

Electronic Supporting Information for

Miscible Polyether/Poly(ether-acetal) Electrolyte Blends

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I. General Considerations

All manipulations of air and water sensitive compounds were carried out under nitrogen in an MBraun Labmaster glovebox or by using standard Schlenk line techniques.

Dichloromethane for air sensitive reactions was purchased from Fisher, sparged with ultrahigh purity (UHP) grade nitrogen, and passed through two columns of alumina and dispensed into an oven-dried Straus flask, followed by three freeze-pump-thaw cycles. Otherwise, solvents (heptane, hexanes, acetonitrile, and isopropanol) were used as received. All other chemicals and reagents, except for 1,3,6-trioxocane (*vide infra*), were purchased from commercial sources (Millipore Sigma, Oakwood Chemical, TCI, and Fisher) and used without further purification.

II. Instrumentation

^1H and ^{13}C NMR spectra were recorded on a Bruker AV III HD (^1H , 500 MHz) spectrometer with a broad band Prodigy cryoprobe or Varian IVarian INOVA 400 (^1H , 400 MHz) spectrometer. Chemical shifts (δ) for ^1H and ^{13}C NMR spectra were referenced to protons on the residual solvent (for ^1H) and deuterated solvent itself (for ^{13}C).

High-resolution mass spectrometry (HRMS) analyses were performed on a Thermo Scientific Exactive Orbitrap MS system equipped with an Ion Sense DART ion source.

Thermogravimetric Analysis (TGA) was performed on a TA Instruments Q500 Thermogravimetric Analyzer. The measurement was performed on 8–10 mg samples, which were heated in a nitrogen atmosphere from 25 °C to 600 °C at a rate of 10 °C/min.

Gel permeation chromatography (GPC) analyses were carried out using an Agilent 1260 Infinity GPC System equipped with an Agilent 1260 Infinity autosampler and a refractive index detector. The Agilent GPC system was equipped with two Agilent PolyPore columns (5 micron, 4.6 mm ID) which were eluted with THF at 30 °C at 0.3 mL/min and calibrated using monodisperse polystyrene standards.

AC impedance measurements were performed on lithium symmetric cells using a Bio-Logic VMP3 potentiostat over a 0.1–10⁶ Hz frequency range at an amplitude of 80 mV.

