Spectroscopic studies of the conversion of poly(*p*-phenylene-vinylene) precursor

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Efforts are made to identify the irregular structures formed in poly(phenylene-vinylene) (PPV), obtained via the conversion of its sulfonium precursor by different physical and chemical methods. Analysis by X-ray photoelectron spectroscopy and Fourier transform infra-red spectroscopy reveals that the ketone structure is a common defect appearing in PPV whenever the conversion is carried out in the presence of oxygen. In contrast to the PPV obtained by pyrolysis of the precursor, the PPV obtained by treatment of the precursor with H_2SO_4 contains no chlorine residue but much more sulfur residue. Ion bombardment of the sulfonium precursor leads to a PPV containing no trace of sulfur or chlorine in the structure. Finally, the nature of bonding between the carbon atom and oxygen, chlorine or sulfur atoms in PPV is discussed and irregular structures are proposed. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Poly(phenylene-vinylene) (PPV) displays a variety of properties (potential electrical conductivity, non-linear optical response, electro- and photoluminescence) that make it an interesting material for many applications[1–6]. Not only is PPV obtained from a water-soluble high polymer precursor[7] which favours fibre or film processing, but it is also a high-molecular-weight, highly crystalline and highly orientable polymer[8,9] which presents excellent inherent mechanical properties together with high conductivity after doping[1,10].

In the Wessling method[7], PPV is obtained via a soluble precursor polysulfonium salt. The conversion of the precursor into PPV proceeds via the elimination of sulfide and halohydric acid (*Scheme 1*).
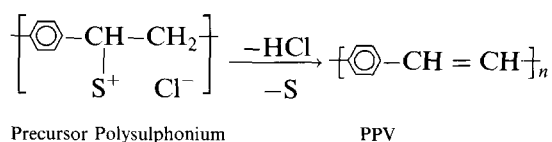
Scheme 1

This conversion can be achieved in many ways, such as via a thermal treatment[11–15] or via pyrolysis under an acid stream[16–21]. The conversion can also be performed by a chemical pathway using a solution of alcoholic sodium hydroxide under reflux[11] or a strong acid[22]. Whatever the method used, the resulting PPV does not have the perfect sequence of repeat units as illustrated in *Scheme 1*, but contains some abnormal structures arising from undesirable side-reactions during conversion. In fact, Lenz and co-workers[23] have identified defect structures in PPV (such as structure I and structure II, *Scheme 2*) formed during pyrolysis and shown that the

Scheme 2

number of such structures depend on the nature of the sulfur in the sulfonium precursor. For instance, the number of defect structures is higher with poly(*p*-xylene-dialkylsulfonium chloride)[23], but is of much less importance with poly(*p*-xylene-tetrahydrothiophenium chloride)[15].

Since the properties of a polymer and its structural regularity are well correlated, in this paper we report the impact of the conversion pathway on the defect structures in PPV, using X-ray photoelectron spectroscopy (X.p.s.) and Fourier transform infra-red spectroscopy (*FT*i.r.). The conversion of the sulfonium precursor into PPV was achieved by various methods: thermal treatment, chemical conversion and heavy-ion-beam bombardment.

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EXPERIMENTAL

PPV precursor was synthesized using the method described in our previous paper[22]. Free-standing films of the PPV precursor, with a thickness of around 20 μm, were obtained by casting poly(p-xylene-tetrahydrothiophenium chloride). Pyrolysis of the cast film was carried out at 180 or 250°C under an inert atmosphere, for about 2 h. Chemical treatment of the cast films was carried out by directly immersing them in H_2SO_4 (97%) for 4 h. Elimination of the excess acid in the films was monitored by rinsing the samples with acetonitrile. All films were then dried under vacuum at 40°C. Ion-beam irradiation of the cast film was performed using a 200 keV Balzers implanter with Ne^+ or Na^+ ions of current density of the order of 0.3 μA cm^{-2}.

I.r. studies of the film samples were carried out on a Nicolet 20SX FT-IR spectrometer, with a spectral resolution of 2 cm^{-1}. For the films irradiated by heavy ions, the spectra were recorded by reflection on both faces of the film.

X.p.s. experiments were performed on a Leybold LH 12 ESCA analyser (CNRS–Université de Nantes). Free-standing films of PPV were mounted on a stainless steel substrate and introduced to the ESCA chamber. Mg $K\alpha$ radiation ($h\nu$ = 1256 eV) was used for the analysis, which was carried out under low pressure conditions (10^{-9} torr). The instrumental resolution was about 0.4 eV under the analysis conditions. Absolute binding energy was referred to the Au $4f_{7/2}$ line (84 eV) of a gold spot evaporated on the film. Shirley non-linear background and satellites were subtracted from the spectra using a computer program.

