

# Vertical orientation of liquid crystal on polystyrene substituted with *n*-alkylbenzoate-*p*-oxymethyl pendant group as a liquid crystal precursor

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## Preparation of *n*-alkylbenzoate-*p*-oxymethyl modified polystyrenes

### 1. P2BO20

The following procedure was used to synthesize P2BO20. A mixture of PCMS (0.300 g, 1.97 mmol), ethyl-*p*-hydroxybenzoate (0.065 g, 0.39 mmol, 20 mol% compared with PCMS), and potassium carbonate (0.065 g, 0.47 mmol, 120 mol% compared with ethyl-*p*-hydroxybenzoate used substituent) in DMAc (50 mL) was heated to 70 °C and magnetically stirred at 200 rpm under a nitrogen atmosphere. The substitution reaction lasted for 24 h. Thereafter, the solution mixture was cooled to room temperature and poured into methanol to obtain a white precipitate. The precipitate was further purified by several reprecipitations from DMAc solution into methanol, and then a Soxhlet extractor was used to remove potassium carbonate and the remaining salts with boiling methanol. P2BO20 was obtained in > 80% yield after drying under vacuum overnight.

<sup>1</sup>H NMR of P2BO20 (400 MHz, CDCl<sub>3</sub>, δ/ppm): δ = 0.74–2.45 (–CH<sub>2</sub>–CH–Ph–CH<sub>2</sub>–Cl, –CH<sub>2</sub>–CH–Ph–CH<sub>2</sub>–O–, –COO–CH<sub>2</sub>–CH<sub>3</sub>, 9H), δ = 4.18–4.41 (–Ph–COO–CH<sub>2</sub>–CH<sub>3</sub>, 2H), δ = 4.42–4.76 (–Ph–CH<sub>2</sub>–Cl, 2H), δ = 4.72–5.12 (–Ph–CH<sub>2</sub>–O–Ph–, 2H), δ = 6.00–8.20 (–CH<sub>2</sub>–CH–PhH–CH<sub>2</sub>–Cl, –CH<sub>2</sub>–CH–PhH–CH<sub>2</sub>–O–PhH–COO–, 12H).

### 2. P2BO40

The following procedure was used to synthesize P2BO40. A mixture of PCMS (0.300 g, 1.97 mmol), ethyl-*p*-hydroxybenzoate (0.131 g, 0.79 mmol, 40 mol% compared with PCMS), and potassium carbonate (0.131 g, 0.95 mmol, 120 mol% compared with ethyl-*p*-hydroxybenzoate used substituent) in DMAc (50 mL) was heated to 70 °C and magnetically stirred at 200 rpm under a nitrogen atmosphere. The substitution reaction lasted for 24 h. Thereafter, the solution mixture was cooled to room temperature and poured into methanol to obtain a white precipitate. The precipitate was further purified by several reprecipitations from DMAc solution into methanol, and then a Soxhlet extractor was used to remove potassium carbonate and the remaining salts with boiling methanol. P2BO40 was obtained in > 80% yield after drying under vacuum overnight.

<sup>1</sup>H NMR of P2BO40 (400 MHz, CDCl<sub>3</sub>, δ/ppm): δ = 0.66–2.60 (–CH<sub>2</sub>–CH–Ph–CH<sub>2</sub>–Cl, –CH<sub>2</sub>–CH–Ph–CH<sub>2</sub>–O–, –COO–CH<sub>2</sub>–CH<sub>3</sub>, 9H), δ = 4.08–4.39 (–Ph–COO–CH<sub>2</sub>–CH<sub>3</sub>, 2H), δ = 4.62–4.73 (–Ph–CH<sub>2</sub>–Cl, 2H), δ = 4.73–5.33 (–Ph–CH<sub>2</sub>–O–Ph–, 2H), δ = 6.02–8.16 (–CH<sub>2</sub>–CH–PhH–CH<sub>2</sub>–Cl, –CH<sub>2</sub>–CH–PhH–CH<sub>2</sub>–O–PhH–COO–, 12H).

### 3. P2BO60

The following procedure was used to synthesize P2BO60. A mixture of PCMS (0.300 g, 1.97 mmol), ethyl-*p*-hydroxybenzoate (0.196 g, 1.18 mmol, 60 mol% compared with PCMS), and potassium carbonate (0.196 g, 1.42 mmol, 120 mol% compared with ethyl-*p*-hydroxybenzoate used substituent) in DMAc (50 mL) was heated to 70 °C and magnetically stirred at 200 rpm under a nitrogen atmosphere. The substitution reaction lasted for 24 h. Thereafter, the solution mixture was cooled to room temperature and poured into methanol to obtain a white precipitate. The precipitate was further purified by several reprecipitations from DMAc solution into methanol, and then a Soxhlet extractor was used to remove potassium carbonate and the remaining salts with boiling methanol. P2BO60 was obtained in > 80% yield after drying under vacuum overnight.

<sup>1</sup>H NMR of P2BO60 (400 MHz, CDCl<sub>3</sub>, δ/ppm): δ = 0.71–2.59 (–CH<sub>2</sub>–CH–Ph–CH<sub>2</sub>–Cl, –CH<sub>2</sub>–CH–Ph–CH<sub>2</sub>–O–, –COO–CH<sub>2</sub>–CH<sub>3</sub>, 9H), δ = 4.18–4.39 (–Ph–COO–CH<sub>2</sub>–CH<sub>3</sub>, 2H), δ = 4.41–4.61 (–Ph–CH<sub>2</sub>–Cl, 2H), δ = 4.73–5.14 (–Ph–CH<sub>2</sub>–O–Ph–, 2H), δ = 6.03–8.07 (–CH<sub>2</sub>–CH–*PhH*–CH<sub>2</sub>–Cl, –CH<sub>2</sub>–CH–*PhH*–CH<sub>2</sub>–O–*PhH*–COO–, 12H).

#### 4. P2BO80

The following procedure was used to synthesize P2BO80. A mixture of PCMS (0.300 g, 1.97 mmol), ethyl-*p*-hydroxybenzoate (0.263 g, 1.58 mmol, 80 mol% compared with PCMS), and potassium carbonate (0.262 g, 1.90 mmol, 120 mol% compared with ethyl-*p*-hydroxybenzoate used substituent) in DMAc (50 mL) was heated to 70 °C and magnetically stirred at 200 rpm under a nitrogen atmosphere. The substitution reaction lasted for 24 h. Thereafter, the solution mixture was cooled to room temperature and poured into methanol to obtain a white precipitate. The precipitate was further purified by several reprecipitations from DMAc solution into methanol, and then a Soxhlet extractor was used to remove potassium carbonate and the remaining salts with boiling methanol. P2BO80 was obtained in > 80% yield after drying under vacuum overnight.

