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13. ABSTRACT (Maximum 200 words) In this project, new polymeric ionic conductors were synthesized, and characterized both chemically and through complex dielectric measurements, which provided information on ionic conductivity. Parallel with this experimental program, a series of theoretical studies were performed to elucidate the mechanisms of ion transport in polymers. Some major accomplishments were the demonstration that cryptands enhance ionic conductivity in phosphazene polyelectrolytes, the theoretical indication of ion clustering and the role of such clusters in ion transport. Considerable insight into the conduction processes in these materials was also gained from conductivity and dielectric constant measurements from DC to 6 GHz, which suggest that the attempt frequency for ion motion is above 6 GHz. The research on polyphosphazenes inspired new research on polyaluminosilicates which have excellent conductivity.				
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**FUNDAMENTAL STUDIES OF POLYPHOSPHAZENE
AND POLYSILOXANE POLYELECTROLYTES FOR
ELECTROCHEMICAL DEVICES**

FINAL REPORT

D. F. SHRIVER AND M. A. RATNER

APRIL 1, 1994

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A. Statement of the problem studied:

This research had the objective of synthesizing new polymer electrolytes and elucidating their conduction through a combination of experimental and theoretical studies.

B. Summary of important results:

New siloxy linked polyethers with good low-temperature performance were synthesized and investigated. We also explored a new polycarbonate polymer; poly(diethylene glycol carbonate), and its salt complexes. The ionic conductivity was found to be low for this material. Apparently the advantages of its high dielectric constant are offset by low segmental motion.

Spectroscopic studies of the very promising phosphazene polyelectrolytes containing Mg^{2+} - cryptand complexes. Ion pairing in this material was found to be greatly reduced by the introduction of cryptands and this resulted in an order of magnitude increase in ionic conductivity.

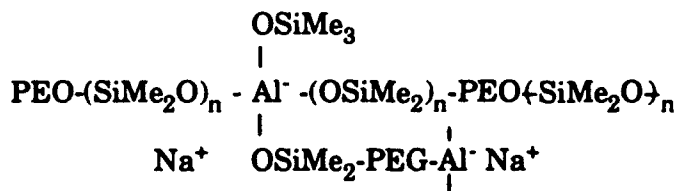
Molecular dynamics studies were performed on ion motion in a Stockmayer fluid. These simulations provide considerable insight into the role of ion pairing and ion screening on the role of ion transport. Molecular dynamics simulations in NaI solutions, where the solvent has been represented by a simplistic Stockmayer fluid (spherical particles with point dipoles), were performed as a function of temperature, salt concentration, magnitude of ionic charge and solvent dipole strength. In a high dielectric solvent where coulomb screening is more efficient, free ions and solvent separated pairs are most prevalent. In a weaker dielectric contact ion pairs and ion clustering occurs. Thermodynamic analysis shows that this temperature behavior is predominantly

entropically driven.

The transport properties calculated in the solutions of lower dielectric constant and charge of 1e confirm the clustered nature of the salt, with strong deviations from Nernst-Einstein predictions for the calculated conductivities. In systems where the solvent-ion interactions increase relative to ion-ion interactions (lower charge or higher solvent dipole moment), less clustering is observed and the transport properties indicate independent motion of the ions, with higher calculated conductivities.

In a second area, we have prepared polysiloxaluminate-polyethylene oxide polymers. The concept here is to incorporate a polyelectrolyte containing a large low basicity and highly flexible anion (the siloxaluminate) into a polymer chain.

The initial synthetic work in this area has yielded:



This rubbery material exhibits a conductivity of 10^{-6} S/cm at room temperature. We have explored the conductivity of this class of materials as a function of aluminosilicate/ethylene oxide ratio. (In effect, this corresponds to higher charge density). The result is a maximum in the conductivity similar to that seen for simple polymer-salt complexes. An increase in conductivity is observed when cryptands are introduced.

These materials are very promising for a variety of applications because they should be chemically robust and have the highest conductivity we have observed for a polymer electrolyte.

