

AD-A200 481

DTIC FILE COPY

④

SECURITY CLASS

## 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) Annual Letter Report No. 2		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION The 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 The University of Texas at Arlington Arlington, Texas 76019		7b. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, Virginia 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, Virginia 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, Krisnan Rajeswar, Dennis S. Marvnick, Timothy D. Shaffer			
13a. TYPE OF REPORT Annual-Letter	13b. TIME COVERED FROM 10/1/87 TO 9/30/88	14. DATE OF REPORT (Year, Month, Day) 1988 October 4	15. PAGE COUNT 8
16. SUPPLEMENTARY NOTATION			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
			Electronically conducting polymers, charge transport, polymer composites, liquid crystalline polymers
19. ABSTRACT (Continue on reverse if necessary and identify by block number) The following results have been achieved or elucidated during 1987-1988: <input checked="" type="checkbox"/> Charge transport properties of electrochemically prepared poly(3-methylthiophene) thin films depends on the morphology of the film; <input checked="" type="checkbox"/> Soluble transition metal bisdithiolenes polymers are electroactive with three distinct oxidation states; <input checked="" type="checkbox"/> Carbon felt electrodes allow fairly large quantities of soluble poly(3-hexylthiophene) to be prepared; <input checked="" type="checkbox"/> The electrical properties of anion exchanged, doped polypyrroles are anion independent; <input checked="" type="checkbox"/> Composite poly(pyrrole-Kevlar sulfonate) films, where the dopant is a thermally stable polyelectrolyte modified Kevlar, have good electrical conductivities of up to $1 \text{ S/cm}$ ; <input checked="" type="checkbox"/> Cation transport dominates in these composites during switching and is a function of ion size. <input checked="" type="checkbox"/> The diffusion coefficients for anion exchange in polypyrrole are a function of polymer morphology; <input checked="" type="checkbox"/> Proton transport accompanies switching of polypyrrole from the conducting to the insulating state; <input checked="" type="checkbox"/> Redox switching of polypyrrole modifies the luminescence behavior of an interfacial probe, (e.g. pyrene) and can be monitored using fluorescent dopant anions; <input checked="" type="checkbox"/> Quantum mechanical calculations indicate that steric effects in polyisothianaphthene and polyisophthothienophene renders them non-planar and increases the band gap; <input checked="" type="checkbox"/> The liquid crystalline properties of aliphatic/aromatic polyazomethine ethers depend on the configuration of atoms in the isomeric mesogenic core and the LC properties of some metal chelates depends on the nature of the transition metal. (R.W.)			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. JoAnn Millikan		22b. TELEPHONE (Include Area Code) 22c. OFFICE SYMBOL (202) 696-1410	

DTIC  
ELECTE  
OCT 14 1988  
S  
E

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. JoAnn Millikan

Contract No.: N00014-86-K-0769

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

Reporting Period: October 1, 1987-September 30, 1988

This is Annual Letter Report No. 2 for 1987-1988

<b>Accession For</b>	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	



88 1013 105

The following is a summary and status report of activities during 1987-1988 and brief plans for the coming year (1988-1989).

### 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 development of electroactive polymers based on polyheterocycles and main chain transition metal complexes is being pursued with the goal of controlling and improving physical and electronic properties of materials for specific applications. These include electrical conductivity, electrochemical response, electrochromism and thermal stability. Fluoropolymers 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. Spectroscopy and electrochemistry are being combined to develop a detailed understanding of the dynamics of charge and ion transport through conductive polymers. 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. They are being used to predict the site of electrochemical polymerization and to understand how various substituents effect the electronic and three dimensional structure of the polymers. Extensive Hückel band structure calculations are being performed on many of these systems to assess qualitative trends in band gaps. Liquid crystalline polyethers and polyazomethines (LCP) are being synthesized and characterized both for their mesomorphic and electroactive properties. Mesogenic core units which are being incorporated in these LCP's include such potential electroactive centers as extended conjugated units and transition metal chelates.

