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High molecular weight poly(3-alkylthiophenes) have been prepared and cast into films and made into fibers. Molecular composites of polypyrrole with polyelectrolytes polystyrene sulfonate and poly(phenyleneterephthalamide propanesulfonate) have been prepared and characterized by electrochemical microgravimetry. By derivatizing doped polypyrrole membranes with 2,6-di-*p*-tolyl-4-phenylpyrylium reagent, dopant ion fluxes during electrochemical reduction down to parts per billion could be measured. Extensive PRDDO conformational and EH band structure calculations have been done on the aromatic and quinoid forms of poly(isothianaphthene), poly(thieno[3,4-b]naphthalene-9,11-diyl) and related systems. Very high molecular weight, low polydispersity, polymers such as poly(octamethylene sulfide) have been made by a novel polythioetherification using phase transfer catalysis and tetrahydrothiophene also as a catalyst.

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Technical Report

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Description of Progress

High molecular weight poly(3-alkylthiophenes) have been prepared by ferric chloride oxidation of the corresponding 3-alkylthiophene in the presence of air. These polymers are extremely soluble in solvents such as chloroform and can be melted at reasonable temperatures. They show gel permeation chromatography molecular weights (M_n) of up to approximately 500,000 using polystyrene standards. High quality elastic films have been cast and stretch oriented to extension ratios of 1.5. Aligned fibers have been pulled from solution as shown by cross polarized optical microscopy. Electron microscopy shows these fibers to have porous surfaces attributable to solvent evaporation. Conductivities of 5 S cm^{-1} have been measured for doped samples of the films.

A collaborative program has been initiated with URI researchers at Hoechst-Celanese (Summit, NJ) for the melt spinning of poly(3-alkylthiophene). Initial results have indicated that the UTA prepared high molecular weight poly(3-decylthiophene) can be made into fibers. Extensive studies of these fibers is underway.

Molecular composites of polypyrrole (PP) with the polyelectrolytes polystyrene sulfonate (PPS) and poly(phenyleneterephthalamide propanesulfonate) (PPTA-PS) have been characterized via electrochemical microgravimetry. The PP/PSS composite shows repeatedly stable cation specific transport during switching with a frequency/mass response proportional to cation mass.

Dopant ion fluxes during the electrochemical reduction of polypyrrole perchlorate and polythiophene tetrafluoroborate membranes were measured in situ at parts per billion sensitivity, and the polymer doping levels assayed via derivatization with 2,6-di-*p*-tolyl-4-phenylpyrylium reagent. This derivatization strategy is completely general and we are currently applying it to the detection of cations and other types of membranes (e.g. redox polymers) as well.

Extensive PRDDO conformational analyses and Extended Hückel band structure calculations have been performed on the aromatic and quinoid forms of polyisothianapthene, poly(thieno[3,4-b]-naphthalene-9,11-diyl), poly(thieno[3,4-b]pyrazine-5,7-diyl) and poly(thieno[3,4-b]quinoxaline-

9,11-diyl). The relative stabilities of the quinoid and aromatic forms have been estimated via a newly developed thermodynamic cycle approach.

In our program on the synthesis of liquid crystalline polymers containing extended conjugation, we have begun to examine ways to enhance the molecular weights, in particular using phase transfer catalyzed polythioetherification with sodium sulfide. We have discovered that these reactions with α,ω-dibromoalkanes can generate a large amount of cyclic sulfide and thus inhibit polymerization. However, with monomers where cyclization is kinetically and themodynamically prohibited, we have found that added catalysts such as tetrahydrothiophene, permit very high molecular weight polymers to form, M_n approximately 1×10^6, with very narrow polydispersities, approximately 1.3 to 1.4. These properties are unobtainable without the added tetrahydrothiophene.

Poly(organophospha-λ^5-azenes) containing organic groups between phosphazene linkages with polyether side chains have been prepared and are being studied.

Publications

Papers Published

Baker, C. K. and Reynolds, J. R., "A Quartz Microbalance Study of the Electrosynthesis of Polypyrrole", *J. Electroanal. Chem.*, **251**, 307-322 (1988).

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.*, **252**, 441-451 (1988).

Papers in Press

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

Panchalingam, V. and Reynolds, J. R., "New Vinylidene Fluoride Copolymers: Poly(vinyl acetate-co-vinylidene fluoride)", *J. Polym. Sci., Polym. Lett. Ed.*, in press.

