

# Influence of Dopant Ion and Synthesis Variables on Mechanical Properties of Polypyrrole Films

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## Synopsis

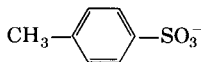
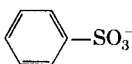
Oxidized, conductive poly(pyrrolylium anion) films [poly(pyrrolylium) =  $PP^+$  where there exists about one cation per three pyrrole rings] have been prepared electrochemically in an effort to study the effect of counteranion structure and preparation conditions on the composition, order (crystallinity), and mechanical properties of the films. The counteranion principally employed was *p*-toluene-sulfonate ( $OTs^-$ ), although benzenesulfonate ( $BZs^-$ ), *p*-ethylbenzenesulfonate ( $EBs^-$ ), and *p*-dodecylbenzenesulfonate ( $DBs^-$ ) were incorporated in several polypyrrole films. It was found that the amount of  $OTs^-$  incorporated increased with increasing potential during synthesis, suggesting a parallel increase in the extent of oxidation of the polymer. Mechanical testing of the same films demonstrated that the ultimate tensile strength decreased as the electrode potential and current density during synthesis increased. X-ray diffraction indicated that the degree of order (reflected by the widths of the diffraction lines), albeit quite small, is dependent upon the anion species and synthesis conditions. Interestingly, samples with the highest degree of order exhibit the highest electrical conductivities.

## INTRODUCTION

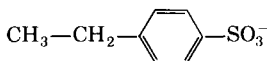
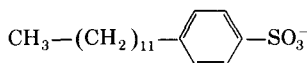
The low oxidation potential of polypyrrole,<sup>1</sup> undoubtedly the result of the  $\pi$ -excessive character of pyrrole and its homologs,<sup>2</sup> allows for the facile formation of conducting (oxidized) derivatives that exhibit quite respectable environmental stability.<sup>1,3</sup> Although such stability is generally considered to be a prerequisite for technological applications, acceptable processability and mechanical properties may be equally important. Only a few studies have focused on the measurement of mechanical properties of electrochemically grown, conductive poly(pyrrolylium anion) films, such as tensile strength,<sup>4-7</sup> and these qualitatively indicate that such properties are sensitive to film growth conditions, electrolyte composition, and the nature of the counteranion. For example, films of  $PP^+ OTs^-$  exhibited tensile strengths about 30% greater than films of  $PP^+ ClO_4^-$ . We were intrigued with the apparent ability of "organic" counterions to impart enhanced mechanical integrity and began a study of the effect of the nature of the anion species (see Chart I) on mechanical properties. The dependence of the latter on polymer film growth conditions, namely applied potential and current density, was also studied. We present data that suggest that the ultimate tensile strengths depend on the degree of order of the poly(pyrrolylium anion) films, which in turn is

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*p*-Toluenesulfonate (OTs)

Benzenesulfonate (BZs)

*p*-Ethylbenzenesulfonate (EBs)*p*-Dodecylbenzenesulfonate (DBs)

Perchlorate

Chart I

sensitive to the anion species and, more significantly, to the electrochemical film growth variables.

## EXPERIMENTAL

Pyrrole (Aldrich) was passed through a column containing 300-mesh activated alumina prior to use. Spectral grade acetonitrile was used without further purification. Tetraethylammonium *p*-toluenesulfonate (Alfa) was used as received. The benzenesulfonate and other *p*-substituted benzenesulfonates were prepared by the reaction of the corresponding acids (Aldrich or Alfa) with an equimolar amount of aqueous  $(\text{C}_2\text{H}_5)_4\text{NOH}$ . The resulting salts were dried in an evacuated desiccator over  $\text{P}_2\text{O}_5$ . Structures and purities ( $\geq 97\%$ ) were determined by 60 MHz proton NMR spectroscopy.

