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Electronic properties of conjugated polymers

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The nature of the proposed defect states in conjugated polymers (solitons and polarons in polyacetylene, polarons and bipolarons in other materials) is expected to be strongly dependent on the morphology and chain conjugation length of the polymer. Polyacetylene prepared by the Durham 'precursor' route has a lower conjugation length than that prepared by the Shirakawa route, and it is expected that polarons or bipolarons rather than solitons should be the defect state introduced during chemical doping. We discuss here a wide range of physical measurements made on Durham polyacetylene. We present data for two other, processible, polymers. Poly(phenylenesulphide) shows strong optical absorption features below the band gap when reversibly doped with AsF_5. Poly(diphenylenediphenylvinylene) shows similar behaviour and evidence for photogeneration and chemical generation of polaron-like states in this material is presented.

1. Introduction

Conjugated polymers form an important class of electronically conducting organic materials, which may combine the desirable properties of a polymer, such as processibility, with conventional semiconductor electronic properties. Conduction in these materials involves the π electrons, which overlap along the conjugated chain to form a π conduction band. Overlap between orbitals along chains is usually large, with intrachain transfer integrals of typically 3 eV. These materials are intrinsically semiconductors, and can be made highly conducting only after chemical doping. Interchain overlap of π electrons, although weaker, is still appreciable for simple polymers such as polyacetylene, and the interchain transfer integral is estimated to be *ca.* 0.1 eV (Grant & Batra 1979, 1983); thus conduction in three dimensions is expected to be easy.

The recent interest in the electronic properties of conjugated polymers stems from the availability of flexible 'films' of semiconducting polyacetylene (Ito *et al.* 1974), and the discovery by the Pennsylvania group that these could be chemically doped with electron acceptors such as AsF_5 and iodine, or electron donors such as sodium, to give values of conductivity up to $10^3\ \Omega\ \mathrm{cm}^{-1}$ at room temperatures (Chiang *et al.* 1977). Polyacetylene had previously only been prepared as an insoluble, infusible powder, and it was the synthesis of these films that allowed the wide range of physical measurements necessary to unravel the nature of the transport processes in this material.

The behaviour of the conductivity with both acceptor and donor dopants is suggestive of the conventional substitutional p and n type doping of a semiconductor. Doping, of course, is not substitutional; the dopant species reside alongside the polymer and there is a charge transfer process to the polymer chain. The doping reaction is more akin to the intercalation chemistry known for graphite and other layer-structure materials (Dresselhaus & Dresselhaus 1981, Friend 1982).

As discussed in §3, charges added to conjugated polymer chains do not behave as low mass particles, as is the case for conventional semiconductors such as silicon, but are intrinsically localized as a result of a relaxation of the polymer chain round the charge to form defects that may be of a soliton, polaron or bipolaron type. Most of the electronic properties of interest in these materials are determined by the behaviour of these defect states, and the theoretical understanding of them that has been achieved in recent years has been a crucial factor in advancing this field (Su *et al.* 1979, 1980; Rice 1979; Takayama *et al.* 1980; Campbell & Bishop 1981).

It can be argued that materials development has lagged behind the advances of the theoretical physicists, and that the materials widely available have few desirable 'polymer' properties. In this paper, therefore, we discuss our recent work on some processible polymers. These include polyacetylene prepared by thermal elimination of a leaving group from a non-conjugated precursor polymer (Edwards & Feast 1980) poly(phenylenesulphide), and poly(diphenylenediphenylvinylene) (PDPV) (Feast & Millichamp 1983). The control of morphology that can be brought about for these materials together with measurements of physical properties gives important information on the nature of the defect states in these materials, and this is discussed in §4.

2. Materials

(*a*) *Shirakawa-route polyacetylene*

Polyacetylene remains the most extensively studied of the conjugated polymers. The synthesis of polyacetylene 'films' by Shirakawa's group (Ito *et al.* 1974) involves the direct polymerization of acetylene gas on, for example, a substrate wetted with a Ziegler–Nata catalyst solution. A thin polymer film can be conveniently grown at a low temperature, usually − 78 °C. At this temperature, polyacetylene grows as the *cis* isomer (*cis*-transoidal) shown in figure 1. The stable isomer is the *trans* isomer (*trans*-transoidal) and conversion from the *cis* to *trans* may be achieved within a few minutes on heating to above 180 °C. The 'films' obtained have about one third the expected density and electron microscopy shows them to consist of randomly oriented fibrils of diameter 20–50 nm (Shirakawa *et al.* 1983); there is considerable crystallinity within the fibrils. The open structure is obviously advantageous for rapid chemical doping to the high molar concentrations required to achieve high conductivities (*ca.* 0.1 M for $\sigma \approx 10^3\ \Omega^{-1}\ \mathrm{cm}^{-1}$).

