

## Supplementary Materials for

# **Polar Thermoplastics with Tunable Physical Properties Enabled by the Stereoselective Copolymerization of Vinyl Ethers**

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## 1. Materials and Methods

### 1.1 General Considerations

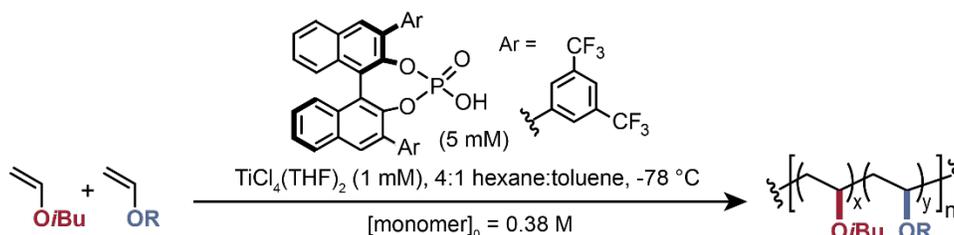
The compounds (*R*)-3,3'-bis(3,5-bis(trifluoromethyl)phenyl)-1,1'-binaphthyl phosphate,<sup>1</sup> tetrachlorobis(tetrahydrofuran)titanium(IV) ( $\text{TiCl}_4(\text{THF})_2$ ),<sup>2</sup> and 1-pyrenebutyryl chloride<sup>3</sup> were prepared according to literature procedures. Vinyl ether monomers were dried over  $\text{CaH}_2$  and distilled under vacuum prior to storage in a  $\text{N}_2$ -filled glovebox for further use. All other reagents and solvents were purchased from commercial sources and used without further purification. Unless otherwise noted, solvents were dried and degassed using a Pure Process Technology solvent purification system and then subsequently stored over molecular sieves (3Å). All syntheses were performed under inert atmosphere ( $\text{N}_2$  or Ar) using flame-dried or oven-dried glassware unless specified otherwise. NMR spectra were recorded using a Bruker DRX 400 MHz, Bruker AVANCE III 500 MHz, or Bruker AVANCE III 600 MHz CryoProbe spectrometer. Chemical shifts  $\delta$  (ppm) are referenced to tetramethylsilane (TMS) using the residual solvent as an internal standard ( $^1\text{H}$  and  $^{13}\text{C}$ ). For  $^1\text{H}$  NMR:  $\text{CDCl}_3$ , 7.26 ppm. For  $^{13}\text{C}$  NMR:  $\text{CDCl}_3$ , 77.16 ppm. Coupling constants ( $J$ ) are expressed in hertz (Hz).

### 1.2 Macromolecular Characterization

Gel permeation chromatography (GPC) was performed on a Waters 2695 separations module liquid chromatograph equipped with either four Waters Styragel HR columns (WAT044225, WAT044231, WAT044237, and WAT054460) arranged in series or two Agilent Resipore columns (PL1113-6300) maintained at 35 °C, and a Waters 2414 refractive index detector at room temperature. Tetrahydrofuran was used as the mobile phase at a flow rate of 1.0 mL/min. Molecular weight and dispersity data are reported relative to polystyrene standards.

Melting-transition temperature ( $T_m$ ) and glass-transition temperature ( $T_g$ ) of precipitated and dried polymer samples were measured using differential scanning calorimetry (DSC) on a TA Instruments Discovery DSC. Unless specifically noted otherwise, values for  $T_m$  and  $T_g$  were obtained from a second heating scan after the thermal history was removed. All heating and cooling rates were 10 °C/min. Decomposition onset temperatures ( $T_d$ ) of precipitated and dried polymer samples were measured by thermal gravimetric analysis (TGA) on a TA Instruments Q5000 Thermogravimetric Analyzer. Polymer samples were heated from ambient temperatures to 600 °C at a heating rate of 10 °C/min. Values of  $T_d$  (temperature at 5% weight loss) were obtained from wt % vs. temperature (°C) plots.

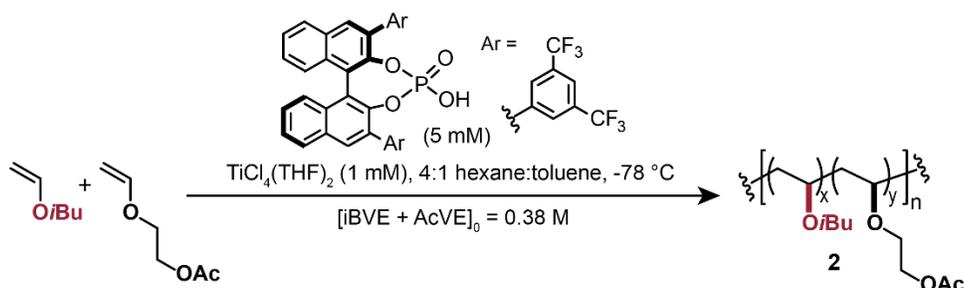
### 1.3 Syntheses and Characterization Data



#### General copolymerization procedure

Copolymerizations were performed in septum-capped reaction vials prepared in a  $\text{N}_2$ -filled glovebox. An oven-dried 8 mL septum-capped vial equipped with a stir bar was charged with isobutyl vinyl ether (iBVE), comonomer, and hexane. In this vial: the total monomer concentration was kept constant at 0.38 M and the total solution volume was kept constant at 1.62 mL. A separate

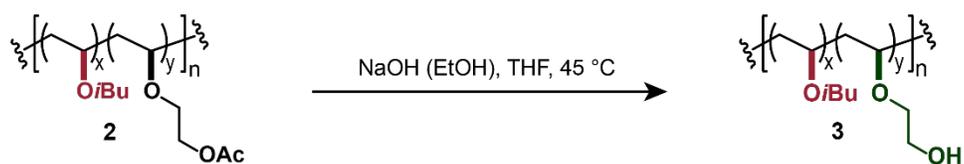
8 mL septum-capped vial equipped with a stir bar was charged with 0.26 mL of a 0.05 M stock solution of (*R*)-3,3'-bis(3,5-bis(trifluoromethyl)phenyl)-1,1'-binaphthyl phosphate in MePh (0.013 mmol) and 0.26 mL of a 0.01 M stock solution of TiCl<sub>4</sub>(THF)<sub>2</sub> in MePh (0.0026 mmol). Both vials were removed from the glove box and cooled to -78 °C in a dry ice/acetone bath. After stirring at -78 °C for 15 min, the entire MePh solution was transferred via syringe to the vial containing monomer solution. The reaction was stirred at -78 °C for 2 h, after which time 1.0 mL of Et<sub>3</sub>N/MeOH solution (5% v/v) was added to quench the polymerization. Upon warming to room temperature, the mixture was washed with 1N HCl and all volatiles removed in vacuo. The crude polymer was dissolved in 1–2 mL CH<sub>2</sub>Cl<sub>2</sub> and filtered through a plug of SiO<sub>2</sub> (4–5 cm) in a glass pipette eluting with additional CH<sub>2</sub>Cl<sub>2</sub>. The resulting purified polymer was dried under vacuum for at least 12 h to a constant weight.



### Copolymerization of iBVE with acyl-protected ethylene glycol vinyl ether (AcVE)

An oven-dried 20 mL septum-capped vial equipped with a stir bar was charged with iBVE (0.29 mL, 2.10 mmol), AcVE (15 mg, 0.11 mmol), and hexane (4.22 mL). A separate 8 mL septum-capped vial equipped with a stir bar was charged with 0.6 mL of a 0.05 M stock solution of (*R*)-3,3'-bis(3,5-bis(trifluoromethyl)phenyl)-1,1'-binaphthyl phosphate in MePh (0.03 mmol) and 0.6 mL of a 0.01 M stock solution of TiCl<sub>4</sub>(THF)<sub>2</sub> in MePh (0.006 mmol). Both vials were removed from the glove box and cooled to -78 °C in a dry ice/acetone bath. After stirring at -78 °C for 15 min, the entire MePh solution was transferred via syringe to the vial containing monomer solution. The reaction was stirred at -78 °C for 4 h, after which time 3.0 mL of Et<sub>3</sub>N/MeOH solution (5% v/v) was added to quench the polymerization. Upon warming to room temperature, the mixture was washed with 1N HCl and all volatiles removed in vacuo. The crude polymer was dissolved in 1–2 mL CH<sub>2</sub>Cl<sub>2</sub> and filtered through a short (5–6 cm) column (diameter = 16 mm) of SiO<sub>2</sub> eluting with additional CH<sub>2</sub>Cl<sub>2</sub>. The resulting purified polymer was dried under vacuum for at least 12 h to a constant weight. Yield: 46%.

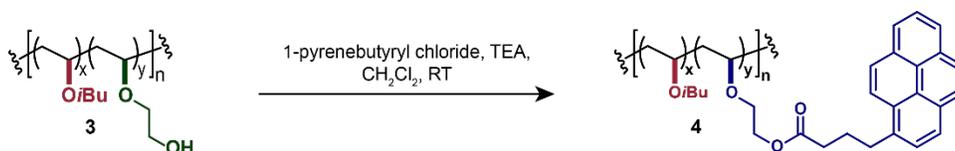
$f_{Ac} = 0.05$ ;  $F_{Ac} = 0.065$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 4.16 (t), 3.62 (br.), 3.56 (br.), 3.47 (br.), 3.25 (br.), 3.16 (br.), 2.07 (s), 1.82 (br.), 1.78 (septet), 1.53 (br.), 0.88 (d). <sup>13</sup>C NMR (125 MHz): δ 171.1, 75.9, 73.9, 41.6, 39.7, 39.4, 29.1, 19.8. GPC:  $M_n = 41$  kDa;  $D = 1.9$ . DSC:  $T_g = -26$  °C,  $T_m = 124$  °C.



## Hydrolysis of copolymer 2

An oven-dried 8 mL septum-capped vial equipped with a stir bar was charged with copolymer **2** (0.215 g, 0.136 mmol AcVE repeat units) and dry THF (2.5 mL). NaOH (55 mg, 1.38 mmol), dissolved in EtOH (0.30 mL), injected into vial containing copolymer solution and mixture heated to 45 °C. After 16 hours, mixture cooled to RT and directly poured into ice-cold H<sub>2</sub>O. Pale yellow precipitate collected by filtration and subsequently triturated with excess MeOH by vigorously stirring for 30 min. The resulting material was dissolved in THF (1-2 mL) and precipitated into ice cold H<sub>2</sub>O a second time. The pure, white copolymer was collected by filtration and dried under vacuum for at least 12 h to a constant weight. Yield: 140 mg (77%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.66 (br.), 3.47 (br.), 3.15 (br.), 1.82 (br.), 1.77 (septet), 1.53 (br.), 0.88 (d). GPC:  $M_n = 37$  kDa;  $D = 2.1$ . DSC:  $T_g = -16$  °C,  $T_m = 131$  °C.



## Functionalization of copolymer 3 with 1-pyrenebutyryl chloride

An oven-dried 8 mL septum-capped vial equipped with a stir bar was charged with copolymer **3** (0.040 g, 0.026 mmol hydroxyl repeat units) and dry CH<sub>2</sub>Cl<sub>2</sub> (5.0 mL). Triethylamine (18 μL, 0.130 mmol) added, followed by a solution of 1-pyrenebutyryl chloride (0.040 g, 0.130 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL). Mixture stirred at room temperature (RT) for 3 hours, at which point it was directly poured into ice-cold MeOH. Pale yellow precipitate collected by filtration, dissolved in THF (1 mL), precipitated into ice cold MeOH a second time. The pure, pale yellow copolymer was collected by filtration and dried under vacuum for at least 12 h to a constant weight. Yield: 33 mg (70%). Note: GPC analysis with photodiode array (PDA) detection (344 nm) confirms the presence of pyrene in copolymer **4**.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.30 (br.), 8.16 (br.), 8.10 (br.), 8.02 (br.), 7.87 (br.), 4.21 (br.), 3.57 (br.), 3.48 (br.), 3.20 (br.), 3.15 (br.), 2.51 (br.), 2.18 (br.), 1.83 (br.), 1.77 (septet), 1.53 (br.), 0.88 (d). <sup>13</sup>C NMR (125 MHz): δ 173.37, 131.4, 130.9, 130.0, 128.7, 127.5, 127.3, 126.7, 125.8, 125.1, 124.9, 123.4, 75.8, 73.8, 41.4, 39.6, 39.3, 28.9, 19.7. GPC:  $M_n = 47$  kDa;  $D = 2.3$ . DSC:  $T_g = -16$  °C,  $T_m = 126$  °C.

## 2. Supplementary Text

### 2.1 Copolymerization of ethyl vinyl ether (EVE) with iBVE

**Table S1.** Summary of copolymerization experiments with iBVE and EVE using **1**.

$f_{\text{Et}}^{\text{a}}$	$F_{\text{Et}}^{\text{b}}$	$M_{\text{n}}$ (kg mol <sup>-1</sup> ) <sup>c</sup>	$\mathcal{D}^{\text{c}}$	$m$ (%)	$T_{\text{g}}$ (°C) <sup>d</sup>	$T_{\text{m}}$ (°C) <sup>d</sup>
0.05	0.09	58	1.7	93	-26	132
0.10	0.13	58	1.9	93	-25	132
0.15	0.22	62	1.9	93	-29	107
0.20	0.34	83	2.0	92	-32	66
0.30	0.38	101	2.4	93	-33	50 <sup>e</sup>
0.40	0.52	41	1.7	93	-37	39 <sup>e</sup>
0.50	0.62	90	2.7	92	-37	40 <sup>e</sup>
0.65	0.74	66	2.0	91	-37	not observed
0.8	0.83	51	1.8	93	-38	41 <sup>e</sup>
0.9	0.91	82	2.6	92	-39	42 <sup>e</sup>

<sup>a</sup> mole fraction of EVE in the monomer feed. <sup>b</sup> mole fraction of EVE in copolymer determined by <sup>1</sup>H NMR integration. <sup>c</sup>  $M_{\text{n}}$  indicates the number average molecular weight of the polymer. Dispersity was calculated according to  $\mathcal{D} = M_{\text{w}}/M_{\text{n}}$  where  $M_{\text{w}}$  is the weight average molecular weight. <sup>d</sup>  $T_{\text{g}}$  and  $T_{\text{m}}$  obtained from a second heating scan (10 °C/min) after the thermal history was removed. <sup>e</sup>  $T_{\text{m}}$  values obtained from first heating scan (10 °C/min) after annealing at room temperature for several days.

