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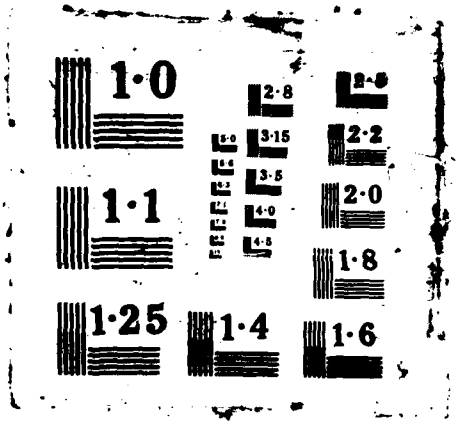
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# POLY (PYRROLIUM ANION) STUDIES: ELECTROCHEMICAL SYNTHESIS AND PHYSICAL BEHAVIOR

by

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NAVAL AIR DEVELOPMENT CENTER
Warminster, Pennsylvania 18974

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Conductive polymers exhibit many unique physical property combinations that lead to a variety of applications which include coatings, sensors, and thin film devices. Conductive polypyrrole has shown the most promise with respect to environmental stability and mechanical integrity. Various poly (pyrrolium anion) materials have been synthesized electrochemically using novel dopant counterions. The counterions (substituted benzenesulfonates) were prepared as tetraethylammonium salts from the acids and ranged in size from small (8 angstroms) to large (25 angstroms) with varying degrees of symmetry. Depending on the dopant anion used in the synthesis, the electrical conductivity, tensile strength and tensile modulus varied greatly. X-ray diffraction studies have shown varying peak breadths indicating a difference in molecular order among the polymers. Interrelationships between molecular structure, electrical conductivity, and mechanical behavior have been addressed. Keywords: polypyrroles, pyrroles

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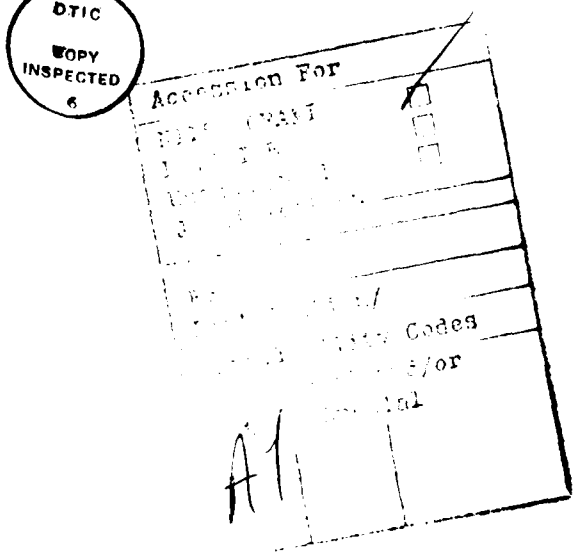

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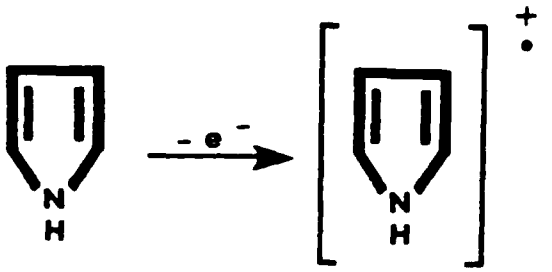
## INTRODUCTION

Oxidized polypyrrole has exhibited exceptionally good environmental stability compared to other electrically conductive polymers. Minimal conductivity changes occur upon exposure to ambient environments [1]. Low density, controllable conductivity, and excellent chemical resistance make this conductive polymer an interesting material choice for photoelectrode protection, chemical sensors and conductive coatings. Changes in the composition and morphology have been found to vary with the synthesis conditions and type of counterion [2]. A more extensive understanding of the molecular structure may allow finer control of the physical behavior.

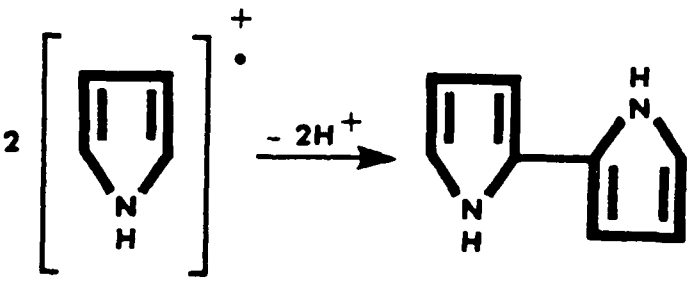
The electrochemical synthesis of conductive polypyrrole was first demonstrated by Dall'Olio in 1968 [3]. In this experiment thin films approximately 1μm thick were prepared by the electrochemical oxidation of pyrrole and were found to have a room temperature conductivity of 8 $(ohm\text{-}cm)^{-1}$. A unique feature of this particular conductive polymer was its environmental stability in the oxidized (conductive) state. This was the first conductive polymer to exhibit minimal loss in electrical conductivity upon exposure to the atmosphere. One of the causes for the stability is the sharing of the positive charge of the backbone by the heteroatom leaving all atoms in the polymer with complete octets. This decreases the reactivity of the molecule to oxygen or moisture.