(*b*) *Durham-route polyacetylene*

An interesting approach to combine the processibility of a conventional polymer with the desirable electronic properties of a conjugated polymer is to make a non-conjugated 'precursor' polymer, with desirable polymer properties such as solubility, which can be transformed in a simple way by, for example, an elimination reaction, to give the conjugated polymer. We have used this approach (Edwards & Feast 1980; Bott *et al.* 1983), and an effective system is shown in figure 2. Monomer A is converted to the 'precursor' polymer B with a metathesis catalyst

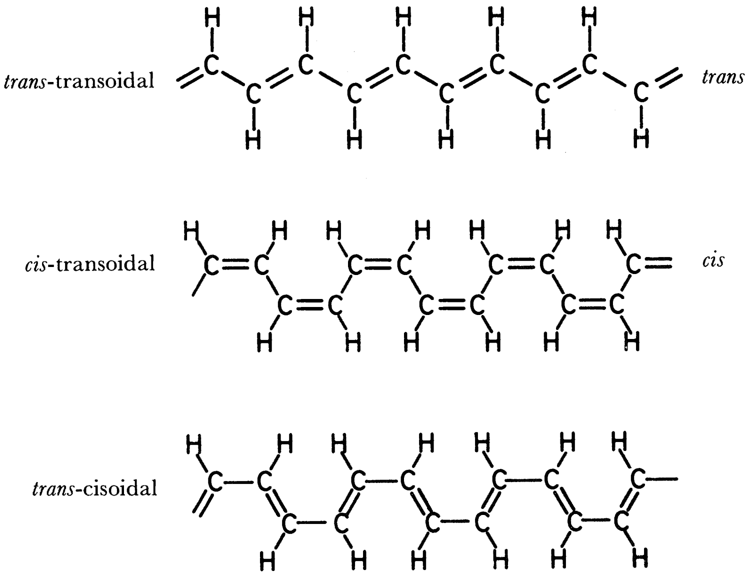


Figure 1. Isomers of polyacetylene.

prepared from tetramethyl tin and tungsten hexachloride. Polymer B is readily soluble in common solvents, but at room temperature and above undergoes the reaction shown to give polyacetylene and a volatile xylene elimination product.

Polyacetylene can be prepared in several forms from this route. Thin films can be made by conversion of a film of the 'precursor' polymer formed by evaporation from solution by a simple heat treatment. In contrast to Shirakawa polyacetylene these films are fully dense ($\rho = 1.05$ g cm^{-3}). X-ray powder diffraction measurements on fully transformed materials indicate a comparable degree of crystallinity to Shirakawa polyacetylene. Highly oriented films can be made if the polymer is transformed in a stress field (White & Bott 1983) and well-oriented fibres can be made by gel-drawing (draw ratios in excess of 10 have been achieved).

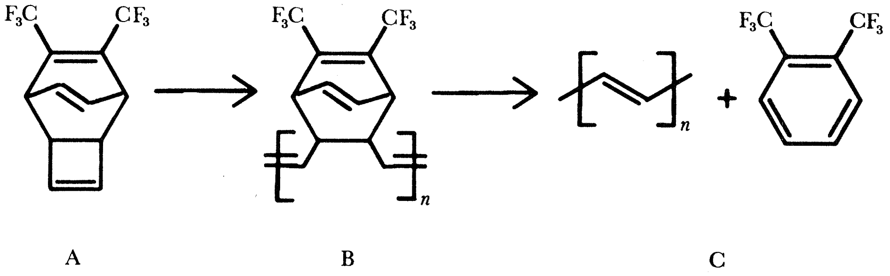


Figure 2. Durham route to polyacetylene.

