Synthesis, doping, and electrical conductivity of high molecular weight poly(*p*-phenylene vinylene)

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High molecular weight poly(*p*-phenylene vinylene) (PPV) has been synthesized starting from the monomer *p*-xylylene-*bis*(dimethylsulphonium chloride). The latter was polymerized to yield a water-soluble sulphonium salt polyelectrolyte, which was converted to PPV by the thermal elimination of $(CH_3)_2S$ and HCl from films cast from aqueous solution. The elimination reaction was studied by elemental analysis and by thermogravimetric analysis and mass spectrometry. The PPV films had good mechanical properties and could be n- and p-doped to yield material with electrical conductivities approaching those of highly doped polyacetylene. The degree of conversion of the intermediate polyelectrolyte to PPV could be controlled and the conductivities of these doped films could be related to the average conjugation length.

(Keywords: poly(*p*-phenylene vinylene); synthesis; doping; electrical conductivity)

INTRODUCTION

Poly(*p*-phenylene vinylene), PPV, has been shown to be a good electrical conductor[1] after being reacted with a strong oxidizing agent ('doping'). However, direct attempts to synthesize high molecular weight PPV by conventional polymerization reactions, such as a Wittig reaction of *p*-xylene *bis*(triphenylphosphonium chloride) with terephthalaldehyde or the dehydrohalogenation of *p*-xylylidene dihalides, have resulted only in the formation of oligomers. These powdered oligomers when pressed into pellets could be doped to yield a limiting electronic conductivity of $1\,\mathrm{S\,cm^{-1}}$.[2] The resistance of a pressed powder includes not only that of the material itself but also that associated with the grain–grain interface. For this reason it is desirable to investigate continuous substrates, preferably films, to obtain information regarding the inherent conductivity and charge transport properties in such materials.

The difficulty in attaining samples of high molecular weight is common to all polymerization reactions that form conjugated polymers because of the premature precipitation of the insoluble unsaturated oligomers. A method to circumvent this problem is through the synthesis of a soluble, polymeric precursor, which can be cast into film form and subsequently converted by thermal or chemical means to yield the desired conjugated polymer. Early attempts by Kanbe and Okawara to synthesize a saturated α-substituted poly(*p*-xylylidene) by the polymerization of *p*-xylylene-*bis*(dimethylsulphonium tetrafluoroborate) resulted in the formation of an insoluble oligomeric PPV[3]. However, similar investigations by Wessling and Zimmerman involving the polymerizations of several *bis*-sulphonium salts yielded high molecular weight, water-soluble polyelectrolytes, which when treated with excess base or when exposed to elevated temperatures in solid form generated PPV directly as fibres, coatings and foams with good mechanical properties[4].

Recently this route has been successfully employed by us[10,11] and by Murase *et al.*[5] to obtain high molecular weight films of PPV, which can be used in studies of conducting polymers. This concept is thus similar to the formation of polyacetylene films, which begins with the synthesis by metathesis of the precursor poly(5,6-*bis*(trifluoromethyl)-bicyclo(2,2,2)-octa-5,7-diene-2,3-diyl) 1-2-ethene diyl), followed by the thermal elimination of 1,2-*bis*(trifluoromethyl)benzene, developed by Edwards and Feast[6]. The latter were able thereby to obtain continuous, orientable films of polyacetylene in contrast to the typical polyacetylene with random fibrillar morphology obtained by the Shirakawa route[7].

The synthetic strategy employed in this study (also used for poly(1,4-naphthalene vinylene)[10] is described for poly(*p*-phenylene vinylene) in *Figure 1*. The versatility of the polymerization of the *bis*-sulphonium salt monomer, **I**, to form the precursor polymer, **II**, and its subsequent thermal conversion also permits the synthesis of many other substituted derivatives and analogues of PPV. Substitution on the phenylene ring of the monomer with groups differing electronegativity changes the electron density along the PPV backbone and thus alters the chemical reactivity, including the reactivity with dopants and the environmental stability of the doped polymer. Substitution with groups of constant electronegativity but with differing size changes the intermolecular packing distances and also significantly alters the conductivity and processability. The results of such studies have been published elsewhere[8-10].

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Another important feature of the precursor route is that during the thermal elimination of $(CH_3)_2S$ and HCl in the third step of the reaction, *Figure 1*, the precursor film can be stretched up to 15 times its initial length. X-ray and electron diffraction studies on these films show the presence of extremely high molecular orientation and have permitted the determination of the parameters of the paracrystalline unit cell[11]. The conductivity of doped, oriented PPV films increases dramatically with increasing draw ratio parallel to the orientation direction, but remains either nearly constant or decreases slightly perpendicular to the orientation direction[12,13]. The ability to prepare a conducting polymer with well characterized, variable degrees of uniform orientation is an important advance in obtaining an understanding of charge transport, which is also currently under investigation in this laboratory.

