

# Supporting information for

## Facile preparation of polycarbonates from Bio-based eugenol and 2-methoxy-4-vinylphenol

Mengqian Huang,<sup>a</sup> De Bai,<sup>a</sup> Qin Chen,<sup>a</sup> Changbo Zhao,<sup>a</sup> Tianhua Ren,<sup>a</sup> Caijuan Huang,<sup>a</sup> Michael North,<sup>b</sup> Haibo Xie<sup>a\*</sup>

<sup>a</sup>Department of Polymeric Materials & Engineering, College of Materials & Metallurgy, Guizhou University, West Campus, Guizhou University, Huaxi District, Guiyang, P. R. China, 550025. Email: [hbxie@gzu.edu.cn](mailto:hbxie@gzu.edu.cn)

<sup>b</sup>Green Chemistry Centre of Excellence, Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK.

### S1. Materials and Methods

**S1.1 Materials.** Eugenol (99%) and triphosgene (99%) were purchased from Macklin and used as received. 2-Methoxy-4-vinylphenol ( $\geq 98\%$ ), 1,2-ethanedithiol (EDT, 97%), 1,3-propanedithiol (PDT, 98%), 1,10-decanedithiol (DDT, 96%), the Hoveyda-Grubbs 2<sup>nd</sup> generation catalyst ( $\geq 97\%$ ) 1,4-benzoquinone (99%), ethyl vinyl ether (98%) and 3-chloroperbenzoic acid (86%) were obtained from Aladdin and used as received. 1,6-hexanedithiol (HDT, 98%) was supplied by Energy Chemical. Other common organic solvents were obtained through commercial resources. Before use, calcium hydride was used to distill dichloromethane, tetrahydrofuran and triethylamine to remove water. They were stored by adding activated Davison 4 Å molecular sieves and placed in a vacuum drying oven. Other chemicals were used as received.

### S1.2 Methods.

NMR spectra were recorded on a JOEL ECX500 spectrometer (400 MHz for <sup>1</sup>H NMR and 101 MHz for <sup>13</sup>C NMR) with tetramethylsilane (TMS) as an internal reference. (DMSO-d<sub>6</sub>,  $\delta$ 2.50 ppm for <sup>1</sup>H NMR and 39.52 ppm for <sup>13</sup>C NMR; CDCl<sub>3</sub>,  $\delta$ 7.26 ppm for <sup>1</sup>H NMR and 77.16 ppm for <sup>13</sup>C NMR). Fourier transform infrared spectra (FTIR) were recorded on a Thermoscientific (Nicolet iS50) FTIR spectrometer at room temperature ranging between 500–4000 cm<sup>-1</sup>. Molecular weights ( $M_n$ ) and dispersities ( $\mathcal{D} = M_w/M_n$ ) were determined by size-exclusion chromatography (SEC). THF or DMF were used as eluent and the system was calibrated with 10 PMMA standards. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to determine thermal properties under a nitrogen atmosphere. Approximately 10 mg of the sample was heated from room temperature to 750 °C at a rate of 10 °C/min for TGA analysis. Polymer samples were first heated from room temperature to 180 °C at a rate of 10 °C/min. After cooling down to -90 °C at the same rate, they were reheated to 250 °C for DSC analysis. The glass transition temperatures ( $T_g$ ) were collected from the second heating scan.

## S1.3. Synthesis of monomers<sup>1</sup>

### S1.3.1 Bis(4-allyl-2-methoxyphenyl) carbonate (2a, BAMC)

Triethylamine (21.0 ml, 150 mmol) was added to a solution of eugenol (18.7 ml, 120 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL), and stirred at 0 °C for 10 min. Triphosgene (6.0 g, 20 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL), and the resulting solution was slowly dropped into the mixture and stirred at 0 °C for 2 h. 1M HCl was used to quench the reaction, and the reaction solution was washed with saturated salt until neutral. Dichloromethane (3×40 mL) was used to extract the inorganic phase. The organic phases were combined and dried over anhydrous sodium sulfate. The final compound was obtained as a white solid, which was purified by recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane. Yield: 94%. Mp 83.1 °C, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.15 (d, 2H, aromatic protons), 6.88–6.72 (m, 4H, aromatic protons), 5.96 (2H, -CH=), 5.19–5.01 (m, 4H, =CH<sub>2</sub>), 3.88 (s, 6H, -OCH<sub>3</sub>), 3.39 (d, 4H, -CH<sub>2</sub>-). <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ 151.00, 150.52, 139.59, 137.77, 137.33, 121.98, 120.32, 116.15, 113.24, 55.89, 39.30.

### S1.3.2 Bis(2-methoxy-4-vinylphenyl) carbonate (2b, BMVC)

Triethylamine (2.1 ml, 15 mmol) was added to a solution of 2-methoxy-4-vinylphenol (1.8 g, 12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL), and stirred at 0 °C for 10 min. Triphosgene (0.6 g, 2 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL), and the resulting solution was slowly dropped into the mixture and stirred at 0 °C for 2 h. 1M HCl was used to quench the reaction, and the reaction solution was washed with saturated salt until neutral. Dichloromethane (3×40 mL) was used to extract the inorganic phase. The organic phases were combined and dried over anhydrous sodium sulfate. The crude product was purified by silica gel chromatography using petroleum ether/ CH<sub>2</sub>Cl<sub>2</sub> (4:1, v/v) to obtain a white product. Yield: 78%. Mp 101.4 °C, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.19 (d, 2H, aromatic protons), 7.06–6.97 (m, 4H, aromatic protons), 6.69 (dd, 2H, -CH=), 5.72 (dd, 2H, =CH<sub>2</sub>), 5.27 (d, 2H, =CH<sub>2</sub>), 3.92 (s, 6H, -OCH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 151.27, 139.89, 137.12, 136.25, 122.37, 118.97, 114.54, 110.26, 56.16.

## S1.4. Synthesis of polymers

### S1.4.1 ADMET polymerizations

α,ω-Dienes (3 mmol) were added to a 50 ml Schlenk flask and dissolved in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The Hoveyda-Grubbs 2<sup>nd</sup> generation catalyst (19 mg, 1 mol%) was added to the flask. 1,4-benzoquinone (16 mg, 5 mol%) was added to limit isomerization. After the flask was subjected to three freeze-thaw-pump cycles, the reaction mixture was stirred under reflux with an inert atmosphere in an oil bath at 40 °C for 24 hours. Then, 5 mL of ethyl vinyl ether was introduced into the flask to quench the reaction. The final polymer was dissolved into 5 mL of THF and reprecipitated in cold methanol. This washing was repeated three times and the product vacuum-dried at 50 °C for 24 h.

**P2a.** BAMC (1.063 g, 3.0 mmol), isolated yield (92%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.10 (t, 2H, aromatic protons), 6.79 (d, 4H, aromatic protons), 5.72 (s, 2H, -CH=CH-), 3.87 (s, 6H, -CH<sub>3</sub>), 3.52 – 3.27 (m, 4H, -CH<sub>2</sub>-). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 151.67, 151.04, 140.11, 138.61, 130.55, 122.16, 120.60, 113.07, 56.14, 38.94.

**P2b.** BMVC (0.98 g, 3.0 mmol), isolated yield (90%). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 7.37–7.28

(m, 4H, aromatic protons), 7.23 (d, 2H, aromatic protons), 5.76 (s, 2H, -CH=CH-), 3.94 (s, 6H, -CH<sub>3</sub>).<sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ 151.07, 139.05, 136.92, 128.49, 122.54, 119.37, 110.62, 56.11. Add 1H J values.

## 1.4.2 Synthesis of poly(thioether carbonates) via Thiol–Ene Click reactions.<sup>2</sup>

These poly(carbonate ester)s with different chain lengths were synthesized by reacting various dithiols with  $\alpha,\omega$ -diene monomers under UV light for 4 h through thiol-ene click chemistry under stoichiometric balance (molar ratio of C=C to sulfhydryl = 1:1). Taking the reaction of BAMC and EDT as an example, the experimental steps are as follows. BAMC (1.063 g, 3 mmol), EDT (260  $\mu$ l, 3 mmol), and benzoin dimethyl ether (DMPA, 0.04 g, 5 mol%) as the photoinitiator, were transferred into a 10 mL glass bottle and adequately mixed into a homogeneous phase with 5 ml of tetrahydrofuran. Then the reaction system was irradiated for 4h ( $\lambda = 365$  nm). The reaction mixture was poured into a large amount of methanol to regenerate the polymers, washed three times, collected by centrifugation, then dried at room temperature.

**P2a3a:** EDT (260  $\mu$ l, 3.0 mmol), isolated yield (85%).<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 7.12 (d, 2H, aromatic protons), 7.00 (s, 2H, aromatic protons), 6.78 (d, 2H, aromatic protons), 3.81 (s, 6H, -CH<sub>3</sub>), 2.66 (d, 8H, -CH<sub>2</sub>-), 2.50 (s, 4H, -CH<sub>2</sub>-), 1.81 (s, 4H, -CH<sub>2</sub>-).<sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ 151.06, 150.48, 141.29, 137.64, 121.86, 120.27, 113.19, 55.90, 34.04, 31.35, 30.91, 30.55.

**P2a3b:** PDT (310  $\mu$ l, 3.0 mmol), isolated yield (90%).<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 7.15 (d, 2H, aromatic protons), 7.02 (s, 2H, aromatic protons), 6.81 (d, 2H, aromatic protons), 3.83 (s, 6H, -CH<sub>3</sub>), 2.74–2.42 (m, 12H, -CH<sub>2</sub>-), 1.94–1.64 (m, 6H, -CH<sub>2</sub>-).<sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ 150.99, 150.45, 141.24, 137.62, 121.80, 120.22, 113.16, 55.87, 34.00, 30.80, 30.50, 29.83, 29.06.

**P2a3c:** HDT (470  $\mu$ l, 3.0 mmol), isolated yield (88%).<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 7.16 (d, 2H, aromatic protons), 7.03 (s, 2H, aromatic protons), 6.82 (d, 2H, aromatic protons), 3.85 (s, 6H, -CH<sub>3</sub>), 2.68 (s, 4H, -CH<sub>2</sub>-), 2.56–2.38 (m, 8H, -CH<sub>2</sub>-), 1.85 (s, 4H, -CH<sub>2</sub>-), 1.43 (d, 8H, -CH<sub>2</sub>-).<sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>) δ 151.01, 150.47, 141.30, 137.64, 121.82, 120.24, 113.18, 55.89, 34.06, 30.92 (d, J = 12.6 Hz), 30.57, 29.05, 27.79.

**P2a3d:** DDT (660  $\mu$ l, 3.0 mmol), isolated yield (82%).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.12 (d, 2H, aromatic protons), 6.78 (dd, 4H, aromatic protons), 3.87 (s, 6H, -CH<sub>3</sub>), 2.67 (s, 4H, -CH<sub>2</sub>-), 2.50 (s, 8H, -CH<sub>2</sub>-), 1.97–1.80 (m, 4H, -CH<sub>2</sub>-), 1.63–1.49 (m, 4H, -CH<sub>2</sub>-), 1.39–1.26 (m, 12H, -CH<sub>2</sub>-).<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 151.66, 150.91, 141.08, 138.42, 122.05, 120.51, 112.96, 56.09, 34.77, 32.22, 31.51, 31.14, 29.75, 29.54, 29.30, 28.99.

**P2b3a:** EDT (260  $\mu$ l, 3.0 mmol), isolated yield (87%).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.13 (d, 2H, aromatic protons), 6.82–6.77 (m, 4H, aromatic protons), 3.86 (s, 6H, -CH<sub>3</sub>), 2.87–2.73 (m, 12H, -CH<sub>2</sub>-).<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 151.54, 151.04, 139.82, 138.80, 122.27, 120.59, 113.06, 56.16, 36.36, 33.80, 32.51.

**P2b3b:** PDT (310  $\mu$ l, 3.0 mmol), isolated yield (81%).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.13 (d, 2H, aromatic protons), 6.82–6.77 (m, 4H, aromatic protons), 3.87 (s, 6H, -CH<sub>3</sub>), 2.88–2.60 (m, 12H, -CH<sub>2</sub>-), 1.91–1.82 (m, 2H, -CH<sub>2</sub>-).<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 151.19, δ 151.02, 140.01, 138.76, 122.24, 120.59, 113.05, 56.15, 36.38, 33.66, 31.17, 29.31.

**P2b3c:** HDT (470  $\mu$ l, 3.0 mmol), isolated yield (77%).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.13 (d, 2H, aromatic protons), 6.82–6.78 (m, 4H, aromatic protons), 3.88 (s, 6H, -CH<sub>3</sub>), 2.88–2.73 (m, 8H, -CH<sub>2</sub>-), 2.53 (t, 4H, -CH<sub>2</sub>-), 1.64–1.57 (dd, 4H, -CH<sub>2</sub>-), 1.39–1.31 (dd, 4H, -CH<sub>2</sub>-).<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 151.56, 150.98, 140.15, 138.69, 122.21, 120.57, 113.01, 56.14, 36.44, 33.69, 32.39, 29.56, 28.56.

**P2b3d:** DDT (660  $\mu$ l, 3.0 mmol), isolated yield (76%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.13 (d, 2H, aromatic protons), 6.82–6.78 (m, 4H, aromatic protons), 3.88 (s, 6H,  $-\text{CH}_3$ ), 2.88–2.74 (dt, 8H,  $-\text{CH}_2-$ ), 2.53 (t, 4H,  $-\text{CH}_2-$ ), 1.62–1.54 (m, 4H,  $-\text{CH}_2-$ ), 1.36–1.25 (dt, 12H,  $-\text{CH}_2-$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  151.54, 150.94, 140.18, 138.64, 122.17, 120.53, 112.97, 56.10, 36.41, 33.65, 32.45, 29.70, 29.53, 29.31, 28.98.

### S1.4.3 Oxidation of P2a3a (PO2a3a)

**P2a3a** (1.095 g, 2.45 mmol) and m-chloroperoxybenzoic acid (m-CPBA, 1.99 g, 9.8 mmol, 85%) were placed in a flask and dissolved in 15 ml of THF. The system was magnetically stirred for 10 h at room temperature and atmospheric pressure. After the reaction was completed, the mixture was poured into a large amount of methanol to regenerate the polymer and washed three times, collected by centrifugation, then dried at 50  $^\circ\text{C}$  under vacuum for 24 h to obtain a light pink solid. Yield: 96%.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  7.18 (d, 2H, aromatic protons), 7.06 (s, 2H, aromatic protons), 6.84 (d, 2H, aromatic protons), 3.84 (s, 6H,  $-\text{CH}_3$ ), 2.72–2.47 (m, 12H,  $-\text{CH}_2-$ ), 2.03 (s, 4H,  $-\text{CH}_2-$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO-d}_6$ )  $\delta$  150.98, 150.54, 140.43, 137.83, 122.00, 120.34, 113.28, 55.93, 51.50, 44.81, 33.41, 22.93.

