

Supplementary Information

Preparation of lignin/glycerol-based bis(cyclic carbonate) for synthesis of polyurethanes

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Experimental Details

Materials, chemicals and instruments

Creosol (99%) was purchased from Acros and used as received. Epichlorohydrin and 1,6-hexamethylene diamine (HMDA) were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai China). 1,5,7-triazabicyclo[4,4,0]-dec-5-ene (TBD) was obtained from J&K Scientific Ltd.. Diaminehydrate (DAH) (99+%) was supplied by Alfa. Isophorondiamine (IPDA) was purchased from Aladdin. All other chemicals were supplied by local suppliers and used without further purification.

Melting points were determined by X-4 Melting Point apparatus (Beijing Tech Instrument Co. Ltd.). ¹H and ¹³C NMR spectra were recorded on Bruker AVANCE III 500 MHz or 400 MHz. Chemical shifts (δ) were reported in parts per million (ppm). Fourier transform infrared spectroscopy (FT-IR) measurements were recorded on Tensor 27 in the range of 400-4000 cm⁻¹. High-resolution mass spectra (HRMS) were performed on a LTQ Orbitrap Elite (Thermo). Wide-angle X-ray powder diffraction (WAXD) was performed by X'pert Pro-1 X-ray diffractometer using Ni-filtered Cu KR radiation (40 kV, 30 mA) with 5 °/min scanning rate at room temperature. Diffraction intensity was measured in a range of $2\theta = 5-90^\circ$.

Gel permeation chromatography (GPC) analyses were performed on TDA302 equipped with small angle light scattering detector in THF (flow rate 1.0 mL/min) at 30 °C calibration using polystyrenes as standards. Thermogravimetric analyses (TGA) were acquired under nitrogen with a TGA-DSC STA 449F-3 instruments. About 5 mg of sample was heated at 10 °C/min from 40 to 700 °C. Differential scanning calorimetry (DSC) experiments were performed on a DSC 204 HP instruments. The samples (5-10 mg) were enclosed in aluminum pan and placed in the heating cell with an empty pan as reference. All samples were heated under nitrogen flow (20 mL/min) from -

60 °C to 200 °C at a heating rate of 10 °C/min. The glass transition temperature was recorded from the second run heating cycle.

Typical procedure for the synthesis of bisphenol

The lignin-based bisphenol was prepared according to our previous report. Briefly, creosol (0.276 g, 2 mmol), 37% formaldehyde (0.081 g, 1 mmol) and lignosulfonic acid (20 mmol%) were added to the deionized water (2 mL). The reaction was heated at 100 °C under N₂ for 6 h and precipitates were formed. The solution was decanted and the solid was purified by column chromatography using petroleum ether/ethyl acetate (3:1) as eluents.

5,5'-methylenebis(2-methoxy-4-methylphenol) (**1**) yield 52.7%. m.p. 134-136 °C. ¹H NMR(500 MHz DMSO-d₆), δ = 8.54 (s, 2H), 6.73 (s, 2H), 6.30 (s, 2H), 3.72 (s, 6H), 3.57 (s, 2H), 2.09 (s, 6H). ¹³C NMR (125 MHz DMSO-d₆), δ = 145.5, 144.2, 130.8, 126.0, 116.6, 114.4, 55.7, 34.6, 18.6. FT-IR (KBr)_{v_{max}} (cm⁻¹) 1078, 1196 (C-O); 1446, 1511, 1595 (aromatic); 2956, 3458, 3528(O-H). HRMS calcd for C₁₇H₂₀O₄Na [M+Na]⁺: 311.1259, found 311.1252.

Typical procedure for the synthesis of bisepoxide

Compound **1** (1.218 g, 4.22 mmol), BnEt₃NCl (0.1 eq.) and epichlorohydrin (42.2 mmol) were added into a round-bottomed flask and stirred at 80 °C for 1 hour. Then, the solution was cooled down to room temperature and aqueous solution of BnEt₃NCl (0.1 eq.) and NaOH (16.88 mmol) was added. The mixture was stirred at room temperature for 30 min. Ethyl acetate and water were added, and the aqueous phase was extracted with ethyl acetate. The organic layer was dried (Na₂SO₄), and excess amount of ethyl acetate and epichlorohydrin were removed by rotary evaporator, then the product was obtained through column chromatography (petroleum ether/ethyl acetate = 2/1). Yield: 83.7%