In the present study the synthetic method of Wessling and co-workers for the preparation of PPV has been extended to include a study of the electrical conductivity of doped high molecular weight PPV films. We report here on the optimized conditions for the synthesis of the monomer and the polyelectrolyte precursor and on thermogravimetric–mass spectral analyses of the thermal elimination of the precursor to PPV. Conductivity measurements were made for both p- and n-doped PPV films, and conductivity as a function of conversion of the polyelectrolyte to PPV was determined.

EXPERIMENTAL

Synthesis of the monomer, *p*-xylylene-*bis*(dimethylsulphonium chloride), **I**, was achieved by reacting α,α'-dichloro-*p*-xylylene at a concentration of 0.75 M with excess dimethyl sulphide (2.25 M) at 50°C in a methanol: water (80:20) solution for 20 h. This monomer was purified by concentrating the reaction solution, precipitating the product in cold acetone (0°C), filtration and extensive vacuum drying.

The polymerization reaction to form the poly(*p*-xylylene-α-dimethylsulphonium chloride) precursor, **II**, was effected in aqueous solution by the reaction of the monomer with an equimolar quantity of sodium hydroxide (0.2 M) at 0°C for 1 h under rigorous anaerobic conditions. The reaction was quenched by neutralization with 1 M HCl to a slightly acidic pH, 6.8, which yielded a highly viscous solution. The polyelectrolyte was separated from residual monomer and NaOH by dialysis against deionized water for 3 days. The dialysis tubing, Speta/Por 3, has a reported lower-limit molecular weight cut-off of 3500 Da.

The polyelectrolyte, **II**, was wet cast into free-standing films by evaporation of water at or below ambient temperatures. The resulting polymer film was clear and could be redissolved in polar solvents. The solution could also be processed to yield foams or fibres. Simple heating of the polyelectrolyte film resulted in an E1cB elimination of the substituent, yielding a yellow, free-standing film of PPV. The length of time and the temperature at which the film was annealed could be varied to control the extent of this elimination and hence the amount of unsaturation induced in the polymer. To obtain maximum elimination the films were annealed at temperatures greater than 380°C for more than two hours. Alternative protocols yielded differing products. For example, when the clear precursor films were exposed to rapid heating by immersion in a fluidized sand bath at 220°C they expanded by approximately 400% to form an open-celled, flexible foam. In a similar manner, if the polyelectrolyte film was uniaxially stressed when exposed to rapid heating, the material underwent an elongation of up to 15 times its initial length to yield a tough, flexible material.