<sup>1</sup>H NMR of P2BO80 (400 MHz, CDCl<sub>3</sub>, δ/ppm): δ = 0.71–2.55 (–CH<sub>2</sub>–CH–Ph–CH<sub>2</sub>–Cl, –CH<sub>2</sub>–CH–Ph–CH<sub>2</sub>–O–, –COO–CH<sub>2</sub>–CH<sub>3</sub>, 9H), δ = 4.20–4.40 (–Ph–COO–CH<sub>2</sub>–CH<sub>3</sub>, 2H), δ = 4.42–4.64 (–Ph–CH<sub>2</sub>–Cl, 2H), δ = 4.70–5.17 (–Ph–CH<sub>2</sub>–O–Ph–, 2H), δ = 6.09–8.16 (–CH<sub>2</sub>–CH–*PhH*–CH<sub>2</sub>–Cl, –CH<sub>2</sub>–CH–*PhH*–CH<sub>2</sub>–O–*PhH*–COO–, 12H).

#### 5. P4BO

The following procedure was used to synthesize P4BO. A mixture of PCMS (0.300 g, 1.97 mmol), *n*-butyl-*p*-hydroxybenzoate (0.575 g, 2.96 mmol, 150 mol% compared with PCMS), and potassium carbonate (0.491 g, 3.55 mmol, 120 mol% compared with *n*-butyl-*p*-hydroxybenzoate used substituent) in DMAc (50 mL) was heated to 70 °C and magnetically stirred at 200 rpm under a nitrogen atmosphere. The substitution reaction lasted for 24 h. Thereafter, the solution mixture was cooled to room temperature and poured into methanol to obtain a white precipitate. The precipitate was further purified by several reprecipitations from DMAc solution into methanol, and then a Soxhlet extractor was used to remove potassium carbonate and the remaining salts with boiling methanol. P4BO was obtained in > 80% yield after drying under vacuum overnight.

<sup>1</sup>H NMR of P4BO (400 MHz, CDCl<sub>3</sub>, δ/ppm): δ = 0.86–1.81 (–CH<sub>2</sub>–CH–Ph–CH<sub>2</sub>–, –COO–CH<sub>2</sub>–(CH<sub>2</sub>)<sub>2</sub>–CH<sub>3</sub>, 10H), δ = 4.17–4.39 (–Ph–COO–

$\text{CH}_2\text{-CH}_2\text{-}$ , 2H),  $\delta = 4.70\text{--}5.06$  ( $\text{-Ph-CH}_2\text{-O-Ph-}$ , 2H),  $\delta = 6.09\text{--}8.11$  ( $\text{-CH}_2\text{-CH-PhH-CH}_2\text{-O-PhH-COO-}$ , 8H).

#### 6. P6BO

The following procedure was used to synthesize P6BO. A mixture of PCMS (0.300 g, 1.97 mmol), *n*-hexyl-*p*-hydroxybenzoate (0.658 g, 2.96 mmol, 150 mol% compared with PCMS), and potassium carbonate (0.491 g, 3.55 mmol, 120 mol% compared with *n*-hexyl-*p*-hydroxybenzoate used substituent) in DMAc (50 mL) was heated to 70 °C and magnetically stirred at 200 rpm under a nitrogen atmosphere. The substitution reaction lasted for 24 h. Thereafter, the solution mixture was cooled to room temperature and poured into methanol to obtain a white precipitate. The precipitate was further purified by several reprecipitations from DMAc solution into methanol, and then a Soxhlet extractor was used to remove potassium carbonate and the remaining salts with boiling methanol. P6BO was obtained in > 80% yield after drying under vacuum overnight.

$^1\text{H}$  NMR of P6BO (400 MHz,  $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ):  $\delta = 0.76\text{--}1.87$  ( $\text{-CH}_2\text{-CH-Ph-CH}_2\text{-}$ ,  $\text{-COO-CH}_2\text{-(CH}_2\text{)}_6\text{-CH}_3$ , 14H),  $\delta = 4.12\text{--}4.34$  ( $\text{-Ph-COO-CH}_2\text{-CH}_2\text{-}$ , 2H),  $\delta = 4.67\text{--}5.06$  ( $\text{-Ph-CH}_2\text{-O-Ph-}$ , 2H),  $\delta = 5.99\text{--}8.14$  ( $\text{-CH}_2\text{-CH-PhH-CH}_2\text{-O-PhH-COO-}$ , 8H).

#### 7. P8BO

The following procedure was used to synthesize P8BO. A mixture of PCMS (0.300 g, 1.97 mmol), *n*-octyl-*p*-hydroxybenzoate (0.741 g, 2.96 mmol, 150 mol% compared with PCMS), and potassium carbonate (0.491 g, 3.55 mmol, 120 mol% compared with *n*-octyl-*p*-hydroxybenzoate used substituent) in DMAc (50 mL) was heated to 70 °C and magnetically stirred at 200 rpm under a nitrogen atmosphere. The substitution reaction lasted for 24 h. Thereafter, the solution mixture was cooled to room temperature and poured into methanol to obtain a white precipitate. The precipitate was further purified by several reprecipitations from DMAc solution into methanol, and then a Soxhlet extractor was used to remove potassium carbonate and the remaining salts with boiling methanol. P8BO was obtained in > 80% yield after drying under vacuum overnight.

$^1\text{H}$  NMR of P8BO (400 MHz,  $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ):  $\delta = 0.77\text{--}1.78$  ( $\text{-CH}_2\text{-CH-Ph-CH}_2\text{-}$ ,  $\text{-COO-CH}_2\text{-(CH}_2\text{)}_8\text{-CH}_3$ , 18H),  $\delta = 4.16\text{--}4.33$  ( $\text{-Ph-COO-CH}_2\text{-CH}_2\text{-}$ , 2H),  $\delta = 4.74\text{--}5.03$  ( $\text{-Ph-CH}_2\text{-O-Ph-}$ , 2H),  $\delta = 5.95\text{--}8.18$  ( $\text{-CH}_2\text{-CH-PhH-CH}_2\text{-O-PhH-COO-}$ , 8H).

