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By employing NaOH dedoping high/low conductivity interfaces have been prepared. Optoelectrochemical properties of several thiophene-phenylene-thiophene polymers have been studied. Blends of poly(3-decylthiophene) with polyethylene or poly(ethylene terephthalate) have been prepared. The ion binding properties of copolymers of pyrrole and 3-(1-pyrrolyl)propanesulfonate have been studied for the first time using $\text{Ru}(\text{NH}_3)_6^{3+}$ and $\text{Ru}(\text{bpy})_3^{2+}$ (bpy=2,2'-bipyridyl) as the ion probes. Molecular orbital calculations have been used to estimate the equilibrium ground state geometries of alternating copolymers of substituted phenylenes and bithiophenes. Calculated spin populations suggest possible α - β and/or β - β linkages in addition to α - α linkages. Calculated band gaps are between those of poly(p-phenylene) and polythiophene (AW).

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Technical Report No. 17

Electronic and Ionic Transport in Polymers

by

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Description of Progress

The effect of NaOH dedoping on the electrical conductivity of poly(pyrrole tosylate), poly(pyrrole dodecylbenzenesulfonate) and polypyrrole/poly(styrene sulfonate) has been examined. Distinct high conductivity/low conductivity interfaces, ca 2 mm wide across a conducting polymer film, have been prepared with conductivity changes of 2 orders of magnitude across the interface. These interfaces are found to be stable under ambient conditions with no conductivity change on either side and can thus serve as stability models for graded conductivity polypyrrole films.

The optoelectrochemical properties of a series of substituted thiophene-phenylene-thiophene polymers were investigated using $-\text{CH}_3$, $-\text{OCH}_3$, and $-\text{OC}_7\text{H}_{15}$ substituents. A new family of furan-phenylene-furan monomers were synthesized and, in the case of the unsubstituted phenylene, found to electropolymerize to form smooth films. Blends of varying amounts of poly(3-decylthiophene) with several other polymers such as low and high density polyethylene and poly(ethylene terephthalate) have been prepared and their properties are being studied. We have observed thermochromicity in these blends where they change from dark red brown at room temperature to yellow at elevated temperatures.

The ion binding properties of copolymers of 3-(1-pyrrolyl)propanesulfonate and pyrrole (copoly PP-PS) have been studied for the first time using $\text{Ru}(\text{NH}_3)_6^{3+}$ and $\text{Ru}(\text{bpy})_3^{2+}$ (bpy = 2,2'-bipyridyl) as the ion probes. The partition coefficients of these species have been measured from binding studies in aqueous media. Composites of polypyrrole and Prussian blue as the dopant anion have been synthesized.

We have employed the PRDDO molecular orbital method to estimate the equilibrium ground state geometries of the alternating copolymers of substituted phenylenes with bithiophenes. The aromatic form of the unsubstituted phenylene-bithiophene copolymer was found to be preferred over the quinoid counterpart. From our PRDDO UHF calculations, it was predicted that significant spin populations exist on the outer α -carbons of the monomers of the 1,4-bis(2-thieno)-phenylene and 1,4-bis(2-thieno)-2,5-dimethoxyphenylene and 1,4-bis(2-thieno)-2,5-

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dimethylphenylene, although substantial amounts of spin population exists at the other sites. These findings suggest that these copolymers might contain some fractions of α - β and/or β - β linkages. The band structures of the one dimensional polymer chain of the copolymers of phenylene with bithiophene were calculated using the extended Hückel theory within the tight binding approximation. The band gaps of the unsubstituted, methyl and methoxy substituted poly(1,4-bis(2-thienyl)-2,5 disubstituted phenylene) were calculated to be 2.03, 2.58 and 2.18 eV's respectively; these values are intermediate between those of poly(*p*-phenylene) (3.5 eV) and polythiophene (1.71 eV).

The molecular orbital study of the alternating copolymers of substituted phenylenes with bipyrrrole and bifuran is underway in our laboratory. The electronic properties of polyarenemethide (PAM) and polyquinoxaline are also under investigation.

Publications

Papers Published

Pomerantz, M. and Victor, M. W. "Synthesis and Characterization of a Series of Alternating Copolymers (Oligomers) Containing Organophospha- λ^5 -azene Backbone Moieties", *Macromolecules*, **1989**, 22, 3511-3514.

Shaffer, T. D. and Sheth, K. A. "Mesomorphic Transition Metal N_2O_2 Chelates", *Mol. Cryst. Liq. Cryst.*, **1989**, 172, 27-39.

Papers in Press

Tsai, E. W., Basak, S., Ruiz, J. P., Reynolds, J. R. and Rajeshwar, K. "Electrochemistry of Some β -Substituted Polythiophenes. Anodic Oxidation, Electrochromism and Electrochemical Deactivation Behavior", *J. Electrochem. Soc.*, in press.