In 1979 Diaz and co-workers prepared free-standing polypyrrole films approximately 50μm thick [4]. These films were reported to have a room temperature conductivity of 100 $(ohm\text{-}cm)^{-1}$. On the basis of electrochemical and spectroscopic data the pyrrole polymerization is believed to involve oxidative coupling at the alpha-carbons with simultaneous oxidation resulting in the incorporation of a counterion from the electrolyte.

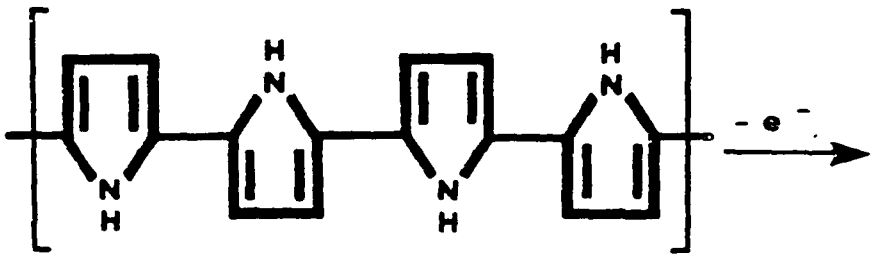
The mechanism of polypyrrole polymerization has been suggested by Street et al., and begins with the generation of radical cations at the anode [5].

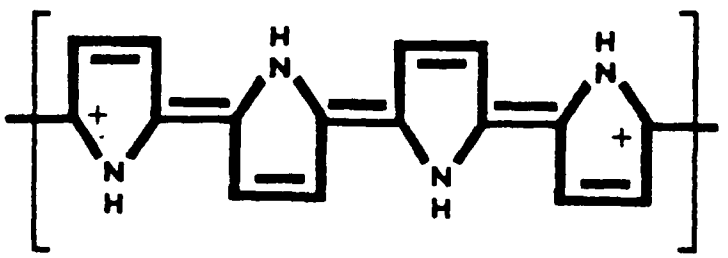


Propagation may then proceed by reaction of two radical cations, pairing the spins and eliminating two protons to produce the neutral dimer.



The dimer and higher oligomers can also be oxidized to form radical cations. Chain propagation continues by reaction of the oligomer radical cation primarily with the radical cation of the monomer, which is present in high concentration in the region of the anode. As the chain grows, the polypyrrole oligomer becomes insoluble and eventually precipitates out on the electrode, where the chain can continue to grow until the oligomer radical cation becomes too unreactive or until it is sterically prevented from reacting. Additional oxidation of the polypyrrole chain leads to the formation of cationic sites with incorporation of the counterion from the electrolyte to maintain charge neutrality. Conductive (oxidized) polypyrrole has the following chemical structure.



## EXPERIMENTAL

An electrolytic cell was used in the synthesis of the polypyrrole/anion films (See Fig. 1). This cell consisted of a 2 liter capacity battery jar with a vitreous carbon anode and a platinum mesh cathode that produced a film of approximately 75 $cm^2$. The carbon anode size was 10.2 cm x 10.2 cm. The cathode consisted of 2 pieces of platinum mesh (each 5.1 cm x 10.2 cm). The platinum was supported by means of a 10.2 cm x 10.2 cm glass plate. A spacing of 3.5 cm between the anode and cathode was used. An $Ag/Ag^+$ (Ag in 0.1 M $AgNO_3$ and acetonitrile) reference electrode was used to determine the potential.

All of the syntheses were performed under constant potential. The current density was monitored throughout each syntheses (See Table I). In addition the syntheses were performed with the battery jar covered to minimize evaporation and at 23°C and approximately 50% relative humidity.