## 2.2 Pseudo-First Order Kinetic Analyses

The cationic polymerization of vinyl ethers, including iBVE, nBVE, EVE, and AcVE, facilitated by catalyst **1** may be represented as:



Under the assumption that there are negligible side-reactions taking place, any of the above listed monomers (M) will always be present in a large excess over the catalyst (C). As such, pseudo-first-order kinetics are valid for rate calculations. In this scenario, the following rate law applies:

$$\frac{d[P]}{dt} = \frac{-d[M]}{dt} = k[M]$$
$$\frac{d[M]}{[M]} = -kdt$$

The integrated form of the rate equation is represented as:

$$\ln[M] = \ln[M]_0 - kt$$

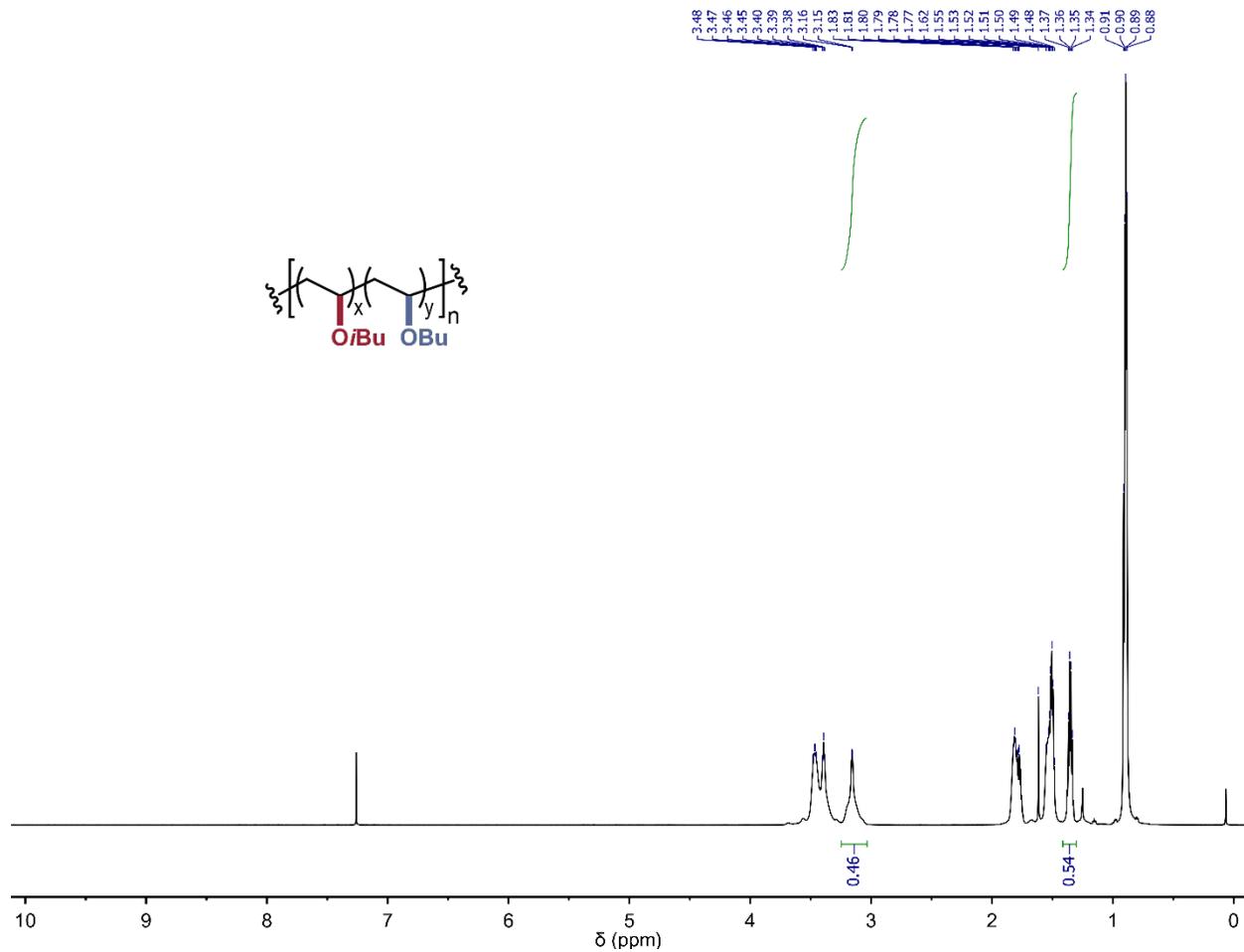
This equation indicates that plotting inverse  $\ln[M]$  versus  $t$  (s) should give a linear plot where  $k$  is equal to the slope of the line. Figure 4 in the main text illustrates this relationship.

During the copolymerization of iBVE and nBVE, significant overlap occurs in the  $^1\text{H}$  NMR spectrum that hinders the ability to monitor the relative consumption of each monomer independently. Peak deconvolution of the vinyl region ( $\delta$  6.40-6.48 ppm,  $\text{CDCl}_3$ ) using OriginPro 8<sup>4</sup> in the presence of an internal standard (*i.e.*, 1,4-dimethoxybenzene), however, enables the accurate determination of individual monomer concentration at various time points (Table S1). A representative example can be seen in Figure S13.

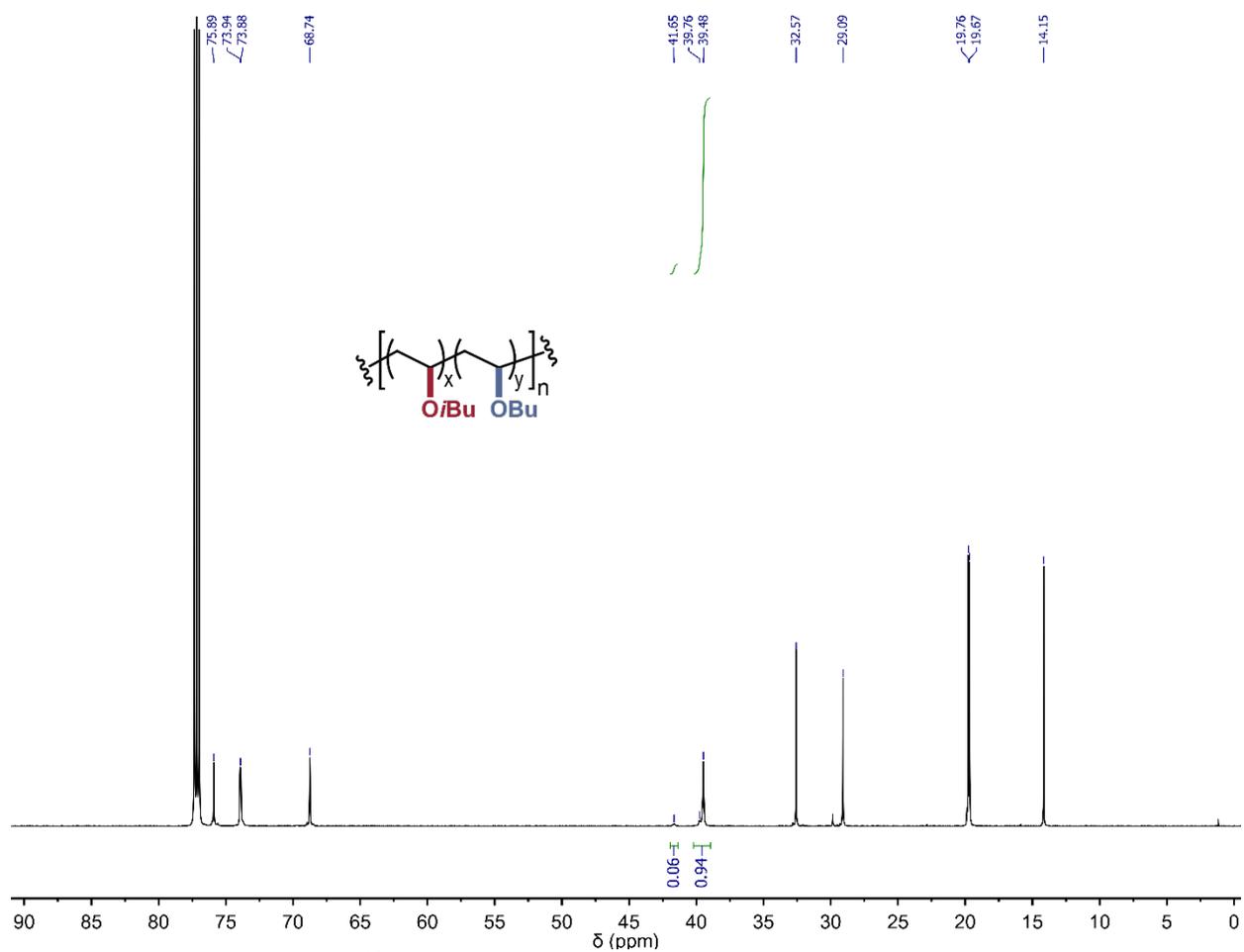
**Table S2.** Summary of peak deconvolution data obtained from a copolymerization of nBVE with iBVE with  $f_{\text{Bu}} = 0.50$  that was quenched at 20 min ( $t = 1200$  s). Peak denominations correspond to those seen in Figure S13.

Monomer	Peak	Area	Total Area
iBVE	1	9.96E-5	4.26E-4
	2	1.10E-4	
	3	1.12E-4	
	4	1.10E-4	
nBVE	5	7.58E-5	3.00E-4
	6	7.98E-5	
	7	8.10E-5	
	8	7.14E-5	

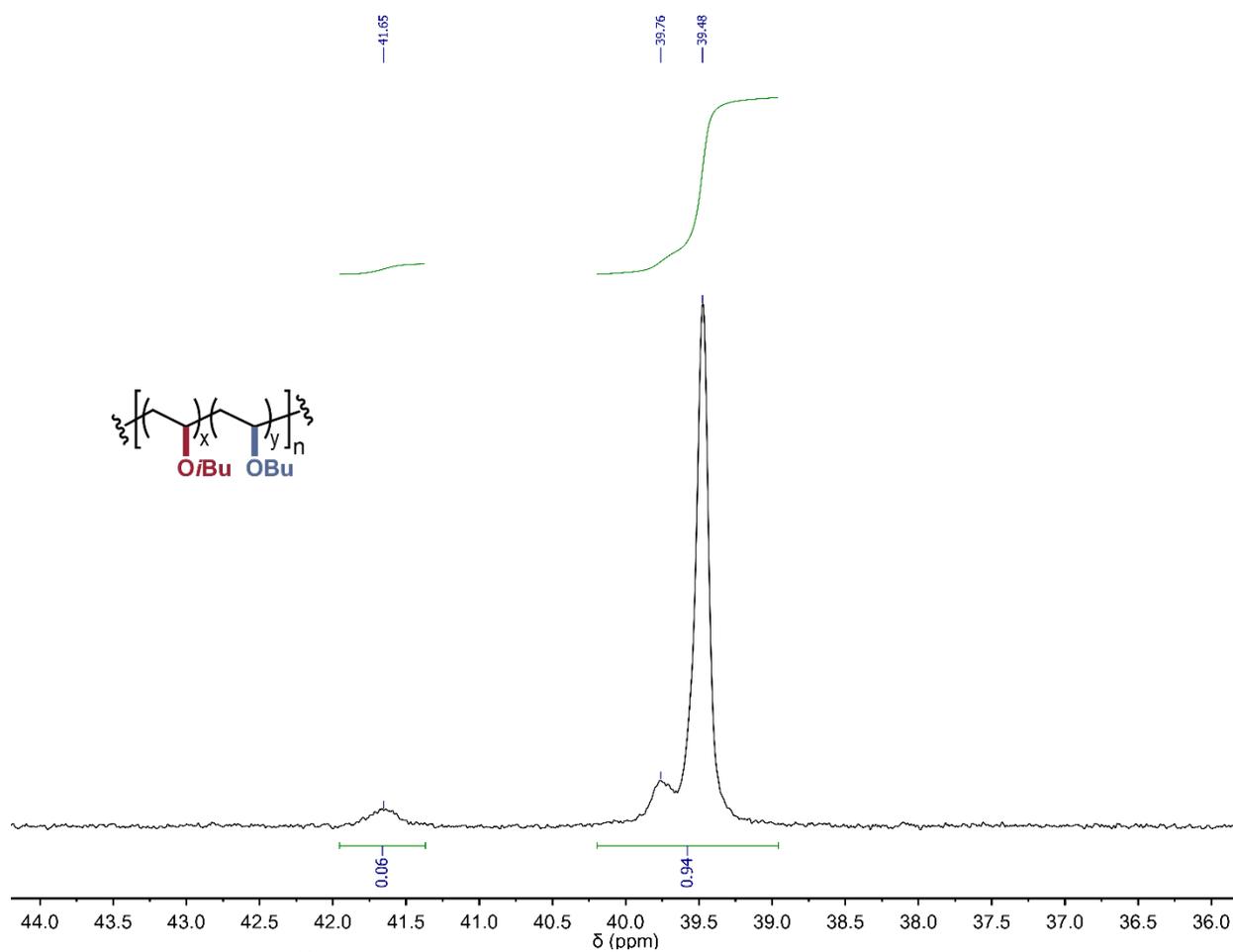
### 3. Figures



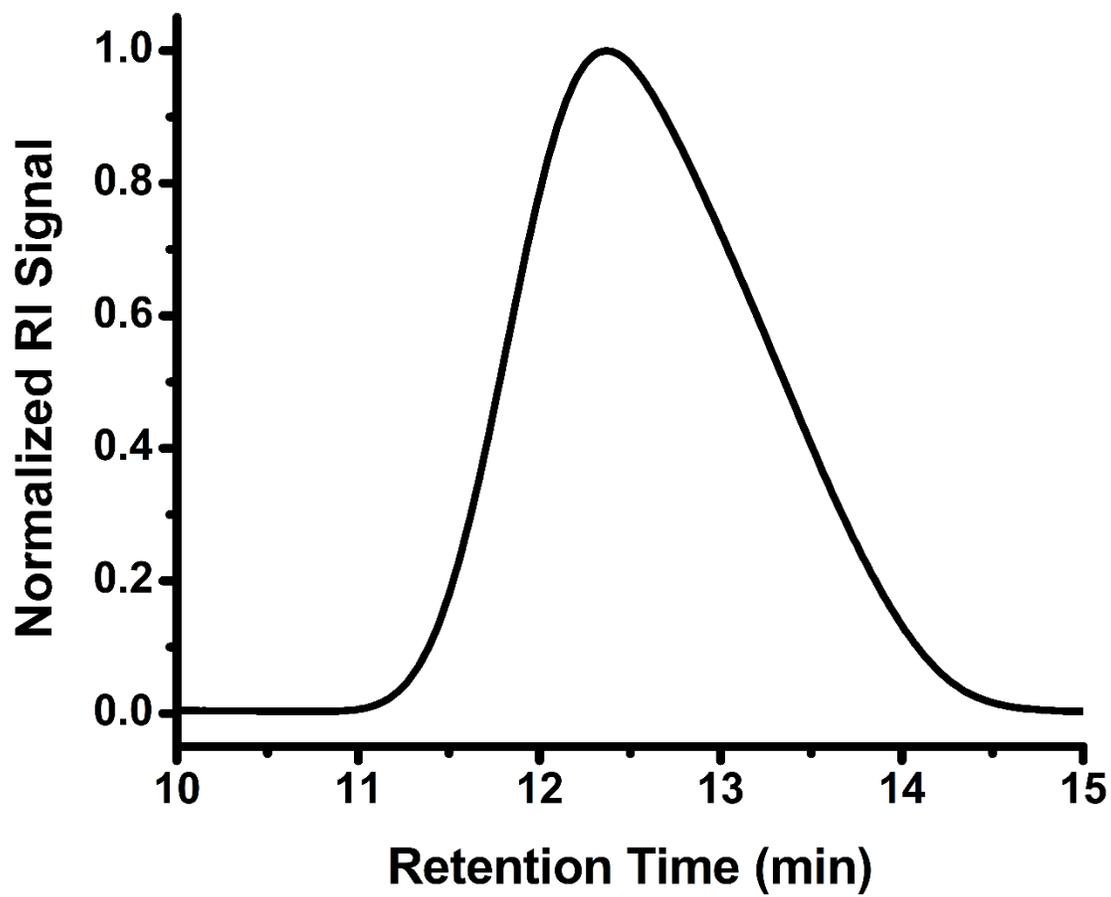
**Figure S1.** Representative <sup>1</sup>H NMR spectrum of isotactic poly(iBVE-co-nBVE). In this example,  $F_{\text{Bu}} = 0.54$  (CDCl<sub>3</sub>).