III. Polymer Characterization

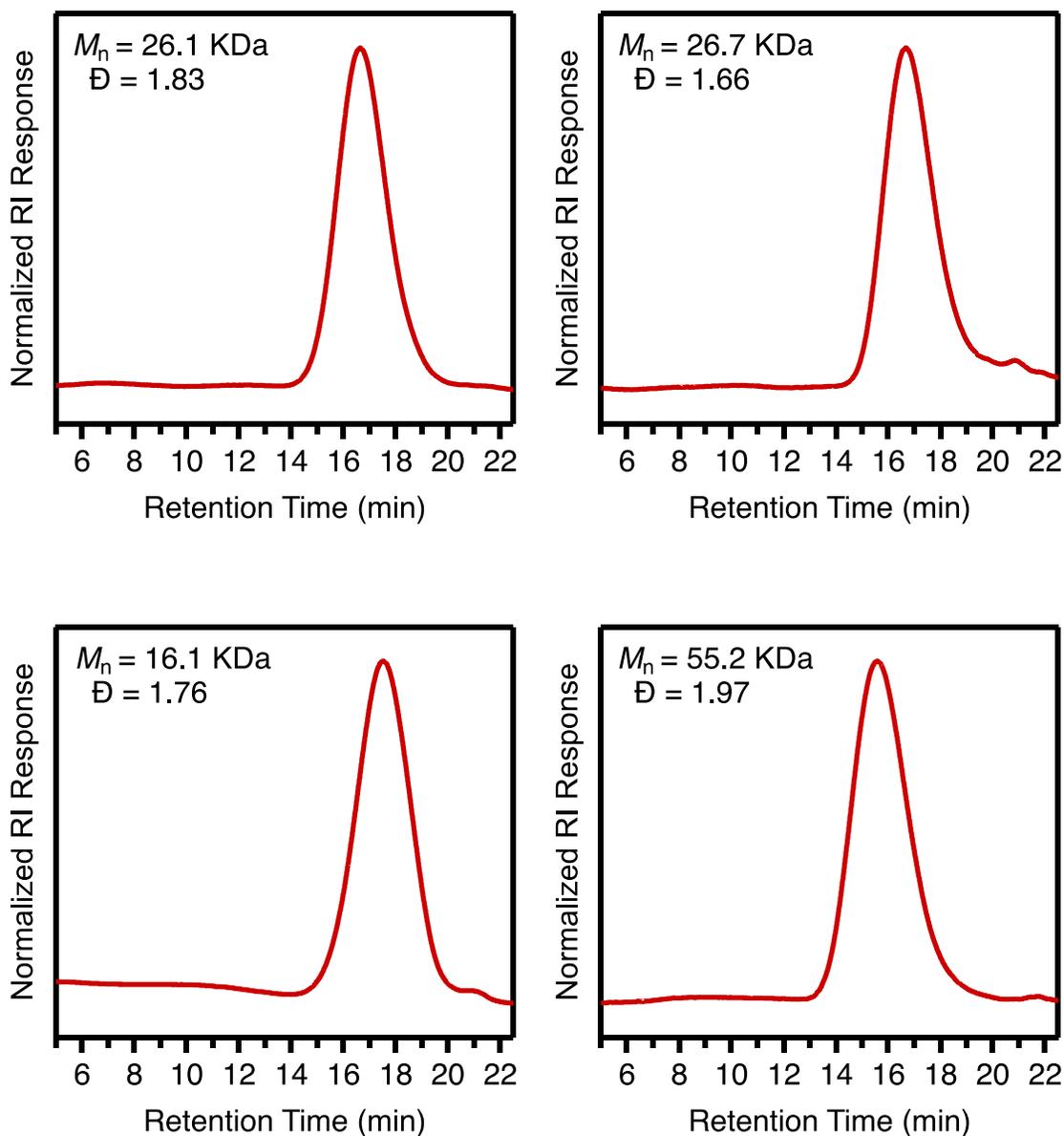


Figure S1. GPC traces of P(2EO-MO) sample 1 (upper left), sample 2 (upper right), sample 3 (lower left) and sample 4 (lower right) show monomodal distributions.

