# An Optical Study of the Arsenic Pentafluoride Doping of Poly(p-phenylene sulphide): Polaron and Bipolaron Transitions

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The oxidative doping of thin films of poly(p-phenylene sulphide) by arsenic pentafluoride has been followed by transmission absorption spectroscopy (near i.r. to u.v.) and transitions are assigned involving cationic states, polaron and bipolaron, formed within the $\pi-\pi^*$ band gap.

There is considerable current interest in electrically conducting polymers such as polyacetylene, poly(p-phenylene), and polypyrrole. The interest has been stimulated partly by the novel properties of such systems and partly by the potential applications to such areas as rechargeable batteries.[1] Poly(p-phenylene sulphide) (PPS) has the advantage of being melt and solution processable and on reaction with arsenic pentafluoride, equation (1), forms an electrically conducting material.[2]

$$2(PPS) + 3AsF_5 \rightarrow 2(PPS)^+ + 2AsF_6^- + AsF_3 \quad (1)$$
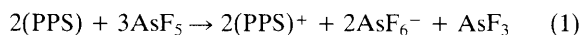
We have followed the changes in the near i.r. to u.v. absorption spectrum of thin films of PPS (Aldrich Chemical Co.) on exposure to arsenic pentafluoride vapour, typical pressure 30 mbar. Films 10—15 μm thick were formed from the evaporation of diphenyl ether or 1-chloronaphthalene solutions at ca. 125 °C, while films less than 0.2 μm were obtained from the polymer melt above 300 °C.
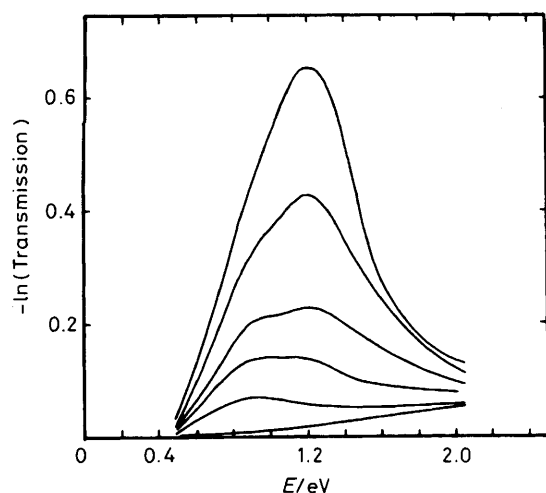
The absorption spectrum of the undoped polymer shows a band-edge at 3.4 eV and lowest energy $\pi-\pi^*$ transition of 3.9 eV. Within two minutes of exposure to AsF$_5$ of films less than 0.1 μm thick, transitions at 0.9 and 3.1 eV were detectable while the inter-band $\pi-\pi^*$ region correspondingly weakened, Figure 1(b). As the extent of doping increased a further transition at 1.2 eV was observed and an isosbestic point was apparent at 3.45 eV (350 nm) as the inter-band transition weakened further. Also the width on the low energy side of the transition centred at 3.1 eV decreased, while increasing in overall intensity, Figure 1(c). As the doping
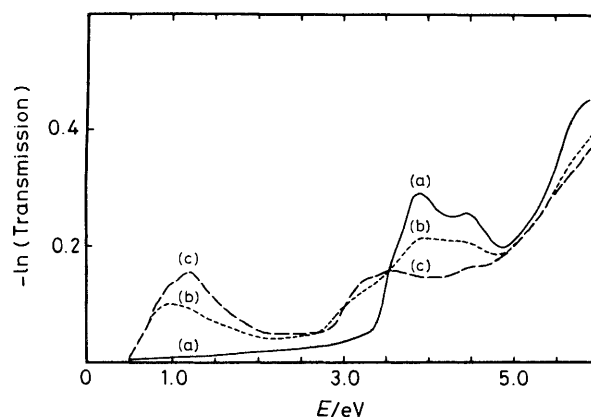

Figure 1. Absorption spectrum of a PPS thin film (<0.1 μm) initially (a), and after successive exposures to AsF$_5$ vapour (b) and (c).

progressed the 0.9 eV peak decayed after first becoming a shoulder to the 1.2 eV transition, which eventually dominated the spectrum. The transitions in the i.r. region are seen more clearly in Figure 2. When the 0.9 eV peak was lost there was a parallel reduction in the intensity of the 3.1 eV transition and a small decay in signal strength in the intervening region (Figure 3).

