

*Supporting Information for*

## **Potential of Polymethacrylate Pseudo Crown Ethers as Solid State Polymer Electrolyte.**

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**A – Experimental section (p.S2)**

**B – Experimental data (p.S4)**

## A – Experimental section

### Materials

The inhibitor of poly(ethylene glycol)-dimethacrylate (PEG<sub>9</sub>DMA, Aldrich, 98%,  $M_n = 562 \text{ g.mol}^{-1}$  by  $^1\text{H}$  NMR, glass transition temperature ( $T_g$ )  $\sim -68^\circ\text{C}$ ) was removed by filtration through a basic alumina column from a diluted THF solution. The PEG<sub>9</sub>DMA macromonomer was then recovered by THF evaporation and dried at  $40^\circ\text{C}$  for 12 h under reduced pressure. Copper bromide (CuBr, from Fluka, 98%) was purified in acetic acid for 24 h and recrystallized in ethanol under inert atmosphere until a white powder was obtained. Bis(trifluoromethane)sulfonimide lithium salt (LiTFSI, Aldrich) was dried by heating under vacuum at  $160^\circ\text{C}$  for 12h. Ethyl-2-bromoisobutyrate (EBI, from Aldrich, 98%), 1,1,4,7,10,10-hexamethyltriethylene tetramine (HMTETA, from Aldrich, 97%), tetraethylene glycol (TCI, > 95%) and acetonitrile(- $d_3$ ) were used as received.

### Analytical techniques

All NMR spectra were performed on a Bruker Avance III spectrometer, operating at  $^1\text{H}$  and  $^7\text{Li}$  frequencies of 500.13 and 194.37 MHz respectively. All data was acquired and processed using TopSpin 3.0 pl6, using standard pulse sequences. For the  $^7\text{Li}\{-^1\text{H}\}$  HOESY sequence, 512 t1 increments obtained from 32 scans each were recorded with a NOE mixing time of 600 ms. Samples were prepared using acetonitrile- $d_3$  (EURISOTOP).

Number-average molecular weights and molecular weight distributions ( $\mathcal{D} = M_w/M_n$ ) values of polymers determined by Size Exclusion Chromatography (SEC) were based on experiments conducted in THF at  $35^\circ\text{C}$  at a flow rate of 1 mL/min, using an isocratic pump (VE 1122, Viscotek) a set of two PLgel 5 mm MIXED-C ultra high efficiency column and a Shodex SE 61 differential refractive index detector. A volume of 100  $\mu\text{L}$  of sample solution in chloroform (concentration 0.3% w/v) was injected. Poly(ethylene oxide) (PEO) standards (Polymer Laboratories) with narrow molecular weight distributions were used to generate a calibration curve. Differential scanning calorimetry (DSC) measurements were carried out with a DSC Q200 apparatus from T.A. Instruments under nitrogen flow (heating rate:  $10^\circ\text{C}/\text{min}$ ).

The electrical conductivity of the complexes was measured by Impedance Spectroscopy (IS). For this purpose, the complexes were coated on alumina substrates patterned with gold electrodes (from C-MAC). The system was calibrated with KCl solutions of known conductivity to be independent from both the electrode geometry and the film thickness (assuming that the film thickness is much higher than the distance between the gold electrodes, which was verified). IS measurements were performed with a combined potentiostat and frequency response analyser (*Parstat 2273* from *Ametek* and were recorded over a frequency range of 0.2 Hz to  $5 \cdot 10^5$  Hz with an AC amplitude of 5 mV rms. The spectra were modelled with the equivalent electrical circuit described in the results and fitted using *ZView* software. The experiments were carried out in air, in the dark, at a temperature varying from  $20^\circ\text{C}$  to  $80^\circ\text{C}$  by heating on a hot plate. The impedance spectrum is composed of a flattened semicircle at high frequencies, corresponding to the response of the electrolyte (modelled by a resistance in parallel with a constant phase element), followed by an almost straight line at low frequencies, characteristic of ion-blocking electrodes (accounting for the gold/electrolyte interface and modelled by a constant phase element). The conductivity was calculated by comparing the value of the electrolyte resistance to the calibration.

### Preparation of tetraethylene glycol dimethacrylate.

In a 200-ml round-bottomed flask filled with nitrogen, methacryloyl chloride (30.9 mmol, 3.02 ml) was added dropwise to a solution of tetraethylene glycol (10.3 mmol, 1.82 ml) and triethylamine (30.9 mmol, 4.31 ml) in dry tetrahydrofuran (30 ml) at 0 °C. The reaction mixture was stirred at 0 °C for 2 h and at 25 °C for an additional 22 h, and then evaporated under reduced pressure. The concentrated crude was diluted with diethyl ether (100 ml) and washed with water (2x35 ml). The aqueous layer was separated and further extracted with diethyl ether (35 ml). The combined ether solution was washed with 2x30 ml of 25% ammonia water three times and with 40 ml of distilled water once, and was dried on sodium sulphate overnight. Into the purified ether solution of PEG<sub>4</sub>DMA, dried cyclohexanone was added. The solution was then evaporated under reduced pressure to remove the ether to give cyclohexanone solution of PEG<sub>4</sub>DMA for cyclopolymerization. <sup>1</sup>H NMR [500 MHz, acetone-d<sub>6</sub>, r.t., δ]: d 6.08 (m, olefin, 2H), 5.62 (m, olefin, 2H), 4.24 (t, 4H, -COOCH<sub>2</sub>CH<sub>2</sub>O-), 3.71 (t, 4H, -COOCH<sub>2</sub>CH<sub>2</sub>O-), 3.62–3.56 (m, 16H, -OCH<sub>2</sub>CH<sub>2</sub>O-), 1.92 (m, 6H, -CCH<sub>3</sub>). Electrospray ionization mass spectrometry m/z ([M+Na<sup>+</sup>): calcd. for C<sub>16</sub>H<sub>26</sub>O<sub>7</sub>Na 353.4, found 353.2.

