

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.

¹H NMR of P2BO20 (400 MHz, CDCl₃, δ/ppm): δ = 0.74–2.45 (–CH₂–CH–Ph–CH₂–Cl, –CH₂–CH–Ph–CH₂–O–, –COO–CH₂–CH₃, 9H), δ = 4.18–4.41 (–Ph–COO–CH₂–CH₃, 2H), δ = 4.42–4.76 (–Ph–CH₂–Cl, 2H), δ = 4.72–5.12 (–Ph–CH₂–O–Ph–, 2H), δ = 6.00–8.20 (–CH₂–CH–PhH–CH₂–Cl, –CH₂–CH–PhH–CH₂–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.

¹H NMR of P2BO40 (400 MHz, CDCl₃, δ/ppm): δ = 0.66–2.60 (–CH₂–CH–Ph–CH₂–Cl, –CH₂–CH–Ph–CH₂–O–, –COO–CH₂–CH₃, 9H), δ = 4.08–4.39 (–Ph–COO–CH₂–CH₃, 2H), δ = 4.62–4.73 (–Ph–CH₂–Cl, 2H), δ = 4.73–5.33 (–Ph–CH₂–O–Ph–, 2H), δ = 6.02–8.16 (–CH₂–CH–PhH–CH₂–Cl, –CH₂–CH–PhH–CH₂–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.

¹H NMR of P2BO60 (400 MHz, CDCl₃, δ/ppm): δ = 0.71–2.59 (–CH₂–CH–Ph–CH₂–Cl, –CH₂–CH–Ph–CH₂–O–, –COO–CH₂–CH₃, 9H), δ = 4.18–4.39 (–Ph–COO–CH₂–CH₃, 2H), δ = 4.41–4.61 (–Ph–CH₂–Cl, 2H), δ = 4.73–5.14 (–Ph–CH₂–O–Ph–, 2H), δ = 6.03–8.07 (–CH₂–CH–*PhH*–CH₂–Cl, –CH₂–CH–*PhH*–CH₂–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.

¹H NMR of P2BO80 (400 MHz, CDCl₃, δ/ppm): δ = 0.71–2.55 (–CH₂–CH–Ph–CH₂–Cl, –CH₂–CH–Ph–CH₂–O–, –COO–CH₂–CH₃, 9H), δ = 4.20–4.40 (–Ph–COO–CH₂–CH₃, 2H), δ = 4.42–4.64 (–Ph–CH₂–Cl, 2H), δ = 4.70–5.17 (–Ph–CH₂–O–Ph–, 2H), δ = 6.09–8.16 (–CH₂–CH–*PhH*–CH₂–Cl, –CH₂–CH–*PhH*–CH₂–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.

¹H NMR of P4BO (400 MHz, CDCl₃, δ/ppm): δ = 0.86–1.81 (–CH₂–CH–Ph–CH₂–, –COO–CH₂–(CH₂)₂–CH₃, 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.

^1H NMR of P6BO (400 MHz, CDCl_3 , δ/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.

^1H NMR of P8BO (400 MHz, CDCl_3 , δ/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. ^1H nuclear magnetic resonance (NMR) spectrum of PCMS.

Figure S2. ^1H nuclear magnetic resonance (NMR) spectrum of P2BO20.

Figure S3. ^1H nuclear magnetic resonance (NMR) spectrum of P2BO40.

Figure S4. ^1H nuclear magnetic resonance (NMR) spectrum of P2BO60.

Figure S5. ^1H nuclear magnetic resonance (NMR) spectrum of P2BO80.

Figure S6. ^1H nuclear magnetic resonance (NMR) spectrum of P4BO.

Figure S7. ^1H nuclear magnetic resonance (NMR) spectrum of P6BO.

Figure S8. ^1H nuclear magnetic resonance (NMR) spectrum of P8BO.

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

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

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

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

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

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

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

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

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

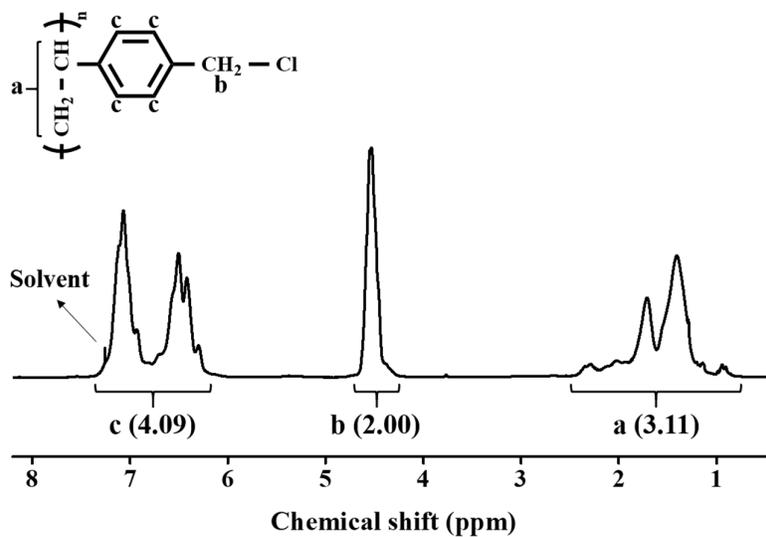


Figure S1. ¹H nuclear magnetic resonance (NMR) spectrum of PCMS.