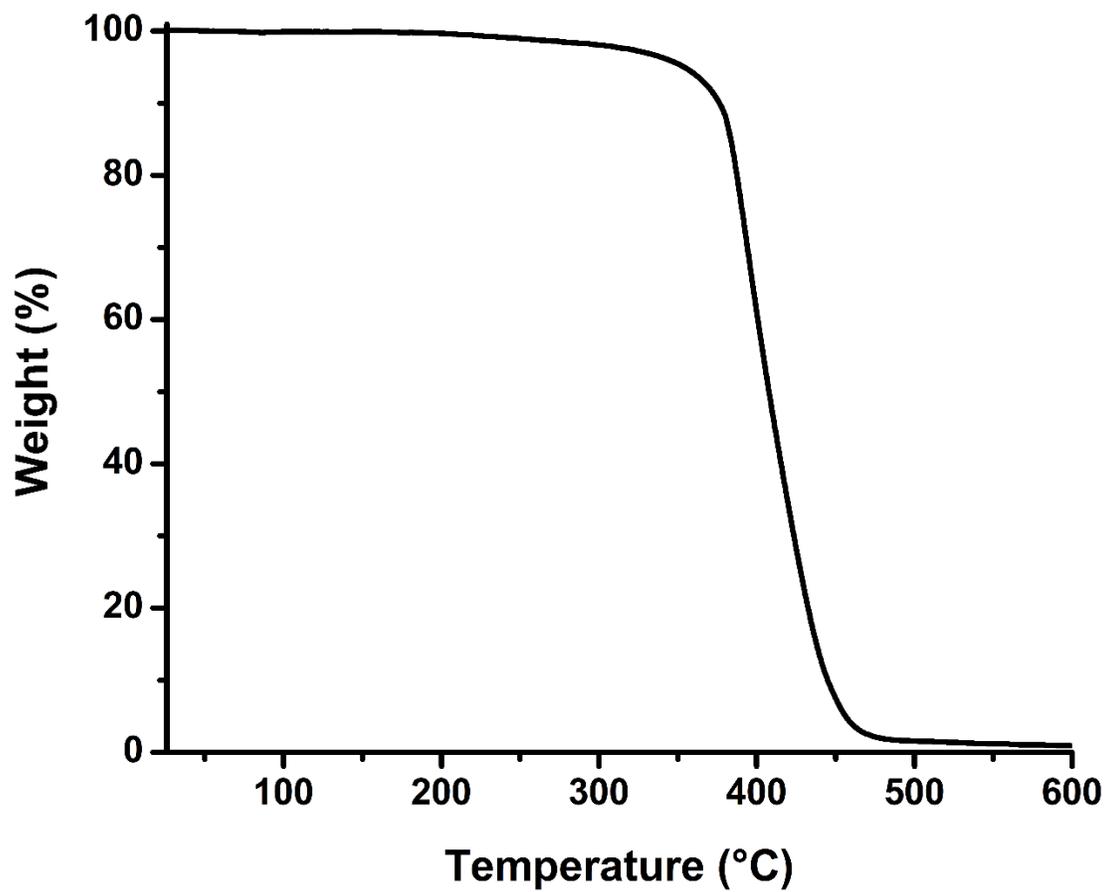
**Figure S2.** Representative  $^{13}\text{C}$  NMR spectrum of isotactic poly(iBVE-co-nBVE) with relative integrations amounting to 94% *meso* diads. In this example,  $F_{\text{Bu}} = 0.54$  ( $\text{CDCl}_3$ ).



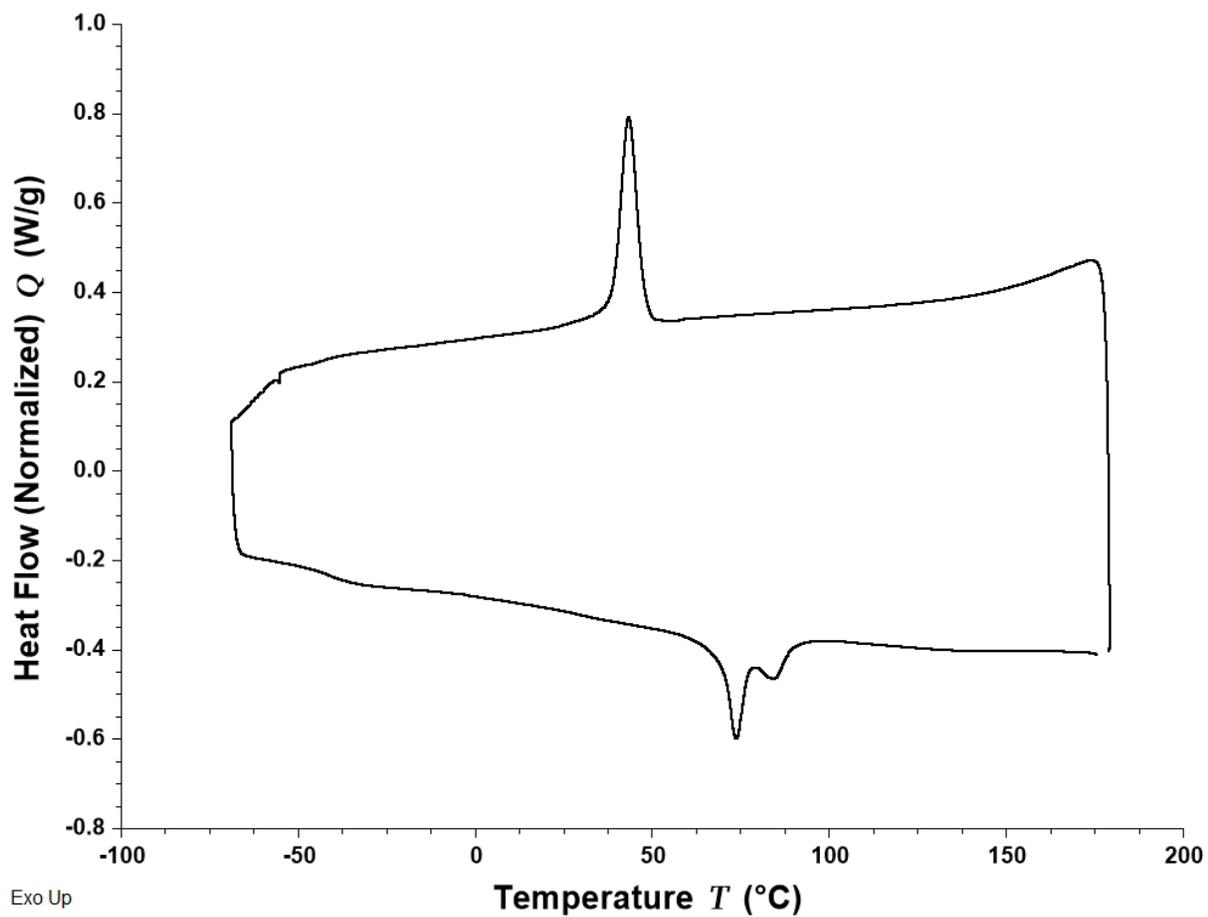
**Figure S3.** Expanded  $^{13}\text{C}$  NMR spectrum of a representative sample of isotactic poly(iBVE-co-nBVE) showing relative integrations amounting to 94% *meso* diads. In this example,  $F_{\text{Bu}} = 0.54$  ( $\text{CDCl}_3$ ).



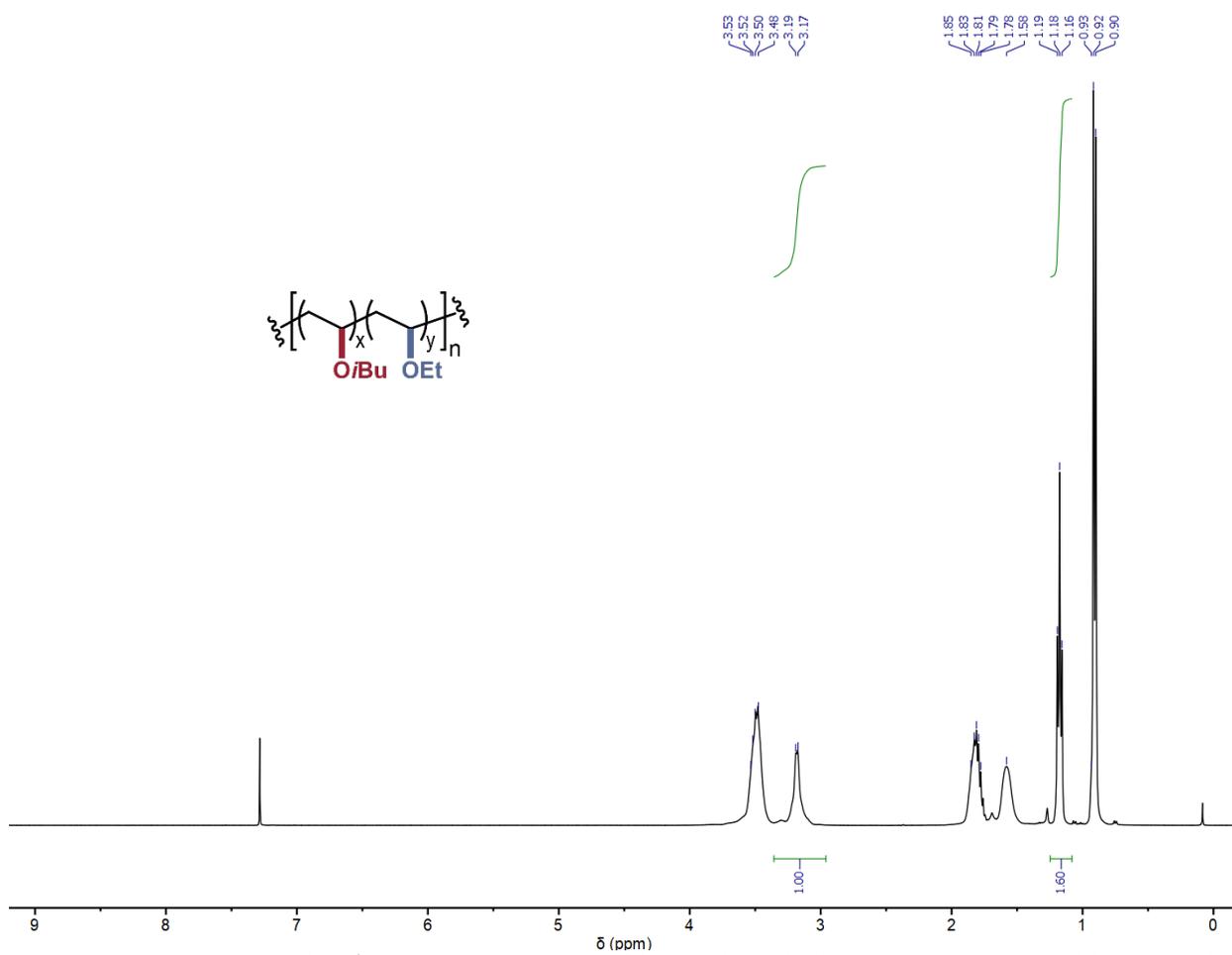
**Figure S4.** Representative GPC RI trace of isotactic poly(iBVE-*co*-nBVE). In this example,  $F_{Bu} = 0.54$ .



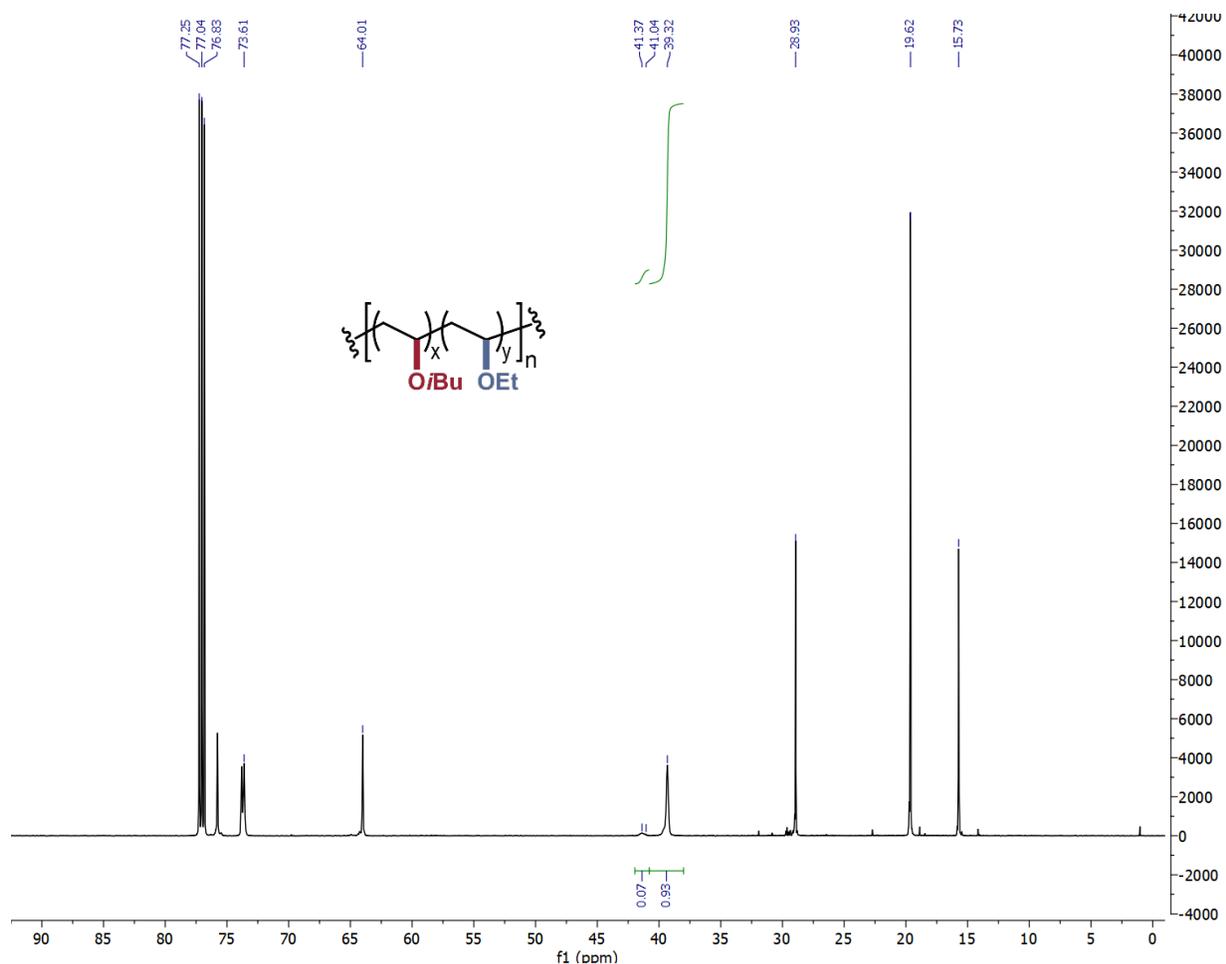
**Figure S5.** Representative TGA curve for isotactic poly(iBVE-co-nBVE). In this example,  $F_{Bu} = 0.54$ .