Bis(5-((oxiran-2-yl)methoxy)-4-methoxy-2-methylphenyl)methane (2) M.p. = 98-99 °C, ¹H NMR(500 MHz CDCl₃), δ = 6.73 (s, 2H), 6.48 (s, 2H), 4.07-4.04 (m, 2 H), 3.91-3.90 (m, 2H), 3.86 (s, 6H), 3.73 (s, 2H), 3.29-3.27 (m, 2H), 3.82-3.80 (t, 4 Hz, 2H), 2.64-2.63 (m, 2H), 2.19 (s, 6H). ¹³C NMR (125 MHz CDCl₃), δ = 147.9, 146.0, 130.7, 129.9, 116.2, 114.4, 70.6, 56.2, 50.3, 45.1, 35.8, 19.2. FT-IR (KBr) _{v_{max}} (cm⁻¹) 1008, 1219 (C=O), 1466, 1525, 1611 (aromatic), 2937. HRMS calcd for C₂₃H₂₈O₆Na [M+Na]⁺: 423.1784, found 423.1780.

1-(5-(5-((oxiran-2-yl)methoxy)-4-methoxy-2-methylbenzyl)-2-methoxy-4-methylphenoxy)-3-chloropropan-2-ol (3) was yellow oil ¹H NMR (500 MHz CDCl₃), δ = 6.72 (s, 2H), 6.49 (s, 1H), 6.47 (s, 1H), 4.09-4.05 (m, 2H), 3.95-3.94 (d, J = 5 Hz, 2H) 3.88-3.85 (m, 1H), 3.82 (s, 3H), 3.81 (s, 3H), 3.71 (s, 2H), 3.69-3.66 (m, 1H), 3.62-3.59 (m, 1H), 3.27 (s, 1H), 2.79-2.77 (t, J = 4.5 Hz, 1 H), 2.61 (m, 1H), 2.18 (s, 6H). ¹³C NMR (125 MHz CDCl₃), δ = 147.8, 147.7, 145.8, 145.7, 130.8, 130.4, 130.2, 129.7, 117.0, 116.1, 114.3, 114.2, 71.4, 70.4, 69.8, 55.9, 55.8, 50.2, 45.5, 44.7, 35.5, 19.0, 18.9. FT-IR (KBr) _{v_{max}} (cm⁻¹) 750 (C-Cl), 1202 (C-O), 1462, 1512, 1609 (aromatic), 2934, 3473 (O-H). HRMS calcd for C₂₃H₂₉O₆ClNa [M+Na]⁺: 459.1550, found 459.1571.

Typical procedure for the synthesis of bis(cyclic carbonate)

Compound **2** (0.5 g, 1.25 mmol) and 12.5 g of a mixture of TBAB and TBAI (1:1, w/w) were added to stainless steel autoclave equipped with a magnetic stirrer. Then, CO₂ was charged in the autoclave and adjusted to 2 MPa. The reaction was carried out at specified temperature for a

desired period of time. After the reaction, the autoclave was cooled and the excess CO₂ was slowly vented. The product was extracted with ethyl acetate and purified by column chromatography (petroleum ether/ethyl acetate = 2/1). Yield: 98.9%

4,4'-(((methylenebis(2-methoxy-4-methyl-5,1-phenylene))bis(oxy))bis(methylene))bis(1,3-dioxolan-2-one) (4). m.p.: 156 °C, ¹H NMR (400 MHz, CDCl₃) δ = 6.74 (s, 2H), 6.49 (s, 2H), 4.89-4.95 (m, 2H), 4.52-4.59 (m, 4H), 4.08-4.16 (m, 4H), 3.83 (s, 6H), 3.73 (s, 2H), 2.20 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ = 154.9, 148.7, 145.7, 131.6, 130.9, 118.5, 114.9, 74.9, 69.9, 60.4, 56.2, 35.4, 19.3. FT-IR (KBr) ν_{max} (cm⁻¹) 1170 (C-O), 1460, 1509, 1609 (aromatic), 1791 (C=O), 2939 (C-H). HRMS calcd for C₂₅H₂₉O₁₀ [M+H]⁺: 489.1761, found 489.1732.

