmwd	0.86	dL/g
Bulk CH3 / 1000C	50.33	
Bulk SCB / 1000C	48.73	
Bulk Comonomer Wt%	38.99	%
Pump Flow Rate	1.00	ml / min
Columns Temp	150	ºC
Detectors Temp	150	ºC
Nominal MHa	0.725	
Nominal MHK	0.00044	

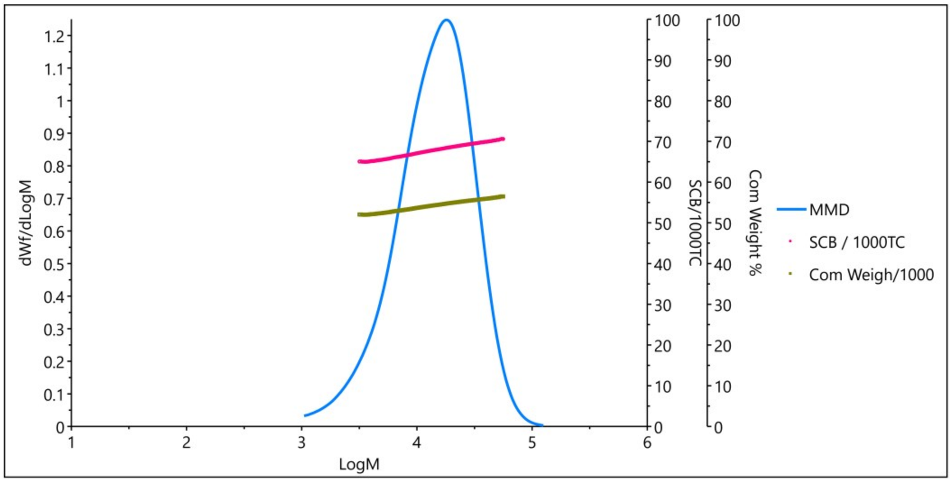
Calibrations

Flow Marker	28.32	mL
Mass constant	0.45	mL·V/mg

Performance

Flow Marker	28.32	mL
Mass recovery	96	%
Plate Count	2027	

Figure S89. GPC trace of poly(E-*co*-AAc) (Entry 3, Table 4).



Results

Mw	18019	g/mol
Mn	9962	g/mol
Mw / Mn	1.81	
Mz	27510	g/mol
Mp	18038	g/mol
Mv	16868	g/mol
IVmwd	0.51	dL/g
Bulk CH3 / 1000C	70.70	
Bulk SCB / 1000C	67.83	
Bulk Comonomer Wt%	54.26	%
Pump Flow Rate	1.00	ml / min
Columns Temp	150	ºC
Detectors Temp	150	ºC
Nominal MHa	0.725	
Nominal MHK	0.00044	

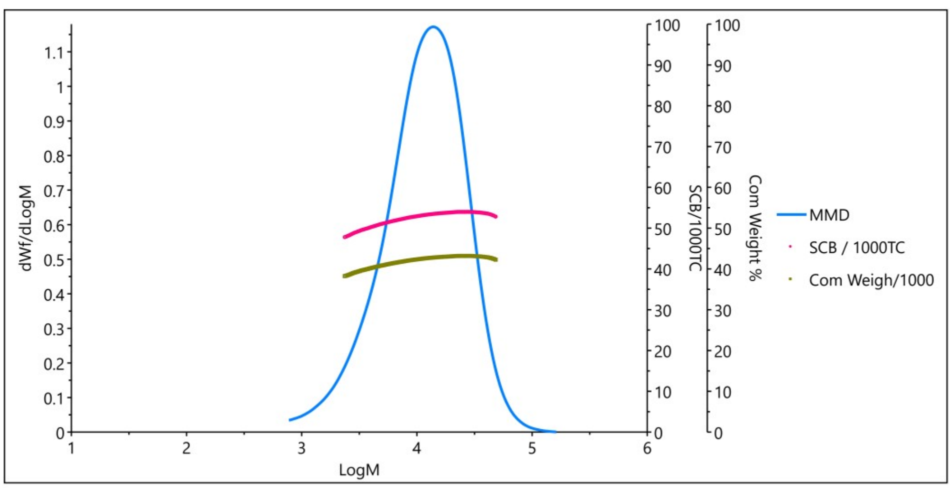
Calibrations

Flow Marker	28.32	mL
Mass constant	0.45	mL·V/mg

Performance

Flow Marker	27.88	mL
Mass recovery	96	%
Plate Count	3794	

Figure S90. GPC trace of poly(E-*co*-AAc) (Entry 4, Table 4).



Results

Mw	15258	g/mol
Mn	7838	g/mol
Mw / Mn	1.95	
Mz	24957	g/mol
Mp	13886	g/mol
Mv	14156	g/mol
IVmwd	0.45	dL/g
Bulk CH3 / 1000C	56.00	
Bulk SCB / 1000C	52.35	
Bulk Comonomer Wt%	41.88	%
Pump Flow Rate	1.00	ml / min
Columns Temp	150	ºC
Detectors Temp	150	ºC
Nominal MHa	0.725	
Nominal MHK	0.00044	

