Synthesis of Poly(vinylene sulphide) and Its Electrical Properties

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A novel polymer of poly(vinylene sulphide), synthesized from *trans*-1,2-dichloroethylene and sodium sulphide, shows enhanced electrical conductivity on doping with iodine, and has an electronic structure consistent with that determined by Brédas *et al.* from theoretical calculations.

Conducting organic polymers have recently been investigated with considerable interest. These are conjugated polymers and can be doped with either electron acceptors or donors to yield electrically conducting derivatives. Some of them, such as poly(*p*-phenylene sulphide) and poly(thiophene), contain sulphur atoms. It is especially interesting that poly(phenylene sulphide) can be doped to give electrical conductivity although it is not a conjugated compound. Poly(vinylene sulphide), $-(CH{=}CH{-}S)_x-$, (PVS), is the simplest sulphur-containing unsaturated polymer, but it has not yet been prepared. The electronic structure of this polymer has been studied by Brédas *et al.*[1] using *ab initio* MO calculations and it is expected to have very promising characteristics. We have succeeded in preparing this novel conducting polymer, and the preparation is described here. PVS has a high conductivity on doping with an electron acceptor and has good processibility. We have also compared the theoretical electronic structure (band gap, XPS theoretical spectrum) of Brédas *et al.*[1] with our experimental data.

PVS was prepared by the condensation polymerization of sodium sulphide and *trans*-1,2-dichloroethylene. *N*-Methyl-2-pyrrolidone was used as solvent. *N*-Methyl-2-pyrrolidone (25 ml) and $Na_2S{\cdot}9H_2O$ (5 g) were added to a reactor equipped with a powerful stirrer under an argon atmosphere. The sodium sulphide solution was stirred vigorously at room temperature, and then *trans*-1,2-dichloroethylene (6.2 g) was added. The reaction mixture was filtered and the filtrate acidified with aqueous HCl and subsequently mixed with water. PVS was extracted with 1,2-dichloroethane from the filtrate. The organic phase was washed repeatedly with water and distilled off. The red brown concentrate containing PVS was dissolved in chloroform and purified by gel permeation chromatography. PVS has a red brown colour when dissolved in organic solvents and it can be obtained as a film by casting.

The structure of PVS was supported by ^1H n.m.r., ^{13}C n.m.r., and i.r. spectra.† The broad signal at *ca.* δ 6.3 in the ^1H n.m.r. spectrum indicates the presence of an olefinic proton and the broad resonance centred at *ca.* 125 p.p.m. in the ^{13}C n.m.r. spectrum is ascribed to the alkenic carbon atom. The i.r. spectrum exhibits absorption bands at 3024, 1540, 910, and 660 cm^{-1}. The band at 3024 cm^{-1} is due to the olefinic C–H stretching. A broad band centred at 1540 cm^{-1} is characteristic of the C=C double bond positioned between two sulphur atoms, such as S–CH=CH–S.[2] The two bands at 910 and 660 cm^{-1} can be assigned to the olefinic C–H deformation vibration out of plane in *trans* and *cis* conformation, respectively, since it is known that a red shift is caused by sulphur atoms neighbouring the C=C double bond.[3]

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† ^1H N.m.r., ^{13}C n.m.r., and i.r. spectra were obtained with a JNM MH-100 n.m.r. spectrometer, a JNM GX-400 Fourier transform (F.t.) n.m.r. spectrometer, and a JIR-40 F.t.-i.r. spectrophotometer, respectively.

The electrical conductivity of PVS film was measured by the two-probe method using a 4140 pA meter/D.C. voltage source (Yokogawa–Hewlett-Packard, Ltd.). Two electrodes were formed on the film by vacuum evaporation of gold.

XPS measurements were performed with a PHI Model 550 ESCA system (Perkin–Elmer Corp.) using monochromatized Mg-K_α radiation. The spectra were calibrated using the Au $4f_{7/2}$ line as a standard.

