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Poly(pyrrol-2-ylium tosylate): Electrochemical Synthesis and Physical and Mechanical Properties

Kenneth J. Wynne*[1] and G. Bryan Street*

IBM Research Laboratory, San Jose, California 95193.

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ABSTRACT: Poly(pyrrolylium tosylate) may be prepared by the electrochemical polymerization of pyrrole in acetonitrile utilizing tetraethylammonium tosylate as a supporting electrolyte without special precautions to exclude air. Pyrolytic carbon electrodes allow the use of high currents, which shortens preparative time (e.g., 80 mA, 3 V, 4 h) and yields large samples (50 mm × 90 mm × 0.13 mm). As-prepared poly(pyrrolylium tosylate) films contain 4–6% by weight acetonitrile and 2–3% water. When an applied potential of 3 V ($\approx$80 mA) is utilized, films of composition $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$ are obtained after removal of volatiles at 100 °C and 10^{-3} torr for 18 h. This is the first time that an analytically pure, anhydrous, poly(pyrrolylium anion) film has been prepared without utilizing dry-atmosphere techniques. The analytical data show that neither irreversible oxidation nor hydrogenation of the pyrrole moiety occurs, even in the presence of water. The anion/polycation segmer ratio found for these films (0.43) is higher than that observed previously (0.28–0.32) and may be due to the higher applied potential utilized. Films of $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$ are hygroscopic, taking up $\approx$3% water to form $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n{\cdot}{}^1/_4H_2O$ within 12 h. Slower water uptake continues, reaching $\approx$5% over the course of 3 months. This water absorption is reversible, the original composition being obtained after removal of water at 100 °C for 24 h. $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$ exhibits a tensile strength of 69 MPa (1×10^4 psi), a Young's modulus of 2 GPa (3×10^5 psi), and an elongation-to-break of 8–18%. Acetonitrile/water, present in freshly prepared films, plasticizes poly(pyrrolylium tosylate) and reduces the modulus and tensile strength by $^1/_3$, while increasing the elongation-to-break to 50%. Poly(pyrrolylium tosylate) has been characterized by conductivity, X-ray, and SEM studies, as well as infrared, ESR, core-level X-ray photoelectron, and ^{13}C NMR spectroscopy. The conductivity of the amorphous films (105 S cm^{-1}) is only slightly affected on exposure to air over long periods of time (months). A variable-temperature study from 273 to 4.4 K showed that the conductivity of $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$ follows that predicted for a variable-range hopping mechanism and that the conductivity remains high (4.9 S cm^{-1}) even at 4.4 K. The narrow ESR line (0.38 G) due to free spins present in $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$ is rapidly broadened on exposure to air but is narrowed back (0.5 G) almost to its original value after heating in vacuo overnight. The picture of poly(pyrrolylium tosylate) that emerges from the above studies is that of an easily prepared polymer film whose composition depends on the applied potential used for electropolymerization and the presence of adsorbed solvent/water. The mechanical properties are strongly dependent on the presence of solvent. While the conductivity of poly(pyrrolylium tosylate) is remarkably unaffected by exposure to air for long periods of time, physical and chemical changes that occur quickly (broadening of the ESR line, water uptake) and on a slower time scale (continued weight gain due to water absorption, attenuated spin density) are easily detected.

Introduction

Conducting polymeric materials containing the polypyrrolylium microstructure (Figure 1) have been the object of a number of investigations since the discovery of the electrochemical synthesis of films by Dall'Olio.[2] Thus, the preparation and characterization of poly(pyrrolylium tetrafluoroborate),[3,4] poly(pyrrolylium perchlorate),[5] and a variety of other poly(pyrrolylium anion) compositions[6,7] have been described. The relative ease of preparation of these films has resulted in numerous efforts directed at elucidating the details of the polymer chain structure as well as the spectroscopic, electronic, and optical properties.[8–11] An interesting conclusion derived from ESR studies is that the charge carriers in poly(pyrrolylium anion) films are spinless.[8] The existence of dications or "bipolarons" (Figure 1) that would allow spinless conductivity has been shown to be favorable energetically.[12–14] Evidence for the existence of these bipolarons has been obtained from optical as well as ESR data. Electrooptical studies have revealed optical absorptions in the band gap consistent with the presence of bipolarons.[14,15]

Poly(pyrrolylium anion) films are coherent and adhere well to the electrode. These properties, the robust nature of the films, and their redox behavior have led to utilization of poly(pyrrolylium anion) films as electrode materials.[16,17] Potential applications as a free-standing film place additional materials requirements, including good mechanical properties, and raise questions concerning the invariance

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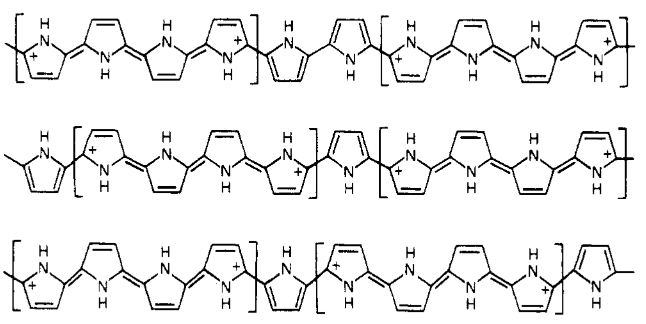

Figure 1. Idealized structure of the polypyrrole cationic portion of poly(pyrrolylium tosylate), with an average charge/segmer of 0.4.

of properties with time. The work of Diaz et al.[6,7] concerning the electrochemical synthesis and physical properties of poly(pyrrolylium tosylate) is important in providing information along these lines, as tensile strengths up to 59 MPa (8.6 × 10^3 psi), good thermal stability, and high conductivity were reported. However, the composition of the films as determined by elemental analysis showed O:S ratios varying from 5.2 to 6.1, whereas tosylate requires 3:1. Furthermore, the anion/polycation segmer ratio, x in the formula $[(C_4H_3N)^{x+}(CH_3C_6H_4SO_3)_x]_n$, varied from 0.28 to 0.32, and tensile strengths varied from 8 to 59 MPa ((1.2–8.6) × 10^3) psi, depending on the solvent used in the film preparation. In view of the importance of the observed mechanical properties together with film stability, we have reinvestigated the electrochemical synthesis of poly(pyrrolylium tosylate) in an attempt to better define the composition of poly(pyrrolylium tosylate) and the observed variation of properties.