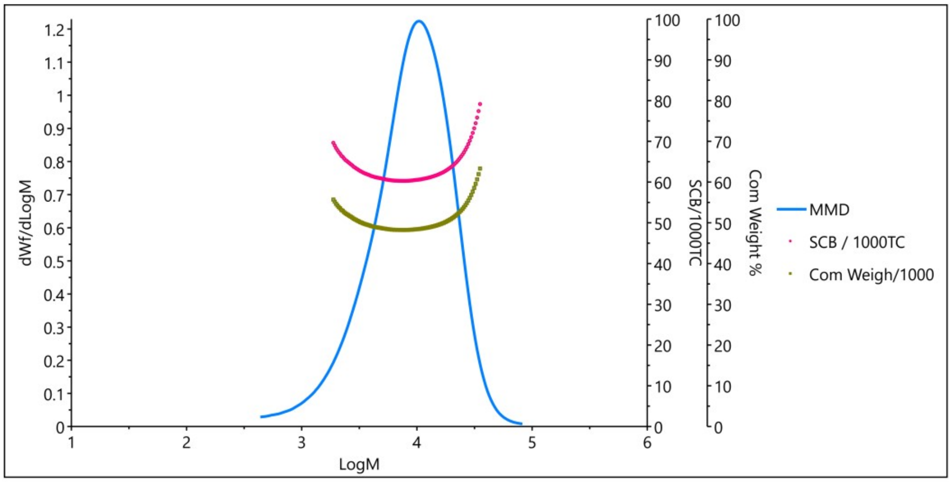
Calibrations

Flow Marker	28.16	mL
Mass constant	0.45	mL·V/mg

Performance

Flow Marker	28.16	mL
Mass recovery	96	%
Plate Count	14676	

Figure S91. GPC trace of poly(E-*co*-AAc) (Entry 5, Table 4).



Results

Mw	11471	g/mol
Mn	5768	g/mol
Mw / Mn	1.99	
Mz	18074	g/mol
Mp	10427	g/mol
Mv	10680	g/mol
IVmwd	0.37	dL/g
Bulk CH3 / 1000C	70.49	
Bulk SCB / 1000C	65.55	
Bulk Comonomer Wt%	52.44	%
Pump Flow Rate	1.00	ml / min
Columns Temp	150	ºC
Detectors Temp	150	ºC
Nominal MHa	0.725	
Nominal MHK	0.00044	

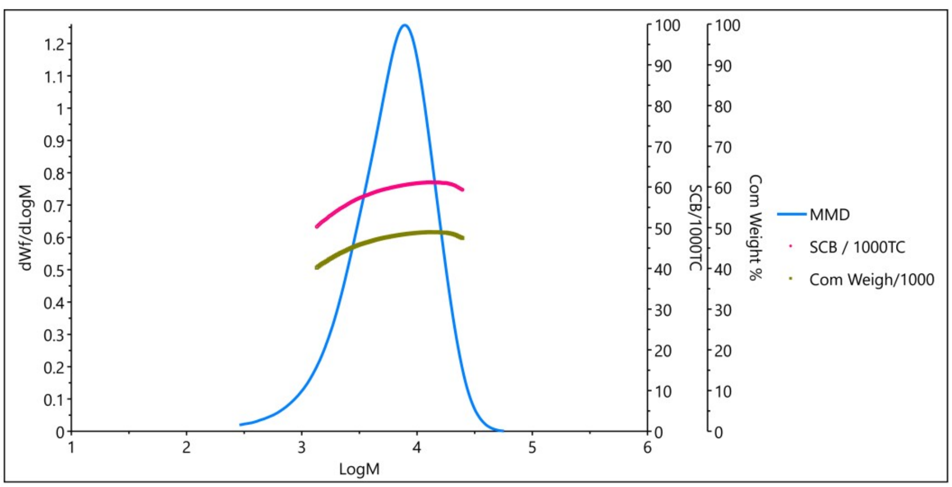
Calibrations

Flow Marker	28.32	mL
Mass constant	0.45	mL·V/mg

Performance

Flow Marker	28.35	mL
Mass recovery	95	%
Plate Count	2368	

Figure S92. GPC trace of poly(E-*co*-AAc) (Entry 6, Table 4).



Results

Mw	7950	g/mol
Mn	4046	g/mol
Mw / Mn	1.97	
Mz	12274	g/mol
Mp	7824	g/mol
Mv	7416	g/mol
IVmwd	0.28	dL/g
Bulk CH3 / 1000C	65.35	
Bulk SCB / 1000C	58.34	
Bulk Comonomer Wt%	46.67	%
Pump Flow Rate	1.00	ml / min
Columns Temp	150	ºC
Detectors Temp	150	ºC
Nominal MHa	0.725	
Nominal MHK	0.00044	

Calibrations

Flow Marker	28.32	mL
Mass constant	0.45	mL·V/mg

Performance

Flow Marker	28.34	mL
Mass recovery	97	%
Plate Count	4500	

Figure S93. GPC trace of poly(E-*co*-AAc) (Entry 7, Table 4).

