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Elimination of Ion-Exchanged Precursors to Poly(phenylenevinylene)

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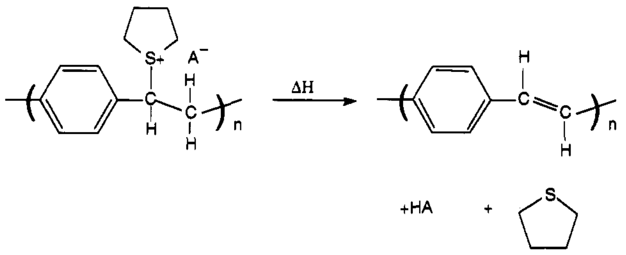
ABSTRACT: Poly(xylylidenetetrahydrothiophenium) (PXT) precursors to poly(phenylenevinylene) (PPV) containing fluoride, chloride, bromide, and acetate counterions were prepared by ion-exchange dialysis of the chloride polyelectrolyte. Thermal gravimetric analysis (TGA) of cast films of PXT's indicates that elimination of the PXT acetate to PPV occurs at a much higher temperature than the halides. In situ conductivity measurements on sulfuric acid doped PPV's show that the identity of the anion has a marked influence on the limiting electronic conductivity. Studies on solution elimination kinetics reveal ion association of acetate with aqueous PXT. The products of elimination were followed by TGA coupled to IR analysis and were found to include tetrahydrothiophene, the conjugate acid of the anion, and water. Evidence for hydrogen bonding of water to PXT was found.

Introduction

The soluble precursor route to poly(arylenevinylene) (PAV) synthesis represents a versatile approach to overcoming the intractability of these polymers.[1-3] The water-soluble sulfonium salt precursor polyelectrolytes can be made with high molecular weights,[4] are easily cast into films, and are readily oriented by mechanical drawing[5] prior to thermal elimination to the final conjugated conductive polymer. The precursor can be rendered soluble in different solvents by controlling the anion[4] or by displacement of the sulfonium group with uncharged groups.[6] Flexibility in the choice of substituents at the 2,5 (3) position on the phenylene (thiophene) ring has stimulated much recent activity in this field, since these substituents exert a strong control over the electrical and optical properties and the morphology of PAV's. For example, introducing electron-donating alkoxy groups in poly(phenylenevinylene) (PPV) decreases the redox potential and the band gap for electronic absorption.[7,8] The band gap for poly(ethoxythienylenevinylene) is such that the doped polymer is color neutral in the visible region.[9] Sulfopropoxy derivatization of PPV yields a polymer which is water-soluble after elimination.[10] In a recent development in nonlinear electro-optic applications of PAV's, Burroughes et al. demonstrated a light-emitting diode based on PPV.[11] The electroluminescent properties of PAV's can also be tailored through design of the polymer.

Thermal conversion of the precursor proceeds with elimination of the acid form (HA) of the counterion (A^-), which balances the charge on the sulfonium group, as illustrated by poly(xylylidenetetrahydrothiophenium) conversion to PPV (Scheme I). An important step in the evolution of poly(arylenevinylene) synthesis was taken when the dimethyl sulfide group in the poly(phenylenevinylene) precursor was replaced by tetrahydrothiophene.[12] The resulting precursor could be eliminated at lower temperatures and to a greater extent, yielding polymers that attained significantly higher conductivities when doped. In the course of our studies on PPV's we observed that when polymers prepared with different anions were eliminated under the same conditions, marked differences in conductivity of the doped material resulted. The anion present in the precursor polyelectrolyte is determined by the composition of the monomer and by the acid employed to quench the polymerization. For example, the bis(sulfonium chloride) form of the monomer is often used, with subsequent neutralization of the reaction mixture by HCl, which would lead to a chloride polyelectrolyte. Changing the anion has been employed to control solubility of the polyelectrolyte[4] and to demonstrate the novel possibility of using the evolved acid as the doping agent, obviating the need for an additional doping step.[13,14] If, on elimination, no reaction of polymer with anion is observed, the tacit assumption has been that the role of the anion in the elimination is passive. Since the anion is a key and easily accessible variable in PAV synthesis, we were interested in exploring the effect of changing the anion on elimination conditions and on the conductivity of the final doped polymer.

Scheme I



Experimental Section

Poly(xylylidenetetrahydrothiophenium chloride) (PXT Cl) precursor to poly(phenylenevinylene) was prepared according to previously published procedures.[12] The chloride ion in the precursor was exchanged with bromide, fluoride, iodide, or acetate by dialyzing the chloride polyelectrolyte against a large excess of the exchanging ion (0.1 M, sodium salt) with 3500 molecular weight cutoff dialysis tubing. The exchanged polymer was then dialyzed against 18 MΩ deionized distilled water. Complete replacement (>95%) of chloride was verified by elemental analysis for chlorine performed on cast films of the precursor (Galbraith Laboratories). The iodide polymer precipitated during exchange and was thus not used to make films. Films of ca. 10-μm thickness were cast under vacuum onto silanized glass. Precursor polymers were eliminated at 250 °C under dynamic vacuum.

