# Direct conversion of sulfonium precursors into poly(*p*-phenylene vinylene) by acids

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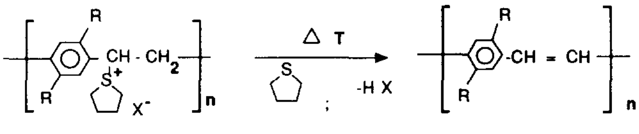
A novel method for the conversion of sulfonium precursor into poly(*p*-phenylene vinylene) (PPV) has been developed. The treatment of the sulfonium precursor with strong acids at room temperature leads to doped PPV. The materials obtained have the same optical properties and slightly higher conductivity in comparison to PPV prepared by pyrolysis of the precursor. Finally, the chemically converted PPV material appears to be of lower density, therefore the dopants can easily diffuse into the polymer matrix and subsequently enhance the electrical conductivity of the system.

**(Keywords: sulfonium; conversion; poly(phenylene vinylene))**

## *Introduction*

Recently, poly(*p*-phenylene vinylene) (PPV) has been intensively studied owing to its promising potential applications. PPV is a high molecular weight polymer, highly crystalline and highly orientable[1–3]. It has excellent inherent mechanical properties together with high conductivity after doping[4]. Moreover, it is obtained from a water-soluble high polymer precursor[5], so it can be easily processed as fibre or film.

However, the conversion of the precursor into PPV, which needs a rather long thermal treatment at 200°C or more, may constitute a drawback to the production of PPV on an industrial scale. In fact, the first PPV was obtained by pyrolysis of the polyelectrolyte sulfonium at a temperature as high as 300–400°C to eliminate sulfide and halohydric acid[6–8]. However, the low temperature conversion of sulfonium precursor has been reported[9,10]. In the thermal treatment, besides the energy and time required, many undesired reactions take place, though some improvement has resulted either from using a cyclic sulfonium[10] instead of a dialkyl sulfonium salt to lower the conversion temperature of sulfonium precursors:



**Sulfonium Precursor** **P P V**

or by the introduction of a hydrochloric acid flow during annealing of the presursor[11–13].

The transformation of the poly(*p*-xylylidene sulfonium) precursor into PPV by methods other than pyrolysis has been the subject of many recent studies. For instance, in the elimination of sulfonium groups of the precursor by a chemical process, Kanbe and Okawara[14] tried to perform the conversion using a solution of 10% alcohol sodium hydroxide under reflux. More recently, Han and Elsenbaumer[15] and Tokito *et al.*[16] substituted the sulfonium group in the precursor by an alkoxy and the modified precursor was then pyrolysed under an acid stream. These methods introduce supplementary reactions which take time and also induce many side reactions.

We report here a novel method by which PPV may be obtained rapidly and directly, and with almost no side reactions. This method, described in our patent[17], consists in treating the sulfonium precursor PPV with strong acids at room temperature. Some characterizations of the PPV obtained are presented.

## *Experimental*

The dichloro-*p*-xylene, tetrahydrothiophene and acetonitrile used were products from Aldrich. All the acids were from Aldrich or Prolabo. Dialysis tubing was from Medicell International Ltd. In the synthesis of the monomer (tetrahydrothiophenium chloride derivative), we adapted the method of Lenz *et al.*[10] and could obtain yields higher than 90% by optimization of the experimental parameters. For example, 1 g (5.75 mmol) of dichloro-*p*-xylene was dissolved in 2 ml of methanol, then 2 ml (22.7 mmol) of tetrahydrothiophene was added to the solution. The system was left at room temperature for 60 h. A white precipitate was formed and 10 ml of cold acetone was added to the reactor with stirring. On filtration, 1.8 g (5.17 mmol) of monomer sulfonium salt was obtained[18]. The precursor sulfonium polymer was synthesized according to the method described in ref. 5. The polymerization of equimolar amounts of 0.4 N water solution of sodium hydroxide and of the monomer was carried out under nitrogen at 0°C with constant stirring. After 1 h, the residual amount of sodium hydroxide was quenched by an excess of hydrochloric acid (1 N). To eliminate the oligomer and the non-reactant residue, the solution was put into dialysis tubing (6.3 mm i.d.) and immersed in deionized water. After dialysis, the solution was cast under a vacuum of $10^{-3}$ bar (100 Pa) at 40°C in the hope that the morphology of the film would be lower density[19]. The cast films were 10–30 $\mu$m thick.