### Typical procedure of cation template-assisted living radical cyclopolymerization of PEG<sub>9</sub>DMA.

In a typical experiment (Table 1, entry 1), a previously flamed round bottom flask was charged with ACN (42 mL), LiTFSI (2.08 g, 10 eq., 7.2mmol), PEG<sub>9</sub>DMA (4 g, 10 eq., 7.1 mmol), and EBi (0.142 g, 1 eq., 0.73 mmol). The contents of the vial were then transferred to a nitrogen-filled Schlenk flask containing CuBr (0.104 g, 1 eq., 0.72 mmol) and HMTETA (0.336 g, 2 eq., 1.5 mmol). Three cycles of freeze-pump-thaw were used to degas the system. The flask was charged with N<sub>2</sub> at room temperature and then placed in an oil bath at 70 °C. Samples were taken out from the reaction mixture with a degassed syringe at the desired period for <sup>1</sup>H NMR and SEC analyses. The conversion was determined from the integration ratio of resonances at 0.65-1.3 ppm for the CH<sub>3</sub> unit in polymer backbone and 1.87 ppm for the CH<sub>3</sub> unit in monomer (reaction time: 90 min; conversion: 73 %; M<sub>n,SEC</sub> = 4,300 g/mol, Đ = 1.51).

The resulting crude was dialysed in water with a regenerated cellulose membrane (Spectra/Por ; MWCO 2,000) for 5 days. The inner solution was evaporated to dryness under reduced pressure to give P(*cyclo*PEG<sub>9</sub>DMA). <sup>1</sup>H NMR [500 MHz, CDCl<sub>3</sub>, δ, Figure S4]: 6.2, 5.6 (residual olefin), 4.2–4.0 (-COOCH<sub>2</sub>CH<sub>2</sub>O-), 3.8–3.5 (-CH<sub>2</sub>CH<sub>2</sub>O-), 2.1–1.3 (-CH<sub>2</sub>CCH<sub>3</sub>), 1.3–0.8 (-CCH<sub>3</sub>). Yield = 75%.

### Typical procedure of cation template-assisted living radical cyclopolymerization of PEG<sub>4</sub>DMA.

The same procedure than the one used to polymerize the PEG<sub>9</sub>DMA was applied by using 1 eq. of LiTFSI as compared to the PEG<sub>4</sub>DMA. Once again, samples were taken out from the reaction mixture with a degassed syringe at the desired period for <sup>1</sup>H NMR and SEC analyses. The conversion was determined from the integration ratio of resonances at 0.65-1.3 ppm for the CH<sub>3</sub> unit in polymer backbone and 1.87 ppm for the CH<sub>3</sub> unit in monomer (reaction time: 180 min; conversion: 33 %; M<sub>n,SEC</sub> = 1,600 g/mol, Đ = 1.32, estimated DP ~ 15).

The resulting crude was purified by fractionation in a THF/Heptane mixture: 1.5 g of the crude was initially solubilized by 30ml of THF before the slow addition of cold heptane (~ 30 ml). The polymer was then dry under reduced pressure to give P(*cyclo*PEG<sub>4</sub>DMA). <sup>1</sup>H NMR [500 MHz, CDCl<sub>3</sub>, δ]: 6.2,

5.6 (residual olefin), 4.2–4.0 (-COOCH<sub>2</sub>CH<sub>2</sub>O-), 3.8–3.5 (-CH<sub>2</sub>CH<sub>2</sub>O-), 2.1–1.3 (-CH<sub>2</sub>CCH<sub>3</sub>), 1.3–0.8 (-CCH<sub>3</sub>). Yield = 34%.

### **Polymer-Salt Complexation.**

Polymer-LiTFSI complexes were prepared by mixing lithium salts with the polymers in an excess of ACN. After homogenization, solutions were slowly evaporated at r.t. then extensively dried at 40°C for 12 hours. Compositions of solutions are defined using the usual [Li]/[EO] ratio where [EO] is the number of ether oxygen atoms per Li<sup>+</sup>.

### **Theoretical Methodology**

In order to characterize the three-dimensional structure of a PEG<sub>9</sub>DMA monomer and the complex with two lithium cations, their geometries have been first optimized at the molecular mechanics level using the Universal force field [1], as implemented in the Materials Studio 6.0 package [2]. All default parameters have been selected except for the cutoff distance for non-bonded interactions which has been increased up to 100 Å so that none of them was neglected; the conjugated gradient has been selected to achieve the geometry optimizations. The atomic charges used are those implemented in the COMPASS force field [3]. Based on the optimized geometries, 100 ps-long quenched dynamics (NVT; T = 298K, snapshots optimized every 1ps) were performed to explore the potential energy surface. The resulting lowest energy structures were then used as the starting point for two successive 1 ns-long molecular dynamics (MD) at room temperature (NVT; T = 298K, snapshots saved every 1 ps). The second runs have been used to analyze the structural characteristics of the systems. The distribution profiles in Figure 2 have been built from the measured distances between the two reactive groups for the 1000 frames saved during the last MD runs.