## 2. Figures

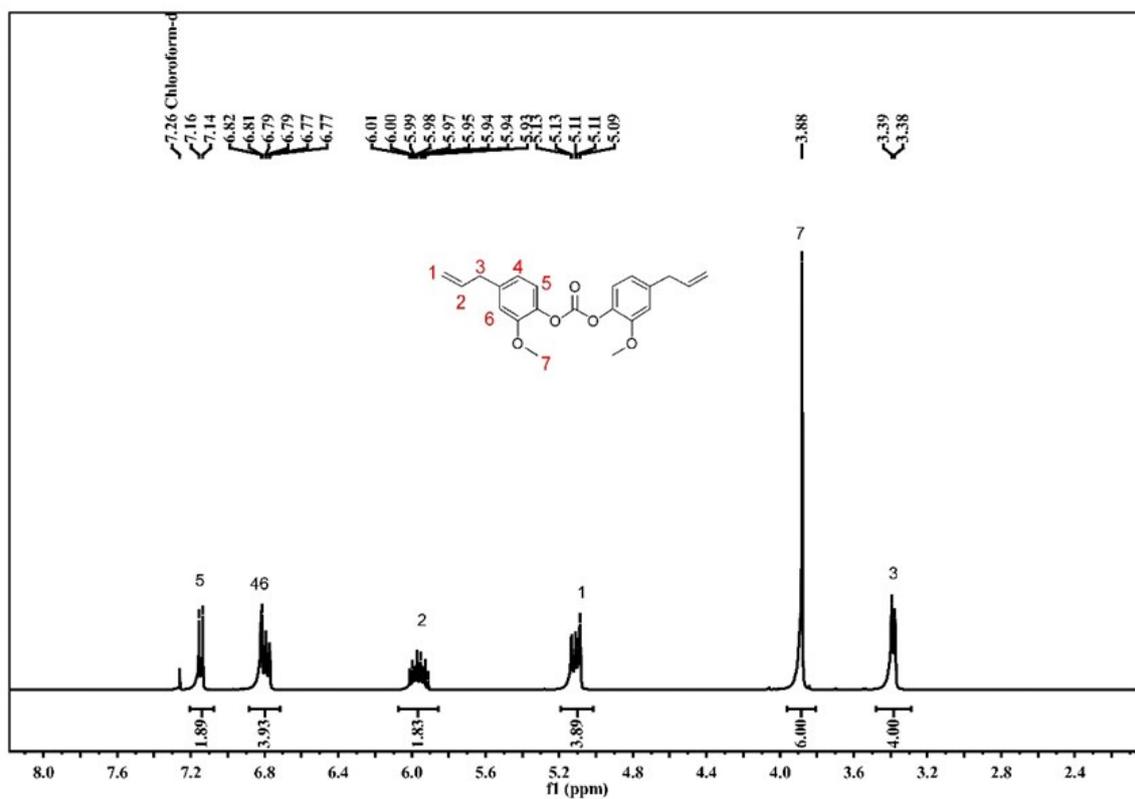


Figure S1. <sup>1</sup>H NMR spectrum of **2a** (400 MHz CDCl<sub>3</sub>).

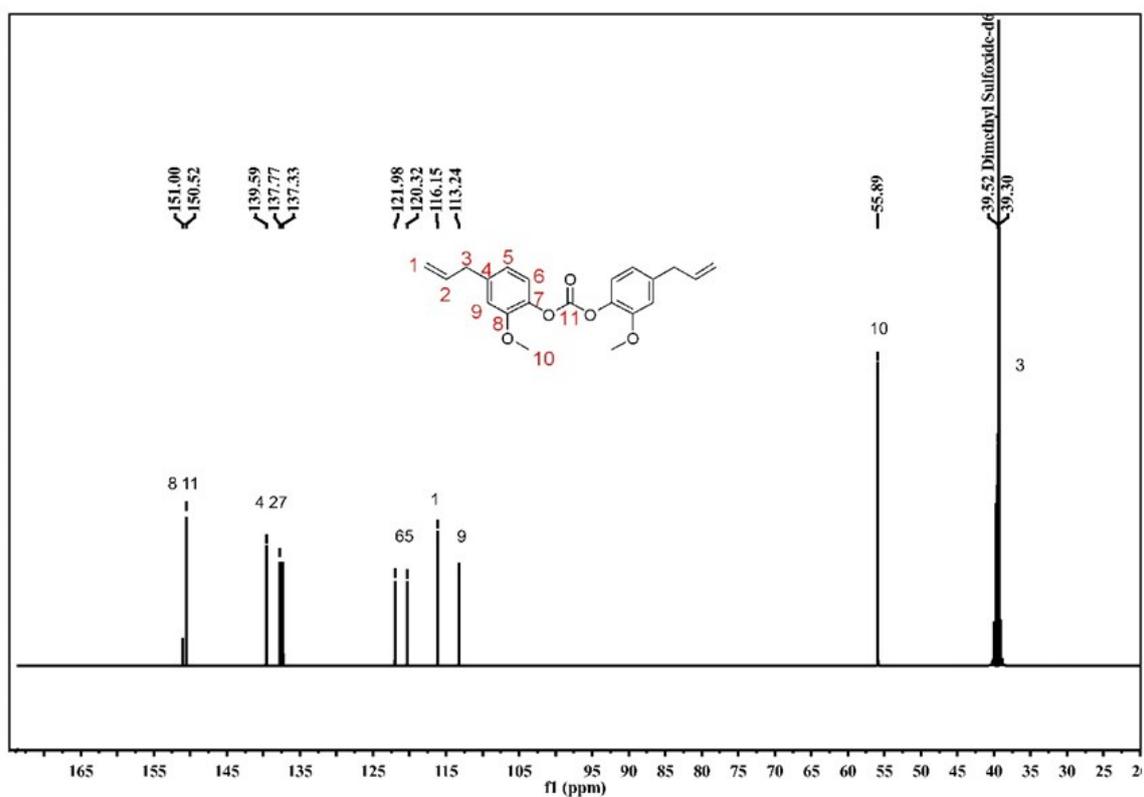


Figure S2. <sup>13</sup>C NMR spectrum of **2a** (101 MHz DMSO-d<sub>6</sub>).

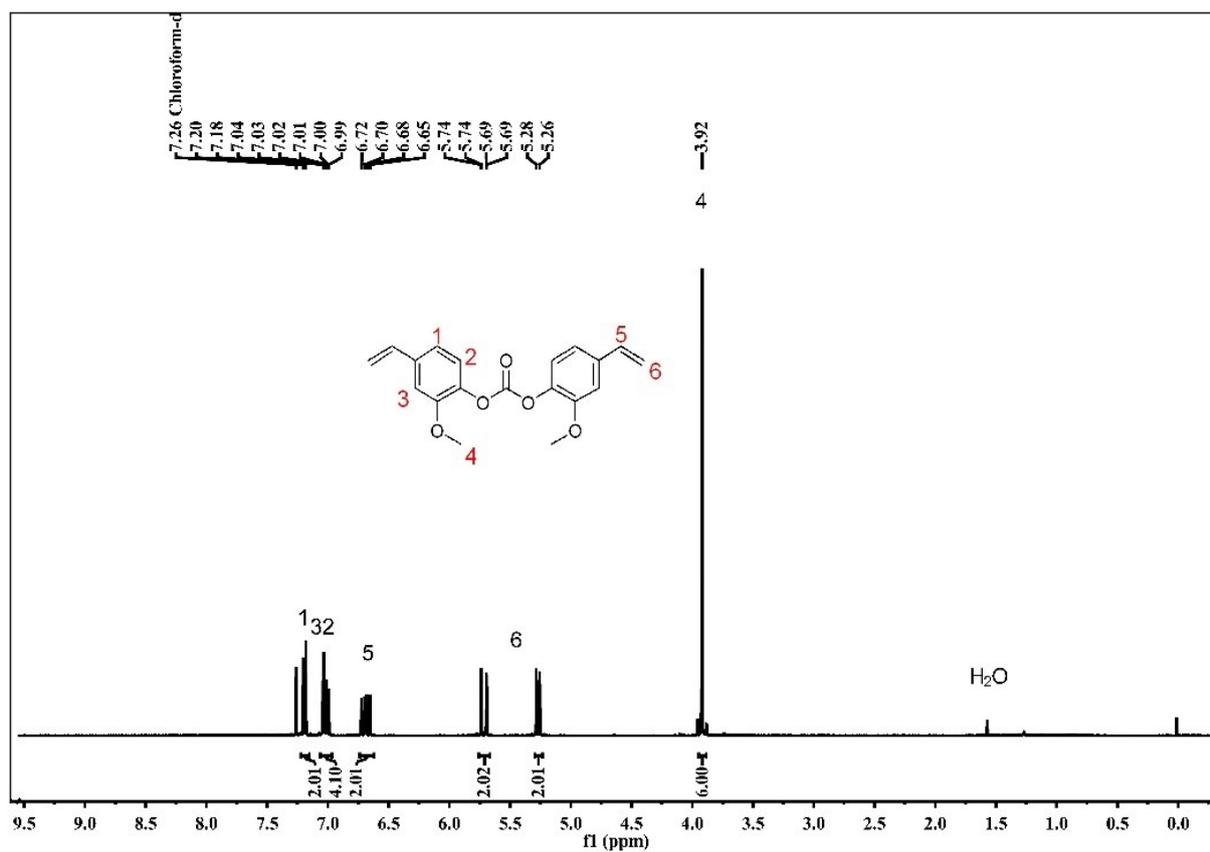


Figure S3. <sup>1</sup>H NMR spectrum of **2b** (400 MHz CDCl<sub>3</sub>).

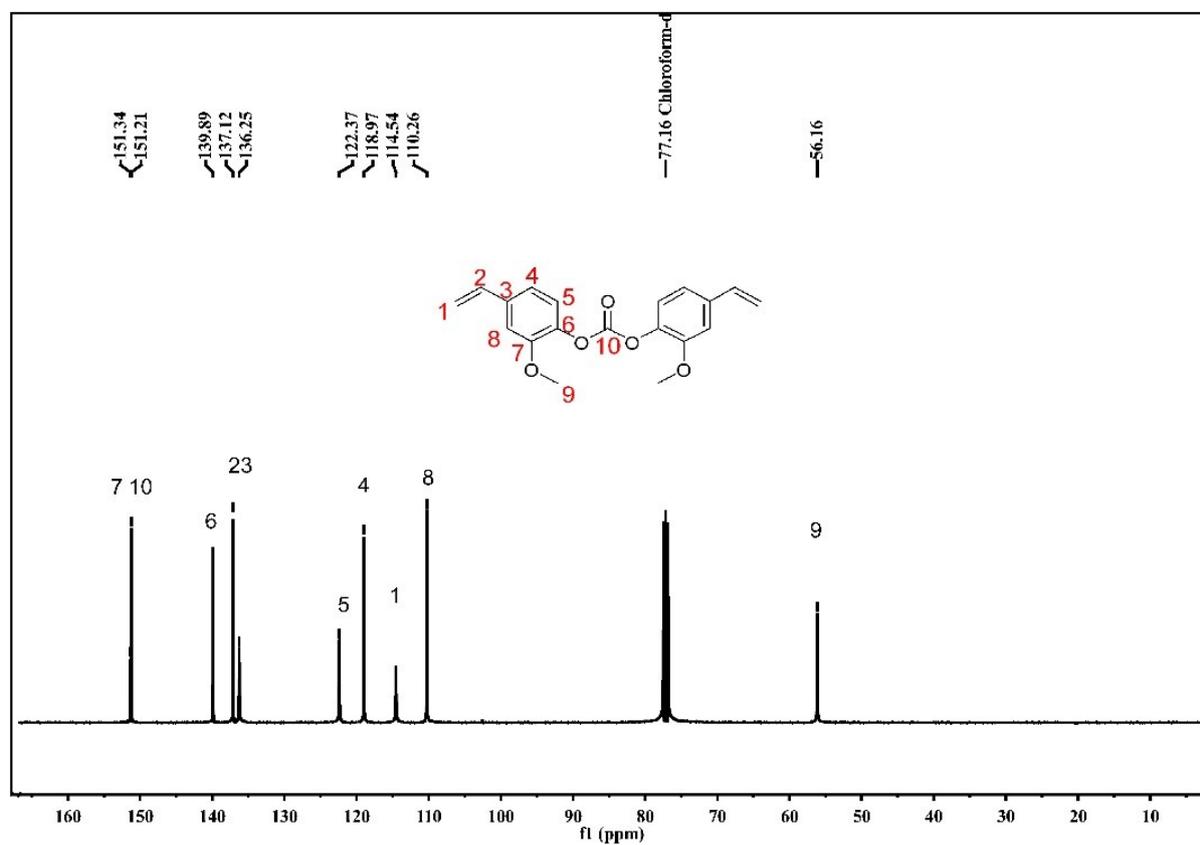


Figure S4. <sup>13</sup>C NMR spectrum of **2b** (125 MHz CDCl<sub>3</sub>).

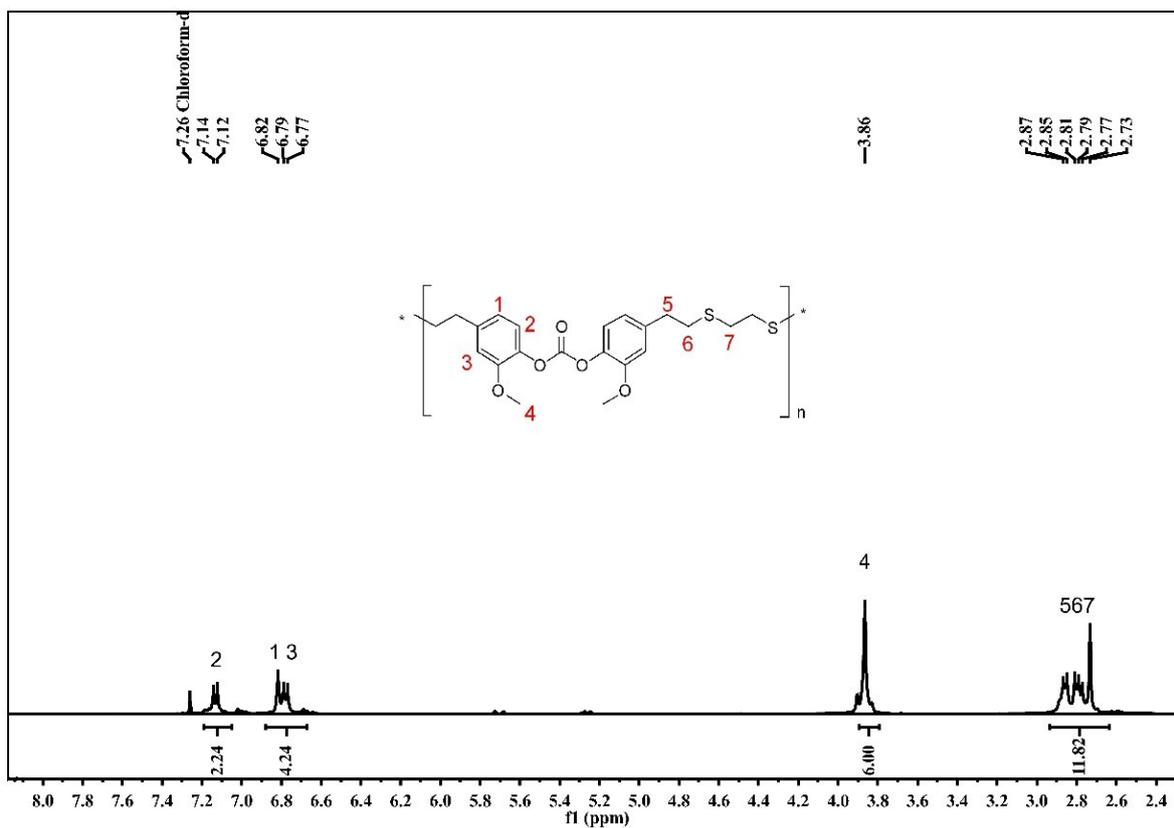


Figure S5.  $^1\text{H}$  NMR spectrum of **P2b3a** (400 MHz  $\text{CDCl}_3$ ).

