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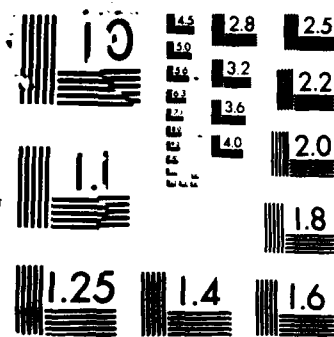
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An optoelectrochemical study of poly(1,2-dithienylethylene) showed a lower band gap than the parent polythiophene and that it is electrochemically switchable between oxidized and reduced states. Free standing films exhibit conductivities up to 15 Scm^{-1} . The quartz crystal microbalance has been used to monitor charge transport in polypyrrole and the self-doped copolymer, poly{pyrrole-co-[3-pyrrol-1-yl]propanesulfonate} in a variety of electrolytes. Scanning electron microscopy has shown that the morphology of these polymers is similar. A recently developed spectroelectrochemical technique has demonstrated that proton migration accompanies redox switching in polypyrrole. PRDDO calculations of many N-substituted pyrroles has shown that the oxidation potential of benzylpyrroles most closely match that of pyrrole. C-1s binding energies of polypyrrole with α - α linkages and with α - β and β - β defects have been calculated for comparison with XPS data. An extended series of metal Cu(II) and Ni(II) chelate model compounds of bis(2,5-dihydroxybenzaldehyde)ethylenediimine has been prepared which contain ether end-cap spacers of 6-10 methylene units. Thermal analysis has revealed that the Ni(II) complexes show only nematic behavior while the Cu(II) complexes show both smectic and nematic behavior.

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Technical Report

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Description of Progress

a) Electronically Conducting Polyheterocycles

The synthesis of two new soluble polythiophenes, poly[(3-ethylmercapto)thiophene] and poly[(3,4-bis-ethylmercapto)thiophene], has been accomplished chemically using a Grignard coupling reaction of the 2,5-dibromo substituted monomers. Their band gaps have been measured in solution and preliminary doping experiments show that they have elevated conductivities. Free standing films of each have been cast from solution.

A full study of the optoelectrochemistry of poly(1,2-dithienylethylene) has been completed and shows it to have a lower band gap than the parent polythiophene and to be electrochemically switchable between oxidized and reduced states. Free standing films, of known composition, which exhibit conductivities as high as 15 Scm^{-1} , have been obtained.

The quartz crystal microbalance has been used to monitor charge transport in polypyrrole and the self-doped copolymer, poly{pyrrole-co-[3-(pyrrol-1-yl)propanesulfonate]} in a variety of electrolytes. These results, coupled with a complete chronocoulometric analysis of both systems, lends significant insight into the mechanism of charge transport in self doped conductive polymers. Scanning electron microscopic investigations have been carried out on films of poly(pyrrole fluoroborate) and the self-doped poly{pyrrole-co-[3-(pyrrol-1-yl)propanesulfonate]}. Both have similar morphologies which suggest that the polymers are initially significantly swelled with electrolyte. Microbalance studies of the electropolymerization of various heterocyclic monomers is continuing.

Equipment is being constructed to monitor mass changes during the gas phase doping of thin conductive polymer films. Initial studies have begun by coupling changes in FTIR spectra of SO_3 doped poly(phenylene vinylene) to quantitatively determined oxidation levels.

Poly(isonaphtho[2,3,c]thiophene) has been prepared from 2,3-naphtho(2,5-dihydrothiophene) by FeCl_3/O_2 oxidation. It was a deep blue-black powder which had a pressed pellet (four probe) conductivity of 10^{-2} Scm^{-1} .

Continuing our efforts to verify proton transport in polypyrrole thin films, we have recently completed a new set of spectroelectrochemical measurements. Using a new technique which was recently developed in our laboratory,¹ we have been able to conclusively show that proton migration accompanies redox switching in polypyrrole. There have been previous suggestions as to the importance of proton transport in this material;² however, this is the first demonstration, to our knowledge, of this double-injection electrochemical phenomenon.

The crux of these experiments is as follows. Polypyrrole is deposited on an optically-transparent gold minigrid electrode. The film is then rapidly brought to the insulating (reduced) form. On incremental switching to the conductive (oxidized) form, protons are expelled from the polypyrrole film into the contacting electrolyte. A light beam probes the interfacial pH changes using a dye indicator. These measurements also reveal that cation movement is an important component of redox switching. Previous mechanistic interpretations have involved predominantly anion transport.