The pyrolysis of the cast film was carried out at 210 or 240°C under an inert atmosphere, for about 3 h.

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All spectroscopic studies of the film samples were carried out on Nicolet 20SX FTIR apparatus.

The electrical conductivity of the films was measured by a Keithley 617 Programmable Electrometer according to the conventional four-point probe technique. The four electrodes of the electrometer were applied to the film surface.

## *Results and discussion*

The cast films obtained from poly(*p*-xylylidene tetrahydrothiophenium chloride) solution, according to the method quoted above, were immersed directly in various acids at room temperature, for variable times according to the thickness of the film. The appearance of bubbles in the solution indicates that gaseous products are released from the reaction, supposedly HCl. After a few seconds the colour of the sulfonium precursors changes from yellow to a dark colour then black, with metallic lustre after 1 h. After about 2 h, the characteristics (electrical conductivity, structure) of the treated films of 10–15 $\mu$m thickness do not evolve. To ensure that the elimination of sulfide is complete for the thicker films (20–30 $\mu$m), the reaction time is about 6 h. Elimination of the excess acid in the film was monitored by rinsing the samples with acetonitrile. All films were then dried under vacuum at 40°C before the conductivity measurements. The reaction takes place spontaneously with $H_2SO_4$ (97%), $HSO_3CH_3$ (98%) and $HClO_4$ (70%); however, other acids, such as trifluoroacetic (99%), phosphoric (85%), tetrafluoroboric (50%), nitric (65%), *p*-toluene sulfonic (50%), bromhydric (47%), chlorhydric (35%) and hydriodic (67%) acids, seem not to interact with the precursor sulfonium salt.

As shown in *Table 1*, after reaction the conductivities of the precursor treated by acids (hereafter referred to as chemical PPV) are higher than those of the PPV obtained from the pyrolysis of the sulfonium precursor (thermal PPV) and doped later with the same acids. $H_2SO_4$ is the best acid while $HSO_3CH_3$ does not have a doping effect with thermal PPV. It is noteworthy that in our experimental conditions, we cannot obtain high values of the conductivity for thermal PPV doped with acid, as reported in the literature[14,19]. However, both the colour change and the increased conductivity observed in the treated precursor can be explained by the simultaneous formation of PPV followed by *in situ* doping of PPV by the acids. Furthermore, a comparison between the conductivity of chemical PPV and thermal PPV is of considerable interest. As shown in *Figure 1*, although their conductivities have the same order of magnitude,

**Table 1** Conductivity of thermal PPV doped with acids and of chemical PPV

| Material | Acid | Colour | Conductivity, $\sigma$ ($S\,cm^{-1}$) |
|---|---|---|---|
| Precursor | None | Yellowish | $\ll 10^{-12}$ |
| PPV, 250°C | None | Brown–orange | $\ll 10^{-12}$ |
| Precursor | $CH_3SO_3H$ (98%) (2 h) | Dark | $5\times10^{-3}$ |
| PPV, 210°C | $CH_3SO_3H$ (98%) (2 h) | Brown | $\ll 10^{-12}$ |
| Precursor | $H_2SO_4$ (95–97%) (2 h) | Dark | $5\times10^{-1}$ |
| PPV, 250°C | $H_2SO_4$ (95–97%) (2 h) | Dark | $10^{-1}$ |
| Precursor | $HClO_4$ (70%) (6 h) | Dark | $10^{-3}$ |
| PPV, 210°C | $HClO_4$ (70%) (6 h) | Chestnut | $3\times10^{-5}$ |

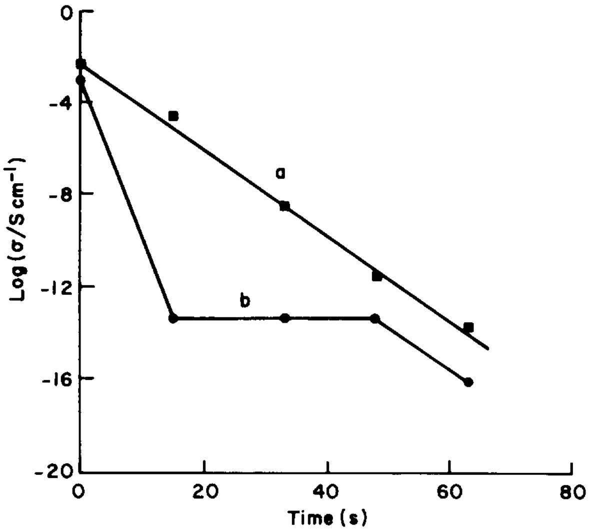

**Figure 1** Evolution of conductivity with time during dedoping, by an acetonitrile solution, of (a) chemical PPV and (b) thermal PPV