The polypyrrole films were prepared according to the method developed by Wynne and Street for the synthesis of Polypyrrole/Tosylate films without special precautions to exclude air [6]. The cell solution consisted of pyrrole (0.3M), the dopant species (0.15M) and 1050 ml of acetonitrile. The pyrrole was passed through activated alumina prior to use. Chromatography grade acetonitrile was used without further purification. A small amount of demineralized water (0.5%) was added to the solution to enhance the cathode reaction (reduction of protons.) During the syntheses, the amount of solution covered approximately 10.2 cm x 7.2 cm of the carbon anode. Film thickness ranged from 0.127 mm to 0.254 mm.

Benzene sulfonates and substituted benzene sulfonates were synthesized for use as the dopant counterions. All were synthesized with the exception of the tetraethylammonium-p-toluene sulfonate which was obtained from Alfa Products. Each of the electrolyte salts was prepared in the following manner:

The respective sulfonic acid and base (tetraethylammonium hydroxide, 40%) were mixed on a 1:1 molar basis. The reaction mixture was then stirred for 1 hour at ambient temperature using a magnetic stirrer. Aliquots were then diluted 50/50 with methanol and stripped under vacuum using a Buchi roto-vap. When completed, the remaining salt solution was again diluted with methanol, heated and then filtered. The filtrate was then evaporated in an open beaker while being stirred. The remaining salt was then refrigerated overnight. The salt was then dried in a vacuum oven overnight. Proton Nuclear Magnetic Resonance was then run on the resultant products.

All dopant preparations were routine with the exception of the dodecyl salt. Upon mixing of the dodecylbenzenesulfonic acid and base, the resultant product was a viscous fluid. This problem was alleviated by adding methanol to the mixture before stirring.

