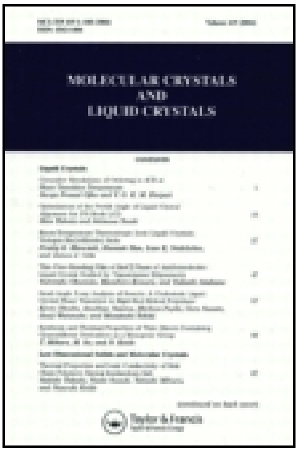

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Mixed Ionic and Electronic Conducting Polymers

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Mixed Ionic and Electronic Conducting Polymers

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Both polymeric electrolytes and electronically conducting polymers have been the focus of considerable research during the past decade. Polymeric electronic conductors may find applications as either the anode or cathode in solid state batteries while solid ionic conductors function as the electrolytes in these devices.[1] High ionic conductivities have been achieved in salt complexes of[2]; 1) amorphous polymeric hosts with 2) highly flexible chains and correspondingly low Tg values. Finally, salt complex formation is most favorable for 3) polymers with polar groups and salts with low lattice energies such as alkali metal cations with large anions. In this report we describe materials that are similar to the polymer electrolytes but instead of an electrochemically "inert" anion such as $[SO_3CF_3]^-$ these materials contain polyiodides which impart electronic conductivity to the salt complexes.

In previous work from this laboratory the conductivity and physical properties of PEO_xNaI_n complexes were examined.[3] In particular, the complex PEO_4NaI_3 is a blue-black crystalline compound with an electronic (hole) conductivity of 2×10^{-5} S cm^{-1} and a band in the resonance Raman spectrum at 171 cm^{-1}. Raman investigations of the other polyiodide PEO complexes contained one or two bands. The first at 111 cm^{-1} is characteristic of I_3^- while the second occurs at 171 cm^{-1} and is indicative of I_5^- and higher polyiodides.[4]

In the present research polyiodide salt complexes of higher conductivity were sought. Polyiodide complexes of the totally amorphous polymer poly[bis-(methoxyethoxyethoxy)phosphazene] (MEEP) have been synthesized and their electronic and physical properties examined. The room temperature conductivity of the lithium triflate/MEEP complexes[5] has been observed to be several orders of magnitude greater than analogous polyethylene oxide complexes at room temperature,[6] and this prompted our investigations of polyiodide/MEEP salt complexes.

$MEEP_xNaI_n$ and $MEEP_xLiI_n$ complexes were prepared in reactions of stoichiometric amounts of I_2 vapor and dry, solid $MEEP_xMI$ (M = Na, Li) to prepare the desired polyiodide complex. $MEEP_xNaI_n$ complexes were prepared with $x = 2, 4, 8, 16$ and $n = 1, 3$; and $x = 4$, $n = 5, 7$. Lithium complexes of $x = 4$ and $n = 1, 3, 5, 7$ were also prepared.

AC conductivity measurements of the polyiodide complexes resulted in complex impedance spectra with two arcs. Based on DC polarization experiments the first arc was assigned to the ionic conductivity and the second to a charge transfer process (an electronic component of the total conductivity) indicating that these complexes are mixed ionic/electronic conductors. In more highly doped polyiodide samples and at elevated tempertures only electronic and no ionic conductivity was observed. Furthermore, ohmic current-voltage behavior was observed in these complexes. The highest room temperature ionic conductivity (2.4×10^{-3} S cm^{-1}, $n = 5$, $T = 298.15$ K) was observed for the series of complexes $MEEP_4NaI_n$ where sixteen ether oxygens complex the sodium cation. The total conductivity, however, increases as the amount of the dopant I_2 increases. Comparing the sodium and lithium complexes, the sodium complexes have higher ionic conductivities while the temperature dependence of the ionic conductivity follows VTF behavior in both the sodium and lithium complexes.

Although we describe the conductivity of the polyiodide materials as ionic and electronic, this is an operational definition based on the polarization behavior and ohmic response. It is possible that the portion of the conductivity that we term electronic involves an ion transfer between polyiodide chains as has been suggested for fluid solutions of polybromides.[7]

Resonance Raman spectra of the $MEEP_xNaI_n$ ($x = 0.5, 1, 2, 4$; $n = 3, 5, 7$) have two bands at circa 112 cm^{-1} and circa 175 cm^{-1} indicating the presence of triiodide moieties and higher polyiodide species in these complexes. The lithium complexes have similar spectra.

The MEEP/polyiodide complexes recently prepared exhibit both ionic and electronic conductivity. Over a rather narrow concentration range where the ionic and electronic components to the conductivity can both be measured, the ionic conductivity as well as the electronic conductivity increase with added I_2.

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