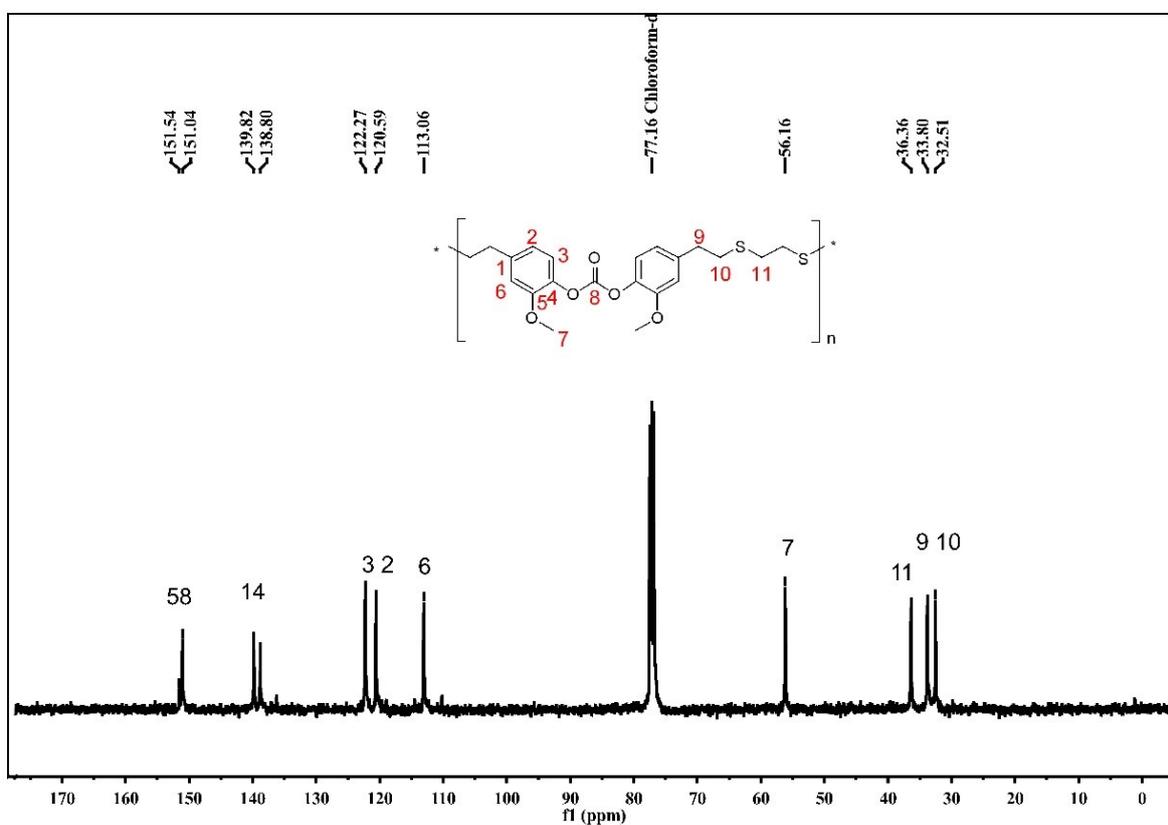


Figure S6.  $^{13}\text{C}$  NMR spectrum of **P2b3a** (125 MHz  $\text{CDCl}_3$ ).

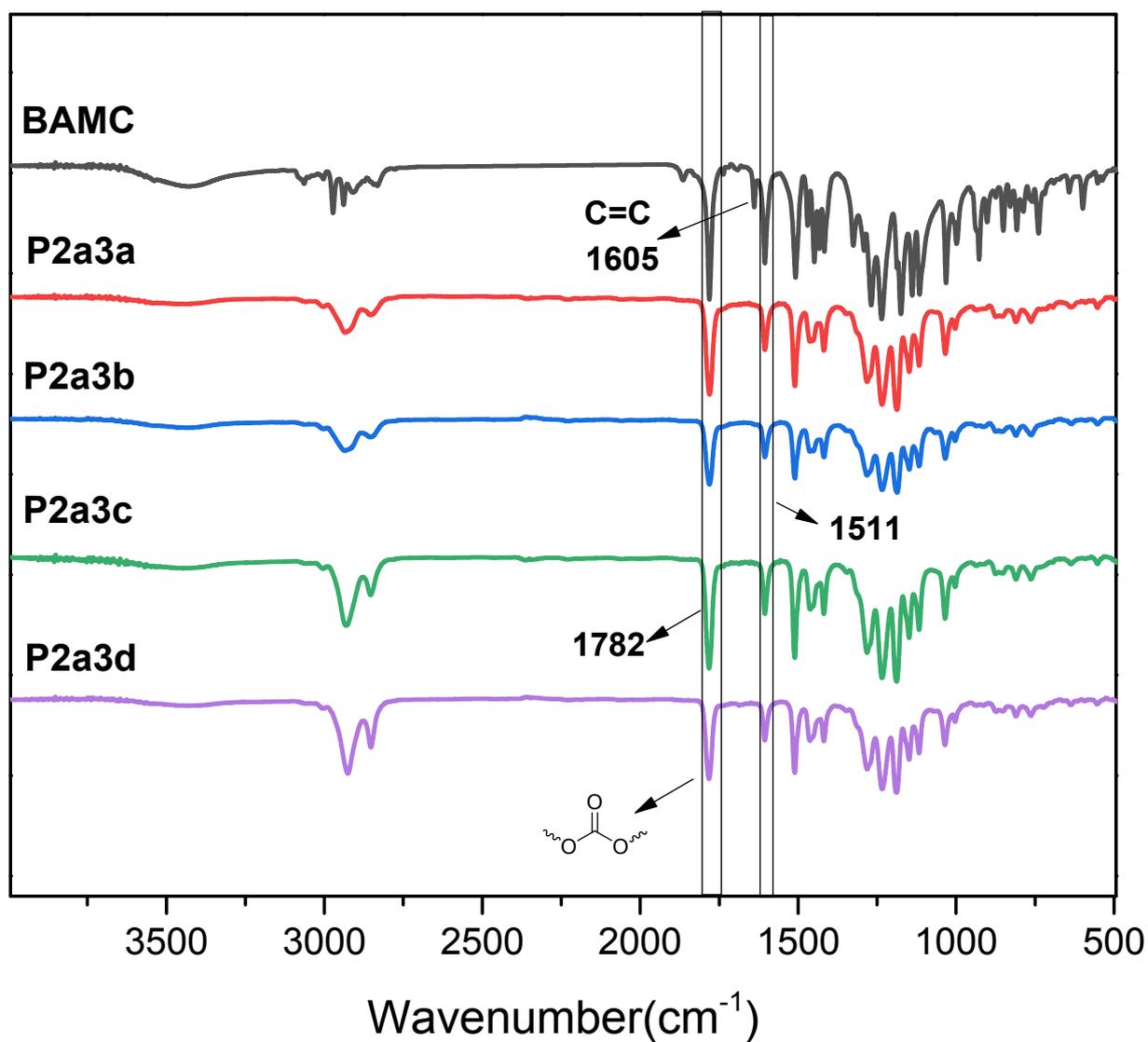


Figure S7. FTIR spectra of BAMC and representative resulting polymers.

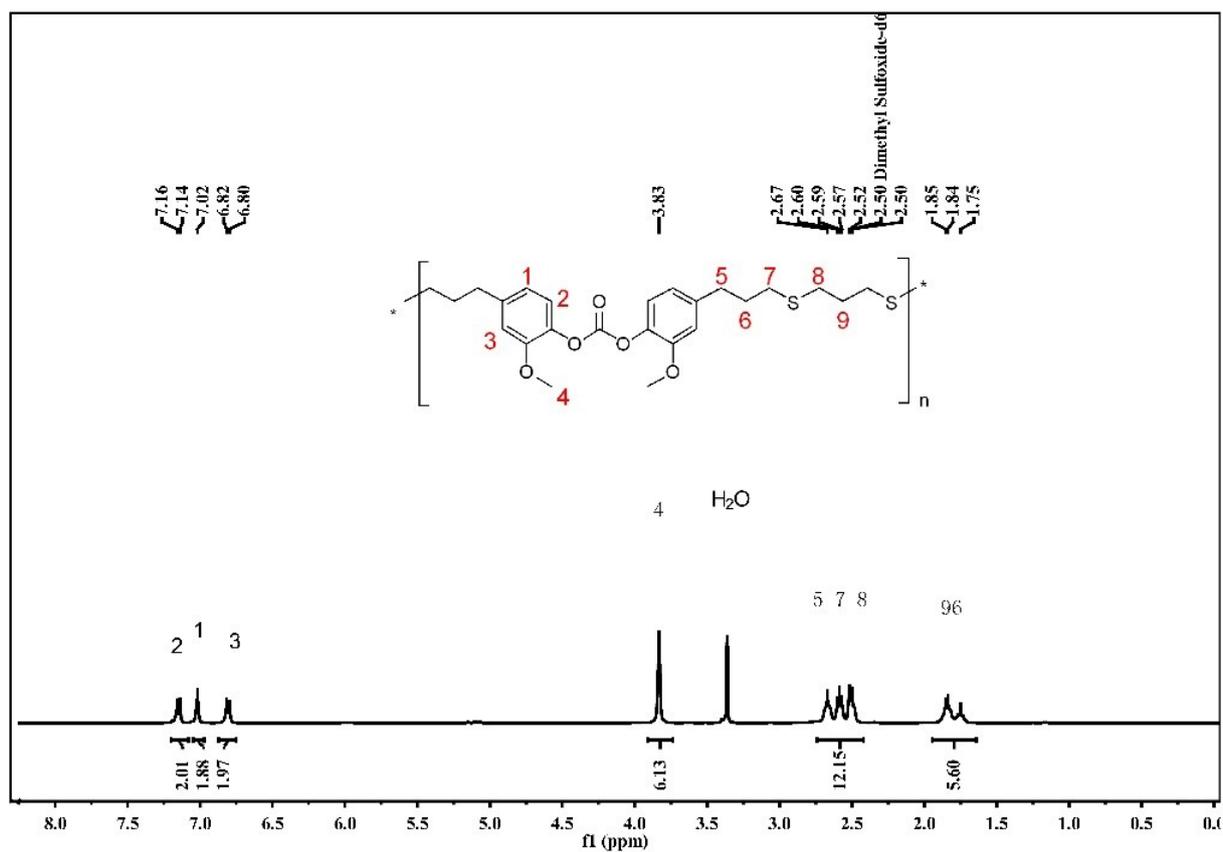


Figure S8. <sup>1</sup>H NMR spectrum of **P2a3b** (400 MHz DMSO-d<sub>6</sub>).

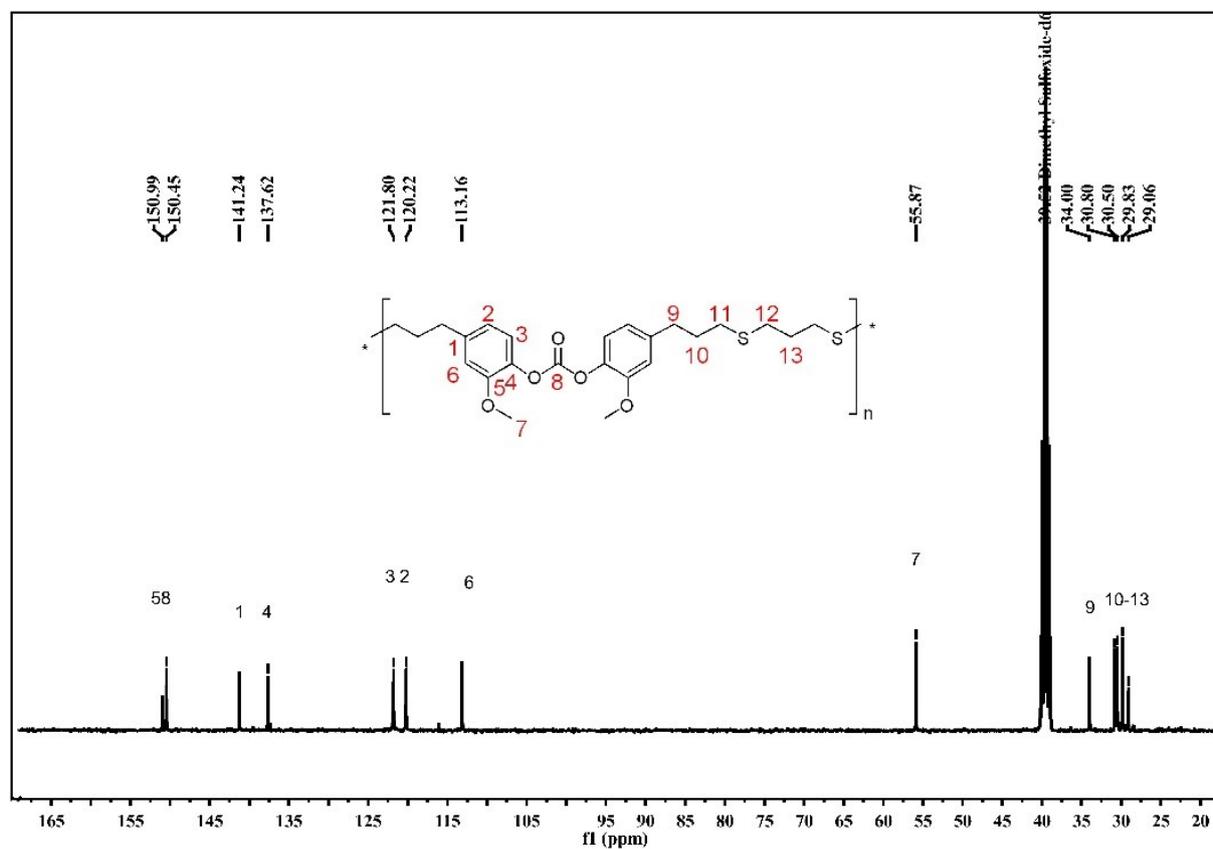


Figure S9. <sup>13</sup>C NMR spectrum of **P2a3b** (101 MHz DMSO-d<sub>6</sub>).

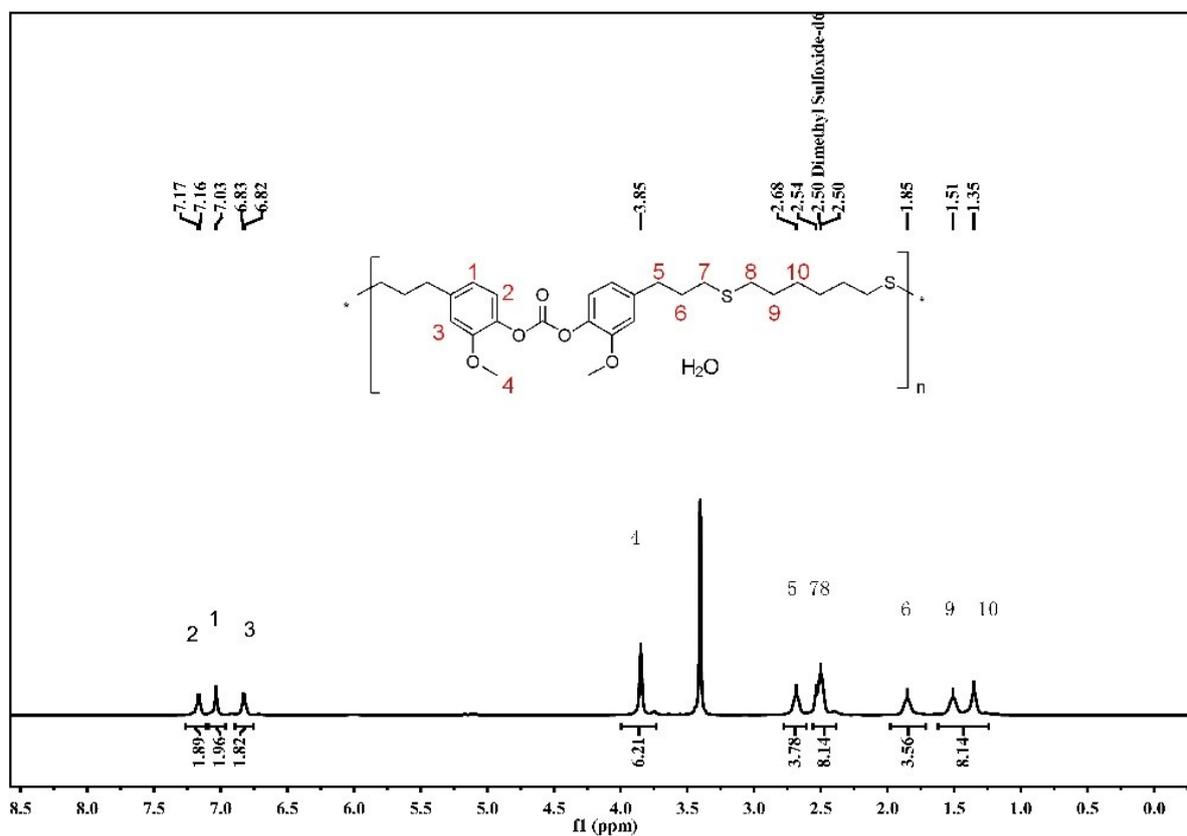


Figure S10.  $^1\text{H}$  NMR spectrum of **P2a3c** (400 MHz DMSO- $d_6$ ).