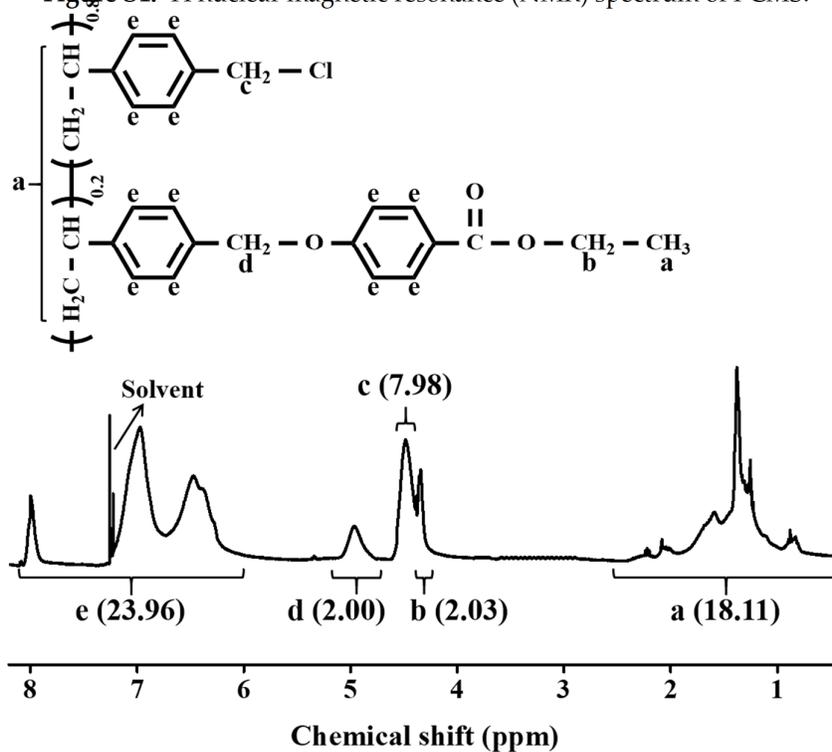


Figure S2. ¹H nuclear magnetic resonance (NMR) spectrum of P2BO20.

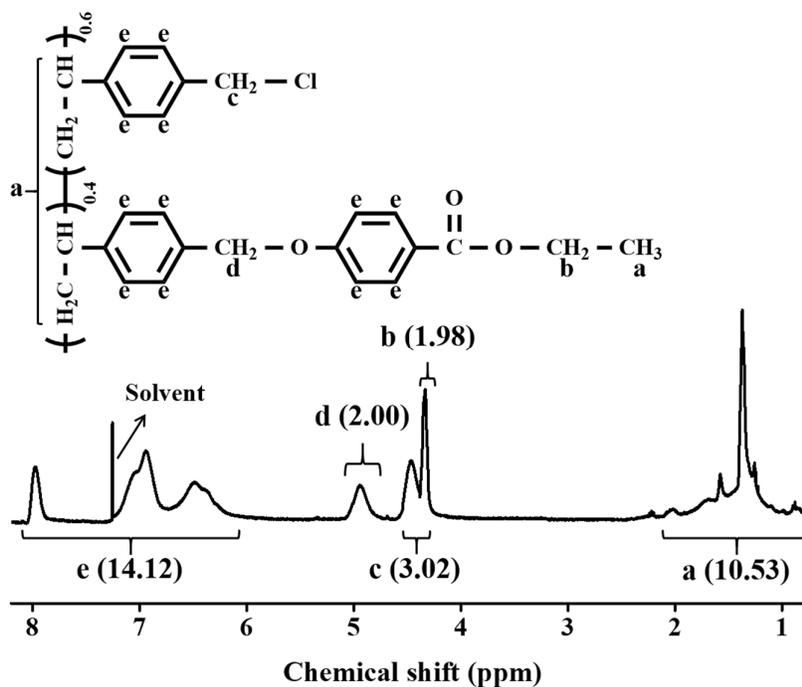


Figure S3. ¹H nuclear magnetic resonance (NMR) spectrum of P2BO40.

