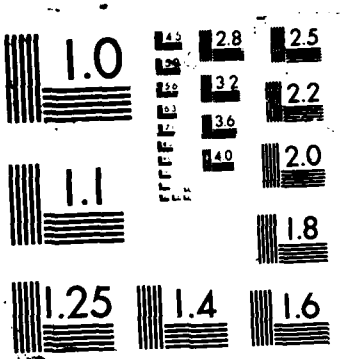
AD-A187 253 ELECTRONIC AND IONIC TRANSPORT IN POLYMERS(U) TEXAS UNIV AT ARLINGTON DEPT OF CHEMISTRY M POMERANTZ ET AL. 10 SEP 87 N00014-86-K-0769 1/1

UNCLASSIFIED F/G 7/6 NL


1.0
2.8
2.5
3.2
2.2
3.6
4.0
2.0
1.1
1.8
1.25
1.4
1.6

Annual Letter Report

Principal Investigators: Martin Pomerantz, Grant Administrator, John R. Reynolds, Krishnan Rajeshwar, Dennis S. Marynick and Timothy D. Shaffer

Contractor: The University of Texas at Arlington

Telephone No. (817) 273-3811

Cognizant ONR Scientific Officer: Dr. Kenneth J. Wynne

Contract No.: N00014-86-K-0769

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

Reporting Period: September 15, 1986-September 30, 1987

This is Annual Letter Report No. 1 of 1986-1987

The following is a summary and status report of activities during 1986-1987 and brief plans for the coming year (1987-1988).

Principal Investigators

Martin Pomerantz, Grant Administrator - 817-273-3811

John R. Reynolds - 817-273-3813

Krishnan Rajeshwar - 817-273-3810

Dennis S. Marynick - 817-273-3814

Timothy D. Shaffer - 817-273-3808

Brief Description of Project

The synthesis and study of electrically conducting polymers, particularly polyheterocycles, is being carried out with the ultimate goal of producing materials with a variety of electronic and ionic transport properties while, at the same time, gaining an improvement in their processibility. Polymers based on monomer systems containing a high density of attached dipoles are being developed with the goal of producing materials with elevated permittivities while retaining low loss behavior. Polymers containing phosphorus, nitrogen and organic groups in the main chain and polyether sidechains are being prepared and studied as ion conductors for possible solid electrolyte applications. The kinetics of the insulating to conductive switching process in conducting polymers is being examined including the development of techniques to probe the ionic fluxes which accompany the redox processes in the polymer films.

Theoretical calculations (PRDDO and ab initio) are being used to calculate structures, conformations, spin densities, HOMO-LUMO gaps, and potential energy surfaces for a wide variety of heterocyclic monomers and oligomers and will be used to predict the site of electrochemical polymerization and to understand how various substituents affect the electronic structure of the polymers. Finally, main-chain liquid crystalline polymers which contain potential electroactive centers are being synthesized. Some of these will contain oligomeric unsaturated organic groups.

Significant Results During the Last Year (1986-1987)

The following has been achieved.

1) Preparation and study of self-doped conducting polymers that have ion-specific transport and are water soluble.

2) Use of a quartz crystal microbalance to analyze electropolymerization and charge transport in polyheterocycles.

3) Synthesis of variable conductivity copolymers of pyrrole and N-substituted pyrroles; substantiated with theoretical calculations.

4) The conductivity of polypyrrole free standing films has been shown to be relatively insensitive to dopant anion but dependent on morphology.

5) Spectroelectrochemical demonstration of proton transport through a Au-supported polypyrrole film during redox switching.

6) Theoretical calculations of pyrrole and thiophene monomers and oligomers correlate with electropolymerization tendencies.

7) Model compound studies have been carried out in the ares of high permittivity, ion-conducting and liquid crystalline polymers.

8) Ethylmercapto substituted polythiophenes have been prepared and their optical properties shown to be controlled by the extent of substitution.

Brief Summary of Plans for Next Years Work

Future work will involve new conducting polyheterocycles, for improved processibility and better understanding of electronic and ionic transport. Self-doped conductive polymers will be pursued vigorously. Optoelectrochemical, temperature dependent conductivity, thermoelectric power, quartz microbalance and standard analytical characterization methods will be employed. With our current results we intend to develop a comprehensive model for the anion exchange behavior of polypyrrole to help us fully understand the dynamic redox switching process in these conductive polymers. We plan to extend the spectroelectrochemical method to other heterocyclic conductive polymers and will further study the temporal aspects of proton transport at the polypyrrole/electrolyte interface. These studies will have implications in the effective use of polypyrrole and other analogs for device and sensor applications.

