

Supplementary information

Upcycling Waste Poly(Ethylene Terephthalate) into Polymer Electrolytes

Ming Yan Tan,^a Leonard Goh,^a Dorsasadat Safanama,^a Wei Wei Loh,^a Ning Ding,^a Sheau Wei Chien,^a Shermin S. Goh,^a Warintorn Thitsartarn,^a Jason Y. C. Lim^{*a,b} and Derrick W. H. Fam^{*a,c,d}

a. Institute of Materials Research and Engineering (IMRE)
2 Fusionopolis Way, Singapore 138634 (Singapore)

E-mail: jason_lim@imre.a-star.edu.sg; derrickfamwh@imre.a-star.edu.sg

b. Department of Materials Science and Engineering
National University of Singapore (NUS), 9 Engineering Drive 1
Singapore 117576 (Singapore)

c. School of Materials Science and Engineering
Nanyang Technological University, 50 Nanyang Ave, Singapore 639798,
College of Design and Engineering

d. Department of Mechanical Engineering
National University of Singapore, 9 Engineering Drive 1, Block EA #07-08, Singapore 117575

1. Experimental section

Materials

Used PET beverage bottles were washed and cut into small flakes. EMITFSI was purchased from Solvionic (99.9%). LITFSI (98%) was purchased from TCI. Tetrahydrofuran (99.9%), hexamethylene diisocyanate (HMDI), dibutyltin dialurate (95%) (DBTL) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) (98%) were purchased from Sigma Aldrich. Anhydrous dimethyl sulfoxide was purchased from Kanto Chemical Co. Inc. PEG (17,500Da) was bought from Fluka. N,N-dimethylformamide (99.8%) was purchased from Arcos Organics. Dichloromethane was purchased from Tedia. Diethyl ether was purchased from Fisher Scientific.

Characterization

Samples dissolved in deuterated DMSO (Cambridge Isotopes Laboratory) were tested using a JEOL ECA 500 MHz NMR spectrometer. ATR spectra of samples were recorded on a Bruker Vertex 80v spectrometer in the region of 4000 to 400 cm^{-1} . Thermogravimetric analysis (TGA) using TGA Q500 (TA Instruments) was carried out from room temperature to 800°C under N_2 . DSC was conducted from using TGA Q1000 (TA Instruments) to obtain the melting temperature and glass transition temperature T_g . Moisture content was tested using Karl Fischer coulometer (C20).

Synthesis of bis(2-hydroxyethyl) terephthalamide (BHETA)

5.2 g of PET flakes were mixed with ethanolamine (20 mL) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) (189 mg, 5 mol% w.r.t. PET repeating units). The mixture was heated to 130 °C for 4 h, where the solid PET flakes were observed to dissolve to form a slurry. The resultant slurry was precipitated using dichloromethane (400 mL) and filtered under vacuum. The residue is washed using THF and dried under vacuum to afford the product as an off-white solid in excellent purity (5.8 g, 85.1%). ^1H NMR (500 MHz, DMSO-d_6): δ / ppm = 8.55 (t, J = 5.6 Hz, 2H, CONH), 7.91 (s, 4H, Ar-H), 4.75 (t, J = 5.6 Hz, 2H, OH), 3.52 (q, J = 5.7 Hz, 4H, CH_2OH), 3.35 (q, J = 5.9 Hz, 4H, CH_2NH); ^{13}C NMR (125 MHz, DMSO-d_6): δ / ppm = 165.8, 136.7, 127.2, 59.7, 42.3.

The characterisation data for BHETA matches that published earlier.¹

Synthesis of BHETA:PEG polyurethanes

In a typical synthesis, PEG (17,500 Da) was first dried under azeotropic distillation using anhydrous toluene (2 x 20 mL). To the dried PEG macromonomers was added BHETA (appropriate ratio by mass)

and the mixture was stirred at 120 °C under high vacuum for an hour to remove further traces of moisture from the reaction. Thereafter, anhydrous DMF was added to dissolve all the monomers under stirring, followed by HMDI (such that the molar ratio of OH: NCO = 1.00 : 1.03) and DBTL catalyst, and the reaction mixture was stirred till just before gelation was observed, whereupon the reaction was quenched by adding ethanol and stirring for an additional 15 minutes. The resulting solution was poured into vigorously-stirred diethyl ether (10x volume of DMF used) to precipitate the polymer, which were filtered and left to dry in air overnight. The polymers were then dried in a vacuum oven at 150°C for 2 days to remove moisture and traces of organic solvents to afford a beige solid (generally >80 % yield). ¹H NMR (500 MHz, DMSO-d₆): δ/ ppm = 8.66 (CONH), 7.91 (Ar-H), 7.12 (CONH on urethane), 4.08 (CH₂O on BHETA component), 3.50 (CONHCH₂ on BHETA + PEG-CH₂s), 2.9 (OCONHCH₂ on HMDI segment), 1.35 (CONHCH₂CH₂CH₂ on HMDI segment) and 1.2 ppm (CONHCH₂CH₂CH₂ on HMDI segment). ¹³C NMR (125 MHz, DMSO-d₆): δ/ ppm = 165.7, 156.1, 136.8, 127.2, 69.8, 61.8, 29.4, 26.0 (2 peaks hidden under DMSO peak, see Figure S3).

Preparation of BHETA:PEG films

Varying amounts of BHETA:PEG polymer and/or PEO 100K, LITFSI salt and/or EMTFSI ionic liquid was added to anhydrous DMSO and stirred at 80-150°C for at least 3 hours until they are fully solvated inside an Ar glovebox (<1 ppm H₂O and <1ppm O₂). The anhydrous DMSO and ionic liquid solutions were tested using KF to be <30ppm before use. The resultant solution was degassed and transferred into a teflon petri dish and dried in a 100°C oven for 3 days, followed by 80°C drying under vacuum for 1 day. The film was further dried in a vacuum oven at 150°C for 2 days to remove moisture.