Thermal gravimetric analysis (TGA) of precursors was performed under nitrogen with a Dupont 2100 thermal analysis system on samples weighing ca. 7 mg, using a temperature program of 30–500 °C at 10 °C min^{-1}. On-line infrared vapor phase spectroscopy of the products from elimination was performed on

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a Dupont TGA system connected to a Nicolet 720 FTIR through a Nicolet TGA interface. Transmission infrared spectra of precursor and eliminated films were collected with a Nicolet 520 FTIR. Electron impact (70 eV) mass spectra of elimination products were recorded on a Finnigan 4510 mass spectrometer fitted with an insertion probe wherein polymers were loaded and heated at 10 °C min^{-1}. Solid-state ^{13}C CP MAS NMR were acquired with a Bruker WP200SY spectrometer using a spinning rate of 3.2 kHz.

In situ conductivity was measured by using the four-probe technique. Samples of dimension ca. 2 mm × 10 mm × 0.01 mm were attached to 0.27-mm Pt wires with carbon paint (Electrodag 502, Acheson Colloids) and were exposed to concentrated H_2SO_4 in Teflon-sealed vessels. A potential of 50 mV, supplied by a General Resistance E-35 voltage reference source, was applied to the outer two wires. Current was measured with Keithley 197 multimeter in series, and voltage drop across the inner two wires was recorded with a Keithley 617 electrometer. The minimum measurable electronic conductivity, limited by the parallel ionic conductivity of the sulfuric acid, was ca. 2 Ω^{-1} cm^{-1}.

For solution elimination studies, 20 mL of aqueous precursor solution was placed in a glass jar (sealed to prevent escape of volatile acids) which was then maintained at 70° C in a silicone oil bath for up to 100 h. For pH measurements solutions were allowed to cool to room temperature and pH measured with a freshly calibrated Corning 250 ion analyzer. UV-vis spectra on solutions heated at 70 °C for 100 h were recorded with a Cary 14 spectrometer.

Results and Discussion

(1) Ion Exchange. In the past, the identity of the anion in the polyelectrolyte precursor has been determined by the choice of monomer, or by precipitating the water-soluble polymer with an ion that forms a water-insoluble product. The latter approach was used to prepare tetrafluoroborate PPV precursor, which, unlike its chloride counterpart, is soluble in a wide range of organic solvents, including those used in gel permeation chromatography.[4] The precipitation technique was employed by Stenger-Smith et al., who examined SbF_6^-, ClO_4^-, $Fe(CN)_6^{3-}$, PF_6^-, BF_4^-, and tosylate-containing PPV precursor.[15] We found that spontaneous room temperature elimination appeared to be accelerated on precipitation, in that redissolved polymers were yellower. Also, several additional precipitation/dissolution steps are needed to remove excess counterion.

In comparing the elimination of precursors, we wished to rule out any effects that an ion might have on molecular weight or structure during synthesis. Our dialysis technique, which avoids precipitation, allowed us to obtain a water-soluble precursor with different counterions starting from the same batch of chloride polyelectrolyte. Ion-exchange proceeded smoothly with fluoride, chloride, bromide, and acetate, whereas the iodide precursor precipitated. Attempts to exchange hydroxide ion led to premature room-temperature elimination and precipitation of polymer. We also prepared "copolymers" containing two anions in varying proportion by mixing pure exchanged polymer solution in the appropriate ratios. This was considered preferable to performing the original exchange with a mixture of ions, since it is not certain that the ions will be incorporated in the same ratio present in solution.

Our selection of anions did not include any fluorine-containing species, such as PF_6^-, BF_4^-, and AsF_6^-, since these are prone to decomposition at high temperature. Precursors containing these turn black upon heating, due to protonic acid type doping by the evolved acid[13,14] or anion decomposition. Our films were always pale straw-yellow after elimination.

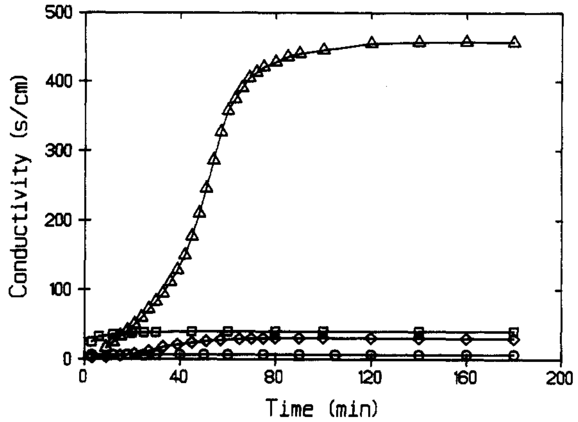


Figure 1. In situ conductivity of eliminated PXT's doped with sulfuric acid: (□) PXT fluoride; (△) PXT chloride; (◇) PXT bromide; (○) PXT acetate.

