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ELECTRONIC AND IONIC TRANSPORT IN PROCESSABLE CONDUCTING POLYMERS

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EPR spectroscopy/electrochemical measurements have shown polaron and bipolaron states in the redox switching of poly(di-2-thienylphenylenes) substituted with alkoxy groups. The longer side chains stabilize the polaronic form of the polymers. In aqueous perchlorate and tetrafluoborate electrolytes, pyrrole electropolymerizes using only ca. 0.1 electrons per monomer. This suggests that in these cases a chain-growth polymerization is occurring rather than the more typical cation-radical coupling. Continued studies on our Pt/polypyrrole nanocomposites (a 3-dimensional array of catalytically active colloidal Pt particles in a polypyrrole matrix) has demonstrated unusual catalytic activity toward O_2 and H_2. A new modified extended Hückel band structure calculation method has been developed which reproduces band gaps of polyheterocycles to within 0.4 eV. A new soluble derivative of poly(thieno[3,4-b]pyrazine) with a solution band gap of 1.1 eV and which changes color from dark blue to light yellow upon doping has been prepared.

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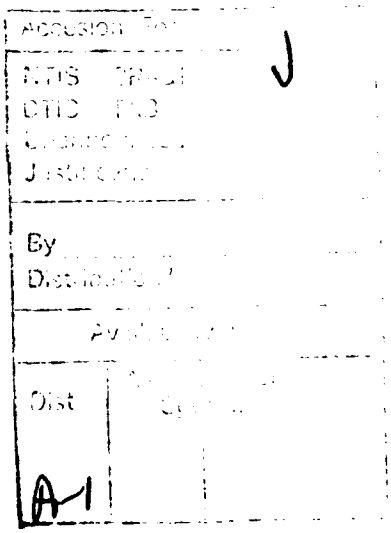
Technical Report 32

Electronic and Ionic Transport in Processable Conducting Polymers



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October 21, 1991

Description of Progress

We have utilized in situ electron paramagnetic resonance (EPR) spectroscopy/electrochemical measurements to probe the redox switching of alkoxy substituted poly(di-2-thienylphenylenes). The diheptoxy derivative shows two distinct electrochemical processes suggesting three redox states. Correlation of EPR signal intensity with electrode potential shows the fully reduced and fully oxidized states to be diamagnetic while the intermediate oxidation state is paramagnetic. This is consistent with the initial formation of polarons upon oxidation which are subsequently converted to bipolarons. The longer side chains are observed to stabilize the polaronic form of the polymers since no paramagnetism is observed for the dimethoxy substituted polymer during switching.

The generally accepted electrochemically activated step-growth mechanism for oxidative polymerization of pyrrole has been found to not be universal. In aqueous perchlorate and tetrafluoroborate electrolytes, electrochemical deposition rates monitored microgravimetrically at an oscillating quartz crystal are found to have extremely high coulometric yields. In certain phases of electropolymerization, *ca.* 0.1 electrons are required per monomer unit. This is highly suggestive of an electrochemically initiated chain-growth polymerization. The more typical cation-radical coupling mechanism is found to occur in many other electrolytes including Cl^-, NO_3^-, dodecyl sulfate, copper phthalocyanine tetrasulfonate and poly(styrene sulfonate).

Studies on the Pt/polypyrrole nanocomposites (comprising a three-dimensional array of catalytically active colloidal Pt particles within the polypyrrole matrix) are continuing. Unusual catalytic activity has been noted for these materials towards H_2 and dioxygen. For example, comparable catalytic activity with bulk Pt is achieved by immobilizing only ~3.6% of the corresponding amount of Pt^0 within the polymer matrix. Quartz crystal microbalance studies of the ion transport at polypyrrole/aqueous electrolyte interfaces are in progress. The goal of these studies is to acquire a complete partitioning of all the ion fluxes (cation, anion and proton) in response to redox switching of the conductive polymer.

Final parameterizations have been completed for a new, modified Extended Hückel band structure calculation method. The new approach consistently reproduces band gaps of polyheterocycles to within ~0.4 eV. The first application of the new method was to phenylene-pyrrole and phenylene-furan copolymers with methyl and methoxy substituents on the phenylene ring. The calculated electronic properties of the copolymers were found to be similar to those of the homopolymers and were in excellent agreement with experiment.

Work on "transparent" (color neutral), processable conducting polymers is continuing. Poly(2,3-dihexylthieno[3,4-b]pyrazine) has been prepared by $FeCl_3$ polymerization of the corresponding monomer. This polymer forms a dark blue solution which can be doped to a light yellow solution. The solution phase band gap of the polymer is ca. 1.1 eV.

Publications

Papers Published

Baker, C. K.; Qiu, Y.-J.; Reynolds, J. R. "Electrochemically Induced Mass Transport in Poly(pyrrole)/Poly(styrene sulfonate) Molecular Composites", *J. Phys. Chem.* **1991**, *95*, 4446-4452.