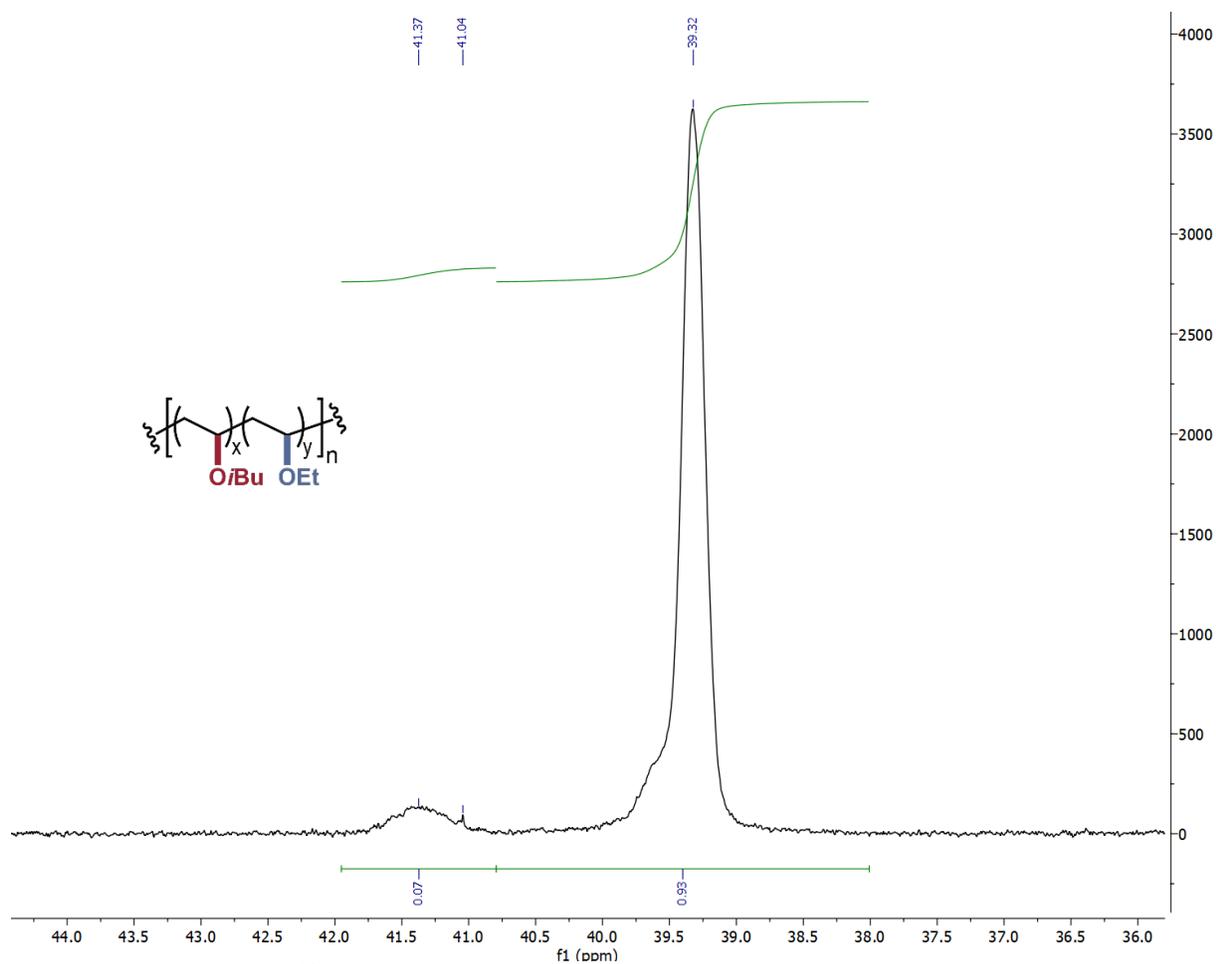
**Figure S6.** Representative DSC curves for isotactic poly(iBVE-co-nBVE). In this example,  $F_{Bu} = 0.54$ .



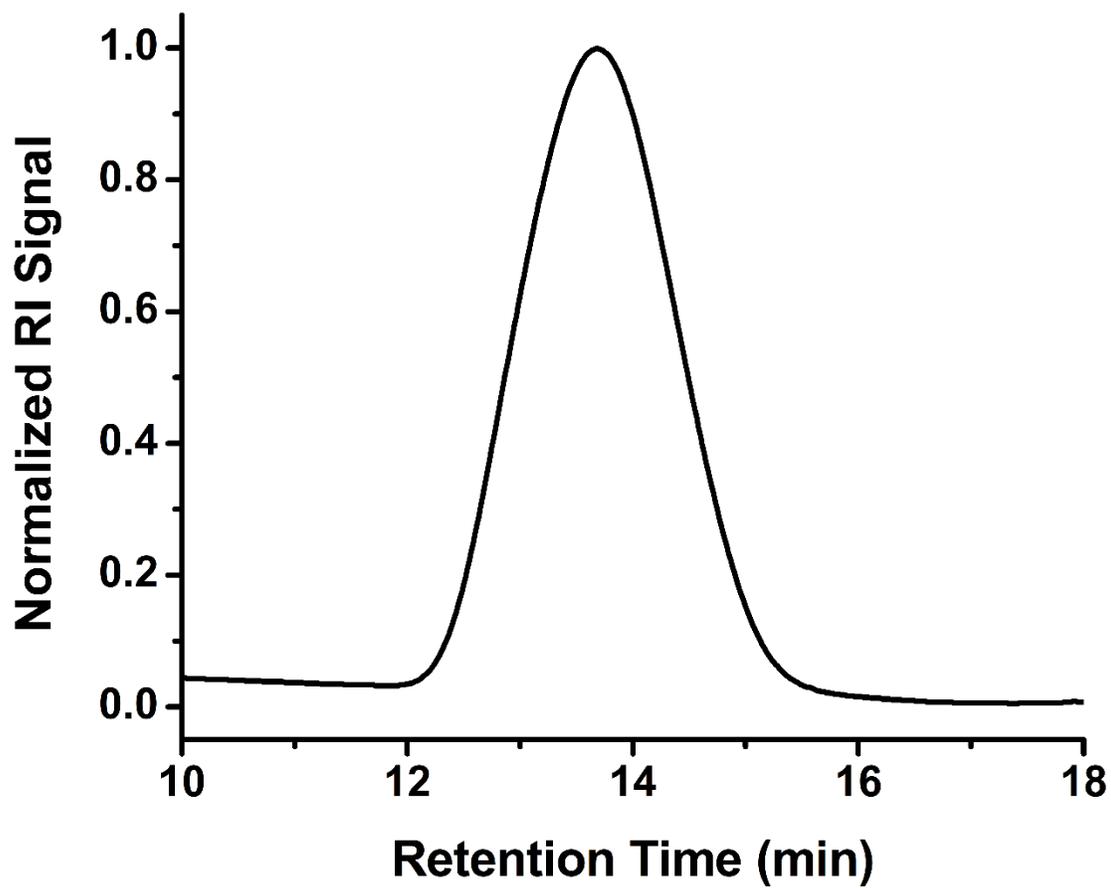
**Figure S7.** Representative <sup>1</sup>H NMR spectrum of isotactic poly(iBVE-co-EVE). In this example,  $F_{\text{Et}} = 0.52$  (CDCl<sub>3</sub>).



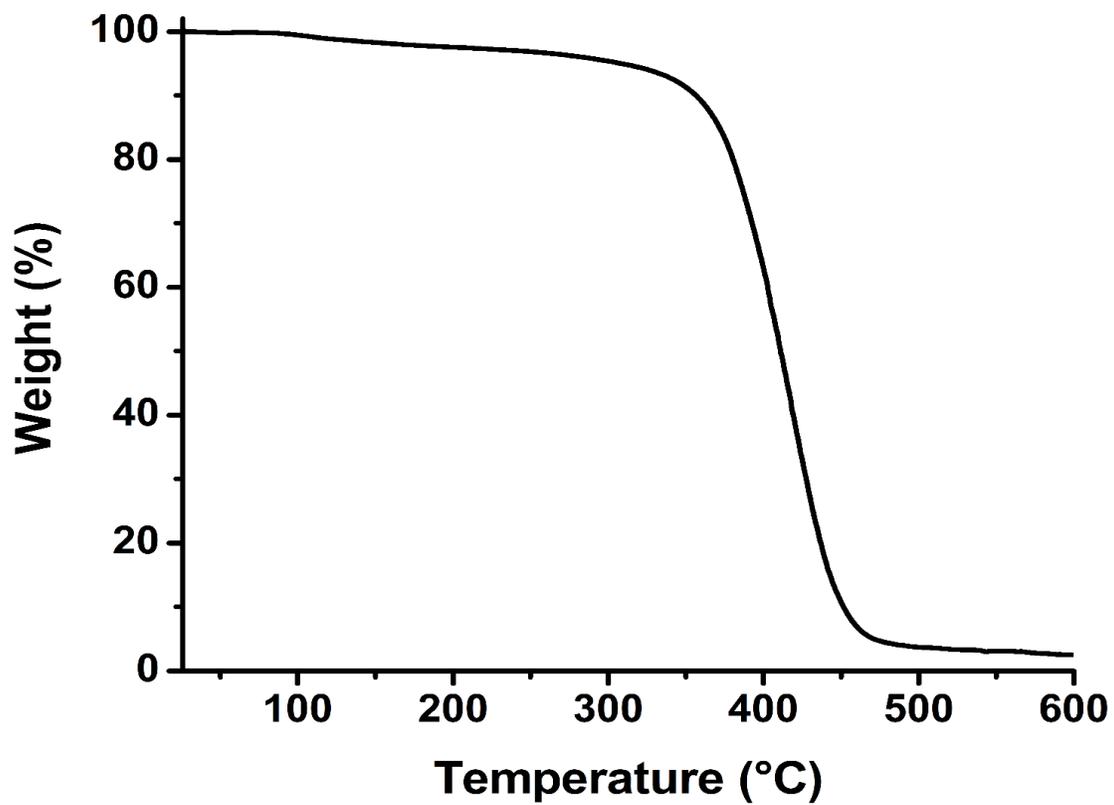
**Figure S8.** Representative  $^{13}\text{C}$  NMR spectrum of isotactic poly(iBVE-co-EVE) with relative integrations amounting to 93% *meso* diads. In this example,  $F_{\text{Et}} = 0.52$  (CDCl<sub>3</sub>).



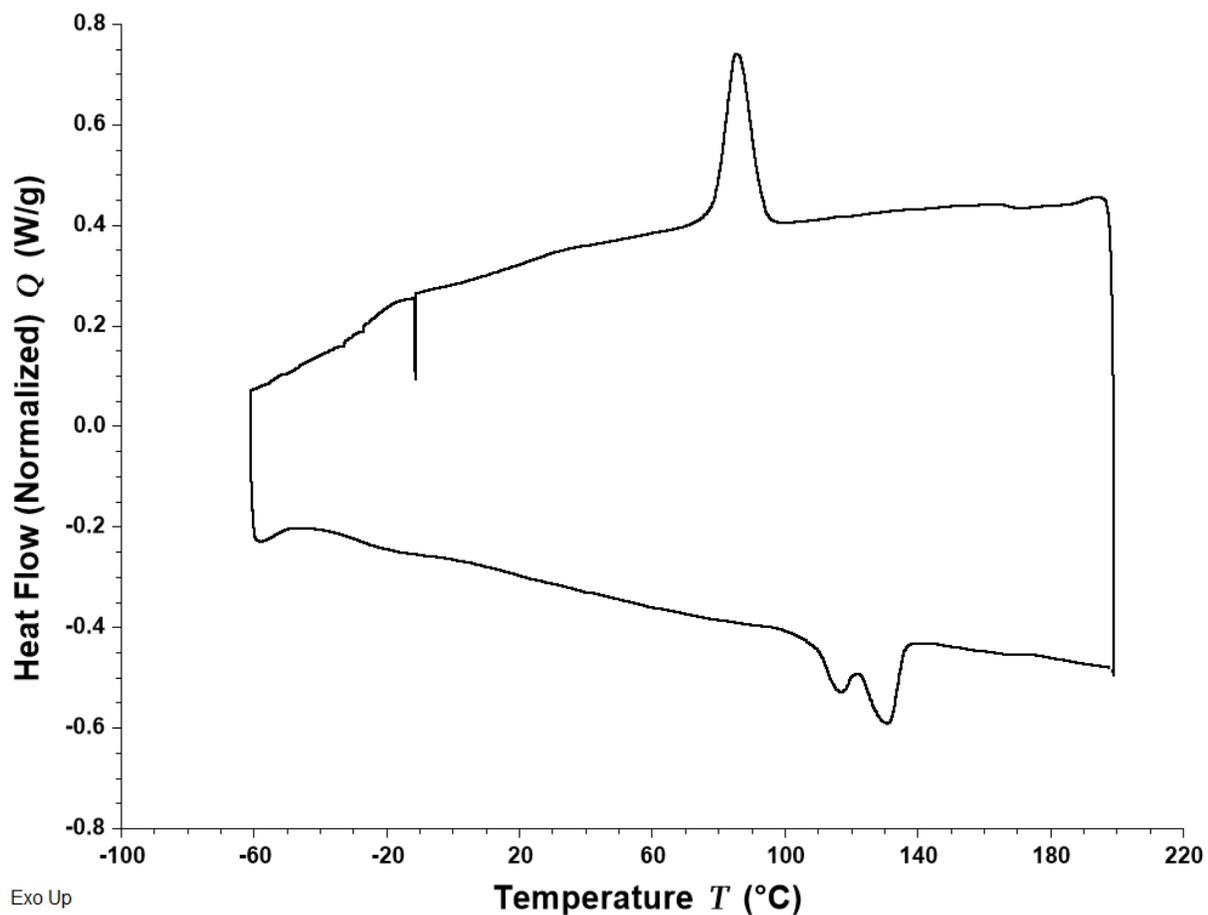
**Figure S9.** Expanded  $^{13}\text{C}$  NMR spectrum of a representative sample of isotactic poly(iBVE-co-EVE) showing relative integrations amounting to 93% *meso* diads. In this example,  $F_{\text{Et}} = 0.52$  ( $\text{CDCl}_3$ ).