(2) In Situ Sulfuric Acid Doping. The utility of strong, nonoxidizing protonic acids in doping conductive polymers has been known for some time, and both polyacetylene and PPV have been doped in this way.[16,17] Han and Elsenbaumer recently pointed out the general applicability of protonic acid doping of conductive polymers.[18] Although the mechanism of doping remains unclear, it is well established that protonic acid doping is rapid, reproducible, and yields materials with purely electronic conductivities equal to, or greater than, values that can be obtained by oxidizing agents (such as I_2 or AsF_5). While an oxidizing mechanism can be proposed for sulfuric acid doping, it is more likely that the strong doping tendencies are due to the low pK_a.[18]

The apparatus used herein permits in situ monitoring of the conductivity of eliminated films as they are being doped by sulfuric acid. The conductivity is electronic as long as the measured resistance is less than the parallel ionic resistance of the acid between the platinum wire contacts. For samples of the dimensions we were using, this limited the lowest measurable electronic conductivity to about 2 Ω^{-1} cm^{-1}. For all anions doping was rapid (Figure 1) and a plateau in conductivity was reached within about an hour. Figure 1 shows that the limiting conductivity is highly stable with respect to time, in contrast[19] to PPV doped by AsF_5. Conductivities are stable even in air, as long as the polymer remains wetted by the acid. The large differences in conductivity between chloride and bromide were unexpected, in view of the close similarity in composition of the eliminated films, as revealed by IR. The low ultimate conductivity of the acetate sample can be rationalized in terms of incomplete elimination at the temperatures used (250 °C). There does not seem to be any correlation between speed of doping and limiting conductivity, since the fluoride film doped much more quickly than the bromide film, yet the latter had a lower conductivity.

(3) Solution Elimination. Solutions of precursor polyelectrolyte to PAV's are known to undergo slow elimination on standing at room temperature, limiting the shelf life of these materials. Whereas elimination conditions for cast films of PAV's have been studied and optimized, little is known about the kinetics of elimination of PAV precursors when they are in dilute solution. The release of one proton for every double bond formed in the polymer backbone provides a convenient opportunity for determination of the average degree of elimination along the polymer backbone: pH electrodes are highly selective toward protons.

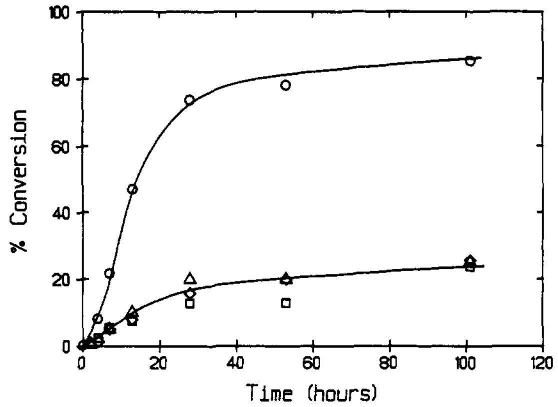


Figure 2. Percent conversion vs time, calculated from measured pH, for aqueous solutions of PXT's maintained at 70 °C: (□) PXT fluoride; (◇) PXT chloride; (△) PXT bromide; (○) PXT acetate.

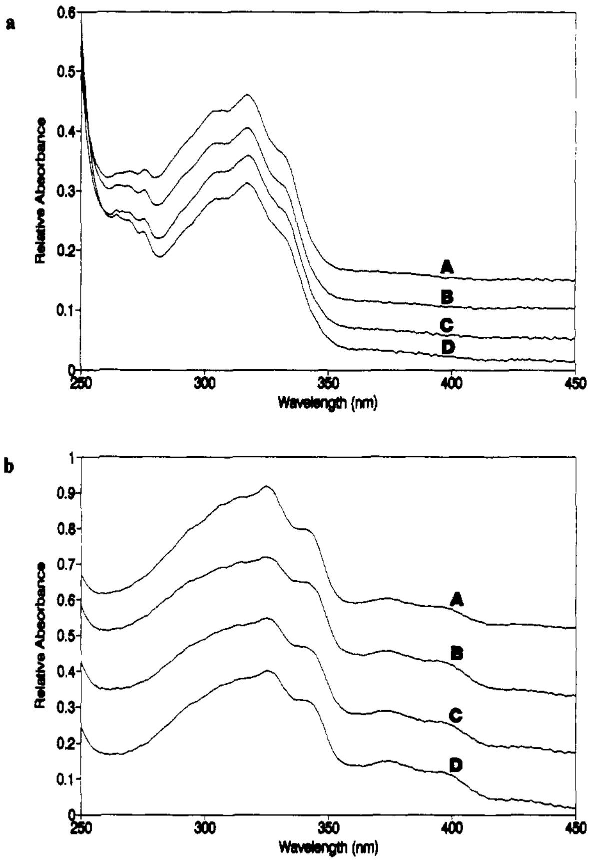


Figure 3. UV-vis spectroscopy of solutions of PXT's before elimination (a) and 100 h at 70 °C (b): A, PXT acetate; B, PXT fluoride; C, PXT chloride; D, PXT bromide.

