Supporting Information

Optimizing Ion Transport in Polyether-based Electrolytes for Lithium Batteries

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# Contents

1. Synthesis Details

1.1 General Considerations

The synthesis of P(2EO-MO) has been briefly reported[1–3] but previous work has not explored its application as a polymer electrolyte. Step-growth polymerization between diethylene glycol and paraformaldehyde was not successful in obtaining a high molecular weight polymer, instead, an oligomer was synthesized with an $M_n \sim 1$ kDa. However, the resulting oligomer can be heated under vacuum and depolymerized to yield the cyclic ether monomer, 1,3,6-trioxocane, which can then be polymerized subsequently under cationic conditions to yield higher molecular weight P(2EO-MO). All air and water sensitive reactions were carried out under dry nitrogen conditions using standard Schlenk techniques or MBraun UniLab drybox.

1.2. Materials

Diethylene glycol, paraformaldehyde, polyphosphoric acid, BF$_3$·OEt$_2$, α-bromoisobutyryl bromide was purchased from Sigma-Aldrich and used as received. *n*-Heptane was purchased from Fisher Scientific. Dichloromethane and tetrahydrofuran (THF) was purchased from Fisher Scientific and dried using a Phoenix solvent drying system and degassed by freeze-pump-thaw method for three cycles before use. All the other chemicals were purchased from commercial vendors and used as received unless otherwise noted. NMR solvent (CDCl$_3$) was purchased from Cambridge Isotope Laboratories (CIL) and used as received.

1.3 Synthesis of 1,3,6-trioxocane Monomer
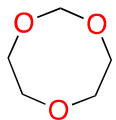
Diethylene glycol (15.92 g, 150 mmol), paraformaldehyde (5.86 g, 195 mmol), and polyphosphoric acid (~0.2 mL) was dissolved in 30 mL *n*-heptane. The resulting mixture was

refluxed at 110 °C for 16 h with a Dean-Stark head to remove the water generated from the reaction. Solvent was removed and the resulting white solid was melted by heating and distilled at 150 °C under static vacuum (0.2 torr). The collected liquid was a mixture of the desired product and diethylene glycol. The collected liquid was fractional distilled at 28 °C under static vacuum (0.2 torr) to yield the product as a colorless liquid (13.4 g, 75%). The ^{1}H NMR spectra and ^{13}C NMR for 1,3,6-trioxocane are shown in Figure S1 and Figure S2.

1.4 Synthesis of P(2EO-MO) Polymer
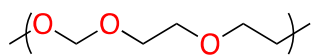
The monomer 1,3,6-trioxocane (4.00 g, 33.9 mmol) was dissolved in 10 mL dichloromethane. To this solution was added a 0.5 mol/mL stock solution of BF$_3$·OEt$_2$ (0.677 mL, 0.339 mmol). The mixture was stirred at room temperature for 2 h and quenched with water. The resulting mixture was washed with water and the organic layer was separated and dried over anhydrous Na$_2$SO$_4$. The organic layer was concentrated under rotavapor and added dropwise into hexanes. A white solid was precipitated out. The solid was filtered and dried under vacuum to yield the polymer product as a white solid (3.30 g, 83 %). The ^{1}H NMR spectra and ^{13}C NMR for P(2EO-MO) are shown in Figure S3 and Figure S4.

Table S1 summarizes the P(2EO-MO) synthesis with different mol% of BF$_3$·OEt$_2$ catalysts and temperatures. The polymerization exhibits very fast rates and the reaction normally started to become viscous after 30 minutes and reached full conversion in 2 hours. The yielded polymer has an alternating sequence of 2EO and MO units, and no regio-defects are observed based on ^{13}C-NMR. It is noteworthy that there is an equilibrium between the high molecular weight polymer and oligo-macrocycles in the cationic ring-opening polymerization (see Figure S5 for an exemplary crude GPC of Table S1 entry 3) possibly because of backbiting from the

active chain end. The oligo-macrocycles can be removed by precipitation in hexanes. The formation of oligo-macrocycles was greatly suppressed when the reaction temperature was lowered and an increased M_ns was observed for all initiator loadings. The M_ns of the synthesized P(2EO-MO) at all loadings were all higher than the theoretical M_n, suggesting that not all initiators initiated the polymerization. A similar discrepancy between experimental and theoretical M_ns has been reported by Chien and co-workers[1] in polymerizing 1,3,6-trioxocane in toluene with the $BF_3 \cdot OEt_2$ catalyst.