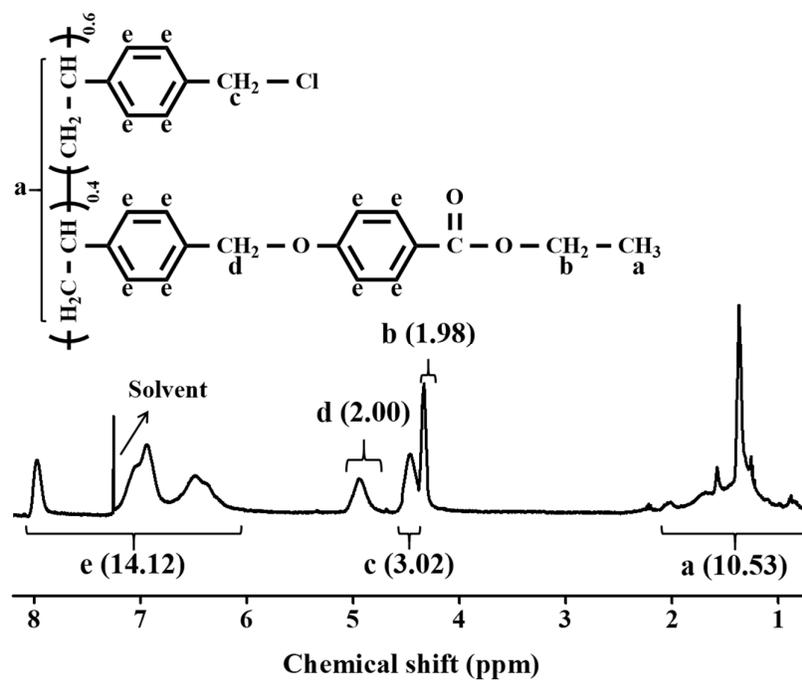


Figure S4. ^1H nuclear magnetic resonance (NMR) spectrum of P2BO60.

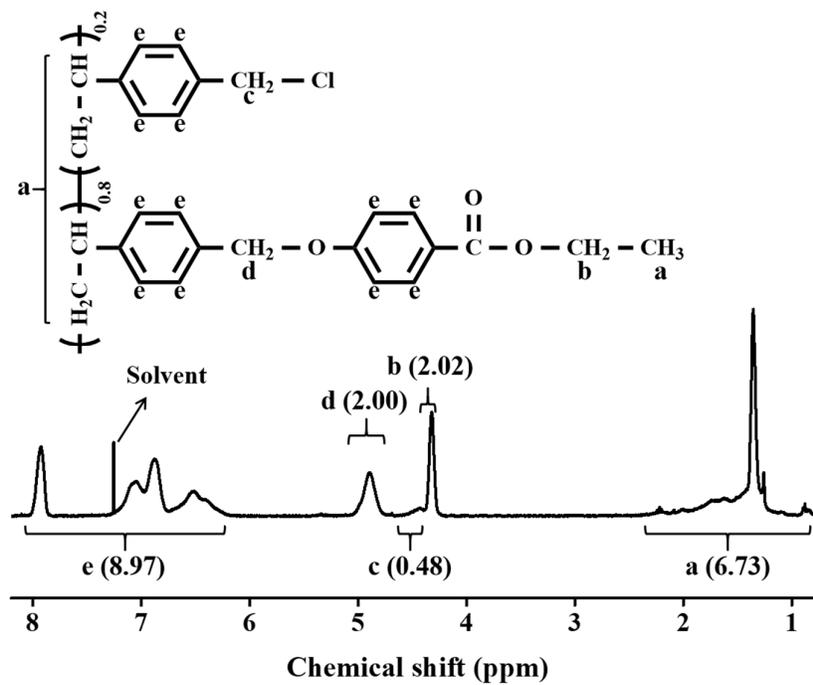


Figure S5. ^1H nuclear magnetic resonance (NMR) spectrum of P2BO80.

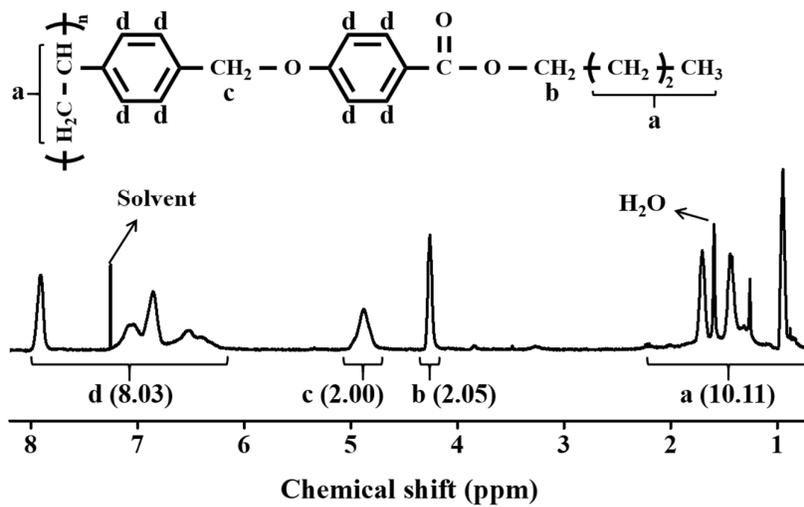


Figure S6. ¹H nuclear magnetic resonance (NMR) spectrum of P4BO.