The concentration of the ion-exchanged polymers employed in the present study was about 0.25 wt % in water. Solutions were used immediately after dialysis to prevent premature buildup of protons. The pH, measured at room temperature, was converted to percent elimination, assuming, initially, that the polyelectrolyte was completely dissociated. Results for the solutions containing weak acids—HF and CH_3COOH—were corrected for association using their room temperature pK_a's. Figure 2 shows that the apparent rates of solution elimination for the halide ions are all approximately the same, whereas the actetate ion seemed to eliminate much more rapidly, in apparent disagreement with our findings for elimination of acetate-containing films (vide infra). However, any association of acetate ion with polyelectrolyte molecules would lead us to overestimate the degree of elimination. In order to verify the relative degrees of elimination of different polyelectrolytes we performed UV-vis absorbance spectroscopy on samples before and after elimination at 70 °C for 100 h. Studies on films have shown that elimination of PAV's causes a red shift due to increasing conjugation lengths, as documented by Gagnon et al.[20] and others.[21] Figure 3a, which depicts UV-vis spectra of PXT's before elimination, shows a peak with a low energy edge at 350 nm, corresponding to uneliminated material.[20] Upon warming, spectral features with an edge of 410 nm evolve (Figure 3b). This spectrum may be identified as belonging to "partially eliminated" PPV.[20] In an observation that has been made previously, rather than a monotonic shift in the peak wavelength, one sees a relative growth and decrease in the peaks centered at 375 and 325 nm, respectively, suggesting that elimination occurs in blocks, rather than randomly. In the case of the halides, we are able to assign a degree of elimination of 25% from our pH results. The acetate polymer has clearly undergone less elimination than the halides, and if we assume that the relative peak heights are a measure of the degree of elimination, we can estimate a true value of 17% for the acetate polymer, considerably less than would be deduced from Figure 2. Thus, ion association occurs in the acetate polymer. Using the following equilibria:

$$Ac^- + H^+ = HAc$$

$$K_a = \frac{[H^+][Ac^-]}{[HAc]} = 1.8 \times 10^{-5}$$

$$P^+ + Ac^- = PAc$$

$$K_f = \frac{[PAc]}{[P^+][Ac^-]}$$

where Ac^- is acetate ion, P^+ is dissociated polyelectrolyte, and PAc is associated polymer, we calculate a formation constant (K_f) for PXT acetate of 7.7×10^3 mol^{-1} L^{-1}, implying 81% of the polymer exists in associated, or ion-paired, form. Since HCl is a strong acid, ion pairing of Cl^- with polymer will not affect the measured H^+ concentration.

(4) Thermal Elimination of Films: Analysis of Films. The progress of elimination of cast films of the various PXT electrolytes was followed with TGA, as shown in Figure 4. As criteria for "optimum" elimination of these materials, we specified that the elimination should proceed in one step and at as low a temperature as possible. These goals were determined in response to the trend that had been observed when dimethyl sulfide was replaced with tetrahydrothiophene (THT) whereupon a lower elimination temperature and more complete elimination was observed.[12] The results in Figure 4 illustrate that the elimination temperature is a strong function of anion. The PXT halides appear to be fully eliminated by 200 °C, if small transitions around 425 °C for bromide and fluoride are discounted. PXT acetate clearly requires significantly higher temperatures, since the last weight loss is not complete until 350 °C. Thus, PXT acetate will suffer from the same type of side reactions that are presumed to limit the cleanness of elimination in the dimethyl sulfide precursor.[22] Following our criteria, it would seem that the halides should yield equivalent material, with bromide giving polymer that can be doped to the highest conductivities, since it appears to eliminate in one step at the lowest temperature. As seen from the in situ doping studies

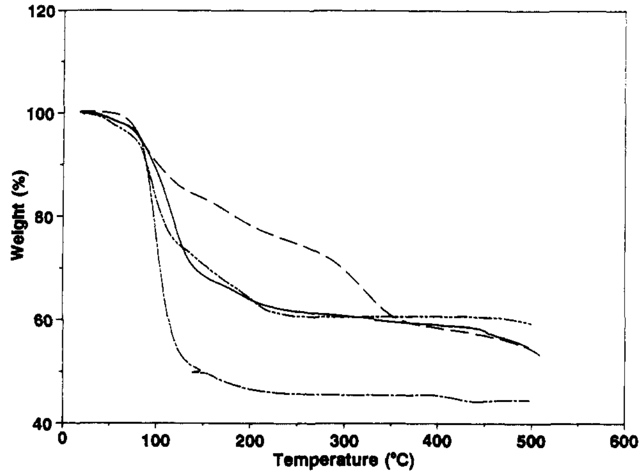


Figure 4. Thermal gravimetric analysis of PXT films under a nitrogen atmosphere (heating rate of 10 °C min^{-1}): (—) PXT fluoride; (- - -) PXT chloride; (- -) PXT bromide; (- -) PXT acetate.

above, this is not the case. It may well be that the small features observed at high temperatures (425 °C), not seen for PXT chloride, represent residual decomposition reactions which lead to chain branching or backbone saturation, rather than elimination. For polymers having high conductivities (greater than 100 Ω^{-1} cm^{-1}) a marked decrease is conductivity is seen with the introduction of small numbers of defects along the polymer chain.[23]