Preparation of Solid Polymer Electrolytes

Varying amounts of BHETA:PEG polymer, 100kDa PEO and LITFSI salt (as shown in Table S1) were added to anhydrous DMSO and stirred at 80-150°C for at least 3 hours until they are fully dissolved. The DMSO was tested using KF to be < 30ppm before use. The resultant solutions were degassed and transferred to a Teflon petri dish. All solutions were prepared inside an Argon glovebox (<1ppm H₂O and <1ppm O₂). The solution was dried in a 100°C oven for 3 days, followed by 80°C drying under vacuum for 1 day. The obtained free-standing film was further dried in a vacuum oven at 150°C for 2 days to remove moisture.

Table S1. Solid polymer electrolyte formulations.

Sample description	EO:LITFSI	BHETA:PEG polymer/mg	100kDa PEO/mg	LITFSI/mg	DMSO/g
1BHETA:2PEG	8:1	450	-	201	5
1BHETA:2PEG	10:1	300	-	107	3
1BHETA:4PEG	10:1	500	-	262	5
1BHETA:6PEG	10:1	750	-	365	5
1BHETA:2PEG + 29% 100kDa PEO	10:1	750	300	466	10
1BHETA:6PEG + 28% 100kDa PEO	10:1	750	300	565	10

Preparation of Gel Polymer Electrolytes

Varying amounts of 1BHETA:2PEG polymer, LiTFSI salt and EMITFSI ionic liquid (as shown in Table S2.) were added to anhydrous DMSO and stirred at 80-150°C for at least 3 hours until they are fully dissolved. The DMSO and EMITFSI were tested using KF to be < 30ppm before use. The resultant solutions were degassed and transferred to a 25 mm Teflon petri dish. All solutions were prepared inside an Argon glovebox (<1ppm H₂O and <1ppm O₂). The solution was dried in a 100°C oven for 3 days, followed by 80°C drying under vacuum for 1 day. The obtained free-standing film was further dried in a vacuum oven at 150°C for 2 days to remove moisture.

Table S2. Gel polymer electrolyte formulations.

Sample description	EO:LITFSI	BHETA:PEG polymer/mg	LITFSI/mg	EMITFSI/mg	DMSO/g
1BHETA:2PEG + 24% EMITFSI	8:1	450	200	200	5
1BHETA:2PEG + 38% EMITFSI	8:1	450	200	400	5

Electrochemical Impedance Spectroscopy (EIS) measurement

Ionic conductivities of the solid and gel electrolytes were measured using an RHD piezo cell connected to an Autolab FR32 M frequency response analyzer. Discs of 12 mm diameter were cut and mounted onto cell with symmetric stainless steel current collectors. Impedance spectra were obtained in the frequency range of 1MHz-100Hz from 20 to 80°C. An equivalent circuit of (RCPE)CPE was used to fit the Nyquist plots. The ionic conductivities were accordingly calculated using the following equation: $\sigma =$

$\frac{l}{RA}$, where σ is the ionic conductivity at a certain temperature (K), l is the film thickness, R is the resistance and A is the contact area (8 mm diameter of RHD cell's electrodes).

Determination of Li⁺ Transference Number

The Li⁺ transference for the BHETA-PEG gel polymer electrolyte is estimated based on the Bruce-Vincent method² and corresponding equation (below) which is the most commonly used method for polymer electrolytes:

$$T_{Li^+} = \frac{I_{ss}R_{bs}(\Delta V - I_0R_{i0})}{I_0R_{b0}(\Delta V - I_sR_{is})}$$

The symmetrical coin cell with Li metal electrodes and the gel electrolyte in the middle is polarized under voltage of 10 mV for 24 hours to reach a steady state. The EIS measurement is performed for the cell before and after the DC polarization in the frequency range of 3MHz-100Hz and the Nyquist plots are fitted using the open-source EISSA software. The electrochemical tests are carried out using a Biologic SP300 potentiostat. I_0 and I_{ss} are the initial current and the steady state current respectively (collected from DC polarization). R_{bx} and R_{ix} refer to the bulk and interfacial resistances, respectively (for initial state $x = 0$ and after polarization ($x = s$))

Battery fabrication containing the 1BHETA:2PEG gel polymer electrolyte

The LTO:BHETA-PEG:LFP cells were assembled by sandwiching the gel polymer electrolyte between the $Li_4Ti_5O_{12}$ anode and $LiFePO_4$ cathode using a CR2032 coin cell. The loading for active material (LTO or LFP) is 52 wt% ($\approx 2 \text{ mg/cm}^2$) with 3.5 wt% of carbon (Super C-65) and 44.5 wt% of binder (PVdF) and PEO:LiTFSI (EO:Li ratio of 10:1). The cell was charged and discharged at constant current density of 0.1C in the voltage range from 1.5-2.5 V. All batteries were assembled in an Ar-filled glovebox (O_2 and $H_2O < 0.1 \text{ ppm}$). The galvanostatic measurement were carried out using Arbin Instruments battery tester at room temperature and at elevated temperature of 60°C. The coulombic efficiency (CE) was calculated using the following equation:

$$CE = \frac{\text{discharge capacity}}{\text{charge capacity}} \times 100\%$$

Dynamic Mechanical Analysis (DMA)

DMA was conducted using TA Instruments Q800 DMA. The elastic modulus was measured from at least 3 specimens with dimensions length 10 mm x width 6 mm. The test was conducted under controlled force mode, with constant force ramp of 1N/min up to a maximum of 18N. The test was conducted at room temperature.

Measurement of Electrochemical Window

The 2032 coin cells with Li metal as negative electrode, BHETA-PEG as gel polymer electrolyte and stainless steel as positive electrolyte were assembled in an Ar-filled glovebox (similar condition as above). The cyclic voltammetry was performed using Biologic SP300 potentiostat under voltage sweep rate of 5 mV/s and data was collected from open circuit voltage (OCV) to 5 V for two cycles.