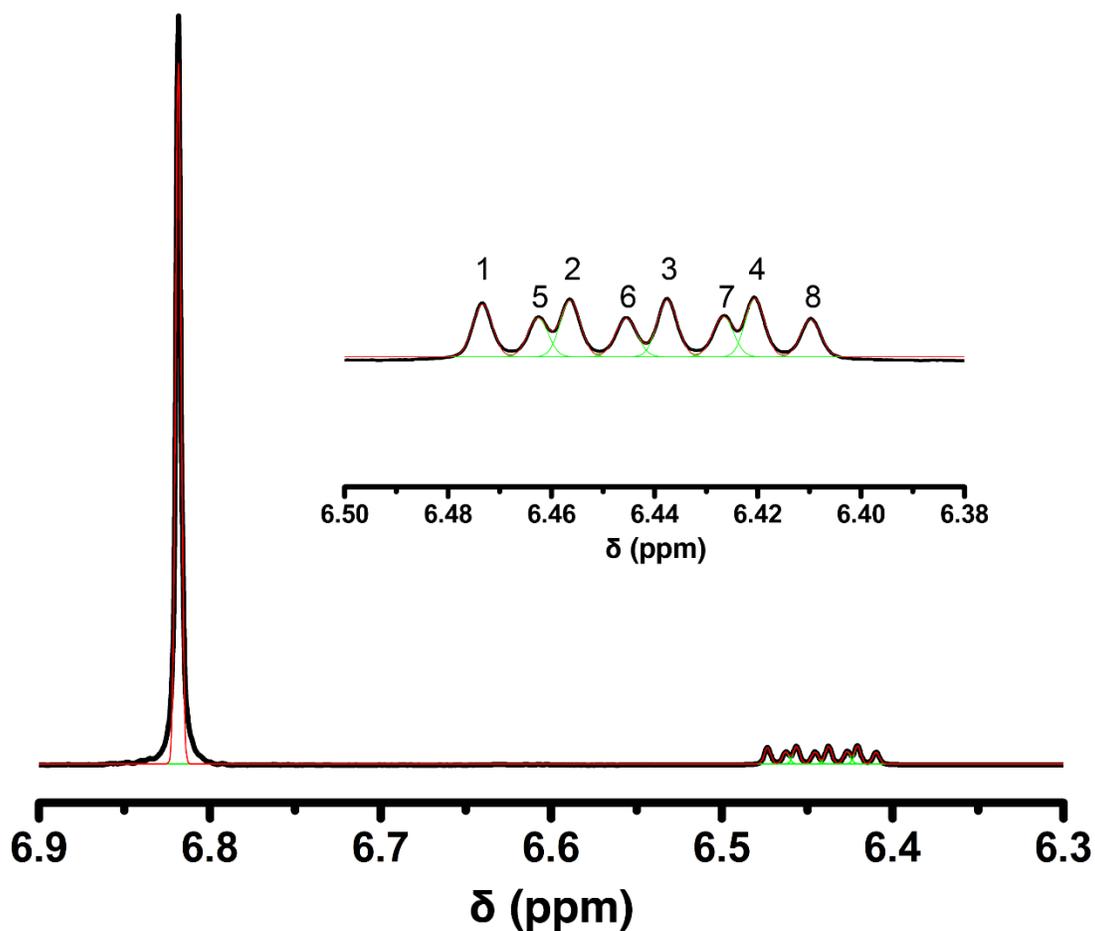
**Figure S10.** Representative GPC RI trace of isotactic poly(iBVE-*co*-EVE). In this example,  $F_{Et} = 0.09$ .



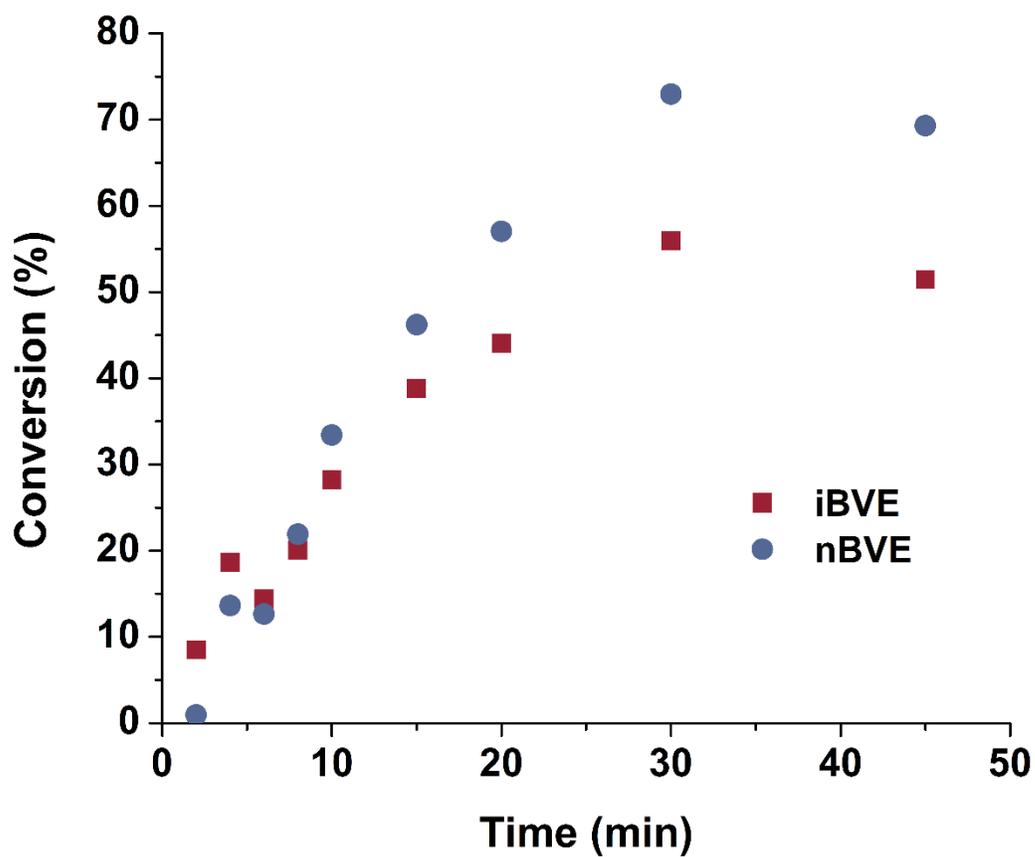
**Figure S11.** Representative TGA curve for isotactic poly(iBVE-co-EVE). In this example,  $F_{Et} = 0.52$ .



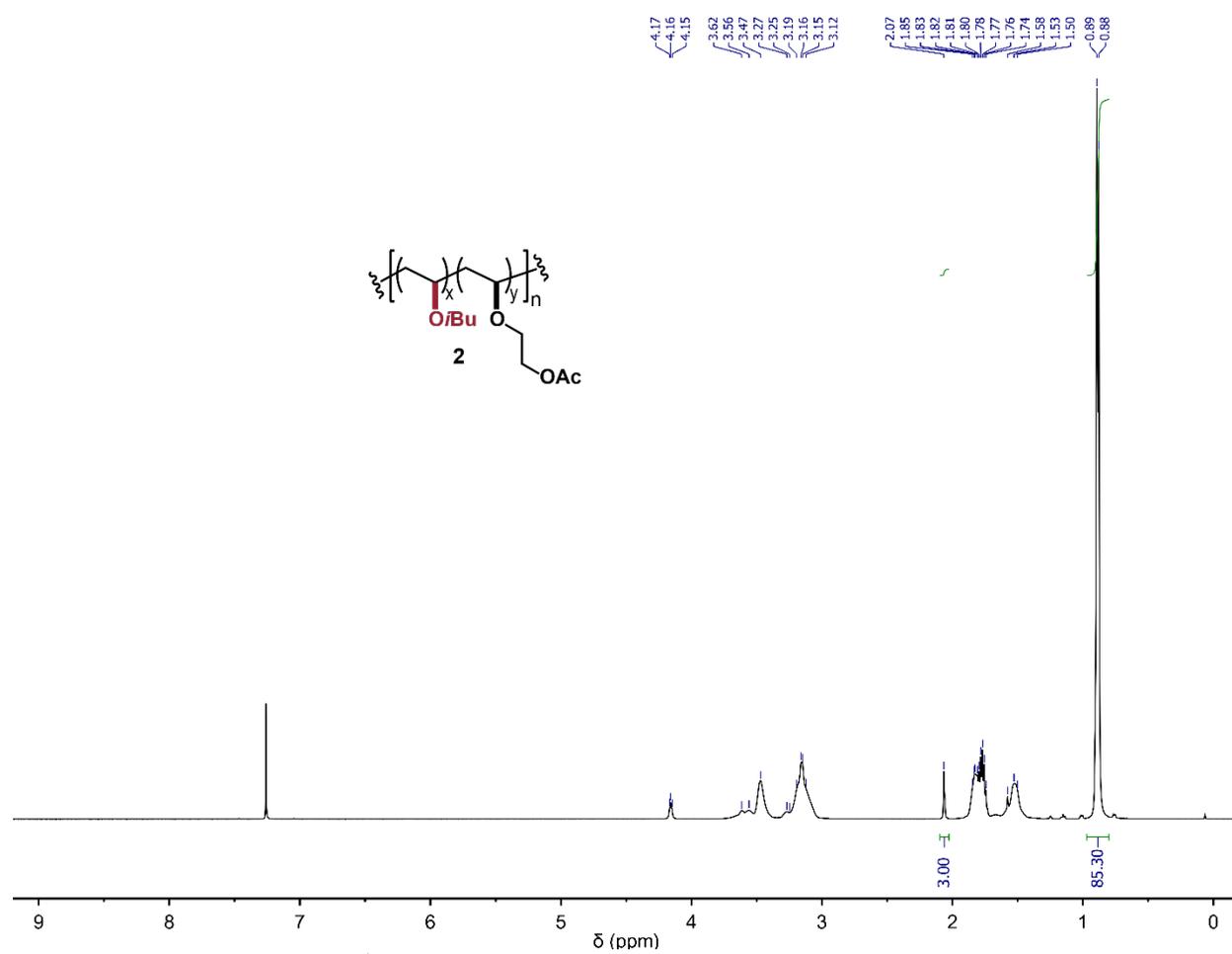
**Figure S12.** Representative DSC curves for isotactic poly(iBVE-co-EVE). In this example,  $F_{Et} = 0.09$ .



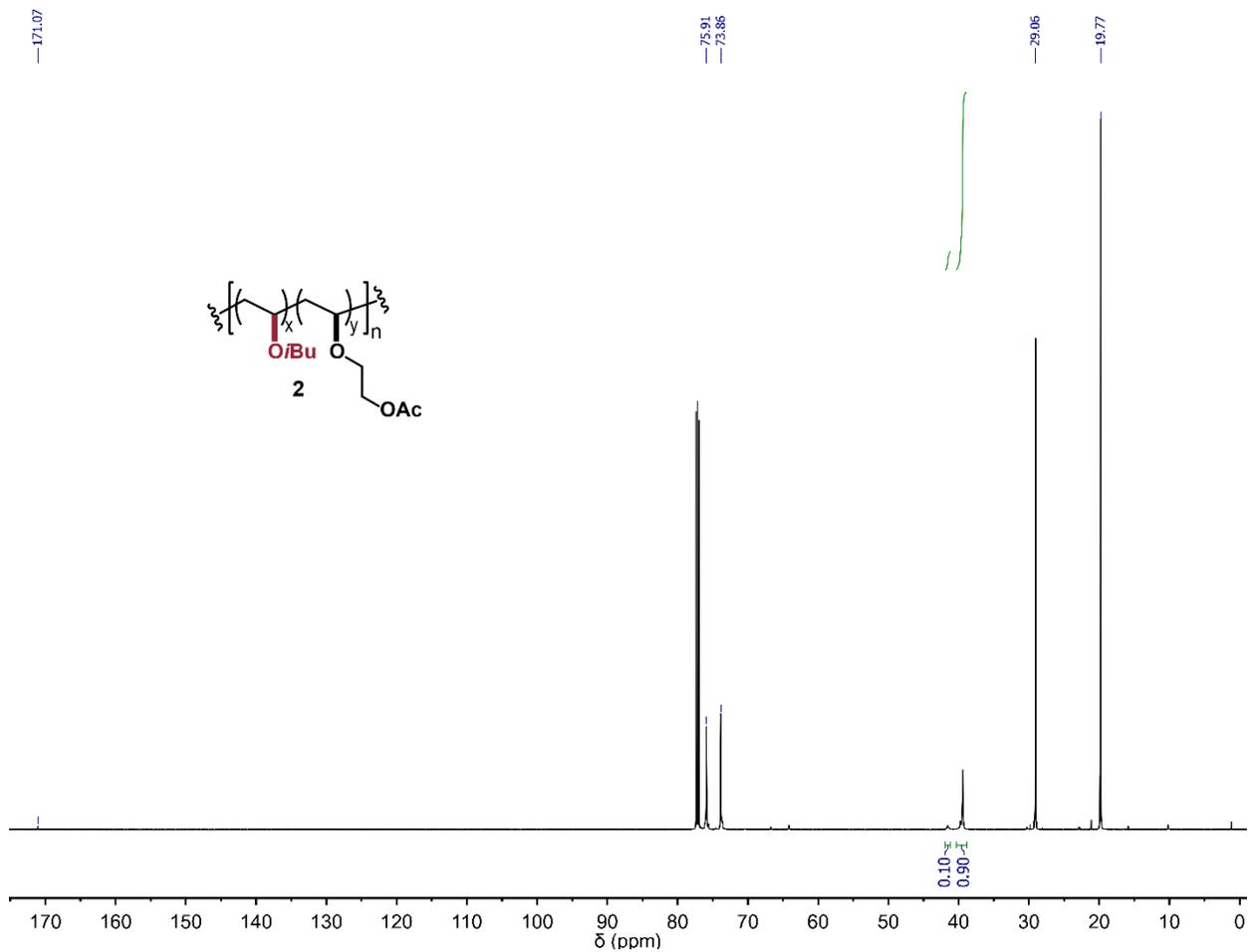
**Figure S13.** Representative example of peak deconvolution using OriginPro 8 to determine the relative consumption of individual vinyl ether monomers. The aryl resonance of the 1,4-dimethoxybenzene internal standard can be seen at  $\delta$  6.8 ppm, while the overlapped vinyl resonances for iBVE and nBVE are between  $\delta$  6.40 – 6.48 ppm (expanded in inset). This example represents a copolymerization of nBVE with iBVE with  $f_{Bu} = 0.50$  that was quenched at 20 min ( $t = 1200$  s). Fitted peaks (green) and peak sum (red) are shown overlaid on the original spectrum (black).