In order to reveal differences in structure and mechanism that would yield polymers with varying doped conductivity, transmission IR spectra of eliminated and uneliminated films were recorded. These are depicted in Figure 5. Assignments of vibrational bands are made following Bradley.[24,25] In the uneliminated films, band are seen at 2941 and 666 cm^{-1}, due to CH_2 and C–S stretching, respectively. Eliminated films show the appearance of characteristic strong bands at 965 and 838 cm^{-1} corresponding to the *trans*-vinylene CH out-of-plane bend and the *p*-phenylene out-of-plane ring bend, in addition to the *trans*-vinylene CH stretch at 3024 cm^{-1}. Chloride and bromide PXT films show large water peaks at ca. 3300 cm^{-1} (absent in the eliminated polymer), and acetate PXT contains no water. These spectra were typically recorded after about 10 min in the dry nitrogen purge environment of the spectrometer. Although fluoride PXT exhibited a water band in the usual position immediately after mounting in the spectrometer, after a short time, the precursor spectrum corresponded to the one given in Figure 5a. The fluoride PXT spectrum shown contains some very unusual features in the range 2200–2600 cm^{-1}, and a broad peak at 1792 cm^{-1} is also seen. We believe that these features are derived from water which is very strongly hydrogen bonded to HF, evolved as a result of room-temperature elimination. From the prominence of the 965 and 838 cm^{-1} bands it may be deduced that PXT fluoride precursor has undergone more elimination at room temperature than the other PXT's.

There are some additional puzzling aspects concerning the IR spectrum of the eliminated fluoride polymer, shown in Figure 5a. While the number and positions of the bands in the PXT fluoride are the same as in the other PXT halides, the intensity of the peak at 1595 cm^{-1} is considerably enhanced in the former. If hydrofluorination of vinylene bonds were occurring, one would expect to see additional strong bands between 1000 and 1400 cm^{-1} due to C–F and at ca. 2950 cm^{-1} from saturated C–H. The lack of new bands indicates the absence of new structures.

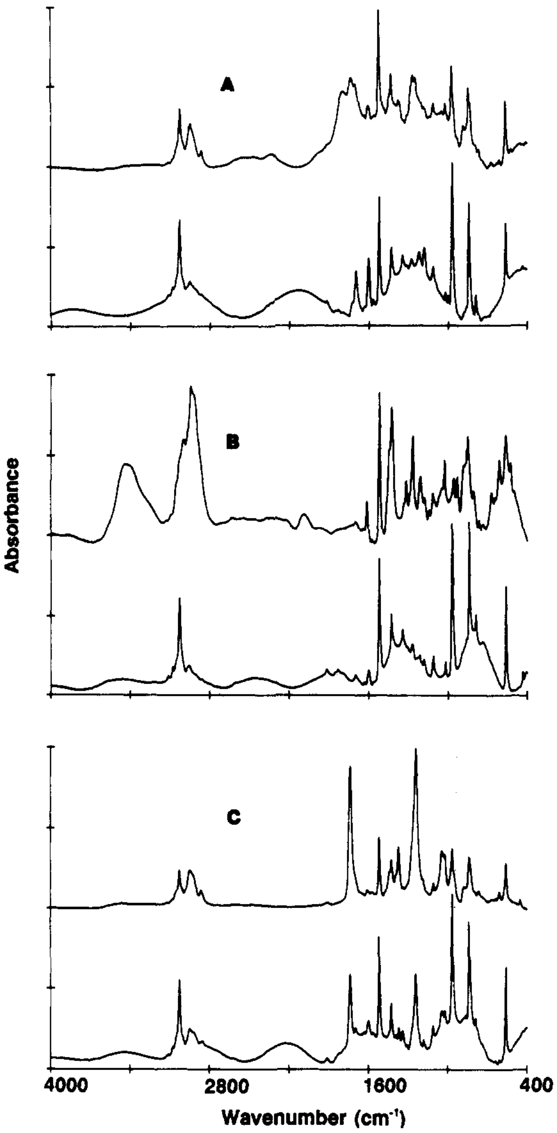


Figure 5. Transmission infrared spectra of films of PXT fluoride (A); PXT bromide (B); and PXT acetate (C). The top spectrum of each pair was taken before elimination, and the bottom spectrum, after elimination at 250 °C. Corresponding spectra for PXT chloride before elimination are depicted in Figure 10. The spectrum of eliminated PXT chloride was indistinguishable from that of eliminated PXT bromide.

According to Bradley,[24] the 1595-cm^{-1} band can be attributed to "quadrant" ring stretching and is expected to be infrared inactive for symmetrically substituted *p*-phenylene. The enhancement of this peak may be due, therefore, to symmetry breaking, the mechanism of which is unclear.

The IR spectra of the PXT acetate shows clear evidence of incomplete elimination, with a strong band at 1736 cm^{-1} due to C=O remaining in the polymer after thermal treatment. The solid-state ^{13}C CP MAS NMR of eliminated chloride and acetate PXT's (Figure 6) shows resonances at 165 ppm and 16 ppm, from residual C=O and CH_3 carbons, respectively. From the literature[26] the peak at 133 ppm is assigned to 1,4-phenyl carbons, and the peak at 124 ppm contains unresolved 2,3-phenyl and vinylene carbons.