[1] Casewit, C.J.; Colwell, K.S.; Rappé, A.K. *J.Am.Chem.Soc.* **1992**, *114*, 10035-10046

[2] MS Modelling v6.0.0, Accelrys Software Inc: San Diego **2011**

[3] Sun, H. *J. Phys. Chem. B* **1998**, *102*, 7338-7364

## B- Experimental data

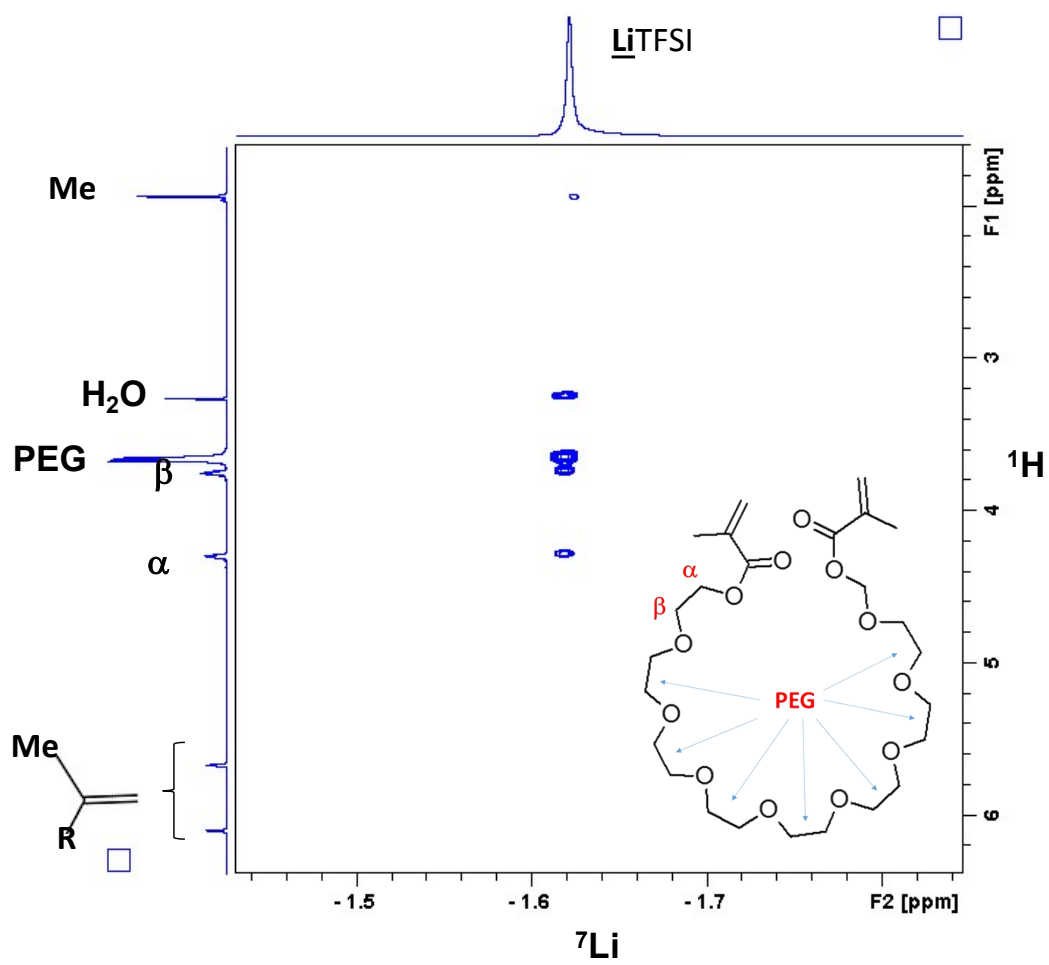


Figure S1. 600 ms  $^7\text{Li}\{-^1\text{H}\}$  HOESY spectrum of a LiTFSI:PEG<sub>9</sub>DMA solution in 2:1 ratio. The identity of the PEG<sub>9</sub>DMA resonances are indicated on the 1D  $^1\text{H}$  spectrum on the left. Note the absence of NOE contacts between the lithium resonance and the dimethacrylate moieties.

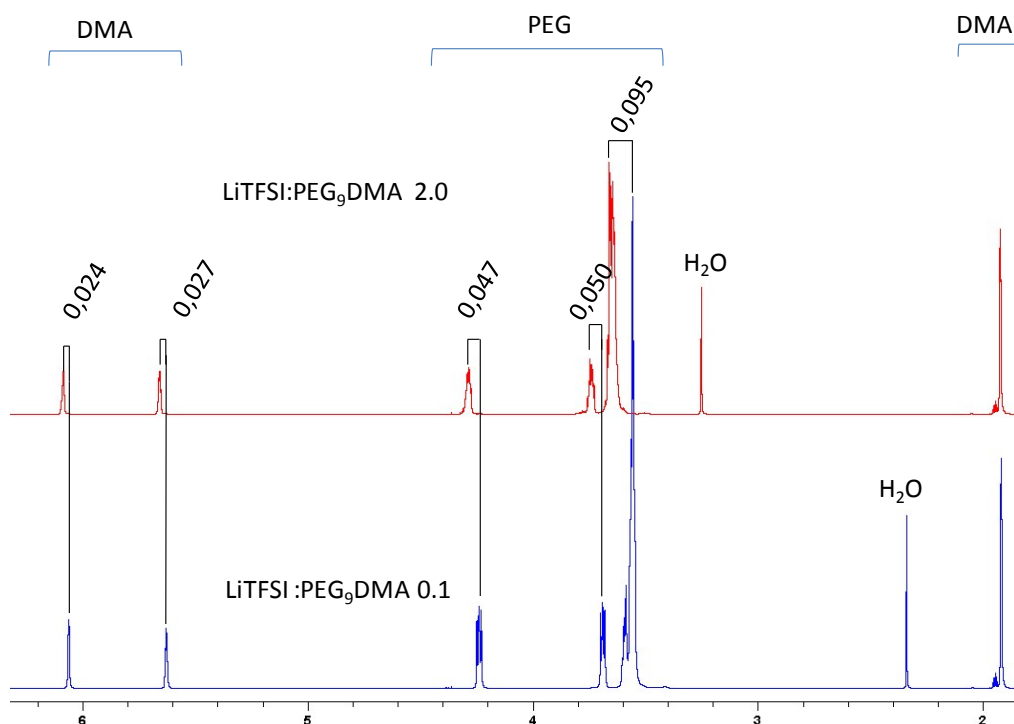


Figure S2. Comparison of the 1D  $^1\text{H}$  spectra of PEG<sub>9</sub>DMA in acetonitrile-*d*<sub>3</sub> in the presence of LiTFSI at the mutual ratio's as indicated. Observable shifts are highlighted together with the values of the chemical shift change. The PEG<sub>9</sub>DMA resonances as seen in the bottom spectrum shift progressively towards the positions observed in the top spectrum as the concentration ratio with LiTFSI changes from 0.1 to 2.0. The observation of a concentration sensitive single set of resonance throughout the titration is indicative for a  $\text{Li}^+$  to PEG<sub>9</sub>DMA binding equilibrium that is fast on the NMR time scale.

