Macromolecules

Volume 37, Number 14 July 13, 2004

Communications to the Editor

Network Single Ion Conductors Based on Comb-Branched Polyepoxide Ethers and Lithium Bis(allylmalonato)borate

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Received April 5, 2004
Revised Manuscript Received May 21, 2004

In the past several decades polyelectrolyte single ion conductors, either dry or as gels, have attracted attention due to the absence of concentration polarization, a common problem encountered in the conventional solid polymer electrolytes (SPEs) where both cation and anion are mobile.[1−18]

Different strategies have been used to synthesize new single ion conductors, and the best ambient temperature conductivities reported are in the range 10^{-6}−10^{-5} S cm^{-1}.[1−18] However, higher ionic conductivities are usually found for mobile oligomers whose poor mechanical properties cannot fulfill the requirements of commercial devices. To obtain single ion conductors with both high ambient temperature conductivity and appropriate mechanical strength, we have recently synthesized and characterized new network single ion conductors based on the lithium salt, lithium bis(allylmalonato)borate (LiBAMB), and polyacrylate and polymethacrylate ethers.[19,20] These single ion conductors possess good mechanical strength due to the formation of the network structure, and 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 polyacrylates and polymethacrylates. It was also shown that the (meth)acrylate single ion conductors were not stable against lithium metal due to attack of metallic lithium on the vulnerable ester bond during cell cycling.[20]

In general, polyepoxide ethers have lower glass transition temperatures than those of corresponding polyacrylates and polymethacrylate derivatives,[21,22] so higher mobility of the lithium ions is expected. In addition, the ether bond of polyepoxide is less easily reduced than the ester bond of polyacrylate and polymethacrylate and should be more stable against the lithium metal when cycled under charge/discharge conditions. In this Communication we report the results of network single ion conductors based on LiBAMB and comb-branched polyepoxide ethers (Scheme 1).

The obtained single ion conductors are all self-standing transparent films. Figure 1 shows a comparison of the ionic conductivities of the polyacrylate and polyepoxide single ion conductors (SIC) with the same side chain length of three EO units at the same salt concentration of EO/Li = 20 (PAE_3XLAE_1 and $PEPE_3$, respectively). The ionic conductivity of polyepoxide ether based SIC is nearly 1 order of magnitude higher than that of the polyacrylate ether based SIC. Marchese et al.[21] also noticed that in binary salt systems at the same side chain length and same salt concentration the conductivity of polyepoxide ethers was higher than that of polyvinyl ethers. These results suggest that the backbone structure of the polyepoxides contributes significantly to the total ionic conductivity. Figure 1 also shows the ionic conductivities of the single ion conductors having the same cross-linker consisting of two ethylene oxide (EO) units and different side chain lengths (Scheme 1, $n = 2-5$) at the same salt concentration of EO/Li = 20. The conductivity systematically increases with increasing the side chain length, as observed for polyacrylate/polymethacrylate ether based network single ion conductors,[20] which can be explained by the increased mobility of the ions associated with the more mobile polymer side chains. This result is consistent with observations in binary salt ($LiClO_4$) solutions of polyepoxide ethers where it was reported that the

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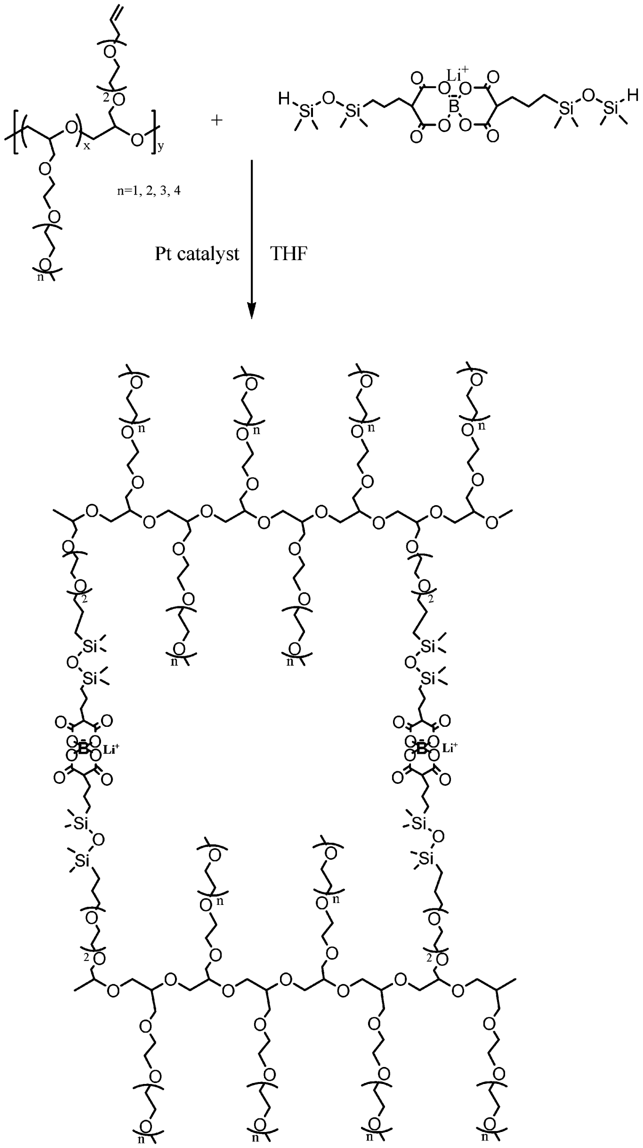
10.1021/ma049331c CCC: $27.50