### Significant Results During the Last Year (1987-1988)

The following have been achieved or elucidated.

- 1) Charge transport properties of electrochemically prepared poly(3-methylthiophene) thin films depends on the morphology of the film.
- 2) Soluble transition metal bisdithiolene polymers are electroactive with three distinct oxidation states.
- 3) Carbon felt electrodes allow fairly large quantities of soluble poly(3-hexylthiophene) to be prepared.
- 4) The electrical properties of anion exchanged, doped polypyrroles are anion independent

5) Composite poly(pyrrole-Kevlar sulfonate) films, where the dopant is a thermally stable polyelectrolyte modified Kevlar, have good electrical conductivities of up to  $1 \text{ Scm}^{-1}$ . Cation transport dominates in these composites during switching and is a function of ion size.

6) The diffusion coefficients for anion exchange in polypyrrole are a function of polymer morphology.

7) Proton transport accompanies switching of polypyrrole from the conducting to the insulating state.

8) Redox switching of polypyrrole modifies the luminescence behavior of an interfacial probe (e.g. pyrene) and can be monitored using fluorescent dopant anions.

9) Quantum mechanical calculations indicate that steric effects in polyisothianaphthene and polyisobenzothienophene renders them non-planar and increases the band gap.

10) The liquid crystalline properties of aliphatic/aromatic polyazomethine ethers depend on the configuration of atoms in the isomeric mesogenic core and the LC properties of some metal chelates depends on the nature of the transition metal.

### Brief Summary of Plans for Next Years Work

We will utilize our new conductive polymer systems in novel processing techniques and specific device applications. We will collaborate with General Dynamics on thermally stable electroactive composites and with Celanese, Inc. on the spinning of electroactive fibers. Larger scale preparations of these polymers will be developed. Due to their intense near-IR absorptions, which are useful in optical data storage and non-linear optics, a full series of soluble transition metal bisdithiolenes will be prepared and electrochemically characterized. We will continue the development of *in situ* electrochemistry/spectroscopy techniques for the study of conductive polymers including the use of luminescence probes for monitoring ion transport. The mechanistic aspects of polymer film growth will also be examined. Cation transport will be studied in polymers with phosphorus, nitrogen and organic groups in the main chain and polyether side chains. Polyheterocycles will be prepared, which theoretical calculations suggest should be planar and have lower band gaps. We will continue our theoretical calculations on monomers, oligomers and polymers, using the PRDDO, ab initio and VEH methods, both to understand and predict physical and chemical properties. We will study the potential conductivity of doped liquid crystalline polyazomethine ethers, particularly those containing oligo(oxyethylene) spacers and mesogenic units of relatively long conjugation lengths. Also, liquid crystalline transition metal complex polymers will be prepared and studied.

### Papers Published in Refereed Journal

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. Electroanal. Chem.*, **1988**, *250*, 355. Other support: Texas Advanced Technology Research Program, Petroleum Research Fund of the American Chemical Society, and the Robert A. Welch Foundation.

Martinez, M., Reynolds, J. R., Basak, S., Black, D., Marynick, D. S., and Pomerantz, M., "Electrochemical Synthesis and Optical Analysis of Poly[(2,2'-dithienyl)-5,5'-diylvinylene]", *J. Polym. Sci. Phys. Ed.* **1988**, *26*, 911. 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., "Structural Analysis of the Alternating Copolymer Poly(chloroacrylonitrile-*alt*-cyclohexadiene)", *Macromolecules*, **1988**, *21*, 960. Other support: Center for Energy Conversion Research, University of Texas at Arlington.

Tsai, E. W., Pajkossy, T., Rajeshwar, K., and Reynolds, J. R., "Anion Exchange Behavior of Polypyrrole Membranes", *J. Phys. Chem.*, **1988**, *92*, 3560. Other support: Texas Advanced Technology Research Program.

Reynolds, J. R., "Electrically Conductive Polymers: Processible, Stable and Useful", *Chemtech* **1988**, *18*, 440.

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.*, **1987**, *134*, 2377. Other support: Center for Energy Conversion Research, University of Texas at Arlington.