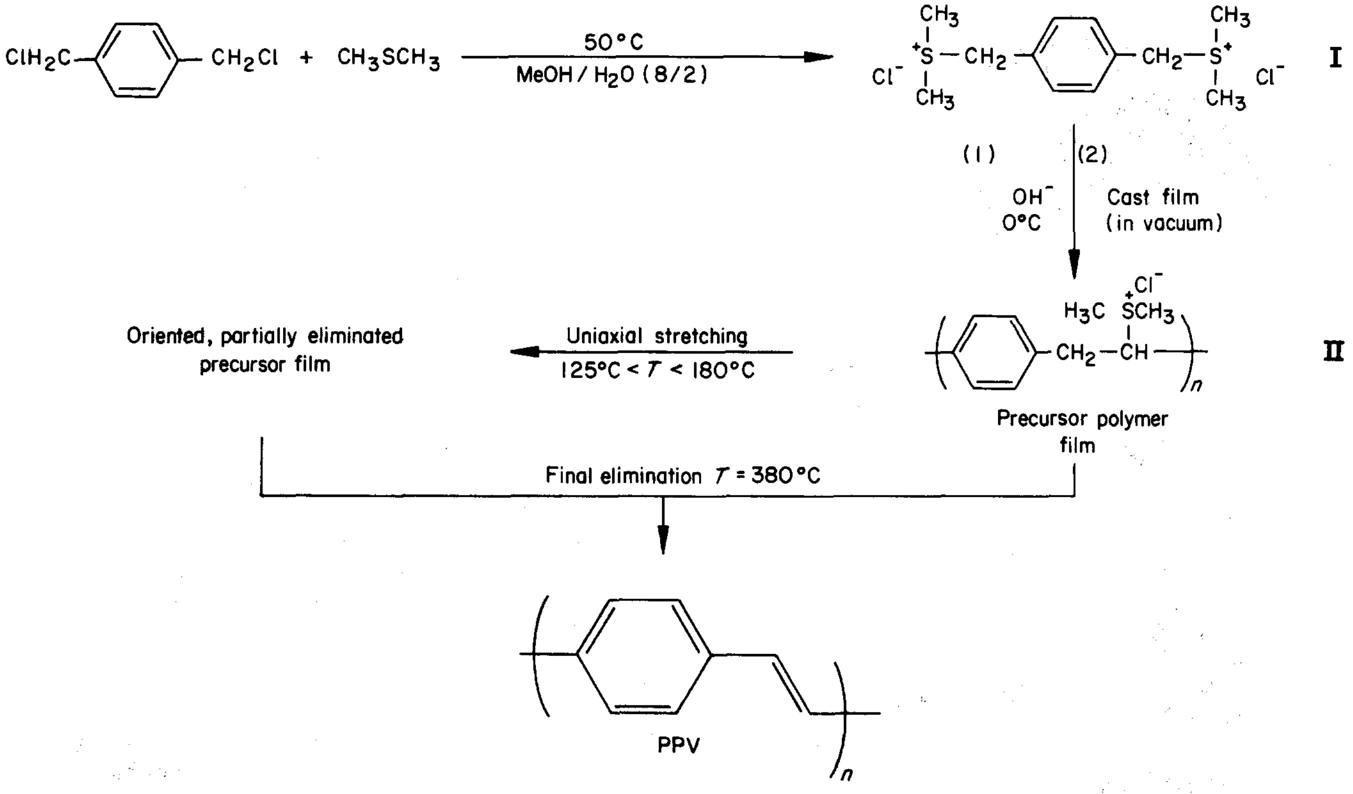


Figure 1 Synthesis and processing scheme of PPV

Doping of the polymers was accomplished by mounting the samples across four platinum electrodes with a conductive adhesive (Electrodag 502) and by using vacuum line techniques, with vacuums of 10^{-4} to 10^{-5} Torr, for degassing and vapour phase reactions[14]. P-type doping was studied by exposing the samples to AsF_5, I_2 or H_2SO_4, which had been prepurified by freeze–thaw cycles. For AsF_5, doping was achieved at a reduced pressure of approximately 200 Torr by cooling the dopant to −76°C in the cold finger of a 1 l reservoir before sample exposure. I_2 doping was attempted by both vapour-phase doping and by immersion of the sample in a degassed 2% I_2 in pentane solution. Doping with H_2SO_4 was achieved by continuous cryogenic distillation of H_2SO_4 vapour over the sample.

In all the vapour-phase doping reactions the conductivity was monitored continuously until the sample resistivity stabilized, at which point the dopant was removed by condensation in a liquid-nitrogen trap followed by sample-chamber evacuation. The dopant was then reintroduced and the resistivity again monitored. This procedure was repeated many times resulting in progressively smaller conductivity changes until no further changes were noted.

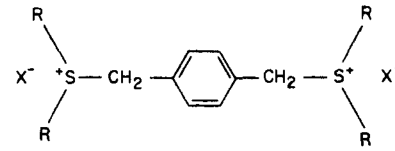
N-type doping was effected by immersing the sample in a purified solution of 1 M sodium naphthalide in THF until the resistivity stabilized. The dopant solution was removed and the sample washed by repeated distillation of pure THF into the four-probe vessel to remove excess dopant. Reference samples were included in the reaction vessel for determination of dopant weight uptake.

Some characterization of the thermal elimination reaction of the precursor polymers was achieved by using a custom t.g.a./mass spectrometer (Cahn microbalance/Granville Research Finnigan 200 Quadrupole Mass Spectrometer). These data were obtained by Systems Research Laboratories (Dayton, Ohio). The samples were heated at a scan rate of 3 K min^{-1} under an initial vacuum of about 10^{-7} Torr. Further characterization was achieved by elemental analysis, by infra-red spectroscopy (Perkin-Elmer IR-283 and IBM FT-IR30S), by ultra-violet–visible spectroscopy (Perkin-Elmer Lambda 9), by thermogravimetric analysis (Perkin-Elmer TGS-2), and by differential scanning calorimetry (Perkin-Elmer DSC-2). Molecular weight determinations were obtained by using membrane osmometry and with a sedimentation/low-angle laser light scattering technique.

RESULTS AND DISCUSSION

Synthesis and characterization

As previously mentioned, the PPV products obtained by Kanbe and Okawara from sulphonium salt monomers were oligomeric powders with a degree of polymerization of about 10. The formation of these low molecular weight products may be attributed to the elevated reaction temperatures (80°C), the use of the tetrafluoroborate counterion, and the excess concentration of base used (molar ratio of base to monomer 3:1) because the elimination reaction to form PPV, which is facilitated by both heat and base, can compete with the polymerization reaction and can impart insolubility to the polymer even at low degrees of polymerization. The success of Wessling and co-workers was primarily due to their choice of sulphonium chloride monomers and the use of low reaction temperatures (0°C) and reduced base to monomer ratios (typically equimolar), and also to the rigorous exclusion of oxygen from the polymerization reaction. The monomers studied were of the following general type



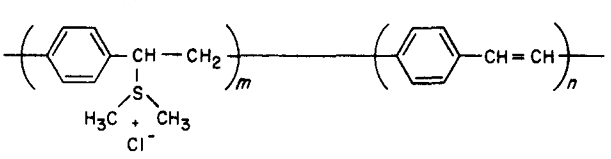
where $R = CH_3, C_2H_5, C_3H_7, C_4H_9$ and $X = Cl, Br, OH$.