Scheme 1. Synthesis of Single Ion Conductors



ionic conductivities increased with increasing side chain length up to six EO units.[21]

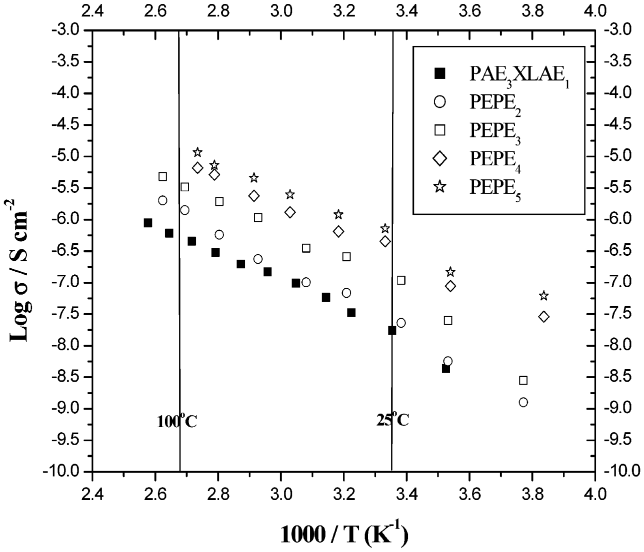


Figure 1. Arrhenius ionic conductivities of single ion conductivities based on polyacrylate and polyepoxide ethers and AllylE$_2$ cross-linker at the same salt concentration of EO/Li = 20.

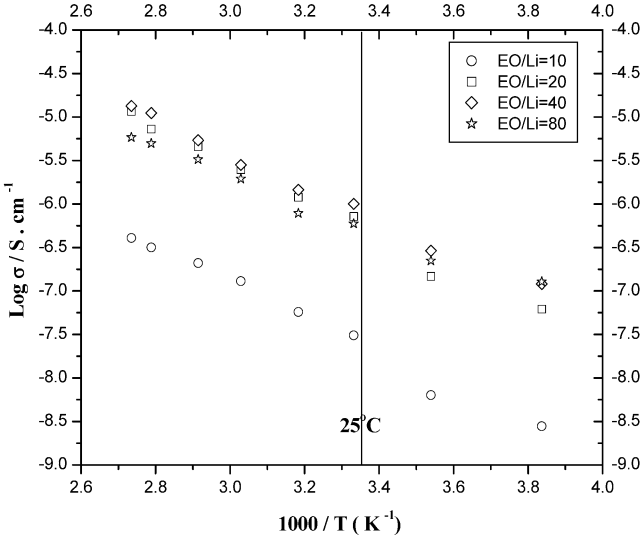


Figure 2. Arrhenius ionic conductivities of single ion conductivities based on PEPE$_5$ with AllylE$_2$ cross-linker at different salt concentrations.