### Figure captions

**Figure S1.**  $^1\text{H}$  nuclear magnetic resonance (NMR) spectrum of PCMS.

**Figure S2.**  $^1\text{H}$  nuclear magnetic resonance (NMR) spectrum of P2BO20.

**Figure S3.**  $^1\text{H}$  nuclear magnetic resonance (NMR) spectrum of P2BO40.

**Figure S4.**  $^1\text{H}$  nuclear magnetic resonance (NMR) spectrum of P2BO60.

**Figure S5.**  $^1\text{H}$  nuclear magnetic resonance (NMR) spectrum of P2BO80.

**Figure S6.**  $^1\text{H}$  nuclear magnetic resonance (NMR) spectrum of P4BO.

**Figure S7.**  $^1\text{H}$  nuclear magnetic resonance (NMR) spectrum of P6BO.

**Figure S8.**  $^1\text{H}$  nuclear magnetic resonance (NMR) spectrum of P8BO.

**Figure S9.**  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectrum of PCMS.

**Figure S10.**  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectrum of P2BO20.

**Figure S11.**  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectrum of P2BO40.

**Figure S12.**  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectrum of P2BO60.

**Figure S13.**  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectrum of P2BO80.

**Figure S14.**  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectrum of P2BO.

**Figure S15.**  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectrum of P4BO.

**Figure S16.**  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectrum of P6BO.

**Figure S17.**  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectrum of P8BO.

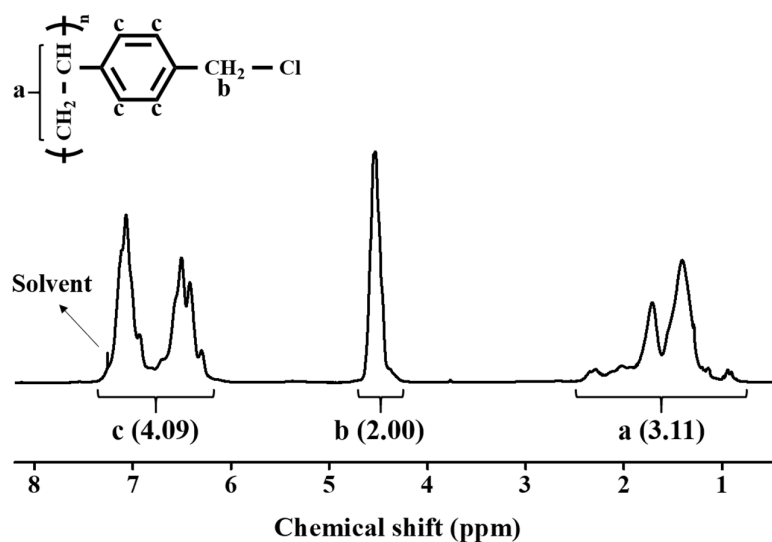


Figure S1.  $^1\text{H}$  nuclear magnetic resonance (NMR) spectrum of PCMS.

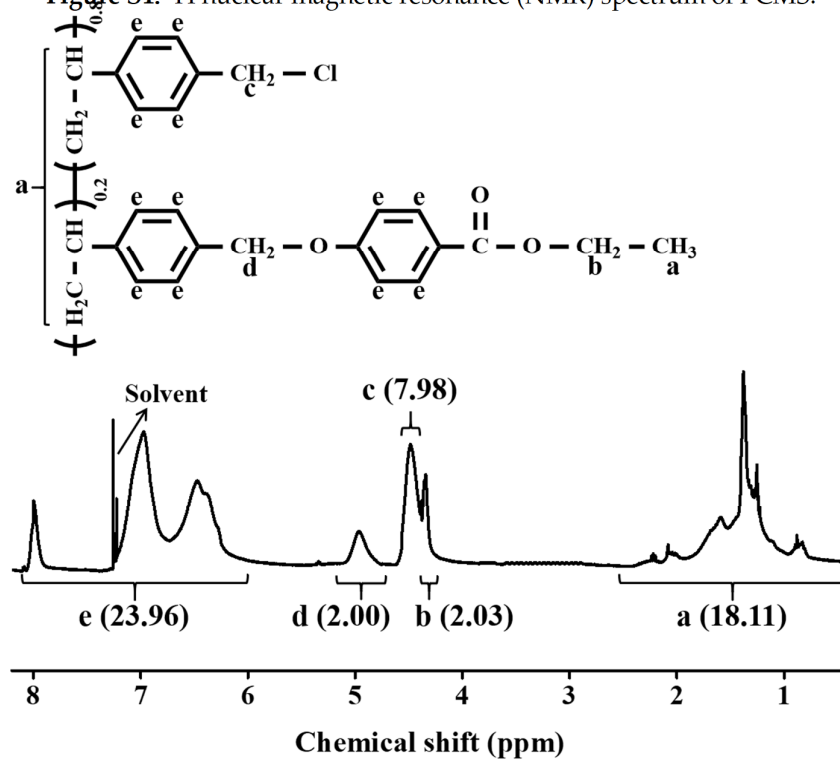


Figure S2.  $^1\text{H}$  nuclear magnetic resonance (NMR) spectrum of P2BO20.

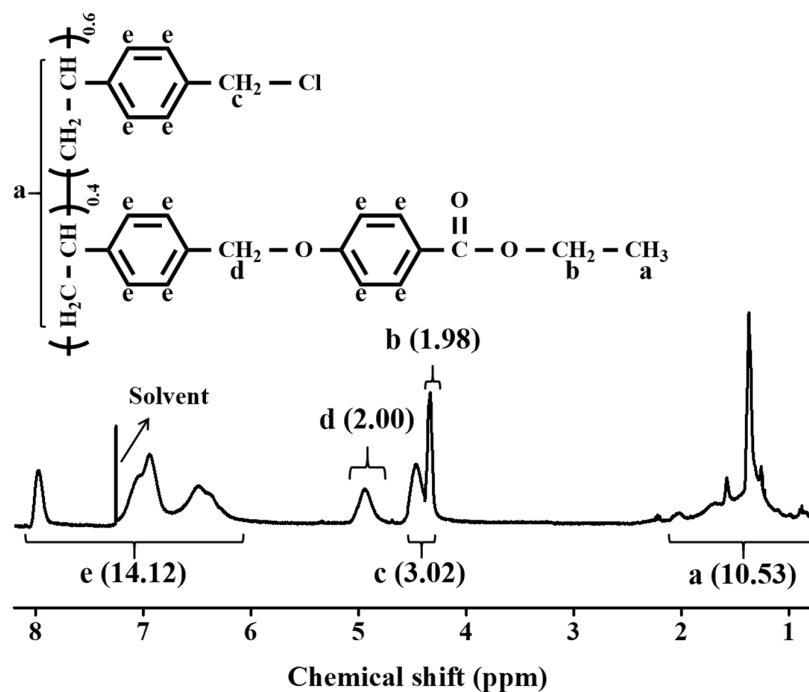


Figure S3.  $^1\text{H}$  nuclear magnetic resonance (NMR) spectrum of P2BO40.