The molecular weights of the polyelectrolyte intermediates obtained by Wessling were reported to be in the range from 15 kDa to 2 MDa, but more typically polymers in the range of 50 kDa to 600 kDa were obtained[4], and these could be cast into films or coatings and thermally treated to yield fibres or foams of PPV.

The polymerization system chosen here for detailed study is the monomer with $R = CH_3$, and $X = Cl$ as the counterion. The reaction of α,α′-dichloro-*p*-xylylene with dimethyl sulphide yields the monomer *p*-xylylene-*bis*(dimethylsulphonium chloride), **I**. The product obtained by Wessling and co-workers by this reaction was described as light greenish-white in colour and was obtained in moderate yields with no clear melting point. It was reported[4] to decompose at temperatures over 100°C with the liberation of $(CH_3)_2S$. In the present study the monomer was obtained in 95% yield by a slight modification of the synthesis and purification procedures and by extensive drying *in vacuo*. It was a white crystalline powder with a clearly defined melting point of 149°C–151°3. Elemental analysis confirmed the purity; the results are listed in *Table 1*.

The monomer was found to be very hygroscopic, and if not thoroughly dried was obtained as a lumpy solid with a reduced, broad melting point. The compound is relatively stable at room temperature, but after several months partial degradation was observed with the loss of $(CH_3)_2S$, indicating a slow reversal of the reaction.

The intermediate polyelectrolyte, which resulted from the reaction of **I** with sodium hydroxide in aqueous solution is in fact a copolymer of structures **II** and **III**, shown below:



II **III**

because under these polymerization conditions, some base-facilitated elimination of $(CH_3)_2S$ apparently always occurs. Thus the aqueous polyelectrolyte solution shows blue fluorescence upon u.v. irradiation, presumably because of the presence of the unsaturated structural units, **III**.

Table 1 Elemental analysis of the monomer, *p*-xylylene-*bis*(dimethylsulphonium chloride)

	Percentage (by mass)			
	%C	%H	%S	%Cl
Calc.	48.16	6.72	21.44	23.67
Found	48.16	6.92	20.91	23.71

The control of reaction temperature and concentration was found to be critical in limiting the amount of **III** formed. The standardized polymerization conditions in this study used a monomer concentration of 0.2 M and a reaction temperature of 0°C to yield a clear polyelectrolyte solution having an intrinsic viscosity of 2.5 dl g^{-1} (in H_2O:CH_3OH (80:20) solvent containing 0.05 M Na_2SO_4). Polymerization reactions at higher concentrations, for example at 0.5 M, resulted in the formation of yellow gels that could not readily be redissolved. If the reactions were effected at or above ambient temperatures, a bright yellow, highly viscous solution was obtained with an increase in the unsaturation of the polymer backbone. The films obtained from these highly coloured solutions were brittle because some precipitation occurred before a coherent film was formed. It was found that precipitation of the polyelectrolyte from the aqueous solution occurred at a ratio of **II** to **III** units of approximately 1:4. The standard reaction conditions previously stated (0°C for 1 h) yielded a copolymer having a **II** to **III** unit ratio of about 10:1, which could easily be cast into films by solvent removal at 25°C *in vacuo* to yield coherent clear films of controllable thickness. Dissolution of the films in polar solvents other than water results in yellow solutions with an increase in unsaturation, indicating that the sulphonium ion units, **II**, are stabilized by water.

The overall mechanism for this polymerization is as yet unresolved. However, our results are not inconsistent with the reaction scheme proposed by Wessling[15] involving ylid formation and elimination to form either a diradical or a *p*-xylylene intermediate which polymerized to yield **II**. Kanbe and co-workers also proposed a diradical polymerization reaction[3]. It has been found that addition of an aqueous radical initiator (Fenton's reagent) accelerated the reaction; upon addition of trace amounts of this solution the viscosity of the reaction solution increased markedly. When the polymerization reaction was effected in the presence of oxygen a solution of low viscosity was obtained, and the product could not be cast into a coherent film. This evidence tends to support a radical polymerization reaction but not necessarily one involving diradicals. More definitive evidence is needed before any conclusions can be drawn concerning the mechanism of chain propagation.