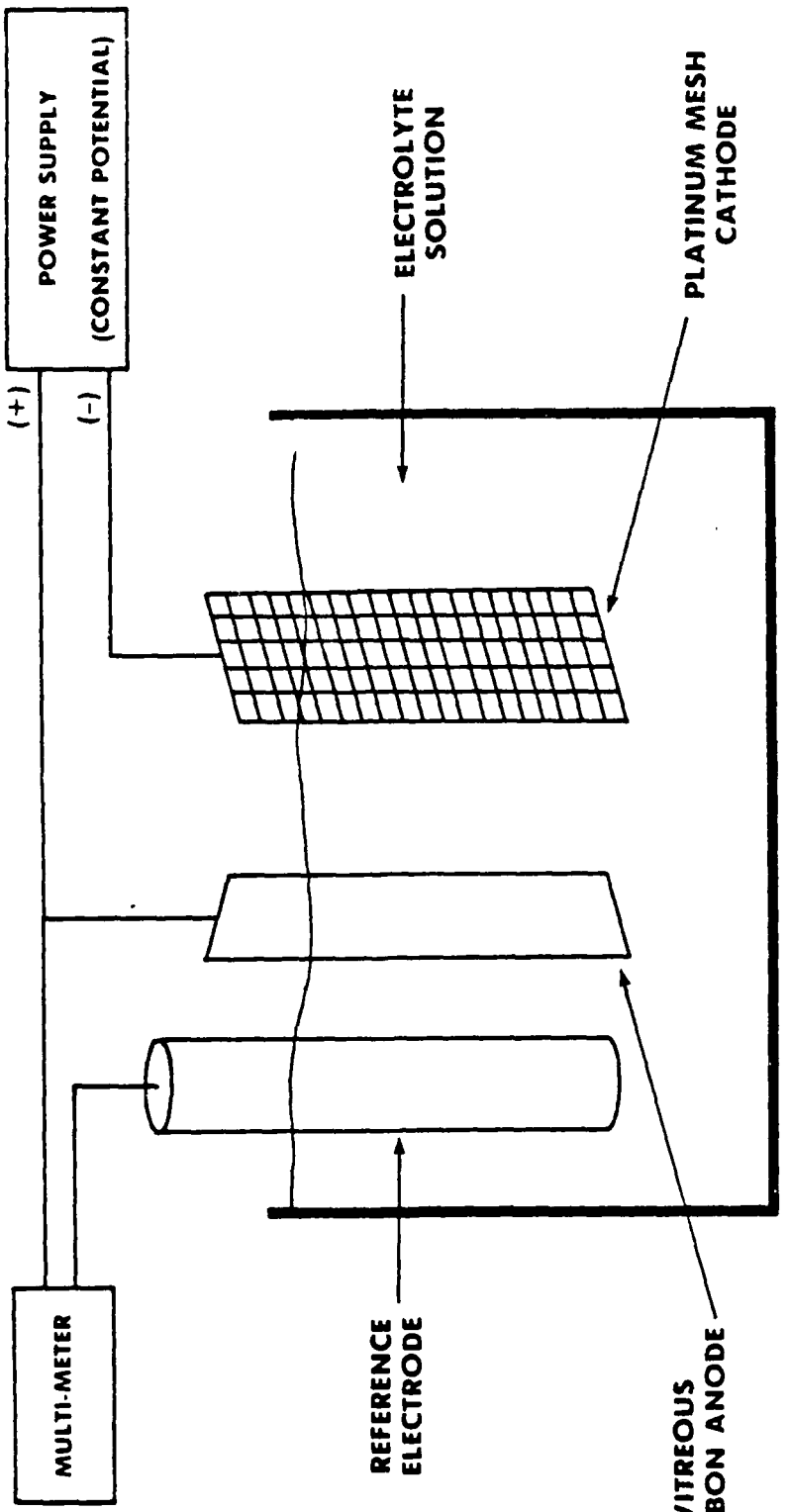



Figure 1. Electrolytic Cell for Poly(Pyrrollum Anion) Synthesis.

TABLE I. SYNTHESIS CONDITIONS

| MATERIAL | APPLIED VOLTAGE (V) | $Ag/Ag^+$ REFERENCE (V) | CURRENT DENSITY ($mA/cm^2$) |
|---|---|---|---|
| $PP^+/BS^-$ | 3.0 | 0.55 | 0.76 |
| $PP^+/OTs^-$ | 3.0 | 0.54 | 0.54 |
| $PP^+/2,5\text{-}DMBS^-$ | 3.0 | 0.54 | 0.58 |
| $PP^+/EBS^-$ | 3.0 | 0.55 | 0.74 |
| $PP^+DBS^-$ | 3.0 | 0.55 | 0.75 |
| $PP^+BPS^-$ | 3.0 | 0.55 | 0.65 |

1

The chemicals and materials used for the syntheses were the following:

| CHEMICAL | SUPPLIER |
|---|---|
| Benzene Sulfonic Acid | Kodak Laboratory Chemicals |
| 2,5 Dimethylbenzene Sulfonic Acid | Kodak Laboratory Chemicals |
| Ethylbenzene Sulfonic Acid | Alfa Chemicals |
| Dodecylbenzene Sulfonic Acid | Alfa Chemicals |
| Biphenylbenzene Sulfonic | Alfa Chemicals |
| Aluminum Oxide | Camag |
| Tetraethylammonium Hydroxide | Alfa |
| Acetonitrile, HPLC Grade | Fisher Scientific<br>Burdick & Jackson |
| Pyrrole | Alfa Chemicals<br>Aldrich Chemicals |
| Tetraethylammonium-p-Toluene Sulfonate | Alfa Chemicals |
| Carbon Electrode | Atomeric Chemetals |

Electrical conductivity was determined by a four point probe technique as described by Wieder [7]. The mechanical behavior was assessed by determining the ultimate tensile strength, strain to failure, and tensile modulus using an Instron Test Machine. A strain rate of 0.05 inch/min. was used. Samples were cut to 0.5 inch width strips approximately 3.5 inches in length. Testing was done under ambient conditions (23°C and 50% RH). Scanning electron microscopy (SEM was performed with an Amray-1000 instrument.

X-ray diffraction studies were performed using a Rigaku D/MAX-11TB system with a Theta/Theta Goniometer. The power level was 50 kV and 20 mA. The geometry of the X-ray set-up is shown in Fig. 2. The sample was kept stationary while scattering angles from 0° to 40° were scanned in the Reflection Mode [See Fig. 3]. The scanning rate was 5°/min and the data was summed over 10 scans. This process provided greater intensity than is normally seen for a single scan which is needed due to the weak scattering of the thin film polymers.