2. Supplementary figures and tables

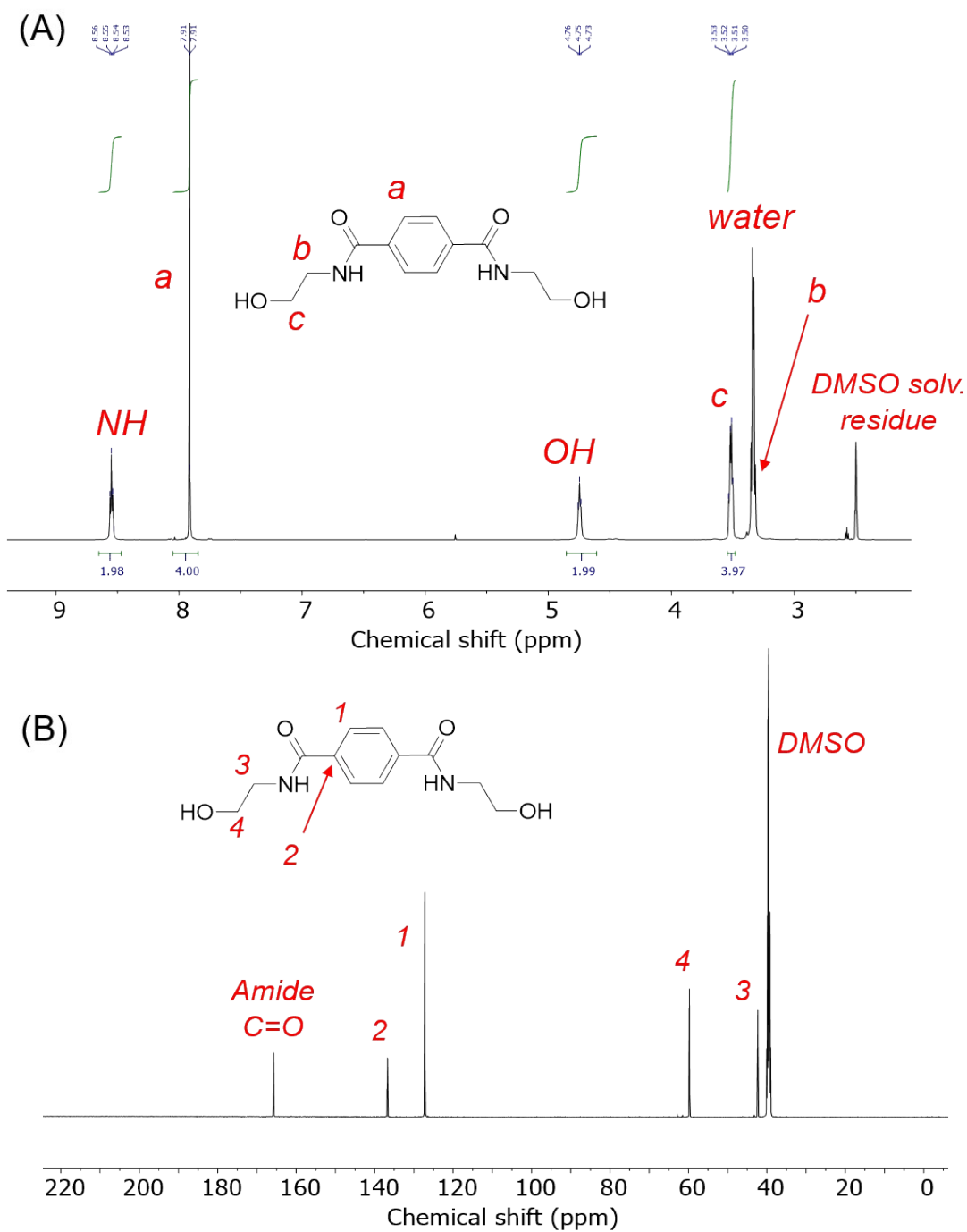


Figure S1. (A) ^1H and (B) ^{13}C NMR spectra ($\text{d}_6\text{-DMSO}$, 298 K) of the BHETA monomer obtained from catalytic PET aminolysis.

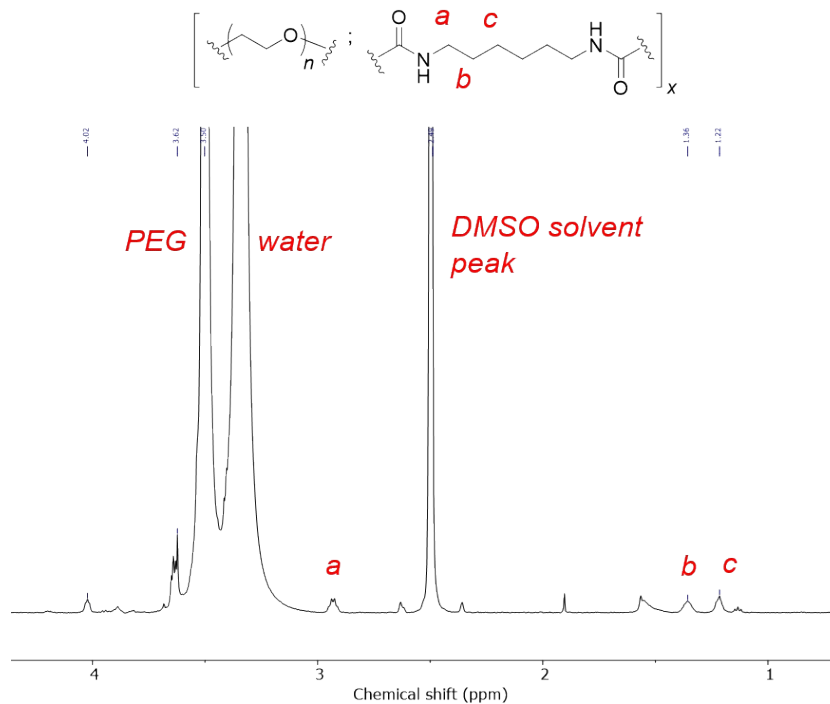


Figure S2. ¹H NMR spectrum of polyurethane containing only PEG without BHETA.