The poly(pyrrolylium anion) films were prepared according to the method developed by Wynne and Street<sup>5</sup> in an ambient atmosphere. The electrolytic cell consisted of a 200 mL beaker with a vitreous carbon anode (Atomergic Chemetals, 18 cm<sup>2</sup>) and a Pt mesh cathode. In a few cases, a larger cell (2 L battery jar and 75 cm<sup>2</sup> carbon anode) was employed to study the influence of current density on the properties of the resulting films. The cell solution consisted of pyrrole (0.3 mol/L) and the tetraethylammonium salt (0.15 mol/L) in acetonitrile. A small amount of water was added (0.5%) to facilitate the cathode reaction, which is the reduction of protons. Applied potentials (VIZ 703 power supply) as well as actual working electrode potentials (versus the Ag/Ag<sup>+</sup> reference; Ag<sup>0</sup> in 0.1M AgNO<sub>3</sub>/CH<sub>3</sub>CN) were measured. Current

densities were determined simply from the steady-state current and the area of the anode.

Poly(pyrrylium anion) films were extracted with  $\text{CH}_3\text{CN}$  in a Soxhlet apparatus for a minimum of 4 h and dried under a dynamic vacuum (about  $10^{-3}$  torr) for 8 h. Elemental analyses were performed by Schwarzkopf Laboratories, Woodside, N.Y. Flotation densities were determined using a  $\text{CCl}_4$ /toluene density-gradient column with a calibrated range of 1.35–1.38  $\text{g}/\text{cm}^3$ . An Instron universal testing machine was used to determine tensile strengths, strains to failure, and moduli of the films; data are reported as averages of 14 samples. Air grips were employed to prevent slippage. A strain rate of 1.27 mm/min was used in all cases. The testing was performed in air at room temperature. X-ray diffraction studies were performed at the Army Materials Technology Laboratory, Watertown, Mass., on the polymer films in the reflection (incident beam nearly parallel [about  $7^\circ$ ] to the film plane) and transmission (beam perpendicular to film plane) modes. The equipment consisted of a TEC 210 proportional counter, Picker x-ray diffractometer, Ortec power supply, and a Lecroy 3500 minicomputer. Integral breadths of the diffraction lines were obtained using the minicomputer.

Electrical conductivities (four point probe) were measured using a Magnetron Conductivity Tester. The probe spacings (1.575 mm) were significantly greater than typical polymer film thicknesses (0.1–0.2 mm), allowing the use of the equation

$$\frac{1}{\sigma} = \frac{V\pi t}{i \ln 2}$$

for an essentially two-dimensional sample,<sup>8</sup> where  $\sigma$  is the conductivity ( $\text{S}/\text{cm}$ ),  $t$  is the thickness (in cm), and  $V/i$  is the sample resistance (in ohms).

## RESULTS AND DISCUSSION

Elemental analytical data for four  $\text{PP}^+ \text{OTs}^-$  films prepared at different applied potentials and current densities are given in Table I. Two samples (Table I, 5-OTs and 6-OTs) were prepared using electrodes of larger area and hence were grown at lower current densities than those of companion samples 1 and 4. There are two points worth noting. First, all films contain a significant amount of water. This is not surprising since water was purposely added to the electrolyte, the syntheses were done in laboratory air, and the films were not rigorously dried. The second point concerns the increase of the S/N ratio (reflecting the  $\text{OTs}^-$ /pyrrylium segment ratio; see Table I) with increasing applied potential, which suggests that the polymer becomes progressively more oxidized as the potential increases. Films grown at an applied potential of 3V in our hands have an S/N value of 0.37 as compared with an S/N near 0.43 prepared elsewhere<sup>5</sup> at the same potential. The reason for this difference is not clear, although our films were washed with acetonitrile for a much longer period, which may have removed residual tetraethylammonium tosylate. The fact that residual electrolyte is not occluded in the films is demonstrated with two samples prepared using  $\text{Ag}^+ \text{OTs}^-$  that showed negligible Ag by elemental analysis.