Tsai, E. W., Jang, G-W., and Rajeshwar, K., "Proton Transport Accompanies Redox Switching of Polypyrrole: A Spectroelectrochemical Study", *J. Chem. Soc., Chem. Commun.*, **1987**, 1776.

Wang, S.J., Naidu, 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  $YBa_2Cu_3O_{7-\delta}$  Studied by Positron Annihilation", *Phys. Rev. B.*, **1988**, *37*, 603. Other support: The Robert A. Welch Foundation.

Wang, F., and Reynolds, J. R., "Soluble and Electroactive Nickel Bisdithiolene Complex Polymers", *Macromolecules* **1988**, *21*, 2887. Other support: The Robert A. Welch Foundation.

#### **Papers Accepted for Publication in Refereed Journals**

Baker, C. K., and Reynolds, J. R., "A Quartz Microbalance Study of the Electrosynthesis of Polypyrrole", *J. Electroanal. Chem.*, accepted for publication. Other support: Petroleum Research Fund of The American Chemical Society.

Pomerantz, M., Cardona, R., and Rooney, P., "The Application of the PMO Method to Aromatic Conducting Polymers", *Macromolecules*, accepted for publication.

Shaffer, T. D., "Phase Transfer Catalyzed Polymerization of  $\alpha,\alpha'$ -Dibromoxylene Isomers", *J. Polym. Sci. Polym. Lett. Ed.*, accepted for publication.

Tsai, E. W., Phan, L. and Rajeshwar, K., "Electrochemical Modulation of Luminescence from an Interfacial Probe during Redox Switching of Polypyrrole", *J. Chem. Soc., Chem. Commun.*, accepted for publication.

Tsai, E. W., Pajkossy, T., Rajeshwar, K., and Reynolds, J. R., "Anion Exchange Behavior of Polypyrrole Membranes", *J. Phys. Chem.*, accepted for publication. Other support: Texas Advanced Technology Research Program.

Mori, E., Baker, C. K., Reynolds, J. R., and Rajeshwar, K., "Aqueous Electrochemistry of Tellurium at Glassy Carbon and Gold: A Combined Voltammetry-Oscillating Quartz Crystal Microgravimetry Study", *J. Electroanal. Chem.*, accepted for publication. Other support: Research Corporation.

Ruiz, J. P., Reynolds, J. R., Nayak, K., and Marynick, D. S., "Soluble Ethylmercapto Substituted Polythiophenes", *Macromolecules*, accepted for publication. Other support: The Robert A. Welch Foundation.

### Papers Submitted to Refereed Journals

Tsai, E. W., Basak, S., Ruiz, J. P., Reynolds, J. R., and Rajeshwar, K., "Electrochemistry of Some  $\beta$ -Substituted Polythiophenes. Anodic Oxidation, Electrochromism and Electrochemical Deactivation Behavior", *J. Electroanal. Chem.*, submitted.

Nayak, K., and Marynick, D. S., "The Interplay Between the Geometric and Electronic Structures of Polyisothianaphthene and Polyisophonothiothiophene", *Macromolecules*, submitted.

Jang, G-W., Tsai, E. W., Abraham, P., and Rajeshwar, K., "Charge Storage and Transport in Thermal Ruthenium Oxide Thin Films", *J. Am. Chem. Soc.*, submitted. Other support: Center for Energy Conversion Research, University of Texas at Arlington.

Shaffer, T. D., and Sheth, K. A., "Mesomorphic Transition Metal  $N_2O_2$  Chelates", *Mol. Cryst. Liq. Cryst.*, submitted. Other support: The Robert A. Welch Foundation.

Shaffer, T. D., and Shaffer, M. L., "Constitutional Isomerism and Structural Characterization of Mesomorphic Aliphatic-Aromatic Polyazomethine Ethers", *Macromolecules*, submitted. Other support: The Robert A. Welch Foundation.