4-((2-methoxy-5-(4-methoxy-2-methyl-5-(oxiran-2-ylmethoxy)benzyl)-4-methylphenoxy)methyl)-1,3-dioxolan-2-one (5) ¹H NMR (500 MHz, CDCl₃) δ = 6.72 (s, 2H), 6.48 (s, 1H), 6.46 (s, 1H), 4.92-4.87 (m, 1H), 4.52-4.50 (m, 2H), 4.11-4.02 (m, 3H), 3.83 (s, 3H), 3.80 (s, 3H), 3.28-3.25 (m, 1H), 2.79-2.78 (t, J = 2.5 Hz 1 H), 2.63-2.61 (m, 1H), 2.19 (s, 3H), 2.17 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ = 154.8, 148.3, 147.9, 145.9, 145.5, 131.3, 130.9, 130.4, 129.8, 117.9, 116.3, 114.7, 114.4, 74.6, 70.6, 69.6, 66.3, 56.0, 55.9, 50.3, 44.7, 35.4, 19.1, 19.0. FT-IR (KBr) ν_{max} (cm⁻¹) 1302 (C-O), 1460, 1512, 1608 (aromatic), 1797 (C=O), 2928 (C-H). HRMS calcd for C₂₄H₂₈O₈Na [M+Na]⁺: 467.1682, found 467.1637.

Polyaddition of bis(cyclic carbonate) with diamine

The bis(cyclic carbonate) (0.244 g, 0.5 mmol) was dissolved in DMSO (0.5 mL) and vacuum degassed, followed by diamine (0.5 mmol) and TBD (5 mol%) addition. The reaction mixture was stirred at 25 °C for 24 h under N₂ atmosphere. After the reaction, the resulting mixture was poured into water and the precipitate was washed with water then lyophilized to obtain non-isocyanate polyurethanes (NIPUs).

6a-2: ¹H NMR (400 MHz, DMSO-d₆) δ = 7.13-7.06 (-NH), 6.80 (-ArH), 6.48 (-ArH), 5.09 (-CH₂OH), 4.83-4.77 (-OCH(CH₂OH)CH₂-), 4.01-3.87 (-CH₂OH, -OCH₂CH(OH)CH₂O-, -CH₂O-), 3.73-3.70 (-ArCH₂Ar-, -ArOCH₃, ArOCH₂-), 3.53 (-CHOH), 2.92 (-NHCH₂-), 2.13 (-ArCH₃), 1.34-1.20 (-CH₂CH₂CH₂CH₂-). ¹³C NMR (100 MHz, DMSO-d₆) δ = 156.7, 147.8, 146.3, 130.9, 129.3, 116.1, 115.1, 73.0, 71.1, 68.3, 67.9, 65.6, 60.3, 56.1, 35.6, 29.8, 26.4, 19.2.

6b-2: ¹H NMR (400 MHz, DMSO-d₆) δ = 7.08-7.02 (-NH), 6.80 (-ArH), 6.50 (-ArH), 5.09 (-CH₂OH), 4.78 (-OCH(CH₂OH)CH₂-), 3.99-3.90 (-CH₂OH, -OCH₂CH(OH)CH₂O-, -CH₂O-), 3.73 (-ArCH₂Ar-, -ArOCH₃, ArOCH₂-), 3.53 (-CHOH), 2.70 (-NHCH₂-), 2.14 (-ArCH₃), 1.45-0.84 (-CH₂-, -CH₃). ¹³C NMR (100 MHz, DMSO-d₆) δ = 157.3, 147.8, 146.3, 130.9, 129.3, 116.2, 115.1, 71.1, 70.5, 67.9, 63.3, 56.1, 35.7, 31.9, 19.2.

6c-2: ¹H NMR (400 MHz, DMSO-d₆) δ = 6.85-6.80 (-ArH), 6.53-6.49 (-ArH), 5.18 (-CH₂OH), 5.07-5.01 (-OCH(CH₂O)₂-), 4.80-4.79 (-OCH(CH₂OH)CH₂-), 4.59-4.52, 4.38-4.34, 4.10-3.99 (-CH₂OH, -OCH₂CH(OH)CH₂O-, -CH₂O-), 3.74-3.71 (-ArCH₂Ar-, -ArOCH₃, ArOCH₂-), 3.55 (-CHOH), 3.41-3.31 (-NH), 2.15-5.14 (-ArCH₃). ¹³C NMR (100 MHz, DMSO-d₆) δ = 155.3, 148.0, 147.6, 146.6, 146.3, 145.8, 131.1, 130.4, 128.8, 117.2, 115.6, 115.3, 115.1, 75.6, 71.1, 70.5, 69.7, 66.5, 63.3, 56.1, 35.5, 19.1.