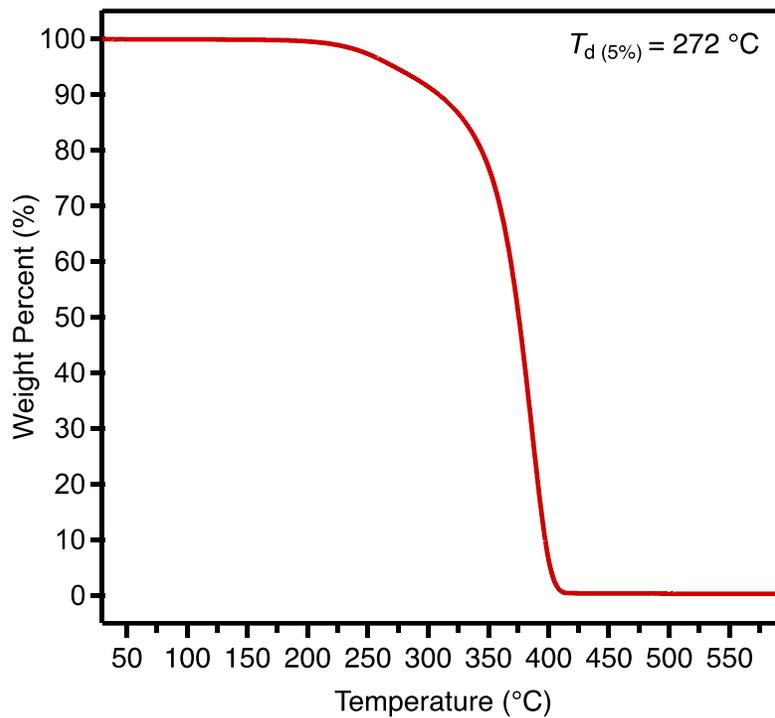


Figure S2. Representative thermogravimetric analysis of poly(1,3,6-trioxocane) shows weight loss due to thermal degradation begins near 230 °C and reaches 5% loss at 272 °C.

IV. NMR Spectra

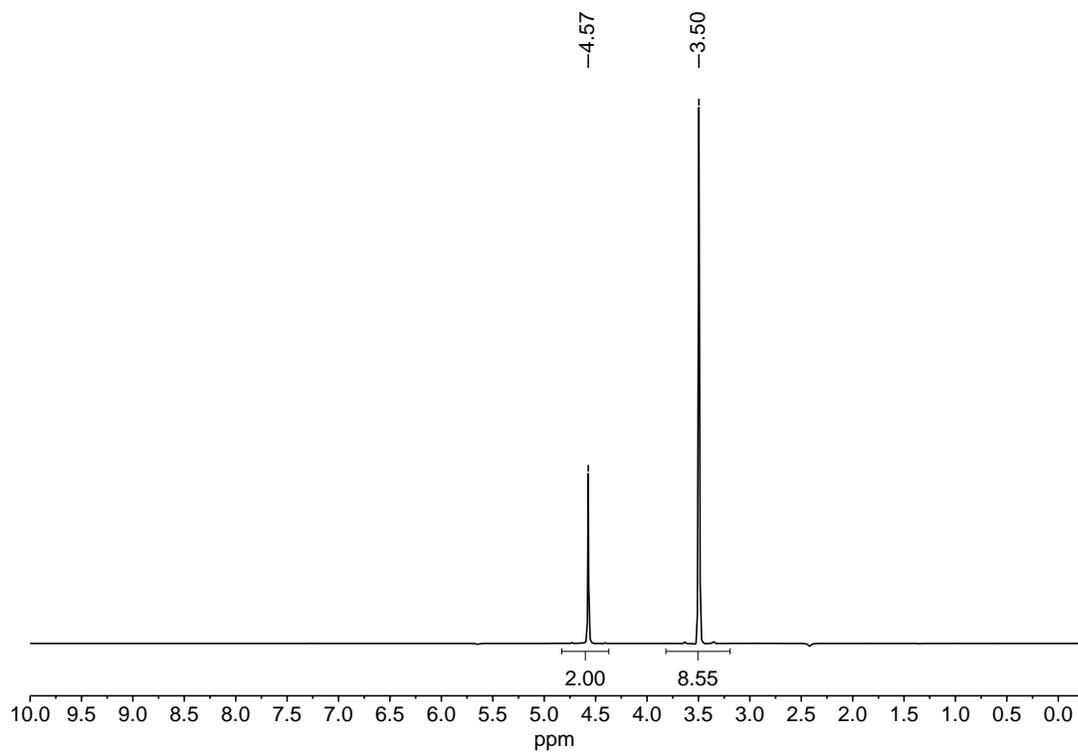


Figure S3. 1,3,6-trioxocane (2EO-MO) ¹H NMR Spectrum (500 MHz, CDCl₃)