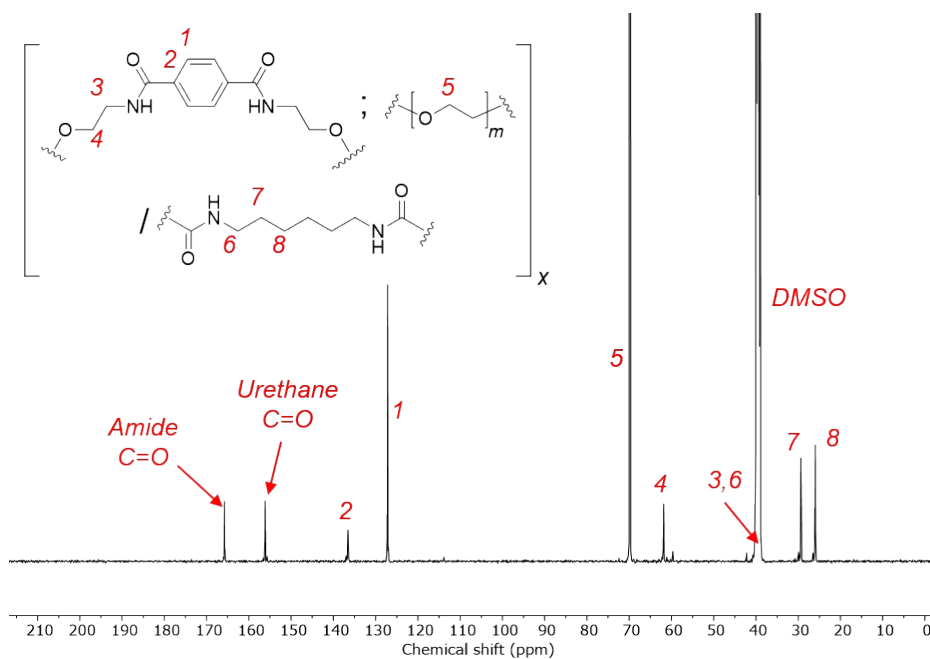


Figure S3. ¹³C NMR spectrum (*d*₆-DMSO, 298 K) of the 1BHETA-2PEG polyurethane.

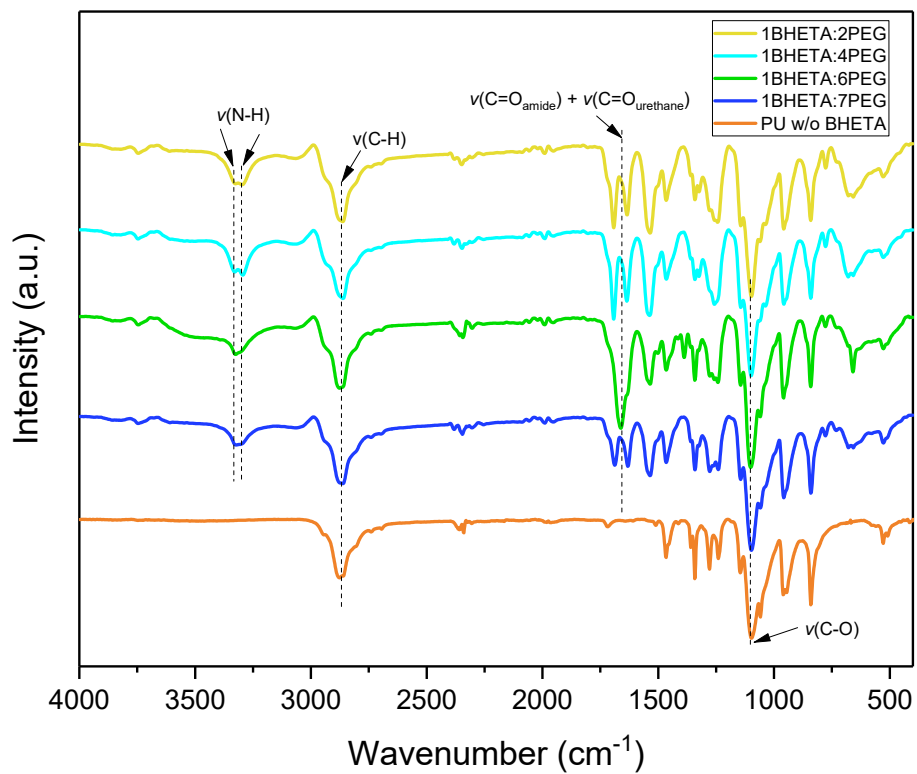


Figure S4. Stacked FTIR spectra of polyurethane electrolytes containing different ratios of BHETA:PEG.