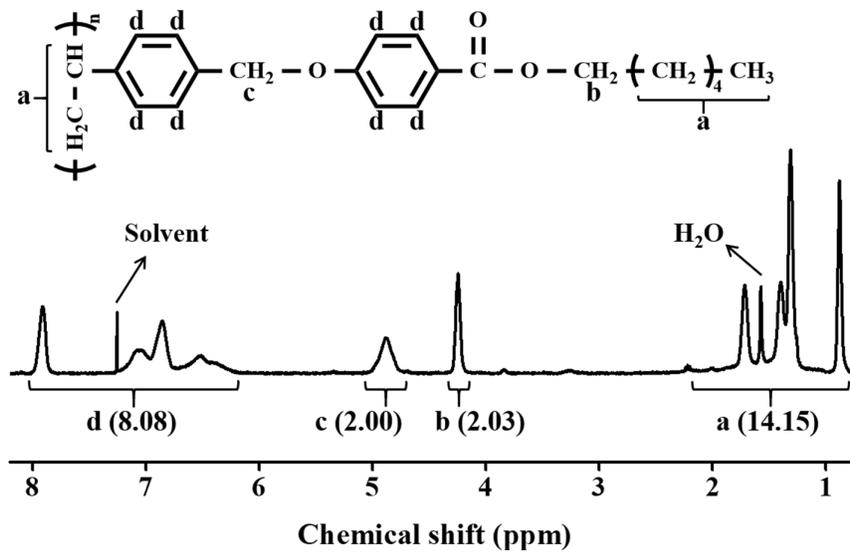


Figure S7. ¹H nuclear magnetic resonance (NMR) spectrum of P6BO.

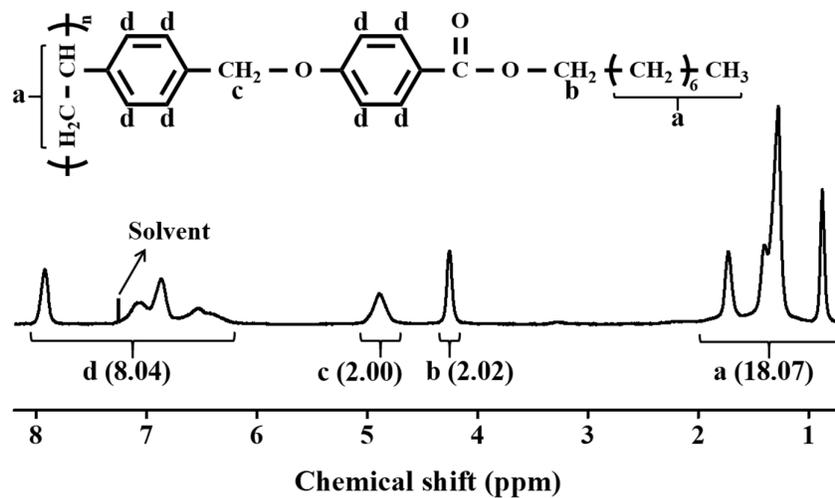


Figure S8. ^1H nuclear magnetic resonance (NMR) spectrum of P8BO.

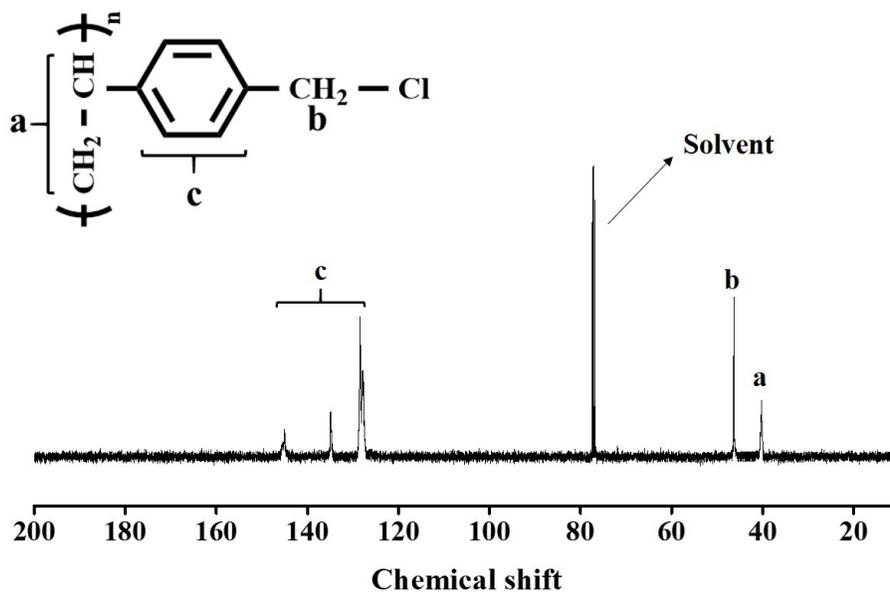


Figure S9. ^{13}C nuclear magnetic resonance (NMR) spectrum of PCMS.