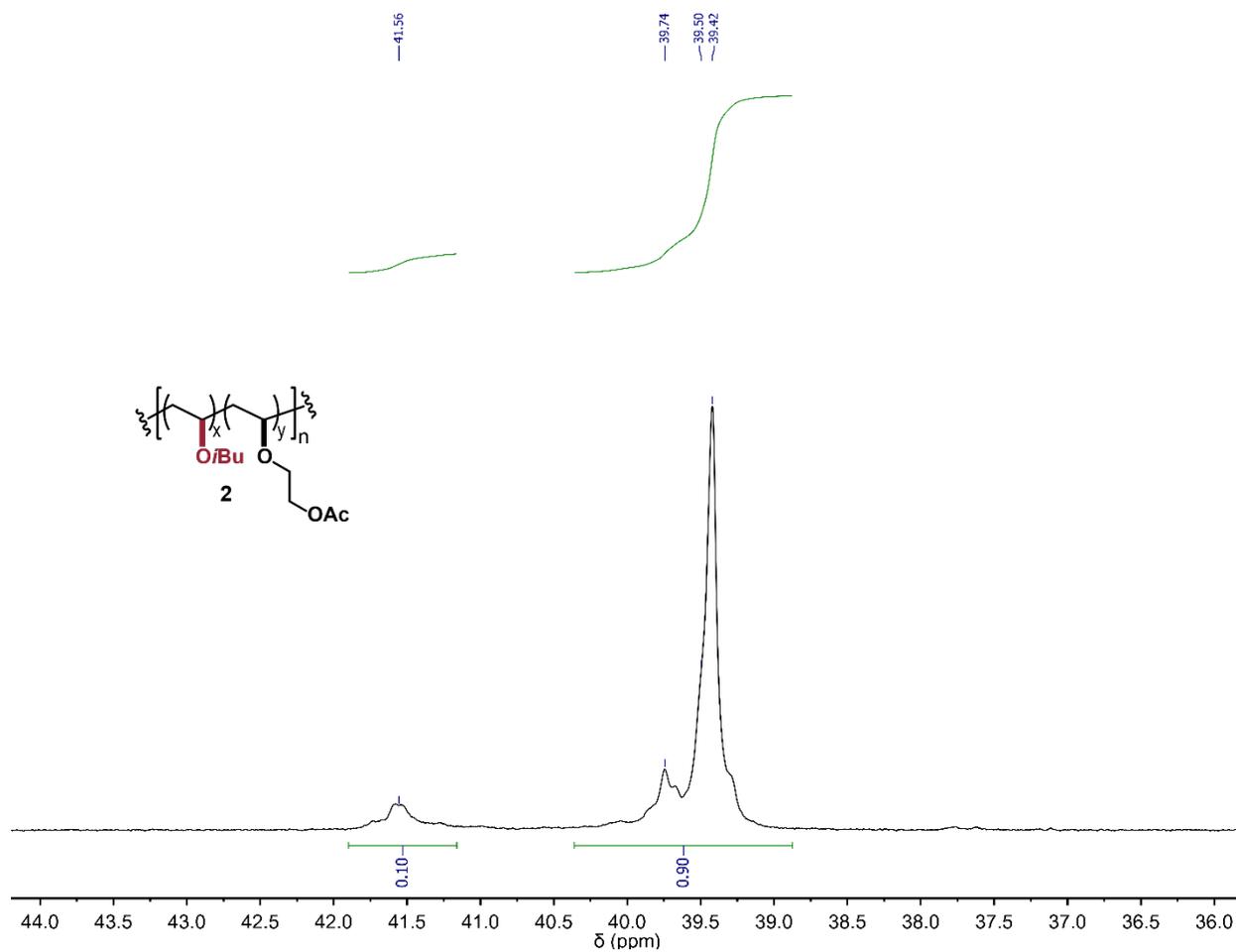
**Figure S14.** Plot of % conversion versus time of the copolymerization ( $f_{Bu} = 0.50$ ) of iBVE and nBVE. Conversions of iBVE (■) and nBVE (●) monitored independently by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ).  $[\text{iBVE}]_0 = 0.19 \text{ M}$ .  $[\text{nBVE}]_0 = 0.19 \text{ M}$



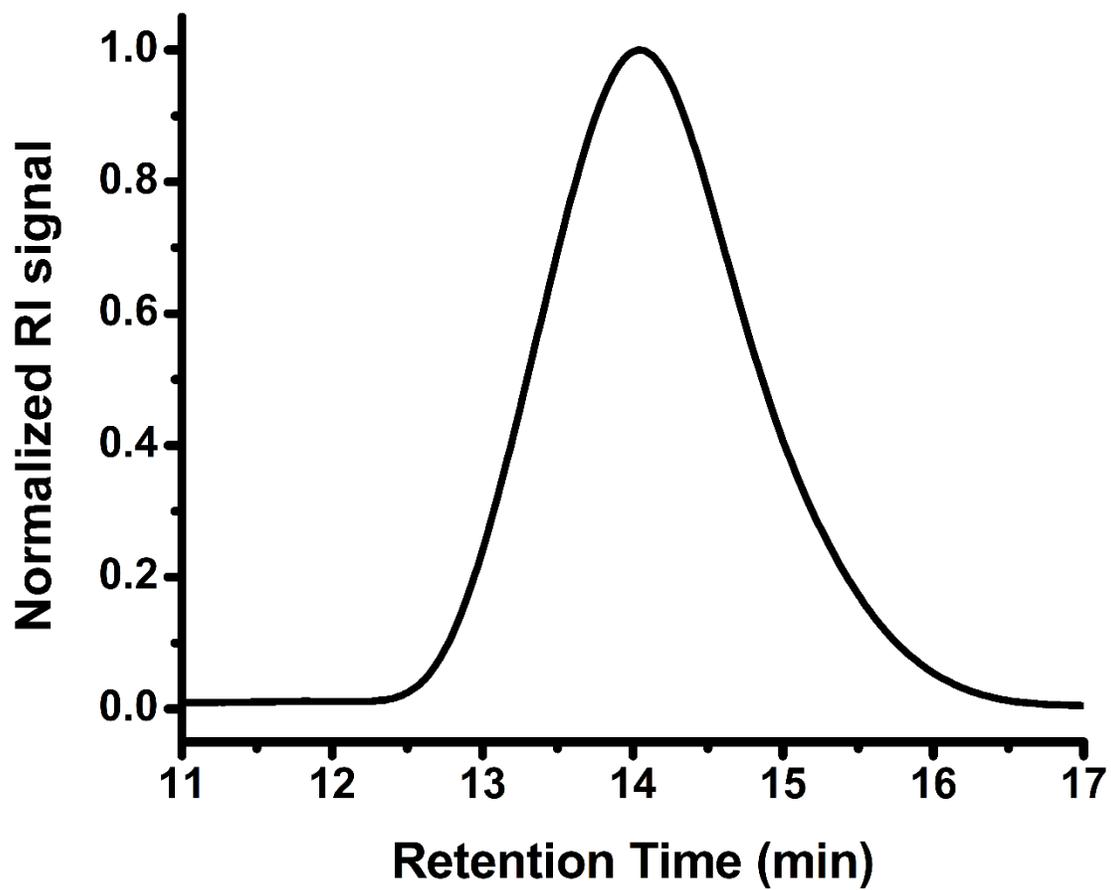
**Figure S15.** Representative <sup>1</sup>H NMR spectrum of isotactic poly(iBVE-co-AcVE). In this example,  $F_{Ac} = 0.07$  (CDCl<sub>3</sub>).



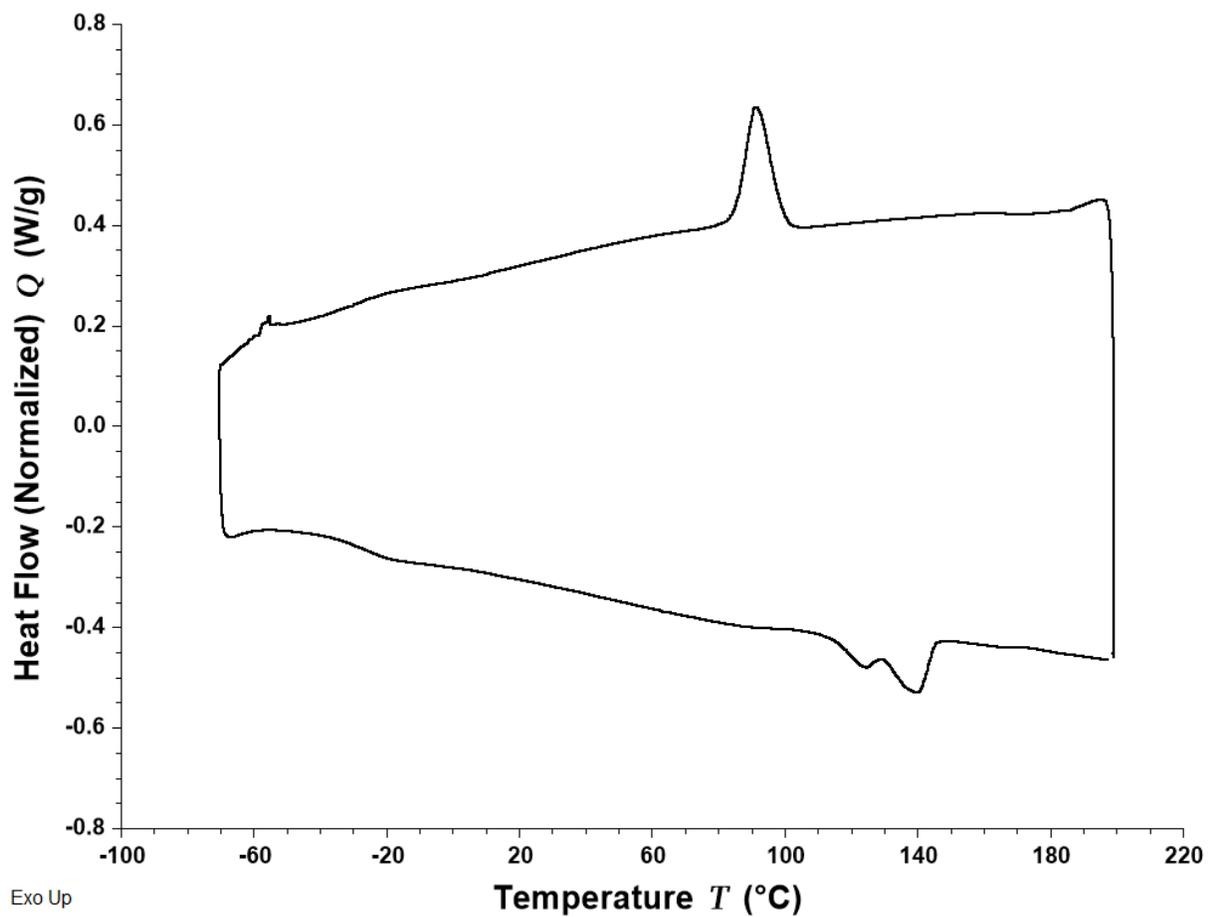
**Figure S16.** Representative  $^{13}\text{C}$  NMR spectrum of isotactic poly(iBVE-co-AcVE) with relative integrations amounting to 90% *meso* diads. In this example,  $F_{\text{Ac}} = 0.02$  ( $\text{CDCl}_3$ ).



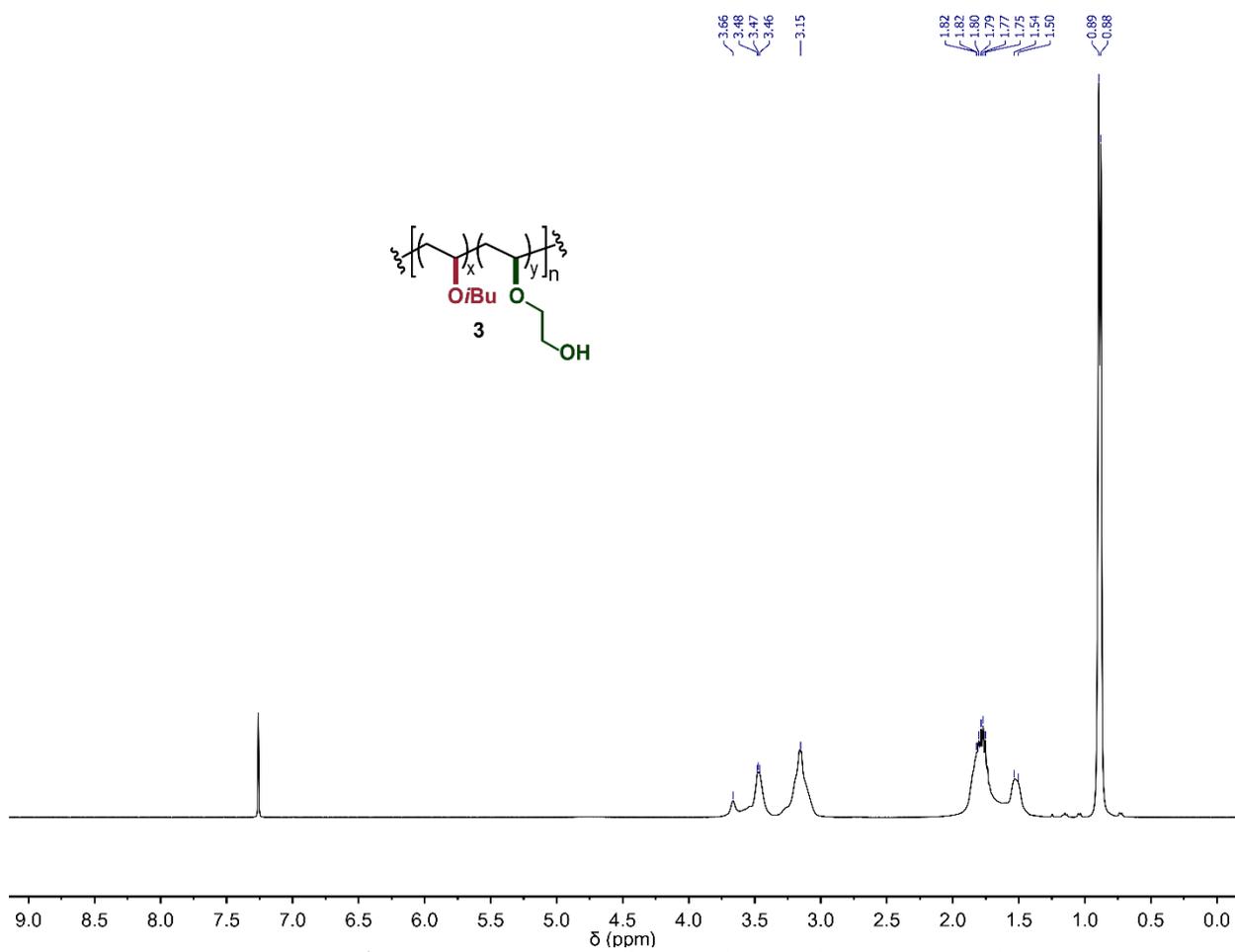
**Figure S17.** Expanded  $^{13}\text{C}$  NMR spectrum of a representative sample of isotactic poly(iBVE-co-AcVE) showing relative integrations amounting to 90% *meso* diads. In this example,  $F_{\text{Ac}} = 0.02$  ( $\text{CDCl}_3$ ).



