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ELECTRONIC AND IONIC TRANSPORT IN PROCESSABLE CONDUCTING POLYMERS

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A series of poly[1,4-bis(2-furanyl)-2,5-disubstituted-p-phenylenes] has been prepared electrochemically. They exhibit conductivities of up to 0.1 S cm^{-1} when doped electrochemically. The nature of the substituent has been shown to affect the cyclic voltammetric $E_{1/2}$ potentials and bandgaps, but these are independent of the length of the alkyl chain in the substituents. Interestingly, electrogravimetric analysis has shown greater mass increase upon electrochemical oxidation with longer alkoxy chains. Poly[(p-phenyleneterephthalamido)propane sulfonate] (PPTA-PS) has been prepared and studied extensively. The ternary phase behavior of poly(p-phenylene benzobisthiazole)/PPTA-PS/methane sulfonic acid has been examined, collaboratively (Wright-Patterson Air Force Base) and the intermolecular coil/rod interactions have been shown to cause the phase behavior to deviate from Flory's theory for molecular composites. The mechanistic aspects of the chemical reduction of polypyrrole/naphthalene sulfonate thin films by hydrazine have been elucidated. The self oxidation of polypyrrole in N_2 and O_2 , and the involvement of polaron and bipolaron states, has been studied by UV-visible spectroelectrochemistry. Conformational analyses and electronic structures have been calculated for a variety of systems including copolymers of heterocyclic rings (e.g., furan and pyrrole) and disubstituted (methyl or methoxy)-p-phenylene systems, copolymers of heterocyclic rings and dimethoxyvinylene and a thienothiophene system.

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Electronic and Ionic Transport in Processable Conducting Polymers

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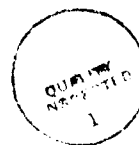
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Description of Progress

A series of 1,4-bis(2-furanyl)-2,5-disubstituted-*p*-phenylene monomers have been synthesized and electropolymerized. Dimethyl, dimethoxy and longer chain dialkoxy pendants were investigated. These new polymers exhibit conductivities of up to 10^{-1} S/cm when electrochemically doped in the presence of ClO_4^- . Cyclic voltammetry has revealed that $E_{1/2}$ potentials are dependent on the nature of the substituent, however, the potentials are not affected by the length of the alkoxy chain. The band gap of each polymer has been determined using optoelectrochemical techniques, and follow a similar trend. Nernst plots of each system, determined from an optical absorption technique, have revealed the n value for oxidation to be dependent on the nature of the pendant group, but also independent of the pendant chain length. PRDLO calculations on the monomers have shown them to be essentially planar with low barriers to rotation. Electrogravimetric studies using a quartz crystal microbalance have demonstrated that the longer chain alkoxy substituted polymers have a larger amount of mass increase associated with electrochemical oxidation.

Poly[(*p*-phenyleneterephthalamido)propane sulfonate] (PPTA-PS) with various extents of sulfoalkylation, were synthesized by reacting poly(*p*-phenyleneterephthalamide) (PPTA, Kevlar) with sodium hydride to prepare the PPTA anion and subsequently with 1,3-propanesultone. Characterization and structural analyses of the polyelectrolytes formed were carried out by a combination of ^{13}C NMR and FT-IR spectroscopies. The NMR spectra indicate the polymer backbone to be stable to the derivatization reaction with mainly N-sulfoalkylation and a small amount of O-sulfoalkylation. The IR spectra reveal an increased chain flexibility with extent of sulfoalkylation as evidenced by comparison of hydrogen bonded and non-hydrogen bonded N-H stretching modes. Viscosity measurements, as a function of concentration, showed the highly sulfoalkylated polymer to exhibit typical polyelectrolyte behavior with maximum viscosities in extremely dilute solutions. In a collaborative program with researchers at Wright Patterson Air Force Base, the ternary phase behavior of the poly(*p*-phenylene benzobisthiazole) (PBZT)/PPTA-PS/methane sulfonic acid system has been investigated. In this rod/coil/solvent system, intermolecular coil/rod interactions cause the phase behavior to deviate from Flory's theory for molecular composites.

Studies on the chemical reduction of polypyrrole/naphthalene sulfonate thin films by hydrazine have been completed. The use of polypyrrole film thickness and hydrazine concentration as variables has enabled us to develop a quantitative model which reveals hydrazine adsorption on the polymer surface, subsequent permeation of reactant, and reaction with the polymer backbone as the key steps in the overall reduction. Diffusion coefficients have been computed as well as the reaction stoichiometric coefficients from these data.

The self-oxidation of neutral polypyrrole in N_2 and O_2 ambients has been studied by UV-visible spectroelectrochemistry. In N_2 , the sequence $PP^0 \rightarrow PP^{+\bullet} \rightarrow PP^{2+}$ was established from the spectral signatures. On the other hand, in an O_2 ambient, the polaron state is bypassed.

We have performed conformational analyses and investigated the electronic structures of the following polymers: (1) copolymers of heterocyclic rings such as pyrrole or furan with disubstituted (methyl or methoxy groups) benzene; (2) copolymers of thiophene, pyrrole or furan with dimethoxyvinylene; and (3) poly(thieno-[3,4-b]-thiophene) systems using theoretical calculations. The latter system has been found to have a calculated band gap of only 1.0 eV and experiments directed towards its synthesis are being vigorously pursued.

Also we have successfully modified the extended Hückel program by introducing modified off-diagonal Hamiltonian elements such that a reasonable 1-dimensional band gap ($p \rightarrow p^*$ transition energy, which corresponds to the peak position of the optical spectrum of polymers) can be predicted.