Experimental Section

Preparation and Analysis of Poly(pyrrolylium tosylate) Films. A. From Acetonitrile Solution. Poly(pyrrolylium tosylate) films were prepared by a modification of a previously reported method.[7] Pyrrole (Aldrich, 98%) was passed over neutral, activated alumina contained in a graduated column prior to use. Spectral grade acetonitrile was used without further purification. Tetraethylammonium tosylate of varying water content (Aldrich) was used as received.

The electrochemical cell was constructed by connecting a section of rectangular glass tubing (80 mm long × 30 mm wide × 100 mm high) to a glass plate (70 mm × 120 mm) with clear epoxy resin. The cell was then fitted with two pyrolytic carbon electrodes (3 mm × 50 mm × 100 mm, Atomergic Chemetals, Plainview, NY) separated by Teflon spacers and connected to a suitable dc power source.

In a typical preparation, Et_4NTos (7.0 g, 0.023 mol, 0.15 M) and pyrrole (3.0 mL, 0.043 mol, 0.29 M) were dissolved in 150 mL of acetonitrile. This solution was added to the electrochemical cell, which was sealed with Parafilm "M" and placed in an ice bath to reduce the loss of solvent during the film growth. The electrochemical polymerization was carried out at a constant applied potential (3 V, 80 mA, 1156 C) for 4 h. When anhydrous tetraethylammonium tosylate was used, 1 mL of water was added to provide sufficient water concentration for the cathode reaction, i.e., for a current of 80 mA. The anode was removed from the cell and rinsed with acetonitrile. Poly(pyrrolylium tosylate) was removed from the electrode with a single-edge razor blade and immersed in acetonitrile for 15 min. Volatiles were removed as described below. The yield of film was 0.68 g (calculated yield, based on an equivalent weight of 57.4, 0.69 g).

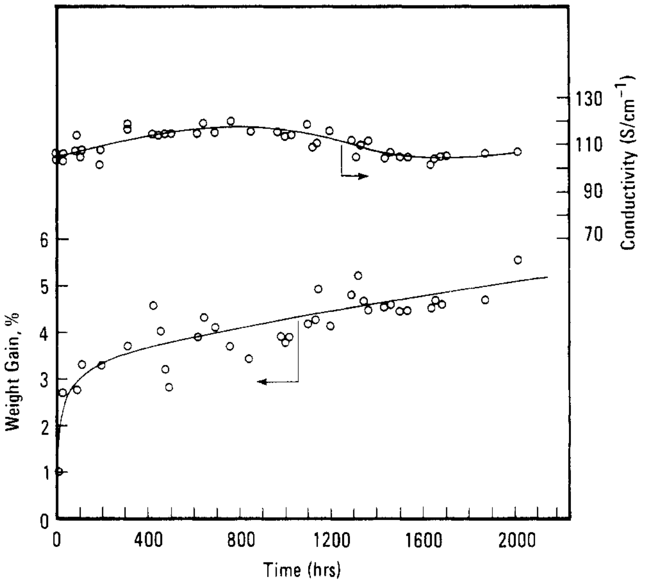

Figure 2. (a) Conductivity and (b) Percent weight uptake of poly(pyrrolylium tosylate) vs. time exposed to ambient air.

Table I
Analytical Results for Poly(pyrrolylium tosylate)

sample	% C	% H	% N	% S	% O
			A. Acetonitrile Solvent		
IA	59.99	4.67	10.06	9.87	15.41
	60.26	4.57	10.23	9.96	14.98
IB	60.15	4.20	9.978	9.89	15.79
	60.18	4.42	10.19	10.08	15.13
mean[19]	60.15	4.47	10.12	9.95	15.33
	(0.10)	(0.18)	(0.10)	(0.08)	(0.31)
calcd[a]	60.70	4.38	10.10	9.94	14.88
			B. Aqueous Solvent		
IIA	61.23	4.24	11.46	8.76	14.31
	61.26	4.39	11.27	8.70	14.38
mean[19]	61.25	4.32	11.37	8.73	14.35
	(0.02)	(0.08)	(0.10)	(0.03)	(0.04)
calcd[b]	61.46	4.32	11.30	8.66	14.26
IIB	60.62	4.52	10.86	8.82	15.18
	60.42	4.74	10.90	8.90	15.04
mean[19]	60.52	4.63	10.88	8.86	15.11
	(0.10)	(0.11)	(0.02)	(0.04)	(0.07)
calcd[c]	60.74	4.28	10.91	8.89	15.18

[a] Based on the formula $[(C_4H_3N)(C_6H_7SO_3)_{0.43}]_n$. [b] Based on the formula $[(C_4H_3N)(C_7H_7SO_3)_{0.335}(O)_{0.1}]_n$. [c] Based on the formula $[(C_4H_3N)(C_7H_7SO_3)_{0.356}(O)_{0.15}]_n$.

B. Volatiles Content. Samples prepared in this way contain a substantial weight fraction of volatiles. One sample prepared by the above method (1.1874 g) was heated at 10^{-3} torr for 2 days at 80–100 °C. The resulting material (1.1162 g) lost 6.0% of its initial weight. Chemical analysis of the evolved liquid (C, 39.86; H, 8.30; N, 23.04) indicated a C:N ratio of 2.0:1 in the liquid. Water content by the Karl Fischer method was 29.03%. ^1H NMR spectroscopy of the liquid recovered from other samples showed two peaks with chemical shifts characteristic of acetonitrile and water. The integrated intensities showed a sample-dependent acetonitrile:water ratio from 1.1 to 1.8.

To determine if the absorption of water was reversible and to evaluate whether irreversible oxygen uptake occurred, a 0.4788-g sample of $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$ was exposed to air for 3 months. The percent weight uptake as a function of time is shown in Figure 2. At the end of this time, the sample weighed 0.5052 g. After heating at 105 °C for 23 h at 10^{-3} torr the sample returned to its original weight (0.4785 g) within experimental error.

