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ELECTRONICS AND IONIC TRANSPORT IN POLYMERS(U) TEXAS
UNIV AT ARLINGTON DEPT OF CHEMISTRY M POMERANTZ ET AL.
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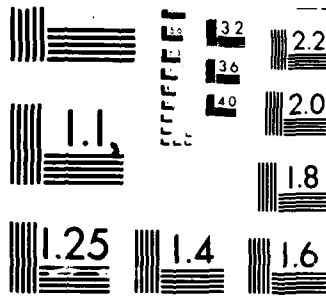
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			19. ABSTRACT (Continue on reverse if necessary and identify by block number) Ion transport studies of the "self-doped" copolymer, poly[pyrrole-co-3-(pyrrol-1-yl)propane sulfonate] have shown that Li^+ mobility is 50% higher than Bu_4N^+ . Polymerization of 3-(pyrrol-1-yl)propane sulfonate with $FeCl_3$ has provided a water soluble polymer. A study of anodic polymerization of pyrrole using a quartz crystal microbalance, set up to be used in solution, shows poor polymerization efficiency at the beginning but improves as the reaction proceeds. The band gap of poly(1,2-dithienylethylene) has been measured as 1.77eV. Ion exchange in self-standing films of polypyrrole has been measured with bathing medium composition, pH and counter-diffusing ion charge as variables and the data show good adherence to the Helfferich and Plesset diffusion model. PRDDO calculations on a number of thiophene systems have provided information about HOMO-LUMO gaps, conformations, spin densities in radical cations and ease of polymerizations. Copolymerization of 1,3-cyclohexadiene and 2-chloroacrylonitrile has been shown to give mainly 1,2-polymerization with smaller amounts of 1,4-polymerization. Thermotropic liquid crystalline behavior has been observed in molecules containing square planar Cu(II) metal chelates of bis(2,5-dihydroxybenzaldehyde) ethylenediimine. Two polymers have been prepared from this system, neither of which appears to show liquid crystalline behavior.			
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Technical Report

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Short Title of Work: "Electronic and Ionic Transport in Polymers"

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Description of Progress

a) Electronically Conducting Polyheterocycles

Ion transport studies have been carried out in the "self-doped" copolymer; poly[pyrrole-co-3-(pyrrol-1-yl)propane sulfonate]. It has been found that Li^+ has *ca.* 50% higher mobility in these films than $(\text{C}_4\text{H}_9)_4\text{N}^+$ which suggests the material is behaving as a cation specific membrane. Mass changes during redox cycling are presently being analyzed to examine this. This material has slower transport rates relative to poly(pyrrole tetrafluoroborate). A paper entitled "Conductive Polymers Containing Bound Dopant Ions" will be presented in the symposium on chemical characterizations of Ion-Containing Polymers in the Analytical Chemistry Division at the upcoming Denver ACS meeting.

In addition we have examined the chemical polymerization of 3-(pyrrol-1-yl)propane sulfonate by FeCl_3 in H_2O . Water soluble fractions of poly[3-(pyrrol-1-yl)propane sulfonate] are obtained which form films when cast onto glass. The electronic and optical properties of this material is under investigation as a potential *water soluble conductive polymer*.

A quartz crystal microbalance has been set up to operate in solution to be used to examine both electropolymerization of heterocycles and mass changes occurring during redox cycling and ion exchange. Studies carried out during the anodic polymerization of pyrrole indicate the electrochemical efficiency of the polymerization is poor in the initial stages and improves as the reaction proceeds. This suggests different mechanisms of polymerization at clean metal surfaces and polypyrrole covered electrodes.

Work has been initiated in the synthesis of polymers having controlled optical gaps by looking at thiophene derivatives. Initial studies have centered on poly(1,2-dithienylethylene). This polymer, which has a conjugated repeat unit of 2 thiophene rings and 1 vinylene unit, has a band gap of 1.77 eV and can be obtained as free standing films. This gap is approximately 200 mV lower than polythiophene homopolymer.