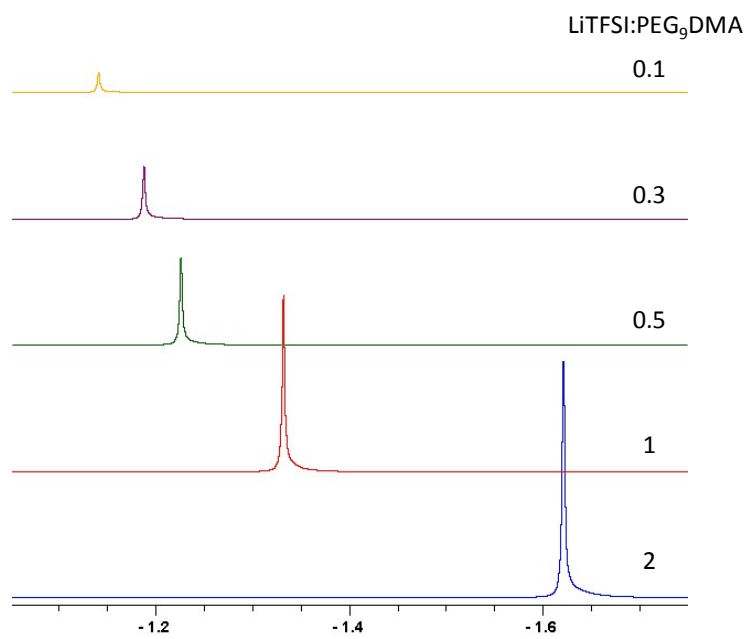


Figure S3. Titration of PEG<sub>9</sub>DMA with LiTFSI in acetonitrile-*d*<sub>3</sub> monitored using <sup>7</sup>Li NMR. The LiTFSI:PEG<sub>9</sub>DMA ratio is indicated.

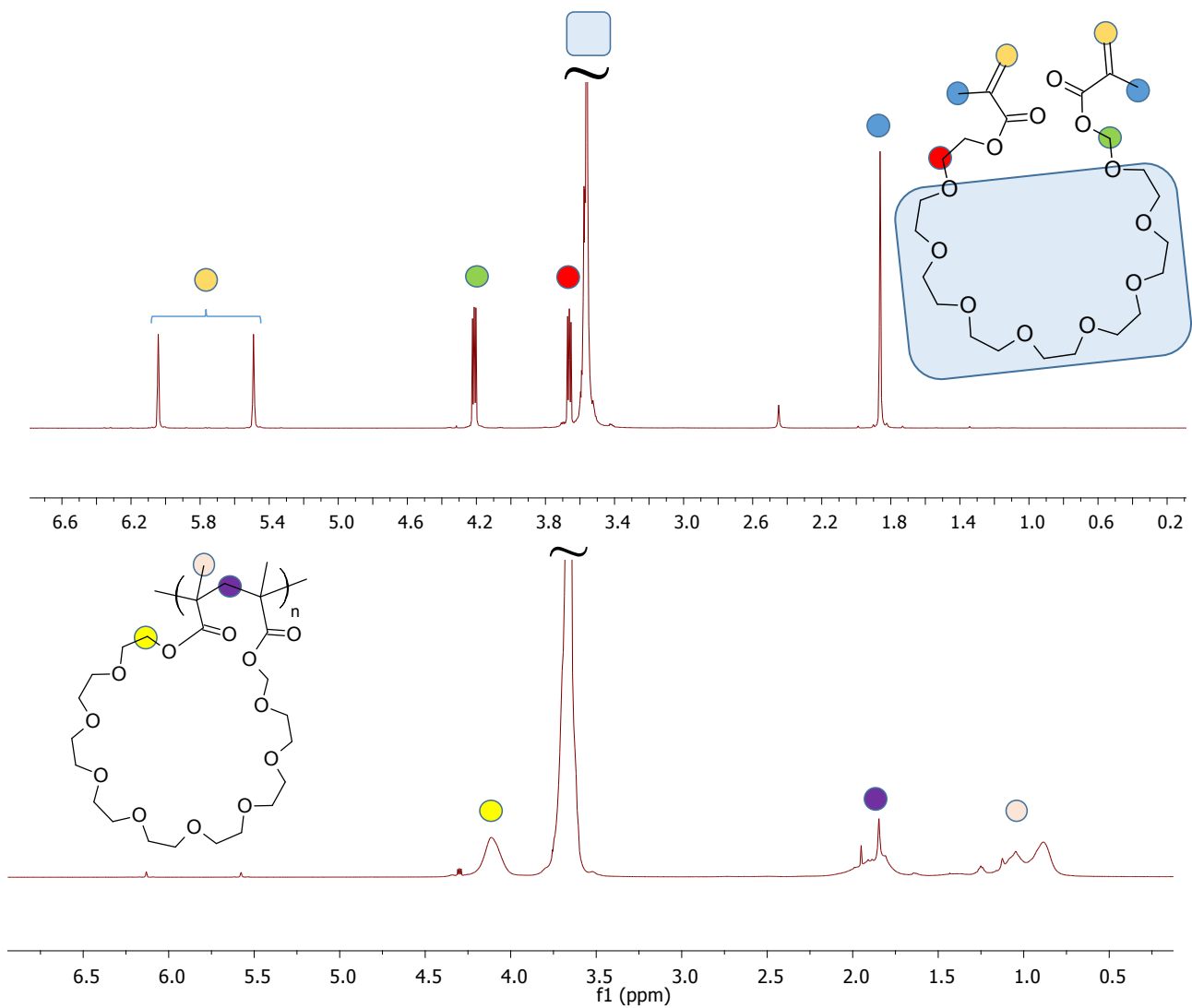


Figure S4.  $^1\text{H}$  NMR analyses of PEG<sub>9</sub>DMA (top) and P(*cyclo*PEG<sub>9</sub>DMA) (bottom) [purified from PEG<sub>9</sub>DMA macromonomer] recorded at 500 MHz in  $\text{CDCl}_3$  at 21°C.