Shaffer, T. D. and Sheth, K. A., "Mesomorphic Transition Metal N_2O_2 Chelates", *Mol. Cryst. Liq. Cryst.*, in press.

Shaffer, T. D., "Phase Transfer Catalyzed Polyetherification Through Nitro Displacement", *J. Polym. Sci., Polym. Lett. Ed.*, in press.

Shaffer, T. D., "Phase Transfer Catalyzed Polymerization of α,α'-Dibromoxylene Isomers", *J. Polym. Sci. Polym. Lett. Ed.*, in press.

Ruiz, J. P., Reynolds, J. R., Nayak, K. and Marynick, D. S., "Soluble Ethylmercapto Substituted Polythiophenes", *Macromolecules*, in press.

Jang, G.-W., Tsai, E. W., Abraham, P. and Rajeshwar, K., "Charge Storage and Transport in Thermal Ruthenium Oxide Thin Films", *J. Electroanal. Chem.*, in press.

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.*, in press.

Pomerantz, M. and Victor, M. W., "Synthesis and Characterization of a Series of Alternating Copolymers Containing Organophospha-λ^5-azene Backbone Moieties", *Macromolecules*, in press.

Reynolds, J. R., Jolly, C. A., Krichene, S., Cassoux, P., and Faulmann, C., "Poly(metal tetrathiooxalates): A Structural and Charge Transport Study", *Synth. Met.*, in press.

Papers Submitted for Publication

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. Electroanal Chem.*, submitted.

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

Shaffer, T. D., and Shaffer, M. L., "Configurational Isomerism and Structural Characterization of Mesomorphic Aliphatic-Aromatic Polyazomethine Ethers", *Macromolecules*, submitted.

Martinez, J. R., Chien, J. C. W., and Reynolds, J. R., "Nuclear Magnetic Resonance of Conductive Polypyrrole", *J. Chem. Phys.*, submitted.

Reynolds, J. R., Hsu, S. G., and Arnott, H. J., "The Effect of Electrolyte Controlled Growth Morphology on the Charge Transport Properties of Poly(3-methylthiophene)", *J. Polym. Sci., Polym. Phys.*, submitted.

Shaffer, T. D., and Sheth, K. A., "Mesomorphic Polyazomethine Ethers Containing Dibenzo-18-crown-6 Units", *Makromol. Chem. Rapid Commun.*, submitted.

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

Ho, Y.-H., Basak, S., Tsai, E. W., and Rajeshwar, K., "Optical Probes of Ion Transport in Electrochemical Processes Based on *In Situ* Derivatization: Monitoring of Ion Transport and Assay of Doping Levels in Polypyrrole and Polythiophene Membranes", *J. Chem. Soc., Chem. Commun.*, submitted.

Meetings Attended and Papers Presented

Invited Paper

Shaffer, T. D., "Liquid Crystalline Behavior in Macromolecules: A New Era in Ordered Polymers", 44th Southwest Regional Meeting of the American Chemical Society, Corpus Christi, TX, December, 1988.

Contributed Papers

Basak, S., Tsai, E. W., Phan, L. and Rajeshwar, K., "Electrochemical Modulation of Luminescence From a Conducting Polymer Surface", Paper No. 668, 174th National Meeting of the Electrochemical Society, Chicago, IL, October, 1988.

Tsai, E. W., Basak, S., Ruiz, J., Reynolds, J. R. and Rajeshwar, K., "Electrochemistry of β-Substituted Soluble Polythiophenes", Paper No. 669, 174th National Meeting of the Electrochemical Society, Chicago, IL, October, 1988.

Reynolds, J. R., Hsu, S. G. and Arnott, H. J., "The Effect of Electrolyte and Growth Morphology or the Electrochemical Properties of Poly(3-methylthiophene)", 44th Southwest Regional Meeting of the American Chemical Society, Corpus Christi, TX, November, 1988.

Invited Seminar

Rajeshwar, K. gave an invited seminar entitled "In Situ Optical Probes of Electrochemical Processes", at The University of North Texas, Denton, TX, November, 1988.

Visitor to UTA

Professor Charles E. Hoyle from The University of Southern Mississippi, Department of Polymer Science, visited The UTA Chemistry Department and presented a talk entitled "Photochemically Initiated Polymerization" on November 15, 1988.