Publications

Papers Published

Reynolds, J. R. and Pomerantz, M. "Processable Electronically Conducting Polymers," in *Electroresponsive Molecular and Polymeric Systems*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1991; Vol. 2, Chapter 4, pp. 187-256.

Reynolds, J. R.; Ruiz, J. P.; Child, A. D.; Marynick, D. S. and Nayak, K. "Electrically Conducting Polymers Containing Alternating Substituted Phenylene and Bithiophene Repeat Units," *Macromolecules* **1991**, *24*, 678-687.

Basak, S.; Rajeshwar, K. and Kaneko, M. "In Situ Photogeneration of a Catalyst on a Chemically-Modified Electrode Surface: Application to a Mixed Valent Hexacyanoferrate System," *J. Electroanal. Chem.* **1990**, *295*, 403-407.

Papers in Press

Krishna, V.; Ho, Y.-H.; Basak, S. and Rajeshwar, K. "A Luminescence Probe and Voltammetry Study of Ion Transport During Redox Switching of Polypyrrole Thin Films," *J. Am. Chem. Soc.*, in press.

Sundaresan, N. S.; Reynolds, J. R. and Ruiz, J. P. "Photocurrent Response of Poly(3-ethylmercaptothiophene)," *J. Mat. Sci.*, in press.

Qiu, Y. J. and Reynolds, J. R. "Dopant Anion Controlled Ion Transport Behavior of Polypyrrole," *Polym. Eng. and Sci.*, in press.

Baker, C. K. and Reynolds, J. R. "Electrochemically Induced Mass Transport in Poly(pyrrole)/Poly(styrene sulfonate) Molecular Composites," *J. Phys. Chem.*, in press.

Pomerantz, M.; Tseng, J. J.; Zhu, H.; Sproull, S. J.; Reynolds, J. R.; Uitz, R.; Arnott, H. J. and Haider, M. I. "Processable Polymers and Copolymers of 3-Alkylthiophenes and Their Blends," *Synth. Met.*, in press.

Reynolds, J. R. and Pomerantz, M. "The International Conference on Science and Technology of Synthetic Metals," *ESN Information Bulletin* (ONR European Office), in press.

Stickle, W. F.; Reynolds, J. R. and Jolly, C. A. "Surface Characterization of Electrically Conducting Nickel Tetrathiooxalate/Poly(Vinyl Alcohol) Composites," *Langmuir*, in press.

Wang, F.; Qiu, Y. J. and Reynolds, J. R. "Synthesis and Characterization of Nickel Bis(dithiolene) Complex Polycarbonates and Polyurethanes," *Macromolecules*, in press.

Papers Submitted for Publication

Qiu, Y. J. and Reynolds, J. R. "Charge and Ion Transport in Poly(pyrrole copper phthalocyanine-sulfonate) During Redox Switching," *J. Electroanal. Chem.*, submitted for publication.

Prezyna, L. A.; Wnek, G. E.; Qiu, Y. J. and Reynolds, J. R. "Interaction of Cationic Polypeptides with Electroactive Polypyrrole/Poly(styrene sulfonate) and Poly(N-methylpyrrole)/Poly(styrene sulfonate)," *Macromolecules*, submitted for publication.

Son, Y. and Rajeshwar, K. "Potential-Modulated UV-Visible and Raman Spectra of Polypyrrole Thin Films in Aqueous Electrolytes: Combination with Voltammetric Scanning and the Influence of Dioxygen on the Stability of Radical Cations and Dications of the Conducting Polymer," *J. Phys. Chem.*, submitted for publication.

Basak, S.; Zacharias, P. S. and Rajeshwar, K. "Binding and Surface Coordination Chemistry of Copper(II) Macrocycles at Nafion-Modified Glassy Carbon Electrodes," *J. Electroanal. Chem.*, submitted for publication.

Papers Acknowledging DARPA Support for Instrumental Purchases

Pomerantz, M. and Levanon, M. "Carbene Addition to the 2,3-Bond of Naphthalene and Thermal Wolff Rearrangement of Bis(methoxycarbonyl)carbene," *Tetrahedron Lett.* **1991**, 32, 995-998.

Brown, K. L.; Brooks, H. B.; Zou, X.; Victor, M.; Ray, A. and Timkovich, R. "Heteronuclear NMR Studies of Cobalamins. 11. ^{15}N NMR Studies of the Axial Nucleotide and Amide Side Chains of Cyanocobalamin and Dicyanocobalamin," *Inorg. Chem.* 1990, 29, 4841-4844.

Talks Presented

John Reynolds presented a talk entitled "Electrically Conducting Polymers: Academic Research to Aerospace Applications," with G. Worrell of General Dynamics to the Dallas/Fort Worth Section of the American Chemical Society, Dallas, Texas, March 1991.

Krishnan Rajeshwar presented a seminar entitled "Ion Transport During Redox Switching of Biconductive Chemically-Modified Electrodes" at Southern Methodist University, February 14, 1991.

Visitors to The University of Texas at Arlington

Professor David Tirrell from the Polymer Science and Engineering Department, the University of Massachusetts, visited on February 1, 1991, and presented a seminar entitled "On The Role of Molecular Genetics in Materials Chemistry."

Dr. Barry Miller of AT&T Bell Laboratories visited on February 8, 1991, and presented a seminar entitled "Electrochemical Aspects of High Temperature Superconductors."

Dr. Joel Miller of DuPont visited on February 12, 1991, and presented a seminar entitled "Molecular Magnets: Chemistry and Physics."

Dr. Robert Crowe from NRL/DARPA visited on February 21, 1991, and we discussed various aspects of our research programs.