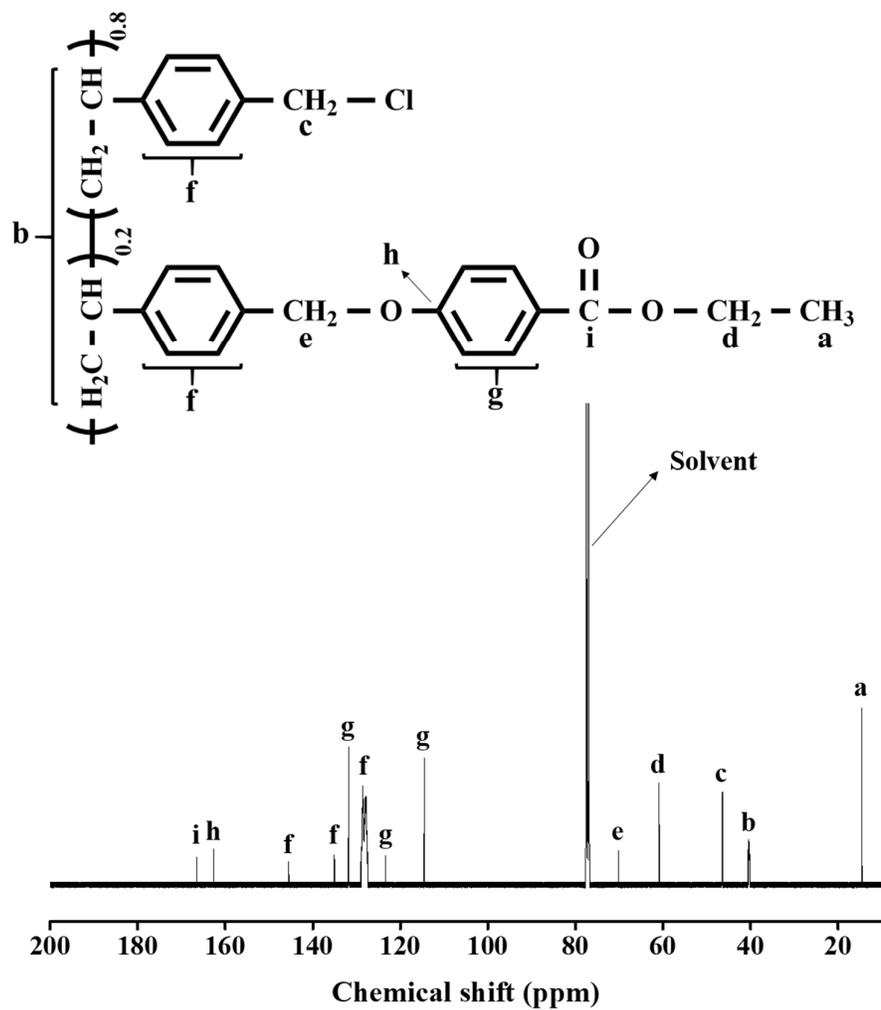


Figure S10. ¹³C nuclear magnetic resonance (NMR) spectrum of P2BO20.

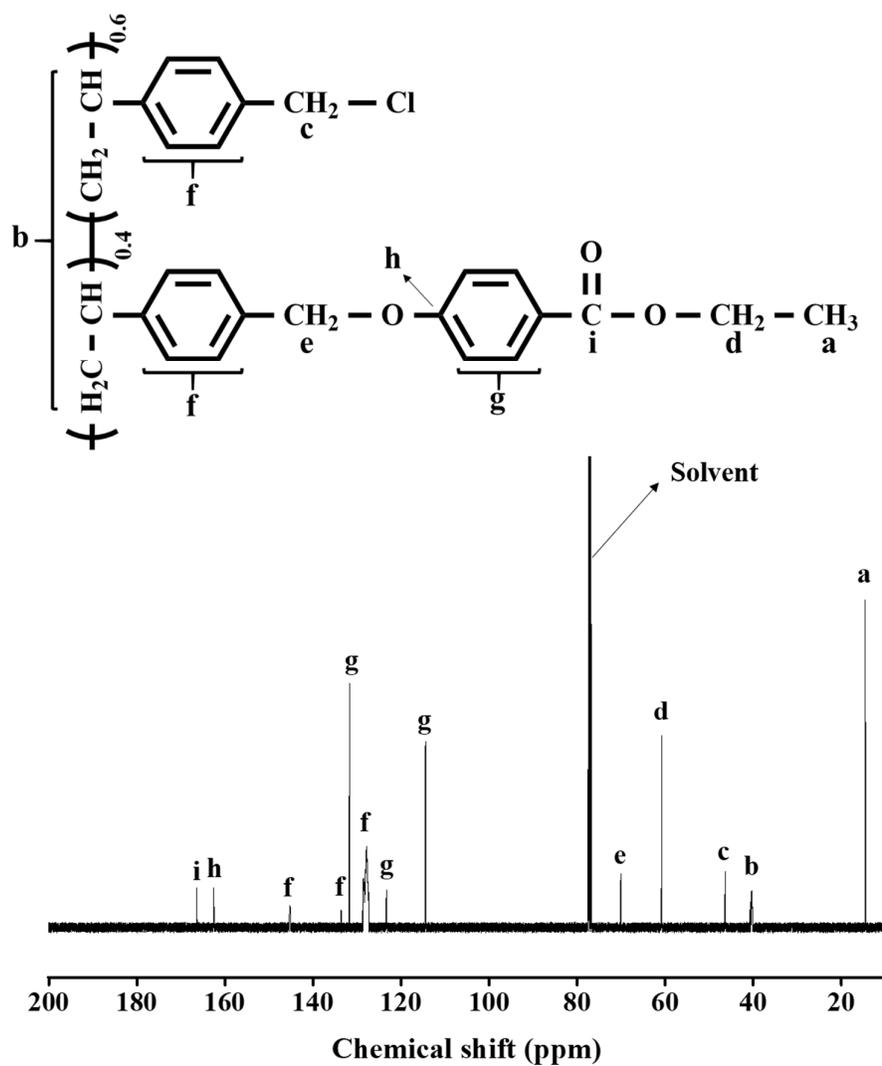


Figure S11. ^{13}C nuclear magnetic resonance (NMR) spectrum of P2BO40.