7. X-ray Crystallography

Table S1. Crystal data and structure refinement for **4c**

Identification code	mo_d8v18750_0m
Empirical formula	C39 H61 Br3 N2 Ni2 O3
Formula weight	963.04
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/c
Unit cell dimensions	a = 14.9658(9) Å
	b = 19.0661(9) Å
	c = 16.9642(9) Å
Volume	4786.8(4) $Å^3$
Z	4
Density (calculated)	1.336 Mg/m^3
Absorption coefficient	3.323 mm^{-1}
F(000)	1976
Crystal size	0.200 x 0.170 x 0.130 mm^3
Theta range for data collection	2.541 to 26.000°.
Index ranges	-15<=h<=18, -23<=k<=23, -17<=l<=20
Reflections collected	23698
Independent reflections	9366 [R(int) = 0.0416]
Completeness to theta = 25.242°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5430
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9366 / 0 / 454
Goodness-of-fit on F^2	0.975
Final R indices [I>2sigma(I)]	R1 = 0.0453, wR2 = 0.1112
R indices (all data)	R1 = 0.0793, wR2 = 0.1222
Extinction coefficient	0.0026(3)
Largest diff. peak and hole	0.820 and -0.535 e.$Å^{-3}$

Table S2. Bond lengths [Å] for **4c**

Ni(1)-O(1)	1.988(3)	C(17)-H(17)	0.9800
Ni(1)-N(1)	2.031(3)	C(18)-H(18A)	0.9600
Ni(1)-O(2)	2.093(3)	C(18)-H(18B)	0.9600
Ni(1)-Br(1)	2.4350(6)	C(18)-H(18C)	0.9600
Ni(1)-Br(2)	2.5959(6)	C(19)-H(19A)	0.9600
Ni(2)-O(1)	1.979(2)	C(19)-H(19B)	0.9600
Ni(2)-N(2)	2.054(3)	C(19)-H(19C)	0.9600
Ni(2)-O(3)	2.106(3)	C(20)-C(25)	1.386(6)
Ni(2)-Br(3)	2.4058(7)	C(20)-C(21)	1.397(6)
Ni(2)-Br(2)	2.4609(7)	C(21)-C(22)	1.389(6)
N(1)-C(1)	1.286(5)	C(21)-C(29)	1.545(7)
N(1)-C(8)	1.456(5)	C(22)-C(23)	1.373(7)

N(2)-C(3)	1.283(5)	C(22)-H(22)	0.9300
N(2)-C(20)	1.445(5)	C(23)-C(24)	1.353(7)
O(1)-C(2)	1.396(4)	C(23)-H(23)	0.9300
O(2)-C(35)	1.433(6)	C(24)-C(25)	1.395(6)
O(2)-C(32)	1.452(6)	C(24)-H(24)	0.9300
O(3)-C(39)	1.440(5)	C(25)-C(26)	1.508(7)
O(3)-C(36)	1.446(5)	C(26)-C(27)	1.518(8)
C(1)-C(5)	1.514(6)	C(26)-C(28)	1.519(9)
C(1)-C(2)	1.537(6)	C(26)-H(26)	0.9800
C(2)-C(3)	1.518(6)	C(27)-H(27A)	0.9600
C(2)-C(6)	1.561(5)	C(27)-H(27B)	0.9600
C(3)-C(4)	1.509(6)	C(27)-H(27C)	0.9600
C(4)-H(4A)	0.9600	C(28)-H(28A)	0.9600
C(4)-H(4B)	0.9600	C(28)-H(28B)	0.9600
C(4)-H(4C)	0.9600	C(28)-H(28C)	0.9600
C(5)-H(5A)	0.9600	C(29)-C(31)	1.503(7)
C(5)-H(5B)	0.9600	C(29)-C(30)	1.521(7)
C(5)-H(5C)	0.9600	C(29)-H(29)	0.9800
C(6)-C(7)	1.500(6)	C(30)-H(30A)	0.9600
C(6)-H(6A)	0.9700	C(30)-H(30B)	0.9600
C(6)-H(6B)	0.9700	C(30)-H(30C)	0.9600
C(7)-H(7A)	0.9600	C(31)-H(31A)	0.9600
C(7)-H(7B)	0.9600	C(31)-H(31B)	0.9600
C(7)-H(7C)	0.9600	C(31)-H(31C)	0.9600
C(8)-C(13)	1.390(6)	C(32)-C(33)	1.507(8)
C(8)-C(9)	1.399(6)	C(32)-H(32A)	0.9700
C(9)-C(10)	1.389(6)	C(32)-H(32B)	0.9700
C(9)-C(17)	1.527(7)	C(33)-C(34)	1.428(9)
C(10)-C(11)	1.370(8)	C(33)-H(33A)	0.9700
C(10)-H(10)	0.9300	C(33)-H(33B)	0.9700
C(11)-C(12)	1.340(8)	C(34)-C(35)	1.477(8)
C(11)-H(11)	0.9300	C(34)-H(34A)	0.9700
C(12)-C(13)	1.403(7)	C(34)-H(34B)	0.9700
C(12)-H(12)	0.9300	C(35)-H(35A)	0.9700
C(13)-C(14)	1.509(7)	C(35)-H(35B)	0.9700
C(14)-C(16)	1.507(7)	C(36)-C(37)	1.464(7)
C(14)-C(15)	1.546(8)	C(36)-H(36A)	0.9700
C(14)-H(14)	0.9800	C(36)-H(36B)	0.9700
C(15)-H(15A)	0.9600	C(37)-C(38)	1.482(8)
C(15)-H(15B)	0.9600	C(37)-H(37A)	0.9700
C(15)-H(15C)	0.9600	C(37)-H(37B)	0.9700
C(16)-H(16A)	0.9600	C(38)-C(39)	1.490(7)
C(16)-H(16B)	0.9600	C(38)-H(38A)	0.9700
C(16)-H(16C)	0.9600	C(38)-H(38B)	0.9700
C(17)-C(19)	1.514(7)	C(39)-H(39A)	0.9700
C(17)-C(18)	1.542(7)	C(39)-H(39B)	0.9700