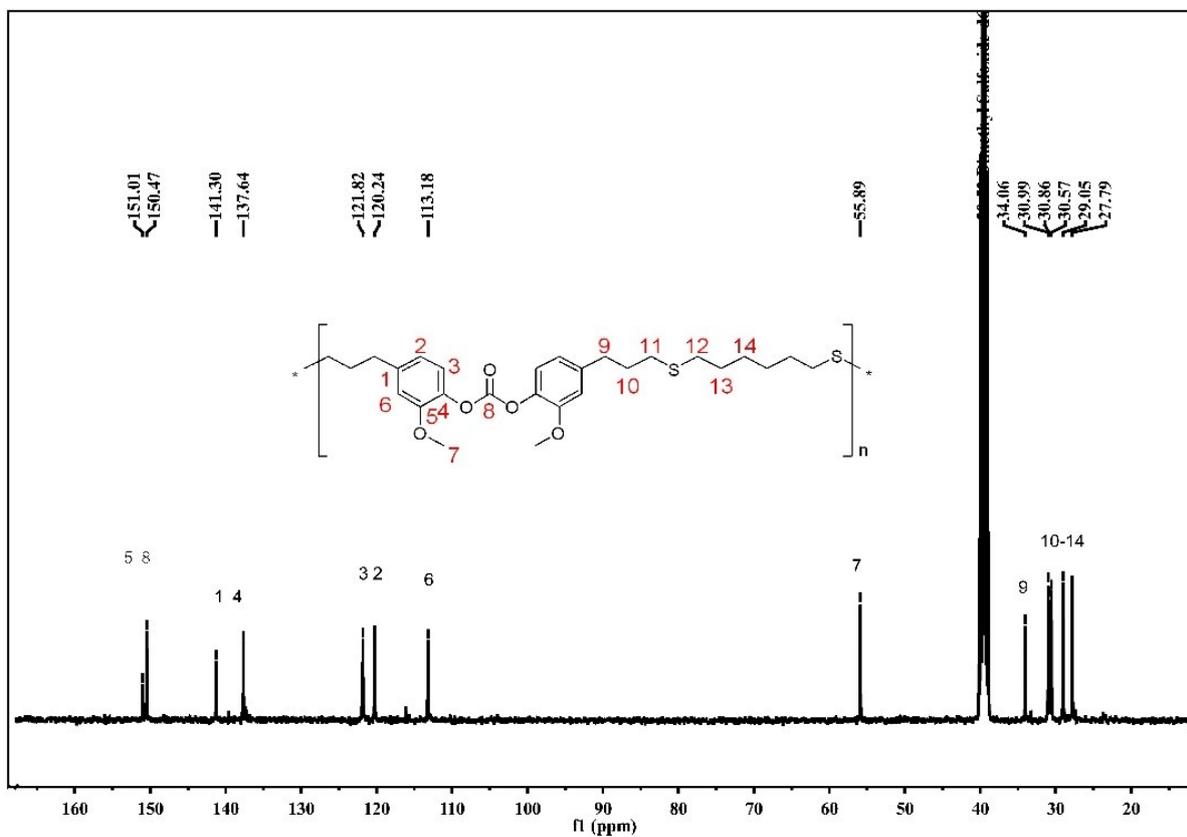


Figure S11.  $^{13}\text{C}$  NMR spectrum of **P2a3c** (101 MHz DMSO- $d_6$ ).

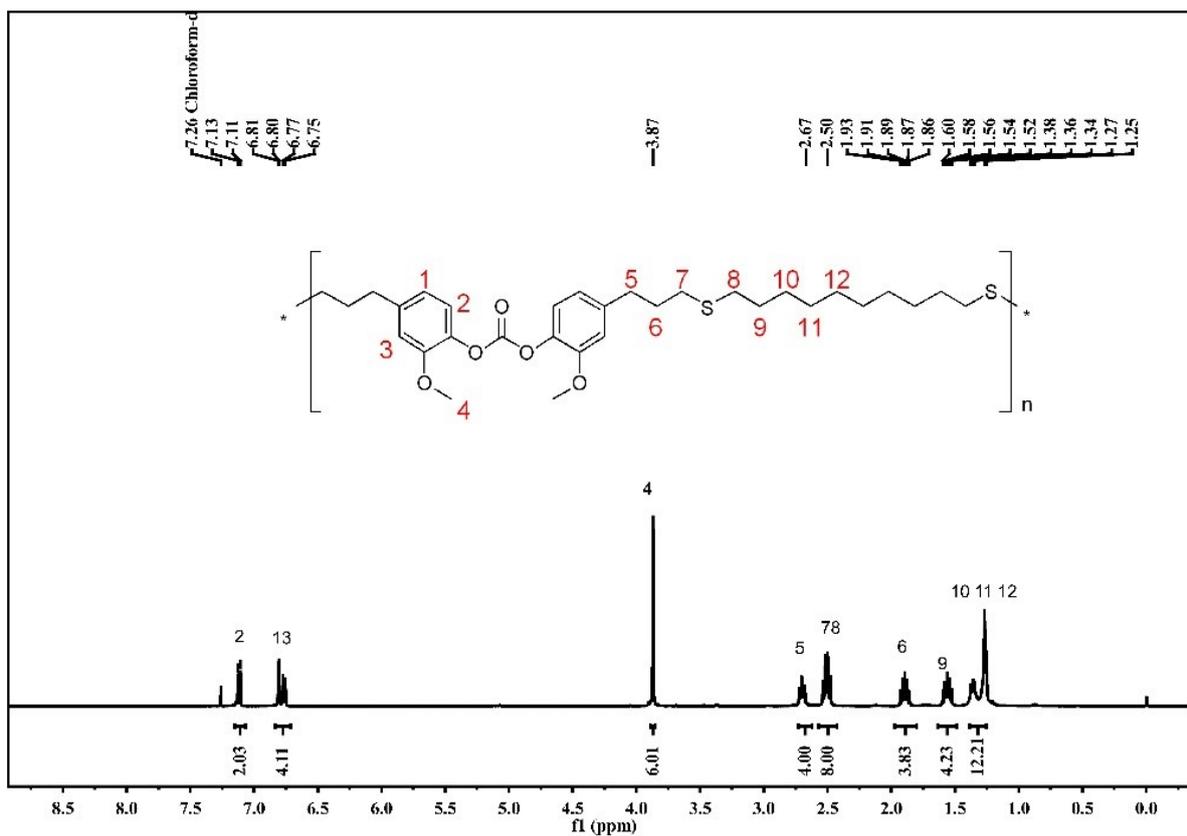


Figure S12. <sup>1</sup>H NMR spectrum of **P2a3d** (400 MHz CDCl<sub>3</sub>).

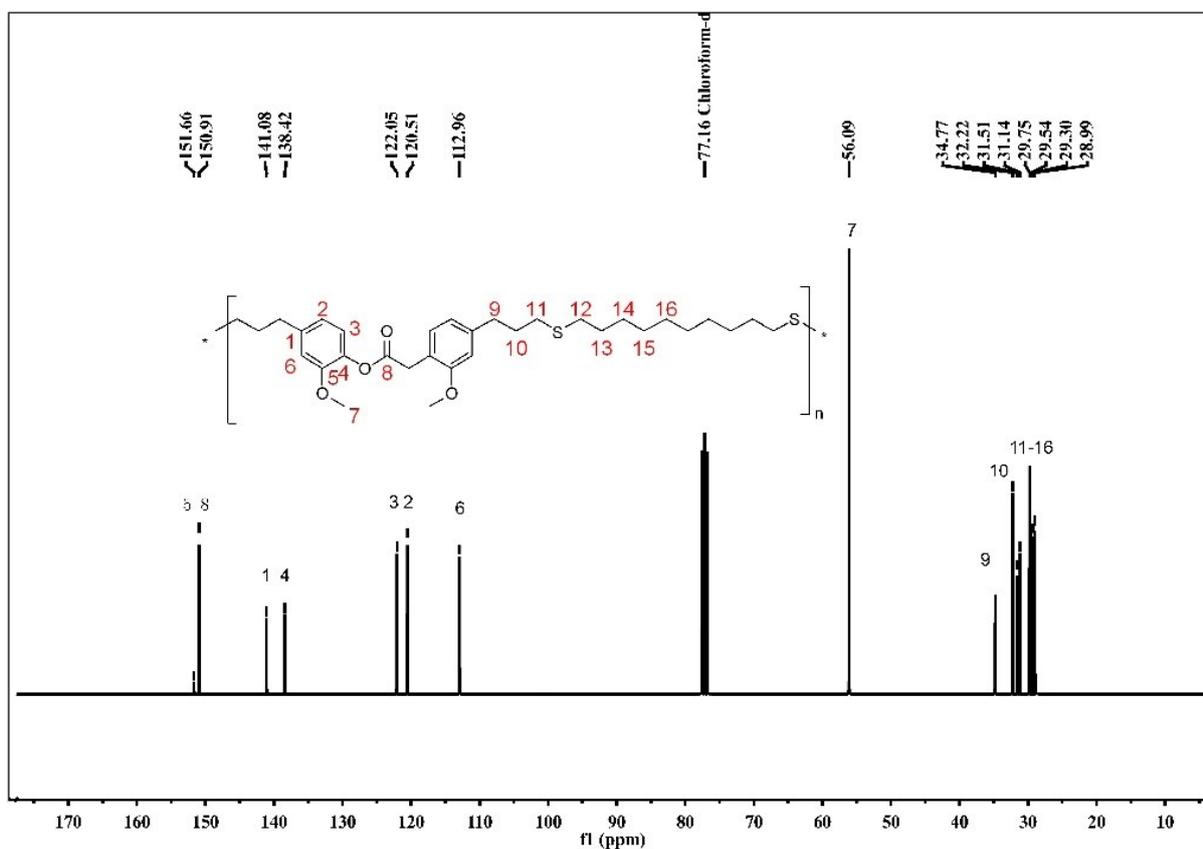


Figure S13. <sup>13</sup>C NMR spectrum of **P2a3d** (125 MHz CDCl<sub>3</sub>).

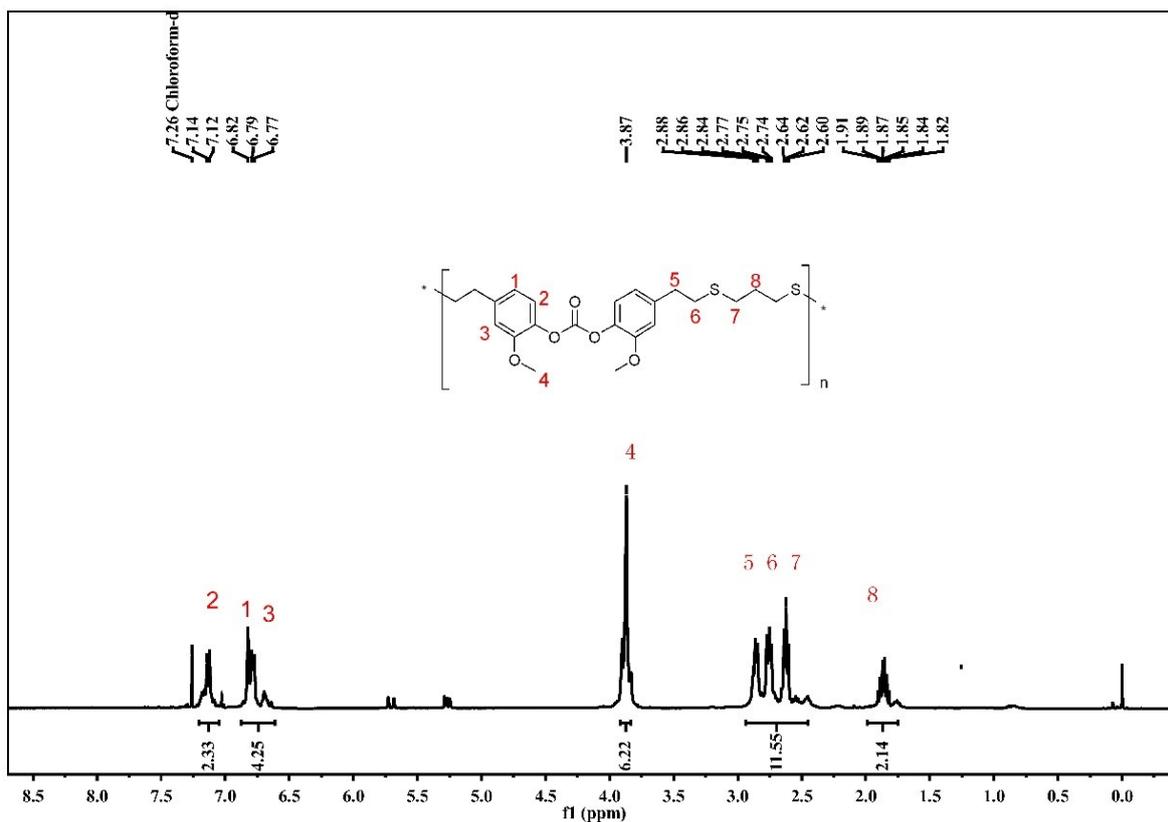


Figure S14.  $^1\text{H}$  NMR spectrum of **P2b3b** (400 MHz  $\text{CDCl}_3$ ).

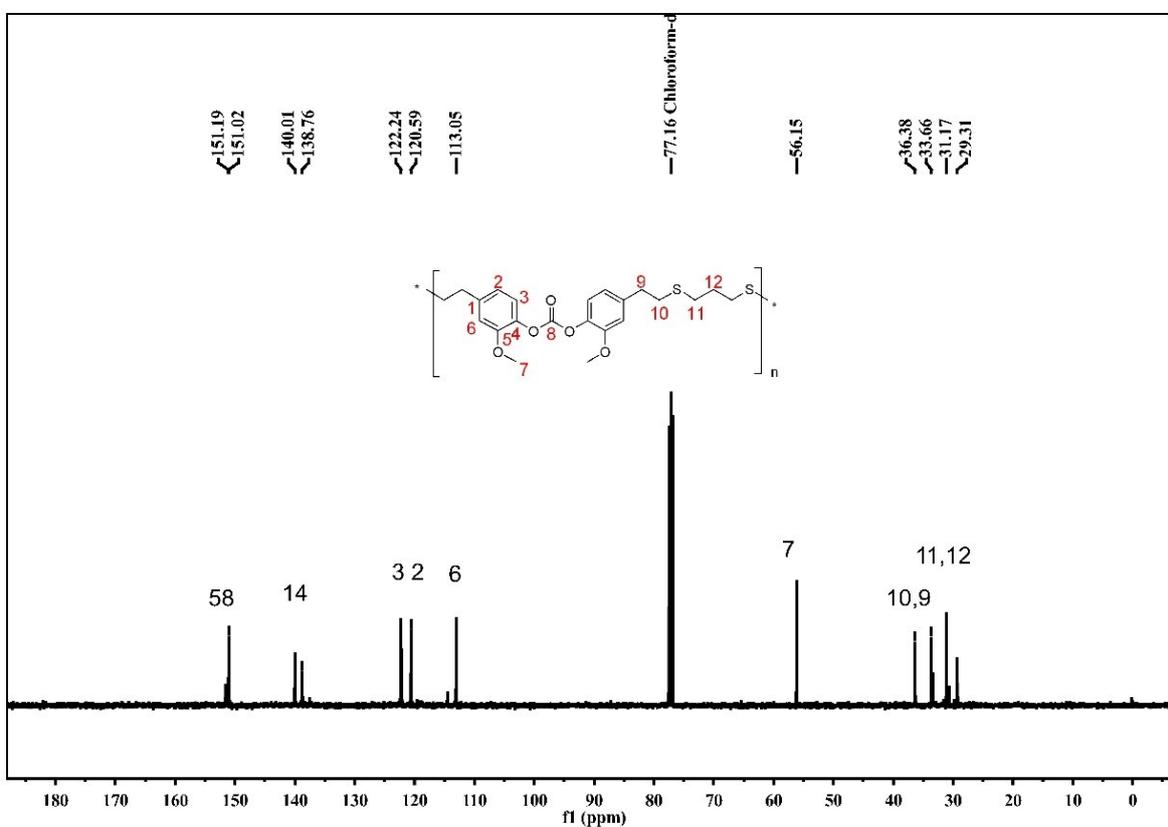


Figure S15.  $^{13}\text{C}$  NMR spectrum of **P2b3b** (125 MHz  $\text{CDCl}_3$ ).

