

## A Study on the Elimination Reaction of Sulfonium Polyelectrolyte Precursor Polymers to Poly(*p*-phenylenevinylene)

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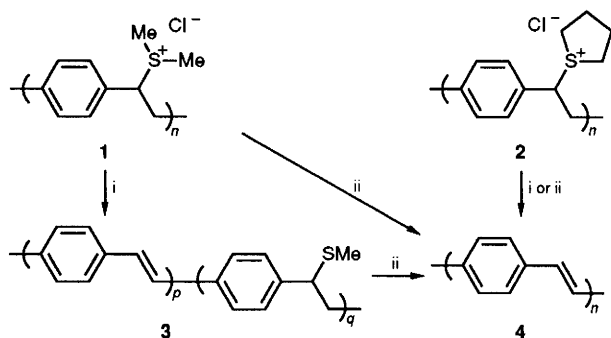
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The dimethylsulfonium polyelectrolyte precursor polymer **1** afforded high quality poly(*p*-phenylenevinylene), PPV, when the sulfonium elimination was performed under acidic conditions; it is proposed that the elimination of the sulfonium group to form a vinylene unit proceeds by an E1 mechanism in the solid state.

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Conjugated polymers are an important class of materials, which can have both electrical conducting or semiconducting properties. Poly(*p*-phenylenevinylene) (PPV) prepared *via* a soluble and processible sulfonium polyelectrolyte precursor polymer was originally of interest as an organic conductor

exhibiting conductivities well into the metallic region when doped.<sup>1-3</sup> We have utilised the intrinsic semiconducting properties of PPV by incorporating it as the light-emitting layer in an electroluminescent polymer device (ELPD).<sup>4,5</sup> The thermal treatment of sulfonium precursor polymers **1** and **2**



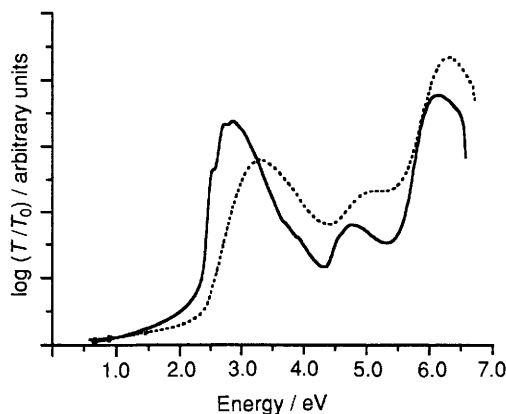
**Scheme 1** Conditions: i, 300 °C, 12 h under vacuum; ii, 220 °C, 12 h under a constant flow of a hydrogen chloride–argon mixture

(Scheme 1) affords conjugated polymers **3** and **4**, respectively by elimination of a dialkyl sulfide moiety and hydrogen chloride. PPV produced from precursor polymer **1** has been reported to have inferior optical and conductive properties compared with that produced from precursor polymer **2**, owing to nucleophilic attack by the counter anion on the methyl groups of the dimethylsulfonium moiety.<sup>6–8</sup>

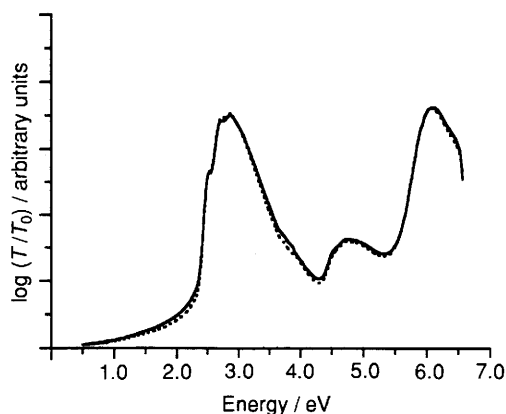
In this communication we report a method of conversion which overcomes the inferior optical properties of PPV prepared from **1**. We also propose that the elimination of the sulfonium groups proceeds predominantly *via* an E1 mechanism in the solid state.

Films for UV–VIS characterisation studies were prepared by spin-coating the precursor polymers onto wide-field spectroscopic substrates from methanol. Films for characterisation by IR spectroscopy were cast [spin-coated films were too thin for standard Fourier transform (FT) IR techniques] on poly(tetrafluoroethylene) from the same solutions and used as free-standing films. Precursor polymers **1** and **2** were thermally treated at 300 °C for 12 h *in vacuo* and 220 °C for 12 h *in vacuo*, respectively in order to achieve the maximum formation of conjugated sequences. The optical absorption spectra of PPV obtained from **1** and **2** are shown in Fig. 1(a) and Fig. 2(a), respectively. Samples of **1** and **2** were also heated at 220 °C for 12 h under a constant flow of a hydrogen chloride–argon mixture and the absorption spectra are shown in Fig. 1(b) and Fig. 2(b), respectively. Essentially no difference was observed between the optical absorption spectra of PPV prepared from **2** by the two methods. However, when **1** is utilised as the precursor polymer a stark contrast exists between the optical absorption spectra of PPV prepared under the two different reaction conditions. Under the thermal and acid treatment the PPV formed has a narrower, stronger and lower energy delocalised  $\pi$ – $\pi^*$  absorption band [Fig. 1(b)] than PPV prepared by thermal treatment alone [Fig. 1(a)]. The absorption spectrum also shows phonon peaks at the same energies as seen in PPV prepared from **2** [Fig. 2(a) and (b)]. IR spectra showed that the PPV whose optical spectra are shown in Figs. 1(b), 2(a) and 2(b) had the same chemical structure with the vinylene double bonds in the *trans* configuration.