Table S3. Bond angles [°] for **4c**

O(1)-Ni(1)-N(1)	81.74(12)	C(17)-C(18)-H(18A)	109.5
O(1)-Ni(1)-O(2)	170.52(11)	C(17)-C(18)-H(18B)	109.5
N(1)-Ni(1)-O(2)	100.29(13)	H(18A)-C(18)-H(18B)	109.5
O(1)-Ni(1)-Br(1)	96.05(7)	C(17)-C(18)-H(18C)	109.5
N(1)-Ni(1)-Br(1)	113.36(9)	H(18A)-C(18)-H(18C)	109.5
O(2)-Ni(1)-Br(1)	91.64(9)	H(18B)-C(18)-H(18C)	109.5
O(1)-Ni(1)-Br(2)	83.91(7)	C(17)-C(19)-H(19A)	109.5
N(1)-Ni(1)-Br(2)	97.27(9)	C(17)-C(19)-H(19B)	109.5
O(2)-Ni(1)-Br(2)	86.64(9)	H(19A)-C(19)-H(19B)	109.5
Br(1)-Ni(1)-Br(2)	149.10(3)	C(17)-C(19)-H(19C)	109.5
O(1)-Ni(2)-N(2)	79.45(11)	H(19A)-C(19)-H(19C)	109.5
O(1)-Ni(2)-O(3)	83.53(10)	H(19B)-C(19)-H(19C)	109.5
N(2)-Ni(2)-O(3)	154.10(12)	C(25)-C(20)-C(21)	122.6(4)
O(1)-Ni(2)-Br(3)	165.73(8)	C(25)-C(20)-N(2)	117.6(4)
N(2)-Ni(2)-Br(3)	99.32(9)	C(21)-C(20)-N(2)	119.8(4)
O(3)-Ni(2)-Br(3)	92.42(8)	C(22)-C(21)-C(20)	117.4(5)
O(1)-Ni(2)-Br(2)	87.79(8)	C(22)-C(21)-C(29)	119.2(4)
N(2)-Ni(2)-Br(2)	109.64(9)	C(20)-C(21)-C(29)	123.3(4)
O(3)-Ni(2)-Br(2)	88.91(9)	C(23)-C(22)-C(21)	121.1(5)
Br(3)-Ni(2)-Br(2)	105.85(3)	C(23)-C(22)-H(22)	119.5
Ni(2)-Br(2)-Ni(1)	75.60(2)	C(21)-C(22)-H(22)	119.5
C(1)-N(1)-C(8)	120.8(3)	C(24)-C(23)-C(22)	119.9(5)
C(1)-N(1)-Ni(1)	114.1(3)	C(24)-C(23)-H(23)	120.1
C(8)-N(1)-Ni(1)	125.1(3)	C(22)-C(23)-H(23)	120.1
C(3)-N(2)-C(20)	119.3(3)	C(23)-C(24)-C(25)	122.4(5)
C(3)-N(2)-Ni(2)	115.4(3)	C(23)-C(24)-H(24)	118.8
C(20)-N(2)-Ni(2)	125.3(3)	C(25)-C(24)-H(24)	118.8
C(2)-O(1)-Ni(2)	117.4(2)	C(20)-C(25)-C(24)	116.5(5)
C(2)-O(1)-Ni(1)	115.3(2)	C(20)-C(25)-C(26)	122.9(4)
Ni(2)-O(1)-Ni(1)	102.88(11)	C(24)-C(25)-C(26)	120.6(4)
C(35)-O(2)-C(32)	108.9(4)	C(25)-C(26)-C(27)	112.1(5)
C(35)-O(2)-Ni(1)	117.9(3)	C(25)-C(26)-C(28)	110.2(5)
C(32)-O(2)-Ni(1)	122.0(3)	C(27)-C(26)-C(28)	112.9(5)
C(39)-O(3)-C(36)	109.0(3)	C(25)-C(26)-H(26)	107.1
C(39)-O(3)-Ni(2)	112.0(3)	C(27)-C(26)-H(26)	107.1
C(36)-O(3)-Ni(2)	124.5(3)	C(28)-C(26)-H(26)	107.1
N(1)-C(1)-C(5)	122.4(4)	C(26)-C(27)-H(27A)	109.5
N(1)-C(1)-C(2)	117.3(3)	C(26)-C(27)-H(27B)	109.5
C(5)-C(1)-C(2)	120.3(4)	H(27A)-C(27)-H(27B)	109.5
O(1)-C(2)-C(3)	109.3(3)	C(26)-C(27)-H(27C)	109.5
O(1)-C(2)-C(1)	110.2(3)	H(27A)-C(27)-H(27C)	109.5
C(3)-C(2)-C(1)	112.8(3)	H(27B)-C(27)-H(27C)	109.5
O(1)-C(2)-C(6)	107.8(3)	C(26)-C(28)-H(28A)	109.5
C(3)-C(2)-C(6)	111.7(3)	C(26)-C(28)-H(28B)	109.5
C(1)-C(2)-C(6)	105.0(3)	H(28A)-C(28)-H(28B)	109.5