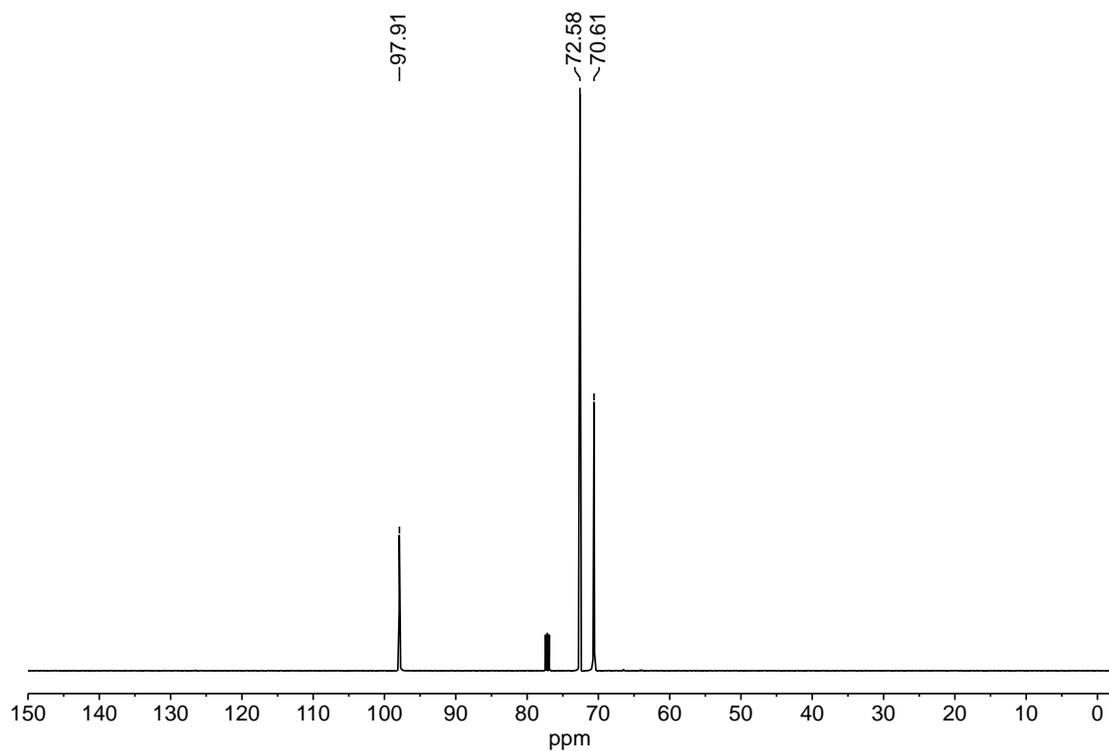
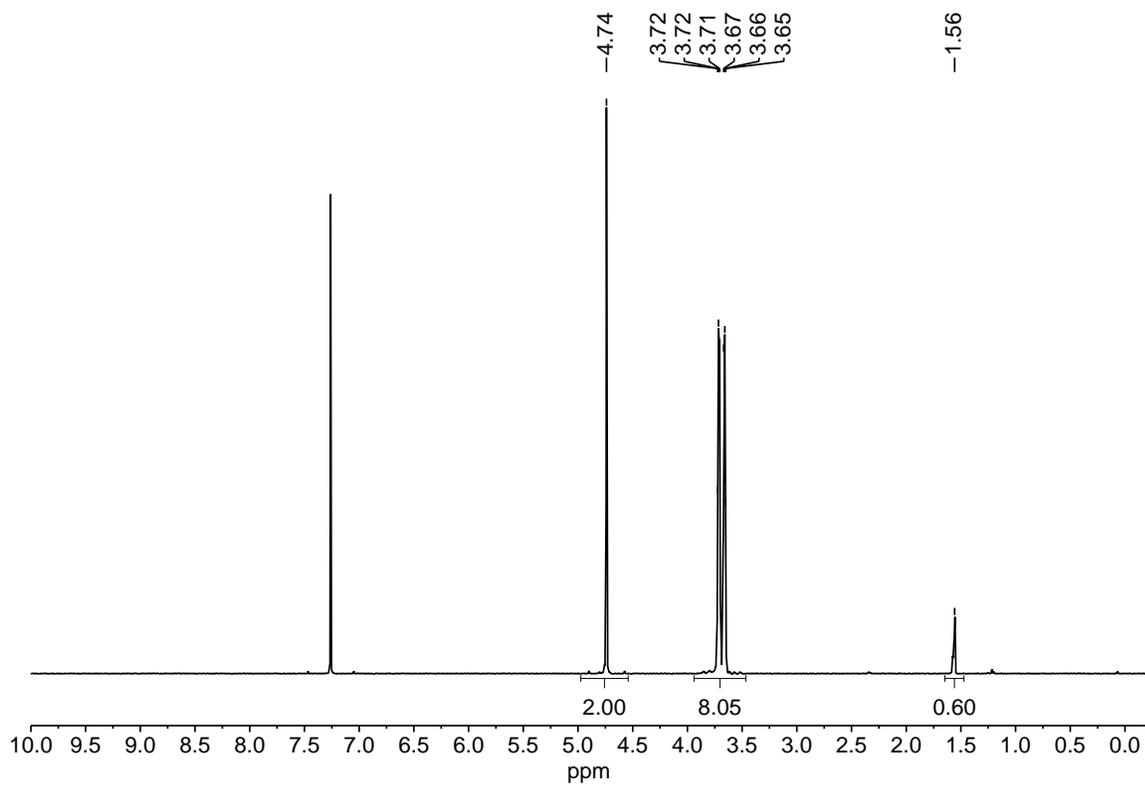