The transformation reaction is virtually complete within one hour at 50 °C, leaving a material, which is shown by i.r. analysis to contain 75% *cis* and 25% *trans* sequences. The carbon–carbon double bond created during the transformation reaction as the xylene group leaves is necessarily *cis*, and a *cis*:*trans* ratio of 1:1 for the double bonds present in the precursor thus accounts for this distribution. Complete isomerization can be achieved by further thermal treatment. Typical optical absorption spectra as a function of transformation are shown in figure 3. The onset of the π–π^* transition is at about 1.5 eV, but the peak in absorption, at 2.3 eV is higher than that reported for Shirakawa polyacetylene, and indicates that the length of uninterrupted conjugated sequences is smaller than in Shirakawa material, with most sequences of 30–40 carbon–carbon bonds. This is also evident from the resonant Raman spectra. When irradiated with a laser line of 674.4 nm the C=C stretching frequency is measured at 1474 cm^{-1}, in contrast with a value of 1460 cm^{-1} for Shirakawa polyacetylene.

(*c*) *Other polymers*

Some of the other conjugated polymers investigated are shown in figure 3. Poly(paraphenylene) has usually been prepared in a powder form with a relatively low degree of polymerization. It has a larger band gap than polyacetylene of 3–3.5 eV, but is still dopable with strong acceptors such as AsF_5 to give a high conductivity (Shacklette *et al.* 1980). Poly(phenylene vinylene) has been prepared in a similar morphology (Wnek *et al.* 1979). Poly(phenylenesulphide) (PPS) is a commercially available processible polymer that does show an increase in conductivity on doping with AsF_5 of up to 3 Ω^{-1} cm^{-1} (Clarke *et al.* 1982; Shacklette *et al.* 1981).

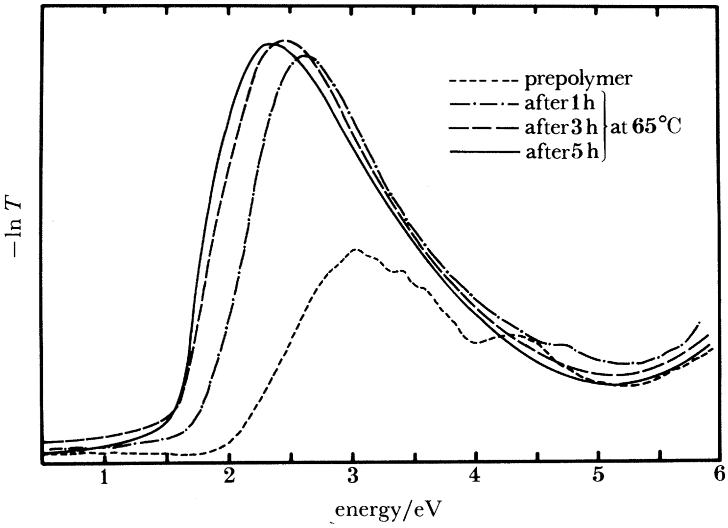


FIGURE 3. Optical absorption spectra on partly transformed and transformed Durham polyacetylene.

It has been shown that AsF_5 initiates some linking of the phenyl groups across the sulphur bridge, to give thiophene linkages, and that it is the presence of this more obviously conjugated structure that is responsible for the increase in conductivity. Poly(diphenylenediphenylvinylene) (PDPV) has recently been synthesized and dissolves in common solvents (Feast & Millichamp 1983). It shows the same 3–3.5 eV band gap of poly(paraphenylene), and is a promising representative material for this group of polymers for experimental work. Presumably the solubility is related to the presence of the two phenyl groups on the vinylene carbons, which are not involved in the conjugation sequence. The degree of polymerization is quite large with g.p.c. measurements, indicating a molecular mass of about 30 kDa (polystyrene equivalent).

3. Band and defect models

(*a*) *Bands*

The electrons contributing to the interesting electronic properties of these conjugated polymers are the p_z electrons left after the sp^2 hybridization that gives the σ bond backbone along the polymer chain. Many calculations on these materials use Huckel theory, which, in spite of the neglect of correlation (Ovchinnikov *et al.* 1973), gives an adequate basis for calculation because parallel bandwidths are large and the π electrons are well delocalized along the chain.

