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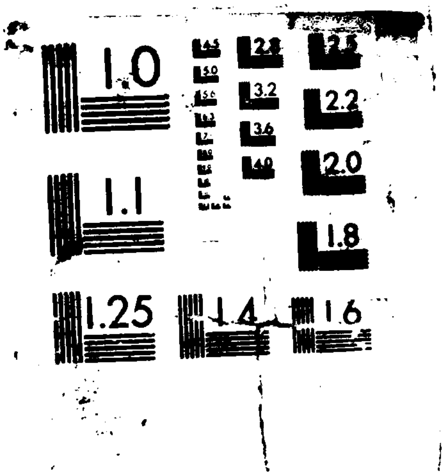

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A series of fully substituted poly(phosphazenes) with alkoxy sidechains, and/or dialkoxy crosslinks were synthesized and investigated as electrolyte host materials. All of the polymers readily formed complexes with $LISO_3CF_3$, $LISO_3C_4F_9$ and $Li_2(SO_3)_2C_2F_2$. The polymer with seven ether oxygens in its sidechain gives the highest conducting polymer salt complex at 30 °C. The crosslinked polymers were found to be totally amorphous with comparable conductivity and increased resistance to flow at elevated temperatures.

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Effect of Sidechain Length and Crosslinking on Ionic Conductivity in Polyphosphazene Solid Electrolytes.

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INTRODUCTION

The use of ethylene oxide (CH_2CH_2O) main and side chain polymers with alkali metal salts as solvent-free polymer electrolytes has developed from the parent Polyethylene oxide (PEO)[1] to the more exotic and highly conducting Poly(bis(2-(2-methoxyethoxy)ethoxy)phosphazene (MEEP).[2,3] We report here the thermal, ac and dc conductivity, and x-ray diffraction properties of a new class of polyphosphazenes that possess polyether side groups linked to the flexible inorganic backbone. Also details of the initial study on the effect of crosslinking MEEP with Poly(ethylene glycol), (PEG), on the ionic conductivity and mechanical properties are presented.

NOMENCLATURE

A series of fully substituted poly(alkoxyphosphazenes), $\{NP[O(C_2H_4O)_xCH_3]_2\}_n$ ($n \geq 15,000$ and X = 1,2,7,12,17) along with MEEP (X = 2) crosslinked with PEG (mol wt. 1000) were synthesized.[4] A systematic nomenclature based on the number X, of ethoxy groups in the sidechains is employed in this work, (MEX-P), eg. for both side chains X = 7 we write ME7P. For the mixed substituent polymers, we use ME(X/X')P(A,B) where A and B denote the relative percentage of X and X' respectively eg. ME2/12P (50,50) which is a 50:50 mixture of X = 2 and X = 12 sidechains.

RESULTS

All the polymers synthesized formed complexes with the following lithium polyfluoro-sulphonic acid salts: $LiSO_3CF_3$, $LiSO_3C_4F_9$ and $Li_2(SO_3)_2C_2F_2$.

Previously,[5] it was found that a ratio of sixteen ether oxygens to one lithium ion gave the highest conducting MEEP complexes (the oxygen in the P-O-CH_2 link is not included in this count). This stoichiometry was again found to give the optimum conductivity with the new polyphosphazenes.

The highest conducting polymer salt complexes were found to be amorphous at room temperature by DSC and x-ray diffraction. Only the ME12P and ME17P polymer salt complexes showed low melting complexes at +5 and +15°C respectively.

The ionic conductivity was determined by complex impedance measurements using Platinum, ion blocking, electrodes. Figure 1 gives the conductivity of the polymer salt complexes at the optimum stoichiometry of sixteen ether oxygens to one lithium ion. The figure also includes the glass transition temperature, Tg, of the pure polymers. Plots of $Ln(\sigma T^{1/2})$ or $Ln(\sigma)$ versus 1/T gave a gentle curve similar to those observed for MEEP complexes.

In the crosslinked polymer salt complexes there is a significant reduction in flow at temperatures above 70°C, with only a small reduction in conductivity compared to uncrosslinked MEEP complexes

CONCLUSION

The highest room temperature conductivity was reached for ME7P ($5 \times 10^{-5} \Omega^{-1} cm^{-1}$); this is the highest known for any solvent-free polymer electrolyte. Polymers with sidechain lengths of X = 7 to 12 seem to represent an optimum between lower Tg and a less effective "hand to hand" ion transport mechanism.

The polyphosphazenes with their ease of substitution continue to provide an array of polymers suitable as electrolyte host materials.

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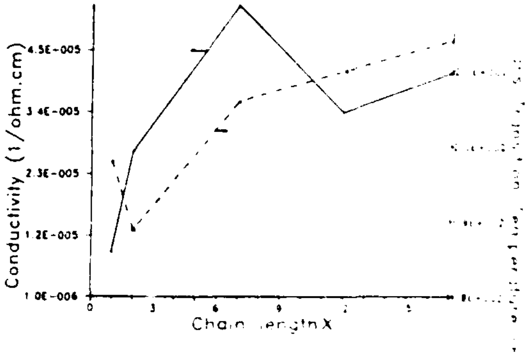

Figure 1. The variation of the optimum ionic conductivity (———) and glass transition temperature (pure polymers, ---) with sidechain length X at 30

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