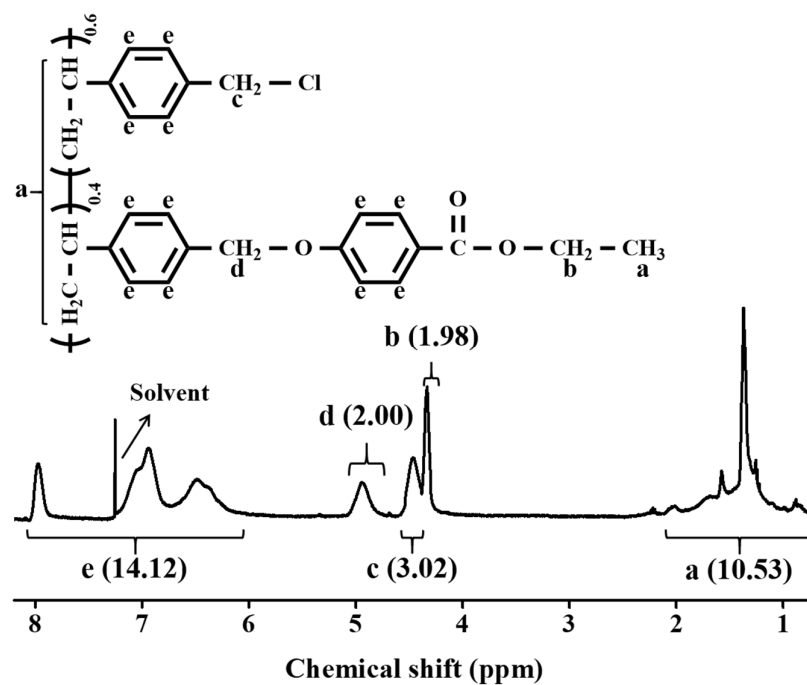


Figure S4. <sup>1</sup>H nuclear magnetic resonance (NMR) spectrum of P2BO60.

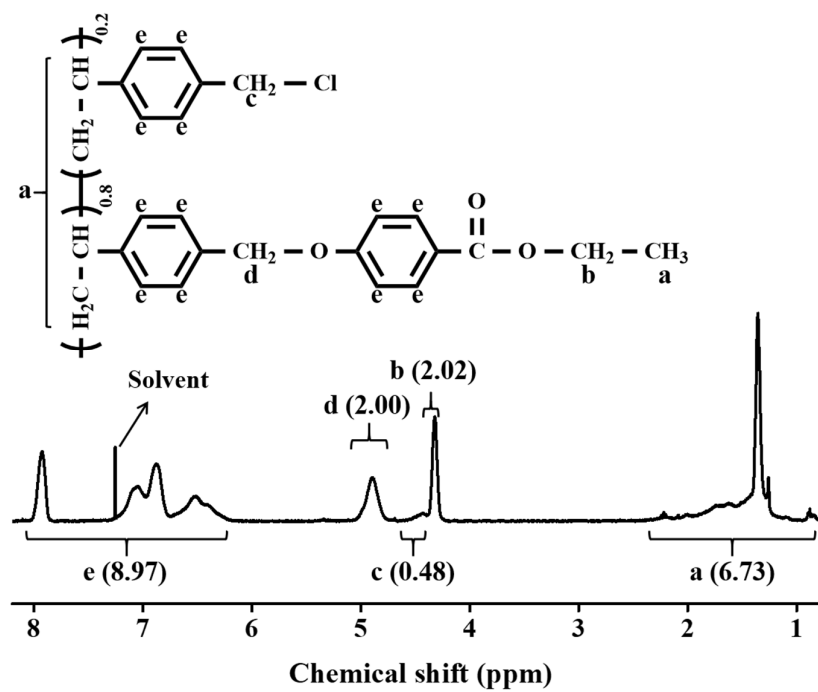


Figure S5. <sup>1</sup>H nuclear magnetic resonance (NMR) spectrum of P2BO80.

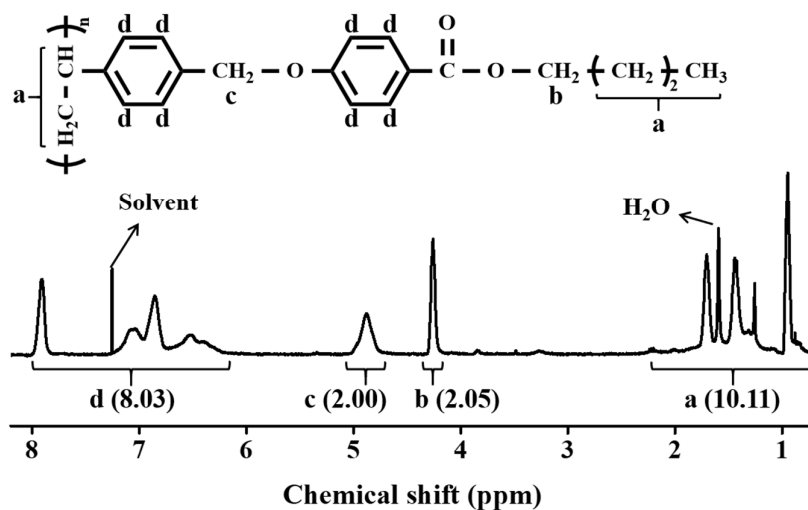


Figure S6.  $^1\text{H}$  nuclear magnetic resonance (NMR) spectrum of P4BO.