Chemical diffusion measurements summarized in the previous report have been refined and completed. A manuscript describing these data is being readied for publication.

A large number of PRDDO calculations on N-substituted pyrroles have been performed, with the goal of finding a substituent which closely matches the oxidation potential of pyrrole. Substituted benzyl pyrroles appear to be the best candidates. In related work, we have calculated the C-1s binding energies of polypyrrole with all α - α linkages and with α - β or β - β defects as a first step towards in understanding of the XPS results for this polymer.

References

1. G-W. Jang, E.W. Tsai, and K. Rajeshwar, *J. Am. Chem. Soc.*, submitted for publication.
2. O. Inganäs, R. Erlandsson, C. Nylander and I. Lundström, *J. Phys. Chem. Solids* **45**, 427 (1984).

b) High Permittivity Dielectric Polymers

A high pressure polymerization reactor system has been set up to study the emulsion polymerization and copolymerization of vinylidene fluoride. Synthetic experiments have been carried out which utilize techniques learned from Pennwalt Incorporated to synthesize PVF₂.

c) Novel Liquid Crystalline Conductors

As a continuation of the preparation of model compounds of metal chelates of bis(2,5-dihydroxybenzaldehyde)ethylenediimine (BDHED), we have prepared an extended series of ether model materials with Ni(II) as the metal core. Both Cu(II) and Ni(II) model chelates have been synthesized to contain from six to ten methylene units as ether end-cap spacers. Thermal characterization of these molecules have indicated only nematic behavior for the Ni(II) complexes and both smectic and nematic behavior for the Cu(II) complexes. Thermal transitions are generally lower for Ni(II) complexes. In addition, the Ni(II) complexes are significantly more thermally stable in air. These observations may be the first to identify a systematic change in LC properties with respect to a metal center.

Publications:**Paper which has appeared in print**

"Electroactive Copolymers of Pyrrole Containing Covalently Bound Dopant Ions: Poly{pyrrole-co-[3-(pyrrol-1-yl)propanesulphonate]}", Sundarasan, N.S.; Basak, S.; Pomerantz, M.; Reynolds, J. *J. Chem. Soc. Chem. Comm.* **1987**, 621.

Meetings, Oral Presentations and Visitors

J.R. Reynolds presented two invited talks on research carried out by the URI group at the 193rd National Meeting of the American Chemical Society, Denver, Colorado, April, 1987.

1. "Conductive Polymers Containing Bound Dopant Ions" (with N.S. Sundaresan, S. Basak and M. Pomerantz) at the Symposium on Chemical Characterization of Ion Containing Polymers in the Analytical Division.

2. "Control of the Physical and Electronic Properties of Polyheterocycles" (with S. Basak, D. Black, D.S. Marynick, T. Pajkossy, M. Pomerantz, P.A. Poropatic, K. Rajeshwar, N. Sundaresan, and R. Toyooka) at the Symposium on the Emergence of Conductive Polymers in the Industrial and Engineering Chemistry Division.

J.R. Reynolds presented an invited seminar on the "Synthesis and Characterization of Electrically Conductive Polyheterocycles" to the Chemical Engineering department at Auburn University.

M. Pomerantz and J.R. Reynolds presented an overview of The University of Texas at Arlington URI program to the DARPA polymer program review in Washington D.C., April 21-22, 1987.

Presentations which were given on URI related research at the 20th Annual Meeting-in-Miniature of the Dallas-Fort Worth Section of the American Chemical Society, Fort Worth, TX, April, 1987 are as follows:

1. "Electrochemical Microbalance Studies of Polypyrrole", presented by Charles Baker.
2. "Polypyrroles: Composites and Copolymers", presented by Paul Poropatic.
3. "Transition Metal Tetrathiooxalates: A Structural and Electronic Study", presented by Cindy Jolly.
4. "Optoelectrochemistry of Poly(2,2'-dithienyl)-5,5'-diylvinylene]", presented by Maria Martinez.
5. "Studies on the Synthesis and Properties of Phosphorus and Nitrogen Containing Polymers", presented by Mark Victor.

Visitors to our laboratories included:

1. Professor Tom McCarthy of the University of Massachusetts who presented a seminar entitled "Organic Chemistry at Chemically Resistant Polymer Surfaces"
2. Professor Andrew Jonscher of London College who discussed aspects of dielectric polymers for capacitor applications.
3. Dr. Ivan Goldfarb, Polymer Branch, Wright Patterson Air Force Base who discussed polymer research at WPAFB and potential further interactions.

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