TP Fig. 2

- RIGAKU D/MAX-11TB (2.0 kW)
- THETA/THETA GONIOMETER (STATIONARY SAMPLE)
- 50 kV; 20 mA




Figure 2. Geometry of X-Ray Diffraction Set-Up

TP Fig 3

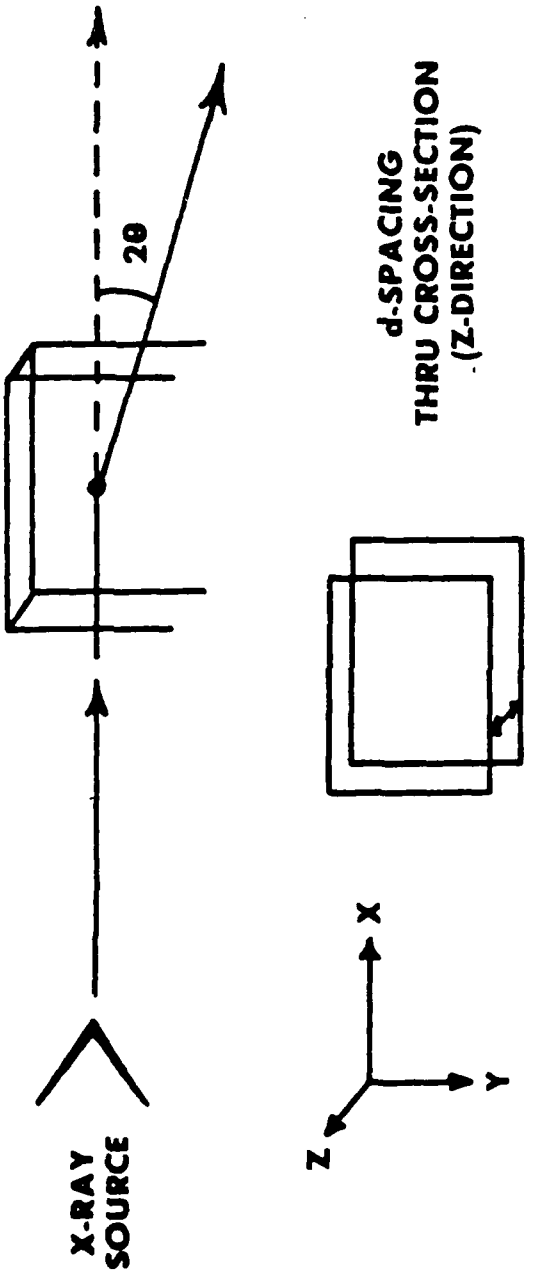



Figure 3. Description of X-Ray Diffraction Reflection Mode

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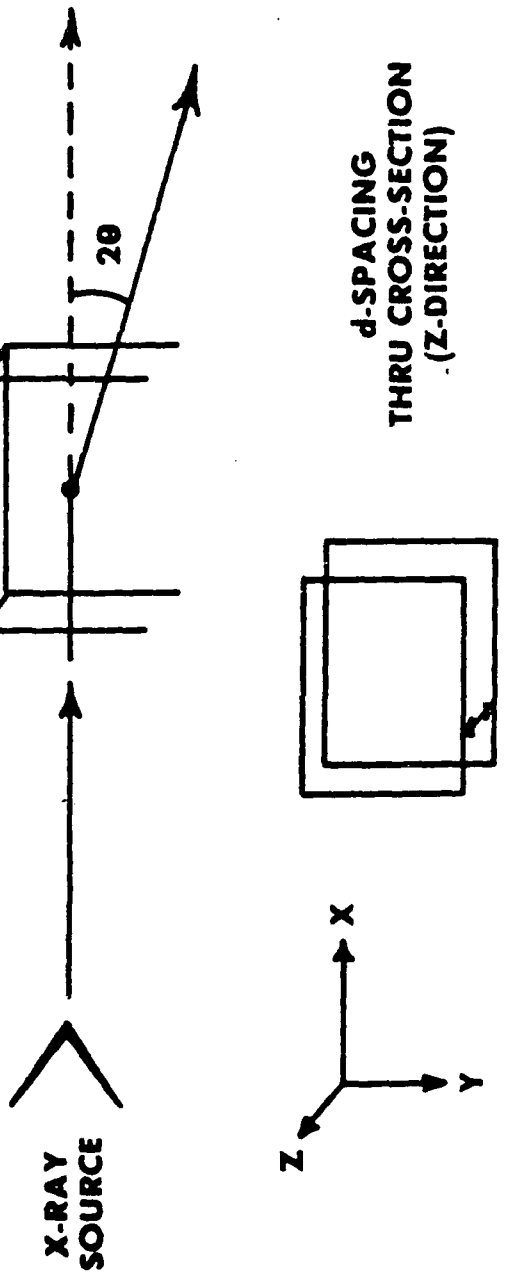
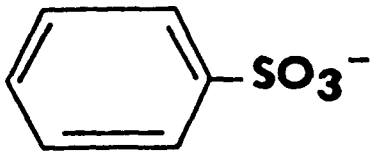
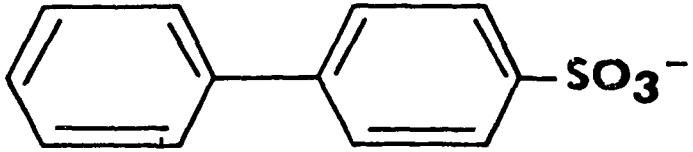