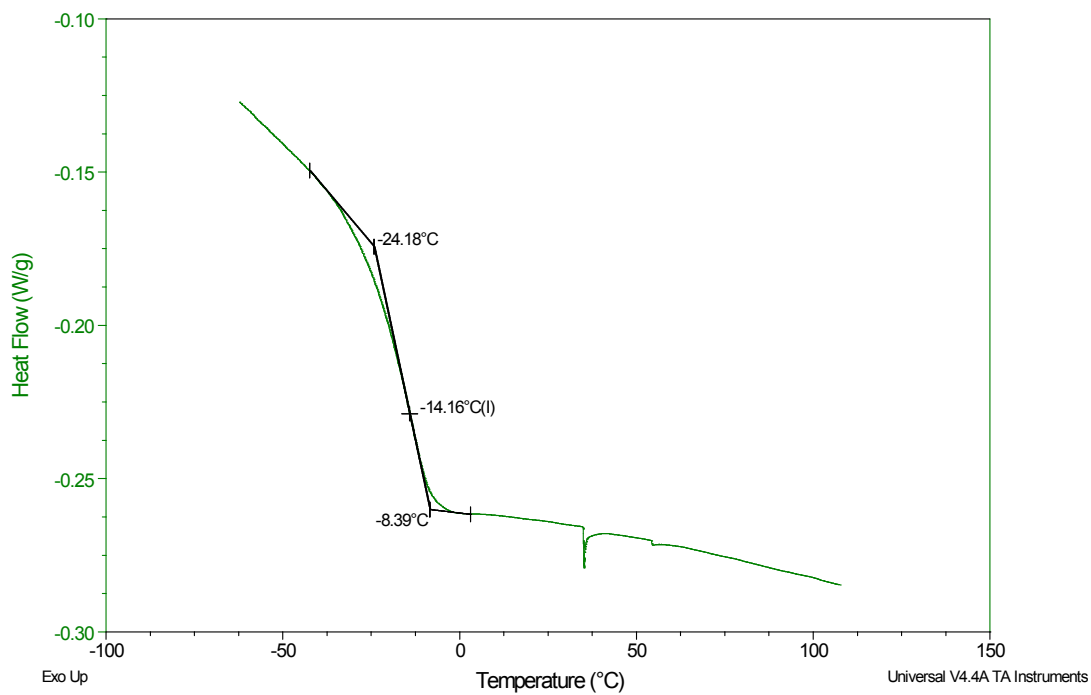


Figure S5. DSC analysis of P(*cyclo*PEG<sub>9</sub>DMA)<sub>8</sub> recorded under N<sub>2</sub> from -60°C to 100°C (10°C/min)

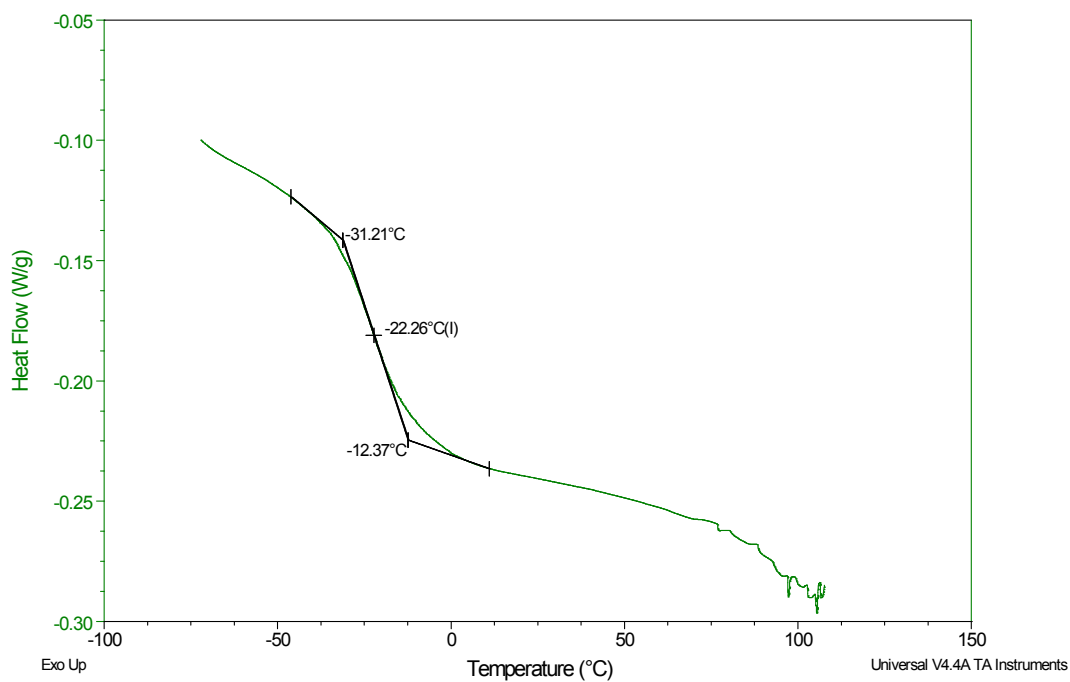


Figure S6. DSC analysis of P(*cyclo*PEG<sub>9</sub>DMA)<sub>8</sub>/LiTFSI complex ([EO]<sub>0</sub>/[Li]<sub>0</sub> = 20) recorded under N<sub>2</sub> from -60°C to 100°C (10°C/min)

