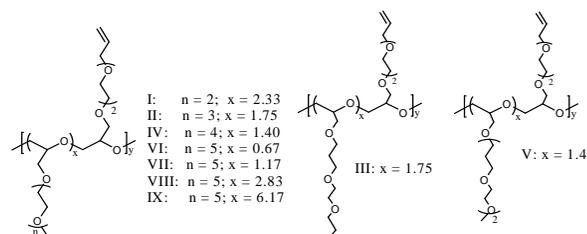


# IONIC CONDUCTIVITY, ELECTROCHEMICAL AND VISCOELASTIC PROPERTIES OF NETWORK SINGLE ION CONDUCTORS BASED ON POLYEPOXIDE ETHERS AND LITHIUM BIS(ALLYLMALONATO)BORATE

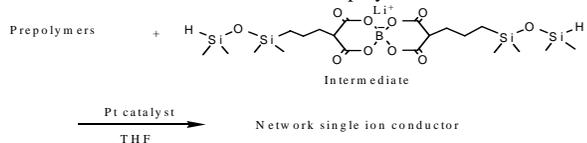
Xiao-Guang Sun, John B. Kerr, Gao Liu, Craig L. Reeder, Yonghong Han

Lawrence Berkeley National Laboratory, MS 62-203, One Cyclotron Road, Berkeley, CA 94720

The focus of this paper is on synthesis of new single ion conductors that could provide high mechanical strength and at the same time present higher ambient ionic conductivity<sup>1,2,3</sup>. This was first realized by synthesis of a new lithium salt, lithium bis(allylmalonato)borate (LiBAMB), which has allyl groups at both ends. After grafting onto allyl group containing polyacrylate<sup>1</sup> and polymethacrylate ethers<sup>1, 2</sup> through 1,1,3,3-tetramethyldisiloxane in the presence of a Pt catalyst, network type single ion conductors were obtained. These single ion conductors possess good mechanical strength and also the Li/Li symmetric cell cycling showed no concentration polarization as expected for true single ion conductors. Unfortunately the conductivity is low due to the unexpectedly poor dissociation of the LiBAMB ion-pair and the high glass transition temperature of the polyacrylate and polymethacrylate backbones. In a previous communication we demonstrated that the ionic conductivity of the network type single ion conductors could be improved by using a more flexible polyepoxide backbone.<sup>3</sup> We also showed that at the same salt concentration the trimethylene oxide (TMO) containing polyepoxide ethers have lower glass transition temperature than those corresponding pure ethylene oxide (EO) based polyepoxide ethers<sup>4,5</sup>, so higher mobility of ions and thus higher ionic conductivity is expected. The focus of this paper is to synthesize TMO containing polyepoxide ether based network single ion conductors and to fully characterize the polyepoxide ethers based single ion conductors (both TMO containing and pure EO based) by means of rheology and electrochemical measurements.



Scheme 1. Prepolymers



Scheme 2. Synthesis of Network single ion conductors

Figure 1 shows the ionic conductivities of the network single ion conductors having the same crosslinker consisting of two ethylene oxide (EO) units and different side chain lengths at the same salt concentration of EO/Li=20. The conductivity systematically increases with increasing the side chain length, which can be explained by the increased mobility of the ions associated with the more mobile polymer side chains (reflected from the corresponding  $T_g$  in Table 1). This result is also consistent with the observations in

binary salt ( $\text{LiClO}_4$ ) solutions of polyepoxide ethers in which the ionic conductivities increased with increasing side chain length up to six EO units<sup>6</sup>.

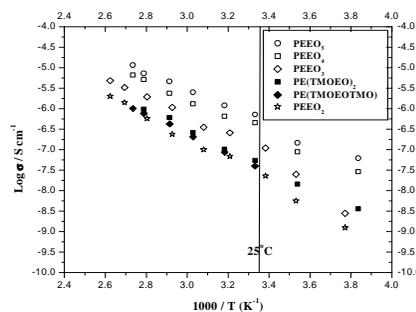


Figure 1. Conductivities of polyepoxide ethers based network single ion conductors at the same salt concentration of EO/Li=20

All the TMO containing materials have lower glass transition temperatures than the pure EO ones, indicating higher chain mobility of the TMO containing polymers. However, the ionic conductivities shown in Figure 1 for those TMO containing single ion conductors were at least half order of magnitude lower than those pure EO based single ion conductors. This is believed to be due to the lower dielectric constant of those TMO containing polymer.

The viscoelastic properties of these new materials will be described both as neat polyelectrolytes and mixed with filler materials such as carbon black to examine the polymer behavior at surfaces. Results of electrochemical testing of both the dry and gel polyelectrolyte membranes in symmetrical Li/Li cells and full Li/ $\text{V}_6\text{O}_{13}$  cells will also be described.

**Acknowledgement:** The authors are grateful for the financial support from NASA PERS programs (NASA Glenn).

## References

- Sun, X.G; Reeder, C.L; Kerr, J.B. *Macromolecules*, **2004**, 37(6), 2219.
- Sun, X.G; Liu, G; Xie, J; Han, Y; Kerr, J. B. *Solid State Ionics*, **2004**, in press.
- Sun, X.G; Kerr, J. B; Reeder, C.L; Liu, G; Han, Y. *Macromolecules*, **2004**, submitted.
- Kerr, J. B.; Liu, G.; Curtiss, L. A.; Redfern, P.C. *Electrochimica Acta*, **2003**, 48, 2305
- Kerr, J.B; Sloop, S.E; Liu, G; Han, Y.B; Hou, J; Wang, S. *Journal of Power Sources*, **2002**, 110, 389.
- Marchese, L; Andrei, M; Roggero, A; Passerini, S; Prosperi, P; Scrosati, B. *Electrochimica Acta*, **1992**, 37(9), 1559.