Figure S4. 1,3,6-trioxocane (2EO-MO) ¹³C NMR Spectrum (125 MHz, CDCl₃)



Figures S5. Poly(1,3,6-trioxocane) (P(2EO-MO)) ^1H NMR Spectrum (500 MHz, CDCl_3)

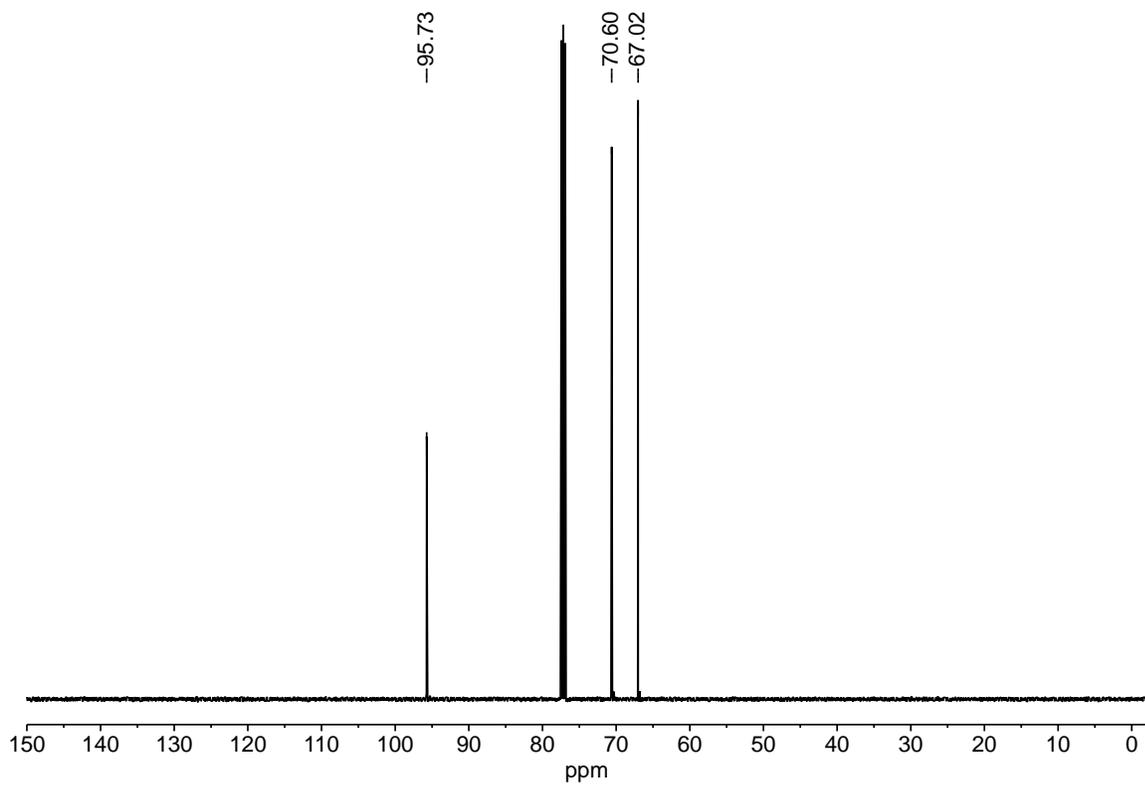


Figure S6. Poly(1,3,6-trioxocane) (P(2EO-MO)) ^{13}C NMR Spectrum (125 MHz, CDCl_3)

V. AC Impedance Spectroscopy

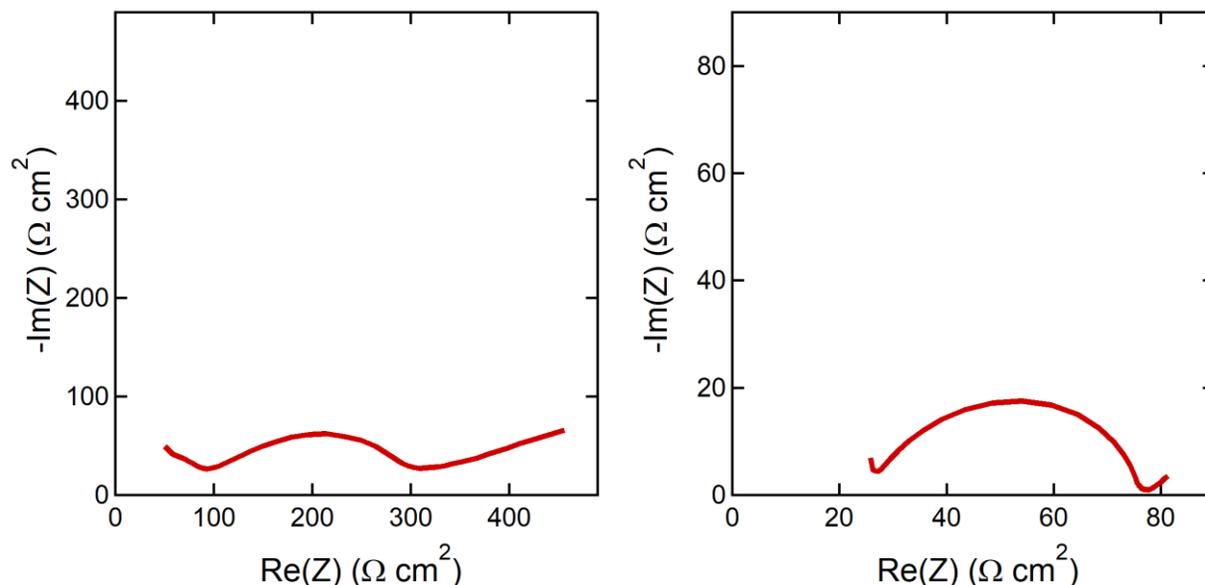


Figure S7. Nyquist plots at 90 °C for lithium symmetric cells of PEO/P(2EO-MO)/LiTFSI blends with salt concentration $r = 0.04$ (left) and $r = 0.10$ (right). The $r = 0.04$ blend is immiscible while the $r = 0.10$ blend is miscible. The difference in magnitude between the two plots is directly proportional to differences in ionic conductivity and interfacial resistance.

VI. Disclaimer

The statements, findings, conclusions and recommendations are those of the authors and do not necessarily reflect the view of NIST or the U.S. Department of Commerce. Certain commercial equipment, instruments, suppliers and software are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.