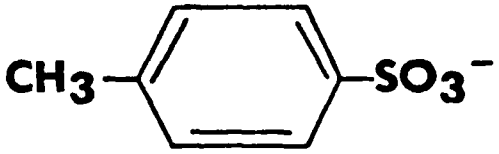

Figure 3. Description of X-Ray Diffraction Reflection Mode



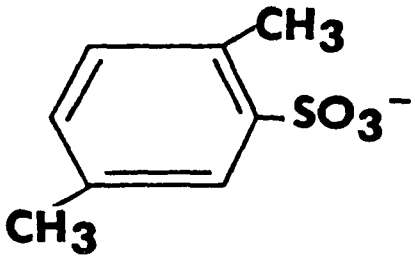

BENZENE SULFONATE (BS)



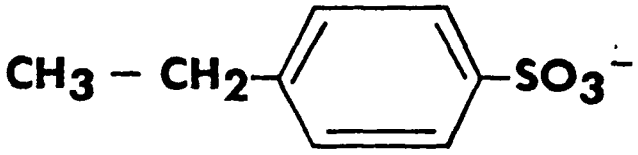

BIPHENYL SULFONATE (BPS)



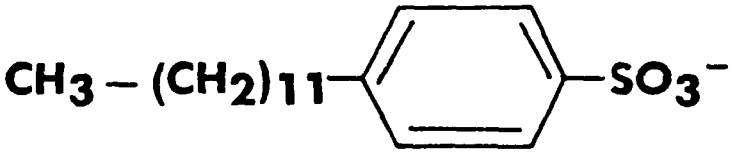

P-TOLUENE SULFONATE (OTs)




2,5-DIMETHYLBENZENE
SULFONATE (2,5-DMBS)




ETHYLBENZENE SULFONATE (EBS)




DODECYLBENZENE SULFONATE (DBS)

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Figure 4. Chemical Structures of Dopant Anions

TABLE II. ELECTRICAL CONDUCTIVITY

| MATERIAL | CONDUCTIVITY ($OHM^{-1}$ $CM^{-1}$) |
|---|---|
| $PP^+/EBS^-$ | 2 |
| $PP^+/BPS^-$ | 2 |
| $PP^+/DBS^-$ | 10 |
| $PP^+/2,5\ DMBS^-$ | 15 |
| $PP^+/BS^-$ | 100 |
| $PP^+/OTs^-$ | 100 |

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TABLE III. MECHANICAL BEHAVIOR

| MATERIAL | $\sigma_{UTS}$ (PSI) | $E_T$ (KSI) | $\epsilon_F$ |
|---|---|---|---|
| $PP^+/OTs^-$ | 10589 | 208 | 0.27 |
| $PP^+/BS^-$ | 7292 | 160 | 0.37 |
| $PP^+/DBS^-$ | 6072 | 124 | 0.09 |
| $PP^+$/2,S-DMBS$^-$ | 4903 | 359 | 0.01 |
| $PP^+/OTs^-$ (DRY) | 10227 | 235 | 0.13 |
| $PP^+/ClO_4^-$ | 9220 | 160 | 0.22 |

Figure 5. Scanning Electron Microscopy Photographs of Polypyrrole/Tosylate Fracture Surfaces Showing the As-Grown Solution Side Morphology. [Top-500X; Middle-1000X; Bottom-2000X]