Using both microwave spectroscopy and theoretical modeling based on our dynamic percolation picture, we have been able to quantify the understanding that segmental

motions of the polymeric host facilitate ion transport. Figure 1 shows a comparison of the results for conductivity on the one hand, and for glass transition relaxation maxima on the other, in a series of ether based polymer electrolytes. When scaled by the reduced temperature, these two quantities lie essentially on the same line. This means that knowledge of the glass transition frequency in the parent polymer will fix the mobility contribution to the conductivity in the polymer electrolyte. This quantification of the statement that has been made for the last decade in the literature, that segmental motions of the polymer assist ion transport, is an important quantitative improvement in the understanding how to prepare more effective electrolytes.

An important result, based purely on modeling elucidates the temperature dependence of ion pairing and clustering in these materials. We used molecular dynamics to demonstrate clearly that ion clustering is entropy driven, and that it increases with increasing temperature. This increase of the clustering competes with the increase in mobility, to produce the overall temperature dependence of the conduction process. Figure 2, for example, shows the dependence of the potential mean force active between two ions (sodium iodide) in a characteristic polymer electrolyte. Notice that the depth of this potential increases with temperature, corresponding to an increase of tight ion pairing (average distance is .95, in the reduced units used in the figure). This temperature dependence arises both from the change with the dielectric constant of the host fluid, and from entropic considerations. It implies that the clustering processes will lead to a correlation that decreases conductivity at higher temperatures.

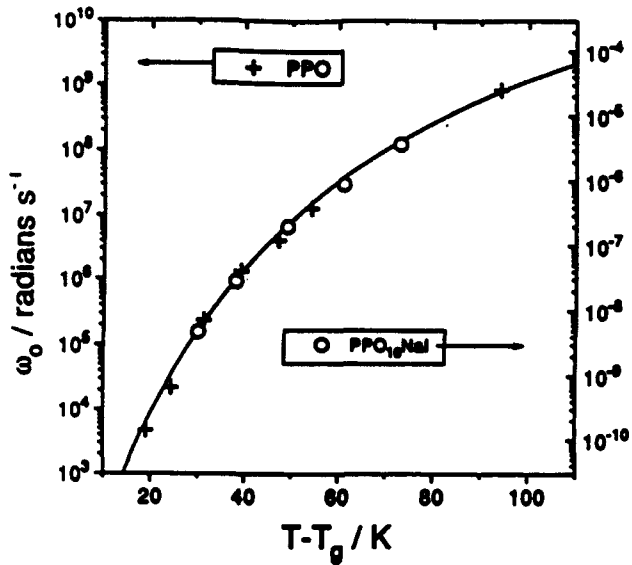


Figure 1

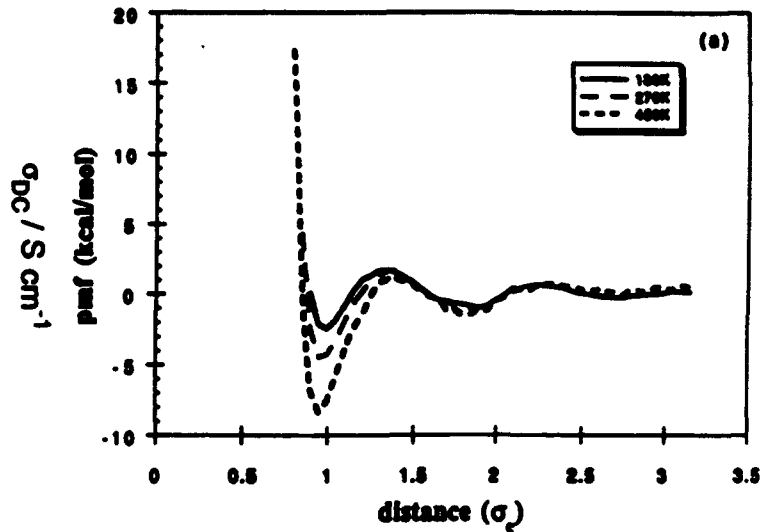


Figure 2

C. List of Publications and Technical Reports.

"Influence of Macrocyclic Ligands on Ion Transport in Solid Polyelectrolytes", K. Chen, K. Doan, S. Ganapathiappan, M. A. Ratner, and D. F. Shriver Proc. Mater. Res. Society Symposium in Solid State Ionics II, Nazri, Huggins, Balkanski and Shriver, eds., 210, (1991) p211.