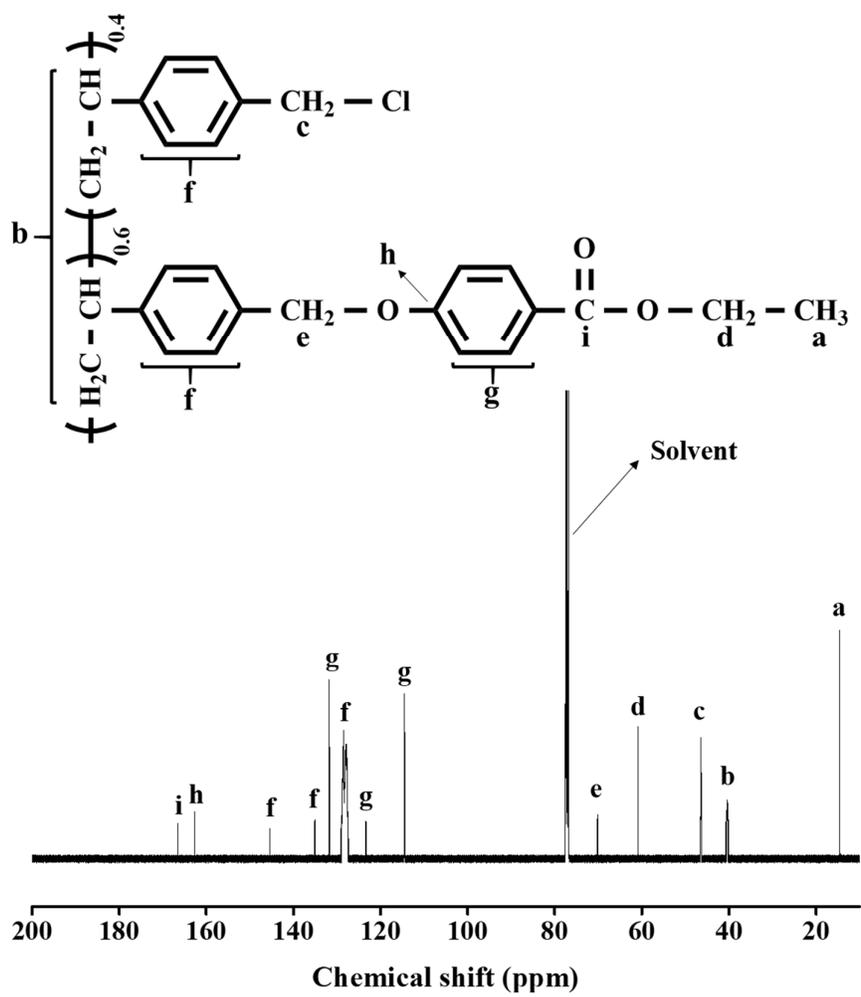


Figure S12. ¹³C nuclear magnetic resonance (NMR) spectrum of P2BO60.