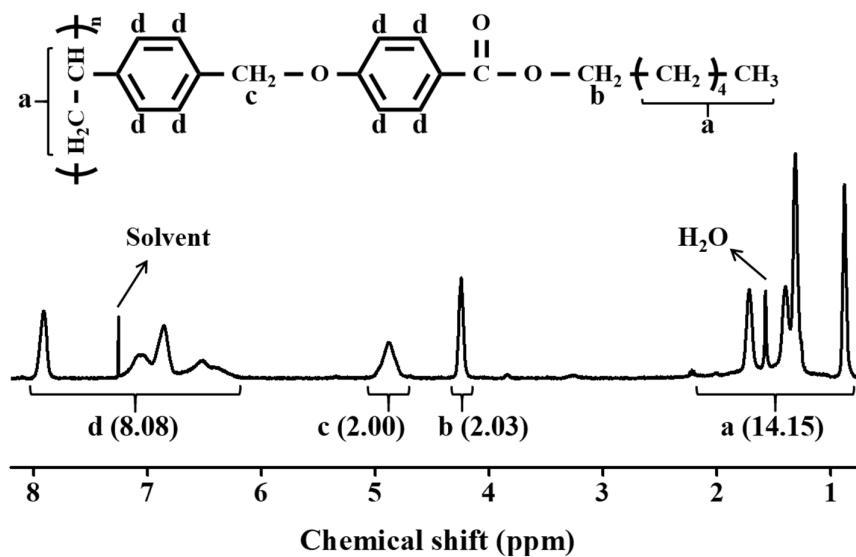


Figure S7.  $^1\text{H}$  nuclear magnetic resonance (NMR) spectrum of P6BO.

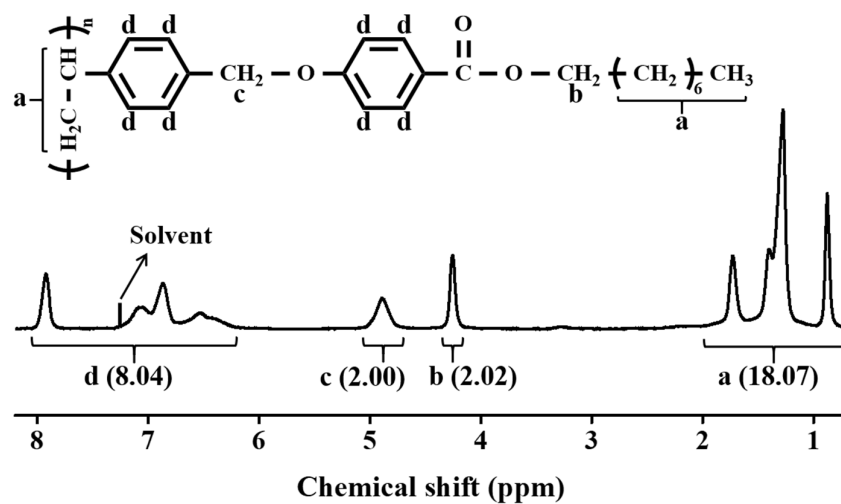


Figure S8.  $^1\text{H}$  nuclear magnetic resonance (NMR) spectrum of P8BO.

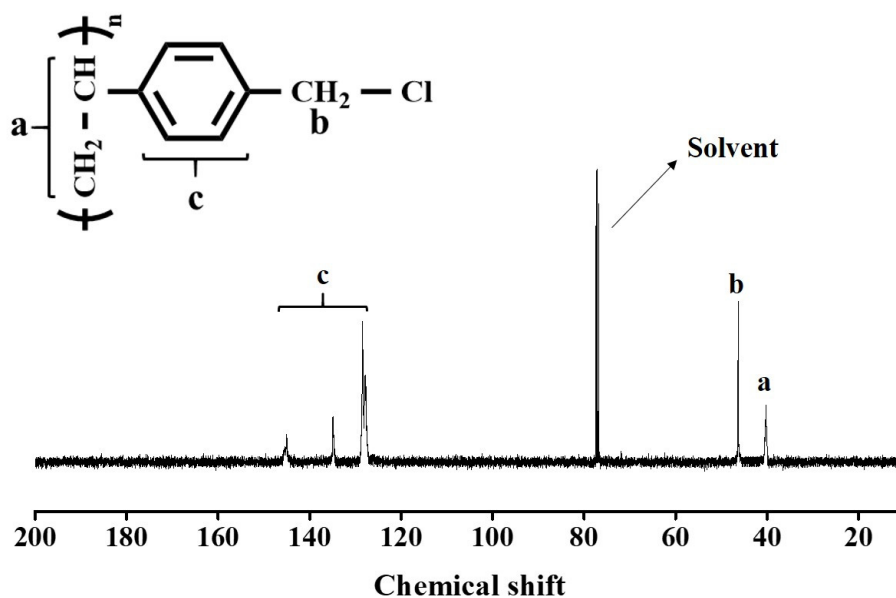


Figure S9.  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectrum of PCMS.