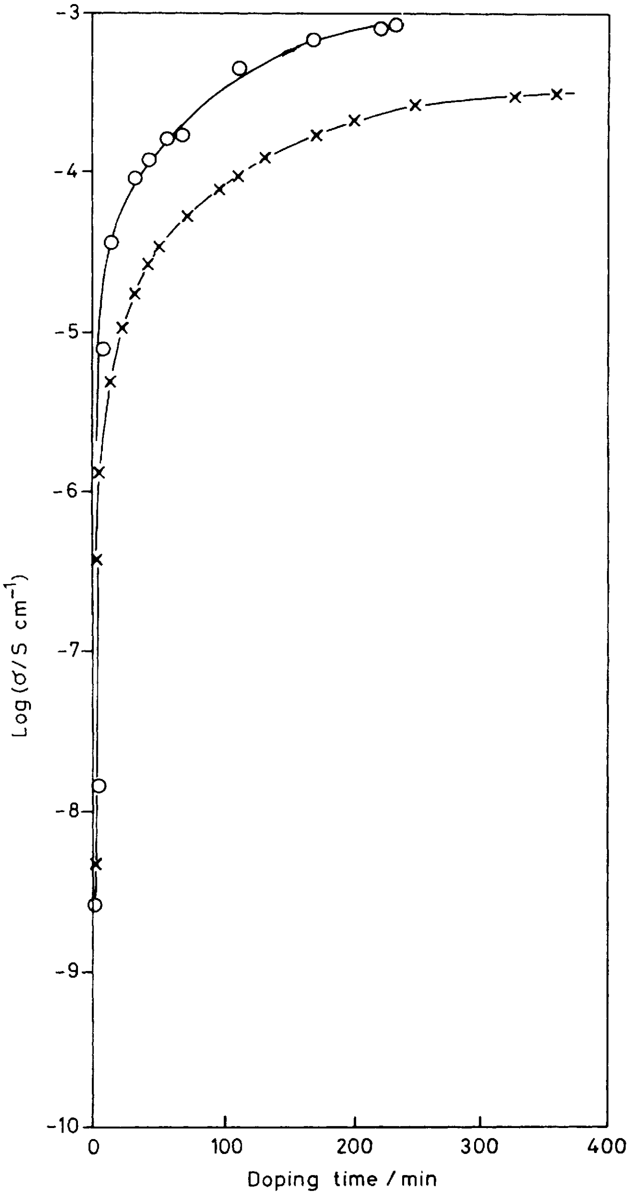

Figure 1. Electrical conductivity (log σ) *versus* iodine doping time; ○ : prepared at 40 °C; × : prepared at room temperature.

The electrical conductivity of PVS, measured by the two-probe method,[†] is 2.7×10^{-9} S cm^{-1}.

On exposure to iodine vapour at room temperature (vapour pressure *ca.* 0.2 Torr), the conductivity σ is rapidly enhanced as shown in Figure 1. A plot of log time *vs.* log σ gives a straight line with slope 1.6. Results of reproducible experiments show this slope to be in the region 1.5—1.7. The conductivity increases rapidly in the first few minutes, and then levels out to 7.9×10^{-4} S cm^{-1}. The colour of the specimen film changes to dark brown, and finally to shiny black.

An *ab initio* valence effective Hamiltonian (VEH) calculation has been performed on PVS by Brédas *et al.*,[1] and they give theoretical results for the parameters ionization potential, band width, and band gap (E_g). These values are 5.6, 3.3, and 3.3 eV, respectively. Brédas *et al.*[1] have also computed the VEH theoretical XPS spectrum.

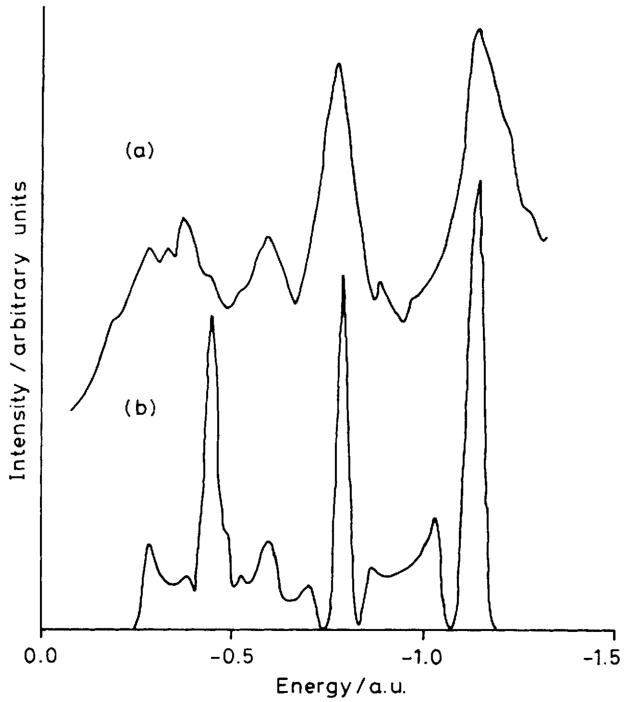

Figure 2. A comparison between the experimental and theoretical XPS spectra: (a) the experimental XPS spectrum rescaled in order to get a good fit with (b); (b) the theoretical XPS spectrum of Brédas *et al.*

It is often observed in amorphous semiconductors that the frequency dependence[4] of the absorption coefficient α is given by equation (1), where r and $\hbar\omega$ are a constant and the

$$\alpha\hbar\omega = \text{constant}\ (\hbar\omega - E_g)^r \qquad (1)$$

photon energy, respectively. In the case of PVS, the constant $r = 1$ (from the electronic absorption spectrum). Therefore, the optical gap E_g is determined by extrapolation of the linear region in the $\hbar\omega$ *vs.* $\alpha\hbar\omega$ plot. We obtained $E_g = 3.6$ eV from this plot, which is in good agreement with the result obtained by Brédas *et al.*,[1] $E_g = 3.3$ eV. The XPS spectrum of PVS[†] is shown in Figure 2(a) and the theoretical spectrum of Brédas *et al.* is shown in Figure 2(b). The experimental peak positions were rescaled by multiplying by a factor of 1.3 in order to get a better fit with the theoretical spectrum. It should be noted that the experimental XPS spectrum is in good agreement with the theoretical XPS spectrum of Brédas *et al.*

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