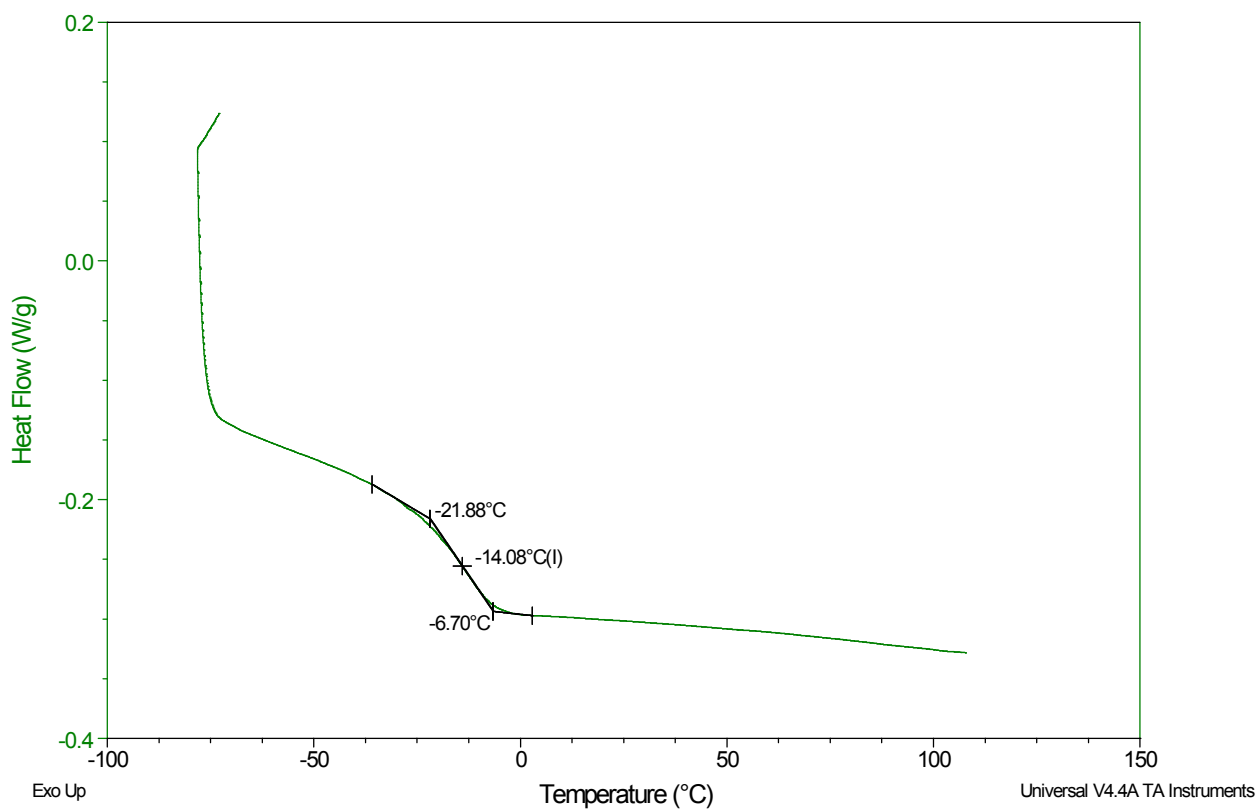


Figure S7. DSC analysis of P(*cyclo*PEG<sub>9</sub>DMA)<sub>35</sub> recorded under N<sub>2</sub> from -60°C to 100°C (10°C/min)