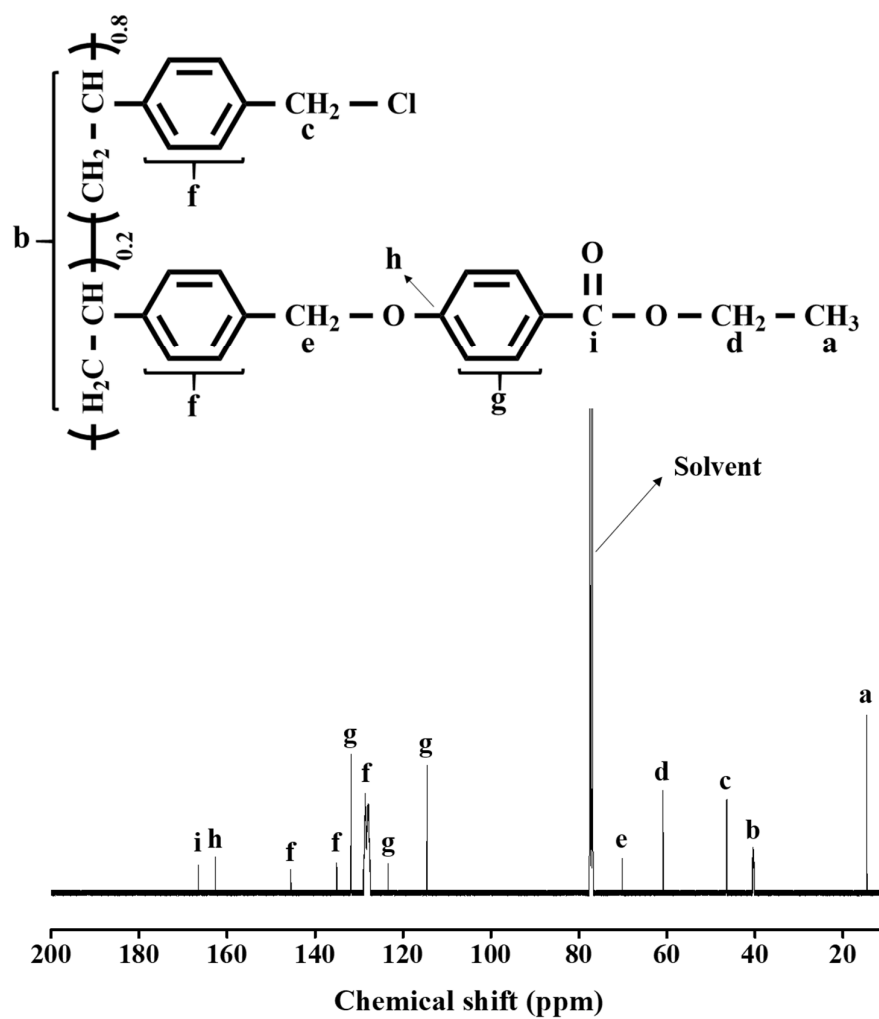


Figure S10.  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectrum of P2BO20.

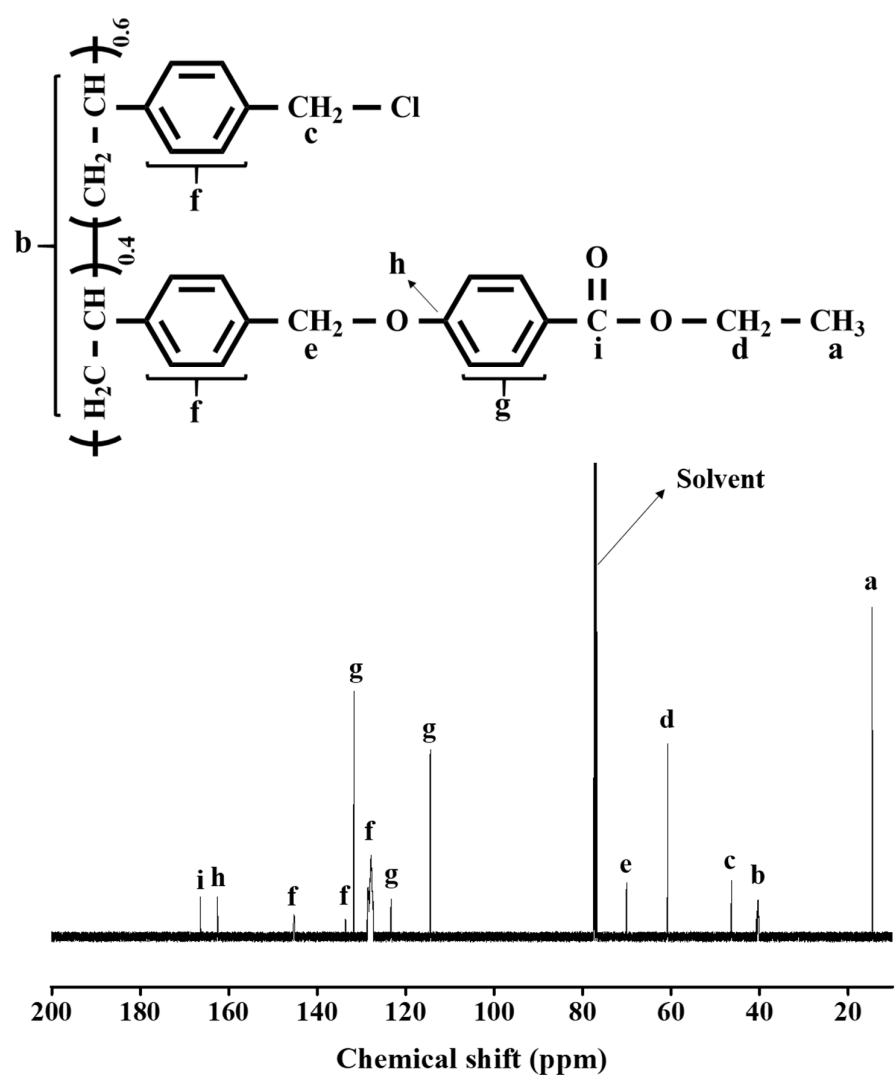


Figure S11. <sup>13</sup>C nuclear magnetic resonance (NMR) spectrum of P2BO40.

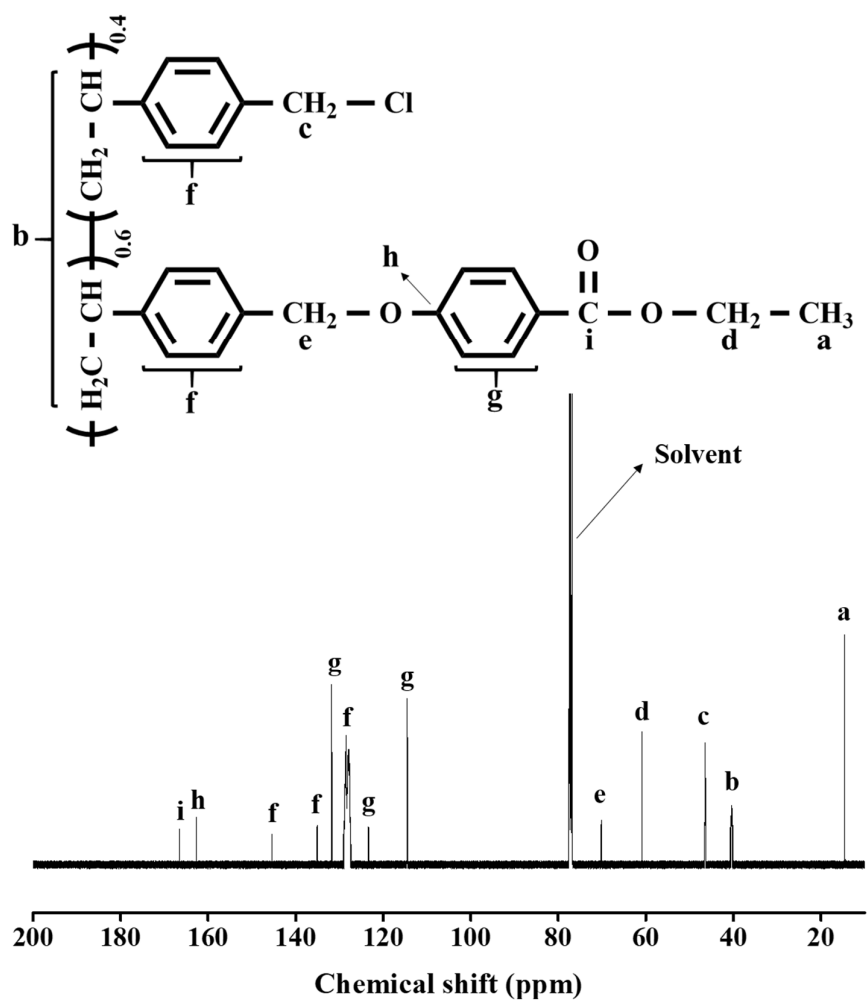


Figure S12.  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectrum of P2BO60.