Deconvolution of the spectra was performed using a curve-fitting program which describes each of the components of a complex envelope as a Gauss–Lorentzian sum function. For each of the envelopes five parameters were allowed to vary simultaneously: the intensity at energy E, $F(E)$; the peak height, H; the peak centre, EO; the full-width at half maximum, $FWHM$; and the mixing ratio, m (1 is pure Gaussian, 0 is pure Lorentzian). They were adjusted by minimizing the L2 value, taking account of the chemical and physical meaning of the bonds between atoms in the polymer network.

Analysis of the spectra corresponding to different elements was based on general considerations of the X.p.s. results obtained on polymers as outlined by Clark and Thomas[24]. The C $1s$ line of carbon linked to hydrogen or other carbon is located at 284.5 eV with a $FWHM$ of 1.5 eV. Broadening of this line implies that bonding of carbon with other atoms can occur. For instance, the substituent effect of sulfur on the C $1s$ line corresponds to a shift of 0.4 eV to higher binding energy. The effect of replacing hydrogen by chlorine produces a 1.6 eV shift to higher binding energy, which is almost comparable to the oxygen substituent effect.

RESULTS AND DISCUSSION

Precursor polymer film (sample P)

X.p.s. spectra obtained on the precursor polymer show that the film is significantly oxidized, with the O $1s$ line situated at 531.5 eV. Shoulders are also observed at 528.5 and 533.5 eV (*Figure 1*). The high binding energy components can be assigned to C–O (533.5 eV) and
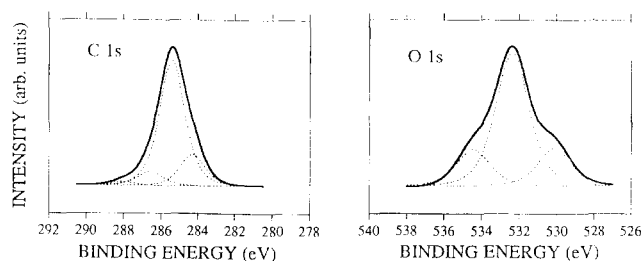

Figure 1 Core-level spectra of carbon and oxygen in sulfonium precursor film

C=O (531.5 eV). As for the low binding energy component (528.5 eV), its origin is not well understood. It may result from contamination in the precursor solution. The C $1s$ line is found at 284.9 eV, which is higher than the binding energy of carbon linked to hydrogen or another carbon. In addition, its $FWHM$ (2.1 eV) is greater than that expected for these bonds and suggests that carbon atoms may be linked to sulfur or chlorine. The presence of these elements is evidenced by the S $2p$ and Cl $2p$ lines situated at 163.9 and 200.4 eV, respectively. Deconvolution of these spectra gives a 2:1 doublet and thus evidence for the single saturated environment of sulfur and chlorine. These lines indicate that both covalent sulfur and chlorine are bonded to carbon atoms[24,25]. The resolved spectrum of C $1s$ gives four components with equal $FWHM$ (1.6 eV) and with peak positions at 284.3 (C–C or b carbon), 284.9 (C–S or a carbon), 286 and 287.5 eV (C=O). The component at 286 eV may correspond to either C–Cl or C–O bonding. We observe that the component at 284.9 eV is predominant, showing that the precursor contains a large amount of sulfonium. The S $2p$/C $1s$ intensity ratio is about 2%.

The i.r. spectrum of P (*Figure 2A*) shows a strong absorption at around 3500 cm^{-1} due to the water in the sulfonium precursor and a peak at 2940 cm^{-1} (sp^3 C–H stretching) due to the sulfonium moieties in the precursor polymer. The absorption at 1200–1400 cm^{-1} can also be assigned to the sulfonium salts. The absorption band in the region 1652–1772 cm^{-1} indicates the presence of the ketone(C=O) group in sample P. The oxygen-containing units observed by X.p.s. and the ketone group evidenced by i.r. lead to the structure assignment shown in *Scheme 3* for sample P. This structure III is not surprising,

$$-\langle\bigcirc\rangle-\overset{\textstyle O}{\underset{\textstyle \|}{C}}-CH-$$

Structure III
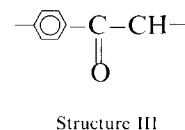
Scheme 3

because oxidation of the precursor by oxygen has been reported by many authors[21,26,27]. Furthermore, it was also observed that the action of light accelerates the degradation and leads to the formation of aggregates[26].