"MD Studies of Transport in Polymer-Salt Complexes: A Progress Report", M. Forsyth, V. A. Payne, M. A. Ratner, S. W. deLeeuw and D. F. Shriver, Solid State Ionics II, Proc. Mat. Res. Soc. Symp., Vol. 210, (1991).

"Characterization of Polyiodide-Polymer Complexes of Resonance Raman Spectroscopy", M. Forsyth, H. C. zur Loye, M. Lerner, A. Tipton, D. C. DeGroot, C. R. Kannewurf, M. A. Ratner and D. F. Shriver, Solid State Ionics II, Proc. Mat. Res. Soc. Symp., Vols 210, (1991).

"Polymer Solid Electrolytes: Charge Transport Mechanisms", M. A. Ratner, Materials Forum, 15, 1-15 (1991).

"Molecular Dynamics Simulations of Highly Concentrated Salt Solutions: Structural and Transport Effects in Polymer Electrolytes", M. Forsyth, V. A. Payne, M. A. Ratner, S. W. deLeeuw, and D. F. Shriver, Solid State Ionics, 53-56, 1011-1026 (1992).

"Structure, Conductivity and Raman Spectrum of 4,7,13,16-tetraoxa-1,10-dithiacyclooctadecanebis(diiodine)", A. L. Tipton, M. C. Lonergan, C. Stern and D. Shriver, Inorg. Chim. Acta, **201**, 23-27 (1992).

"Polymer Nanomaterials: Ionic Conductivity, Relaxation and Chromophore Nonlinear Optics", D. Li, M. Firestone, D. R. Kanis, D. F. Shriver, T. J. Marks, and M. A. Ratner, Nanostructures Based on Molecular Materials, VCH publishers, W. Göpel and Ch. Ziegler, eds., (1992) p125.

"Dipole Time Correlation Functions of the Stockmayer Fluid in the Microcanonical and Canonical Ensembles", V. A. Payne, M. Forsyth, J. Kolafa, M. A. Ratner, and S. de Leeuw, Journal of Physical Chemistry, **97**, 10478 (1993).

"Conductivity Percolation in Polyiodide/Polymer Complexes", M. Forsyth, D. F. Shriver, M. A. Ratner, D. C. DeGroot and C. R. Kannewurf, Chem. Mater., **5**, 1073 (1993).

"Dynamically Disordered Hopping, Glass Transition Relaxation, and Polymer Salt Complexes", M. C. Lonergan, D. F. Shriver and M. A. Ratner, Abstract from the ACS meeting, August, 1993, Chicago, IL.

"Polymer Electrolytes and Ion Pairing: Molecular Dynamics Simulations", V. A. Payne, M. Forsyth, M. A. Ratner, D. F. Shriver and S. W. deLeeuw, Abstract from the ACS meeting, August, 1993, Chicago, IL.

"Conductivity and Dielectric Constant of PPO and PPO-based Solid Electrolytes from DC to 6 GHz", A. L. Tipton, M. C. Lonergan, M. A. Ratner and D. F. Shriver, T. T. Y. Wong and K. Han, Journal of Physical Chemistry, in press.

"Highly Concentrated Salt Solutions: Molecular Dynamics Simulations of Structure and Transport", V. A. Payne, M. Forsyth, M. A. Ratner, D. F. Shriver, S. W. deLeeuw, The Journal of Chemical Physics, submitted.

"Ionic Conductivity in Poly(diethylene glycol-carbonate)Sodium Triflate Complexes", M. Forsyth, A. L. Tipton, D. F. Shriver and M. A. Ratner, manuscript in preparation.

"Aluminosilicate/Polyethylene Glycol Copolymers: A New Class of Polyelectrolytes", G. C. Rawsky, T. Fujinami and D. F. Shriver, submitted to Chem. Mater., (1994).

D. List of Personnel:

Mark C. Lonergan - Graduate student.

Glenn C. Rawsky - Graduate student.

Vilia A. Payne - Graduate student/NSF fellow.

Andrew L. Tipton - Graduate student, Ph.D. September, 1992.

Maria Forsyth - Postdoctoral/Fulbright fellow.

Kaimin Chen - Graduate student, Ph.D., 1991.

Griffith Liang - Undergraduate research assistant.

Theodore Lin - Undergraduate research assistant.
Stephen Druger - Research Associate.

E. Report of Inventions.

None.