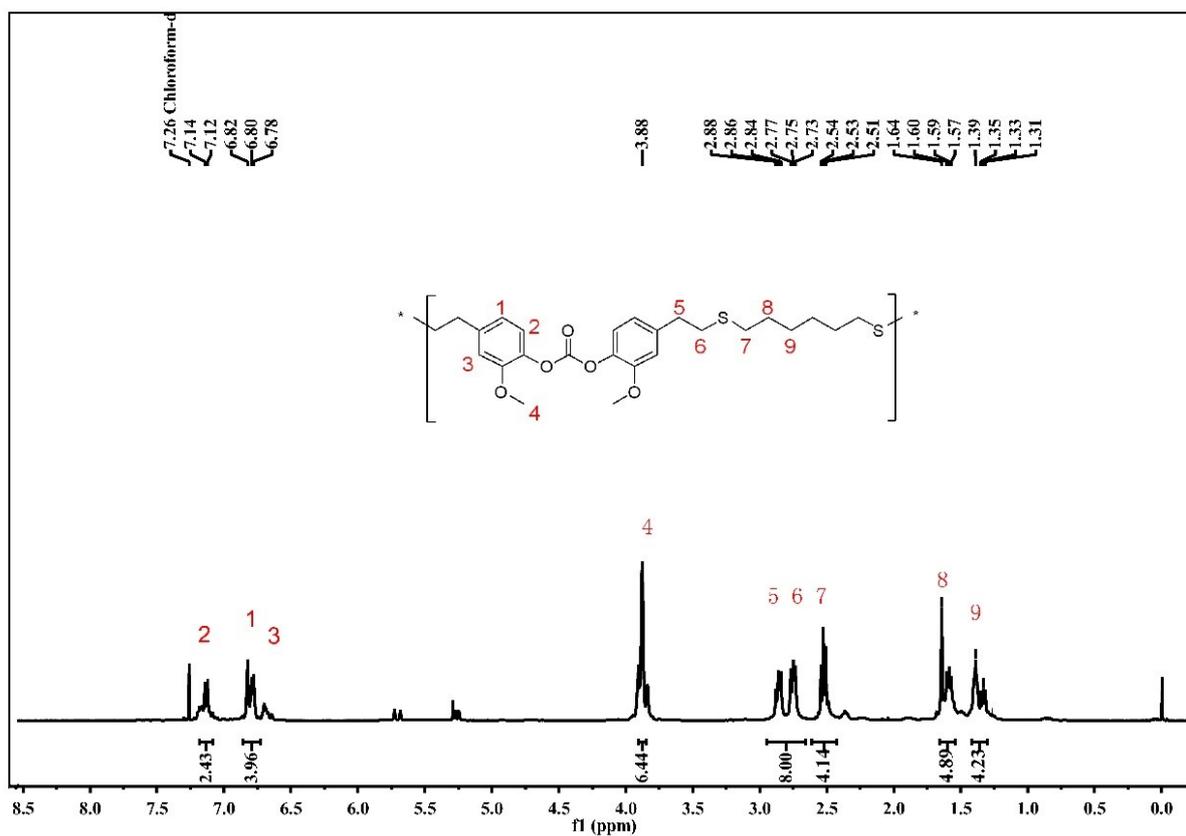


Figure S16. <sup>1</sup>H NMR spectrum of **P2b3c** (400 MHz CDCl<sub>3</sub>).

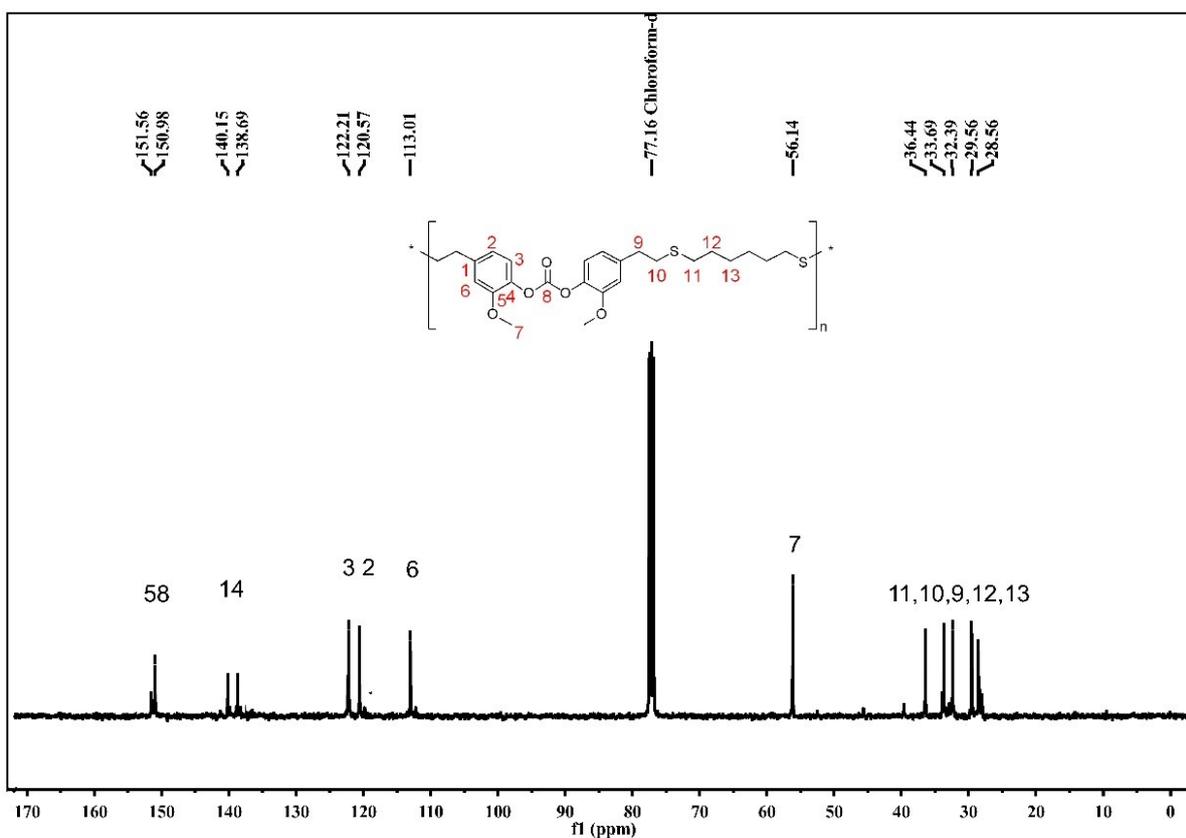


Figure S17. <sup>13</sup>C NMR spectrum of **P2b3c** (125 MHz CDCl<sub>3</sub>).

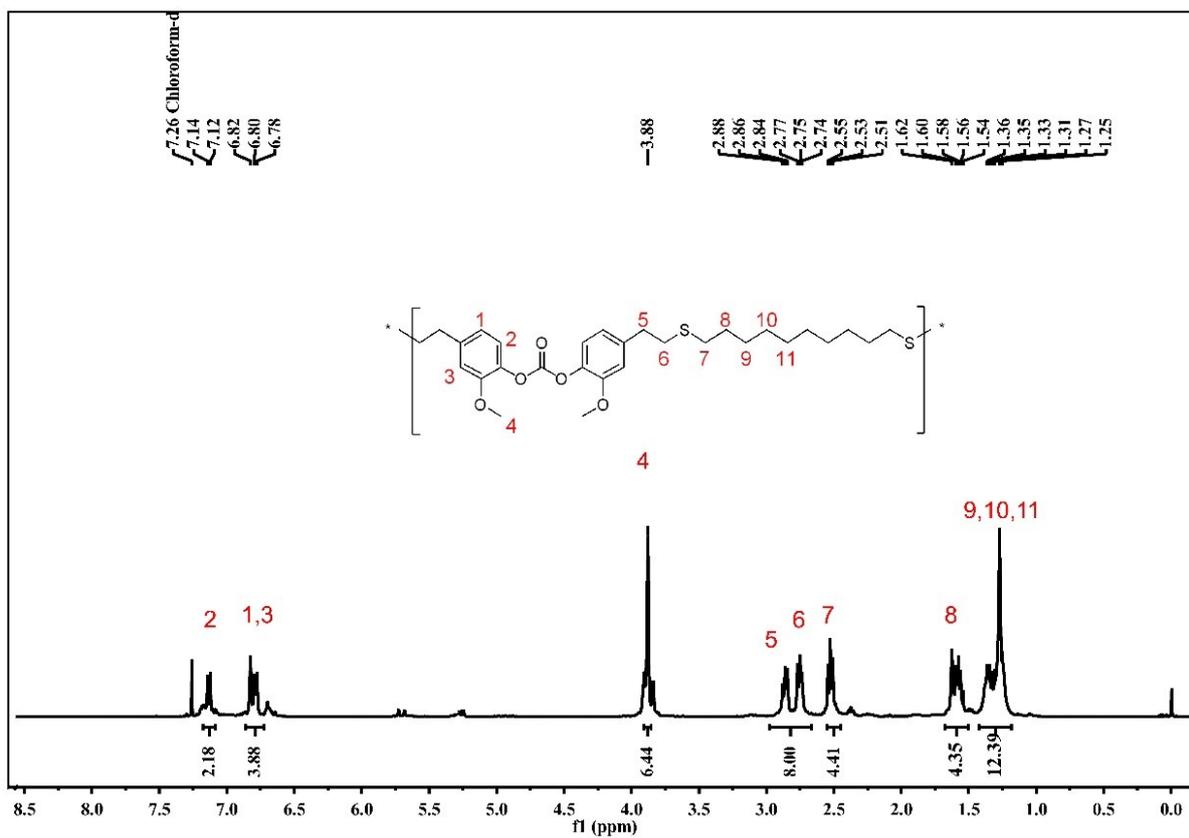


Figure S18. <sup>1</sup>H NMR spectrum of **P2b3d** (400 MHz CDCl<sub>3</sub>).

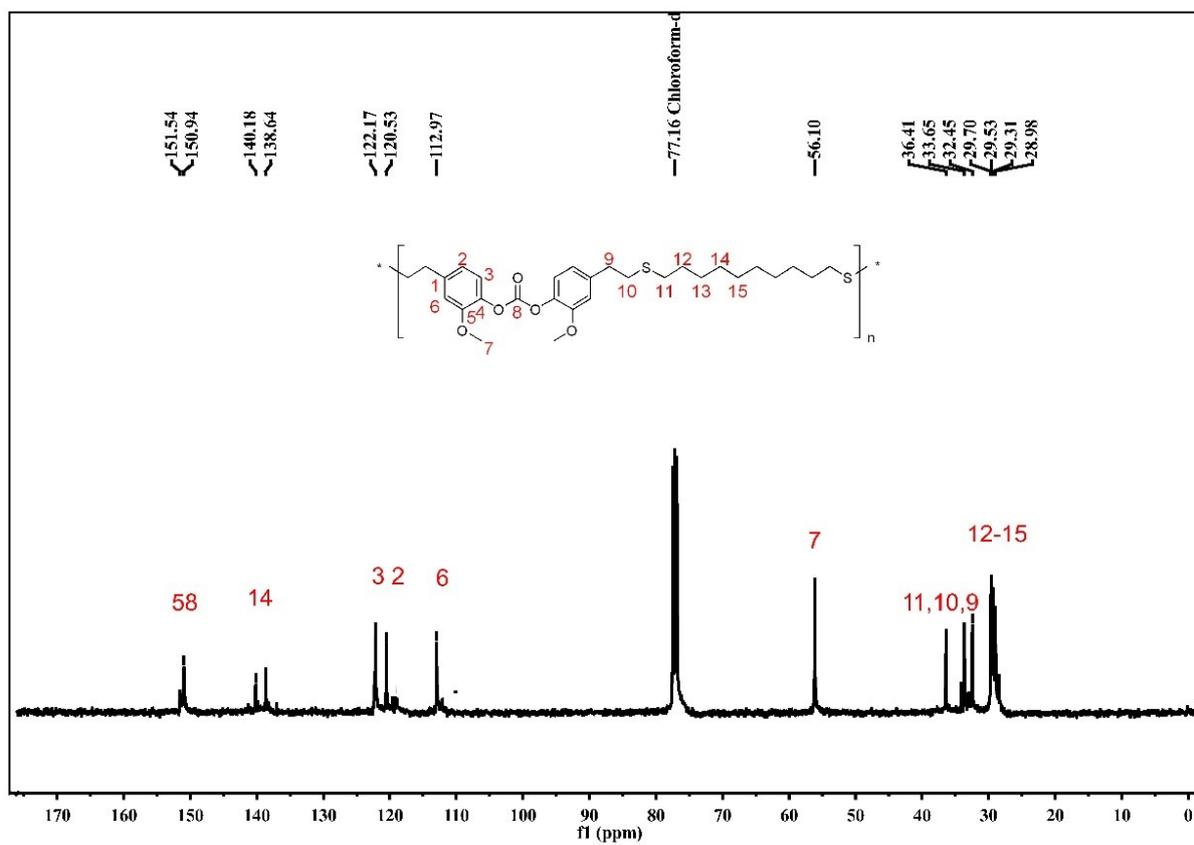


Figure S19. <sup>13</sup>C NMR spectrum of **P2b3d** (125 MHz CDCl<sub>3</sub>).

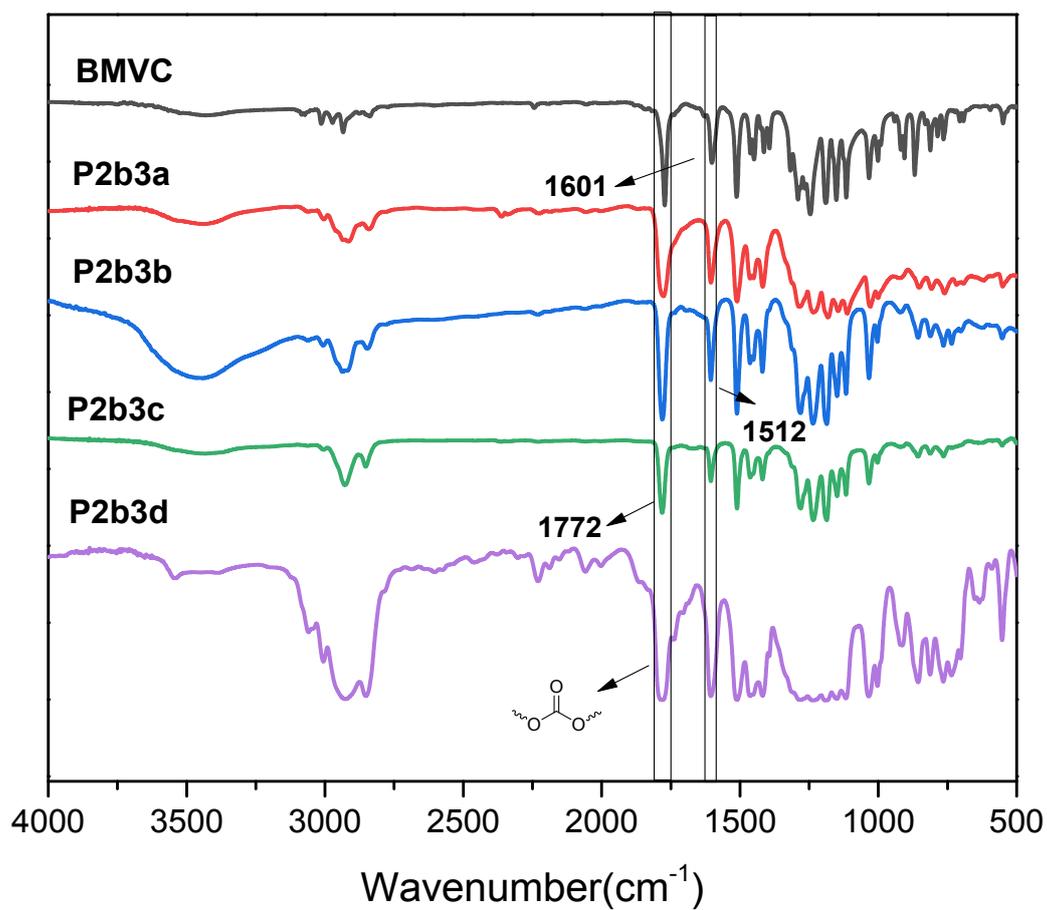


Figure S20. FTIR spectra of BMVC and representative resulting polymers.