C. Water Solvent. The electropolymerization of pyrrole was carried out in water by using experimental conditions similar to those described above. Thus, one experiment utilized 0.2 M sodium tosylate and pyrrole and 2.6 V (50 mA) and gave sample IIA. In a similar experiment (2.7 V, 60 mA), except incorporating toluenesulfonic acid (2 × 10^{-3} M) to ensure that the solution remained acidic, sample IIB was prepared. Sample IIA was pumped at 10^{-3} torr for 43 h at 110 °C, while IIB was pressed dry between filters for 1 h and pumped for 15 h at 90 °C. Weight difference showed that as-prepared IIB contained 11% water.

Composition. Elemental analyses on samples I and II (C, H, N, S, Galbraith Laboratories) were obtained on material quickly transferred in air to ampules that were sealed in vacuo. Oxygen analysis was determined by difference. The results are summarized in Table I. Consistent analyses were obtained only for films from which volatiles were removed as described above.

Characterization Techniques. Thermal gravimetric analysis was carried out by means of a Du Pont 1019 thermal analyzer. A nitrogen atmosphere and a heating rate of 10 °C/min were used.

Conductivity at ambient temperature was measured with a Magne-Tron Model M-700 resistivity/conductivity system with a four-point probe. Conductivity as a function of temperature was measured in vacuo with a previously described method.[18]

Tensile measurements were made under ambient conditions with an Instron universal testing instrument. The samples were cut with a strip cutter to produce specimens with a gauge length of 2.0 in. and a width of 0.25 in. A tensile strain rate of 1.67×10^{-3} s^{-1} was maintained for all determinations.

ESR spectra were obtained with a Varian E-15 spectrometer, operating at X-band frequency (9.3 GHz).[8,19] To avoid a Dysonian line shape due to excess sample thickness, ESR spectra were obtained on thin (~5 μm) samples removed from the back of the carbon electrode, i.e., that side facing away from the counter electrode. The sample was contained in a quartz ESR tube fitted with a stopcock/joint arrangement that facilitated atmosphere control.

^{13}C NMR spectra were recorded with cross-polarization and magic-angle spinning (CPMAS) techniques as described by Yannoni.[20] The sample was prepared from a 0.12-mm-thick film by cutting the film into ~2-mm squares and packing the resulting material into the rotor. Chemical shifts are reported in ppm vs. tetramethylsilane as a standard.

X-ray data were collected on 0.12-mm films by step scanning with a computer-controlled diffractometer described by Parrish.[21]

Infrared measurements were made with an IBM IR98 FTIR interferometer equipped with a room-temperature DTGS detector, utilizing a grazing-incidence IR technique, as described by Rabolt.[22] A 0.35-μm film of poly(pyrrolylium tosylate) was prepared on a glass microscope slide coated with 300-Å Cr and 2000-Å Pt by electropolymerization at 1.2 V (1 mA) for 25 min. The sample was kept in an evacuated tube fitted with a stopcock/joint arrangement until the brief transfer (in air) to the instrument.

XPS measurements were taken with a Hewlett-Packard 5950B spectrometer with monochromatized Al Kα radiation and an energy resolution of ≈0.7 eV.[10]

Results and Discussion

Composition and Analysis. Poly(pyrrolylium tosylate) may readily be prepared without special precautions to exclude air by the electrochemical polymerization of pyrrole in acetonitrile at 0 °C utilizing tetraethylammonium tosylate as a supporting electrolyte.[6,7] The use of pyrolytic carbon electrodes allows the electrochemical reaction to be carried out at high applied potential (3 V, 80 mA) utilizing a simple dc power source. In this way, relatively large samples of poly(pyrrolylium tosylate), typically 50 mm × 90 mm × 0.13 mm, may be prepared in 4 h. The films are easily removed from the electrode, facilitating characterization. Previous preparative methods[6-11] have utilized a platinum anode for film growth. In our hands, attempts to extend this method to thick films led to poly(pyrrolylium tosylate) films that did not adhere well to the Pt anode and displayed increasing roughness with thickness.

Under these high-voltage/high-current conditions the cathode reaction appears to be the reduction of water.[23] During the course of the electrochemical polymerization, gas (presumably hydrogen) is continuously evolved at the cathode. The current increases if the water concentration is increased, and the solution is basic at the end of the reaction, which is consistent with eq 1 for a material prepared at 3 V. An advantage of this gas evolution is the continual purging of dissolved oxygen.

The as-prepared poly(pyrrolylium tosylate) films contain 4–6% by weight acetonitrile and 2–3% water. Both acetonitrile and water are tenaciously held by the film. Thus, in one experiment a 1.265-g sample of poly(pyrrolylium tosylate) released 3.3% volatiles after heating at 80 °C and 10^{-3} torr for 2 h. The composition of the recovered liquid was 57% acetonitrile and 43% water. After an additional 12 h of heating, 2.6% additional volatiles was recovered, of which about 20% was acetonitrile. It is somewhat surprising that the second volatile fraction contained acetonitrile. This observation makes clear that the removal of volatiles before chemical analysis is essential.

$$0.43\mathrm{Et_4N^+} + 0.43\mathrm{CH_3C_6H_4SO_3^-} + \mathrm{C_4H_5N} + 0.43\mathrm{H_2O} \rightarrow [(\mathrm{C_4H_3N})(\mathrm{CH_3C_6H_4SO_3^-})_{0.43}]_n + 1.21\mathrm{H_2} + 0.43\mathrm{Et_4N^+} + 0.43\mathrm{OH^-} \quad (1)$$

At 3 V, films of composition $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$ (IA and IB, Table I) are obtained after removal of volatiles at 100 °C and 10^{-3} torr for 12 h. The analytical data, which are comprised of four analyses on two different samples, define the anion/polycation segmer ratio as 0.430 (0.003)[24] in the pure material. This ratio is unequivocally determined, as only the anion contains sulfur, while only the polycation contains nitrogen. Lower ratios were obtained previously,[7,25] perhaps due to the lower applied potentials utilized. The presence of acetonitrile can also lead to low N:S ratios in samples from which volatiles have not been completely removed.