All the features in the absorption spectrum below the band-edge could be removed by exposing the film to compensating reagents, ammonia or water vapour, indicating that no irreversible structural modification of the polymer had taken

Figure 2. The near i.r. region of the absorption spectrum of a thin PPS film showing the development of the peaks after successive periods of AsF₅ doping.
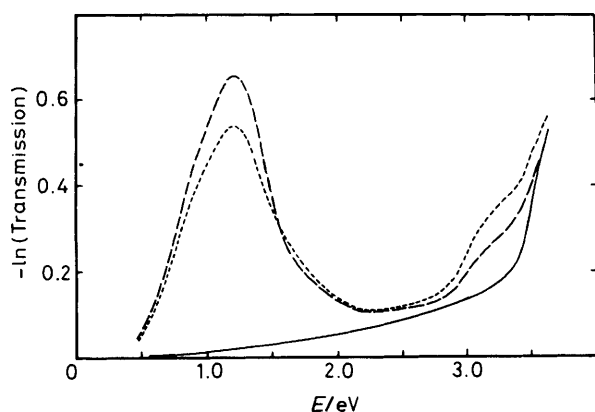
Figure 3. Visible–i.r. region of the absorption spectrum for an AsF₅ doped thin PPS film showing the loss of the polaron (0.9, *ca.* 2.0, and 3.1 eV) and gain in intensity of the bipolaron transitions (1.2 and 3.2 eV) on further doping. The spectra show that α (polaron) $> \alpha$ (bipolaron) in the 3.0—3.4 eV region. The traces cross only at 1.55 eV.

place. Upon prolonged doping further changes in the absorption spectrum[3] occur as the polymer undergoes a predominantly *intra*-molecular cross-linking reaction generating thiophene linkages along the chain, eventually forming a material similar to poly(benzothiophene).[4]

On reacting films *ca.* 10 μm thick with AsF₅ vapour for short periods, the 1.2 eV transition tended to dominate in the near i.r. and there was little change in the u.v. region of the spectrum.

Theoretical calculations predict the initial formation of polaron or radical-cationic defect states along the polymer chain or lattice, at low doping levels, followed by the loss of these states on increased doping when pairs of polarons coalesce to form bipolaron, dicationic states of higher binding energy.[5] The polaron and bipolaron states each generate what may be regarded as a bonding and anti-bonding level between the valence and conduction band as a result of the local structural deformation caused by the charge (Figure 4). As higher doping levels are reached the bipolaron states begin to interact forming separate bands. In the case of *trans*-polyacetylene, which has a degenerate ground-state, the polarons combine to form mid-gap, soliton states. For a
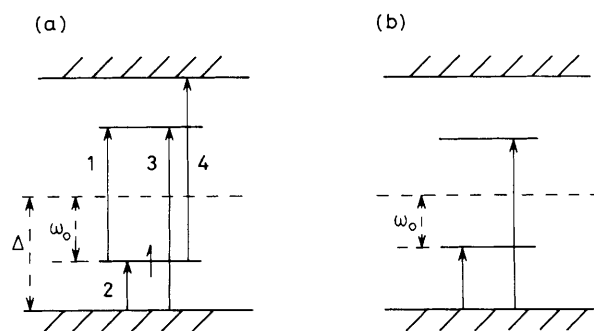
Figure 4. Schematic representation of the additional transitions possible for, (a) a positively charged polaron, (b) a single positively charged bipolaron. The band-gap $= 2\ \Delta$.

positively charged polaron there are four possible transitions in addition to the main π–π^* absorption. The oscillator strengths expected for the transitions have been calculated for a polyacetylene model[6] and depend upon the energy separation of the defect levels from the band edges, measured by ω_0 (Figure 4). The oscillator strength for the below-gap transitions is taken from the π–π^* transitions, a sum rule operating; the total weight removed depends on ω_0. For most values of ω_0, $\alpha_1 = ca.$ $\alpha_2 \gg \alpha_3$ is predicted (α = absorption coefficient).