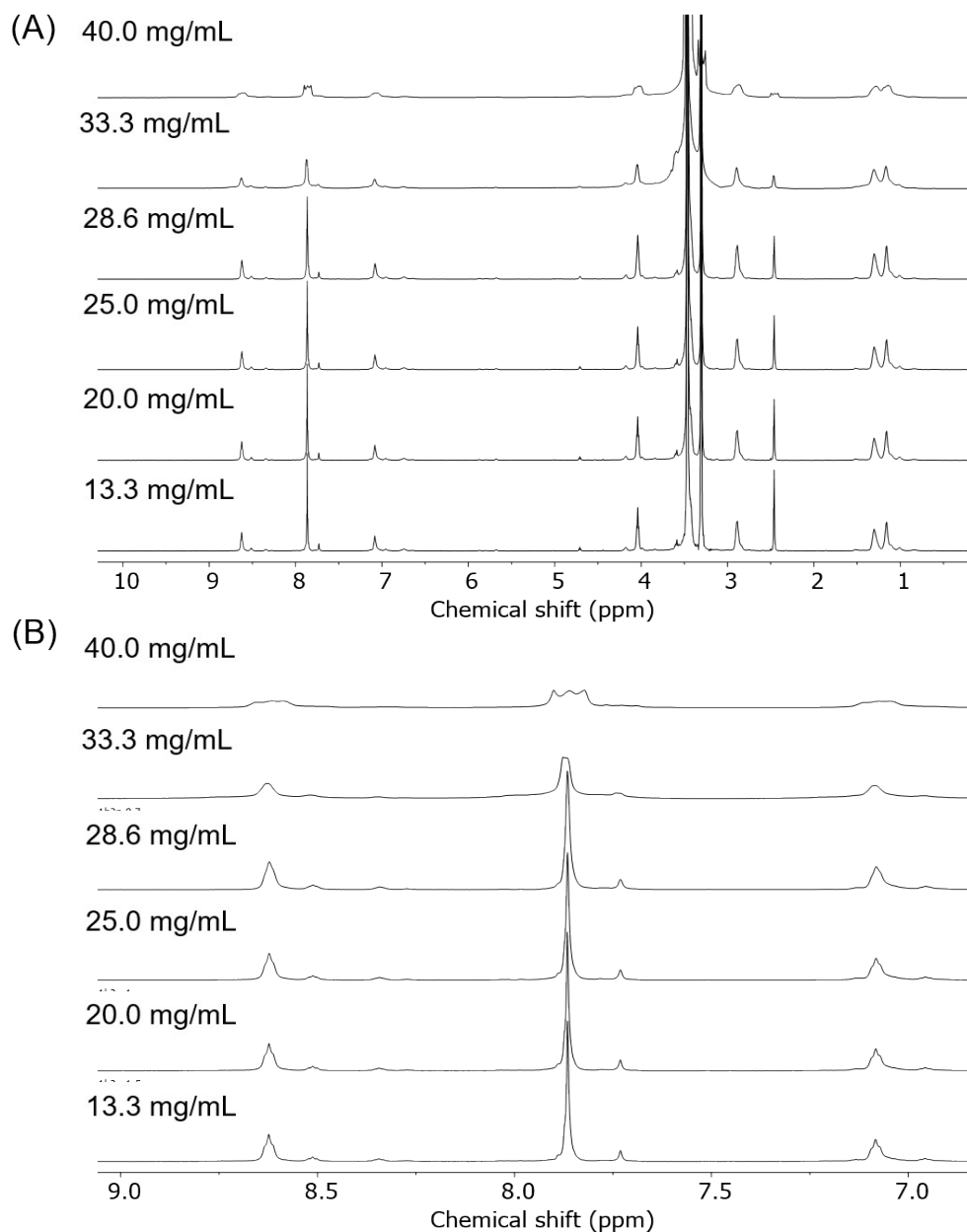


Figure S5. Stacked ¹H NMR spectra of different concentrations of 1BHETA:2PEG polymer in d₆-DMSO: (A) full spectra; (B) expanded aromatic region. Spectra were recorded with 20 mg of the polymer first dissolved in 0.5 mL of d₆-DMSO to give an initial polymer concentration of 40.0 mg/mL, and when different quantities of solvent was subsequently added to afford the concentrations listed.

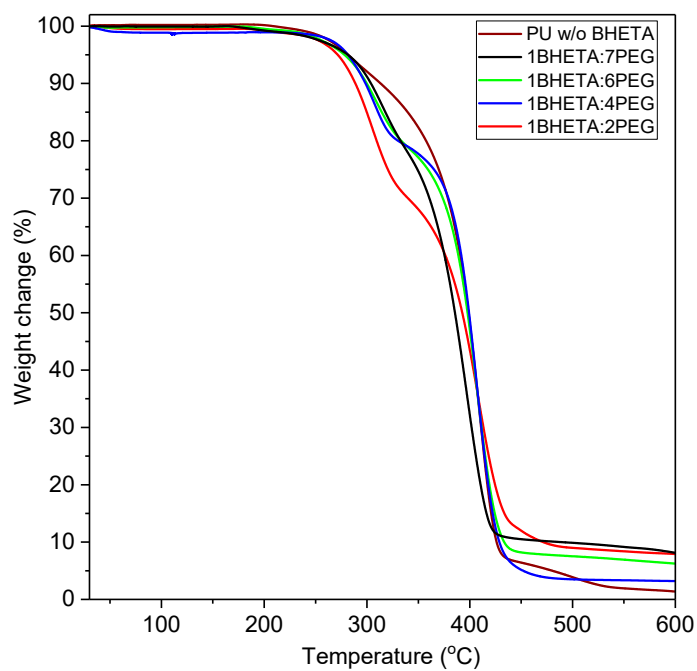


Figure S6. TGA thermograms of all polyurethanes containing different proportions of BHETA.