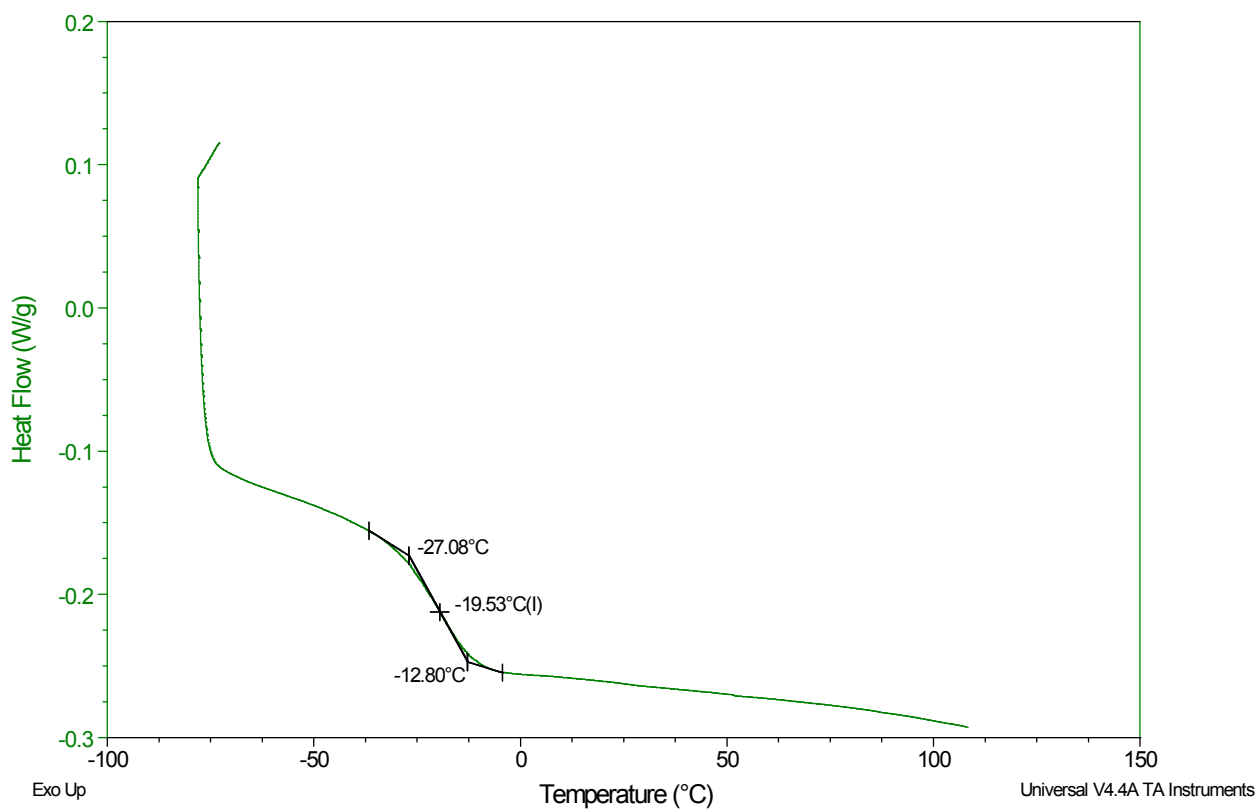


Figure S8. DSC analysis of P(*cyclo*PEG<sub>9</sub>DMA)<sub>35</sub>/LiTFSI complex ([EO]<sub>0</sub>/[Li]<sub>0</sub> = 20) recorded under N<sub>2</sub> from -60°C to 100°C (10°C/min)

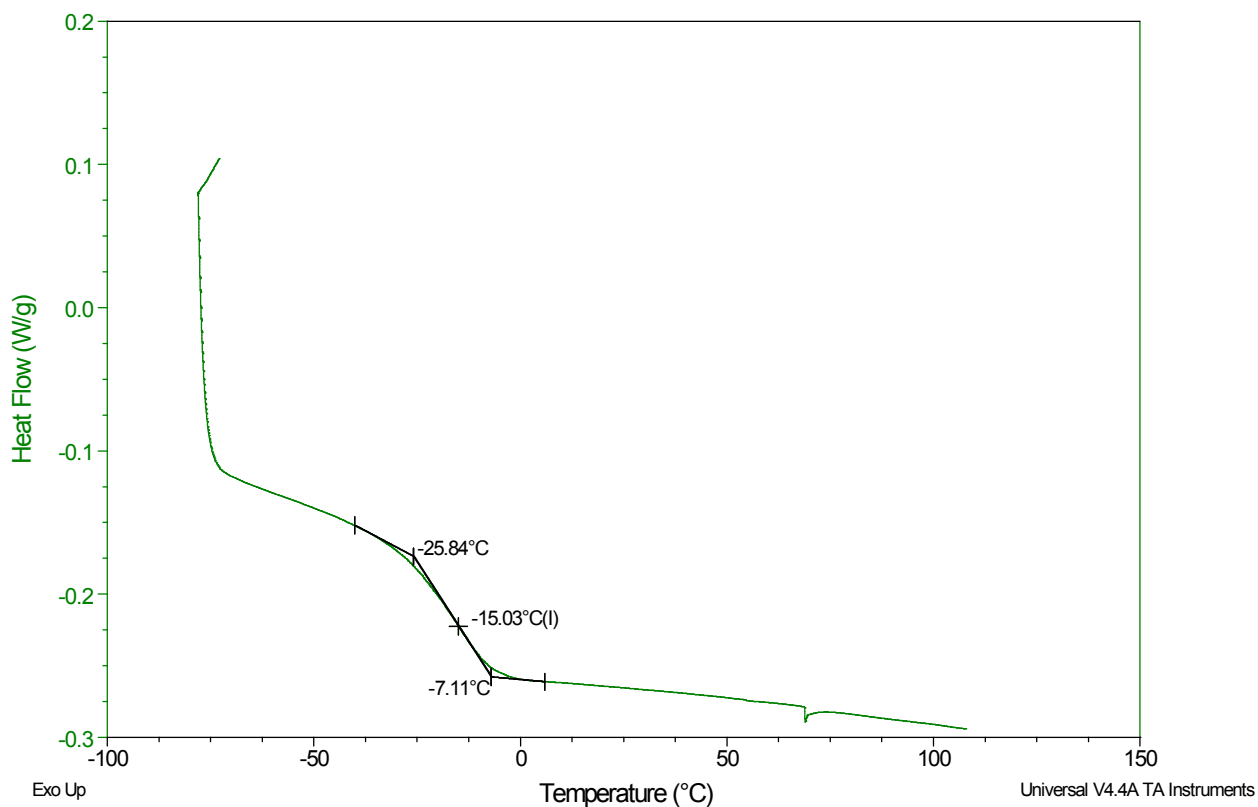


Figure S9. DSC analysis of P(cycloPEG<sub>9</sub>DMA)<sub>70</sub> recorded under N<sub>2</sub> from -60°C to 100°C (10°C/min)

