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ELECTRONIC AND IONIC TRANSPORT IN POLYMERS(U) TEXAS  
UNIV AT AUSTIN DEPT OF CHEMISTRY M POMERANTZ ET AL.  
12 DEC 86 TR-1 N00014-86-K-0769

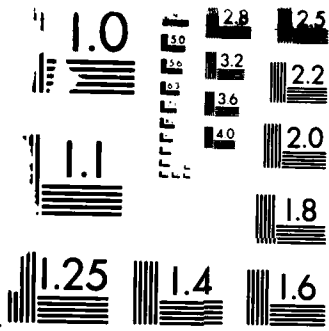
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## DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION / AVAILABILITY OF REPORT Unlimited		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 1			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION University of Texas at Arlington		6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research		
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry, Box 19065 University of Texas at Arlington Arlington, TX 76019			7b. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Defense Advanced Research Projects Agency		8b. OFFICE SYMBOL (If applicable) DARPA	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-86-K-0769		
8c. ADDRESS (City, State, and ZIP Code) 1410 Wilson Boulevard Arlington, VA 22209			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
			WORK UNIT ACCESSION NO.		
11. TITLE (Include Security Classification) Electronic and Ionic Transport in Polymers					
12. PERSONAL AUTHOR(S) Martin Pomerantz, John R. Reynolds, Krishnan Rajeshwar, Dennis S. Marynick, Timothy D. Shaffer					
13a. TYPE OF REPORT Quarterly-Technical		13b. TIME COVERED FROM 9/15/86 TO 12/15/86		14. DATE OF REPORT (Year, Month, Day) 1986-December, 12	
15. SUPPLEMENTARY NOTATION alpha		15. PAGE COUNT 5			
COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	Electronically conducting polymers, ionically conducting polymers, High energy dielectric polymers, liquid crystalline polymers.		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)			100,000 Jan 15 1987		
<p>A "self-doped" copolymer of pyrrole and potassium 3-(1-pyrrolyl)propane sulfonate has been prepared and studied electrochemically and with FT-IR. Ionic mobilities through the film have been measured. Copolymers of pyrrole and N-(3-bromophenyl)pyrrole were shown to have conductivities which decreased by 10<sup>5</sup> with 12% of the bromo compound. Proton mobility and conductivity in polypyrrole tosylate films have been studied as a function of pH. PRDDO calculations of polypyrrole oligomers and of oligomers with an N-phenyl ring on a central pyrrole have been carried out, including geometry optimization in the latter systems to see the effect of the substituent on the twisting of the planar system. Several poly(organophosphazenes) have been prepared and studied and have been shown to be quite thermally stable. Base catalyzed polymerization of <math>\alpha,\alpha'</math>-dibromoxylenes has been shown to give ether linkages, in addition to poly(p-phenylenevinylene), depending on the isomeric starting material. Copolymerization of 1,3-cyclohexadiene and 2-chloroacrylonitrile gives a polymer containing both 1,2 and 1,4 linkages through the cyclohexene rings.</p>					
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Kenneth J. Wynne			22b. TELEPHONE (Include Area Code) (202) 696-4410		22c. OFFICE SYMBOL

## Technical Report

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Contract No.: N00014-86-K-0769

Short Title of Work: "Electronic and Ionic Transport in Polymers"

Reporting Period: September 15, 1986-December 15, 1986

This is Technical Report No. 1 of 1986-1987

Accession For	
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DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
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Distribution/	
Availability Codes	
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## Description of Progress:

### a) Electronically Conducting Polyheterocycles

In order to directly control electronic and ionic properties of conjugated heterocyclic polymers and to prepare such polymers which will be "self-doped" we have synthesized a variety of pyrrole monomers (substituted on the nitrogen and at the 3-position) and thiophene monomers (also substituted at the 3-position). A "self-doped" copolymer of pyrrole and potassium 3-(1-pyrrolyl) propane sulfonate has been prepared and studied by cyclic voltammetry, chronocoulometry and diffuse reflectance FT-IR. Ionic mobilities for several cations, through a film of this copolymer, have been determined. A paper describing this work has been submitted to *J. Chem. Soc. Chemical Communications*. Preliminary ESCA results on this copolymer suggest that the relative composition of the monomer units at the surface (*ca.* 100 Å deep) can be determined. A complete study of the copolymers of pyrrole and N-(3-bromophenyl)pyrrole as a function of composition has shown that a  $10^5$  decrease in conductivity can be achieved with only 12% incorporation of the N-(3-bromophenyl)pyrrole. A paper describing these results has been submitted to *Macromolecules*.

We have also examined proton mobility in polypyrrole during redox switching, by using a tosylate doped polypyrrole free standing film. Chemical exchange studies show that the out-diffusion of tosylate is very sensitive to pH. More importantly, concurrent measurements of the film resistance showed that the conductivity is also pH sensitive. Specifically, tosylate diffusion is rapid in basic medium and the film becomes insulating. If the film is then bathed in acid the conductivity is restored reversibly.