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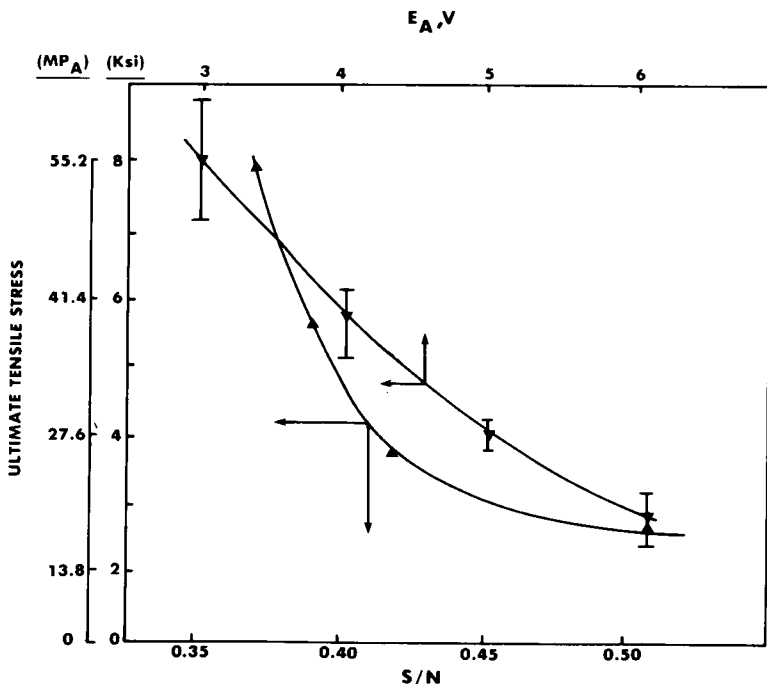


Fig. 1. Ultimate tensile strength versus sulfur/nitrogen ratio (S/N) and applied potential during synthesis ( $E_A$ ) for a series of poly(pyrrrolylium OTs<sup>-</sup>) films.

The dependence of ultimate tensile strength  $\sigma_T$  on the applied potential and S/N ratio for a series of poly(pyrrrolylium tosylate) films is illustrated in Figure 1 (all films were grown in the smaller cell). Clearly,  $\sigma_T$  decreases as applied potential (and current density; see Table I) increases. A similar observation has recently been made by Bloor et al.<sup>7</sup> for PP<sup>+</sup> OTs<sup>-</sup> "plates." Also, we find that the flotation density of our films decreases as the applied potential increases (Fig. 2), suggesting that a more open, mechanically less durable material is formed as the potential increases. Water in the films acts as a plasticizer, as suggested by the strain to failure of a PP<sup>+</sup> OTs<sup>-</sup> film grown in a dry box (by M. A. Druy, GTE Laboratories), which is less than half that of a typical film prepared in laboratory air with a "wet" electrolyte (Fig. 3). A similar influence of water was observed by Wynne and Street<sup>5</sup> and Bloor et al.<sup>7</sup> The stress strain curves of all of the samples prepared (Table I) have the same general characteristics as those of Figure 3: namely, a rather smooth elastic-plastic transition with no distinguishable yield point.

The data of Figure 3 compare the best materials, in terms of ultimate tensile strength, attainable for a series of poly(pyrrrolylium anion) films. It should be noted that both PP<sup>+</sup> OTs<sup>-</sup> films and the PP<sup>+</sup> ClO<sub>4</sub><sup>-</sup> film were prepared in the larger cell (small current density, about 0.5 mA/cm<sup>2</sup>). Attempts to prepare PP<sup>+</sup> BZs<sup>-</sup> and PP<sup>+</sup> DBs<sup>-</sup> films at similar current densities yielded brittle films unsuitable for mechanical testing. These films, therefore, were grown exclusively in the smaller cell ( $i = 2.3$  mA/cm<sup>2</sup>). Interestingly, a PP<sup>+</sup> OTs<sup>-</sup> film grown in the smaller cell exhibits a stress-strain curve (Fig. 4) that is now quite similar (with the exception of the tensile strength at break)

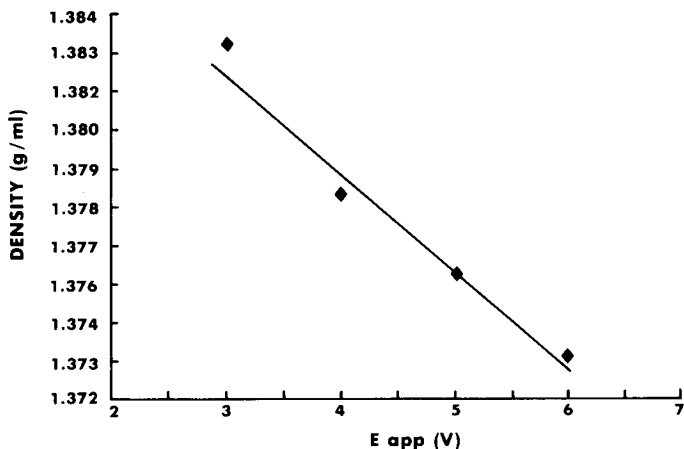


Fig. 2. Flotation density of poly(pyrrylium  $OTs^-$ ) films as a function of applied potential during synthesis.