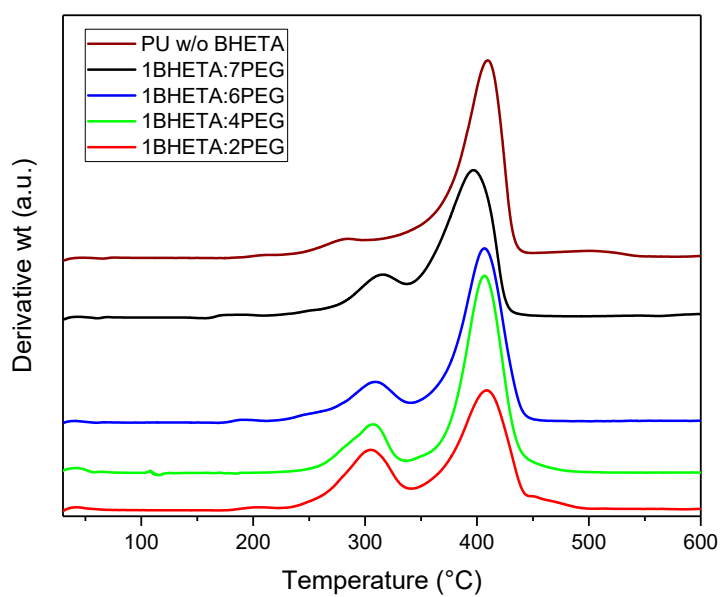


Figure S7. Stacked derivative thermogravimetry of polyurethanes containing different proportions of BHETA components.

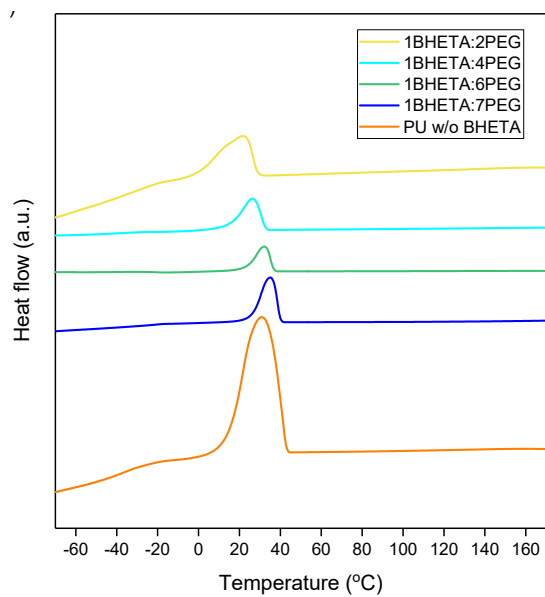


Figure S8. DSC heating curves showing the crystallization temperatures of polyurethanes containing different BHETA:PEG ratios.

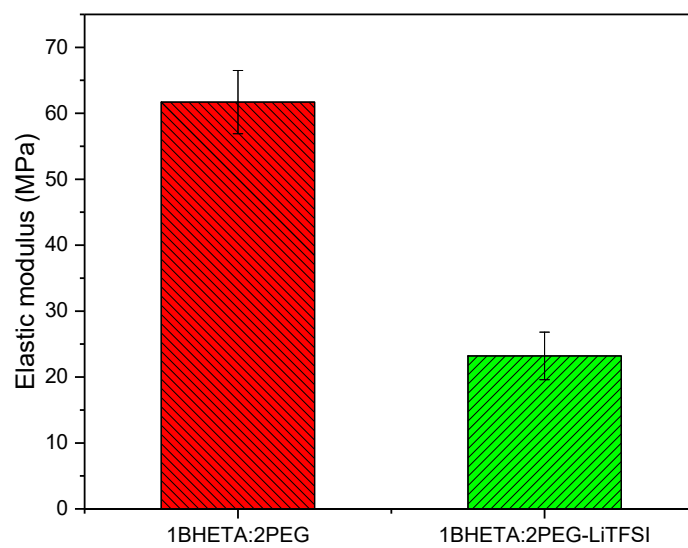


Figure S9. Elastic moduli of 1BHETA:2PEG films with and without LiTFSI

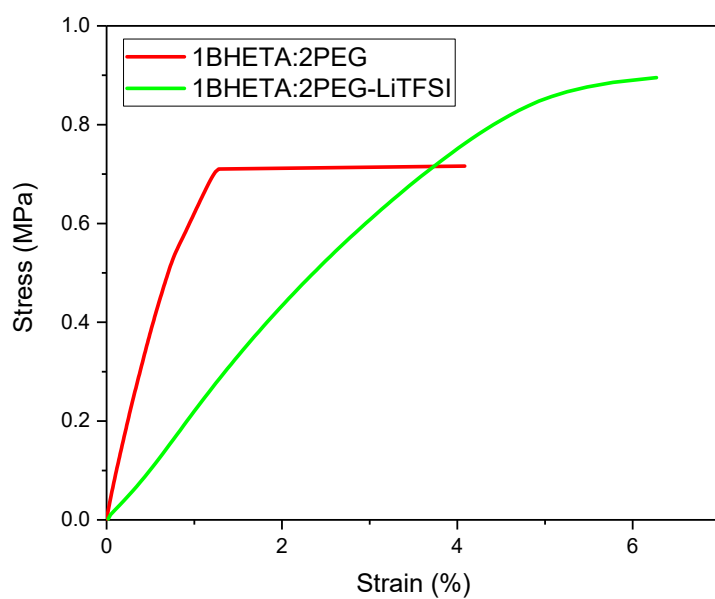


Figure S10. Stress-strain curves of 1BHETA:2PEG films with and without LiTFSI at room temperature and pressure.