N(2)-C(3)-C(4)	121.2(4)	C(26)-C(28)-H(28C)	109.5
N(2)-C(3)-C(2)	117.0(3)	H(28A)-C(28)-H(28C)	109.5
C(4)-C(3)-C(2)	121.7(4)	H(28B)-C(28)-H(28C)	109.5
C(3)-C(4)-H(4A)	109.5	C(31)-C(29)-C(30)	110.6(5)
C(3)-C(4)-H(4B)	109.5	C(31)-C(29)-C(21)	112.9(4)
H(4A)-C(4)-H(4B)	109.5	C(30)-C(29)-C(21)	110.7(5)
C(3)-C(4)-H(4C)	109.5	C(31)-C(29)-H(29)	107.5
H(4A)-C(4)-H(4C)	109.5	C(30)-C(29)-H(29)	107.5
H(4B)-C(4)-H(4C)	109.5	C(21)-C(29)-H(29)	107.5
C(1)-C(5)-H(5A)	109.5	C(29)-C(30)-H(30A)	109.5
C(1)-C(5)-H(5B)	109.5	C(29)-C(30)-H(30B)	109.5
H(5A)-C(5)-H(5B)	109.5	H(30A)-C(30)-H(30B)	109.5
C(1)-C(5)-H(5C)	109.5	C(29)-C(30)-H(30C)	109.5
H(5A)-C(5)-H(5C)	109.5	H(30A)-C(30)-H(30C)	109.5
H(5B)-C(5)-H(5C)	109.5	H(30B)-C(30)-H(30C)	109.5
C(7)-C(6)-C(2)	112.1(4)	C(29)-C(31)-H(31A)	109.5
C(7)-C(6)-H(6A)	109.2	C(29)-C(31)-H(31B)	109.5
C(2)-C(6)-H(6A)	109.2	H(31A)-C(31)-H(31B)	109.5
C(7)-C(6)-H(6B)	109.2	C(29)-C(31)-H(31C)	109.5
C(2)-C(6)-H(6B)	109.2	H(31A)-C(31)-H(31C)	109.5
H(6A)-C(6)-H(6B)	107.9	H(31B)-C(31)-H(31C)	109.5
C(6)-C(7)-H(7A)	109.5	O(2)-C(32)-C(33)	104.9(5)
C(6)-C(7)-H(7B)	109.5	O(2)-C(32)-H(32A)	110.8
H(7A)-C(7)-H(7B)	109.5	C(33)-C(32)-H(32A)	110.8
C(6)-C(7)-H(7C)	109.5	O(2)-C(32)-H(32B)	110.8
H(7A)-C(7)-H(7C)	109.5	C(33)-C(32)-H(32B)	110.8
H(7B)-C(7)-H(7C)	109.5	H(32A)-C(32)-H(32B)	108.8
C(13)-C(8)-C(9)	121.6(4)	C(34)-C(33)-C(32)	106.0(5)
C(13)-C(8)-N(1)	117.5(4)	C(34)-C(33)-H(33A)	110.5
C(9)-C(8)-N(1)	120.8(4)	C(32)-C(33)-H(33A)	110.5
C(10)-C(9)-C(8)	117.7(5)	C(34)-C(33)-H(33B)	110.5
C(10)-C(9)-C(17)	118.7(4)	C(32)-C(33)-H(33B)	110.5
C(8)-C(9)-C(17)	123.6(4)	H(33A)-C(33)-H(33B)	108.7
C(11)-C(10)-C(9)	120.6(5)	C(33)-C(34)-C(35)	106.6(5)
C(11)-C(10)-H(10)	119.7	C(33)-C(34)-H(34A)	110.4
C(9)-C(10)-H(10)	119.7	C(35)-C(34)-H(34A)	110.4
C(12)-C(11)-C(10)	121.6(5)	C(33)-C(34)-H(34B)	110.4
C(12)-C(11)-H(11)	119.2	C(35)-C(34)-H(34B)	110.4
C(10)-C(11)-H(11)	119.2	H(34A)-C(34)-H(34B)	108.6
C(11)-C(12)-C(13)	120.7(5)	O(2)-C(35)-C(34)	107.4(5)
C(11)-C(12)-H(12)	119.6	O(2)-C(35)-H(35A)	110.2
C(13)-C(12)-H(12)	119.6	C(34)-C(35)-H(35A)	110.2
C(8)-C(13)-C(12)	117.8(5)	O(2)-C(35)-H(35B)	110.2
C(8)-C(13)-C(14)	122.3(4)	C(34)-C(35)-H(35B)	110.2
C(12)-C(13)-C(14)	119.8(5)	H(35A)-C(35)-H(35B)	108.5
C(16)-C(14)-C(13)	115.2(5)	O(3)-C(36)-C(37)	106.1(5)
C(16)-C(14)-C(15)	108.7(5)	O(3)-C(36)-H(36A)	110.5

C(13)-C(14)-C(15)	110.8(5)	C(37)-C(36)-H(36A)	110.5
C(16)-C(14)-H(14)	107.2	O(3)-C(36)-H(36B)	110.5
C(13)-C(14)-H(14)	107.2	C(37)-C(36)-H(36B)	110.5
C(15)-C(14)-H(14)	107.2	H(36A)-C(36)-H(36B)	108.7
C(14)-C(15)-H(15A)	109.5	C(36)-C(37)-C(38)	104.5(5)
C(14)-C(15)-H(15B)	109.5	C(36)-C(37)-H(37A)	110.9
H(15A)-C(15)-H(15B)	109.5	C(38)-C(37)-H(37A)	110.9
C(14)-C(15)-H(15C)	109.5	C(36)-C(37)-H(37B)	110.9
H(15A)-C(15)-H(15C)	109.5	C(38)-C(37)-H(37B)	110.9
H(15B)-C(15)-H(15C)	109.5	H(37A)-C(37)-H(37B)	108.9
C(14)-C(16)-H(16A)	109.5	C(37)-C(38)-C(39)	103.5(5)
C(14)-C(16)-H(16B)	109.5	C(37)-C(38)-H(38A)	111.1
H(16A)-C(16)-H(16B)	109.5	C(39)-C(38)-H(38A)	111.1
C(14)-C(16)-H(16C)	109.5	C(37)-C(38)-H(38B)	111.1
H(16A)-C(16)-H(16C)	109.5	C(39)-C(38)-H(38B)	111.1
H(16B)-C(16)-H(16C)	109.5	H(38A)-C(38)-H(38B)	109.0
C(19)-C(17)-C(9)	110.7(5)	O(3)-C(39)-C(38)	105.7(4)
C(19)-C(17)-C(18)	110.1(5)	O(3)-C(39)-H(39A)	110.6
C(9)-C(17)-C(18)	110.9(4)	C(38)-C(39)-H(39A)	110.6
C(19)-C(17)-H(17)	108.4	O(3)-C(39)-H(39B)	110.6
C(9)-C(17)-H(17)	108.4	C(38)-C(39)-H(39B)	110.6
C(18)-C(17)-H(17)	108.4	H(39A)-C(39)-H(39B)	108.7