As for the C–S bond detected by X.p.s., it is difficult to assign it to a side-reaction considering the low temperature during film casting and all the more so as tetrahydrothiophene (THT) is abundant in the sample.

Thermally converted PPV (sample T)

Two samples were used in this analysis: the first was converted from a precursor film at 180°C for 2 h and the second was formed at 250°C under the same condition.
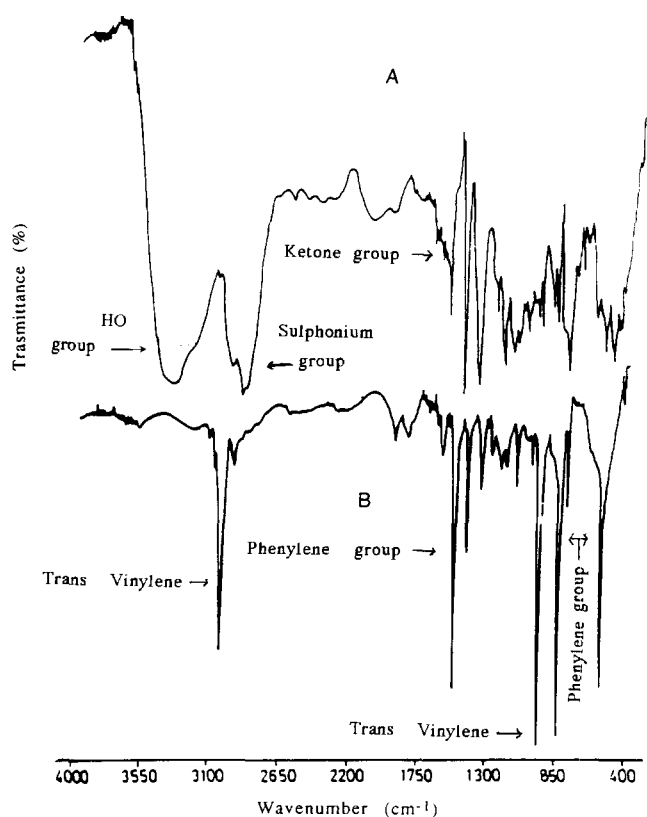
Figure 2 I.r. spectra of (A) sulfonium electrolyte precursor of PPV and (B) A after pyrolysis at 250°C under nitrogen atmosphere for 2 h
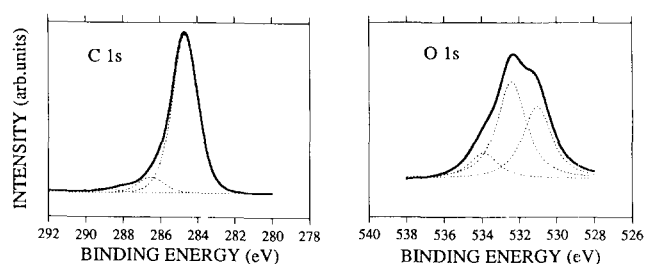

Figure 3 Core-level spectra of carbon and oxygen in PPV film obtained by conversion of the precursor at 250°C for 2 h

The X.p.s. spectra of these samples (*Figure 3*) show that they have been converted but with surface oxidation, since the O 1s line is observed at 531.5 eV with shoulders at binding energies similar to those observed in the precursor polymer. Traces of sulfur and chlorine are also found in the 180°C-converted film. The intensity of the carbon spectrum increases in the thermally converted samples with respect to that of the precursor. For the 250°C-converted sample, the C 1s line appearing at 284.5 eV is in good agreement with that previously reported[28,29]. However, the C 1s peak of the 180°C-converted sample is shifted to higher energy (0.2 eV), indicating that traces of the precursor are still present and corroborating the finding of weak intensity S 2p and Cl 2p lines. The S 2p/C 1s intensity ratio is about 0.7% in the 180°C-converted film and 0.2% in 250°C-converted film. This proves that the elimination reaction (*Scheme 1*) is more complete at a higher pyrolysis temperature, but that the side-reaction also occurs.