PRDDO molecular orbital calculations on oligomeric polypyrroles and their radical cations (1-17 rings) have been carried out and various properties of these species (such as spin density, HOMO-LUMO gap, charges and overlap populations) have been determined. Interestingly, in the N-phenylpyrrole-pyrrole dimer the phenyl is rotated *ca.* 60° out of the pyrrole ring plane while the second pyrrole is rotated about 40°. Pentapyrrole with a phenyl group on the central ring nitrogen

shows that four rings are essentially planar with the central pyrrole is twisted out of the plane. Calculations on other pyrrole systems have also been carried out, and these include the pyrrole trimer with a central N-phenyl substituent, and N-arylpyrroles with a variety of substituents in the aromatic ring.

#### **b) Polymer Solid Electrolytes**

A series of phosha- $\lambda^5$ -azene polymers of the type  $\{[-N=P(Ph_2)-R-P(Ph_2)=N-C_6H_4-]\}$ , where R is one of several different organic groups, has been prepared and studied by thermal analysis, FT-IR and solid state NMR spectroscopy as models for the ion conducting systems with polyether side chains. They show excellent thermal stability and only decompose at temperatures in excess of 300°C, with the temperature of maximum weight loss rate being over 400°C (the exception is where  $R=CH_2$ ). Using  $^{31}P$  solid state NMR spectroscopy (CP/MAS) and end groups analysis, we can estimate that the molecular weights of two of these systems are about 4,000.

#### **c) Novel Liquid Crystalline Conductors**

Preliminary work has shown that in the phase transfer catalyzed polymerization of  $\alpha,\alpha'$ -dibromoxylenes the nature of the isomer used drastically alters the course of the polymerization. Since the meta and para isomers give mainly polyethers (using  $OH^-$  in the reaction) and poly(p-phenylenevinylene) respectively, it is very likely that the latter polymers are contaminated with ether units in the backbone. Solid state NMR spectroscopy (CP/MAS) is consistent with this suggestion. Further mechanistic studies are in progress.

#### **d) High Energy Dielectric Materials**

A family of alternating copolymers of 1,3-cyclohexadiene and 2-chloroacrylonitrile have been synthesized using various initiator systems and their structure analyzed using NMR (including DEPT and 2-D COSY experiments), FT-IR, TGA, GPC and elemental analysis. The polymerization has been shown to proceed through the formation of both 1,2 and 1,4 linkages through the cyclohexene ring. Bromination of these copolymers has been carried out to help in

both structural elucidation and to serve as a precursor for the introduction of fluorine onto the polymer chain.

#### **Personnel:**

Currently there are 2 postdoctoral associates, Dr. S. Krichene and Dr. E. Tsai, and 1 graduate student, Paul Poropatic along with 2 technical assistants, Douglas Black and Bella Khayt supported by the project. Six additional postdoctoral associates and 9 graduate students are involved in research relevant to the project. We have hired a full time administrative secretary as of Nov. 3, 1986. In addition 2 postdoctoral associates have been hired but have not arrived yet.

#### **Summary of Meetings, Oral Presentations and Visitors:**

On October 23 John Reynolds went to the DARPA meeting for URI principal investigations in Arlington, Virginia. There was a presentation by DARPA and a brief presentation by each of the various URI groups describing their programs.

On November 16 John Reynolds and Martin Pomerantz met in Atlanta, Georgia with the PI's involved with the two other DARPA-URI contracts on conducting polymers. The other PI's attending were Alan MacDiarmid (U. of Penn), Arthur Epstein (Ohio State U.), and David Tanner and Kenneth Wagener (U. of Florida). This was an excellent meeting where scientific details about the research of each group was discussed, there were many helpful suggestions concerning research problems and, more importantly, areas of mutual interest and areas where there will be collaboration were delineated.

An oral presentation of aspects of this work entitled "Copolymerization of 1,3-Cyclohexadiene with Polar Vinyl Monomers", was given at The Southwest Regional American Chemical Society Meeting in Houston, TX on November 19.

Another presentation, entitled "High Energy Density Dielectric Polymers", was presented at The Technical Achievements Symposium, Space Power Institute, Auburn University, December 4.

John Reynolds presented an invited talk entitled "Innovations in Conducting Polymers" to the Dallas-Fort Worth section of the American Chemical Society on December 11.

Two papers, entitled "Conductive Polymers Containing Bound Dopant Ions" and "Structural Control of the Electronic and Ionic Properties of Polyheterocycles" will be presented at The National American Chemical Society Meeting in Denver, Colorado, April 5-10, 1987.

Visitors to the Chemistry Department at The University of Texas at Arlington, who consulted with the PI's on research areas directly related to the URI Contract, and who presented seminars are given below along with the title of the talk they presented.

Prof. Frank Karasz  
Polymer Science and Engineering Department  
University of Massachusetts  
Amherst, MA  
"Miscibility of Random Copolymers"

Prof. Lon Mathias  
Polymer Science Department  
University of Southern Mississippi  
Hattiesburg, MS  
"New Polymers and Composites: Synthesis and Characterization"

Dr. Patrick Cassoux  
Director of Research  
Laboratory of Coordination Chemistry, CNRS and Universite Paul-Sabatier, Toulouse,  
France  
"Synthesis, Properties and Structure of Conducting and Superconducting Molecular  
Complexes and Derived Organometallic Polymers."



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