Table S1. Synthesis of P(2EO-MO)

Entry	Temperature (°C)	Initiator loading (mol%)	Conversion %[a]	Theoretical M_n (kg/mol)	Experimental M_n (kg/mol)[b]	$Đ$[b]
1	22	1	>99	11.8	74.8	2.3
2[c]	22	2	>99	5.9	47.5	2.0
3	22	5	>99	2.4	28.5	1.9
4	0	1	>99	11.8	126.9	2.3
5	0	2	>99	5.9	66.6	2.6
6	0	5	>99	2.4	58.5	2.2

[a]The conversion of the polymerization was determined from ^{1}H-NMR from the crude reaction mixture. [b]Number average molecular weight (M_n) and polydispersity index (PDI) were determined by THF gel permeation chromatography calibrated with polystyrene. [c]Polymer from a scale-up reaction of this entry was used for electrochemical study in this paper. The polymer used in this study has an M_n of 55 kDa and polydispersity index of 2.2.

1.5 NMR

^{1}H NMR spectra were collected on a Bruker AV 500MHz spectrometer equipped with liquid nitrogen cooled cryoprobe and referenced with residue non-deuterated solvent shifts ($CHCl_3$ = 7.26 ppm). ^{13}C NMR spectra were collected on a Bruker AV 500 MHz (^{13}C, 125 MHz) spectrometer liquid nitrogen cooled cryoprobe and referenced to chloroform (δ 77.23 ppm). High resolution mass spectrometry (DART-HRMS) analyses were performed on a Thermo Scientific Exactive Orbitrap MS system equipped with an Ion Sense Direct Analysis in Real Time (DART) ion source.