From the data in Table I, an O:S ratio of 3.09 (0.02) may be calculated. Finding the expected 3:1 ratio of O:S in poly(pyrrolylium tosylate) (vs. ratios of 5–6 seen previously)[7] is important as this is the first time that an analytically pure, anhydrous, polypyrrole film has been prepared without utilizing glovebox techniques. This accomplishment is also important in demonstrating that irreversible oxygen incorporation due to oxidation of the pyrrole moiety does not occur, even in the presence of water.

The data in Table I show an average H analysis of 4.47% (0.18%) vs. a calculated value of 4.38% (based on $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$. The observed and calculated C:H ratios are 1.13_2 and 1.167, in agreement within 3%. Surprisingly then, this represents a better hydrogen analysis than that obtained for poly(pyrrolylium tetrafluoroborate)[3] or poly(pyrrolylium perchlorate)[5] films prepared under dry-atmosphere conditions. The excellent agreement in the hydrogen analysis makes the possibility that hydrogenation of some of the pyrrole rings occurs (as previously suggested[5]) seem less likely.

Figure 2 shows that $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$ is hygroscopic, quickly taking up ~3% water to give $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n \cdot {}^1/_4H_2O$. After this initial absorption of water, the films show a slower, additional weight gain, bringing the total to ~5% over the course of 3 months. At this point, the slope of the weight-gain curve is positive, indicating that additional weight gain over longer periods of time can be anticipated. Interestingly, this process is reversible, the entire weight uptake of water being lost on heating in vacuo at 105 °C for 23 h. This result is important in demonstrating that irreversible reaction with oxygen or water does not occur on a large scale over this rather long time period. However, attenuation of the ESR signal discussed below does indicate a small-scale irreversible reaction.

Poly(pyrrolylium tosylate) Films Prepared in Water. The electropolymerization of pyrrole can also be carried out on carbon electrodes with aqueous solutions of pyrrole and sodium tosylate. Despite the tendency for films to show dendritic growth under these conditions, small sections of film were obtained for chemical analysis and examination of mechanical properties so that a com-

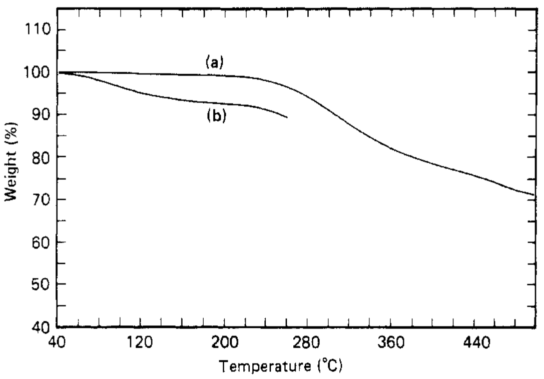

Figure 3. Thermal gravimetric analysis curves for (a) as-prepared (acetonitrile) poly(polypyrrolylium tosylate) and (b) $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$.

parison could be made with acetonitrile-grown films.

The analytical data in Table I for the aqueous-grown films (IIA, IIB) reveal a different stoichiometry for these films relative to acetonitrile-grown films (I). The aqueous-grown films have an anion/polycation segmer ratio of 0.335 (IIA) and 0.346 (IIB) compared to 0.430 (0.003) for I. This may be due to the lower applied potential utilized in the preparation of IIA and IIB. In addition O:S ratios of 3.3 (IIA) and 3.5 (IIB) were obtained despite heating in vacuo under conditions comparable with those used for I (IIB) or more vigorous than those used for I (IIA). The inferior mechanical properties of these films discussed below discouraged a detailed investigation into the nature of the "excess oxygen" present in these films. However, the retention of excess oxygen after heating in vacuo under conditions more vigorous than those used for acetonitrile-grown films suggests that irreversible oxygen incorporation through oxidation of the pyrrole moiety may have occurred.

Low-Voltage/Low-Current Films. To more firmly relate the results of the present study with those obtained previously, poly(pyrrolylium tosylate) films were prepared at low voltage.[7] The polymer prepared in this manner exhibited an anion/polypyrrolylium segmer ratio of 0.27, which is at the lower end of the reported range.[7] These results confirm the previously observed stoichiometry and suggest that the lower anion/polypyrrolylium segmer ratio is due to the lower applied potential.

Thermal Stability. TGA is a useful technique for rapidly evaluating percent volatiles in poly(pyrrolylium tosylate) films (Figure 3). Curve a is for a pure $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$ film and shows that little weight loss occurs below 200 °C. Gradual weight loss above 200 °C is due to the onset of thermal decomposition. Curve b is a result on a film from which volatiles were not removed. The 7.5% weight loss below 180 °C is due to evolution of both acetonitrile and water.

Mechanical Properties. The mechanical properties of poly(pyrrolylium tosylate) films were studied previously,[7] but a reinvestigation seemed appropriate to establish quantitatively the extent to which the presence of water and acetonitrile affects mechanical properties. Figure 4 shows the stress/strain behavior of as-prepared (curve b) and pure poly(pyrrolylium tosylate) (curve a). From these data it is seen that acetonitrile/water has a strong plasticization effect on poly(pyrrolylium tosylate) films. Curve a shows that freshly prepared poly(pyrrolylium tosylate) films containing 8% acetonitrile/water can be stretched by almost 50% of their initial length before fracture. Curve b for a pure poly(pyrrolylium tosylate) sample reveals the intrinsic stress/strain behavior, with an elongation-to-break of 16% (range 8–18%). These data show that, even when plasticized, a yield point is not observed. Rather, a smooth transition occurs from elastic to plastic behavior.

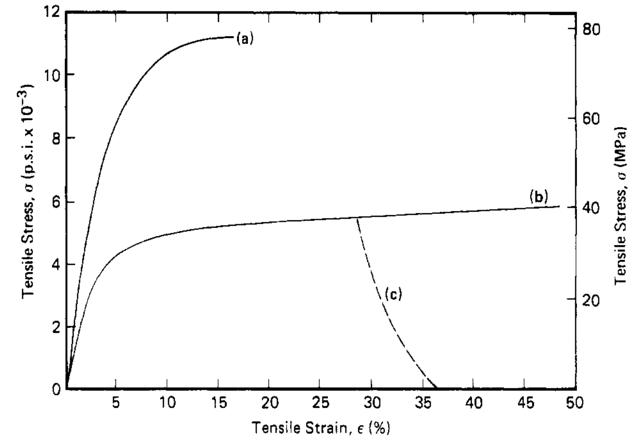

Figure 4. Stress/strain behavior of (a) $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$ and (b) acetonitrile-plasticized poly(pyrrolylium tosylate). (c) Relaxation behavior of acetonitrile-plasticized poly(pyrrolylium tosylate).