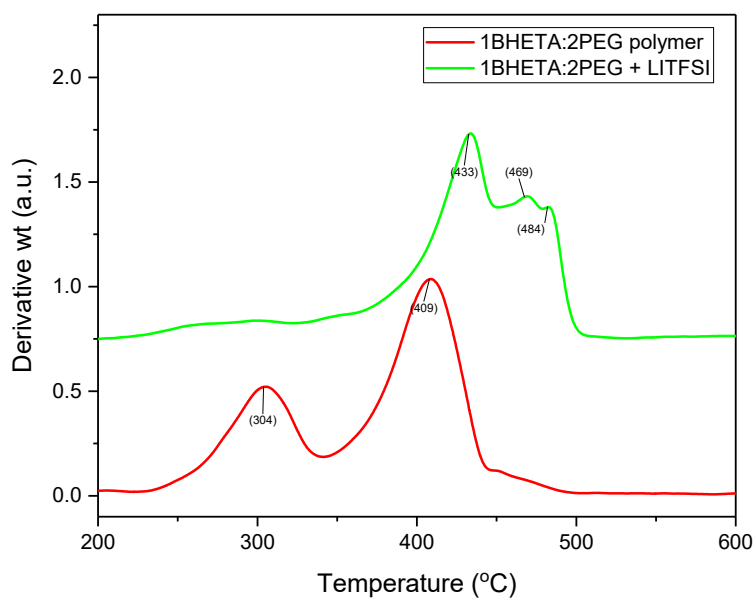


Figure S11. TGA of 1BHETA:2PEG polymer with and without incorporation of LiTFSI salt

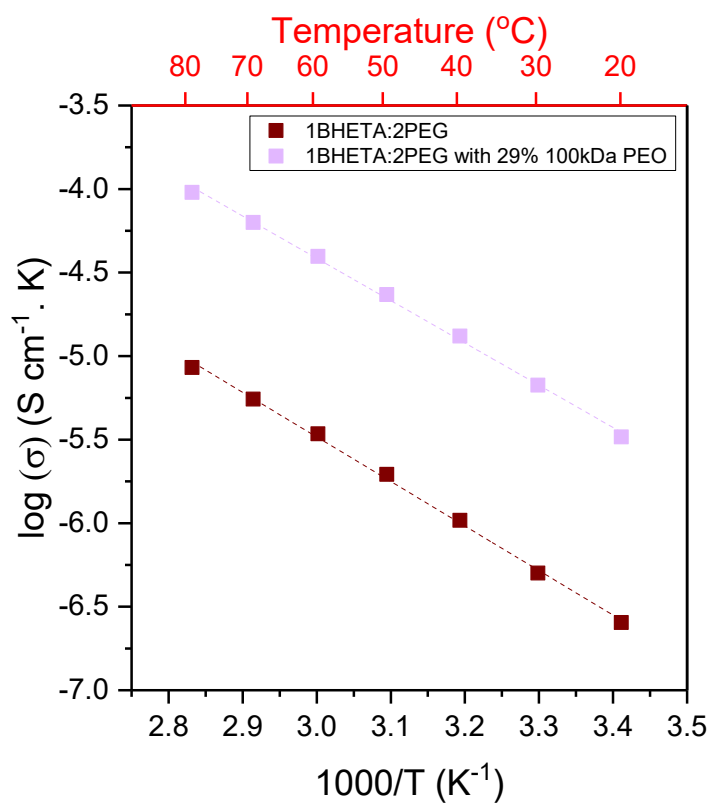


Figure S12. Variation of log conductivity with reciprocal temperature for the 1BHETA:2PEG polymer with and without added PEO.

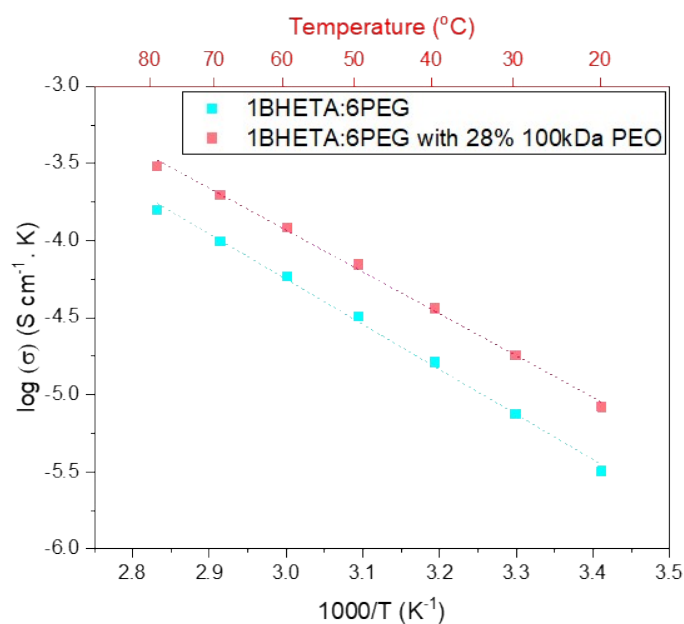


Figure S13. Variation of log conductivity with reciprocal temperature for the 1BHETA:6PEG polymer with and without added PEO.

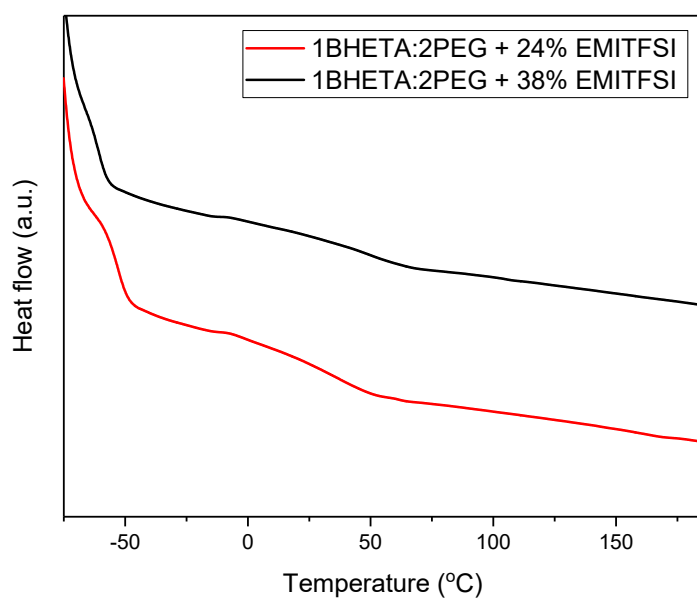


Figure S14. DSC heating curves of the 1BHETA:2PEG/ EMI-TFSI/ LiTFSI gel polymer electrolyte, showing lack of phase transitions.