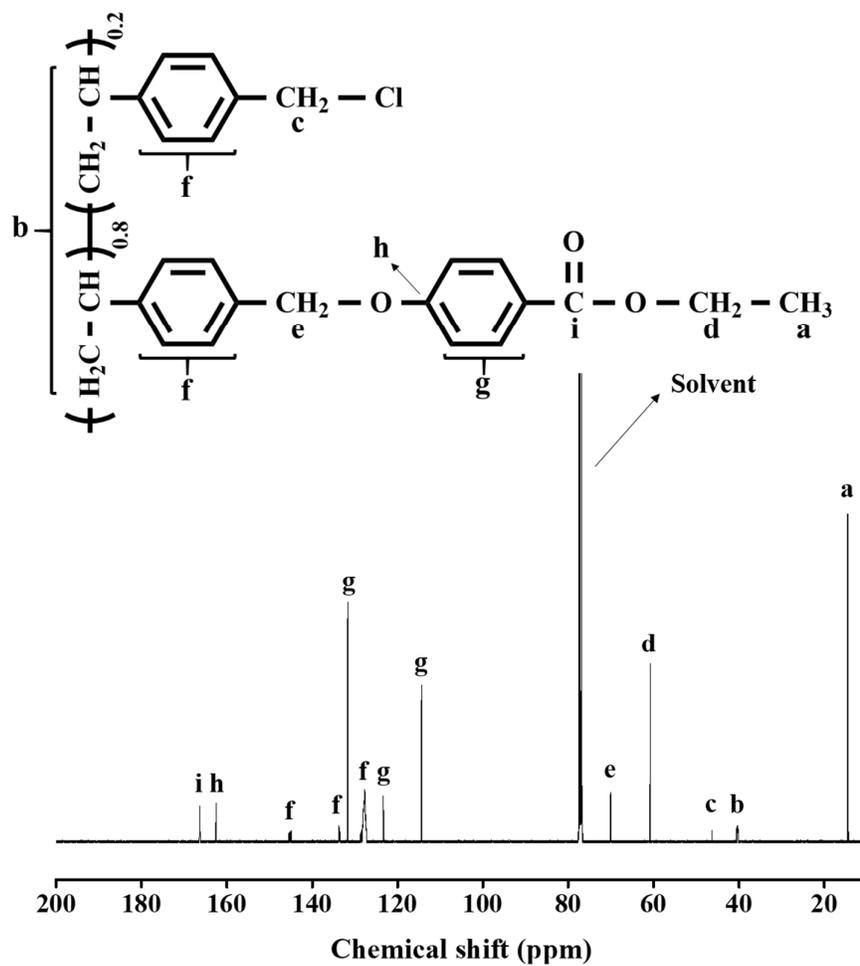


Figure S13. ^{13}C nuclear magnetic resonance (NMR) spectrum of P2BO80.

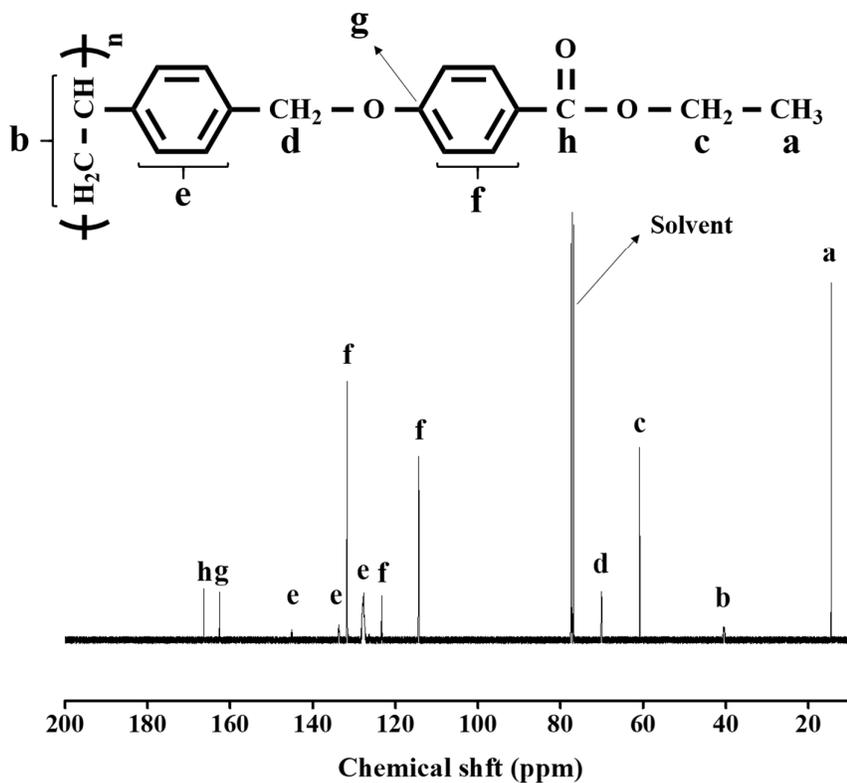


Figure S14. ^{13}C nuclear magnetic resonance (NMR) spectrum of P2BO.

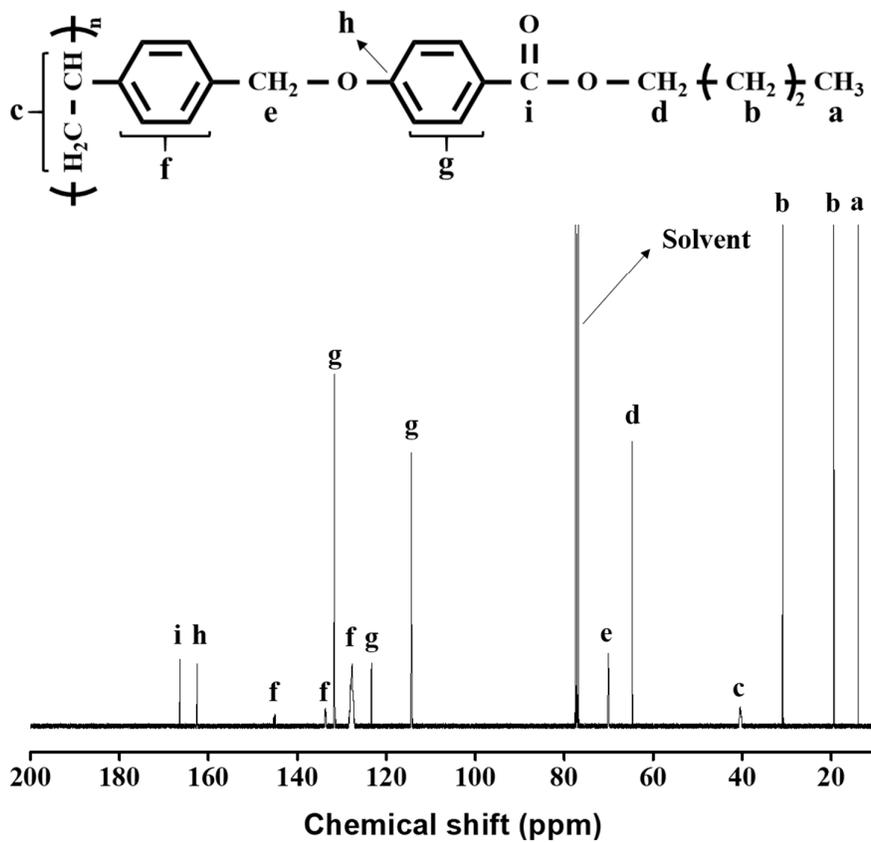


Figure S15. ^{13}C nuclear magnetic resonance (NMR) spectrum of P4BO.