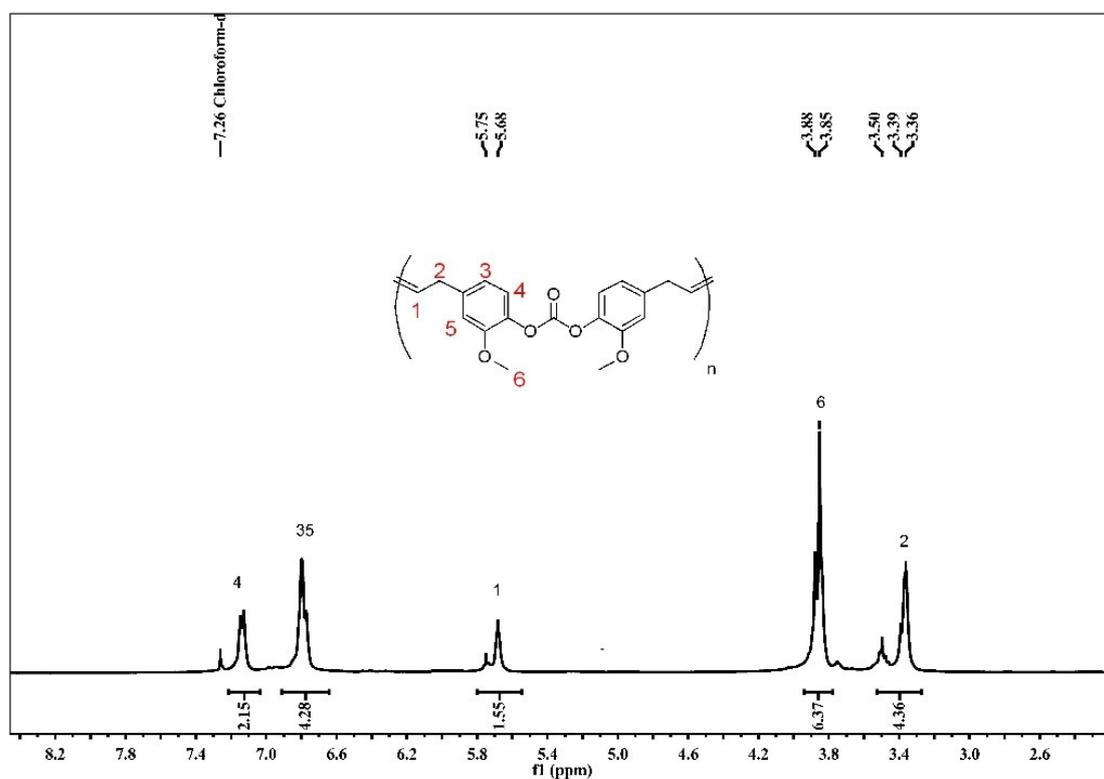


Figure S21.  $^1\text{H}$  NMR spectrum of **P2a** (400 MHz  $\text{CDCl}_3$ ).

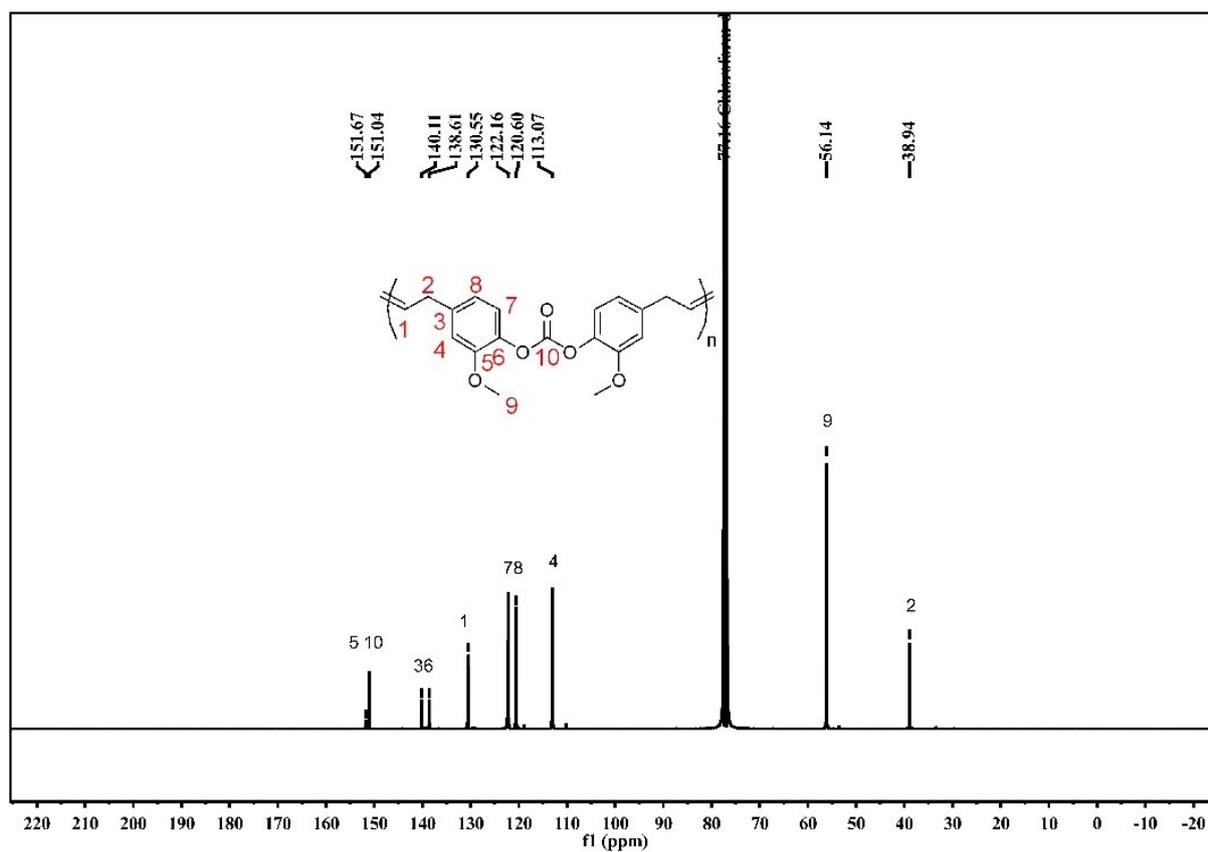


Figure S22.  $^{13}\text{C}$  NMR spectrum of **P2a** (101 MHz  $\text{CDCl}_3$ ).

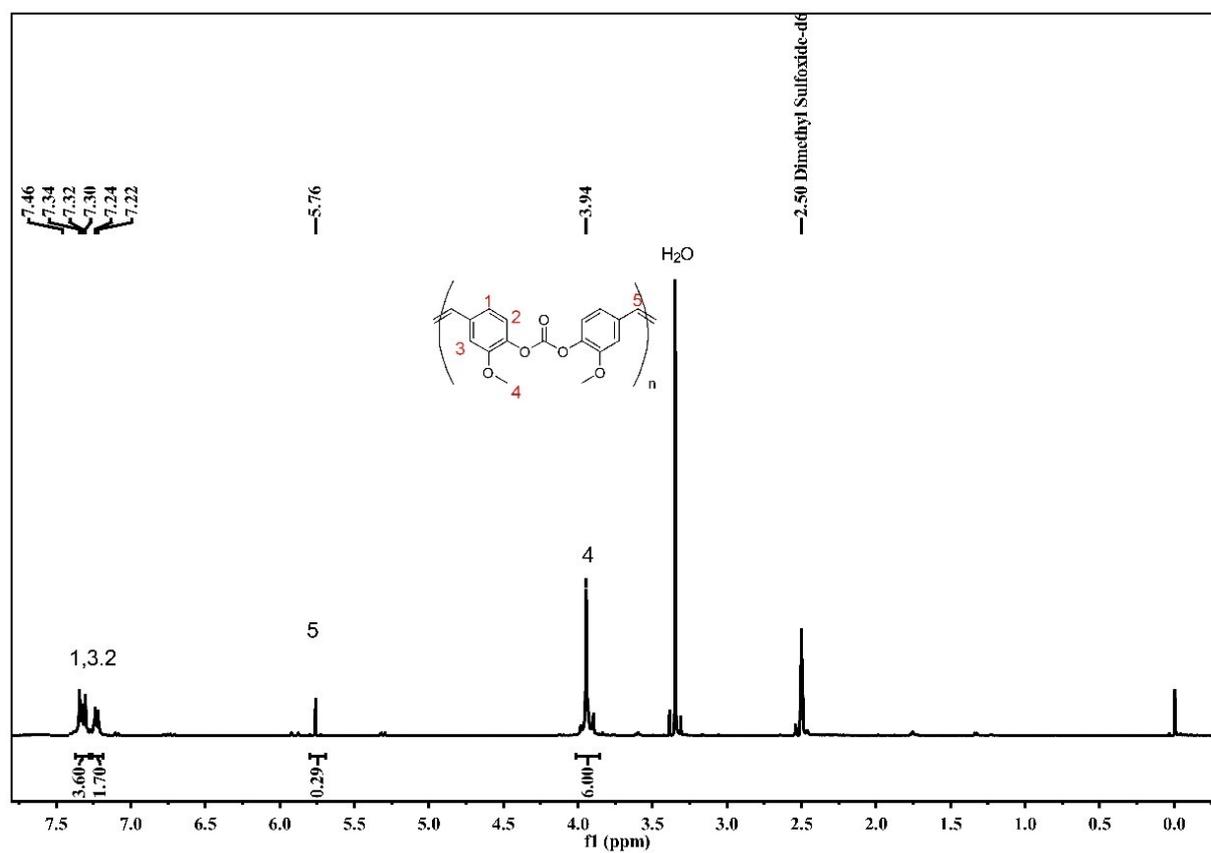


Figure S23.  $^1\text{H}$  NMR spectrum of **P2b** (400 MHz  $\text{DMSO-d}_6$ ).

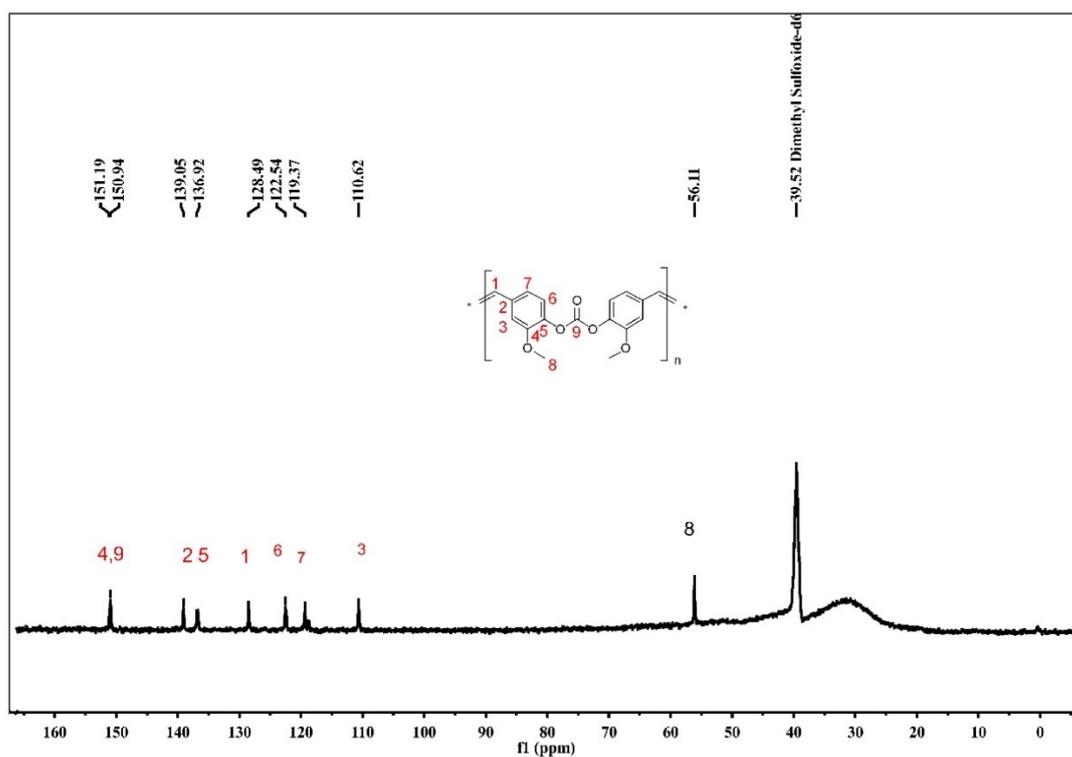


Figure S24.  $^{13}\text{C}$  NMR spectrum of **P2b** (101 MHz DMSO- $d_6$ ).

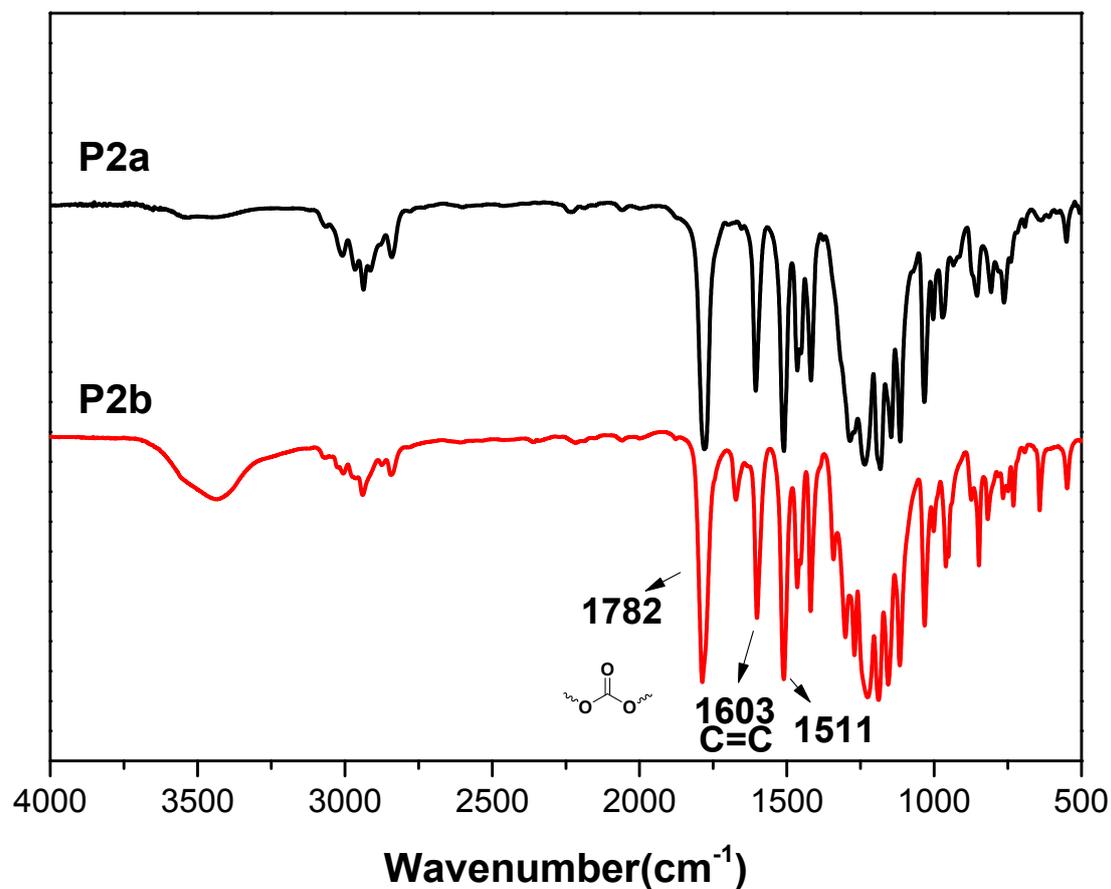


Figure S25. FTIR spectra of **P2a** and **P2b**.