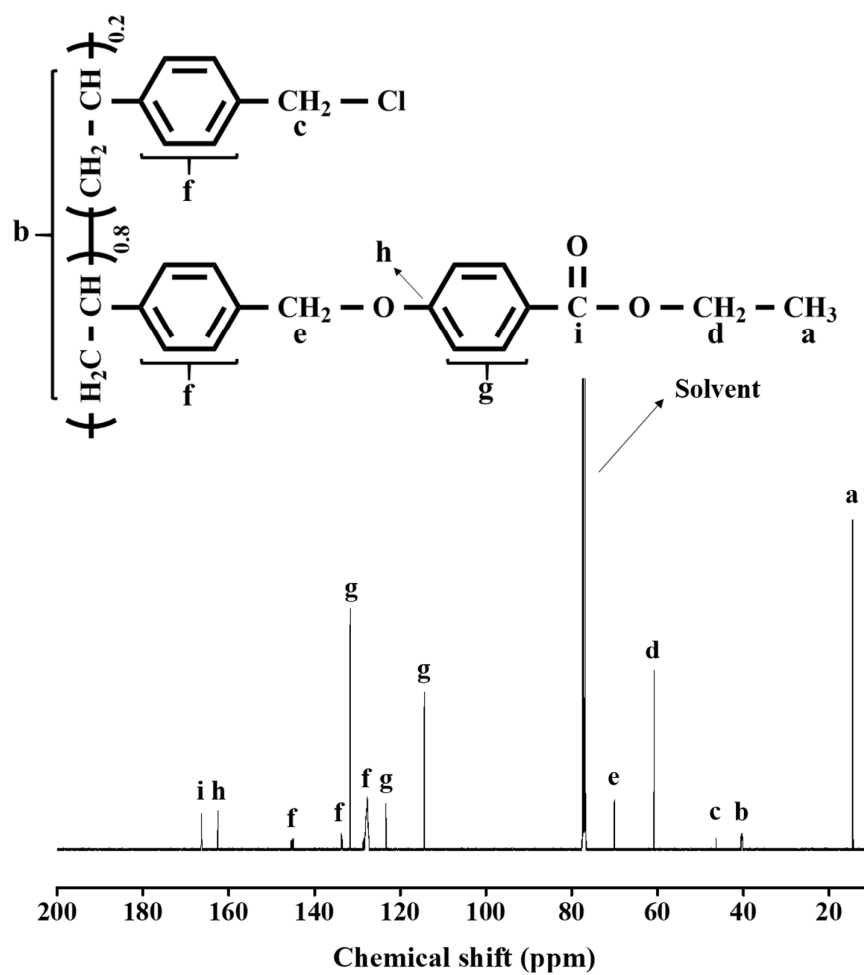


Figure S13.  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectrum of P2BO80.

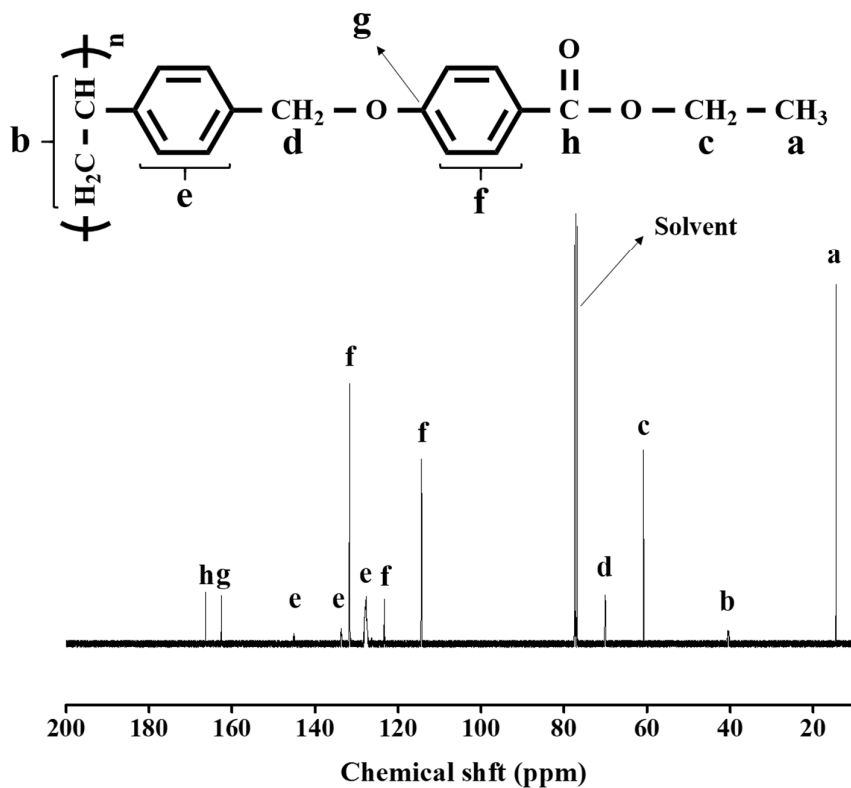


Figure S14.  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectrum of P2BO.