**Figure S18.** Representative GPC RI trace of isotactic poly(iBVE-co-AcVE). In this example,  $F_{Ac} = 0.07$ .



**Figure S19.** Representative DSC curves for isotactic poly(iBVE-co-AcVE). In this example,  $F_{Ac} = 0.07$ .



**Figure S20.** Representative  $^1\text{H}$  NMR spectrum of isotactic copolymer **3** (CDCl<sub>3</sub>).

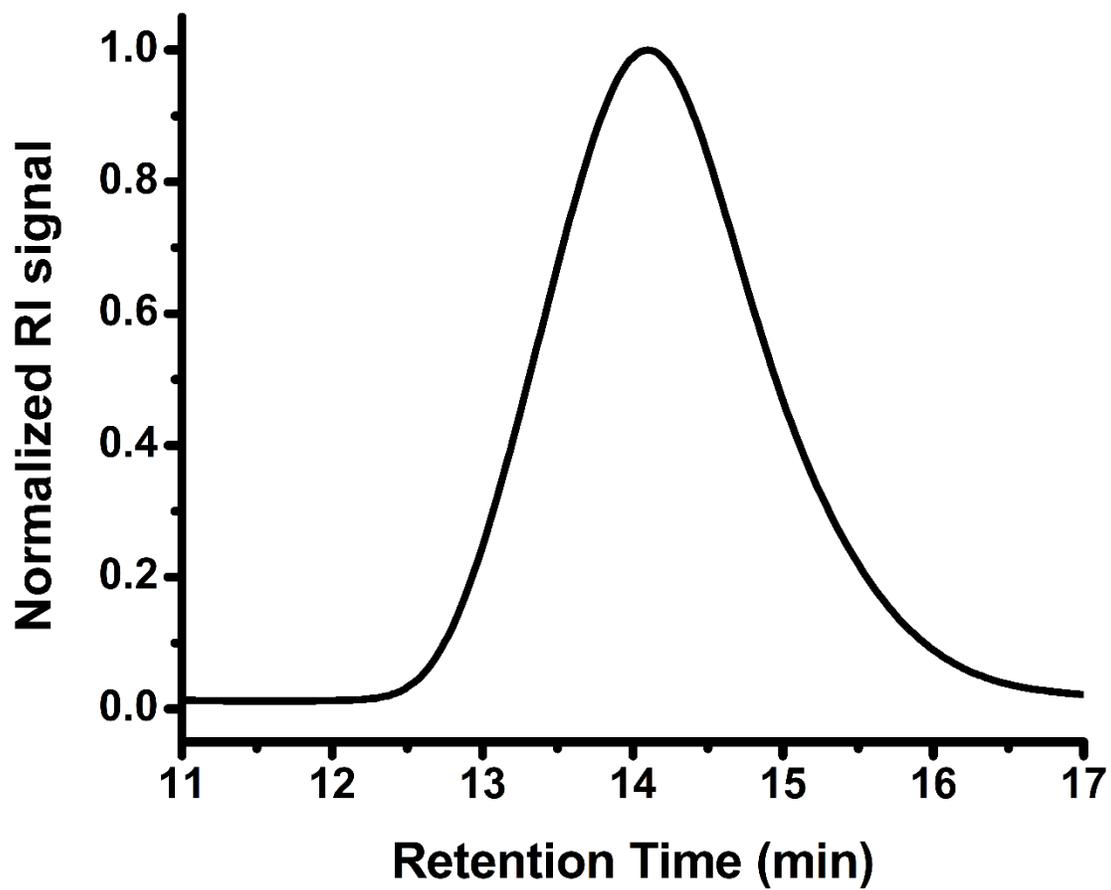
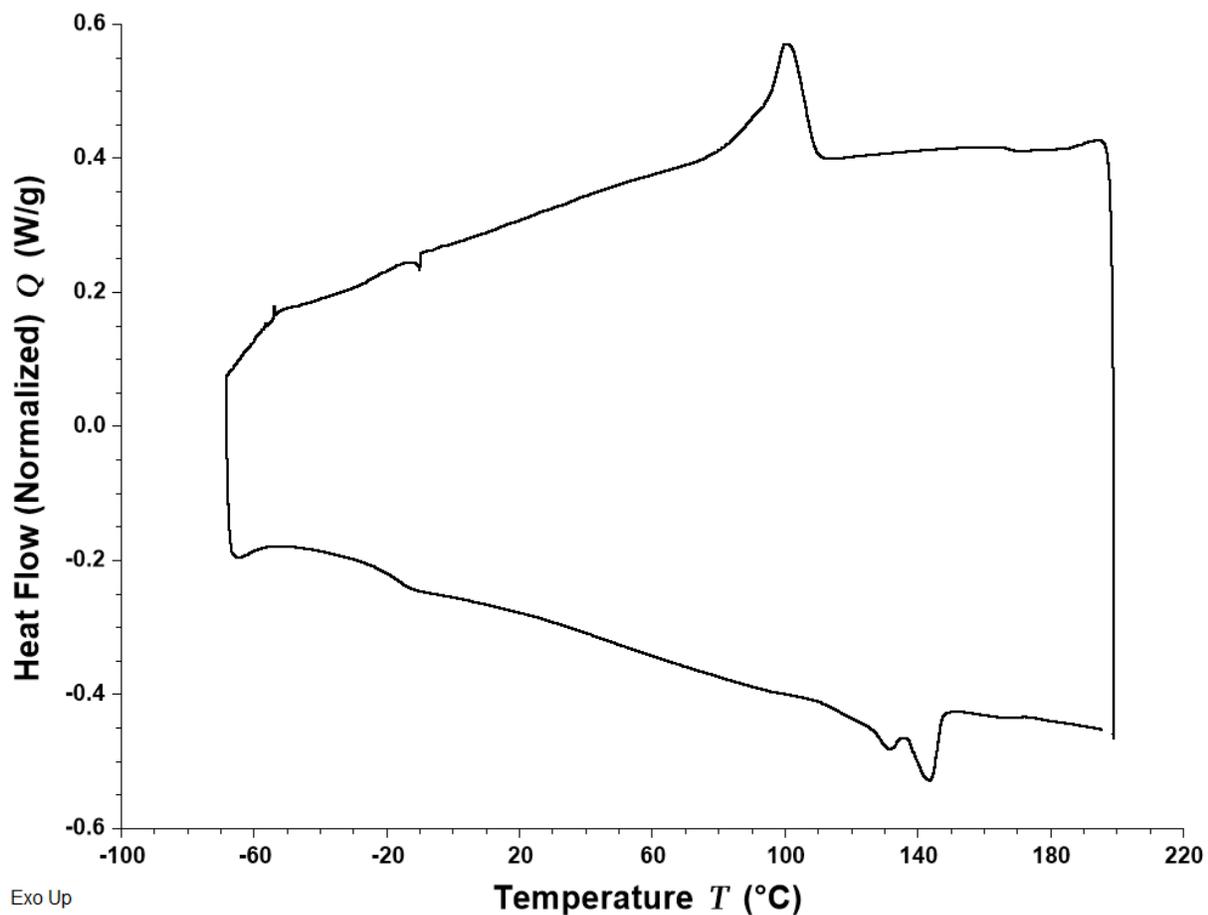
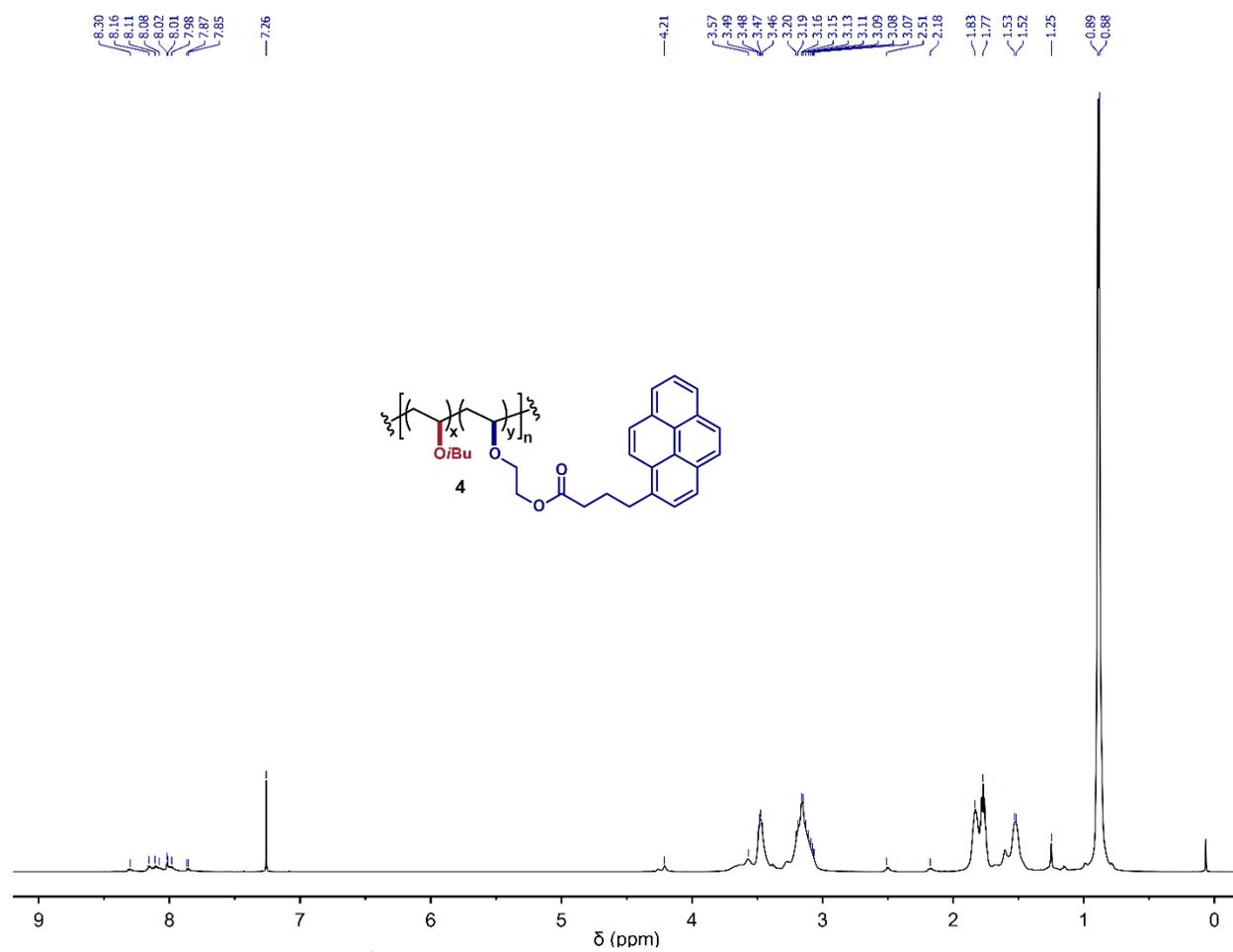


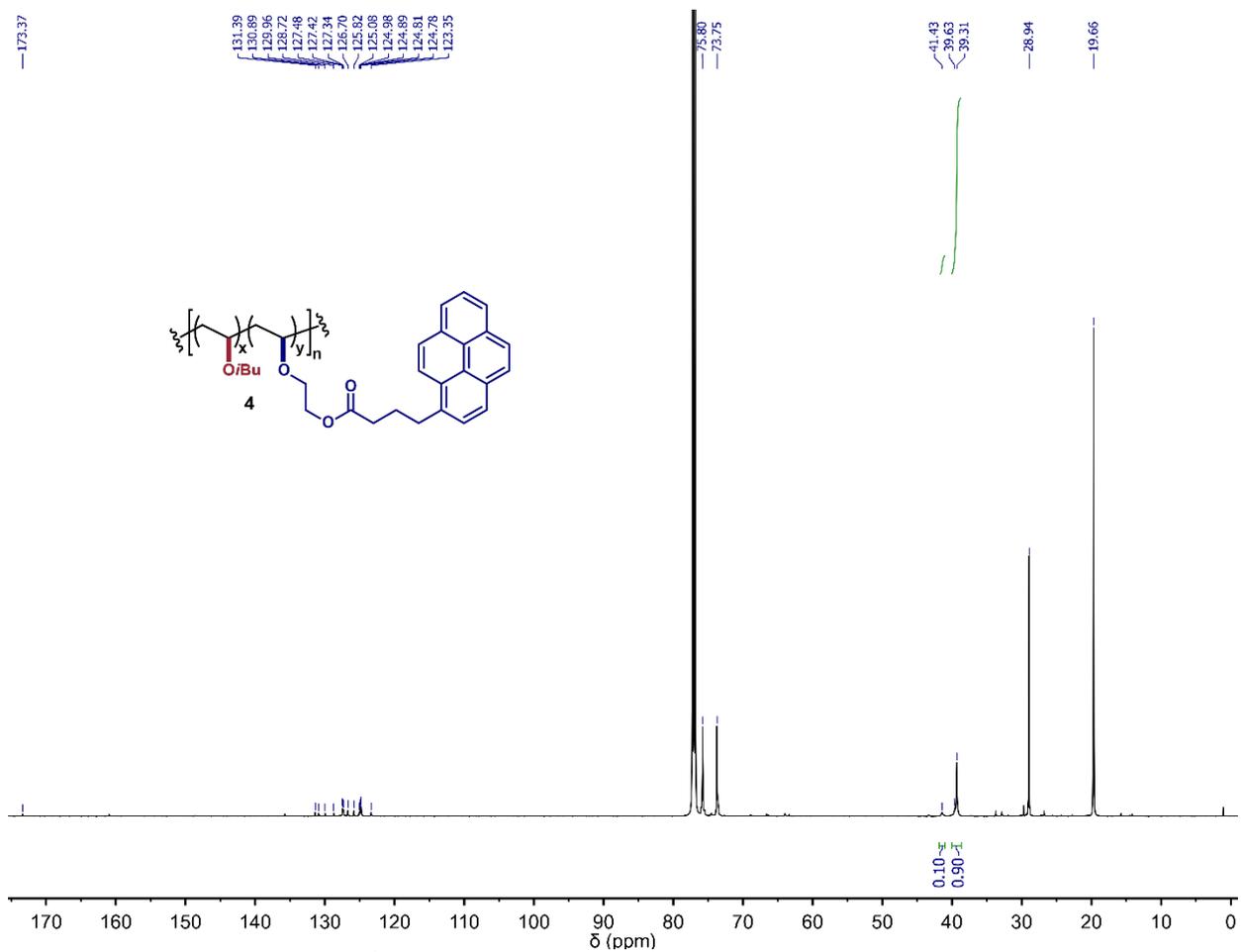
Figure S21. Representative GPC RI trace of isotactic copolymer 3.