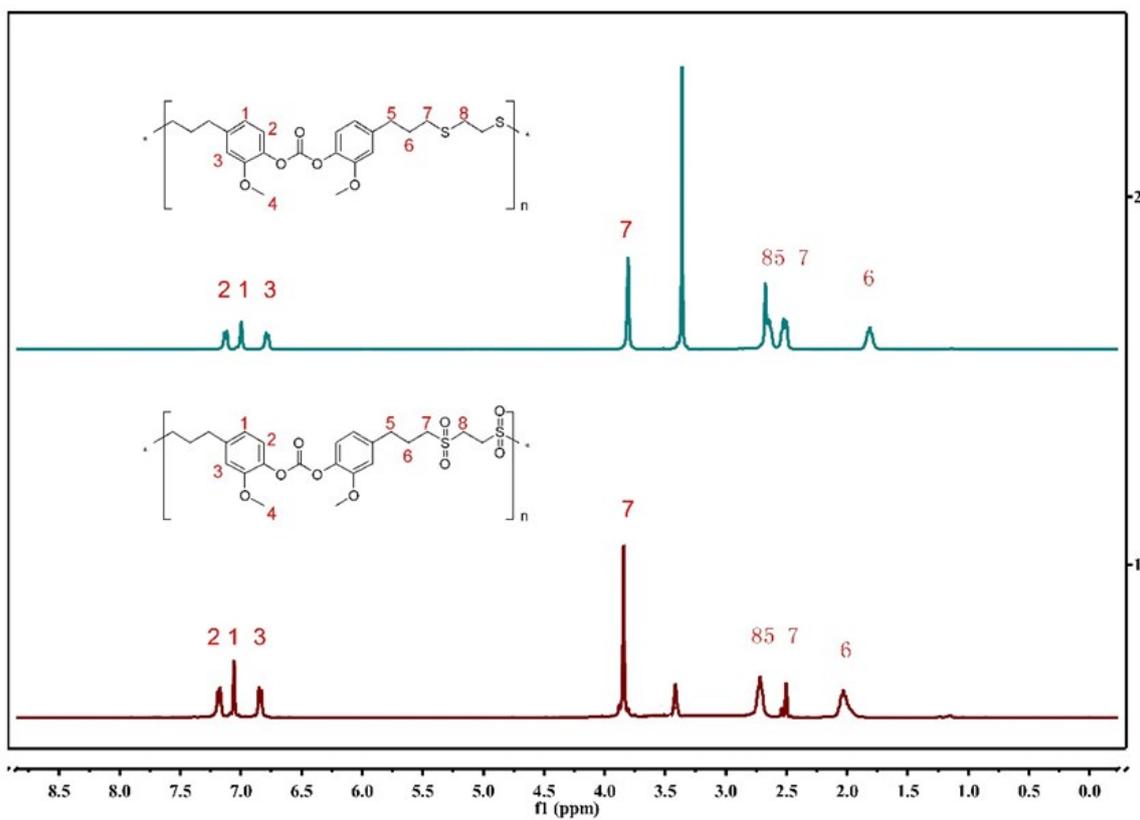


Figure S26. Overlay of  $^1\text{H}$  NMR spectra (DMSO- $d_6$ ) of **P2a3a** and its oxidation product **PO2a3a**.

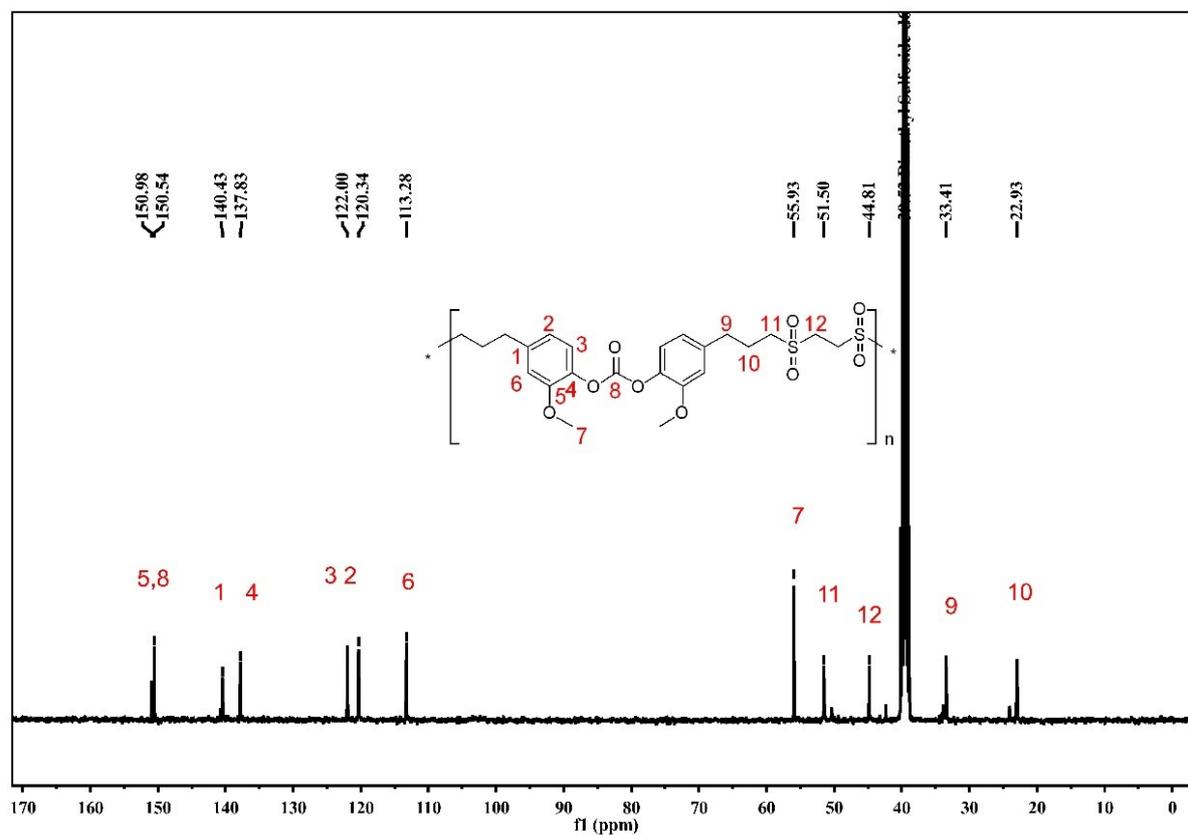


Figure S27.  $^{13}\text{C}$  NMR spectrum of **PO2a3a** (101 MHz DMSO- $d_6$ ).

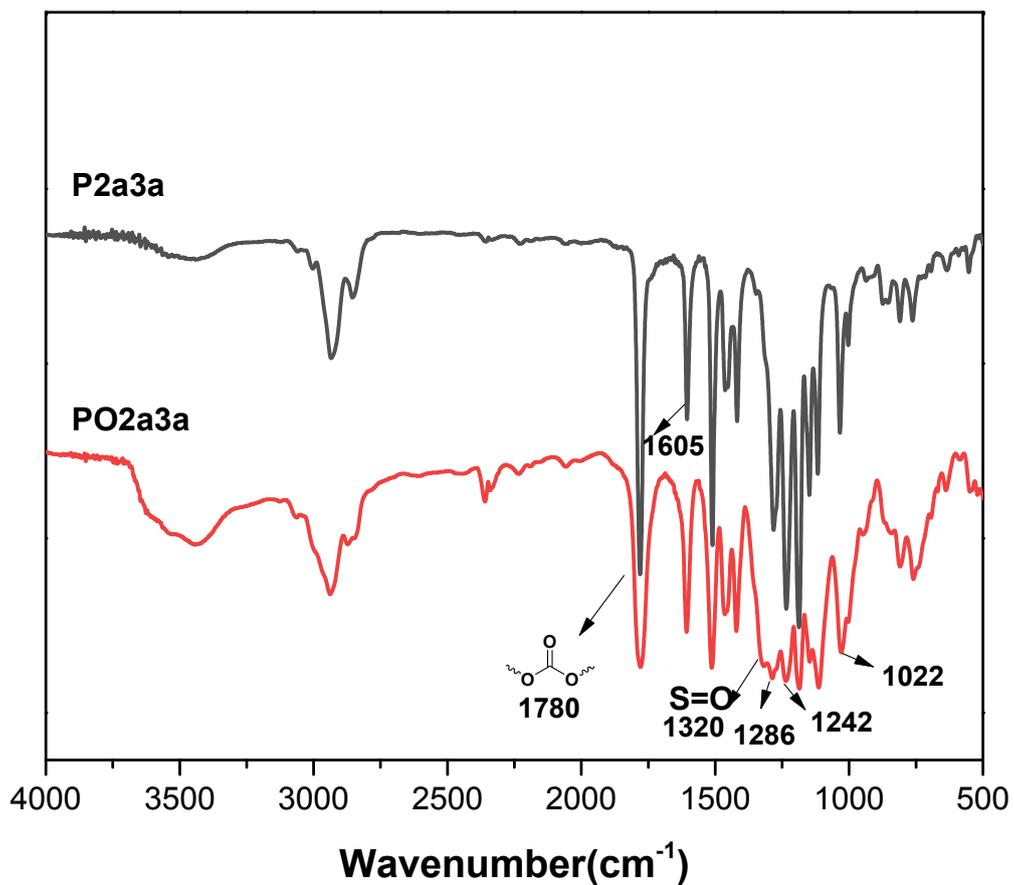


Figure S28. FTIR spectra of **P2a3a** and its oxidation product

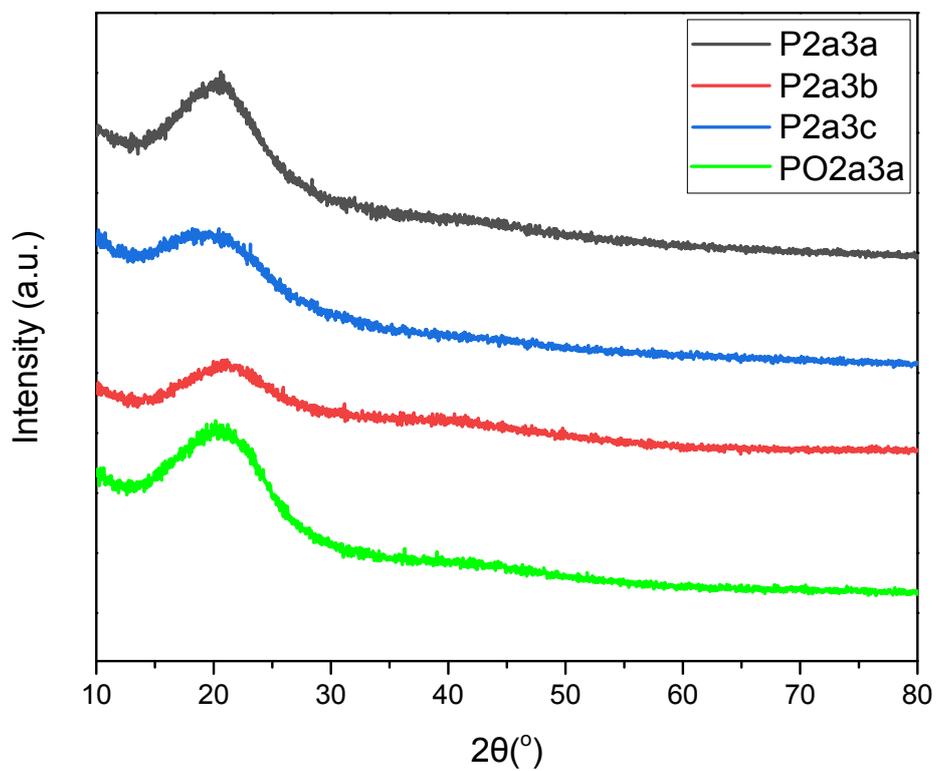


Figure S29. WXR curves of **P2a3a**, **P2a3b**, **P2a3c** and **PO2a3a**.

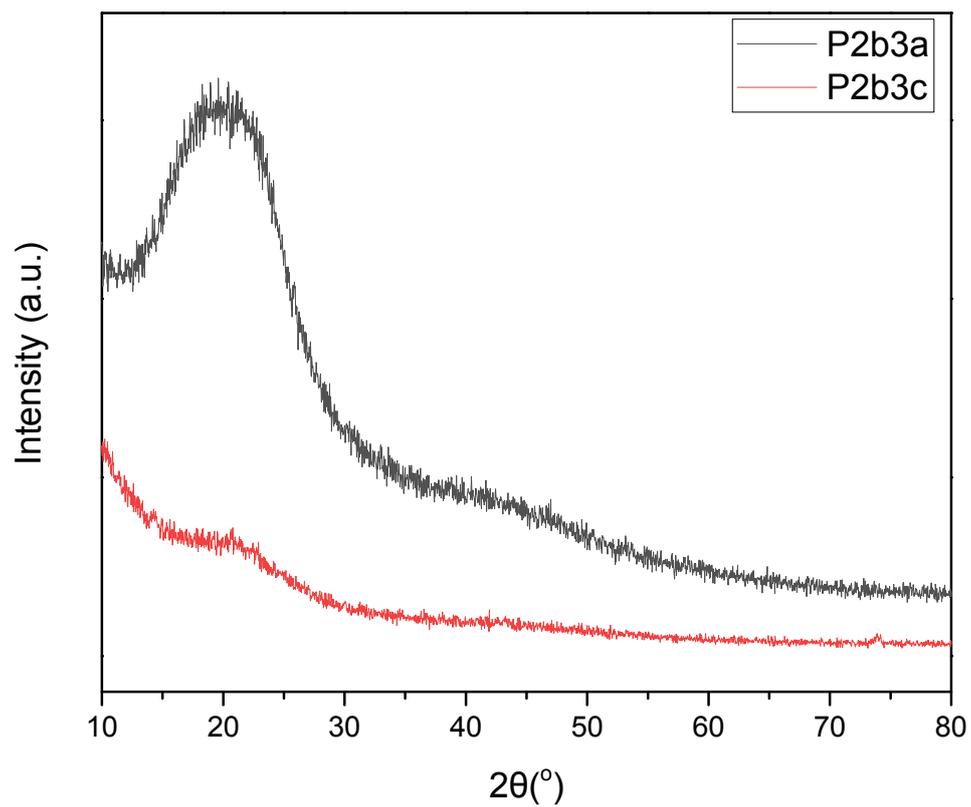


Figure S30. WXR curves of **P2b3a** and **P2b3c**.

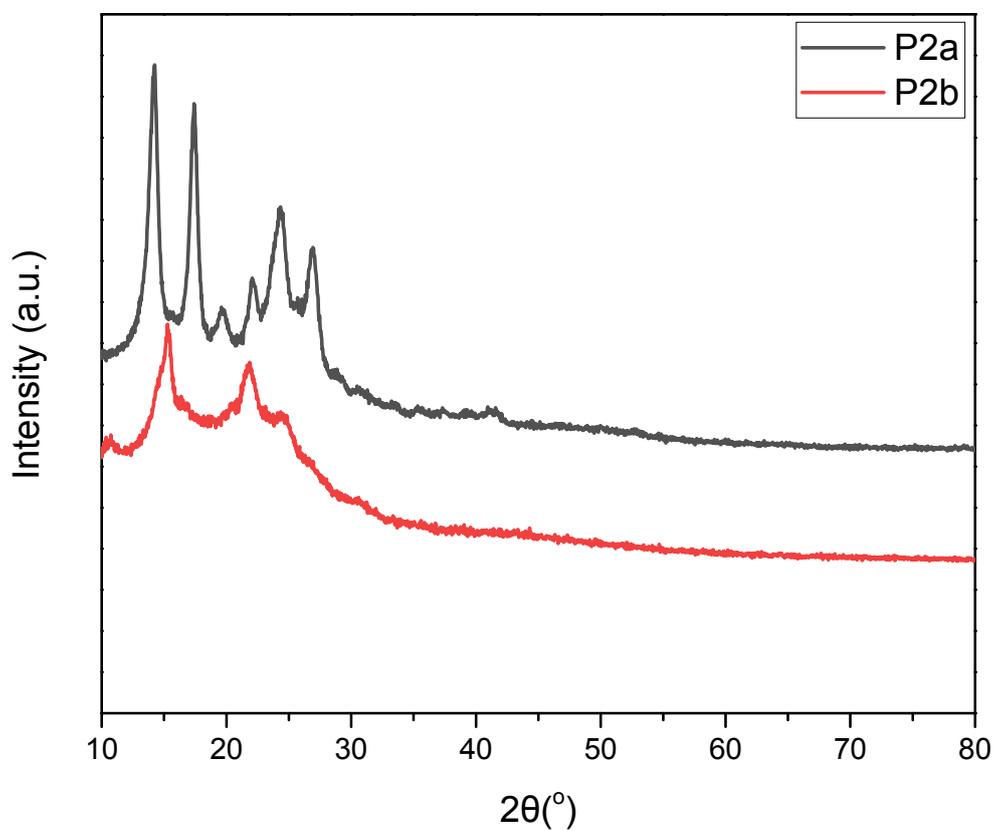


Figure S31. WXR curves of **P2a** and **P2b**.