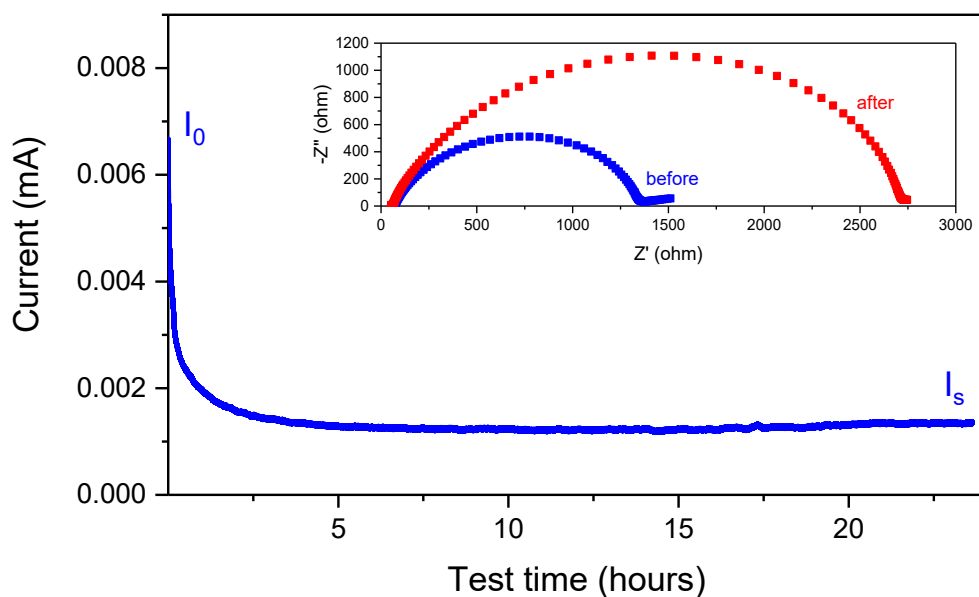


Figure S15. Polarisation curve and Nyquist plots before and after polarization (inset) for symmetrical Li:GPE:Li cell with 1BHETA:2PEG gel electrolyte

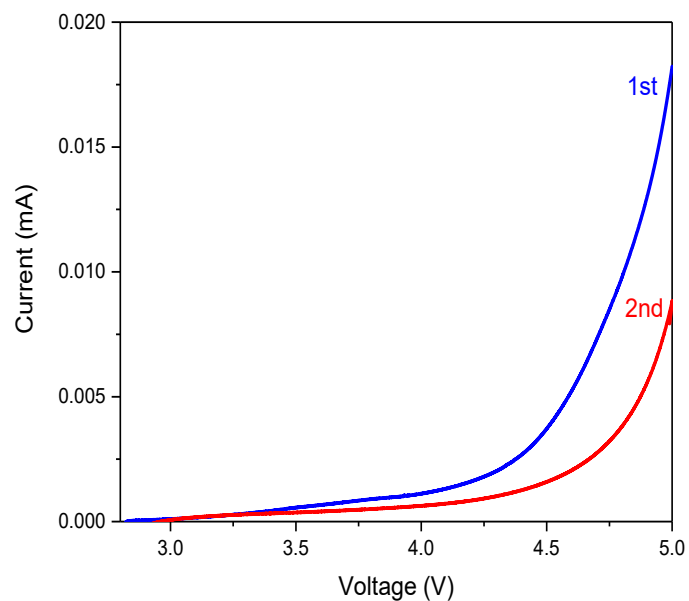


Figure S16. Linear Sweep Voltammetry (LSV) curves of Li:GPE:SS cell with 1BHETA:2PEG gel electrolyte

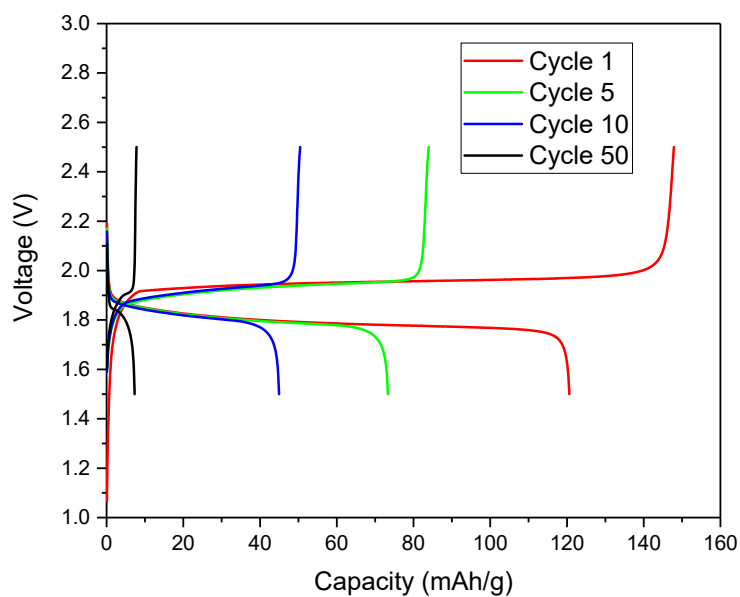


Figure S17. Galvanostatic charge/discharge plots for LTO: BHETA-PEG: LFP cell running at 60°C under 0.1C

References

1. K. Fukushima, J. M. Lecuyer, D. S. Wei, H. W. Horn, G. O. Jones, H. A. Al-Megren, A. M. Alabdulrahman, F. D. Alsewilem, M. A. McNeil, J. E. Rice and J. L. Hedrick, *Polym Chem*, 2013, **4**, 1610-1616.
2. J. Evans, C. A. Vincent and P. G. Bruce, *Polymer*, 1987, **28**, 2324-2328.