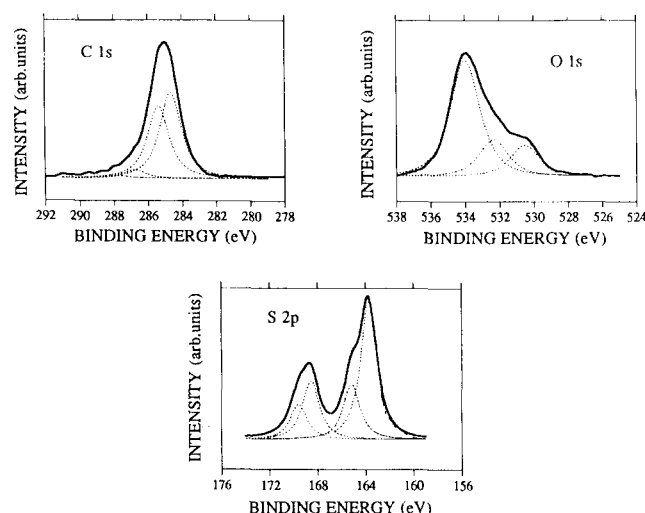The *FT* i.r. spectrum of T (*Figure 2B*) shows the

Figure 4 Core-level spectra of carbon, oxygen and sulfur in chemically converted PPV film

complete disappearance of the water and sulfonium moieties of the precursor and the appearance of bands attributable to PPV, such as those at 3050 cm^{-1} (*trans*-vinylene C–H stretch), 1515 cm^{-1} (semi-circle ring stretching), 970 cm^{-1} (*trans*-vinylene C–H out-of-plane bending), 840 cm^{-1} (*para*-phenylene C–H out-of-plane bend) and 555 cm^{-1} (*para*-phenylene out-of-plane ring bend). Finally, the ketone group C=O, with an absorption band at around 1700 cm^{-1}, is also observed. Furthermore, comparison of the two spectra (*Figures 2A* and *B*) does not reveal any significant difference in the absorption intensity of the ketone band. Therefore, the presence of this group is due to oxidation of the precursor by oxygen during the casting process, and this structure remains unchanged in intensity during conversion which is carried out in the absence of oxygen.

In conclusion, in the thermal conversion of the sulfonium precursor, irregular units such as structures I and II (*Scheme 2*) are formed in PPV as the main defects.

Chemically converted PPV films (samples C)

The X.p.s. spectrum of the PPV film converted by treatment with H_2SO_4 is shown in *Figure 4*. In this case, the precursor is fully converted since no trace of chlorine is found on the film surface. By contrast, two sulfur lines appear at 164.6 and 169.8 eV both of which can be deconvoluted into doublets with 2:1 ratio, indicating two stable bonding states of sulfur. The line with lower binding energy corresponds to sulfur covalently bonded to carbon, whereas the higher one should be consistent with the sulfone group. Oxygen is also present with many components; the strongest intensity is found at 534 eV and two other virtual peaks are situated at 531.5 and 528 eV. The enhancement of the high binding energy peak would correspond to sulfone group formation, since S=O and C=O bondings give the same binding energy. The C 1s line also shows four components at 284.5 (aromatic carbon), 285.3, 286.3 (C–O) and 288.2 (C=O) eV. The component at 285.3 eV could be assigned to C–S bonding[24]. The S 2p/C 1s intensity ratio is about 14%.

FT i.r. analysis (*Figure 5A*) clearly shows that the intensity of the peak at 2940 cm^{-1} (sp^3 C–H stretching)
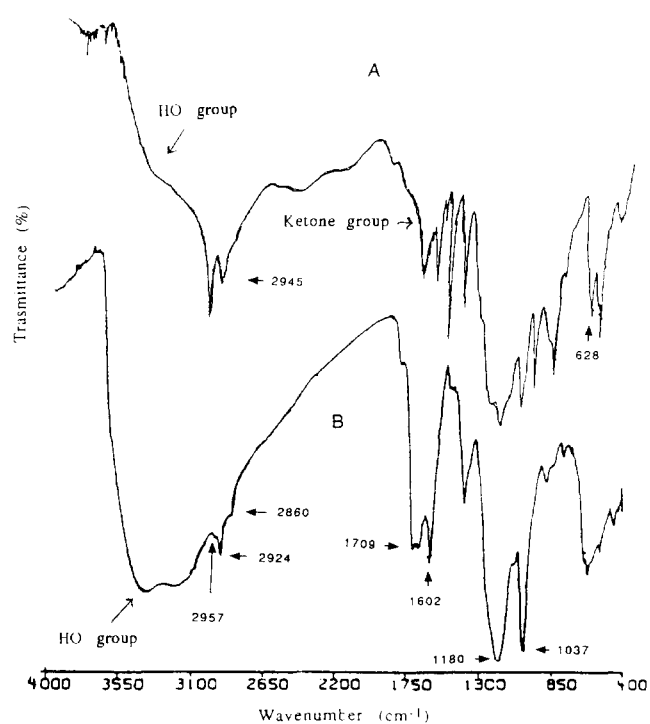
Figure 5 I.r. spectra of (A) the precursor treated with H_2SO_4 (97%) for 2 h and washed with acetonitrile, and (B) PPV treated with oleum for 4 days