The energy of the observed delocalised  $\pi$ – $\pi^*$  transition in the absorption spectra is dependent on the ‘effective’ conjugation length. The ‘effective’ conjugation length can be shortened either by chemical defects (saturated units) or by conformational effects [twisting of the polymer backbone causing a reduction in the overlap of the  $p_z$  ( $\pi$ ) orbitals]. In the case of PPV, prepared *via* the thermal treatment of **1**, the residual  $sp^3$  carbons carrying methyl thioether groups (observed in the IR spectrum) interrupt the delocalised  $\pi$ -electron system, and this is at least in part responsible for the ill-defined delocalised  $\pi$ – $\pi^*$  absorption band. Elemental analysis of PPV prepared from **1** by thermal treatment revealed a sulfur content of *ca.* 8%. The dramatic improvements in the optical properties of PPV prepared by thermal



**Fig. 1** (a) Absorption spectrum of PPV produced from **1** after 12 h at 300 °C under vacuum (dashed). (b) Absorption spectrum of PPV produced from **1** after 12 h at 220 °C under a constant flow of a hydrogen chloride–argon mixture (continuous)



**Fig. 2** (a) Absorption spectrum of PPV produced from **2** after 12 h at 220 °C under vacuum (dashed). (b) Absorption spectrum of PPV produced from **2** after 12 h at 220 °C under a constant flow of a hydrogen chloride–argon mixture (continuous).

and acid treatment of **1** is due to a reduction in the number of both the conformational and chemical defects. The decrease in chemical defects was confirmed by elemental analysis where the level of sulfur was at an undetectable level. PPV prepared *via* thermal treatment of **1** was also treated at 220 °C for 12 h under a flowing hydrogen chloride–argon mixture whereupon the sulfur content was found to have been reduced from *ca.* 8% to an undetectable level by elemental analysis. Under acidic conditions the thioether groups are protonated and form good leaving groups (in an analogous fashion to methoxy leaving group precursor polymer to PPV) for thermal elimination.<sup>9,10</sup> However, the optical absorption spectrum of this sample still exhibited the same broad delocalised  $\pi$ – $\pi^*$  absorption band despite the removal of the thioether groups. This is indicative of the important role that the order in the precursor polymer plays in the optical properties of PPV.<sup>11</sup> Thus, the PPV prepared from **1** by thermal followed by thermal/acid treatment has the saturated units removed by the second treatment but the conformation responsible for the lower ‘effective’ conjugation length is locked in after the initial thermal step.

The elimination of the sulfonium groups is irreversible and has been reported to proceed according to an E1cB mechanism to yield fully *trans* materials.<sup>12–14</sup> However, this mechanism is inconsistent with the data for the elimination of the sulfonium groups in the solid state under neutral reaction conditions. We have found that thermal analysis of **1** by differential scanning calorimetry shows elimination of two different species occurring at 125 and 195 °C and **2** exhibited

endotherms at 150 and 202 °C. Single ion current mass spectrometry has shown that the most abundant product generated upon pyrolysis of **1** was dimethyl sulfide at a temperature around 125 °C.<sup>15</sup> The broad peak centred around 195 °C was assigned to the generation of hydrogen chloride.<sup>15</sup> This data shows that elimination of the dialkyl sulfide takes place before the liberation of a hydrogen chloride molecule in the solid state and this is consistent with an E1 mechanism and inconsistent with either an E1cB or E2 mechanism. In fact under acidic conditions one would expect the elimination reaction to be suppressed instead of enhanced if the mechanism were either E1cB or E2. Although E1 mechanisms are not stereospecific, those *cis*-linkages which are formed would be expected to isomerise thermally to the lower energy *trans*-configuration.<sup>16</sup>

In summary, we have shown that the thermal sulfonium elimination reaction of precursor polymer **1** under acidic conditions gives PPV with the same good optical properties as PPV prepared from precursor polymer **2** owing to the reduction in the number of chemical and conformational defects. The elimination of the dialkyl sulfide and hydrogen chloride under neutral or acidic conditions is consistent with an E1 mechanism in the solid state.

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