Table S4. Crystal data and structure refinement for **4d**

Identification code	mj22149_0m
Empirical formula	C32 H47 Br3 N2 Ni2 O3
Formula weight	864.86
Temperature	235.00 K
Wavelength	1.34139 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 9.1461(2) Å
	b = 9.5974(2) Å
	c = 20.7405(5) Å
Volume	1758.26(7) Å^3
Z	2
Density (calculated)	1.634 Mg/m^3
Absorption coefficient	8.674 mm^{-1}
F(000)	876
Crystal size	0.07 x 0.07 x 0.05 mm^3
Theta range for data collection	4.048 to 55.017°.
Index ranges	-10<=h<=11, -11<=k<=11, -25<=l<=25
Reflections collected	19462
Independent reflections	6668 [R(int) = 0.0605]
Completeness to theta = 53.594°	99.2 %

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7508 and 0.4483
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6668 / 0 / 387
Goodness-of-fit on F^2	1.079
Final R indices [I>2sigma(I)]	R1 = 0.0463, wR2 = 0.1273
R indices (all data)	R1 = 0.0492, wR2 = 0.1302
Extinction coefficient	n/a
Largest diff. peak and hole	0.752 and -1.088 e.Å^{-3}

Table S5. Bond lengths [Å] for **4d**

Br(1)-Ni(1)	2.4215(5)	C(13)-C(14)	1.406(5)
Br(2)-Ni(1)	2.4574(5)	C(14)-C(15)	1.488(6)
Br(2)-Ni(2)	2.5337(5)	C(15)-H(15A)	0.9700
Br(3)-Ni(2)	2.4119(6)	C(15)-H(15B)	0.9700
Ni(1)-O(1)	1.979(2)	C(15)-H(15C)	0.9700
Ni(1)-O(2)	2.081(2)	C(16)-H(16A)	0.9700
Ni(1)-N(1)	2.040(3)	C(16)-H(16B)	0.9700
Ni(2)-O(1)	2.024(2)	C(16)-H(16C)	0.9700
Ni(2)-O(3)	2.137(2)	C(17)-C(18)	1.386(5)
Ni(2)-N(2)	2.007(3)	C(17)-C(22)	1.396(5)
O(1)-C(1)	1.388(3)	C(18)-C(19)	1.393(5)
O(2)-C(25)	1.430(6)	C(18)-C(24)	1.500(5)
O(2)-C(28)	1.441(4)	C(19)-H(19)	0.9400
O(3)-C(29)	1.433(4)	C(19)-C(20)	1.375(6)
O(3)-C(32)	1.453(5)	C(20)-H(20)	0.9400
N(1)-C(2)	1.286(4)	C(20)-C(21)	1.368(6)
N(1)-C(9)	1.446(4)	C(21)-H(21)	0.9400
N(2)-C(4)	1.290(4)	C(21)-C(22)	1.396(5)
N(2)-C(17)	1.458(4)	C(22)-C(23)	1.505(6)
C(1)-C(2)	1.545(4)	C(23)-H(23A)	0.9700
C(1)-C(4)	1.546(4)	C(23)-H(23B)	0.9700
C(1)-C(6)	1.573(4)	C(23)-H(23C)	0.9700
C(2)-C(3)	1.497(4)	C(24)-H(24A)	0.9700
C(3)-H(3A)	0.9700	C(24)-H(24B)	0.9700
C(3)-H(3B)	0.9700	C(24)-H(24C)	0.9700
C(3)-H(3C)	0.9700	C(25)-H(25A)	0.9800
C(4)-C(5)	1.493(5)	C(25)-H(25B)	0.9800
C(5)-H(5A)	0.9700	C(25)-C(26)	1.526(6)
C(5)-H(5B)	0.9700	C(26)-H(26A)	0.9800
C(5)-H(5C)	0.9700	C(26)-H(26B)	0.9800
C(6)-H(6)	0.9900	C(26)-C(27)	1.478(7)
C(6)-C(7)	1.506(5)	C(27)-H(27A)	0.9800
C(6)-C(8)	1.530(5)	C(27)-H(27B)	0.9800
C(7)-H(7A)	0.9700	C(27)-C(28)	1.519(7)