Panchalingam, V., and Reynolds, J. R., "New Vinylidene Fluoride Copolymers: Poly(vinyl acetate-co-vinylidene fluoride)", *J. Polym. Sci., Polym. Lett.*, submitted. Other support: Center for Energy Conversion Research, University of Texas at Arlington.

Martinez, M. R., Chien, J. C. W., and Reynolds, J. R., "Nuclear Magnetic Resonance of Conductive Poly(pyrrole)", *J. Chem. Phys.*, submitted. Other support: NSF/MRL, University of Massachusetts.

Reynolds, J. R., Hsu, S. G., and Arnott, H. J., "The Effect of Growth Morphology on the Electrochemical Response of Poly(3-methylthiophene)", *J. Polym. Sci., Phys. Ed.*, submitted. Other support: The Robert A. Welch Foundation.

Basak, S., Ho, Y.-H., Tsai, E. W., and Rajeshwar, K., "Luminescent Probes of Ion Transport in Polypyrrole: New Strategies for Luminescence Modulation and Assay of Ion Content in Conductive Polymers", *J. Chem. Soc., Chem. Commun.*, submitted.

Shaffer, T. D., and Sheth, K. A., "Mesomorphic Polyazomethine Ethers Containing Dibenzo-18-crown-6 Units", *Makromol. Chem.*, submitted. Other support: The Robert A. Welch Foundation.

Shaffer, T. D., "Liquid Crystalline Side-Chain Polyether Prepared by Phase Transfer Catalysis", *Makromol. Chem.*, submitted. Other support: The Robert A. Welch Foundation.

Shaffer, T. D., "Phase Transfer Catalyzed Polyetherification Through Nitro Displacement", *J. Polym. Sci., Polym. Lett. Ed.*, submitted. Other support: The Robert A. Welch Foundation.

### Books (and sections thereof) Accepted for Publication

Reynolds, J. R., Baker, C.K., Jolly, C. A., Poropatic, P. A., and Ruiz, J. P., "Electrically Conductive Polymers", *Conductive Polymers and Plastics*, Chapman and Hall, accepted for publication.

Reynolds, J. R., Baker, C. K., Martinez, M., Poropatic, P. A., Sundaresan, N., Pomerantz, M., Basak, S., Marynick, D. S., and Black, D. A., "Structural Control of The Electronic and Ionic Properties of Polyheterocycles", Proceedings of the Symposium on the Emergence of Conducting Polymers, 193rd National Meeting of the American Chemical Society, April, 1987, accepted for publication. Other support: Texas Advanced Technology Research Program, Petroleum Research Fund of the American Chemical Society, and The Robert A. Welch Foundation.

#### **Invited Presentations at Topical or Scientific/Technical Society Conferences**

Reynolds, J. R., Ruiz, J. P., Marynick, D. S., and Nayak, K., "The Effect of Structural Modification on the Physical and Electronic Properties of Polythiophenes", American Chemical Society, Middle Atlantic Regional Meeting, Lancaster, PA, May, 1988. Other support: The Robert A. Welch Foundation.

Reynolds, J. R., Ruiz, J. P., Wang, F., Jolly, C. A., Nayak, K., and Marynick, D. S., "Electroactive and Soluble Polyheterocycles and Transition Metal Complex Polymers", International Conference on the Science and Technology of Synthetic Metals, Santa Fe, NM, June, 1988. Other support: The Robert A. Welch Foundation.

#### **Contributed Presentations at Topical or Scientific/Technical Society Conferences**

Reynolds, J. R., Baker, C. K., "Quartz Crystal Microbalance Analysis of Electroactive Conjugated Heterocyclic Polymers", American Physical Society, 1988 March Meeting, New Orleans, LA, March, 1988. Other support: Petroleum Research Fund of the American Chemical Society.

Rajeshwar, K., Reynolds, J. R., Tsai, E. W., and Pajkossy, T., "Chemical Diffusion in Polypyrrole", 172nd National Meeting of the Electrochemical Society, Honolulu, HI, October, 1977.