(5) Analysis of Products of Elimination. Products of the elimination shown in Scheme I are expected to include small, volatile molecules. The identity of these products would suggest possible mechanisms of elimination. In the present work one would expect, at a minimum,

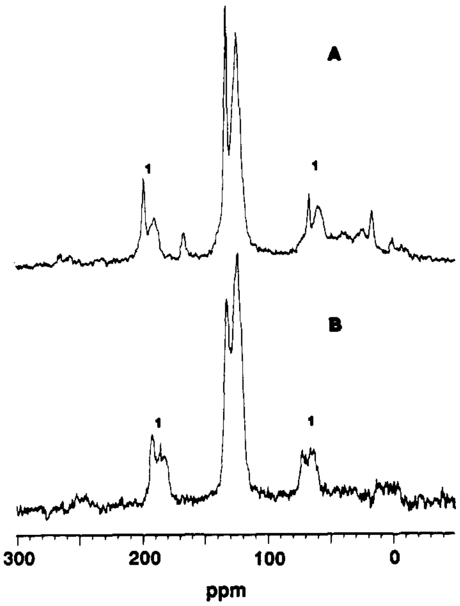


Figure 6. Solid-state ^{13}C CP MAS NMR spectra of eliminated PXT acetate (A); and PXT chloride (B). "1" indicates sidebands.

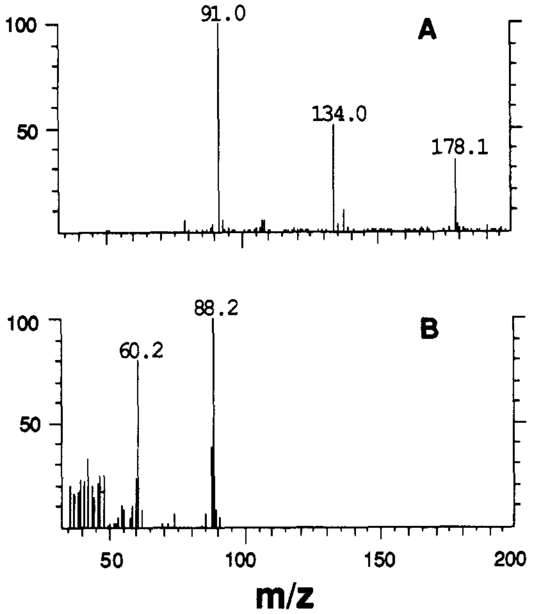


Figure 7. Mass spectra (relative intensity vs mass/change) of the products of elimination for PXT acetate (A); and PXT chloride (B), for films heated at 40 °C.

tetrahydrothiophene, and the acid corresponding to the anion used, if the thermal conversion of precursor to final polymer occurred as depicted. Mass spectrometric (MS) determination of volatile products has been performed by Montaudo et al.[27] and Gagnon et al.[20] on the dimethylsulfonium precursor to PPV. MS measurements on the elimination products of tetrahydrothiophenium precursor are shown in Figure 7 for the chloride and acetate PXT's. The data, recorded at a temperature in the range of the first weight loss, suggest a highly complex mixture of products, as was also observed for the dimethylsufonium precursor. One observes, for the chloride precursor, m/z peaks corresponding to C_2H_4S (60 m/z) and THT (88 m/z). Water and HCl are below the range attainable with our equipment. The identity of PXT acetate products seemed to be quite removed from acetic acid (m/z = 60), m/z peaks at 91, 134, and 178 are seen, corresponding possibly to CH_3CO_2S, $CH_3CO_2SCOCH_3$, and $(CH_3CO_2)_2(CH_2)_2S$.

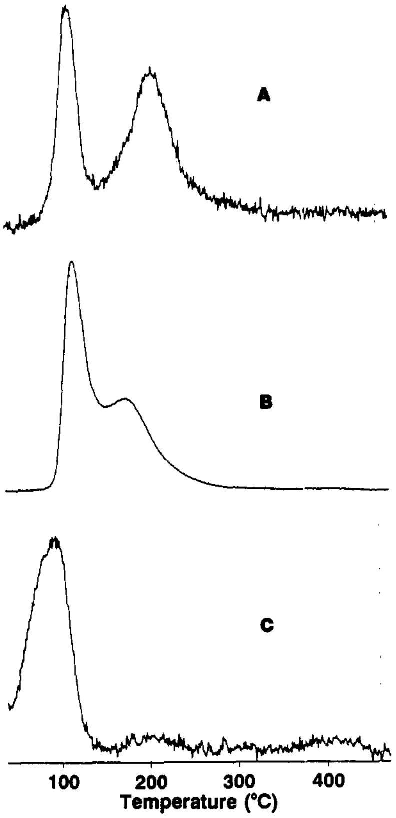


Figure 8. TG–IR of the products of elimination of PXT chloride, showing the relative abundance of HCl (A); THT (B); and water (C), as a function of temperature (heating rate of 10 °C min^{-1}, nitrogen carrier gas).

The MS results would indicate a much greater degree of complexity in elimination than implied by Scheme I. However, we were not able to differentiate between complexity due to elimination chemistry, and complexity resulting from the ionization process in the mass spectrometer. It is quite possible that the majority of species observed in the m/z data are either fragments of thiophene and acid produced by electron impact, or larger molecules resulting from gas-phase chemistry of reactive ions.