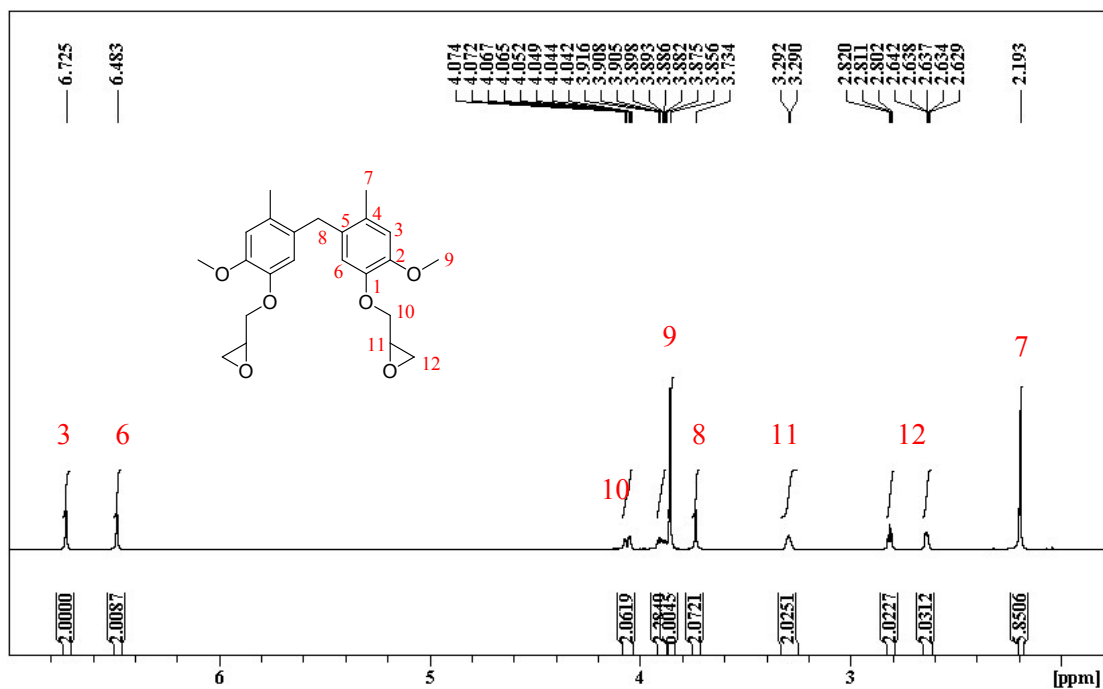


Figure S1. ¹H NMR of bisepoxide **2** (500 MHz CDCl₃).