C(7)-H(7B)	0.9700	C(28)-H(28A)	0.9800
C(7)-H(7C)	0.9700	C(28)-H(28B)	0.9800
C(8)-H(8A)	0.9700	C(29)-H(29A)	0.9800
C(8)-H(8B)	0.9700	C(29)-H(29B)	0.9800
C(8)-H(8C)	0.9700	C(29)-C(30)	1.505(6)
C(9)-C(10)	1.396(5)	C(30)-H(30A)	0.9800
C(9)-C(14)	1.391(5)	C(30)-H(30B)	0.9800
C(10)-C(11)	1.395(6)	C(30)-C(31)	1.450(7)
C(10)-C(16)	1.493(6)	C(31)-H(31A)	0.9800
C(11)-H(11)	0.9400	C(31)-H(31B)	0.9800
C(11)-C(12)	1.383(8)	C(31)-C(32)	1.440(6)
C(12)-H(12)	0.9400	C(32)-H(32A)	0.9800
C(12)-C(13)	1.378(7)	C(32)-H(32B)	0.9800
C(13)-H(13)	0.9400		

Table S6. Bond angles [°] for **4d**

Ni(1)-Br(2)-Ni(2)	77.619(17)	C(9)-C(14)-C(13)	116.8(4)
Br(1)-Ni(1)-Br(2)	100.924(19)	C(9)-C(14)-C(15)	122.9(3)
O(1)-Ni(1)-Br(1)	169.83(6)	C(13)-C(14)-C(15)	120.3(4)
O(1)-Ni(1)-Br(2)	88.79(6)	C(14)-C(15)-H(15A)	109.5
O(1)-Ni(1)-O(2)	85.46(9)	C(14)-C(15)-H(15B)	109.5
O(1)-Ni(1)-N(1)	80.10(9)	C(14)-C(15)-H(15C)	109.5
O(2)-Ni(1)-Br(1)	90.45(7)	H(15A)-C(15)-H(15B)	109.5
O(2)-Ni(1)-Br(2)	96.23(8)	H(15A)-C(15)-H(15C)	109.5
N(1)-Ni(1)-Br(1)	99.78(8)	H(15B)-C(15)-H(15C)	109.5
N(1)-Ni(1)-Br(2)	106.44(8)	C(10)-C(16)-H(16A)	109.5
N(1)-Ni(1)-O(2)	152.70(11)	C(10)-C(16)-H(16B)	109.5
Br(3)-Ni(2)-Br(2)	132.48(2)	C(10)-C(16)-H(16C)	109.5
O(1)-Ni(2)-Br(2)	85.70(6)	H(16A)-C(16)-H(16B)	109.5
O(1)-Ni(2)-Br(3)	97.69(6)	H(16A)-C(16)-H(16C)	109.5
O(1)-Ni(2)-O(3)	170.29(9)	H(16B)-C(16)-H(16C)	109.5
O(3)-Ni(2)-Br(2)	87.97(7)	C(18)-C(17)-N(2)	118.4(3)
O(3)-Ni(2)-Br(3)	92.02(7)	C(18)-C(17)-C(22)	122.2(3)
N(2)-Ni(2)-Br(2)	112.06(7)	C(22)-C(17)-N(2)	119.3(3)
N(2)-Ni(2)-Br(3)	115.21(7)	C(17)-C(18)-C(19)	118.0(3)
N(2)-Ni(2)-O(1)	79.97(9)	C(17)-C(18)-C(24)	121.3(3)
N(2)-Ni(2)-O(3)	95.64(10)	C(19)-C(18)-C(24)	120.7(3)
Ni(1)-O(1)-Ni(2)	102.79(9)	C(18)-C(19)-H(19)	119.6
C(1)-O(1)-Ni(1)	117.77(18)	C(20)-C(19)-C(18)	120.9(4)
C(1)-O(1)-Ni(2)	116.39(17)	C(20)-C(19)-H(19)	119.6
C(25)-O(2)-Ni(1)	116.8(2)	C(19)-C(20)-H(20)	119.9
C(25)-O(2)-C(28)	110.0(3)	C(21)-C(20)-C(19)	120.3(4)
C(28)-O(2)-Ni(1)	125.0(3)	C(21)-C(20)-H(20)	119.9
C(29)-O(3)-Ni(2)	130.0(2)	C(20)-C(21)-H(21)	119.4
C(29)-O(3)-C(32)	107.0(3)	C(20)-C(21)-C(22)	121.2(4)
C(32)-O(3)-Ni(2)	122.8(2)	C(22)-C(21)-H(21)	119.4