As a nondestructive technique for analysis of elimination products TGA interfaced to FTIR was employed. The interface passes volatiles though a heated transfer line to a heated IR gas cell. Spectra were compared to library spectra (Aldrich, vapor phase) for identification. No components other than thiophene, water, and acid were detected. These elimination products are spectrally distinct such that regions unique to each can be selected. The relative amount of each component can then be determined as a function of temperature, as shown in Figures 8 and 9 for PXT chloride and PXT acetate, respectively. The spectral regions selected for each compound were tetrahydrothiophene, 2950–2970 cm^{-1}, water, 3730–3750 cm^{-1}, HCl, 2823–2816 cm^{-1}; and acetic acid, 1780–1800 cm^{-1}. The TG–IR data correlates well to the major weight loss regions in Figure 4. Implications of this data regarding possible elimination mechanisms are discussed below. However, the overall reaction appears to be represented well by Scheme I with no further complications, in contrast to the conclusions drawn from the MS data.

(6) Evidence for H Bonding. Films of PXT precursor, cast from aqueous solution, are known to contain significant quantities of water, which is evolved on elimination. Water is thought to be responsible for "plasticizing" the polymer, facilitating reorganization and molecular align-

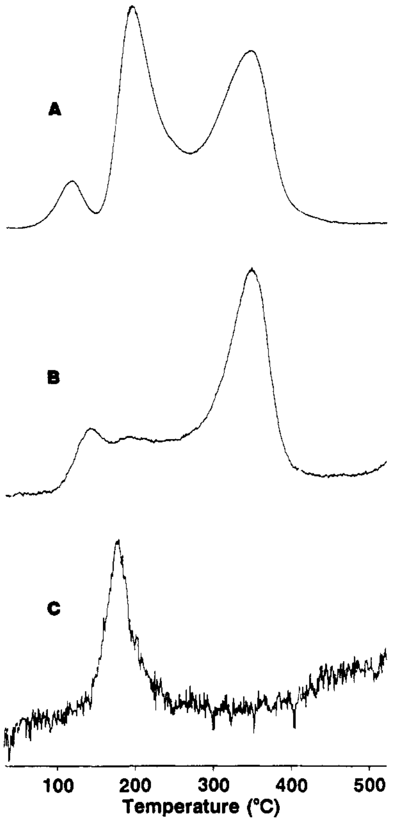


Figure 9. TG–IR of the products of elimination of PXT acetate: acetic acid (A); THT (B); water (C).

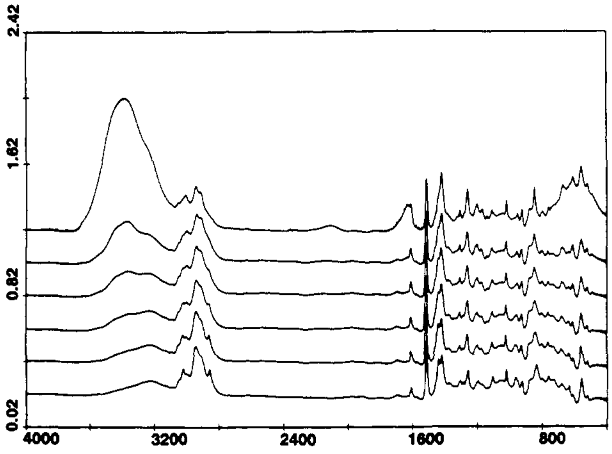


Figure 10. Transmission IR spectra of PXT chloride film, taken while the polymer remains in the nitrogen purge environment of the spectrometer: top curve, after $t = 0$ min; bottom curve, $t = 120$ min.

ment during stretch–orientation.[24] In the course of our studies on ion-exchanged precursors we acquired several pieces of evidence suggesting the occurrence of hydrogen-bonding, involving water and other species, in these materials. Since we believe water plays a critical role in the elimination mechanism, we detail our observations in the following.

Transmission infrared spectra of cast films of PXT chloride indicated loss of occluded water as films were allowed to stand in the dry nitrogen purge environment: Figure 10 shows a clear decrease in the O-H stretching band at ca. 3400 cm^{-1}. However, a residual signal in the same region remained and could not be removed, even on extended exposure to dry nitrogen (Figure 10, bottom spectrum). Closer inspection of Figure 10 reveals that the water band is composed of two components, a large one centered at 3390 cm^{-1}, and a smaller one at 3243 cm^{-1}. The 3234-cm^{-1} band is the one that cannot be removed on drying. We attribute this band to water hydrogen bonded to the phenylene ring or associated with the sulfonium group as water of hydration. Concurrent with the drying, two new peaks evolve at 2860 and 1440 cm^{-1}. These new features are not a result of elimination, since the 965 and 838 cm^{-1} vibrations do not evolve on drying over this time scale. The new bands may be due to the interaction of backbone methylene C–H stretching and bending with H-bonded water. Very recent studies on sulfonated calixarene molecules, which contain four phenyl rings and show some compositional similarities with PXT's, have provided direct crystallographic evidence for hydrogen bonding between water and aromatic π electrons in the solid state.[28]

Table I
Dependence of the C═O Stretching Frequency in PXT Chloride/Acetate Precursors as a Function of Composition

CH_3COO:Cl in PPV precursor	frequency, cm^{-1}
100:0	1735.8
80:20	1734.2
50:50	1731.6
20:80	1730.0