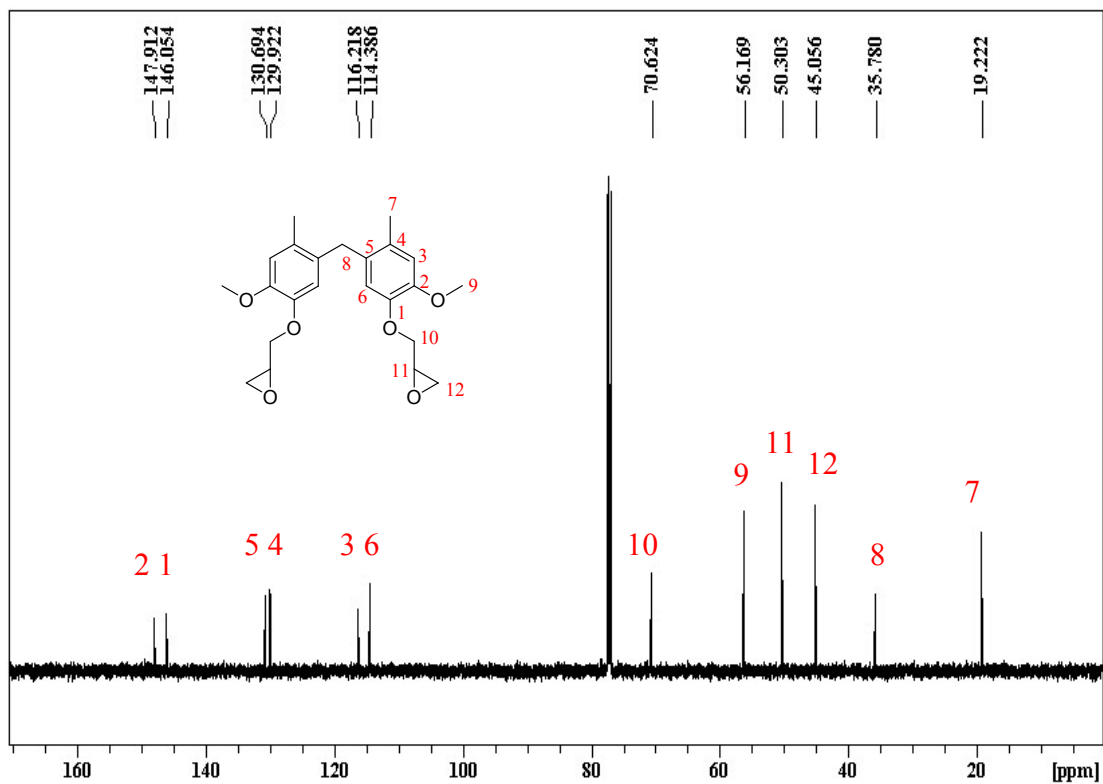


Figure S2. ¹³C NMR of bisepoxide **2** (125 MHz CDCl₃).

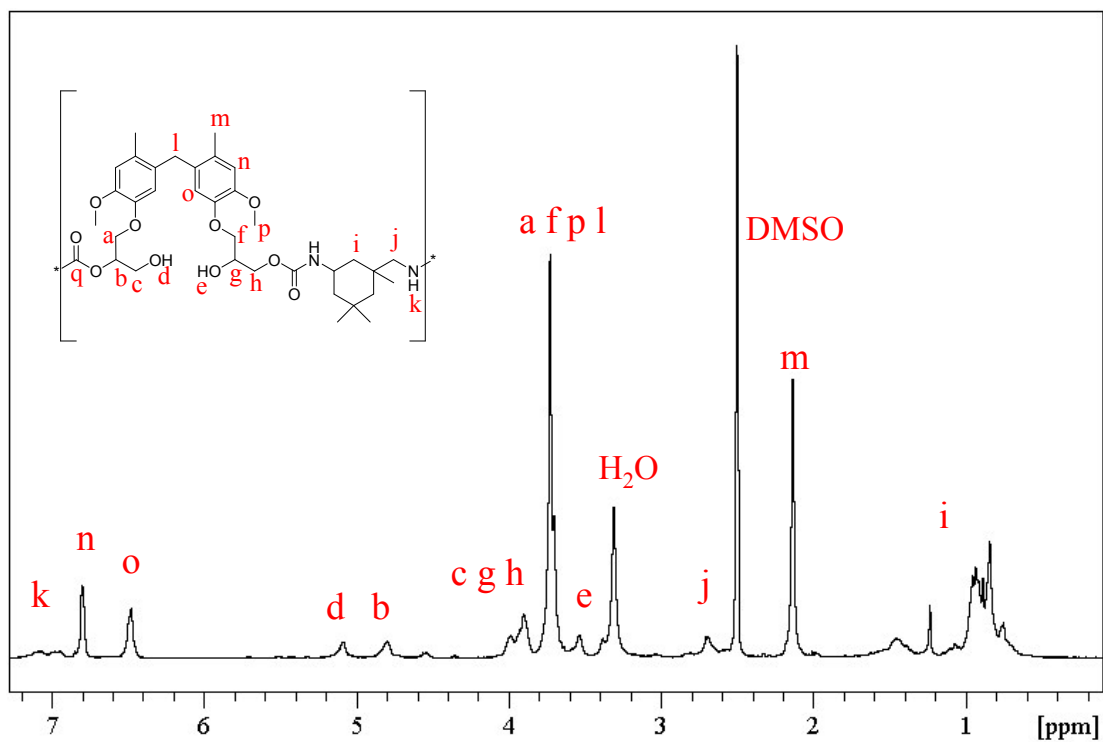


Figure S3. ^1H NMR spectrum of **6b-2** (500 MHz, DMSO- d_6).