to that of the  $PP^+ DBs^-$  film, suggesting that the considerable variation in reported mechanical properties of poly(pyrrylium anion) films may be principally related to differences in growth conditions rather than anion structure. Indeed, Bloor et al.<sup>7</sup> also found improvements in mechanical properties in a series of  $PP^+ OTs^-$  films as current density decreased.

An explanation for the dependence of mechanical properties on current density during synthesis is not immediately obvious, since little is known about the mechanism of film growth and the polymer is intractable and hence difficult to adequately characterize in terms of molecular structure. The dependence may be due to one or a combination of several factors such as molecular weight differences, changes in the number of defects<sup>9</sup> (branches and

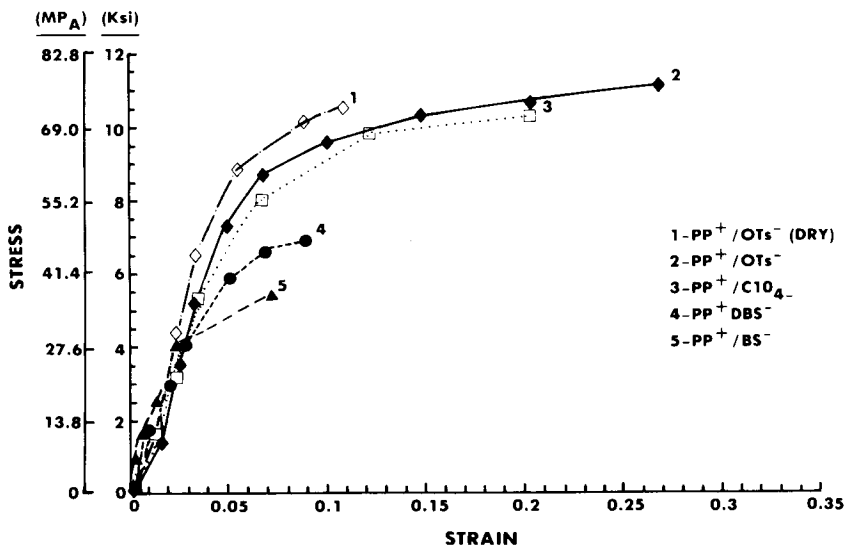


Fig. 3. Stress-strain curves for several poly(pyrrylium anion) films. See text and Table I for synthesis conditions.

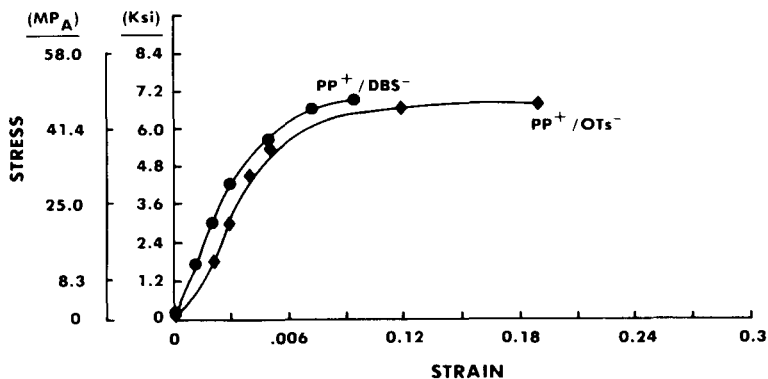


Fig. 4. Stress-strain curves for  $PP^+ DBs^-$  and  $PP^+ OTs^-$  films prepared at a similar current density.

crosslinks), morphological changes, and/or variations in the degree or order (e.g., crystallinity and/or crystallite size). A recent report<sup>10</sup> indicates that the surface morphology of poly(pyrrolylium tetrafluoroborate) films changes from a "smooth" to a "rough" texture as current density increases, whereas no change in internal (fracture surface) morphology<sup>7</sup> was observed in tosylate films prepared at several different current densities. Clearly, morphology/film growth relationships need to be identified in more detail.