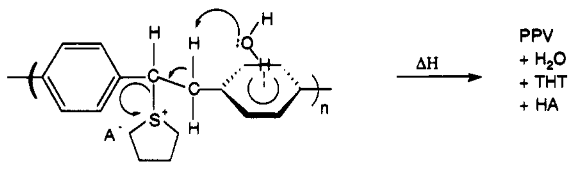
Not all of the precursors contained water. The IR spectrum of the PXT acetate (Figure 5c) showed no detectable concentration of water. Infrared spectra of "copolymers" of chloride and acetate PXT show a red shift in the C═O stretching frequency as chloride content increases (Table I). While this could be due to interaction between acetates, it is more likely that the water introduced into the polymer by the addition of chloride, observed in the IR spectra (not shown), hydrogen bonds with C═O. Finally, the traces of water that were detected in the acetate PXT by TG–IR (Figure 9) evolve at a temperature 90 degrees higher than the water in the chloride precursor, suggesting stronger hydrogen bonding (of water to acetate) in the former.

(7) Mechanism. The elimination of the dimethyl sulfonium precursor to PPV has been shown to follow two routes.[20,27] The first is the process represented by Scheme I, which takes place at low temperature (100–150 °C). A second path involves nucleophilic attack of the counterion on a sulfonium methyl group to form a thio ether, which occurs over an intermediate temperature range (150–250 °C). Heat treatment at higher temperatures leads to elimination of this intermediate and is characterized by a weight loss at about 350 °C.

The results obtained here for THT precursors suggest that, for the halides, elimination takes place at lower temperature and is essentially complete by 200 °C. No intermediate weight loss at 350 °C is observed, in contrast to the behavior of the PXT acetate. TG–IR studies suggest a simple elimination path according to Scheme I, whereas MS indicates further breakdown of reaction products. To determine whether it might be possible that THF and the evolved acid exhibit some unforeseen chemistry following elimination we refluxed acetic acid and thiophene in an aqueous solution. No reaction was seen by ^{1}H NMR.

The detailed mechanism has been presumed to be E1cB[17]—in the present case, a carbanion is created on a vinylene carbon β to the THT, and elimination of THT follows.[29] While the stability of the intermediate carbanion in such a mechanism would certainly be high, due to the adjacent phenyl ring, it is difficult to distinguish between E2 and E1cB mechanisms.[29] Anti E2 elimination would lead to the trans stereochemistry that is clearly

Scheme II



apparent in PPV, whereas E1cB would not necesarily yield the trans polymer if the intermediate carbanion were long-lived. Figure 8 shows that water coevolves with the major loss of THT and HCl in the chloride precursor. At higher temperature, a second weight loss occurs in the absence of water (Figure 8). It is possible that water catalyzes the elimination according to the E2 mechanism in Scheme II where the water is drawn as hydrogen bonded to the phenyl ring, consistent with the findings of Atwood et al.[28] The acetate polymer eliminates at higher temperature, as seen in Figures 4 and 9. The very small amount of water present does not appear to correlate well with any weight loss. The hydrophobic nature of the acetate PXT is illustrated by the absence of a clear water band in the transmission IR (Figure 5c). We believe that the difference in behavior of the acetate PXT cannot be explained in terms of a difference in basicity of the anion, since fluoride PXT showed the same solution elimination kinetics and similar TGA as the other halides and HF and CH_3COOH are both weak acids. Furthermore, any argument founded on differences in basicity and nucleophilicity must be reconciled with the finding that the rates for the halides are similar, whereas the order of nucleophilicity is $Br^- > Cl^- > F^-$ (in protic solvents[29]) and of basicity is $F^- > Cl^- > Br^-$. It is possible that the relatively large acetate (organic) anion forms a hydrophobic environment for the phenyl ring, preventing hydrogen bonding in the film, and preventing the close approach of water molecules in solution. Association of acetate ion with the polymer in solution was demonstrated above. An apparent dichotomy to the above reasoning is that acetate, being a stronger base than water, should speed up the elimination. It may be that acetate associated with tetrahydrothiophenium has a lower basicity.

TGA performed on PXT containing a mixture of chloride and acetate resembled TGA of pure PXT chloride, showing a weight loss at temperatures greater than 200 °C only for acetate/chloride ratios of more than 1:1. Water retained by the chloride segments thus appears to facilitate elimination of acetate segments.

Conclusions

The choice of anion is an important consideration in preparing precursors for poly(phenylenevinylene), and, presumably, other poly(arylenevinylenes). Of the anions investigated chloride appears to be best suited to the production of material which has high electronic conductivity when doped. Doping by sulfuric acid is rapid, reproducible, and yields very stable limiting conductivities. Thermal analysis results indicate that in choosing the best anion, the precursor that eliminates at the lowest temperature with the fewest weight losses does not necessarily lead to a polymer with the highest conductivity. It is probably more important to see a complete absence of residual weight loss at higher temperatures. There is ample evidence for hydrogen bonding in the aromatic polyelectrolyte precursor, which might be a good model for some biological systems. Thermal conversion proceeds to yield simple products with elimination of tetrahydrothiophene and acid, possibly described by an E2 mechanism, and occurs at lower temperatures when accompanied by the evolution of water.

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