Molecular weight studies of the polyelectrolyte proved difficult. Intrinsic viscosity measurements were found to be highly dependent upon the added salt concentration and on the type of salt and the solvent used, with some irreproducibility. Aqueous phase g.p.c. was attempted using both the Waters E-linear Bondagel and Polymer Labs Aquagel columns for water-soluble polymers. The polyelectrolytes in all cases were found to interact with the columns, and retention volumes were highly dependent upon the solvent and salts used. However, reproducible results were obtained by membrane osmometry. The number-average molecular weight of the polyelectrolytes, as determined in an aqueous 0.025 M Na_2SO_4 solvent, was found to be 130 kDa.

Another method of determining molecular weight, which has been developed specifically for high molecular weight polyelectrolytes, combines centrifugation with low-angle laser-light scattering[16]. A sample analysed by this technique yielded $\bar{M}_n = 5.0 \times 10^5$ Da ($\bar{M}_w = 9.9 \times 10^5$ Da and a $\bar{M}_w/\bar{M}_n = 2.0$). This result may differ from that obtained by osmometry because the elimination of low molecular weight products from the precursor polymer occurs to some extent even at room temperature, and these byproducts would significantly lower the number-average molecular weight as measured by membrane osmometry. Because the light scattering method is relatively insensitive to this problem, the molecular weights from this technique are more reliable.

As noted previously, these polymers are fluorescent probably because of the π–π^* transition of electrons in the double bonds. Ultra-violet visible spectra were obtained for the clear polyelectrolyte films, for partially eliminated films and for the fully eliminated PPV films (*Figure 2*). The u.v. spectra for the clear, saturated films displayed three absorption bands with overlapping maxima associated with the phenyl group ($\lambda = 198$, 229 nm), the sulphonium group ($\lambda = 265$, 270, 276 nm), and a small concentration of bathochromically shifted stilbene groups ($\lambda = 305$, 318, 332 nm). As the sample was thermally eliminated, the absorption bands broadened and new bands appeared at longer wavelengths until elimination was complete, at which point the u.v. spectrum showed a broad, continuous absorption with an edge centred at 512 nm (2.43 eV), indicative of a highly conjugated system. The degree of unsaturation in the polymer can be controlled by varying the elimination temperature. It should be noted, however, that u.v.-visible light spectrophotometry becomes insensitive to increasing conjugation above a conjugation length of about six repeat units[17], and thus this method cannot be used as a quantitative technique for assaying polymers with high degrees of elimination.

Elemental analysis of the precursor polymer, which had been eliminated for 24 h at temperatures from 30°C to 250°C showed that the ratio of **II**:**III** repeating units varies from 2:1 to 1:11 over that temperature range. At 250°C there was still a residual sulphur content of about 2.5 wt%, but residual chlorine was less than 0.1 wt%. Clearly the simple elimination reaction involving only $(CH_3)_2S$ and HCl loss is not sufficient to characterize the thermal conversion mechanism of the precursor polymer.

Sulphonium salts can also undergo an S_N2 reaction with formation of the alkyl halide or by displacement of

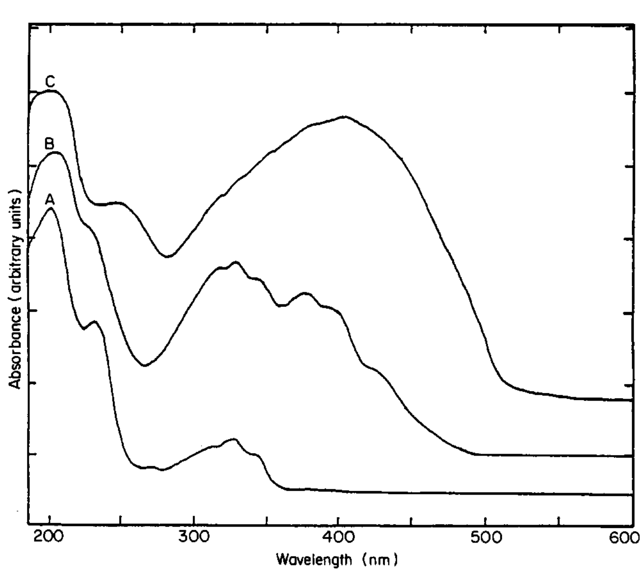
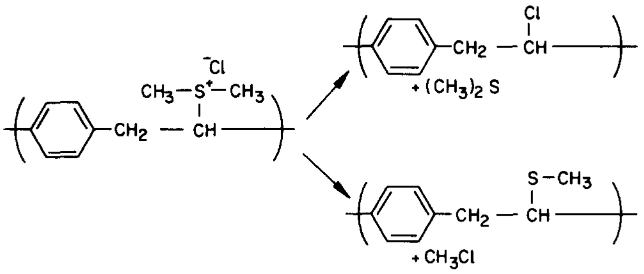
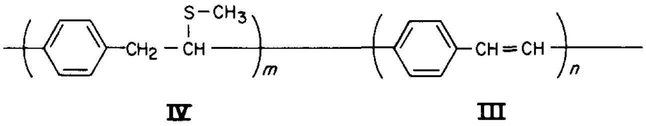


