SUPPORTING INFORMATION

Synthesis of Aliphatic Poly(ether 1,2-glycerol carbonate)s via Copolymerization of CO₂ with Glycidyl Ethers Using a Cobalt Salen Catalyst and Study of a Thermally Stable Solid Polymer Electrolyte

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I. General Information

All manipulations involving air- and/or water-sensitive compounds were carried out in the glovebox. Butyl glycidyl ether was purchased from Sigma-Aldrich. Octyl and stearic glycidyl ether monomers were prepared following previously published procedures.^{1,2} The catalyst was synthesized following a previously reported procedure.³

All monomers and toluene were refluxed over CaH₂ and fractionally distilled under nitrogen atmosphere prior to use (Purification of Common Laboratory Chemicals, ISBN: 978-1-85617-567-8). Carbon dioxide (99.995%, research grade) was purchased from Airgas and used as received. NMR spectra were recorded on Varian Unity Plus 400, and Varian Mercury 500 spectrometers. Chemical shifts for ¹H NMR were reported as δ , parts per million, relative to the signal of residual CHCl₃ in CDCl₃ at 7.26 ppm. Chemical shifts for ¹³C NMR were reported as δ_{13} parts per million, relative to the center line signal of the CDCl₃ triplet at 77.0 ppm. Proton and carbon assignments were established using spectral data of similar compounds. Infrared spectra were recorded on a Nicolet Nexus 670 FT-IR with ATR spectrophotometer. Absorptions are given in wavenumbers (cm⁻¹). Polymer molecular weights were determined by gel permeation chromatography (GPC) versus polystyrene standards using THF as the eluent at a flow rate of 1.0 ml/min through Styragel column (HR4E THF, 7.8 x 300 mm) with a refractive index detector. Thermogravimetric Analysis (TGA) measurements were performed using TGA O50. All samples were heated from 20 to 500 °C at a heating rate of 10 °C/min. All samples were also tested with Differential Scanning Calorimetry (DSC) at a heating rate of 10 °C/min and a cooling rate of 10 °C/min from -50 to 140 °C. The weight of all samples was between 2 to 10 mg and the samples underwent three heat-cool-heat cycles. The rheological measurements were obtained on a TA Instruments RA 1000 instrument. The oscillatory stress sweeps of poly(butyl 1,2-glycerol carbonate) were recorded at a frequency of 1 Hz. The frequency sweeps of the polymer were measured at a frequency of 0.1 to 10 Hz with a controlled strain of 2%. Data are expressed as mean \pm standard deviation (n = 3).

II. General Procedure

Rac-glycidyl ether (25 mmol) was added into a high pressure autoclave, followed by the addition of [*rac*-SalcyCo^{III}DNP] (0.0125 mmol). The autoclave was transferred out of the glovebox and charged with CO₂ to 220 psi. The reaction was allowed to run at 40 °C until the conversion reached 40-60%. Subsequently, the CO₂ pressure was released and the reaction mixture was diluted with 8 mL of DCM and MeOH (7:1) and one drop of aqueous 1M HCl solution. The mixture was added dropwise into MeOH (70 mL) (or acetonitrile for poly(stearyl 1,2-glycerol carbonate)) and the precipitated polymer was collected. The precipitation was repeated until a complete removal of the catalyst, unreacted monomer and cyclic by-product was confirmed by ¹H NMR. Removing solvent *in vacuo* afforded the desired polymer.

Poly(butyl ether 1,2-glycerol carbonate) (Table 2, entry 1)

¹H NMR (500 MHz, CDCl₃): δ 5.03-4.97 (br, 1H), 4.46-4.20 (br, 2H), 3.61-3.56 (m, 2H), 3.48-3.38 (m, 2H), 1.51 (tt, J = 8.7, 6.6 Hz, 2H), 1.33 (qt, J = 14.9, 7.4 Hz, 2H), 0.88 (t, J = 7.4 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 154.3, 74.5, 71.6, 68.4, 66.3, 31.7, 19.3, 13.9; IR (neat): v_{max} 2960, 2934, 2876, 1748, 1459, 1222, 1117, 1075 cm⁻¹; GPC (THF): Mn = 20974 g/mol, Mw = 26376 g/mol, PDI = 1.3.

