New Conducting Polymer Film: Poly(2,5-thienylenevinylene) prepared *via* a Soluble Precursor Polymer

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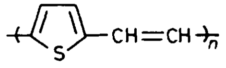
Tough, flexible films of poly(2,5-thienylenevinylene) (PTV), which exhibited conductivity of 60 S/cm on iodine doping, were prepared through a soluble precursor polymer.

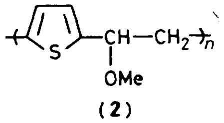
Processibility in preparation is crucially important in the development of conducting polymers for both fundamental research and practical applications. Successful new approaches involving the syntheses of soluble precursor polymers have been developed for polyacetylene,[1] poly(*p*-phenylene),[2] and poly(*p*-phenylenevinylene).[3] We have applied the latter technique to the synthesis of poly(2,5-thienylenevinylene) (PTV) films.

PTV (**1**) is a conjugated polymer regarded as an alternating copolymer of thiophene and acetylene and is expected to exhibit high conductivity on doping. Although PTV was synthesized by Kossmehl *et al.* in 1969, their PTV was in powder form.[5] We describe here the synthesis of stable, flexible PTV films, which were converted to highly conducting, tough films on iodine doping.

The PTV films were prepared *via* a similar route to poly(*p*-phenylenevinylene) films, involving a solution polymerization and a solid state thermal elimination reaction.[3–5]



(**1**)



(**2**)

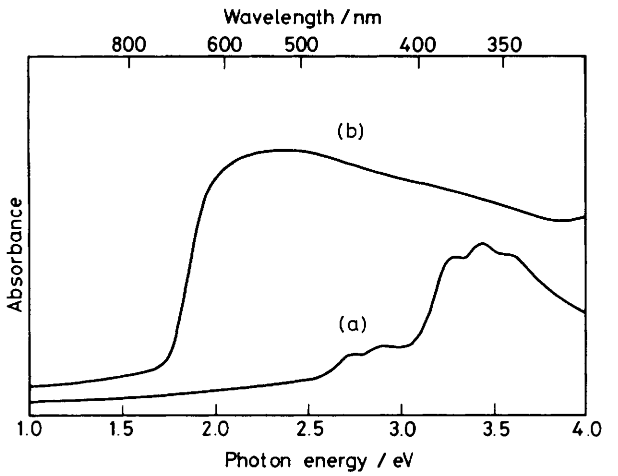


Figure 1. Optical absorption spectra of (a) precursor polymer and (b) poly(2,5-thienylenevinylene) thin films.

Polymerization of the sulphonium monomer, 2,5-thienylenebis(dimethylsulphonium) dichloride, was first examined in aqueous alkaline solution at 0 °C. Although a precursor polymer soluble in dimethylformamide was obtained, partial elimination of the sulphonium salt group during polymerization could not be avoided. The polymerization was then carried out in a methanol–water mixture at −30 °C in the presence of 0.3 M-tetramethylammonium hydroxide, to give a pale yellow solution without precipitate after 4 h. The reaction was quenched by the addition of hydrochloric acid. A yellow precipitate appeared as the solution was warmed to room temperature, suggesting the decomposition of the sulphonium salt structure. The precipitate, however, was completely soluble in both tetrahydrofuran and dichloromethane. Clear, tough films were obtained by casting the precipitate from the dichloromethane solution.

The i.r. spectrum of this film clearly indicated the presence of an -OMe group (C–O stretching at 1090 cm^{-1} and CH$_3$ stretching at 2839 cm^{-1}). Solubility tests and elemental analyses supported our assumption that the precursor polymer contained no sulphonium salt group and possessed structure (**2**).

The precursor polymer films were heated at 200—250 °C under a vacuum of 10^{-2} Torr for 5 h, to give tough, flexible PTV films with a black metallic lustre. The strong absorption at 930 cm^{-1} due to the *trans* C=C linkage and the elemental analyses indicated that the precursor polymer was completely transformed to PTV.

The u.v.–visible absorption spectra of the precursor polymer and PTV films are shown in Figure 1. The precursor polymer showed a small absorption at around 3.4 eV (340 nm), while the PTV film exhibited a large absorption ($\pi \rightarrow \pi^*$ transition) centred at 2.3 eV (540 nm). The peak position is situated midway between those of polythiophene and polyacetylene.[7,8] From the threshold of the optical absorption due to a $\pi \rightarrow \pi^*$ transition in the low energy region, an optical band gap of *ca.* 1.8 eV was obtained, which is very close to that of 1.6 eV calculated by Brédas *et al.*[9] using the Valence Effective Hamiltonian method.

The conductivity of the pristine PTV film was lower than 10^{-13} S cm^{-1} at room temperature. On exposure to iodine vapour at room temperature, the conductivity of the PTV film rapidly increased to 60 S cm^{-1}. The doped film was very stable in air; this conductivity was retained for more than a month.

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