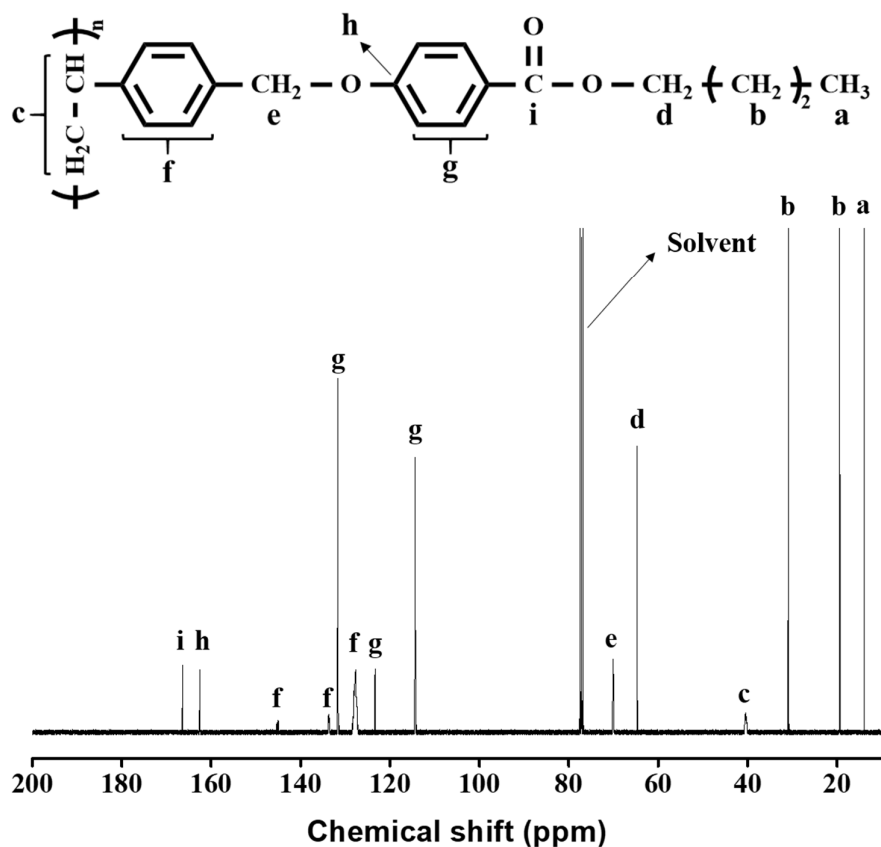


Figure S15.  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectrum of P4BO.

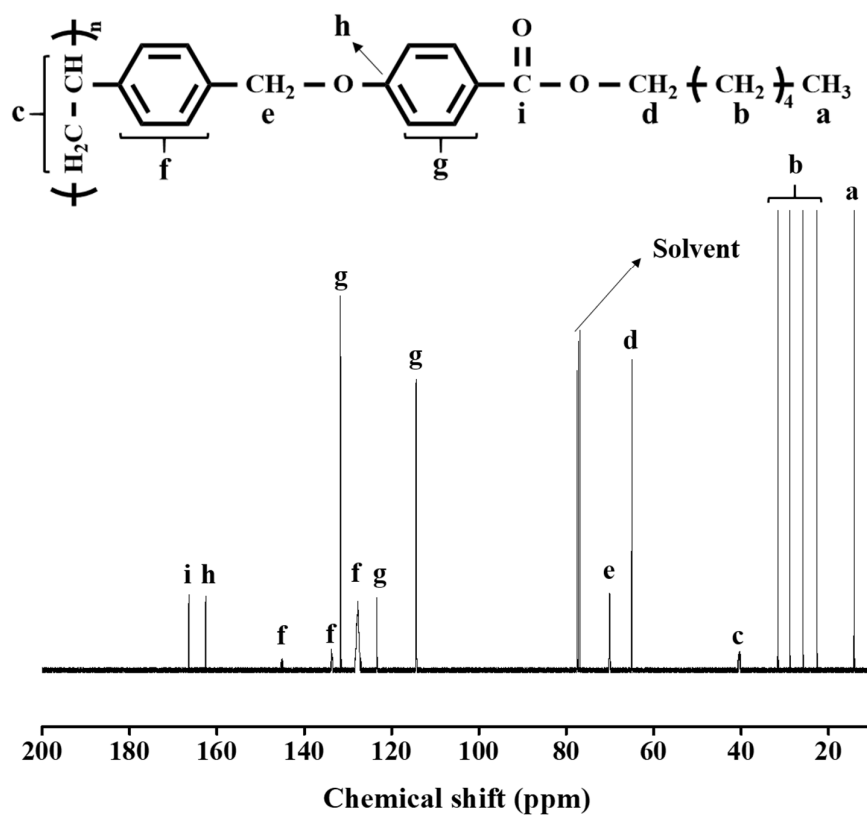


Figure S16.  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectrum of P6BO.

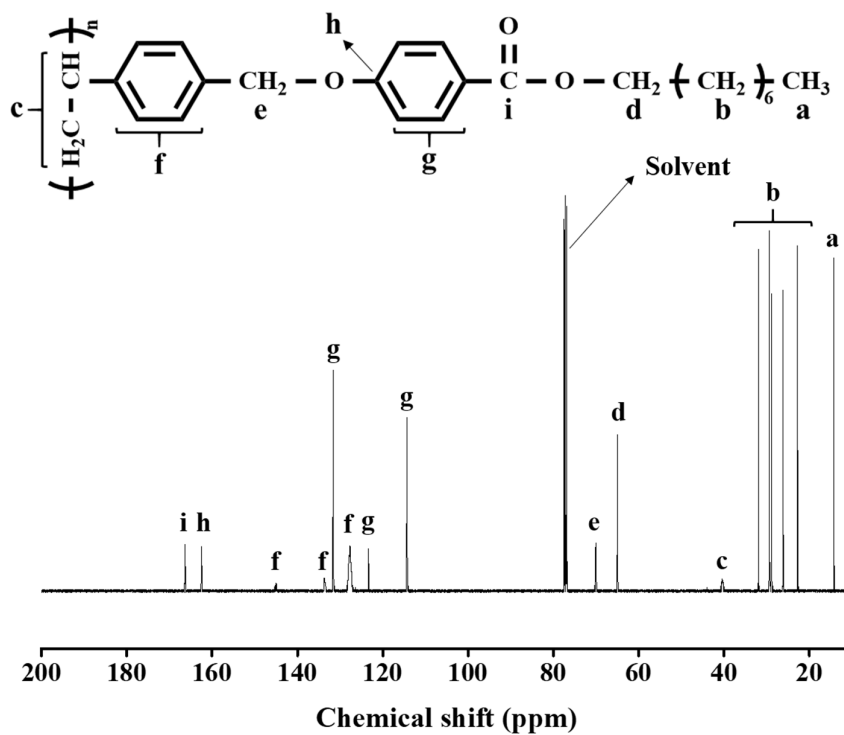


Figure S17.  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectrum of P8BO.