C(2)-N(1)-Ni(1)	116.1(2)	C(17)-C(22)-C(23)	122.0(3)
C(2)-N(1)-C(9)	119.9(3)	C(21)-C(22)-C(17)	117.5(4)
C(9)-N(1)-Ni(1)	123.8(2)	C(21)-C(22)-C(23)	120.5(3)
C(4)-N(2)-Ni(2)	117.6(2)	C(22)-C(23)-H(23A)	109.5
C(4)-N(2)-C(17)	120.2(3)	C(22)-C(23)-H(23B)	109.5
C(17)-N(2)-Ni(2)	122.2(2)	C(22)-C(23)-H(23C)	109.5
O(1)-C(1)-C(2)	109.8(2)	H(23A)-C(23)-H(23B)	109.5
O(1)-C(1)-C(4)	110.2(2)	H(23A)-C(23)-H(23C)	109.5
O(1)-C(1)-C(6)	109.8(2)	H(23B)-C(23)-H(23C)	109.5
C(2)-C(1)-C(4)	110.4(3)	C(18)-C(24)-H(24A)	109.5
C(2)-C(1)-C(6)	108.5(2)	C(18)-C(24)-H(24B)	109.5
C(4)-C(1)-C(6)	108.1(2)	C(18)-C(24)-H(24C)	109.5
N(1)-C(2)-C(1)	116.1(3)	H(24A)-C(24)-H(24B)	109.5
N(1)-C(2)-C(3)	122.2(3)	H(24A)-C(24)-H(24C)	109.5
C(3)-C(2)-C(1)	121.5(3)	H(24B)-C(24)-H(24C)	109.5
C(2)-C(3)-H(3A)	109.5	O(2)-C(25)-H(25A)	110.6
C(2)-C(3)-H(3B)	109.5	O(2)-C(25)-H(25B)	110.6
C(2)-C(3)-H(3C)	109.5	O(2)-C(25)-C(26)	105.6(4)
H(3A)-C(3)-H(3B)	109.5	H(25A)-C(25)-H(25B)	108.7
H(3A)-C(3)-H(3C)	109.5	C(26)-C(25)-H(25A)	110.6
H(3B)-C(3)-H(3C)	109.5	C(26)-C(25)-H(25B)	110.6
N(2)-C(4)-C(1)	115.9(3)	C(25)-C(26)-H(26A)	111.2
N(2)-C(4)-C(5)	122.3(3)	C(25)-C(26)-H(26B)	111.2
C(5)-C(4)-C(1)	121.8(3)	H(26A)-C(26)-H(26B)	109.1
C(4)-C(5)-H(5A)	109.5	C(27)-C(26)-C(25)	102.7(4)
C(4)-C(5)-H(5B)	109.5	C(27)-C(26)-H(26A)	111.2
C(4)-C(5)-H(5C)	109.5	C(27)-C(26)-H(26B)	111.2
H(5A)-C(5)-H(5B)	109.5	C(26)-C(27)-H(27A)	111.2
H(5A)-C(5)-H(5C)	109.5	C(26)-C(27)-H(27B)	111.2
H(5B)-C(5)-H(5C)	109.5	C(26)-C(27)-C(28)	102.7(4)
C(1)-C(6)-H(6)	108.5	H(27A)-C(27)-H(27B)	109.1
C(7)-C(6)-C(1)	111.1(3)	C(28)-C(27)-H(27A)	111.2
C(7)-C(6)-H(6)	108.5	C(28)-C(27)-H(27B)	111.2
C(7)-C(6)-C(8)	109.3(3)	O(2)-C(28)-C(27)	104.0(4)
C(8)-C(6)-C(1)	110.7(3)	O(2)-C(28)-H(28A)	111.0
C(8)-C(6)-H(6)	108.5	O(2)-C(28)-H(28B)	111.0
C(6)-C(7)-H(7A)	109.5	C(27)-C(28)-H(28A)	111.0
C(6)-C(7)-H(7B)	109.5	C(27)-C(28)-H(28B)	111.0
C(6)-C(7)-H(7C)	109.5	H(28A)-C(28)-H(28B)	109.0
H(7A)-C(7)-H(7B)	109.5	O(3)-C(29)-H(29A)	110.4
H(7A)-C(7)-H(7C)	109.5	O(3)-C(29)-H(29B)	110.4
H(7B)-C(7)-H(7C)	109.5	O(3)-C(29)-C(30)	106.6(4)
C(6)-C(8)-H(8A)	109.5	H(29A)-C(29)-H(29B)	108.6
C(6)-C(8)-H(8B)	109.5	C(30)-C(29)-H(29A)	110.4
C(6)-C(8)-H(8C)	109.5	C(30)-C(29)-H(29B)	110.4
H(8A)-C(8)-H(8B)	109.5	C(29)-C(30)-H(30A)	110.6
H(8A)-C(8)-H(8C)	109.5	C(29)-C(30)-H(30B)	110.6

H(8B)-C(8)-H(8C)	109.5	H(30A)-C(30)-H(30B)	108.8
C(10)-C(9)-N(1)	118.2(3)	C(31)-C(30)-C(29)	105.5(4)
C(14)-C(9)-N(1)	118.5(3)	C(31)-C(30)-H(30A)	110.6
C(14)-C(9)-C(10)	123.2(3)	C(31)-C(30)-H(30B)	110.6
C(9)-C(10)-C(16)	122.7(3)	C(30)-C(31)-H(31A)	109.9
C(11)-C(10)-C(9)	117.6(4)	C(30)-C(31)-H(31B)	109.9
C(11)-C(10)-C(16)	119.7(4)	H(31A)-C(31)-H(31B)	108.3
C(10)-C(11)-H(11)	119.6	C(32)-C(31)-C(30)	108.9(4)
C(12)-C(11)-C(10)	120.9(4)	C(32)-C(31)-H(31A)	109.9
C(12)-C(11)-H(11)	119.6	C(32)-C(31)-H(31B)	109.9
C(11)-C(12)-H(12)	119.9	O(3)-C(32)-H(32A)	110.3
C(13)-C(12)-C(11)	120.1(4)	O(3)-C(32)-H(32B)	110.3
C(13)-C(12)-H(12)	119.9	C(31)-C(32)-O(3)	106.9(4)
C(12)-C(13)-H(13)	119.3	C(31)-C(32)-H(32A)	110.3
C(12)-C(13)-C(14)	121.4(5)	C(31)-C(32)-H(32B)	110.3
C(14)-C(13)-H(13)	119.3	H(32A)-C(32)-H(32B)	108.6

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