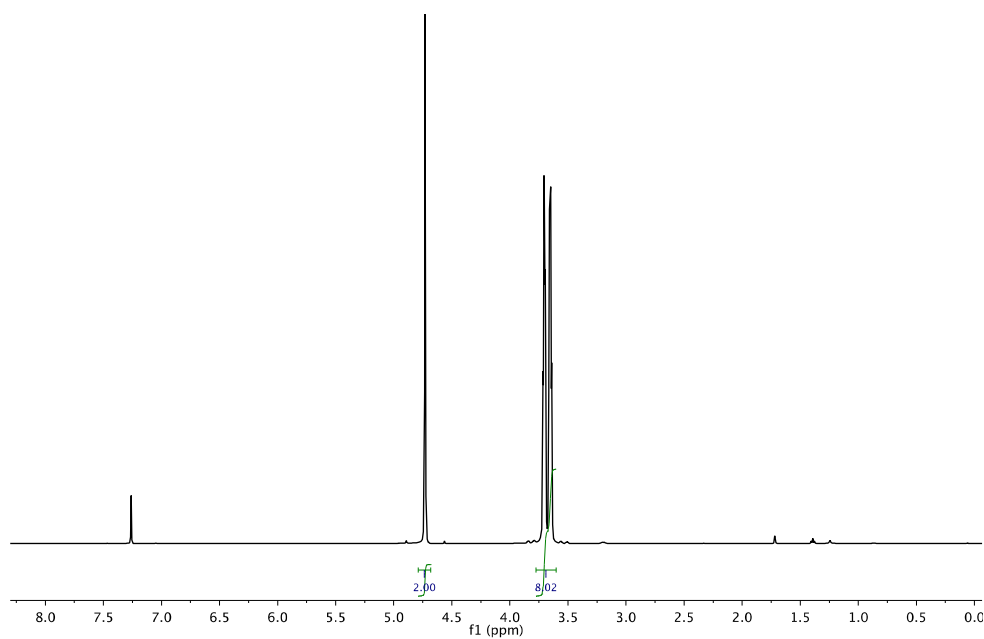
HRMS (DART) *m/z* calculated for $C_5H_{11}O_3^+$ [M + H]$^+$ 119.07027, found 119.07095.
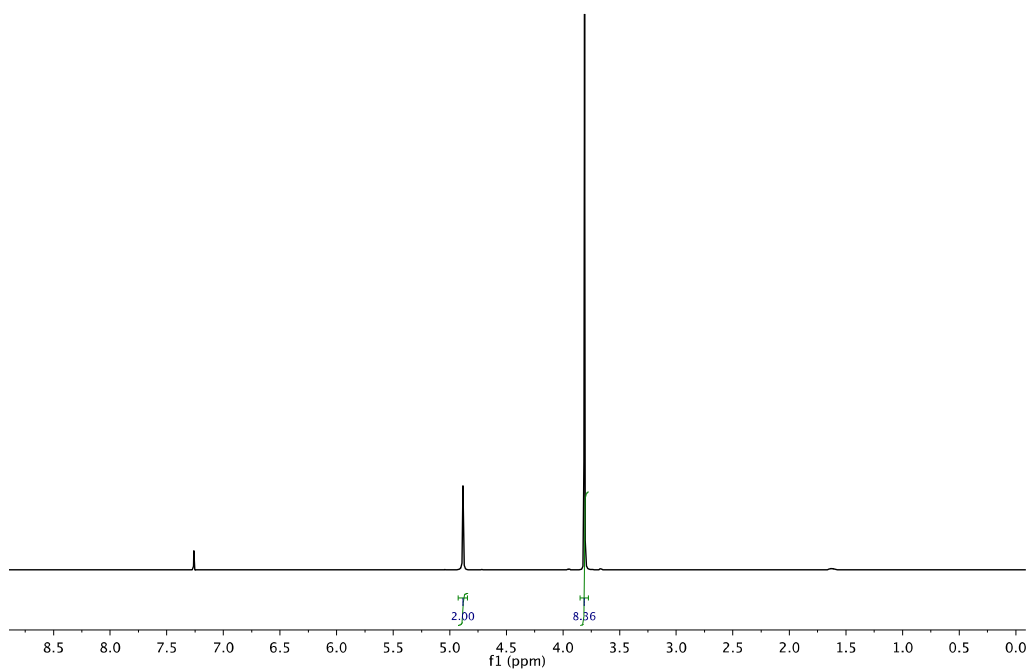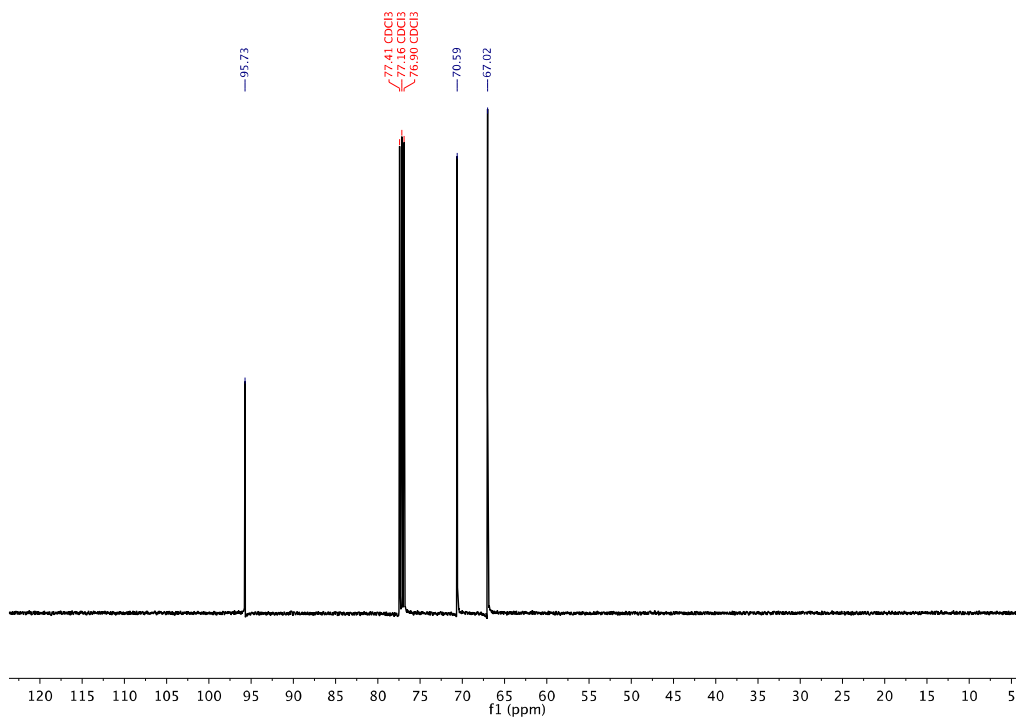
Figure S1. ^{1}H-NMR (500 MHz, CDCl3) δ 4.88 (s, 2H), 3.81 (s, 8H) spectrum of 1,3,6-trioxocane. Signal at 7.26 ppm is residue $CHCl_3$.
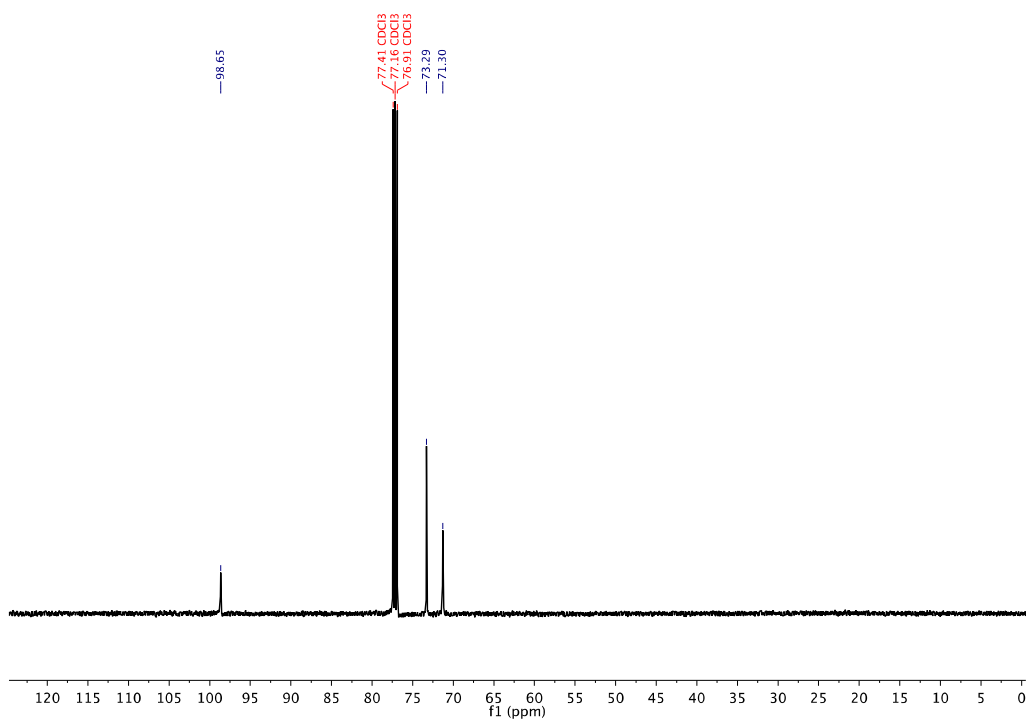
Figure S2. ^{13}C-NMR (125 MHz, CDCl3) δ 98.65, 73.29, 71.30 spectrum of 1,3,6-trioxocane. Signal at 77.16 ppm is residue CHCl$_3$.