Studies on the reaction of alcohols with 1,3-propanesultone are being carried out as a means of preparing thiophene and pyrrole monomers containing pendant sulfonate anions. This

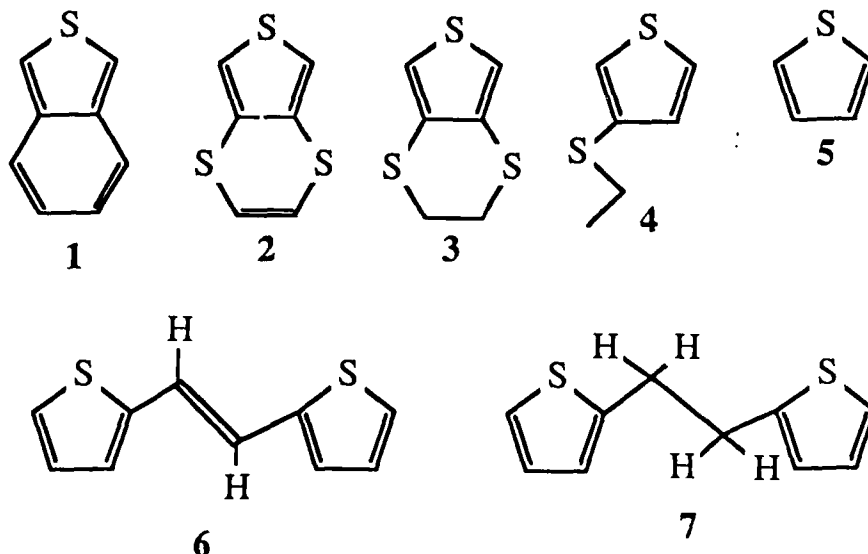
will be used to prepare other "self doped" conducting polymers. A sulfonate containing thiophene monomer has been prepared and is being polymerized and studied.

Ion exchange in self-standing films of polypyrrole has been studied with bathing medium composition, pH, and counter-diffusing ion charge as variables. The data show good adherence to the diffusion model of Helfferich and Plesset.¹ For these studies, the out-diffusing tosylate anion was used as a chromophoric diffusion probe. Microgravimetry and ion-reflective potentiometric detection of chloride were additionally employed.

AC impedance studies continue with respect to the role of proton diffusion (double-injection mechanism) in the redox switching of polypyrrole.

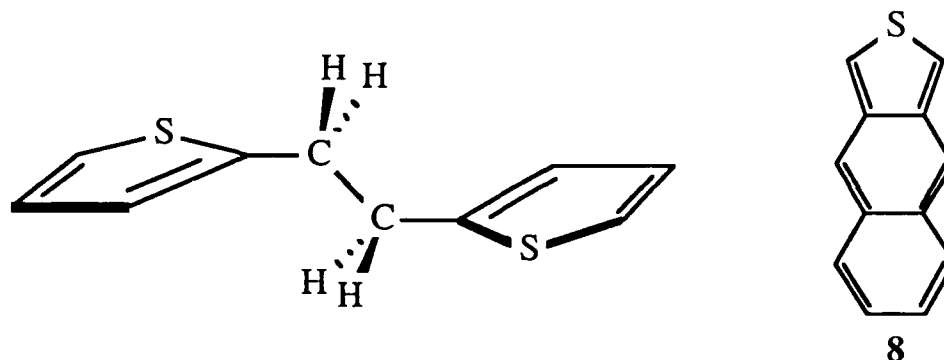
In addition a new thin-layer spectroelectrochemical technique has been developed which permits sensitive detection of the hitherto elusive interfacial pH parameter. This technique will be used to examine the validity of the double-injection mechanism for the redox switching of conductive polymers such as polypyrrole and polyanilene.

PRDDO and ab initio calculations have been performed on the neutral species and radical cations of the molecules 1-7.



Near complete geometry optimization were done on all molecules. 1, 5, 6, and 7 show large spin populations on the α carbons, suggesting the possibility of electrochemical polymerization

[obviously correct for 5]. 2, 3, and 4 do not show spin density on the α carbons, and indeed 4 cannot be polymerized electrochemically. 2 and 3 are non-planar, with out-of-plane angles of $\sim 21^\circ$. The calculated HOMO-LUMO gaps vary in the order $7 > 5 > 3 > 4 > 6 > 1$. The most stable conformation of 2 is quite interesting, with the thiophene rings co-planar and nearly perpendicular to the plane of the "back-bone". Preliminary calculations have been performed on 8,



which show a much lower HOMO-LUMO gap. Geometry optimizations are now in progress.

References

- (1) Helfferich, F.; Plesset, M.S. *J. Chem. Phys.* **1958**, *28*, 418.

b) Polymer Solid Electrolytes

Work here has focused mainly on synthetic strategies directed toward preparing $(RO)_2P-C_6H_4-P(OR)_2$ where R is $-(CH_2)_2OCH_3$. This has involved preparing $Cl_2P-C_6H_4-PCl_2$ and $(RO)_2PCl$. We have also begun thermal analysis studies of the monomers to compare with the polymers we have prepared and which we will prepare.

c) High Permittivity Dielectric Polymers

An in depth structural analysis has been carried out on the alternating copolymer of 1,3-cyclohexadiene and 2-chloroacrylonitrile which indicates the copolymer contains both 1,2 and 1,4 linkages, with a higher content of the 1,2 type.