Figure 2 Ultra-violet–visible spectra of, A, uneliminated polyelectrolyte film, B, partially eliminated film heated at 200°C and, C, PPV after thermal treatment at 360°C

the alkyl sulphide, as shown below, but since no residual chlorine was present after treatment above 150°C, the latter reaction cannot be a major elimination route. The former reaction most probably occurs, however, and could account for the residual sulphur content of the polymer after heating:



Thus at elimination temperatures between 150°C and 250°C the partially eliminated copolymer can best be described as having the following structure:



IV III

Further evidence supporting this elimination scheme has been obtained by using thermogravimetric analysis coupled with mass spectrometry (*Figures 3* and *4*). The upper curve of *Figure 3* shows the rate of weight loss and the lower curve shows total ion intensity data as a function of temperature. Three major thermal transition maxima occurred at 106°C (with a shoulder at 134°C), 360°C and 536°C corresponding, respectively, to two distinct elimination reactions and a degradation reaction.

Figures 4a, *b* and *c* show the mass spectrometry analyses. The intensities of the peaks are approximately proportional to the amount of gas evolved, but are not strictly quantitative because of a dependence on the electronic cross-sectional area of the molecules, the fragmentation of the ion and the sensitivity of the mass spectrometer. The major components in the first peak were the water of hydration and the expected $(CH_3)_2S$ and HCl products formed from the E1cB elimination reaction. There was also a significant contribution from CH_3Cl formation by the decomposition of the sulphonium salt as shown above. The second peak centred at 360°C was associated with the elimination of CH_3SH, and the radical combination products CH_3SSCH_3 and a small amount of CH_3SSSCH_3. Thus t.g.a.–m.s. data demonstrated that near quantitative conversion to PPV was only achieved above 360°C, consistent with the elemental analysis data referred to above.

Infra-red spectroscopy of the fully eliminated PPV showed a strong absorbance at 963 cm^{-1}, consistent with the *trans*-CH out-of-plane bending mode, while no absorbance was observed near 630 cm^{-1}, where the *cis*-CH bending mode would be expected (*Figure 5*). Thus the elimination reaction yielded *trans*-PPV exclusively. The presence of a small peak in the 2900 cm^{-1} sp^3 C–H stretch region indicated, however, that there was a small residual fraction of uneliminated units. The concentration of these units is not expected to significantly alter the electrical properties of the resulting PPV.

Analysis by d.s.c. over a −196°C to 600°C temperature range of the fully eliminated PPV indicated that no glass or melt transitions were observable. The onset of degradation occurred at about 550°C in a nitrogen atmosphere. Wide-angle X-ray diffraction analysis of an unoriented PPV film revealed only rather diffuse rings at d-spacings of 4.45 Å, 3.23 Å and 2.13 Å, consistent with an amorphous structure. In contrast the oriented PPV films were highly crystalline; these results are described elsewhere[18].

