EFFECT OF SIDECHAIN LENGTH AND CROSSLINKING ON IONIC CONDUCTIVITY IN POLY. (U) NORTHWESTERN UNIV EVANSTON IL DEPT OF CHEMISTRY J S TONGE ET AL. 24 AUG 87 016
**Effect of Sidechain Length and Crosslinking on Ionic Conductivity.**


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**Abstract**

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$_3$CF$_3$, Li$_2$(SO$_4$)$_3$C$_2$F$_7$, and Li$_2$(SO$_4$)$_3$. 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.
Effect of Sidechain Length and Crosslinking on Ionic Conductivity in Polyphosphazene Solid Electrolytes.

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INTRODUCTION

The use of ethylene oxide (CH₂CH₂O) 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[10g(2-(2-methoxy-
ethoxy)ethoxy)phosphazene] (NEEP).₂,₃ We report here
the thermal, ac and dc conductivity, and x-ray
diffraction properties of a new class of polyphospha-
zenes that possess polyether side groups linked to
the flexible inorganic backbone. Also details of the
initial study on the effect of crosslinking NEEP with
Poly(ethylene glycol). (PEG), on the ionic conduc-
tivity and mechanical properties are presented.

NOMENCLATURE

A series of fully substituted poly(alkoxyphospha-
zenes). [NP[(CH₂CH₂O)ₓCH₃]ₓ]ₙ (n ≥ 15,000 and X =
1, 2, 3, 7, 12, 17) along with NEEP (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. (NEX-P),
g, for both side chains X = 2 we write NEEP. For
the mixed substituent polymers, we use NEX/X/P(A,B)
where A and B denote the relative percentage of X and
X respectively eg. NE2/12P (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: LiSO₃CF₃, LiSO₃CF₂SO₂F and Li₂SO₃CF₂F₂.

Previously,⁵ it was found that a ratio of
sixteen ether oxygens to one lithium ion gave the
highest conducting NEEP complexes (the oxygen in the
P-0-CH₂ 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 NE12P 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
copolymer salt complexes at the optimum stoichiometry
of sixteen ether oxygens to one lithium ion. The
Figure also includes the glass transition tempera-
ture, Tg, of the pure polymers. Plots of Ln(τ) versus 1/T gave a gentle curve similar to
those observed for NEEP complexes.

In the crosslinked polymer salt complexes there is
a significant reduction in flow at temperatures 40⁻⁰
70°C, with only a small reduction in conductivity
compared to uncrosslinked NEEP complexes

CONCLUSION

The highest room temperature conductivity was
reached for NEEP (L x 10⁻⁴ S cm⁻¹) with 4
this is the highest

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

REFERENCES

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![Figure 1](image-url)
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