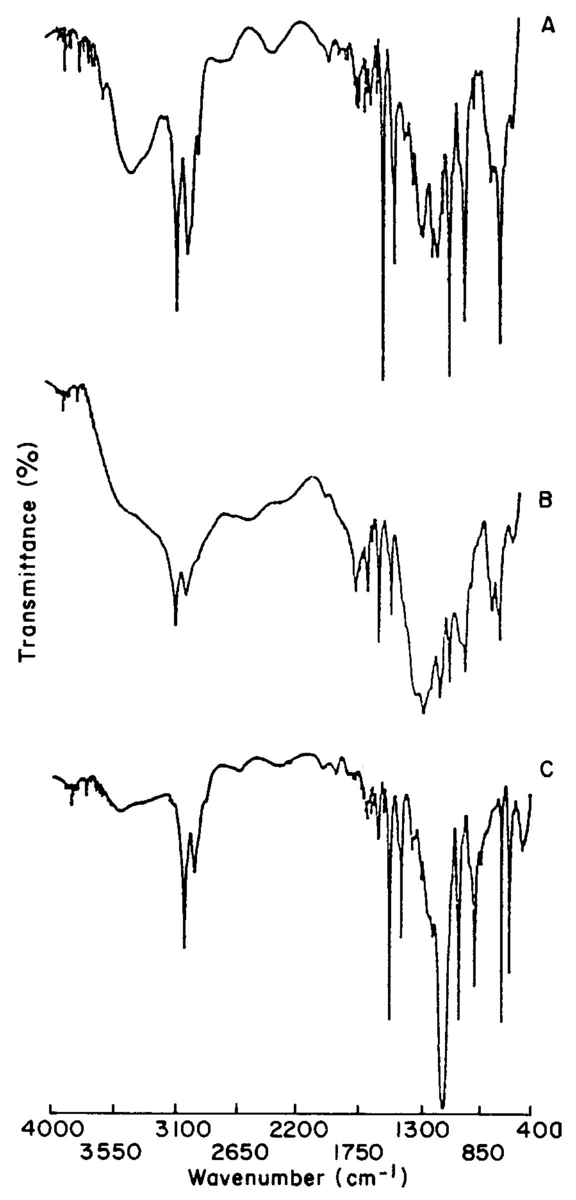

**Figure 2** *FT*i.r. spectra of: A, initial precursor sulfonium (partially converted during drying); B, precursor A treated with $H_2SO_4$, followed by dedoping; C, precursor A treated with $HClO_4$, followed by dedoping

the conductivity of chemical PPV decreases less rapidly than the thermal PPV when the materials are dedoped by immersion in acetonitrile. In view of this result, one would expect that the chemical PPV has a lower density, which allows the dopants to diffuse deeper into the matrix. By contrast, the thermal PPV is more compact, and during doping the dopants give a redox reaction only at the outer face of the materials[16,20], and easily migrate back into the solvent during dedoping.

In order to characterize the structure of chemical PPV, we first proceed to its dedoping by immersing the material in regularly renewed acetonitrile solutions for about 70 h. A comparison between the *FT*i.r. spectra of the precursor and of the dedoped chemical PPV clearly shows that the intensity of the peak at $2940\,\mathrm{cm}^{-1}$ ($sp^3$ C–H stretching) of the sulfonium moieties in the precursor polymer decreases rapidly. At the same time the appearance of PPV bands was observed, particularly the band at $970\,\mathrm{cm}^{-1}$. This band obviously indicates that the chemical PPV has a *trans* configuration. However, a mixture of *trans* and *cis* PPV is not excluded, because the band corresponding to the *cis* structure can be overlapped by the acid bands in the spectra. The $HSO_3CH_3$–chemical PPV and $H_2SO_4$–chemical PPV samples give a broad O–H stretching band centred around $3300\,\mathrm{cm}^{-1}$ and two peaks at 1709 and $1602\,\mathrm{cm}^{-1}$, characteristic of sulfonic acids. On the other hand, the absorbances at 1037 and $1180\,\mathrm{cm}^{-1}$ can be assigned to symmetric and asymmetric stretching in sulfonic acids, and the identification of these groups is well supported by the peaks at 400 and $650\,\mathrm{cm}^{-1}$, which may belong to the C–S stretching (*Figure 2B*). As for the $HClO_4$–chemical PPV samples, two bands at 1100 and $625\,\mathrm{cm}^{-1}$ can be ascribed to the perchlorate (*Figure 2C*). Concerning the acid groups observed in the spectra, it is difficult at present to ascertain whether they are moities grafted on the polymer backbone or free counterions of the dopants entrapped by the polymer matrix. Nevertheless, the sulfonation observed in the heated $H_2SO_4$ doped PPV has been reported by Simpson *et al.*[21]. However, in the case of $H_2SO_4$–chemical PPV there are two pieces of experimental evidence in favour of the grafting of acid: (i) in spite of the prolonged dedoping time, the characteristic band of the acid does not disappear; (ii) after dedoping the conductivity of the chemical PPV becomes very low. These results suggest that the only side reaction in this conversion is the grafting of acid moieties onto the PPV backbone.