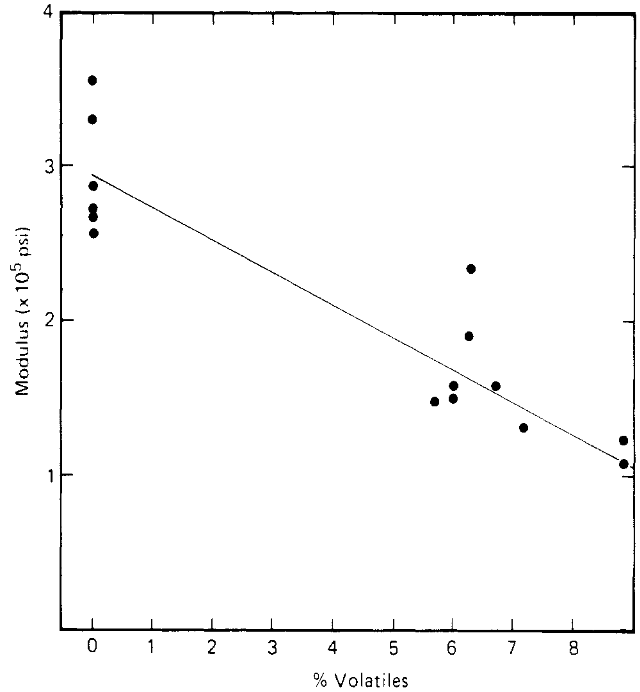

Figure 5. Plot of tensile modulus vs. percent volatiles (acetonitrile, water) in poly(pyrrolylium tosylate).

Figure 4, curve c, the initial portion of which is coincident with curve a, shows the stress/strain behavior of a sample that was strained to 30%, followed by removal of stress at the same rate as initially applied (1.67×10^{-3} s^{-1}). At this rate, only 8% recovery is observed, which is consistent with plastic flow occurring after the elastic region.

Figure 5 shows the effect of acetonitrile/water on Young's modulus. Pure $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$ exhibits a tensile strength of 72 (7) MPa (10.4 (1) × 10^3 psi) and a Young's modulus of 2.9 (0.4) GPa (3 (0.5) × 10^5 psi), while a film containing 8% acetonitrile/water has about one-third these modulus and tensile strength values. The strength values reported here for $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$ are somewhat higher than the maximum values for previously prepared poly(pyrrolylium tosylate).[7] This reflects the different anion/polycation ratios due to different preparative conditions and possibly the presence of varying amounts of volatile plasticizers for the

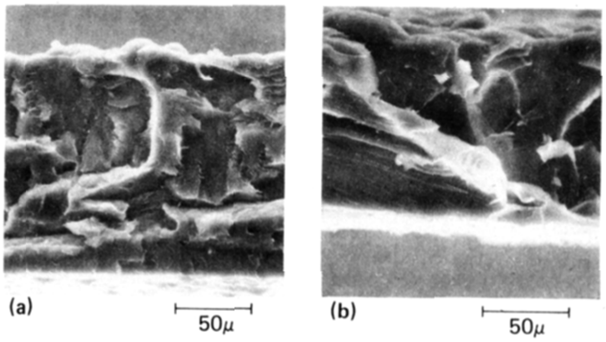

Figure 6. Scanning electron micrographs of the fracture surface of poly(pyrrolylium tosylate): (a) ductile fracture at 25 °C; (b) brittle fracture at −196 °C.

previously prepared materials.

The plasticization of poly(pyrrolylium tosylate) by acetonitrile is reversible. In one experiment, a sample of as-prepared poly(pyrrolylium tosylate) had an initial elongation of 53.6%. This was reduced to 13.1% after removal of volatiles at 80 °C for 30 h, at which point the composition was $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n\cdot{}^1/_4H_2O$ by analysis. Immersion in acetonitrile overnight increased the elongation to 58.4%. This was the highest elongation-to-break observed for any sample.

Quite different mechanical properties were observed for poly(pyrrolylium tosylate) films prepared in water. Combining the chemical analysis of "dry" films with weight loss on removal of labile water, it was found that as-prepared films have a composition approximating IIA·$0.9H_2O$ and IIB·$0.9H_2O$. Although these films have slightly differing compositions, they displayed indistinguishable mechanical properties, and average values are reported. These films exhibited an elongation-to-break of 8%, tensile strength of 22 MPa (3.2×10^3 psi), and a Young's modulus of 0.76 GPa (1.1×10^5 psi). With labile water removed, IIA and IIB showed a reduced elongation-to-break (2.4%) and increased tensile strength (25 MPa (3.6×10^3 psi) and modulus (1.1 GPa (1.6×10^5 psi)). Thus, water plasticizes poly(pyrrolylium tosylate), and the removal of labile water produces a very brittle material with poor strength. The mechanical properties of poly(pyrrolylium tosylate) grown in water are distinctly inferior compared with those of acetonitrile-grown films. The different mechanical properties of materials prepared in water vs. those prepared in acetonitrile can be rationalized in part as due to different materials compositions. Perhaps the difference is also due to the lower molecular weight of polycation chains grown in water, as the viscosity of water is higher than the viscosity of acetonitrile and radical species may be better stabilized in the latter medium.

Scanning Electron Microscopy. SEM was used to examine the fracture behavior of poly(pyrrolylium tosylate). Figure 6a shows the fracture surface of $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n\cdot{}^1/_4H_2O$ (I exposed to air), which underwent fracture at 30% elongation at ambient temperature. Regions of plastic flow and deformation are evident, but there is no sign of fibrillation. Figure 6b shows a similar sample that underwent fracture at −173 °C. A brittle fracture pattern is evident with sharp faces on the fracture surface. These results are in agreement with the observed stress/strain behavior and confirm the idea that liquidlike flow without measurable orientation occurs on stretching poly(pyrrolylium tosylate) under the conditions described.