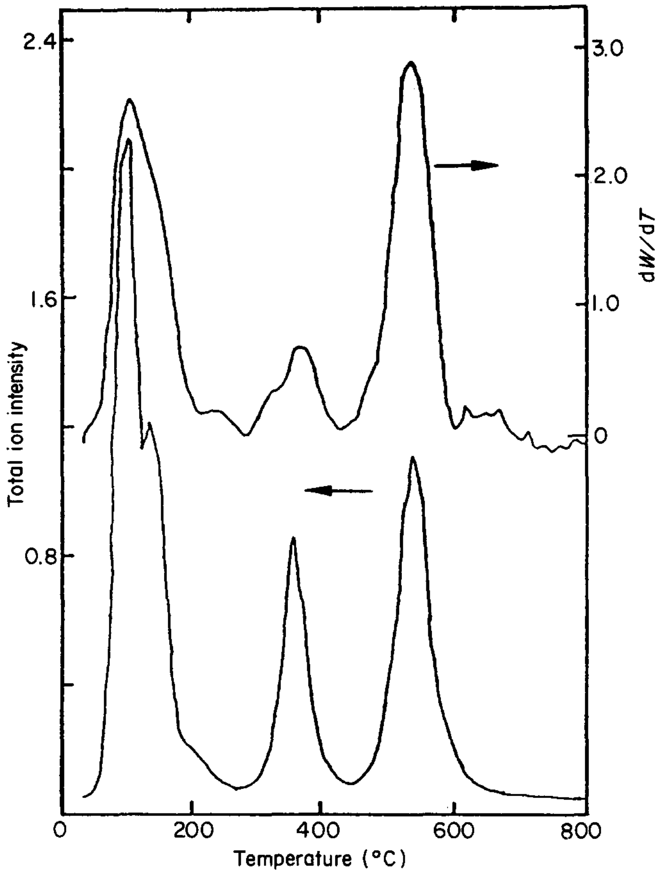


Figure 3 Differential thermogravimetric analysis (upper plot) and mass spectral total ion current (μA) (lower plot) of the volatile products formed by the elimination reaction as a function of temperature

Conductivity

Doping studies of PPV show that conductivities approaching those obtained for doped polyacetylene are attainable. The undoped polyelectrolyte material is an insulator with a conductivity of 10^{-13} S cm^{-1}. For the fully eliminated PPV films having a **II**:**III** ratio greater than 1:11, maximum conductivities of 10 S cm^{-1} with the dopant AsF_5 and 100 S cm^{-1} with H_2SO_4 were consistently achieved. Doping with I_2 in either vapour or solution form resulted in no appreciable increase in conductivity and no change in physical appearance. Murase *et al.* reported I_2 doping of stretched PPV to obtain a conductivity of 10^{-3} S cm^{-1} [5]. However, these samples may not have been fully eliminated and the origin of the measured conductivity is unclear. N-type doping with sodium naphthalide yielded maximum conductivities (σ_{max}), of 2×10^{-4} S cm^{-1} after extensive washing.

The doped materials were metallic in appearance, with colours ranging from a light blue or deep blue lustre for the sodium naphthalide and AsF_5 treatments, respectively, and a copper lustre for the H_2SO_4 dopant.

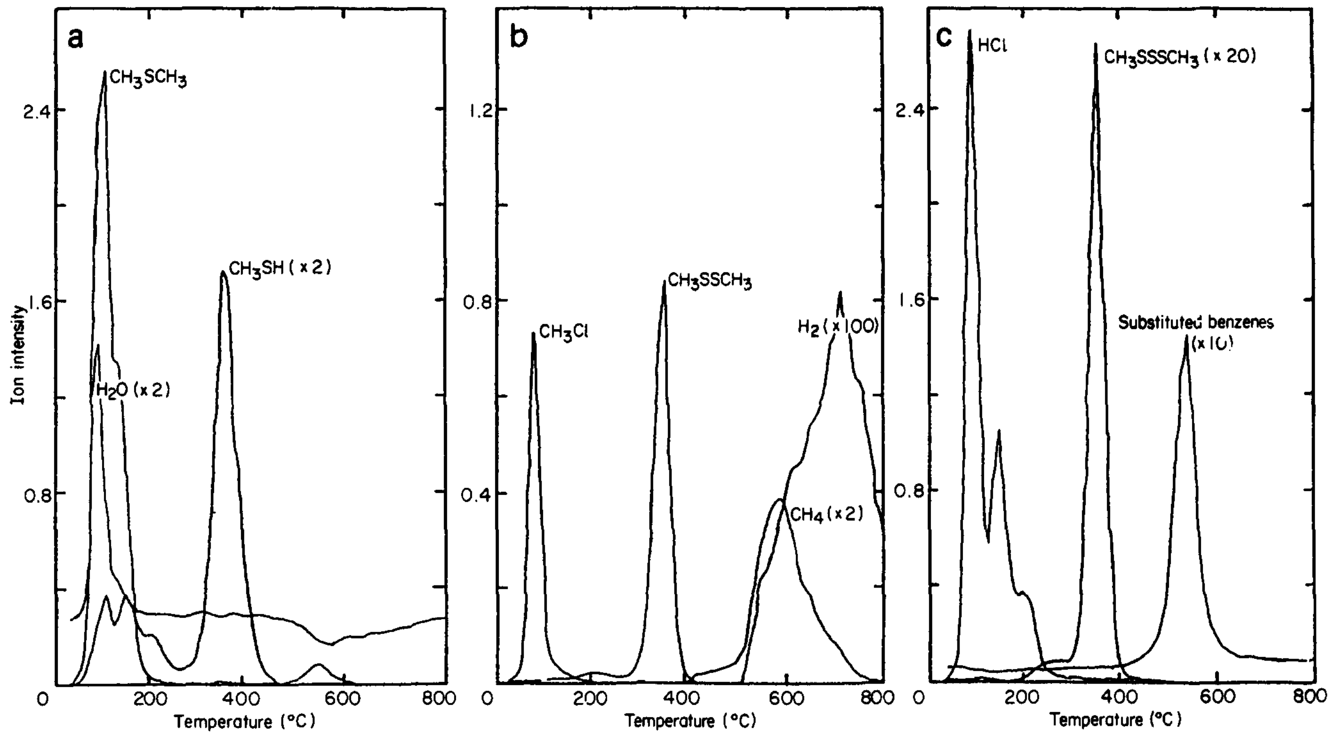


Figure 4 Mass spectral ion intensity (μA) of individual components of precursor elimination as a function of temperature