Figure S3. ^{1}H-NMR (500 MHz, CDCl3) δ 4.73 (s, 2H), 3.74 – 3.61 (m, 8H) spectrum of poly(1,3,6-trioxocane). Signal at 7.26 ppm is residue CHCl$_3$.

Figure S4. ^{13}C-NMR (125 MHz, CDCl3) δ 95.73, 70.59, 67.02 spectrum of poly(1,3,6-trioxocane). Signal at 77.16 ppm is residue CHCl$_3$.

1.6 GPC

Gel permeation chromatography (GPC) analyses were carried out using an Agilent PL-GPC 50 integrated system, equipped with UV and refractive index detectors, and 2 PL gel Mini-MIX C columns (5 micron, 4.6 mm ID). The GPC columns were eluted with tetrahydrofuran at 30 °C at 0.3 mL/min and were calibrated with monodisperse polystyrene standards.
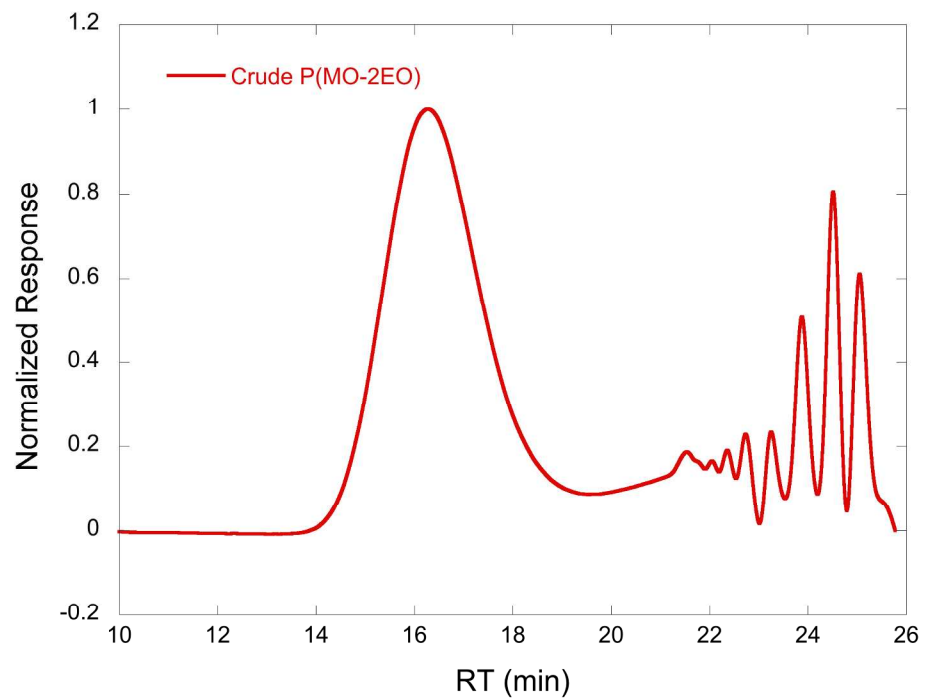
**Figure S5.** GPC traces of the crude mixture of Table 1 entry 3.

2. DSC of PEO and P(2EO-MO) Electrolytes
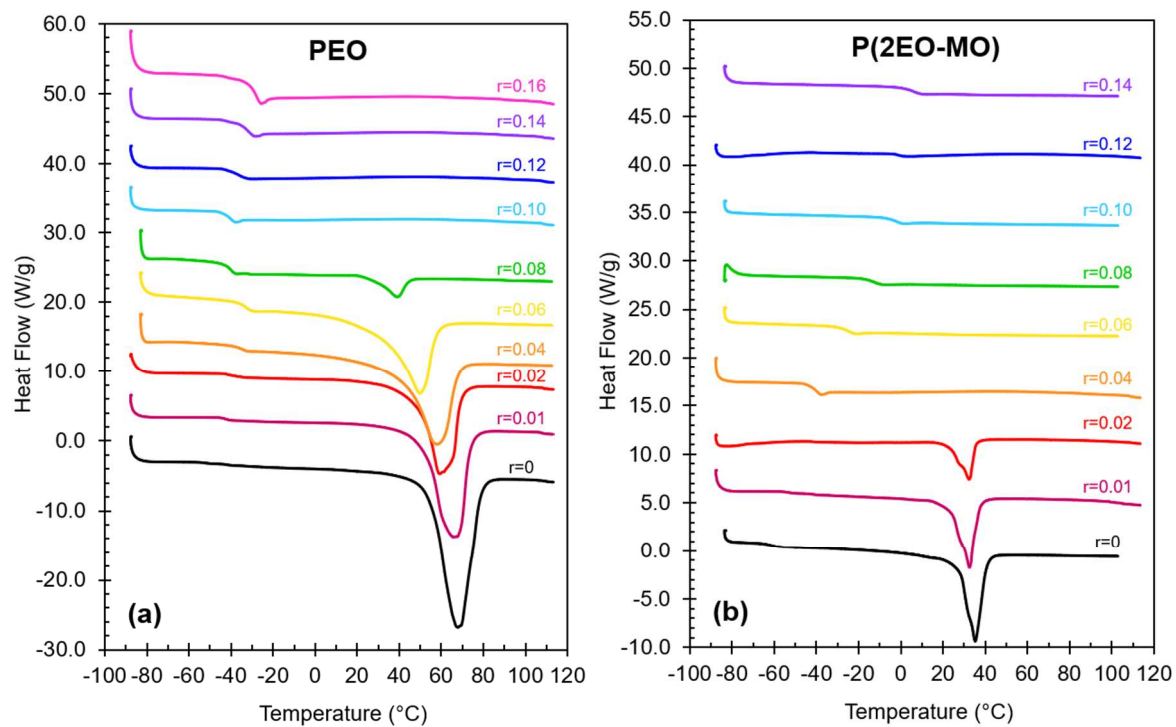
Figure S6. Differential scanning calorimetry (DSC) curves of (a) PEO and (b) P(2EO-MO) electrolytes at different salt concentrations.