X-ray Diffraction. Figure 7 shows a scan of X-ray scattering intensity vs. 2θ for $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$ (curve b) and $[(C_4H_3N)(CH_3C_6H_4SO_3)]_n\cdot{}^1/_4H_2O$ (curve a).

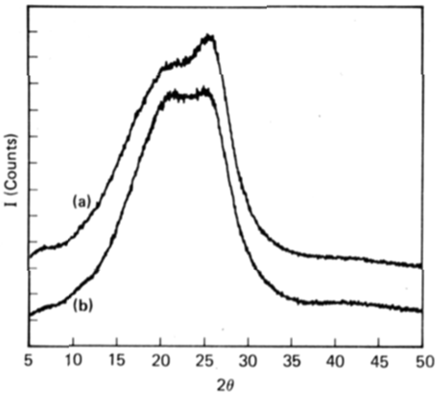

Figure 7. X-ray scattering vs. 2θ for (a) $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n\cdot{}^1/_4H_2O$ and (b) $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$.

The polymer is amorphous to X-rays. Broad scattering maxima for $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$ are observed at 3.55 and 4.13 Å. The peak at 3.55 Å is assigned to scattering from pyrrole chains at interplanar spacings close to the van der Waals distance for aromatic groups. The maximum at 4.13 Å is probably due to pyrrole–tosylate (or intertosylate) scattering, as the "thickness" of the sulfonate group (~5 Å) would increase the interplanar spacing over that of an unencumbered aromatic moiety. Weak scattering at 12.8 Å is possibly due to tosylate, as the van der Waals length of the tosylate group is ~12.1 Å. The weakness of this low-angle peak indicates there is far less anion order present than in poly(pyrrolylium alkyl sulfates), where strong low-angle scattering correlates with the length of the alkyl chain.[11]

The pattern for $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n\cdot{}^1/_4H_2O$ (Figure 7, curve a) is similar to that for the anhydrous polymer with maxima at virtually the same locations (4.21 and 3.48 Å). However, scattering at 4.21 Å is attenuated, probably due to the disruption of tosylate contacts by hydrogen-bonded water.

Scattering by the Laue technique did not reveal any angular dependence for the observed pattern. Furthermore, a Laue photograph on a sample that had been previously stretched to 40% was identical with that observed for an unstretched sample.

Conductivity. The conductivity of $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$ is 105 S cm^{-1} at ambient temperature, close to the previously reported range of 20–100 S cm^{-1}.[7,25] Figure 2 shows that the conductivity of poly(pyrrolylium tosylate) films is relatively insensitive to exposure to ambient air. Over the course of 2 weeks there is a 10% increase in conductivity, after which the conductivity undergoes a very gradual decrease, returning to its original value after 3 months. The initial film conductivity is also unaffected by the presence of acetonitrile/water. The conductivity of stretched films in the direction of tensile stress is the same as that perpendicular to the stretch direction.

The conductivity of poly(pyrrolylium tosylate) vs. temperature is shown in Figure 8. No abrupt changes in conductivity are observed as the temperature is lowered to 4.4 K, at which temperature the conductivity has fallen to 4.9 S cm^{-1}. A plot of log σ vs. $T^{-1/4}$ gave an excellent straight-line fit for the data over the entire temperature range. This $T^{-1/4}$ behavior is similar to that observed previously for poly(pyrrolylium tetrafluoroborate)[18] and polyacetylene[26] and is consistent with a three-dimensional, variable-range hopping mechanism as proposed by Mott.[27] The conductivity is only modestly dependent on temperature, so the activation energy for this process must be small.

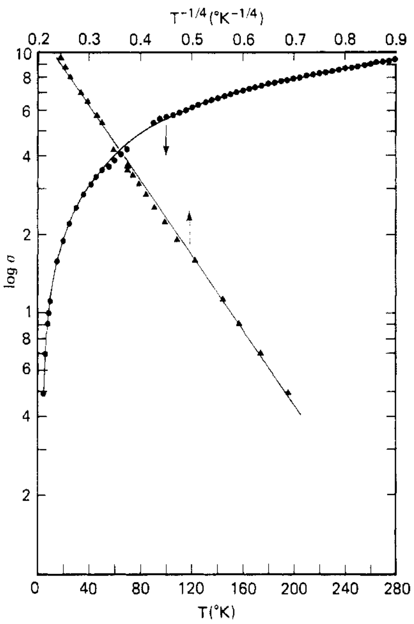

Figure 8. Plot of conductivity (log σ) vs. temperature ((●) T; (▲) $T^{-1/4}$)) for $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$.

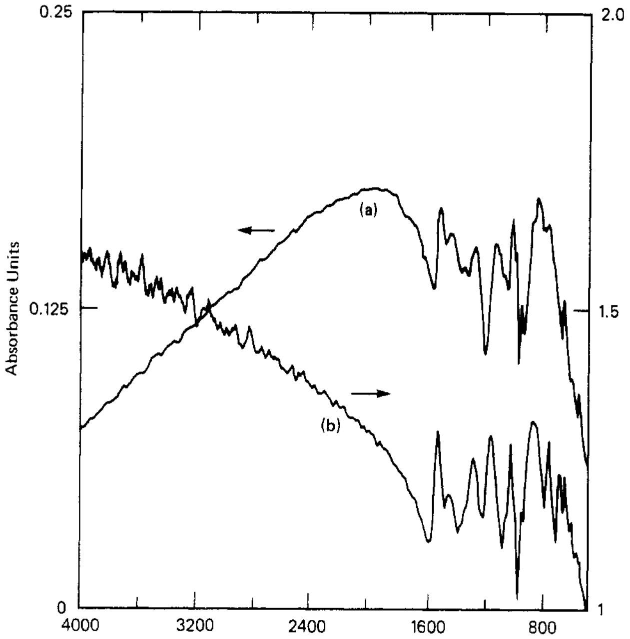

Figure 9. Infrared spectra of (a) poly(pyrrolylium tosylate) and (b) poly(pyrrolylium hexafluoroarsenate(V)).