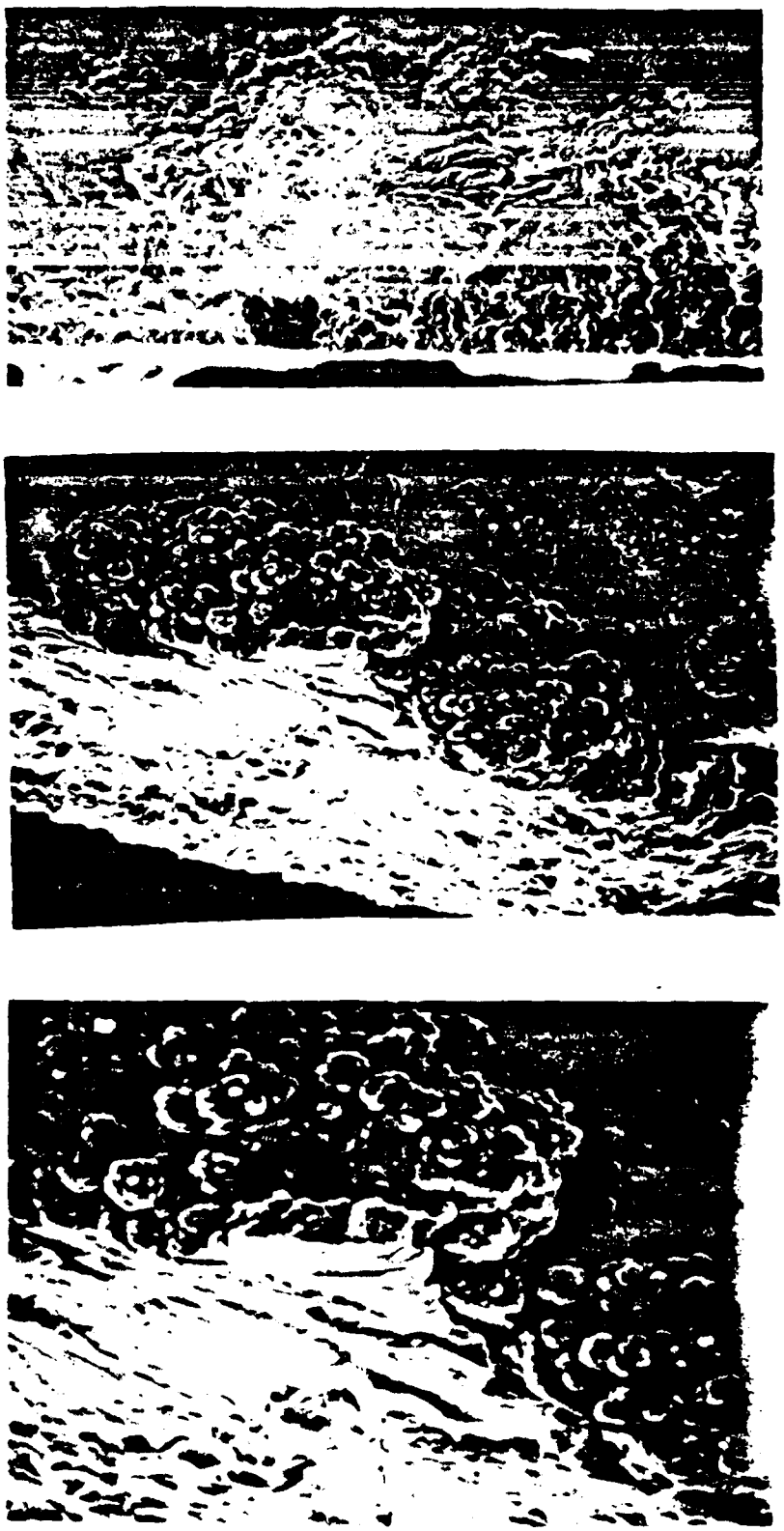

Figure 6. Scanning Electron Microscopy Photographs of Polypyrrole/Ethyl Benzenesulfonate Fracture Surfaces Showing the As-Grown Solution Side Morphology. [Top-500X; Middle-1000X; Bottom-2000X].

X-ray diffraction studies were done to investigate the extent of order within the conductive polymer structures. D-spacings from the reflection mode peaks are given in Table IV. The low-angle peaks correspond to the anions while the wide-angle peaks correspond to the polypyrrole chains. The breadth of the wide-angle peaks is being studied as an indication of the extent of molecular order. The integral breadth is defined as the following [12]:

$$\beta_i = \frac{\int I \, d2\theta}{I_{MAX}}$$

Fig. 7 shows the diffraction peaks for each of the materials (reflection mode). Tosylate, benzene sulfonate, and dodecylbenzene sulfonate materials exhibit structured peaks that are much less broad than the other anions. These materials exhibited the best physical properties which may be due to the increased molecular order or a more well-defined structure. Additional work is being done to understand this technique and how it may be used to investigate the structure of glassy polymeric solids.

TABLE IV. POLY (PYRROLYIUM ANION) X-RAY DATA

| ANION | 2θ | d (Å) | 2θ | d (Å) |
|---|---|---|---|---|
| OTs | 5.3 (S) | 16.6 | 25.3 (S) | 3.5 |
| DBS | 3.6 (SS) | 24.3 | 22.9 (B,S) | 3.9 |
| BS | 5.6 (B,W) | 15.4 | 25.5 (S) | 3.5 |
| BPS | 4.7 (B,W) | 18.5 | 22.7 (B,W) | 3.9 |
| 2,5-DMBS | --- | --- | 23.3 (B,W) | 3.8 |
| EBS | --- | --- | 21.8 (B,W) | 4.0 |