The best ambient temperature conductivity of 1×10^{-6} S cm^{-1} is obtained for the sample with a salt concentration of EO/Li = 40 (Figure 2). This is impressively high for a self-standing membrane and is apparently due to an optimal balance of the charge carrier concentration and ionic mobility. An optimal conductivity at the salt concentration of EO/Li = 40 was also observed in previous results regarding comb-branched and network single ion conductors.[20,23] The sample with the highest conductivity was used to construct a symmetrical Li/Li cell, which was cycled at 85 °C under the current density of 25 μA cm^{-2} and a cycling sequence of 1 h relaxation, 2 h charge, 1 h relaxation, and 2 h discharge. The cycling profile is shown in Figure 3, and as expected for a true single ion conductor, no concentration polarization and relaxation was observed; i.e., when the current is turned on, the cell potential immediately increases from a couple of millivolts to the potential determined by the combined bulk and interfacial impedance, and once the current is turned off the cell potential immediately drops back to the initial value. This cycling behavior is distinctly different from that of binary salt system in which the cell potential increases over a time period of minutes to hours due to the salt concentration polarization.[24] The cycling was stopped after 20 cycles, and the cell impedance was measured using ac electrochemical impedance spectroscopy.[25] It was found that both bulk and interfacial impedance increased. The increase of bulk impedance indicates that the network structure may not have been fully formed due to the film casting technique, and some unreacted siloxane groups may continue to react during cycling. This would result in an increase in the cross-link density of the electrolyte membrane, which would lower the mobility of the polymer chains and thus lead to lower conductivity and higher impedance. The increase of the interfacial impedance suggests a reaction of the single ion conductor with lithium electrode at the electrode/electrolyte interface. This would result in the immobilization of polymer chains at the interface and thus lower the mobility of the ions passing through the interface and yield higher interfacial impedance. Such a process is reflected in the cycling profile by an increase

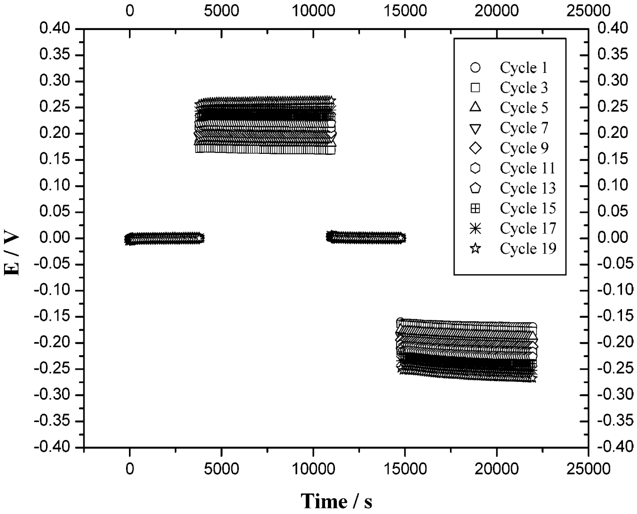


Figure 3. Charge/discharge profile of the Li/polyelectrolyte/Li cell before the impedance measurement (SIC with EO/Li = 40) (electrode area is 1 cm^2, membrane thickness is 100 μm).

in the potential with continued cycling. After the cell cycling was resumed, it quickly failed and signs of polarization and concentration relaxation were observed. This suggests that some small, mobile anionic species were produced, and covalent bond breaking was confirmed from the postmortem gas chromatography analysis of the dichloromethane extract of the cycled SIC in which the side chain fragment (pentaethylene glycol monomethyl ether) and further decomposed smaller fragments (tetraethylene glycol monomethyl ether and triethylene glycol monomethyl ether) were observed. Previously with the polyacrylate SIC's, such decomposition was measured qualitatively.[20] In this case, the decomposition was measured quantitatively by use of an internal standard, and the result showed that the decomposed product was approximately 1.3 wt % of the total amount of the SIC.

The postmortem analysis of the cycled Li/Li symmetric cells suggests that even the polyepoxide ethers are not stable to metallic lithium and may require the use of carbon anodes as used in lithium ion batteries. The instability may be related to the large interfacial impedances observed at the lithium electrodes which are orders of magnitude higher than those observed with binary salt polymer electrolytes.[26] Such large impedances prevent the use of the cells at practical rates and may be attributable to the lower conductivity of the SIC which may be exacerbated by inhibition of the polymer motion at the electrode surface. Whether this is simply due to spatial inhibition or is compounded by some form of self-ordering at the interfaces is an important question and will be pursued in future reports.

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

Supporting Information Available: Complete experimental description, physical properties of the prepolymers and single ion conductors, impedance of Li/Li cell, and postmortem analysis data. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA049331C