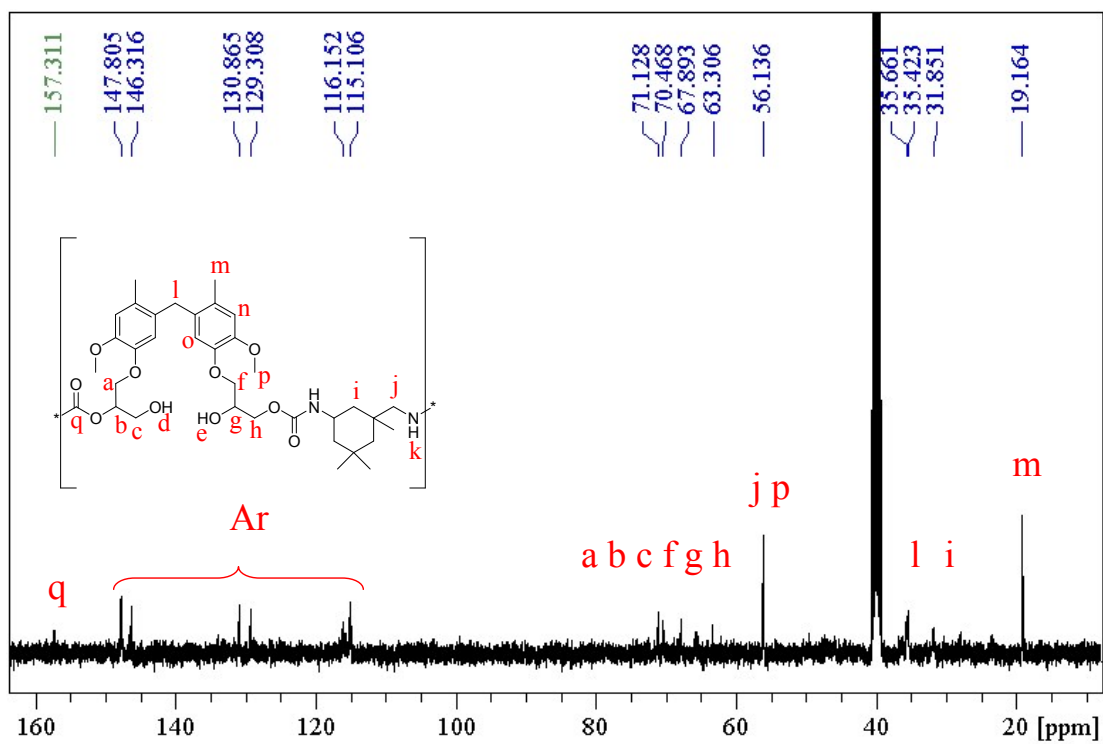


Figure S4. ^{13}C NMR spectrum of **6b-2** (125 MHz, DMSO- d_6).