## *Conclusion*

From these results, it is clear that PPV can be prepared at room temperature by a simple and direct treatment of the precursor sulfonium with certain acids.

This new acidic route is considered to be promising for an industrial scale production of a large number of PPV derivatives from their various precursors[17].

## *References*

1 Granier, T., Thomas, E. L., Gagnon, D. R., Karasz, F. E. and Lenz, R. W. *J. Polym. Sci., Part B: Polym. Phys.* 1986, **24**, 2793
2 Granier, T., Thomas, E. L. and Karasz, F. E. *J. Polym. Sci., Part B: Polym. Phys.* 1989, **27**, 469
3 Murase, I., Ohnishi, T., Noguchi, T. and Hirooka, M. *Polym. Commun.* 1984, **25**, 327
4 Hirooka, M., Murase, I., Ohnishi, T. and Noguchi, T. 'Frontiers of Macromolecular Science', Blackwell Scientific, Oxford, 1989, p. 425
5 Wessling, R. A. and Zimmerman, R. G. US Patent 3 401 152, 1968
6 Montaudo, G., Vitalini, D. and Lenz, R. W. *Polymer* 1987, **28**, 837
7 Gagnon, D. R., Capistran, J. D., Karasz, F. E., Lenz, R. W. and Antoun, S. *Polymer* 1987, **28**, 567
8 Schlenoff, J. B. and Wang, L. J. *Macromolecules* 1991, **24**, 6653
9 Garay, R. O., Baier, U., Bubeck, C. and Muellen, K. *Adv. Mater.* 1993, **5**, 561
10 Lenz, R. W., Han, C. C., Smith, J. S. and Karasz, F. E. *J. Polym. Sci., Part A, Polym. Chem.* 1988, **26**, 3241
11 Halliday, D. A., Burn, P. L., Friend, R. H. and Holmes, A. B. *J. Chem. Soc., Commun.* 1992, 1685
12 Halliday, D. A., Bradley, D. D. C., Burn, P. L., Friend, R. H. and Holmes, A. B. *Synth. Met.* 1991, **41**, 931
13 Burn, P. L., Bradley, D. D. C., Friend, R. H., Halliday, D. A., Holmes, A. B., Jackson, R. W. and Kraft, A. *J. Chem. Soc.: Perkin Trans. I* 1992, 3225
14 Kanbe, M. and Okawara, M. *J. Polym. Sci., A-1* 1968, **6**, 1058
15 Han, C. C. and Elsenbaumer, R. L. *Synth. Met.* 1989, **30**, 123
16 Tokito, S., Momii, T., Murata, H., Tsutsui, T. and Saito, S. *Polymer* 1990, **31**, 1137
17 Massardier, V., Sagnes, O., Dubois, J. C., Tran, V. H. and Guyot, A. French Patent 91 04721, 18 June 1991
18 Massardier, V. Thèse de Doctorat, University Claude Bernard, Lyon, France, 1993
19 Bradley, D. D. C., Evans, G. P. and Friend, R. H. *Synth. Met.* 1987, **17**, 645
20 Hirooka, M., Murase, I., Onishi, T. and Noguchi, 'Frontiers of Macromolecular Science' (Eds T. Saegusa *et al.*), Blackwell Scientific, Oxford, 1989, pp. 425–430
21 Simpson, J. H., Rice, D. M. and Karasz, F. E. *Polymer* 1991, **32**, 2340