We have been interested in the possible connection between changes in the degree of order of the polymer films prepared under different conditions and mechanical properties and, therefore, have examined a series of poly(pyrrolylium anion) films by x-ray diffraction. Figure 5 shows representative plots of x-ray diffraction intensity versus  $2\theta$  for a  $PP^+ OTs^-$  film (Sample 1- $OTs^-$ , Table I) in the transmission and reflection modes, respectively. Values of  $2\theta$  and calculated  $d$  spacings for several films, as well as van der Waals lengths of the various anions (calculated using data in Ref. 11), are presented in Table II. Three points are worth noting. First, the  $d$  spacing derived from the reflection-mode experiments is about  $3.58 \text{ \AA}$  (average value), very close to the  $3.55 \text{ \AA}$  value reported<sup>5</sup> for the polypyrrole interplanar spacing. The fact that this spacing is essentially absent in the transmission mode suggests that the polypyrrole chains lie principally in the plane of the film and thus grow parallel to the surface of the anode. This apparent anisotropy is consistent with the findings from an earlier electron diffraction study.<sup>12</sup> The second point is that the low-angle peaks in the transmission mode appear to scale with the van der Waals length of the counteranions.<sup>5</sup> For example, the  $12.1 \text{ \AA}$  length of  $OTs^-$  combined with calculated van der Waals distances of pyrrole/pyrrole (side-by-side) contacts (about  $4.7 \text{ \AA}$ ) suggests that the pyrrole/ $OTs^-$ /pyrrole intercalation layer thickness should be about  $16.8 \text{ \AA}$ , which is close to the  $16.6 \text{ \AA}$  observed experimentally (see Table II). This assignment of the wide-angle peak is also consistent with the correlation of peak position with chain length in  $PP^+$  tenside materials.<sup>13</sup> Third, the wide-angle peaks in transmission give an average value of  $d = 4.2 \text{ \AA}$ . This spacing has been attributed to pyrrole-tosylate or intertosylate scattering by Wynne and Street.<sup>5</sup> They also find that this scattering maximum is attenuated in "hy-

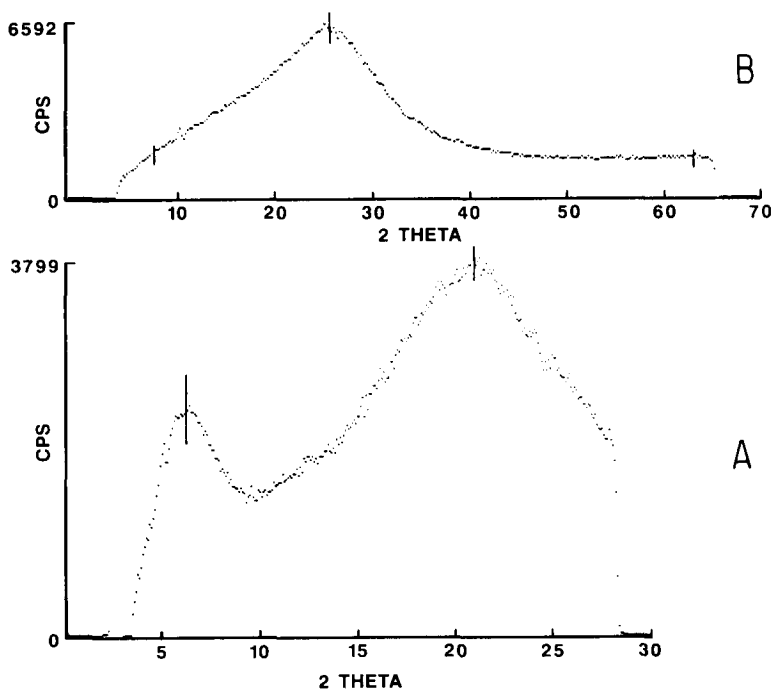


Fig. 5. Representative x-ray scattering raw data for a  $PP^+ OTs^-$  film in (A) transmission and (B) reflection modes.

drated"  $PP^+ OTs^-$  (although the corresponding  $d$  spacing is unchanged) and suggest that water disrupts (via hydrogen bonding) tosylate contacts. The observed weak dependence (Table II) of this spacing on the size of the anion suggests that this scattering maximum might instead be due to pyrrole-pyrrole "side-by-side" contacts, although this interpretation is tenuous.