Several families of high permittivity polymers will be synthesized containing polar groups on aromatic rings and/or on saturated carbon atoms in the main chain. Ion-conducting polymers with phosphorus, nitrogen and organic groups in the main chain and polyether side chains will be prepared and studied.

Theoretical work will concentrate on the substituent effect on the electronic structure of polypyrroles and polythiophenes. Geometries obtained from PRDDO will be used in ab initio calculations. Calculations on actual polymeric systems using the VEH method will be done. Additionally, incorporation of poly(phenylene vinylene) and poly(quinonyl vinylene) oligomers into liquid crystal polymer architectures will be started from directed syntheses of the required monomers followed by standard polymerization to give main chain configured liquid crystalline polymers. We will also focus on incorporation of certain metal chelating centers into the polymer framework but will use a modification of our synthetic methodology.

Paper Published in Refereed Journal

Sundaresan, N.S., Basak, S., Pomerantz, M., and Reynolds, J.R., "Electroactive Copolymers of Pyrrole Containing Covalently Bound Dopant Ions: Poly{pyrrole-co[3-(pyrrol-1-yl)-propanesulphonate]}", *J. Chem. Soc., Chem. Commun.* 621 (1987). Other support: Texas Advanced Technology Research Program, Petroleum Research Fund of the American Chemical Society, and the Robert A. Welch Foundation.

Papers Submitted to Refereed Journals

Reynolds, J.R., Sundaresan, N.S., Pomerantz, M., Basak, S., and Baker, C.K., "Self-Doped Conducting Copolymers: A Charge Transport Study of Poly{pyrrole-co-[3-(pyrrol-1-yl)propanesulfonate]}", *J. Am. Chem. Soc.*, submitted. Other support: Texas Advanced Technology Research Program, Petroleum Research Fund of the American Chemical Society, and the Robert A. Welch Foundation.

Panchalingam, V. and Reynolds, J.R., "Structure of the Alternating Copolymer of 1,3-Cyclohexadiene and Chloroacrylonitrile", *Macromolecules*, submitted. Other support: Center for Energy Conversion Research, UTA.

Jang, G.-W., Tsai, E.W., and Rajeshwar, K., "Electrochemically-Triggered pH Modulation at the Ruthenium Oxide/Electrolyte Interface: A Spectroelectrochemical Probe for the Proton Transport Mechanism", *J. Electrochem. Soc.* in press. Other support: Center for Energy Conversion Research, UTA.

Tsai, E.W., Jang, G.-W., and Rajeshwar, K., "Proton Transport Accompanies Redox Switching of Polypyrrole: A Spectroelectrochemical Study", *J. Chem. Soc., Chem. Commun.* submitted.

Pajkossy, T., Tsai, E.W., Reynolds, J., and Rajeshwar, K., "Anion Exchange in Polypyrrole", *J. Phys. Chem.* submitted. Other support: Texas Advanced Technology Research Program.

Shaffer, T.D., "Phase Transfer Catalyzed Polymerization of α,α'-Dibromoxylene Isomers", *J. Polym. Sci. Polym. Lett. Ed.* submitted.

Wang, S.J., Naidn, S.V., Sharma, S.C., De, D.K., Jeong, D.Y., Black, T.D., Krichene, S., Reynolds, J.R., and Owens, J.M. "High T_c-Superconductor $YBa_2 Cu_3 O_{7-5}$ Studied by Positron Annihilation", *Phys. Rev. B.* submitted. Other support: Robert A. Welch Foundation, Texas Advanced Technology Research Program.

Martinez, M., Reynolds, J.R., Basak, S., Black, D.A., Marynick, D.S., and Pomerantz, M. "Electrochemical Synthesis and Optical Analysis of Poly[(2,2'-dithienyl)-5,5'-diylvinylene], *J. Polym. Sci., Phys. Ed.* submitted. Other support: Texas Advanced Technology Research Program, Petroleum Research Fund and Robert A. Welch Foundation.

Invited Presentations at Topical or Scientific/Technical Society Conferences

Reynolds, J.R., Panchalingam, V.,"Copolymerization of 1,3-Cyclohexadiene with Polar Vinyl Monomers", 42nd Southwest Regional Meeting of the American Chemical Society, Houston, TX, November, 1986. Other support: Center for Energy Conversion Research, UTA.