Poly(octyl ether 1,2-glycerol carbonate) (Table 2, entry 2)

¹H NMR (500 MHz, CDCl₃): δ 5.05-4.95 (br, 1H), 4.50-4.18 (br, 2H), 3.64-3.53 (m, 2H), 3.48-3.36 (m, 2H), 1.58-1.48 (m, 2H), 1.34-1.19 (m, 10H), 0.86 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 154.3, 74.5, 72.0, 68.4, 66.2, 31.9, 29.6, 29.5, 29.3, 26.1, 22.8, 14.2; IR (neat): *v*_{max} 2926, 2856, 1752, 1457, 1225, 1122, 1076 cm⁻¹;

GPC (THF): Mn = 31861 g/mol, Mw = 43716 g/mol, PDI = 1.4.

Poly(stearyl ether 1,2-glycerol carbonate) (Table 2, entry 3)

¹H NMR (500 MHz, CDCl₃): δ 5.07-4.96 (br, 1H), 4.52-4.19 (br, 2H), 3.66-3.56 (m, 2H), 3.52-3.36 (m, 2H), 1.62-1.49 (m, 2H), 1.36-1.19 (m, 30H), 0.88 (t, J = 6.8 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 154.4, 74.5, 72.1, 68.5, 66.3, 32.1, 29.9, 29.7, 29.5, 26.2, 22.8, 14.3; IR (neat): v_{max} 2916, 2850, 1753, 1467, 1229, 1123 cm⁻¹; GPC (THF): Mn = 8965 g/mol, Mw = 12073 g/mol, PDI = 1.3.

III. ¹H and ¹³C NMR, FT-IR, DSC, TGA Spectra



Figure S1. ¹H NMR spectrum of poly(butyl ether 1,2-glycerol carbonate).



Figure S2. ¹H NMR spectrum of poly(octyl ether 1,2-glycerol carbonate).



Figure S3. ¹H NMR spectrum of poly(stearyl ether 1,2-glycerol carbonate).



Figure S4. ¹³C NMR spectrum of poly(butyl ether 1,2-glycerol carbonate).



Figure S5. ¹³C NMR spectrum of poly(octyl ether 1,2-glycerol carbonate).



Figure S6. ¹³C NMR spectrum of poly(stearyl ether 1,2-glycerol carbonate).



Figure S7. FT-IR spectrum of poly(butyl ether1,2-glycerol carbonate).



Figure S8. FT-IR spectrum of poly(octyl ether 1,2-glycerol carbonate).



Figure S9. FT-IR spectrum of poly(stearyl ether 1,2-glycerol carbonate).



Figure S10. Tg spectrum of poly(butyl ether 1,2-glycerol carbonate).



Figure S11. Tg spectrum of poly(octyl ether 1,2-glycerol carbonate).



Figure S12. Tm spectrum of poly(stearyl ether 1,2-glycerol carbonate).



Figure S13. Temperatures at 5 and 50% weight loss on the TGA curve of poly(butyl ether 1,2-glycerol carbonate).



Figure S14. Temperatures at 5 and 50% weight loss on the TGA curve of poly(octyl ether 1,2-glycerol carbonate).



Figure S15. Temperatures at 5 and 50% weight loss on the TGA curve of poly(stearyl ether 1,2-glycerol carbonate).

IV. Rheological Data

Figure S16. Stress sweep at 1 Hz frequency for poly(butyl ether 1,2-glycerol carbonate)



V. Electrochemical Impedance Spectroscopy Data

Polycarbonate electrolytes are prepared using a simple casting method. The polycarbonate is dissolved in acetonitrile with lithium bis-(trifluoromethane sulfonyl) imide (LiTFSI, Sigma Aldrich) at room temperature at a [Li+]:[O] ratio of 1:10. LiTFSI dissolves in chloroform, and the polymer/salt solution is completely transparent. The solution is cast onto a stainless steel disc confined by a stainless steel spacer and dried under vacuum at 40 °C overnight. The other stainless steel disc is placed on top of the sample followed by heating to make a good contact (done in the glovebox). The sandwiched sample is sealed in a coin cell and the ionic conductivities are measured by the electrochemical impedance spectroscopy using a multichannel VersaState 4 potentiostat/galvanostat/EIS analyzer (Princeton Applied Research) in the frequency range from 0.1 Hz to 1 M Hz. The temperature is increased from 25 to 120 °C and the cells are held constant at 10 or 20 °C intervals for at least 30 min, after which each impedance measurement is carried out.





VI. References

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