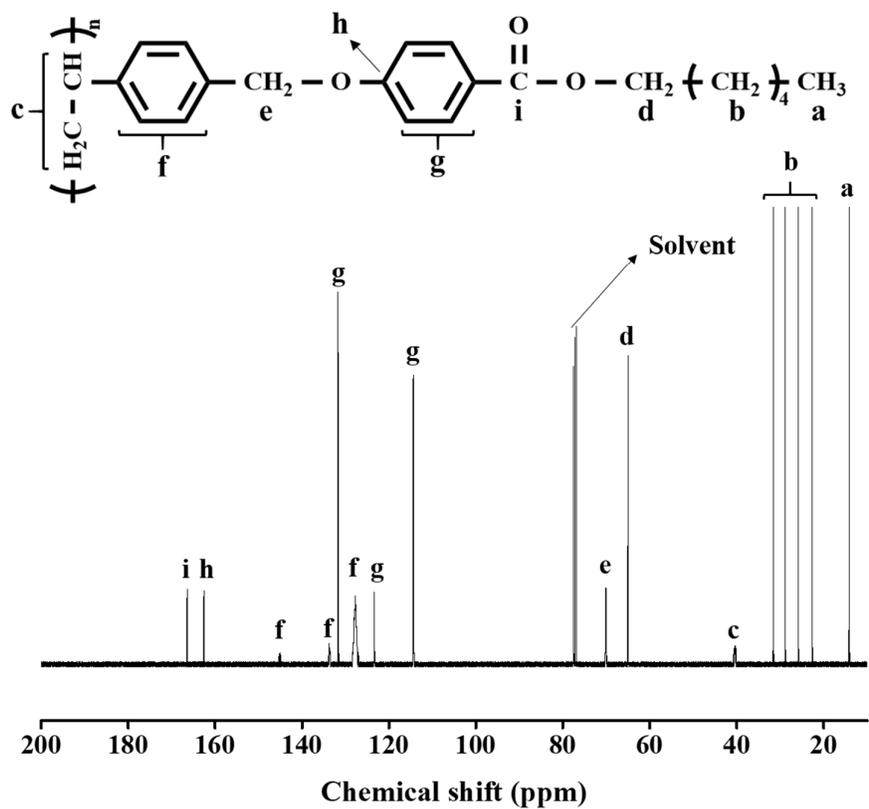


Figure S16. ^{13}C nuclear magnetic resonance (NMR) spectrum of P6BO.

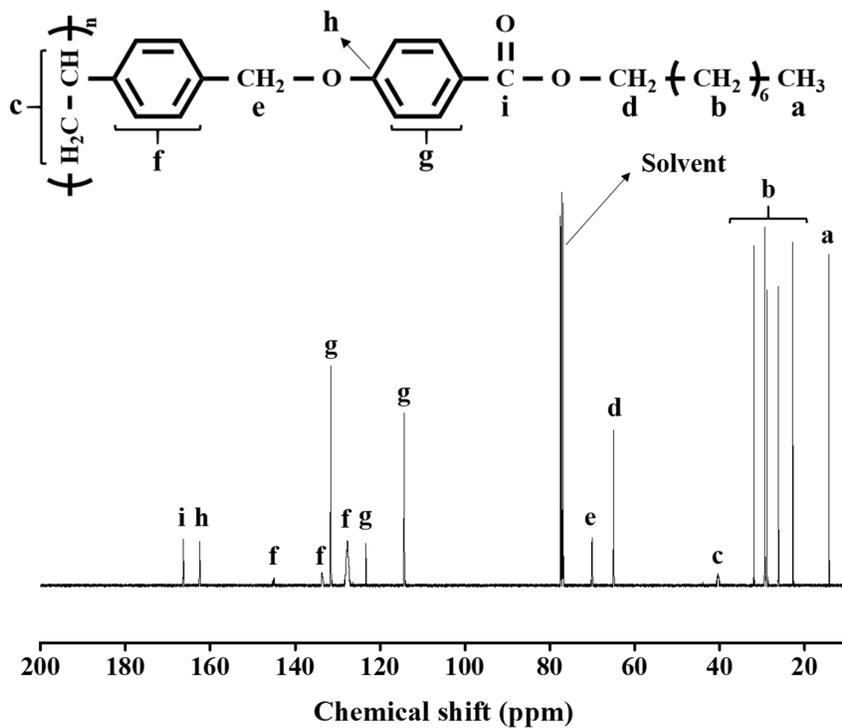


Figure S17. ^{13}C nuclear magnetic resonance (NMR) spectrum of P8BO.