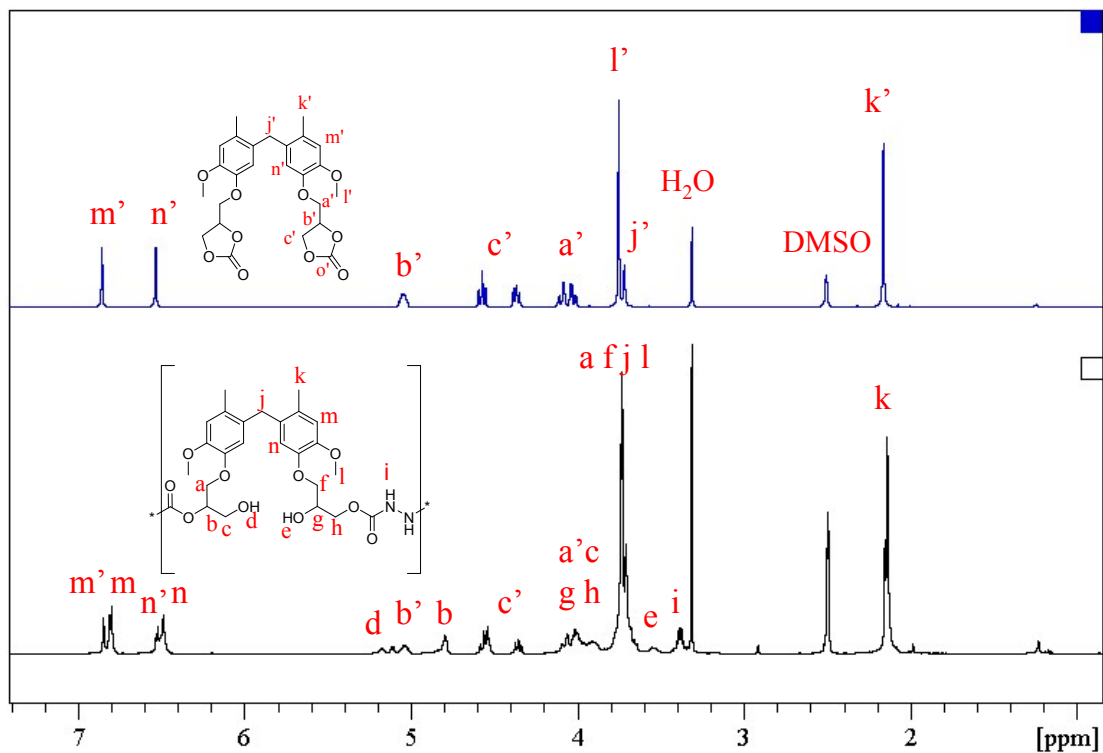


Figure S5. ^1H NMR spectrum of **6c-2** and bis(cyclic carbonate) (500 MHz, DMSO-d_6).

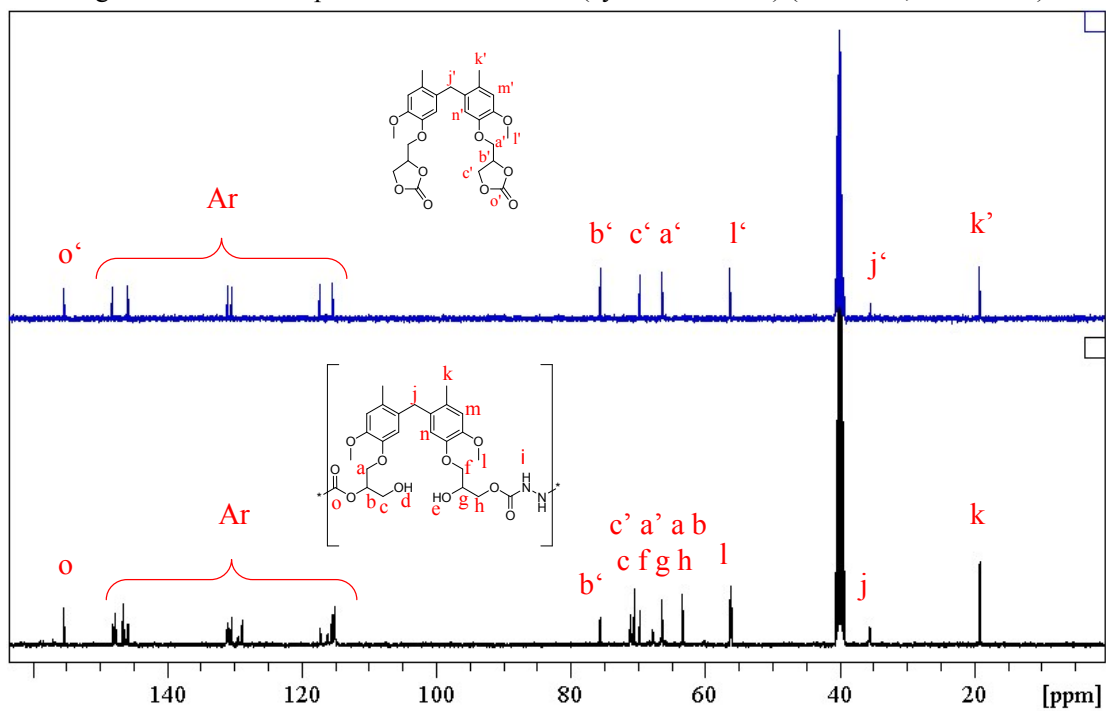


Figure S6. ^{13}C NMR spectrum of **6c-2** and bis(cyclic carbonate) (125 MHz, DMSO-d_6).

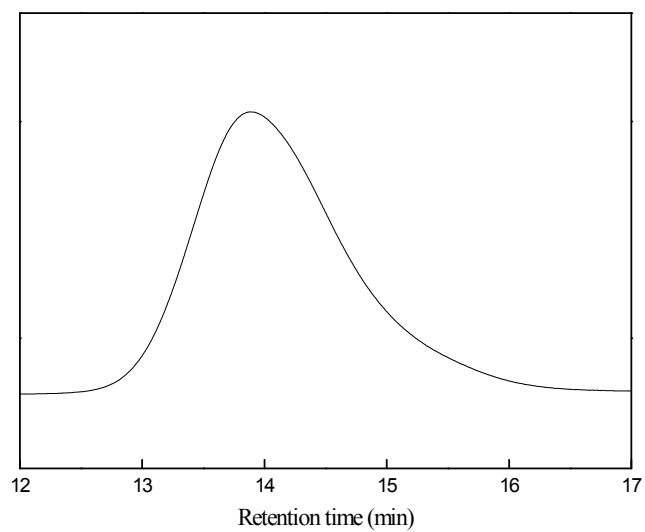


Figure S7. GPC analysis of **6a-1**, $M_n=23000$ g/mol, PDI=1.9.