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.*, in press.

Shaffer, T. D. and Kramer, M. C. "Cyclization vs. Polymerization in Phase Transfer Catalyzed Polythioetherification", *Makromol. Chem.*, in press.

Shaffer, T. D. "PTC Polyetherification Through Nitro Displacement", *J. Polym. Sci., Polym. Lett.*, in press.

Papers Submitted for Publication

Qiu, Y.-J. and Reynolds, J. R. "Poly[3,6-(carbaz-9-yl)propanesulfonate]: A Self-Doped Polymer with Both Cation and Anion Exchange Properties", *J. Electrochem. Soc.*, submitted for publication.

Sharma, S. C., Krishnamoorthy, S., Naidu, S. V., Eom, C. I., Krichene, S. and Reynolds, J. R. "Positron Annihilation and Conductivity Measurements on Poly(pyrrole tosylate) and Poly(pyrrole fluoride)", *Phys. Rev. B.*, submitted for publication.

Basak, S., Nayak, K., Marynick, D. S. and Rajeshwar, K. "Synthesis, Characterization, Theoretical Modeling, and Polymerization of New Fluorophore-Containing Derivatives of Thiophene and Pyrrole", *Chemistry of Materials*, submitted for publication.

Chien, J. C. W., Martinez, M. R., Reynolds, J. R. and Wnek, G. E. "Proton, Carbon-13, Nitrogen-15 NMR of Poly(acetylenes), Poly(pyrroles) and Poly(anilines)", *Macromolecules*, submitted for publication.

Nayak, K. and Marynick, D. S. "The Interplay Between Geometric and Electronic Structure in Polyisothianaphthene, Polyisophthothienophene, Polythieno(3,4-b)pyrazine and Polythieno(3,4-b)quinoxaline", *Macromolecules*, submitted for publication.

Gieselman, M. G. and Reynolds, J. R. "Poly(*p*-phenyleneterephthalamide propane sulfonate): A New Polyelectrolyte for Application to Conducting Molecular Composites", *Macromolecules*, submitted for publication.

Baker, C. K., Qiu, Y. J. and Reynolds, J. R. "Electrochemically Induced Mass Transport in Poly(pyrrole)/Poly(styrene sulfonate) Molecular Composites", *J. Am. Chem. Soc.*, submitted for publication.

Paper Acknowledging DARPA Support for Instrumental Purchase

Marques, H. M., Scooby, D. C., Victor, M. and Brown, K. L. "Optimisation of the Preparation and Purification of Three Monocarboxylic Acid Derivatives of Vitamin B₁₂ and Their Characterisation by ¹³C NMR", *Inorg. Chim. Acta*, **1989**, *162*, 151-155.

New Major Equipment

A Wyatt Technology multiple angle laser light scattering instrument which can be used as a GPC detector and which can give, among other things, absolute molecular weights, weight and number average molecular weights and molecular size information including root mean square radius of gyration and branching ratios, has just been received and is being set up.

An instrument for Raman scattering measurements has been purchased. This system will be used for the study of ion transport during redox switching of polypyrrole.

A computer controlled 4-point probe cryostat system was completed for efficient measurement of conductivities from 4K to 500K.

Personnel Change

Robert Uitz, a postdoctoral associate, has left our group as have graduate students Mark W. Victor (received D.Sc. degree) and Yeung-Haw Ho (received M.S. degree). A new graduate student, Vepa Krishna, has joined our group and several postdoctoral positions will be filled soon.

Meetings Attended and Papers Presented

Reynolds, J. R., Wang, F. and Jolly, C. A. "Electrically Conductive and Electroactive Transition Metal Tetrathiolate Polymers" 198th National Meeting of The American Chemical Society, Miami, FL, September, 1989. *Proc. Am. Chem. Soc. Div. Polym. Mat. Sci. Eng.* **1989**, 61, 340.

Reynolds, J. R., Qiu, Y. J. and Baker, C. K. "Electrochemical Quartz Crystal Microbalance Studies of Polyheterocycles" 198th National Meeting of The American Chemical Society, Miami, FL, September, 1989.

Wnek, G. E., Prezyna, L. A., Lee, J. J., Reynolds, J. R. and Qiu, Y. J. "Interactions of Polycationic Proteins with Electroactive Polypyrrole/Poly(styrene sulfonate) Films" 198th National Meeting of The American Chemical Society, Miami, FL, September, 1989. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1989**, 30, 178.

Visitors to UTA

Dr. M. Kaneko of the Institute of Physical and Chemical Research visited our laboratories for 2 weeks, July 31, 1989 - August 10, 1989, doing collaborative research on conductive polymers. He also presented a seminar entitled: "Polymer Films Incorporating Ru(bpy)₃²⁺ Complex and Their Application to Photochemical and Photoelectrochemical Devices".