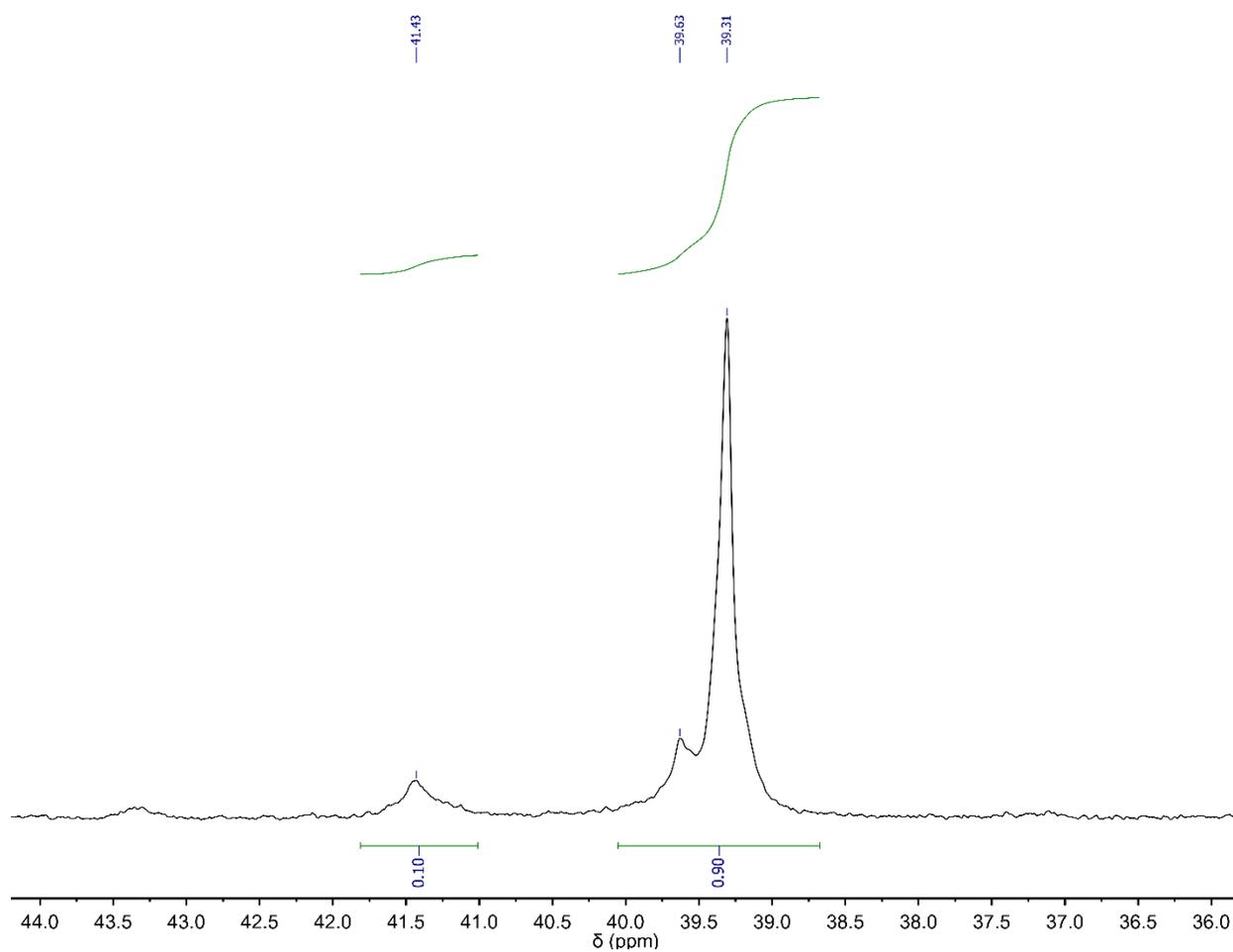
**Figure S22.** Representative DSC curves for isotactic copolymer 3.



**Figure S23.** Representative  $^1\text{H}$  NMR spectrum of isotactic copolymer **4** ( $\text{CDCl}_3$ ).



**Figure S24.** Representative  $^{13}\text{C}$  NMR spectrum of isotactic copolymer **4** with relative integrations amounting to 90% *meso* diads (CDCl<sub>3</sub>).



**Figure S25.** Expanded  $^{13}\text{C}$  NMR spectrum of a representative sample of isotactic copolymer **4** showing relative integrations amounting to 90% *meso* diads ( $\text{CDCl}_3$ ).

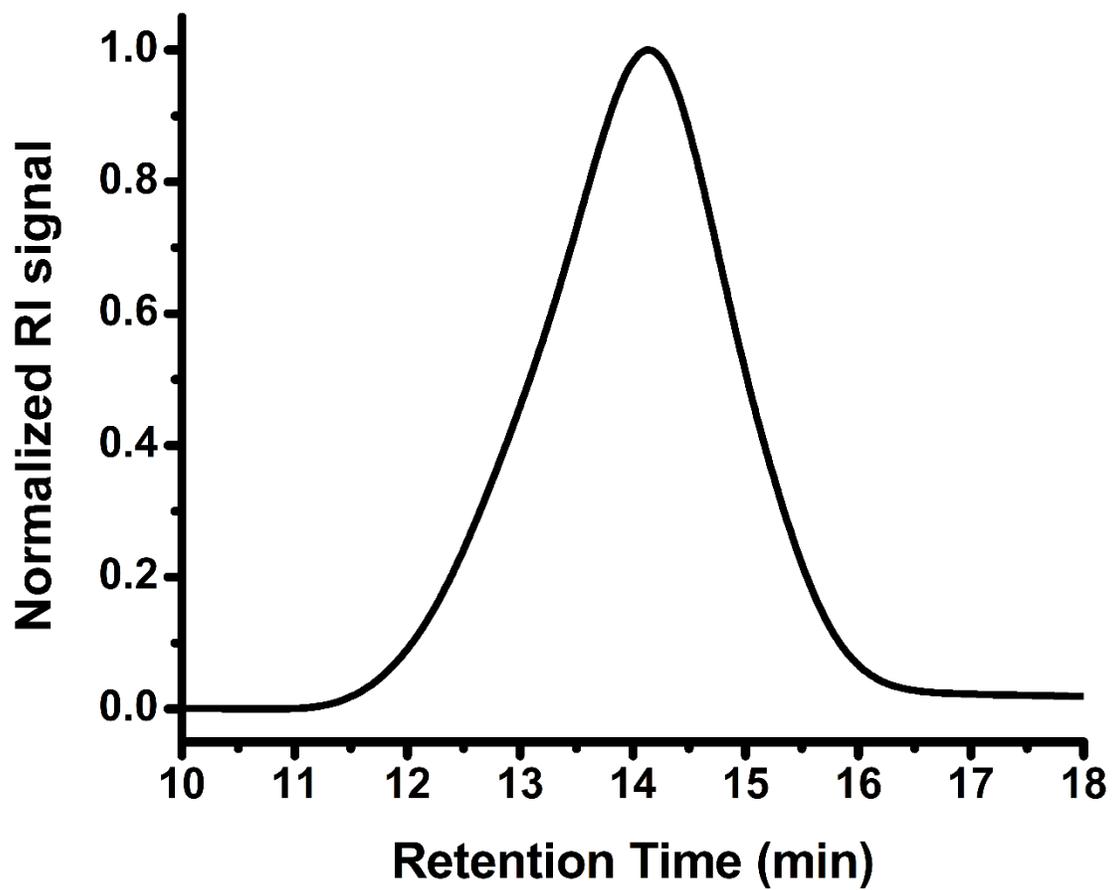
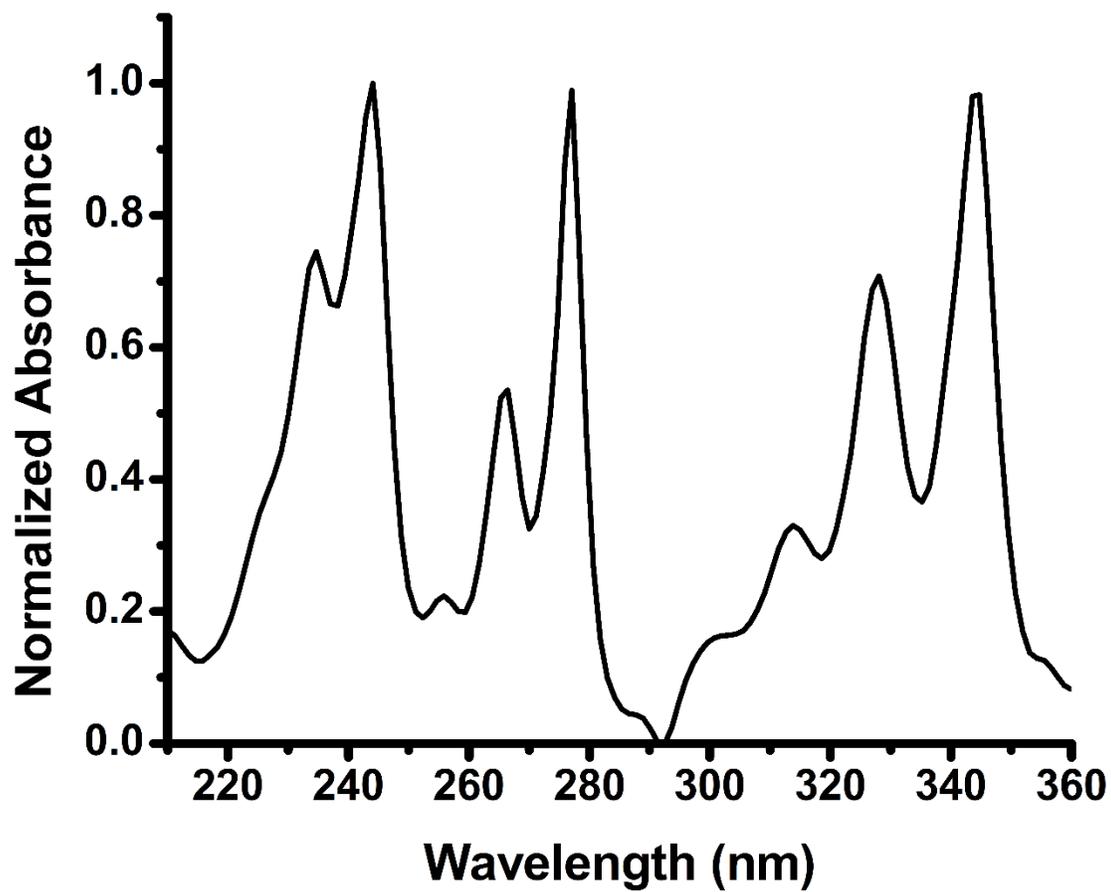
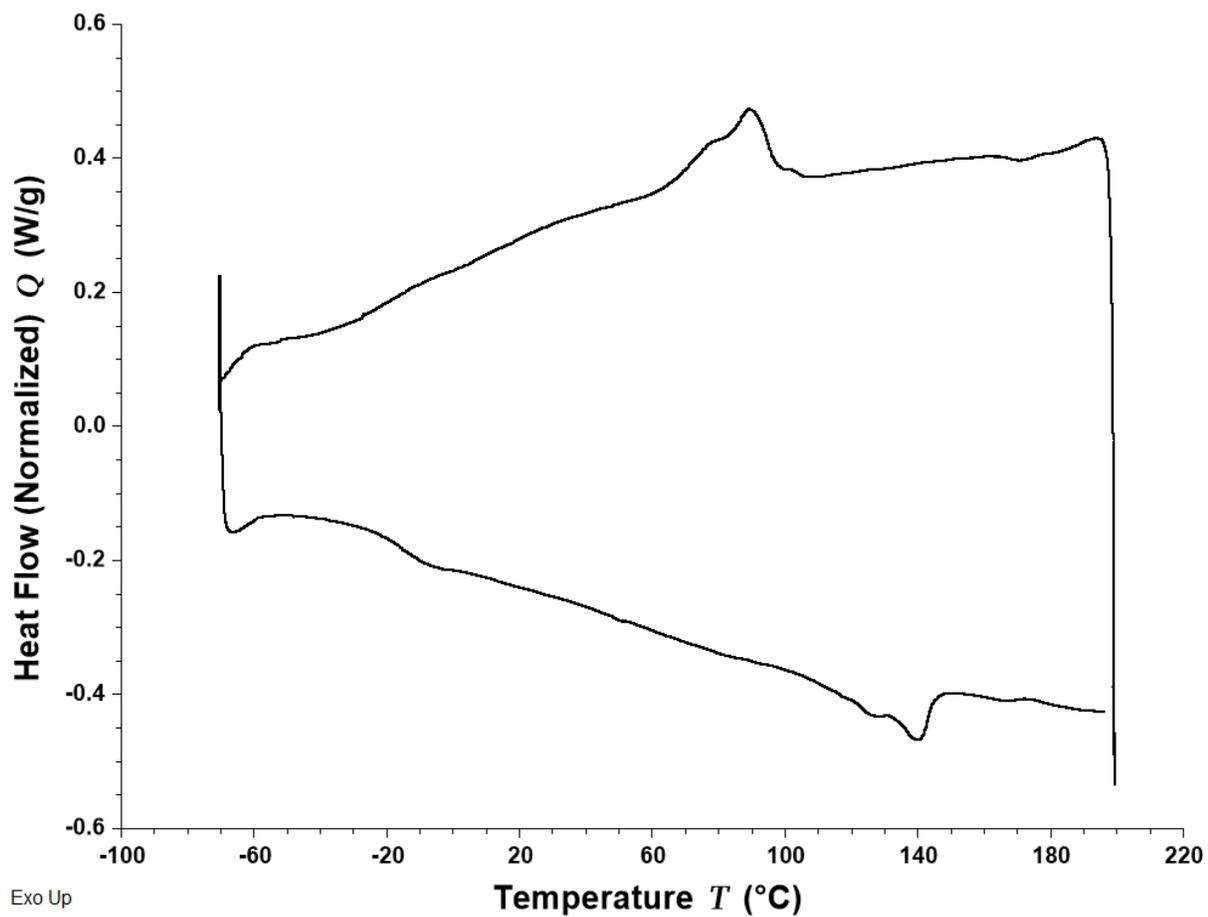


Figure S26. Representative GPC RI trace of isotactic copolymer 4.



**Figure S27.** Representative GPC PDA trace at 344 nm of isotactic copolymer **4**, confirming the presence of pyrene-derived repeat units.



**Figure S28.** Representative DSC curves for isotactic copolymer 4.

#### 4. References

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