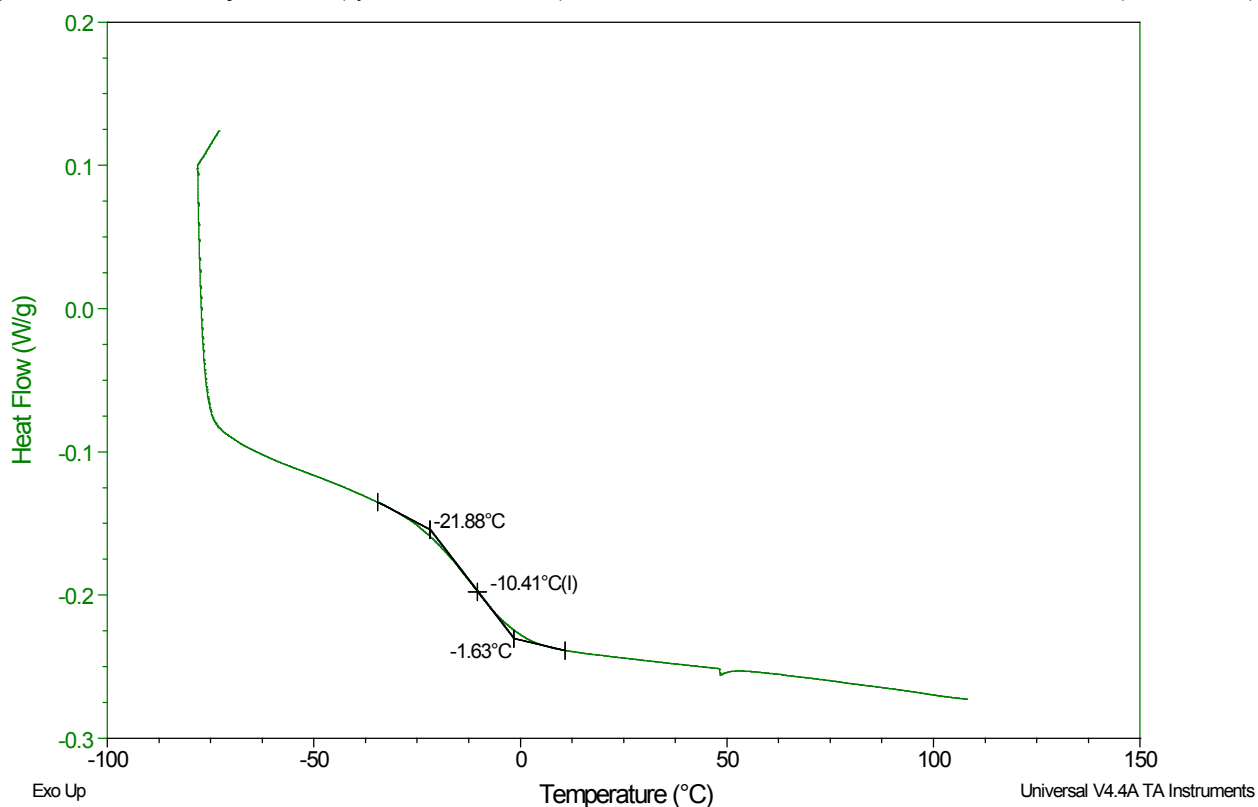


Figure S10. DSC analysis of P(cycloPEG<sub>9</sub>DMA)<sub>70</sub>/LiTFSI complex ([EO]<sub>0</sub>/[Li]<sub>0</sub> = 20) recorded under N<sub>2</sub> from -60°C to 100°C (10°C/min)

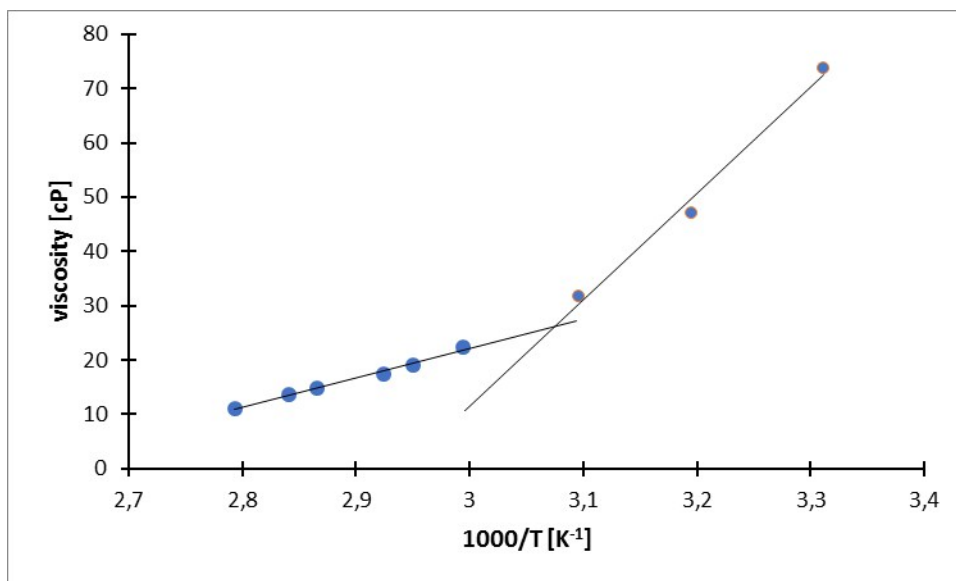


Figure S11. Graphical representation of the viscosity data reported in reference 16.

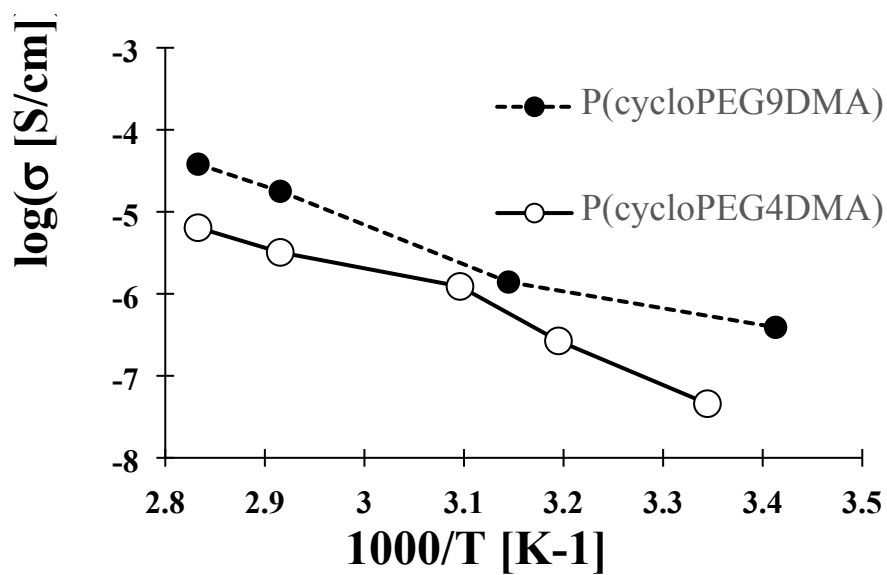


Figure S12. Arrhenius plot of conductivities for P(*cyclo*PEG<sub>9</sub>DMA)<sub>8</sub> and P(*cyclo*PEG<sub>4</sub>DMA)<sub>15</sub>.