From the results for PPS given here the 0.9 and 3.1 eV bands are assigned to the polaron transitions α_2 and (α_3 + α_4) respectively. There is little evidence for the expected transition (α_1) at *ca.* 2.0 eV except an increase in the overall level of absorption in this region on initial doping and the small drop in intensity as the concentration of polarons decreases (Figure 3). The bipolaron state gives rise to two below-gap absorptions, at 1.2 and 3.2 eV with the lower energy transition considerably more intense in agreement with predictions.[6]

The detection of the isosbestic point was possible only on the doping of very thin films and is an indication of relatively uniform dopant penetration.[7] The spectra obtained from doping thick (*ca.* 10 μm) films for short periods, where the 1.2 eV transition dominated and there was little change in the u.v. region, indicate that a surface layer had become relatively heavily doped while the body of the film remained untouched. This agrees with previous results where inhomogeneous doping has been reported and only a 1.2 eV peak was detected in the near i.r.† after short exposure times.[4,9] By comparison with previous data[9] the highest levels of dopant uptake examined here are expected to be less than 5% per monomer unit, whilst the highest attainable level is *ca.* 90% required for conductivities of the order 1 Ω^{-1} cm^{-1}.

Recent spectroscopic investigations[10] of the p-doping of poly(*p*-phenylene) (PPP) films indicate that for an initial band-gap of 4.0 eV the valence band to bipolaron transitions occur at 1.1 and 3.0 eV in close agreement with recent calculated values[11] for a PPP bipolaron defect of strong quinoid character. The distortion extends over about four benzene rings. Similarly the polaron and bipolaron states for PPS may extend over a number of C₆H₄S units, probably with significant charge density at the sulphur atoms. Band structure calculations on PPS using the Valence Effective Hamiltonian technique[12] show that the highest occupied π-band has contributions from the sulphur 3p$_z$ and adjacent carbon 2p$_z$ orbitals, anti-bonding in character. From consideration of the

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† A peak at 2.0 eV, lost when the sample cell was evacuated, was detected (ref. 8) on AsF₅ doping of PPS films and assigned to the product arsenic trifluoride. The spectra reported here were recorded with the cell evacuated.

(A)

(B)
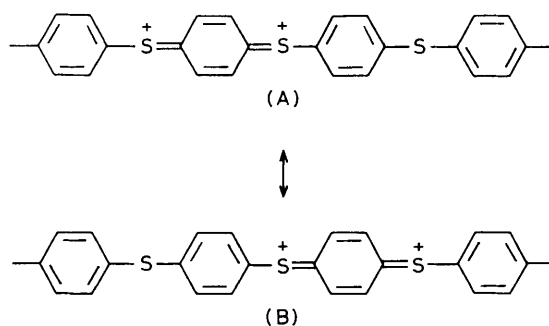
nature of the highest occupied and expected lowest unoccupied π molecular orbitals a quinoid form is also expected for the PPS bipolaron. In valence bond terms this may be represented by the structures (A) and (B).

The optical data show that the bipolaron energy levels shift well into the band-gap, offsetting the ionisation energy requirement, permitted by a strong structural modification along the defect as is seen for PPP.

An e.s.r. study[13] has recently shown that the g-factor for the polaron or radical-cation state of PPS formed on p-doping is similar to the values found for diaryl sulphide radical-cations, where the unpaired electron is π-delocalised from the sulphur over the aryl rings and the g-factor is dominated by S atom spin–orbit coupling.

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