It must be emphasized that the  $PP^+$  anion films are virtually amorphous, exhibiting only broad scattering maxima (see Fig. 5). However, the breadth can be used to determine an average "crystallite" size (i.e., average domain size of short-range order) using the Debye-Scherrer equation<sup>14</sup>

$$D = \frac{K_{\lambda}}{\beta_i \cos \theta}$$

TABLE II  
X-ray Scattering Data for Several Poly(pyrrolylium anion) Films

Anion	van der Waals length (Å)	Transmission				Reflection	
		$2\theta$	$d$ (Å)	$2\theta$	$d$ (Å)	$2\theta$	$d$ (Å)
OTs	12.1	5.317	16.62	20.429	4.35	25.778	3.35
BZs	11.4	6.397	13.82	22.714	3.92	24.635	3.61
EBs	12.6	5.254	16.82	21.413	4.15	25.079	3.55
DBs	24.8	3.413	25.9	19.476	4.56	23.651	3.76
$ClO_4$	8.6	7.508	11.77	22.111	4.02	25.143	3.54



TABLE III

Integral Breadths ( $\beta_i$ ) of X-ray Scattering Peaks in the Reflection (R) and Transmission (T) Modes and Corresponding "Crystallite" Sizes (D) for PP<sup>+</sup>/Anion Films

Anion	$\beta_i$ (R)	D (Å)	$\beta_i$ (T)	D (Å)
OTs <sup>-</sup>	4.24°	22.4	6.00°	15.7
EBs <sup>-</sup>	8.95°	11.2		
DBs <sup>-</sup>	8.75°	11.5	5.42°	17.3
ClO <sub>4</sub> <sup>-</sup>	5.75°	16.5	6.50°	14.5
BZs <sup>-</sup>	5.52°	18.4		

TABLE IV

Four-probe D.C. Conductivity Data for Several Poly(pyrrolylium anion) Films

Anion	$\sigma$ (S/cm)
OTs <sup>-</sup>	100 ( $\pm 15$ )
BZs <sup>-</sup>	100
EBs <sup>-</sup>	2
DBs <sup>-</sup>	10
ClO <sub>4</sub> <sup>-</sup>	100

where  $D$  is the "crystallite" size (in Å),  $K$  is a constant,  $\lambda$  is the wavelength,  $\theta$  is  $\frac{1}{2}(2\theta)$ , and  $\beta_i$  is the integral breadth (in radians). Table III gives values of integral breadths (transmission and reflection) and "crystallite" sizes for a series of PP<sup>+</sup> anion films. Although there appears to be little dependence of short-range order on anion in transmission, the reflection data show a more than twofold decrease in order with PP<sup>+</sup> DBs<sup>-</sup> compared with the tosylate. Interestingly, this decrease in order parallels the decrease in tensile strength observed previously. It is therefore tempting to suggest that the size of the anion directly influences order and therefore mechanical properties. However, a PP<sup>+</sup> OTs<sup>-</sup> film prepared *at the same current density* as a PP<sup>+</sup> DBs<sup>-</sup> film now shows a similar "crystallite" size 11.8Å and, as noted previously (Fig. 4), similar mechanical properties. These results indicate that growth conditions rather than the anion per se determine the extent of order that in turn has a major influence on mechanical properties.

Table IV summarizes electrical conductivity data for several PP<sup>+</sup> anion films. It is interesting that the samples with the least order (PP<sup>+</sup> EBs<sup>-</sup> and PP<sup>+</sup> BZs<sup>-</sup>) have the lowest conductivities, suggesting that ease of hole transport decreases as short-range order decreases. It is difficult to make more quantitative statements owing to the ill-defined structure and possible morphological complexity of the polymer films.

## CONCLUSIONS

The key observations from this work are that the nature of the anion present in oxidized polypyrrole films, as well as film growth variables, can significantly influence the degree of order and mechanical properties of the films. Also, films with the highest degree of order tend to exhibit the highest conductivities.

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