Pomerantz, M.; Tseng, J. J.; Zhu, H.; Sproull, S. J.; Reynolds, J. R.; Uitz, R.; Arnott, H. J.; Haider, M. I. "Processable Polymers and Copolymers of 3-Alkylthiophenes and Their Blends", *Synth. Met.* **1991**, *41*, 825-830.

Wang, F.; Qiu, Y.-J.; Reynolds, J. R. "Electroactive, Near-Infrared Absorbing, Nickel Bis(dithiolene) Complex Polycarbonates and Polyurethanes", *Macromolecules* **1991**, *24*, 4567-4574.

Prezyna, L. A.; Wnek, G. E.; Qiu, Y.-J.; Reynolds, J. R. "Interaction of Cationic Polypeptides with Electroactive Polypyrrole/Poly(styrene sulfonate) and Poly(N-methylpyrrole)/Poly(styrene sulfonate", *Macromolecules* **1991**, *24*, 5283-5287.

Ruiz, J. P.; Child, A. D.; Nayak, K.; Marynick, D. S.; Reynolds, J. R. "Electrically Conducting Polymers Containing Substituted Phenylene and Heterocycle Repeat Units", *Synth. Met.* **1991**, *41*, 783-788.

Prezyna, L. A.; Wnek, G. E.; Qiu, Y.-J.; Reynolds, J. R. "Interaction of Cationic Polypeptides with Electroactive Polypyrrole/Poly(styrene sulfonate) and Poly(N-methylpyrrole)/Poly(styrene sulfonate) Films", *Synth. Met.* **1991**, *41*, 979-981.

Reynolds, J. R. and Pomerantz, M. A report on "The International Conference on Science and Technology of Synthetic Metals", *ESN Information Bulletin* (ONR European Office) **1991**, *No. 4*, pp. 6-9.

Papers in Press

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

Panchalingam, V.; Reynolds, J. R. "Poly(1,3-cyclohexadiene-*alt*-α-fluoroacrylonitrile): A Thermally Stable, Alternating Copolymer", *J. Polym. Sci., Part A, Polym. Chem.*, in press.

Ruiz, J. P.; Dharia, J. R.; Reynolds, J. R.; Buckley, L. J. "Symmetry Effects on the Physical and Electronic Properties of Processable, Electrically Conducting, Substituted Poly(di-2-thienylphenylenes)", *Macromolecules*, in press.

Qiu, Y.-J. and Reynolds, J. R. "Electrochemically Initiated Chain Polymerization of Pyrrole in Aqueous Media", *J. Polym. Sci., Part A, Polym. Chem.*, in press.

Child, A. D. and Reynolds, J. R. "Separation of Neutral-to-Polaron and Polaron-to-Bipolaron Redox Events in Alkoxy Substituted Di-2-thienylphenylene Polymers", *J. Chem. Soc., Chem. Commun.*, in press.

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

Papers Submitted for Publication

Hong, S. Y. and Marynick, D. S. "Modified Extended Hückel Band Calculations on Conjugated Polymers", *J. Chem. Phys.*, 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. Chem. Soc., Farad. Transactions*, submitted for publication.

Bose, C. S. C. and Rajeshwar, K. "Highly Efficient Electrocatalyst Assemblies for Proton and Oxygen Reduction: The Electrosynthesis and Characterization of Polypyrrole Films Containing Nanodispersed Platinum Particles, *J. Am. Chem. Soc.*, submitted for publication.

Papers Acknowledging DARPA Support for Instrumental Purchases

Brown, K. L.; Brooks, H. B.; Gupta, B. D.; Victor, M.; Marques, H. M.; Scooby, D. C.; Goux, W. J.; Timkovich, R. *Inorganic Chemistry* **1991**, *30*, 3430-3438.

Talks Presented

Reynolds, J. R. and Panchalingam, V. "New Fluorinated Copolymers; Poly(1,3-cyclohexadiene-*alt*-α-fuoroacrylonitrile)", presented at the 202nd National American Chemical Society Meeting, New York, New York, August, 1991. *Polym. Prepr., (Am. Chem. Soc. Div. Polym. Chem.)* **1991**, *32*, 185-186.

Reynolds, J. R. and Panchalingam, V. "Dehydrohalogenation Studies of Vinylidene Fluoride/Trifluoroethylene Copolymer and Poly(chlorofluoroethylene)", presented at the 202nd National American Chemical Society Meeting, New York, New York, August, 1991. *Polym. Prepr., (Am. Chem. Soc. Div. Polym. Chem.)* **1991**, *32*, 187-188.

Personnel Changes

Dr. Larry O. Harding, former postdoctoral associate, is now employed at Conoco, Inc., Ponca City, Oklahoma.

Dr. Ronald L. Elsenbaumer, from Allied-Signal Corp., will join the University of Texas at Arlington as Chairman of the Materials Science and Engineering Program on November 1, 1991.

Additional Noteworthy Meeting

John Reynolds met with representatives of General Dynamics, Inc. and E-Systems Inc. to discuss application of conducting polymers in aerospace radar antennae. A plan was put together to develop a joint research program utilizing switchable systems in antennae.