The conductivity of hydrous IIA and IIB films prepared in water was 83 S cm^{-1}, while the conductivity of dried IIA and IIB films was 59 S cm^{-1}. These results, which demonstrate the inferior conductivity of poly(pyrrolylium tosylate) films prepared in water relative to acetonitrile, are in agreement with an earlier report[7] and are explained on the basis of a compositional effect. This observation is also consistent with the possibility that the materials prepared in water have lower molecular weights (as discussed above) and thus shorter conjugation lengths.

Infrared Spectrum. Films of $[(C_4H_3H)(CH_3C_6H_4SO_3)_{0.43}]_n$ are highly absorptive, and an infrared spectrum in transmission could not be obtained on films as thin as 20–30 μm prepared in the normal manner. The IR spectrum shown in Figure 9a was obtained on a poly(pyrrolylium tosylate) film prepared by electropolymerization on a platinum-coated glass slide at 1.2 V. Under these conditions the composition is expected to be close to $[(C_4H_3H)(CH_3C_6H_4SO_3)_{0.27}]_n$. The spectrum shown in Figure 9a was obtained in a reflection mode using a grazing-incidence technique.[22] This spectrum is virtually identical with that of poly(pyrrolylium hexafluoroarsenate) taken in transmission (Figure 9b)[28] and strongly supports similar polycationic structures. The latter material was chosen for comparison, as there are no peaks greater than 500 cm^{-1} due to the anion. The close agreement of the IR spectra stems from the similar applied potentials used for the preparation of both films (1 V for poly(pyrrolylium hexafluoroarsenate)[28]), bringing about comparable anion/polycation segmer ratios, and the use of acetonitrile as a preparative solvent, which may result in similar chain lengths. The close correspondence in spectra is also due to the fact that, as observed previously, the anion absorptions are masked by strong polycation modes. in $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.27}]_n$, the strongest S–O stretching frequency for the tosylate anion (1183 cm^{-1})[29] is apparently shifted and coincident with a polypyrrole absorption at 1150 cm^{-1}. Other weak peaks due to the tosylate anion[29] are observed at 1087 and 1117 cm^{-1}.

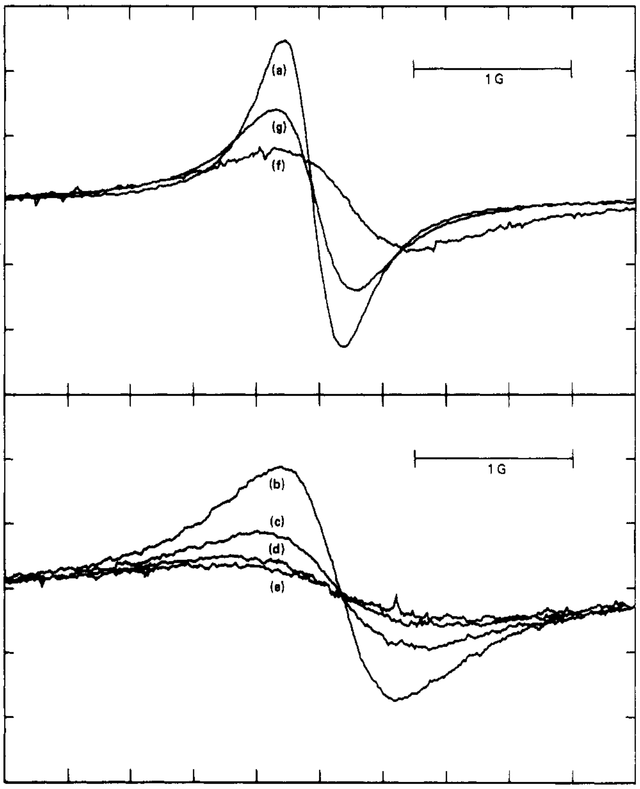

Figure 10. ESR spectrum of poly(pyrrolylium tosylate) as a function of exposure time to ambient air: (a) in vacuo; (b) 5 min; (c) 12 min; (d) 20 min; (e) 45 min; (f) sample reevacuated for 20 min; (g) sample after heating at 111 °C for 11 h.

Electron Spin Resonance Spectroscopy. Figure 10 shows the ESR spectrum of $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$ as a function of time. Curve a shows the ESR spectrum of a freshly prepared film of $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$ exposed to air for 1-min transfer time. The line width of 0.38 G is almost as narrow as that measured for poly(pyrrolylium perchlorate) (0.2–0.3 G) prepared in an argon atmosphere.[5] The 0.38-G line width for $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$ may be compared with that observed for other highly conducting polymeric materials such as *trans*-polyacetylene (0.7 G)[30] and $([Si(Pc)O]I_{1.13})_n$ (2.9 G).[31] The narrow line width for poly(pyrrolylium tosylate) implies highly mobile spins and little hyperfine broadening.

Exposure of $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$ to air broadens the line width to 1.5 G over the course of 45 min (Figure

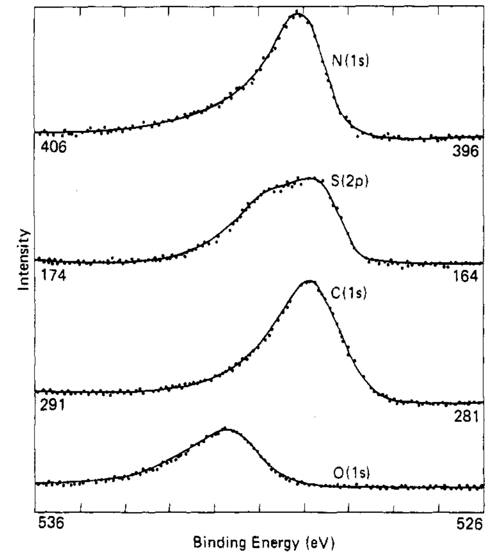

Figure 11. XPS core-level spectrum of $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$. The line through the points is meant as a guide for the eye.