Rajeshwar, K., Jang, G-W., and Tsai, E. W., "A New Spectroelectrochemical Method for Measurement of pH Modulation at an Electrode/Electrolyte Interface", 172nd National Meeting of the Electrochemical Society, Honolulu, HI, October, 1977.

Ruiz, J. P., Nayak, K., Marynick, D. S., and Reynolds, J. R., "The Effect of Structural Modification on the Physical and Electronic Properties of Polythiophenes", American Chemical Society, Rubber Division Meeting, Dallas, TX, April, 1988. Other support: The Robert A. Welch Foundation.

Poropatic, P. A., Huang, C. H., Goolsby, R. D., Marynick, D. S., and Reynolds, J. R., "Electrochemical Copolymerization as a Tool for the Study of the Mechanical and Electronic Properties of Polypyrrole", American Chemical Society, Rubber Division Meeting, Dallas, TX, April, 1988. Other support: Petroleum Research Fund of the American Chemical Society.

Krishnamoorthy, S., Naidu, S. V., Sharma, S. C., Krichene, S., and Reynolds, J. R., "Positron Annihilation Study of Conducting Polymers", American Physical Society, 1988 March Meeting, New Orleans, LA, March, 1988. Other support: The Robert A. Welch Foundation.

Baker, C. K., and Reynolds, J. R., "Gravimetric and Electrochemical Analysis of Polyheterocycles Using the Quartz Crystal Microbalance", International Conference on the Science and Technology of Synthetic Metals, Santa Fe, NM, June, 1988. Other support: Petroleum Research Fund of the American Chemical Society.

Jolly, C. A., Wang, F., Krichene, S., and Reynolds, J. R., "Soluble and Electroactive Transition Metal Complex Polymers", International Conference on the Science and Technology of Synthetic Metals, Santa Fe, NM, June, 1988. Other support: The Robert A. Welch Foundation.

Ruiz, J. P., Gieselman, M., Nayak, K., Marynick, D. S., and Reynolds, J. R., "The Effect of Structural Modification on the Physical and Electronic Properties of Polythiophenes", International Conference on the Science and Technology of Synthetic Metals, Santa Fe, NM, June, 1988. Other support: The Robert A. Welch Foundation.

Faulmann, F., Cassoux, P., Vicente, R., Ribas, J., Jolly, C. A., and Reynolds, J. R., "Conductive Amorphous Metal-Tetrathiolato Polymers: Synthesis of a New Precursor,  $C_6O_2S_8$ , and Its Derived Polymers, and LAXS Structural Studies", International Conference on the Science and Technology of Synthetic Metals, Santa Fe, NM, June, 1988.

Shaffer, T. D., "Polymerization of  $\alpha, \alpha'$ -Dibromoxylene Isomers", 196th National Meeting of The American Chemical Society, Los Angeles, California, September, 1988. *Polym. Prepr., (Am. Chem. Soc. Div. Polym. Chem.)* 1988, 29 (part 2), 322.

Shaffer, T. D. and Shaffer, M. L., "Structural Characterization of Mesomorphic Polyazomethine Ethers", 196th National Meeting of The American Chemical Society, Los Angeles, California, September, 1988. *Polym. Prepr., (Am. Chem. Soc. Div. Polym. Chem.)* 1988, 29 (part 2), 352.

#### Honors/Awards/Prizes

Dennis S. Marynick won The Wilfred T. Doherty Award of The Dallas-Ft. Worth Section of The American Chemical Society, April 22, 1988. Other support: The Robert A. Welch, and Cray Research Foundation.

Dennis S. Marynick won The University of Texas at Arlington Distinguished Research Award, April 12, 1988. Other support: Cray Research Foundation, and The Robert A. Welch Foundation.

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

8

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

7

#### Graduate Students Currently Working on the Project

Charles Baker  
Paul Poropatic  
Jose Ruiz  
Mark Victor  
Lillian Hansen  
Yeung-Haw Ho  
Krisna Kumar

**Postdoctorals Currently Working on the Project**

Sanjay Basak  
Robert Uitz  
John J. Tseng  
Kasinath Nayak