Reynolds, J.R., Panchalingam, V.,"High Energy Density Dielectric Polymers", Technical Achievements Symposium, Space Power Institute, Auburn University, Auburn, AL, December, 1986. Other support: Center for Energy Conversion Research, UTA.

Reynolds, J.R."Conducting Polymers: Past, Present and Future", Dallas-Fort Worth Section of the American Chemical Society Meeting, Arlington, TX, December, 1986. Other support: Texas Advanced Technology Research Program, Petroleum Research Fund of the American Chemical Society, and the Robert A. Welch Foundation.

Reynolds, J.R., Sundaresan, S., Basak, S., and Pomerantz, M., "Conductive Polymers Containing Bound Dopant Ions", 193rd National Meeting of the American Chemical Society, Denver, CO, April, 1987. Other support: Texas Advanced Technology Research Program, Petroleum Research Fund of the American Chemical Society, and the Robert A. Welch Foundation.

Reynolds, J.R., Basak, S., Black, D., Marynick, D.S., Pajkossy, T., Pomerantz, M., Poropatic, P.A., Rajeshwar, K., Sundaresan, N., Toyooka, R., "Structural Control of the Physical and Electronic Properties of Polyheterocycles", 193rd National Meeting of the American Chemical Society, Denver, CO, April, 1987. Other support: Texas Advanced Technology Research Program, Petroleum Research Fund of the American Chemical Society, and the Robert A. Welch Foundation.

Contributed Presentations at Topical or Scientific/Technical Society Conferences

Baker, C. and Reynolds, J.R., "Electrochemical Microbalance Studies of Polypyrrole", 20th Annual Meeting-in-Miniature of the Dallas-Fort Worth Section of the American Chemical Society, Fort Worth, TX, April, 1987.

Poropatic, P., Reynolds, J.R., and Toyooka, R.L., "Polypyrroles: Composites and Copolymers", 20th Annual Meeting-in-Miniature of the Dallas-Fort Worth Section of the American Chemical Society, Fort Worth, TX, April, 1987.

Jolly, C. and Reynolds, J.R., "Transition Metal Tetrathiooxalates: A Structural and Electronic Study", 20th Annual Meeting-in-Miniature of the Dallas-Fort Worth Section of the American Chemical Society, Fort Worth, TX, April, 1987.

Martinez, M., Basak, S., Pomerantz, M., and Reynolds, J.R., "Optoelectrochemistry of Poly[(2,2'-dithienyl)-5,5'-diylvinylene]", 20th Annual Meeting-in-Miniature of the Dallas-Fort Worth Section of the American Chemical Society, Fort Worth, TX, April, 1987.

Victor, M., and Pomerantz, M., "Studies on the Synthesis and Properties of Phosphorus and Nitrogen Containing Polymers", 20th Annual Meeting-in-Miniature of the Dallas-Fort Worth Section of the American Chemical Society, Fort Worth, TX, April, 1987.

Baker, C.K., and Reynolds, J.R., "Electrochemical Quartz Microbalance Studies of Polyheterocyclic Conducting Polymers", 194th National Meeting at the American Chemical Society, New Orleans, LA, September 1987. Other Support: Texas Advanced Technology Research Program, Robert A. Welch Foundation, Research Corporation and Petroleum Research Fund; *Polymer Preprints 28*, 284 (1987).

Panchalingam, V., and Reynolds, J.R., "Structural Analysis of Poly(2-chloroacrylonitrile-co-cyclohexadiene)", 194th National Meeting of the American Chemical Society, New Orleans, LA, September 1987. Other support: Center for Energy Conversion Research, UTA; *Polymer Preprints 28*, 282 (1987).

Honors/Awards/Prizes

John R. Reynolds, University of Texas at Arlington Research Award, April 7, 1987. Other support: Texas Advanced Technology Research Program, Petroleum Research Fund of the American Chemical Society, Research Corporation and the Robert A. Welch Foundation.

Number of Graduate Students Receiving Full or Partial Support on DARPA/ONR Contract

5

Number of Postdoctoral Fellows Receiving Full or Partial Support on DARPA/ONR Contract

5

Graduate Students Currently Working on the Project

Charles Baker
Paul Poropatic
Mark Victor
Leslie Phan
Cynthia A. Jolly

Postdoctorals Currently Working on the Project

S. Krichene
F. El Khatib
E.W. Tsai
K. Nayak

END

FEb.

1988

DTIC