3. Li-TFSI Radial Distribution Functions

Figure S7 shows a comparison of the Li-TFSI radial distribution function (rdf) in PEO and P(2EO-MO) as a function of salt concentration. In each case the rdf is calculated with respect to the Li cations and the oxygen atoms in TFSI. The rdfs show a minimal counter-ion presence in the first solvation shell of the ions. The counter-ion feature in the Li-solvation shell is also much weaker than the corresponding ether oxygen feature in the polymer-Li rdfs. This data is consistent weak ion pairing in both polymers for all studied salt concentrations.
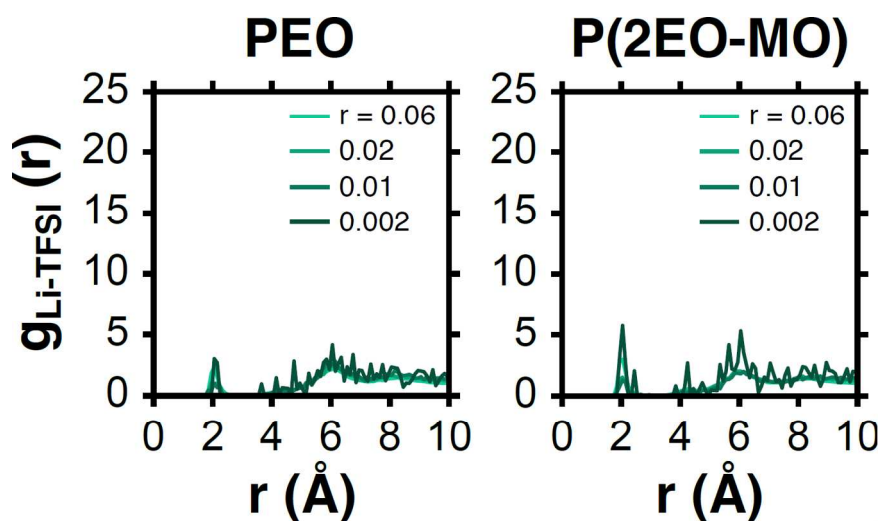
Figure S7. Comparison of Li-TFSI radial distribution functions at different salt concentrations in PEO (left) and P(2EO-MO) (right). Note, "r" in each legend refers to the salt concentration.

4. References

(1)   Xu, B.; Lillya, C. P.; Chien, J. C. W. Cationic Polymerizations of 1,3,6-Trioxocane and 2-Butyl-1,3,6-trioxocane. *Macromolecules* **1987**, *20* (7), 1445–1450.

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(3)   Kawakami, Y.; Yamashita, Y. Macrocyclic Formals. 3. Two-Stage Polymerization of 1,3-Dioxacycloalkanes. *Macromolecules* **1977**, *10* (4), 837–839.