(REFLECTION MODE) W – WEAK, B – BROAD, S – STRONG, SS – STRONG AND SHARP

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TP Fig. 7

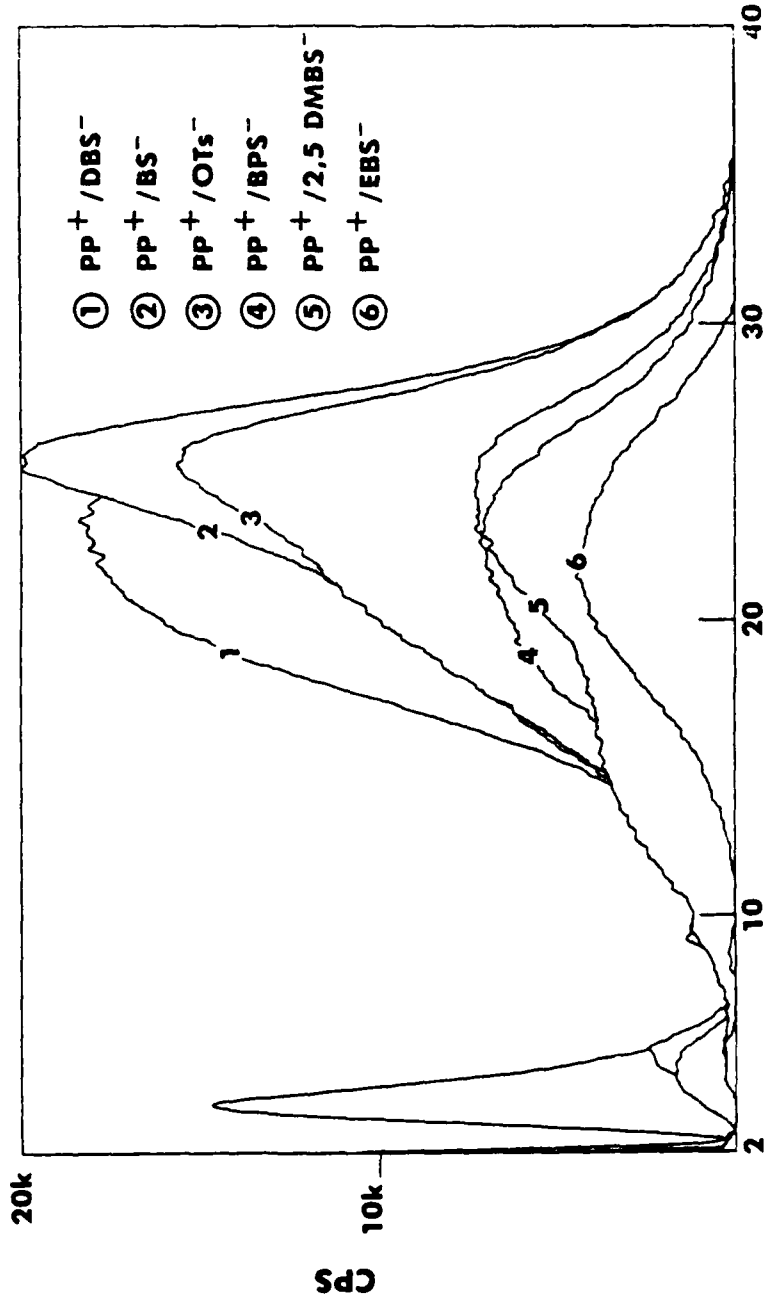


Figure 7. Reflection Mode Diffraction Peaks for Various Poly (Pyrrolium Anion) Materials

## FUTURE STUDIES

Clearly, the physical properties of Poly (pyrrolium anion) materials are strongly influenced by the type of anion used in the synthesis. Future work will consist of investigating additional dopant anions that have not been previously studied. These anions will include sulfonated ferrocenes prepared as sodium and/or ammonium salts. In these materials the cyclopentadienyl rings are freely rotating which may allow for an easier fit into the polymer structure. X-ray diffraction studies will be continued in the transmission mode as well as in the reflection mode. Interrelationships between molecular structure, electrical conductivity, and mechanical behavior will be investigated. The study of diffraction peak broadening for the determination of the extent of molecular order will be continued. The validity of this approach will be examined by investigating the broadening effects due to residual strain and orientation.

The surface properties will also be investigated including the surface tension and morphology. The surface tension shall be determined with a contact angle goniometer and the surface morphology using scanning electron microscopy (SEM).

ACKNOWLEDGEMENTS

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| United Aircraft Corp.<br>United Aircraft Research Labs.<br>E. Hartford, CT 06108 | 1 |
| Army Materials Technology Lab.<br>Polymers & Chemistry Div.<br>Watertown, MA 02172<br>Attn: G.L. Hagnauer<br>R.E. Sacher<br>C.R. Desper | 3 |
| Hercules, Inc.<br>Magna, UT 84044<br>Attn: R.E. Hoffman | 2 |
| University of MA<br>Amherst, MA 01003<br>Attn: Prof. J.C.W. Chien | 1 |

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