Work has begun to prepare polymers with a polystyrene back-bone and phospho- λ^5 -azene pendant side chains. Synthetic work has included putting nitro and then amino groups on the polystyrene.

d) Novel Liquid Crystalline Conductors

Thermotropic liquid crystalline behavior has been observed in molecules containing square planar Cu(II) metal chelates of bis(2,5-dihydroxybenzaldehyde) ethylenediimine (BDHED). The chelates are prepared from BDHED and Cu(OAc)₂ in methanolic solution. The resulting bisphenol serves as a precursor for model compounds and a monomer for polymerization. Etherification of BDHED-Cu^{II} with bromoalkanes (heptyl, octyl, nonyl) has led to model compounds that exhibit thermal behavior suggestive of liquid crystallinity. Evidence from optical polarization microscopy implies the existence of both nematic and smectic character to the mesophases present. Complete characterization of these models has proven difficult because of the decomposition of the materials. Only two polymers have been prepared from this bisphenol. We have found that the bisphenol complex is not stable in the presence of excess base as is required for phase transfer catalyzed polyetherification. After some initial experiments, the polymerization has been shown to be best performed under an inert atmosphere with stoichiometric amounts of KOH with DMF as the solvent. Polymers have been prepared with 1,10-dibromodecane and 1,12-dibromododecane. Neither of these polymers, however, have exhibited evidence suggestive of liquid crystalline behavior.

Personnel Changes:

Two new postdoctoral research associates, Raul Cardona from The University of Texas at Austin and Fayez El Khatib from Paul Sabatier University, Toulouse France (for 5 months) have begun working on this project. A new postdoctoral research associate in theoretical chemistry has been hired and will begin on July 1, 1987. A part-time undergraduate student has also been recently hired.

Major Equipment Ordered:

- 1) Bruker MSL-300 solids-liquids multinuclear NMR spectrometer with a 7.0 T superconducting magnet.
- 2) Bruker ER-300 Electron Spin Resonance Spectrometer.
- 3) Cary 2300 UV-VIS-NIR spectrometer.
- 4) Two Princeton Applied Research Model 273 Potentiostats.

- 5) Vacuum Atmospheres dry box.
- 6) Sigmex 6234 color graphics terminal with ink-jet printer, and graphics software.
- 7) Two Telery VT220 terminals with line drivers.
- 8) Several personal computers.

Publications:**Papers in press:**

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

2. "Electrochemical Copolymerization of Pyrrole with N-Substituted Pyrroles, Effect of Composition on Electrical Conductivity", Reynolds, J.R.; Poropatic, P.A.; Toyooka, R.L. *Macromolecules*, in press.

Papers submitted:

"Electrochemically-Triggered pH Modulation at the Ruthenium Oxide/Electrolyte Interference: A Spectroelectrochemical Probe for the Double-Injection Mechanism" G-W. Jang, E.W. Tsai, and K. Rajeshwar, submitted to *J. Am. Chem. Soc.*

Meetings, Oral Presentations and Visitors

M. Pomerantz visited with Prof. K. Wagener (DARPA-URI principal investigator) at The University of Florida. There were fruitful discussions on monomer and polymer chemistry.

J. Reynolds visited with Prof. A. MacDiarmid (DARPA-URI principal investigator) at The University of Pennsylvania. A research seminar was presented and avenues for possible collaboration were explored.

J. Reynolds visited with Prof. A. Epstein (co-principal investigator with Prof. MacDiarmid on DARPA-URI contract) at Ohio State University. A research seminar was presented and here also possible areas of collaboration were explored.

J. Reynolds visited Pennwalt Inc. (King of Prussia, PA) to discuss suspension polymerization techniques and handling of vinylidene fluoride. Equipment set up used at Pennwalt

was studied and will be used in URI funded research at UTA. A research talk entitled "Electron and Ion Transport in Polyheterocycles" was presented.

A visit was made by J. Reynolds to Westinghouse Research Laboratory to discuss potential collaborative research in conductive polymers and high permittivity polymers. A research talk entitled "Electron and Ion Transport in Polyheterocycles" was presented.

Visitors to the UTA Chemistry Department included Dr. Rudolph E. Cais, AT&T Bell Laboratories who presented a talk entitled "Synthesis of Fluoropolymers with Controlled Regiosequence Microstructure" on February 6 and Prof. Robert E. Neilson from Texas Christian University who presented a talk entitled "New Main Group Monomers and Polymers" on January 30.

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