10b–e). This same effect, which is due to the diffusion of oxygen and water into the film, is observed for poly(pyrrolylium perchlorate), but broadening for the latter occurs in a few seconds.[5,8] Evacuation of the sample causes the line to narrow to 0.9 G (Figure 10f), as was found for poly(pyrrolylium perchlorate). Continued evacuation at 95 °C caused further narrowing to 0.50 G. All spectra show the presence of the same spin concentration.

Defects in the growing polymer chain of various origins could explain the strong ESR signal. In addition, a substantial fraction of chain ends may terminate in a way that traps spins. Such a process would be consistent with the morphology of film growth. Figure 6, in addition to showing the fracture surfaces, gives a glimpse of the surface morphology previously reported.[7] This pebbled morphology apparently arises from the intersection of radially growing microhemispheres of polymer. Interestingly, our own SEM photographs of the growing polymer film show that this morphology is independent of film thickness in the 10–100-μm range. Thus, the trapped spins may be largely a result of physical entrapment occurring when a growing polymer chain "front" encounters a similarly growing front. Whatever the origin of the spin concentration, the trapped spins are surprisingly not correlated with conductivity.[8]

At the termination of the 3-month exposure of $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$ to air, an ESR spectrum was obtained. The signal was difficult to detect as it was relatively broad (1.3 G) and weak. Analysis of relative signal intensities indicated that spin density had decreased between 1 and 2 orders of magnitude during this period. Thus, remnant free radicals present in the film have reacted with oxygen or water, probably giving hydroxy or keto functions at these sites. Such a reaction would not be detectable by the change in weight, as prior studies (on poly(pyrrolylium perchlorate[8]) have demonstrated a spin density corresponding to 1 spin per 50 monomer units. The conversion of all spins to hydroxy groups would thus correspond to a weight gain on the order of 1 part in 400, which is within the experimental weighing error. In view of the continued high conductivity of poly(pyrrolylium tosylate) after 3-month exposure to air, these results offer additional evidence that conduction is not dependent on the presence of free spins.

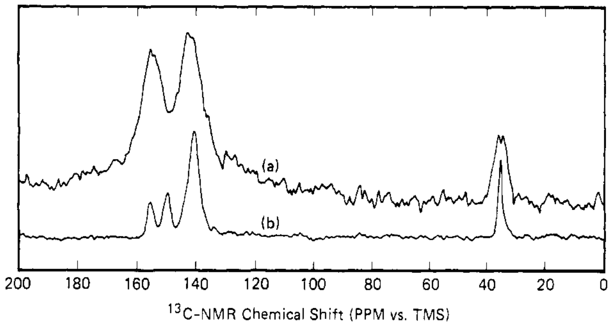

Figure 12. CPMAS ^{13}C NMR spectrum of (a) $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$ and (b) sodium tosylate.

X-ray Photoelectron Spectroscopy (XPS). Core-level XPS is a useful technique for the investigation of gross features of heteroatom conducting polymers.[10,32-34] Figure 11 shows the core-level XPS spectra for the elements in $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$. All the spectra show peaks skewed to the high-energy side. This seems to be a commonly observed feature for conducting polymers, as a similar asymmetry was observed for polyacetylene–AsF_5[32] and poly(pyrrolylium anion).[10,33,34] Salaneck[32] explained the observed skewing as a natural consequence of the metallic state and pointed out that the observed line shapes are similar to the Doniach–Sunjic line shape observed in metals. However, Pfluger et al.[33,34] discussed this broadening in terms of disorder in the case of the carbon peaks and the electrostatic inequivalence in the case of the nitrogen peaks.

^{13}C NMR Spectroscopy. ^{13}C NMR spectroscopy is generally a powerful method for the determination of polymer structure[35] and has proved useful for the investigation of poly(pyrrolylium perchlorate).[5,19] The ^{13}C NMR spectrum of $[(C_4H_3N)(CH_3C_6H_4SO_3)_{0.43}]_n$ is shown in Figure 12a together with the spectrum of anhydrous sodium tosylate (Figure 12b). The tosylate anion shows ^{13}C peaks (with assignments)[36-38] at 35.2 (CH_3), 140.8 (ortho, meta CH), 149.5 (CSO_3^-), and 155.2 ppm (para C). These peaks occur at 35 (CH_3), 142.2 (ortho, meta CH), and 154.6 ppm (CSO_3^- para CH) in poly(pyrrolylium tosylate). Unfortunately, the aromatic tosylate carbons mask the features of the broad signal centered at ~145 ppm due to the polycation, and separate peaks for the α- and β-carbons cannot be discerned. Poly(pyrrolylium perchlorate) also showed a single broad resonance, but at 123 ppm.[5] The observed shift difference is apparently due to the higher charge per pyrrole ring in poly(pyrroylium tosylate) (+0.43) than in poly(pyrrolylium perchlorate) (+0.33) as a result of the different applied potentials used in the preparation of these materials.

Conclusions

Poly(pyrrolylium tosylate) is easily prepared by electropolymerization as a highly conducting polymer film without resort to glovebox conditions. The removal of volatiles results in material of analytical purity. The mechanical properties of the material are remarkably good, and may be controlled to some degree by plasticization with solvent. A limited amount of evidence is available to suggest that the anion/polycation segmer ratio may be controlled over a wide range by the applied potential used in the electropolymerization.

Of the two features that influence composition and properties of poly(pyrrolylium tosylate), the effects of the presence of volatiles have been discussed in some detail. As a result of the preparation of most films at 3 V, little is known of the consequences of changes in anion/polycation segmer ratio. Such changes are expected to affect primarily phenomena that are associated with changes in the π-electron density of the polycation chain. Thus, control of average segmer partial charge may be useful in the study of optical and electronic properties of the polymer. The nature of π-electronic changes can be seen with reference to Figure 1, where the "bipolaron density" has been constructed by use of a valence bond representation to illustrate a polycation partial charge of 0.4. This is close to the composition of poly(pyrrolylium tosylate) films made at 3 V and represents the idealized structure for the polypyrrolylium cation. The pairing of charges over four pyrrole segmers is depicted as a result of recent molecular orbital calculations, which show this structure to be favorable.[13,14,39] Control of the segmer charge may permit study of the evolutionary change in π-electronic structure from predominantly benzenoid-like at low charge/segmer ratios to quinoid-like at high ratios.

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References and Notes

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