of the sulfonium moieties in the precursor polymer decreases rapidly, but levels off after 4 h of treatment. At the same time the appearance of PPV bands is observed, particularly the band at $970 cm^{-1}$. Sample C gives a broad O–H stretching band centred around $3300 cm^{-1}$ and two peaks at 1709 and $1602 cm^{-1}$, characteristic of sulfonic acid and the carbonyl group. In addition, the absorbances at 1037 and $1180 cm^{-1}$ can be assigned to symmetric and asymmetric stretching in sulfonic acids, and the identification of these groups is supported by the peaks at 400 and $650 cm^{-1}$, which may be assigned to C–S stretching. The sulfonation of PPV has been reported by Simpson et al.[30] when heating PPV previously doped with H_2SO_4. Therefore, the sulfonic-containing structures shown in *Scheme 4* can be proposed.
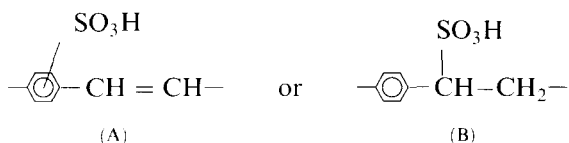
Scheme 4

In conclusion, in the conversion of PPV by H_2SO_4, X.p.s. analysis shows the absence of the C–Cl bond. Therefore, the presence of the C–S bond is expected to arise not from the sulfonium residue but from the sulfonation reaction or from structure I (*Scheme 1*). In this conversion all HCl is eliminated and there is no side-reaction of HCl, therefore structure II is not formed (*Scheme 2*).

To determine the influence of a very strong acid on the structure of PPV, a PPV film obtained from pyrolysis was immersed in oleum (H_2SO_4 + 20% SO_3) for 4 days (samples COL). The spectra reveal the presence of sulfur (S $2p$ peak at 163.7 eV) but no trace of chlorine was

found. This indicates that the polymer was fully converted, but with sulfur being conserved in its network. On the other hand, oxidation of the surface was also found to occur in similar way as in the preceding case (O $1s$ peak located at 530.5 eV). The carbon line with a principal peak at 284.8 eV can be resolved into four components, with a C–S component at 285 eV. The S $2p/$ C $1s$ intensity ratio is about 4%.

Since the PPV treated with oleum turned black, it was impossible to record the i.r. spectrum of the film by transmission, and therefore the i.r. spectra were recorded on a KBr pellet containing 2% of the powder product (*Figure 5B*). Surprisingly, there is no valence band vibration of PPV at 3023 and $2948 cm^{-1}$ nor the band at $960 cm^{-1}$ characteristic of *trans*-vinylene C–H out-of-plane bending, but a large O–H band between 3600 and $3100 cm^{-1}$, two maxima at 1700 and $1600 cm^{-1}$ characteristic of sulfonic acid and the appearance of absorption bands of medium intensity at 2957, 2924 and $2860 cm^{-1}$, bands of *p*-toluene sulfonic acid. Also, the bands between 400 and $650 cm^{-1}$ could correspond to the C–S stretch. Furthermore, there are also two bands of high intensity at 1037 and $1180 cm^{-1}$ which can be attributed to symmetrical and asymmetrical stretch of the SO_3 group of sulfonic acid. Finally, the band at about $1700 cm^{-1}$ could arise from the vibration of C=O groups.

The results of elementary analysis of sample COL clearly indicated the important quantity of oxygen and sulfur (C = 44.4%, H = 4%, S = 9.4% and O = 41.9%). On the other hand, the conductivity of sample COL was very low, as small as $5 \times 10^{-8} S cm^{-1}$. From these facts, we conclude that oleum has totally destroyed the PPV structure but without transforming it into graphite. Therefore, the structure of sample COL is suggested to be formed by units of structure B in *Scheme 4* and the units depicted in *Scheme 5*.