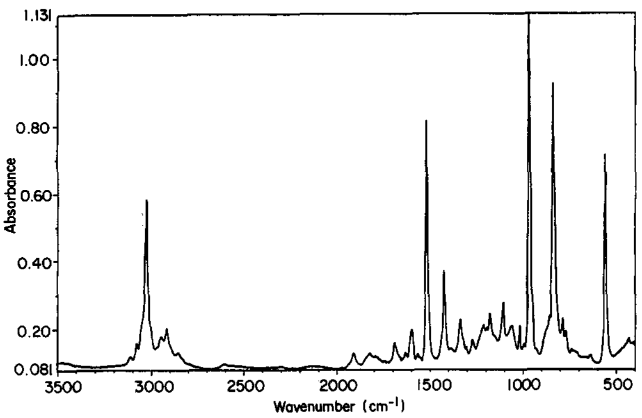


Figure 5 Infra-red spectrum of PPV after complete elimination by thermal treatment at 360°C

The conduction was determined to be electronic (some ionic component was present in H_2SO_4 doped samples) by passing a current through the samples for appropriate times and noting the virtual absence of a resistance change with time.

For AsF_5 doping, a study of conductivity at a doping level of 26–30wt% as a function of elimination temperature, T_{elim}, showed that σ_{max} increased as a function of T_{elim} (*Figure 6*). Above a T_{elim} of about 180°C (a II:III unit ratio of *ca.* 1:6), the conductivity levels off at a value of 10 S cm^{-1}. These data show that the conductivity depended upon the conjugation length, at least until a critical average conjugation length of six units was reached. It is noted that the relation between conjugation length and conductivity is nearly the same as that between conjugation length and the π–π* electronic transition observed in u.v.–visible spectrophotometry.

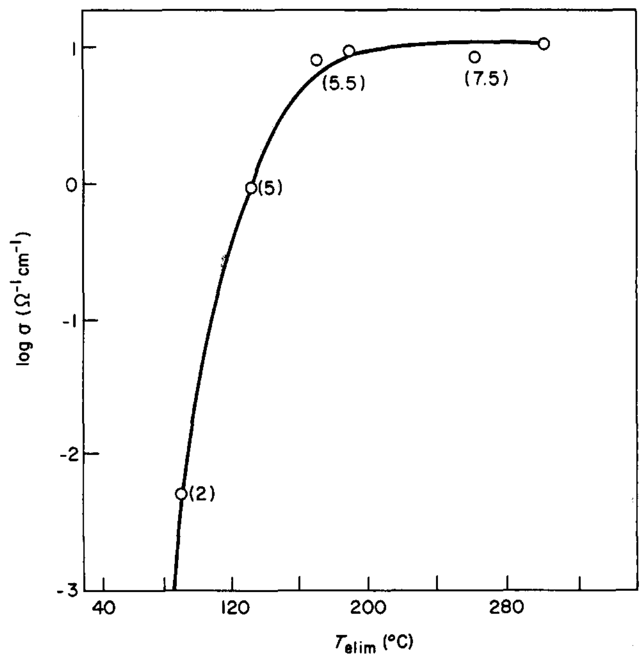


Figure 6 Electrical conductivity, σ, of the doped polymers as a function of their elimination temperatures; the numbers in parentheses indicate the average conjugation length based upon elemental analysis assuming random elimination

CONCLUSIONS

The optimized conditions for the preparation of PPV by the sulphonium salt precursor method has been described in this report. A detailed t.g.a.–m.s. and elemental analysis study of the thermal elimination reaction of the precursor films demonstrates that there are two distinct elimination stages. The first stage is the expected loss of methyl sulphide and HCl leaving a fraction of PPV units but a significant number of sulphonium groups decompose by loss of methyl chloride leaving thiomethyl pendant-group residues. These thiomethyl groups are then eliminated in the second stage at temperatures above 360°C, resulting in near quantitative conversion to PPV. Ultraviolet–visible spectra have also been reported for the first time of the sulphonium precursor polymer as cast, and at partial and fully eliminated stages.

The precursor route to PPV has been found to be a versatile system for studying the effect of conjugation length upon the final doped conductivity attainable. We have shown that the conductivity increases as a function of the conjugation length, but becomes insensitive above a conjugation length of about six units.

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