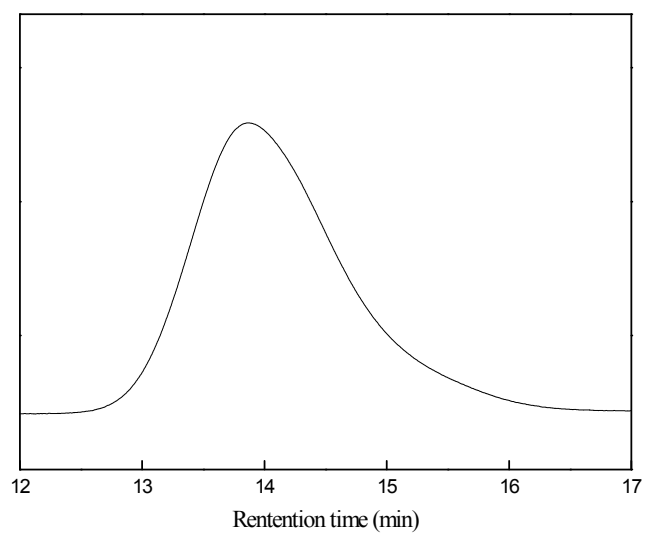


Figure S8. GPC analysis of **6a-2**, $M_n=30000$ g/mol, PDI=1.7.

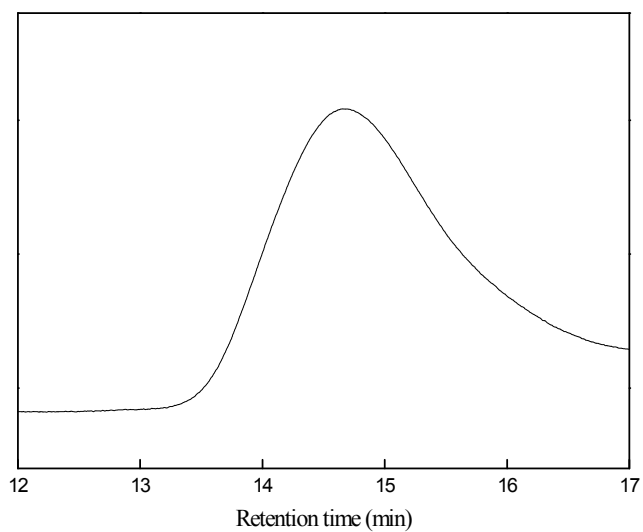


Figure S9. GPC analysis of **6a-3**, $M_n=46000$ g/mol, PDI=1.5.

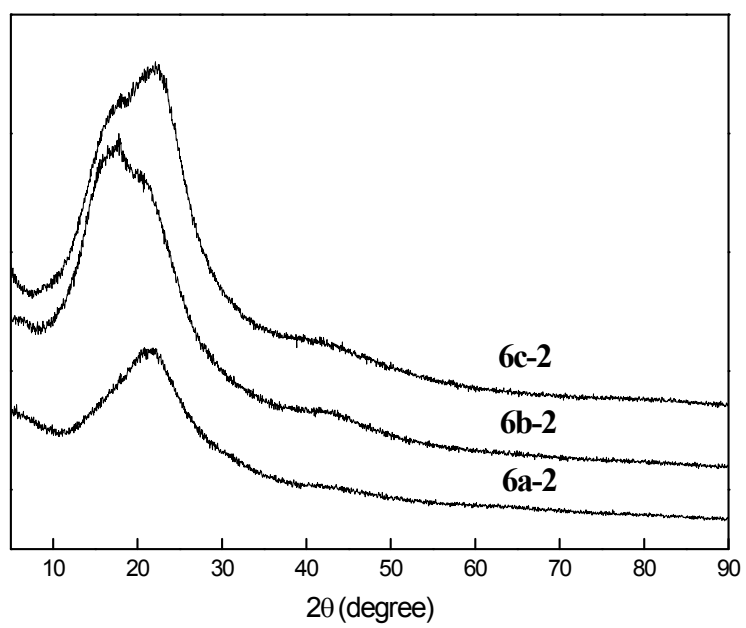


Figure S10. XRD patterns of NIPUs