Scheme 5

As seen, in contrast to the case of thermal conversion where oxygen is absent, in the chemical conversions the formation of ketone becomes much more important because of the oxidation reaction with oxygen present in air or in the SO_3 oleum.

Ion-implanted PPV films with Na^+ and Ne^-

An energy of 100 keV and a density of 10^{15} ions cm^{-2} are insufficient to effect complete conversion of the precursor, as indicated by the i.r. spectra of precursor films implanted with either Na^+ or Ne^+. At a density of 5×10^{15} ions cm^{-2}, the i.r. spectrum of the irradiated surface of the film shows partial conversion of the sulfonium precursor into PPV whereas the spectrum of the unexposed surface is almost identical to that of the precursor. However, at 2×10^{16} ions cm^{-2} the precursor is totally converted into PPV after 3 h of implantation with either Na^+ or Ne^+, and the ketone group is always observed in the structure (*Figure 6*).
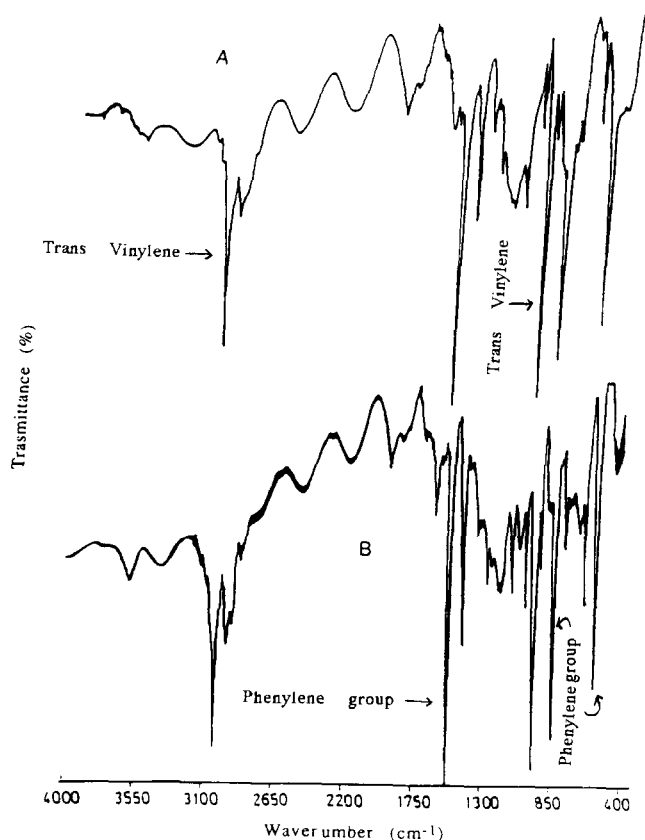
Figure 6 I.r. spectra of the implanted precursors after irradiation with a density of 2×10^6 ions cm^{-2} for 3 h: (A) with Ne$^+$ and (B) with Na$^+$

immersed in acid under air atmosphere or in the presence of an oxidizing agent such as SO_3. Oleum, being a powerful oxidizing agent, induces a radical change of the PPV structure. In contrast, treatment with H_2SO_4 causes sulfonation of the PPV precursor or PPV itself and can lead to a self-doping polymer, owing to the sulfonic acid groups grafted into the polymer backbone.

No trace of sulfur or chlorine was detected by X.P.s. analysis. The surfaces of the films are oxidized as shown by the O 1s line at 530.5 eV (C=O) and a shoulder at 533 eV (C–O). The carbon line shows a peak at 285 eV with a *FWHM* of 1.5 eV. Broadening of the base on the high binding energy side suggests the formation of carbon–oxygen bonds.

To summarize, the bombardment of the polysulfonium precursor by heavy ions gives rise to PPV of perfect structure in comparison to pyrolysis or chemical conversion. The only irregular structure detected is the ketone group, but this is more likely to have been formed initially in the precursor (sample P).

CONCLUSIONS

Depending on the conversion pathway, some irregular structures are formed in PPV during the conversion of the polysulfonium precursor. High temperature during pyrolysis and high density of ions during implantation lead to a more complete conversion. Among these conversion pathways, ion implantation seems to give a more perfect PPV. The ketone structure observed in all converted PPV not only arises from oxidation of the precursor by oxygen during casting, but also from the ketone group initially existing in the precursor. The ketone group increases in quantity when the conversion is carried out in the presence of oxygen; e.g. in chemical conversion during which the polysulfonium precursor is

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