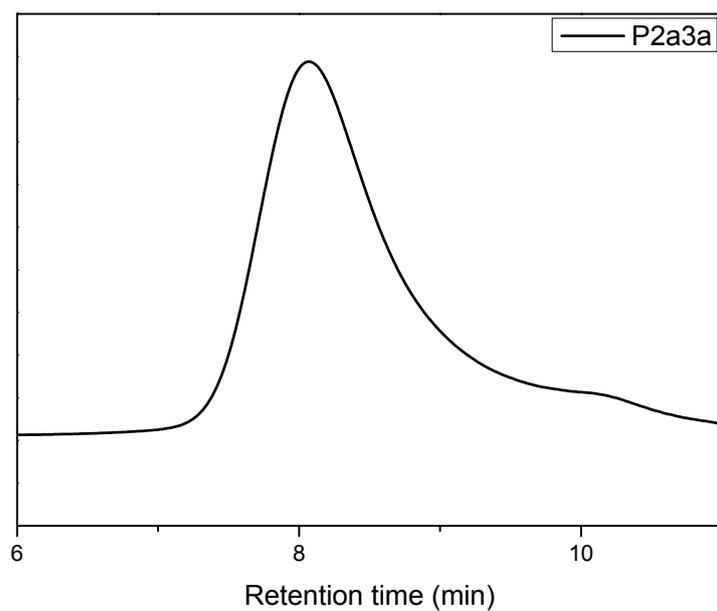


Figure S32. GPC curve of **P2a3a**.

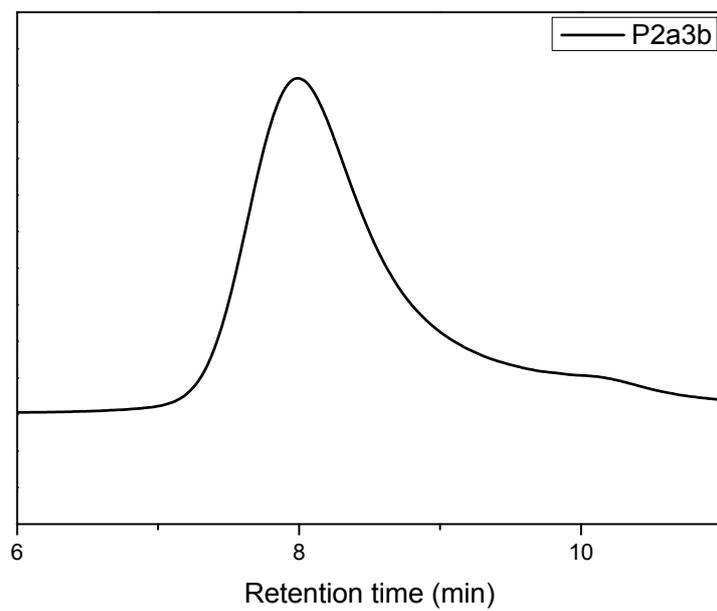


Figure S33. GPC curve of **P2a3b**.

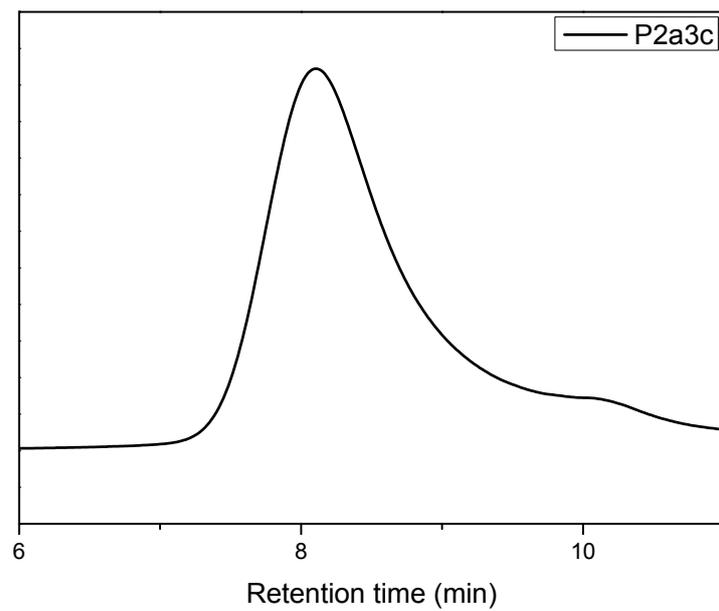


Figure S34. GPC curve of **P2a3c**.

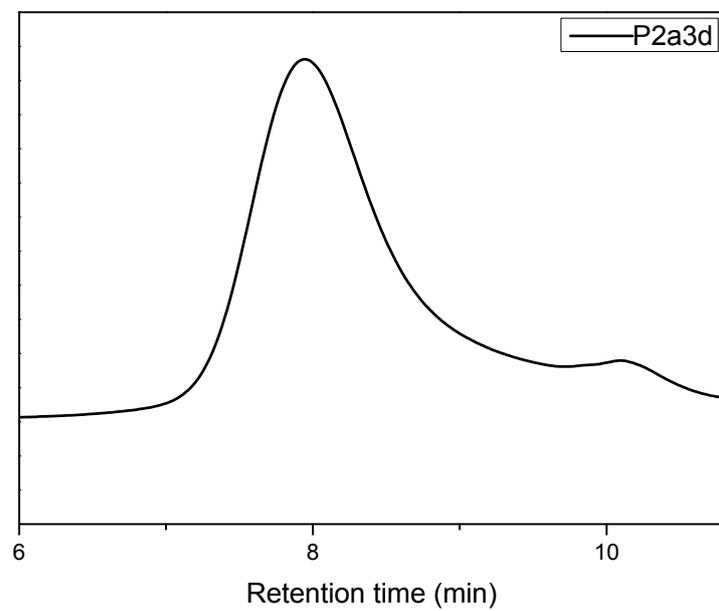


Figure S35. GPC curve of **P2a3d**.

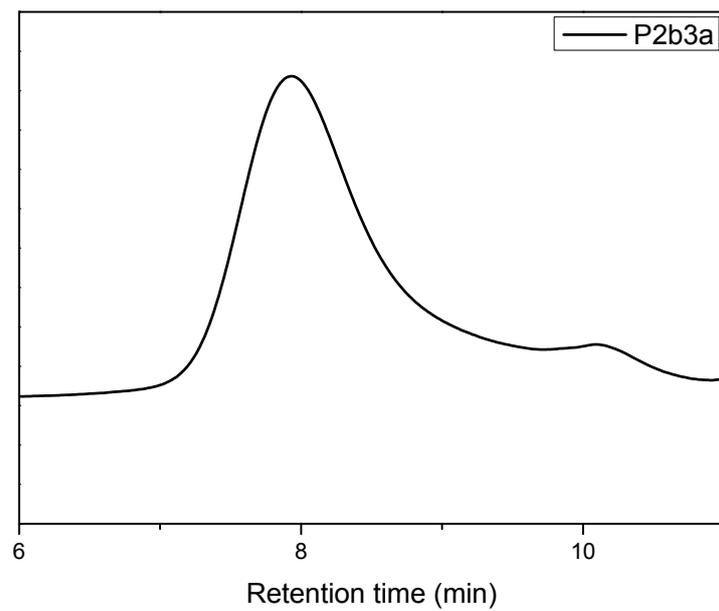


Figure S36. GPC curve of **P2b3a**.

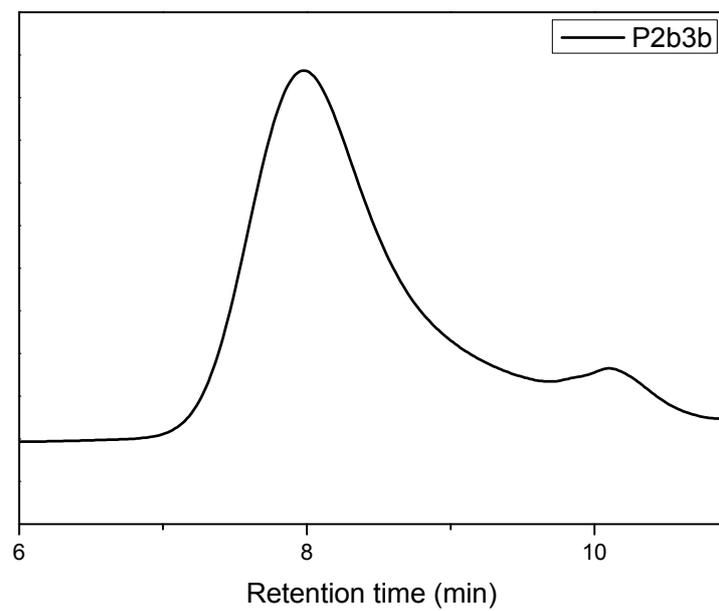


Figure S37. GPC curve of **P2b3b**.

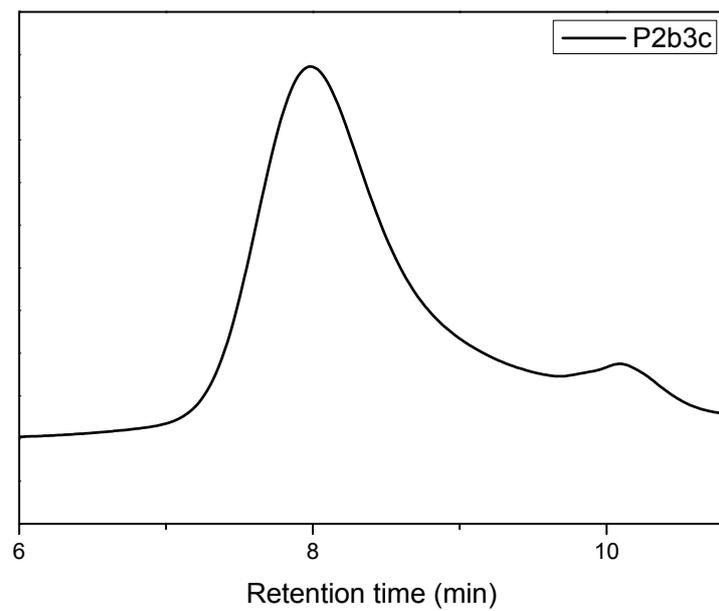


Figure S38. GPC curve of **P2b3c**.

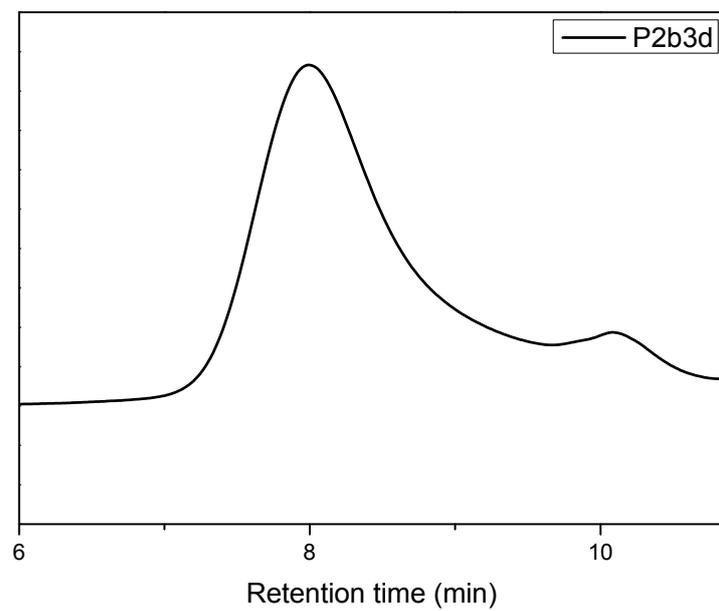


Figure S39. GPC curve of **P2b3d**.

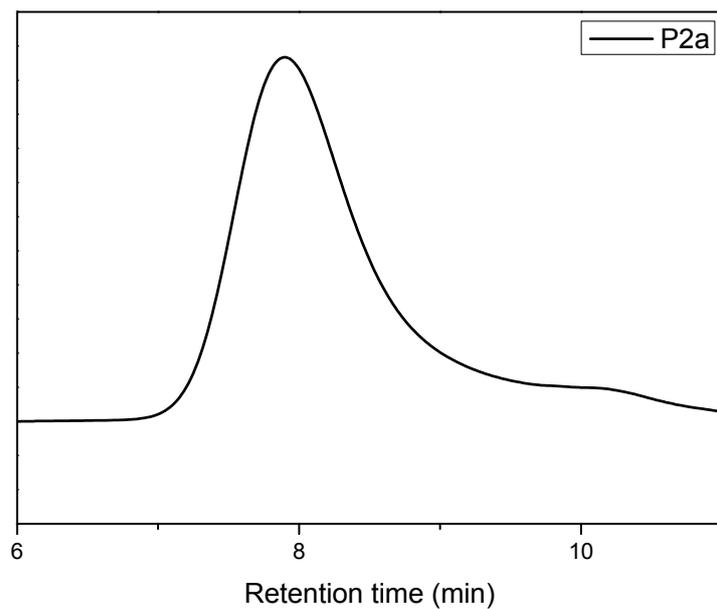


Figure S40. GPC curve of **P2a**.

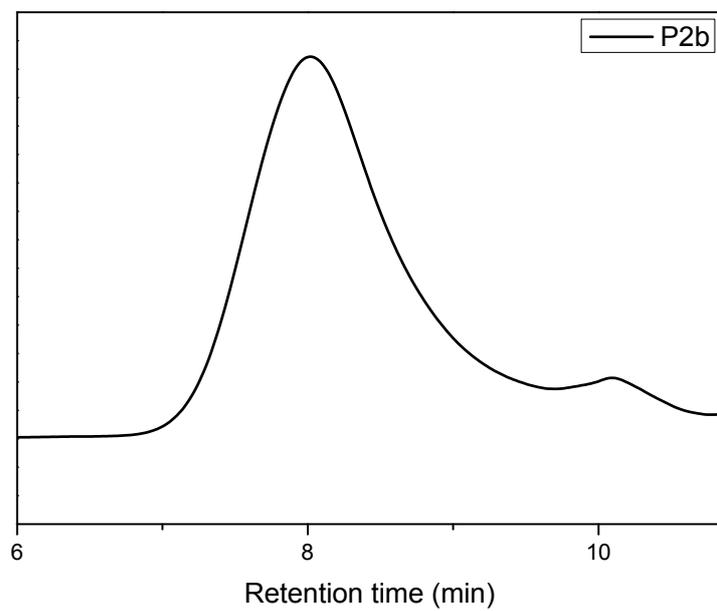


Figure S41. GPC curve of **P2b**.

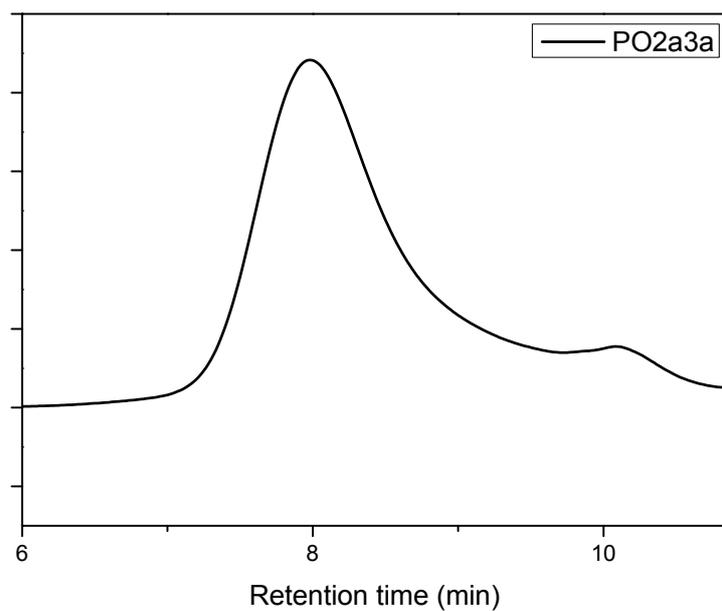


Figure S42. GPC curve of **PO2a3a**.

1. D. Bai, Q. Chen, Y. Chai, T. Ren, C. Huang, I. D. Ingram, M. North, Q. Zheng and H. Xie, *RSC advances*, 2018, **8**, 34297-34303.
2. Q. Zou, L. Ba, X. Tan, M. Tu, J. Cheng and J. Zhang, *Journal of materials science*, 2016, **51**, 10596-10607.