Trans-polyacetylene is a material of particular interest in that without bond alternation (dimerization) along the chain, it would be metallic, with a conduction band half filled by the p_z electrons. Dimerization is driven by the lowering of the band energies of the occupied electron states that result from the opening of a band gap at the Fermi level (Peierls 1955; Longuet-Higgins & Salem 1959). The experimentally measured gap is *ca.* 1.4 eV. In contrast, *cis*-polyacetylene shows an intrinsic dimerization, which is evident from the inequivalence of the *cis*-transoid and *trans*-cisoid structures in figure 1 (the *trans*-cisoid structure is of higher energy). Hence the combination of this and the Peierls mechanism gives an optical gap of few tenths of an electronvolt larger. The other polymers shown in figure 4 all show much larger gaps between conduction and valence bands, but calculations show that the bandwidths along the chains are still of several electronvolts (Bredas *et al.* 1982*a*), so that delocalization along the chain is still effective.

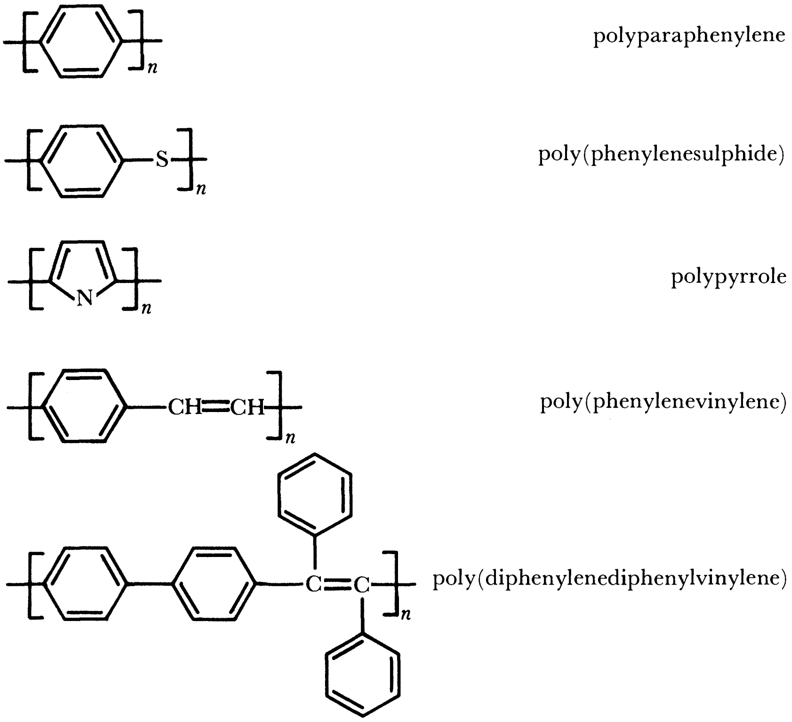


Figure 4. Selected conjugated polymers.

(*b*) *Soliton defects*

As discussed above, *trans*-polyacetylene is unusual among these materials in that the gap is due only to the Peierl mechanism. We can expect, therefore, when the degree of band filling is moved away from $\frac{1}{2}$ as a result of chemical doping that the dimerization is replaced by an incommensurate distortion that attempts to keep the gap at the Fermi level. For incommensurate distortions very close to the $2\times$ commensurate lattice, phase mismatch with the polymer chain periodicity is concentrated at localized domain walls (Rice 1979; Su *et al.* 1979, 1980; Takayama *et al.* 1980). This bond alternation defect is often termed a soliton, and is illustrated for a neutral defect in figure 5*a*. The defect is considerably more delocalized than is indicated in this diagram, and extends over about 14 carbon atoms. The defect formation energy is calculated to be 0.4 eV for a band gap of 2×0.7 eV. It creates a one-electron state that lies at mid-gap (non-bonding p_z orbital). The neutral defect is singly occupied (spin $\frac{1}{2}$), but it may be positively or negatively charged, as illustrated in figure 5*b*. From the energy of formation it is easy to show that charged solitons are expected in preference to occupation of the conduction and valence bands by electrons and holes respectively for donor and acceptor doping. The degeneracy of the A and B phases in figure 5*a* indicates that the domain wall is free to move, and its movement when charged has been put forward as a mechanism for electrical conductivity. An unusual feature of this defect is the separation of spin from charge; when neutral the defect has spin $\frac{1}{2}$, when charged it is spinless.

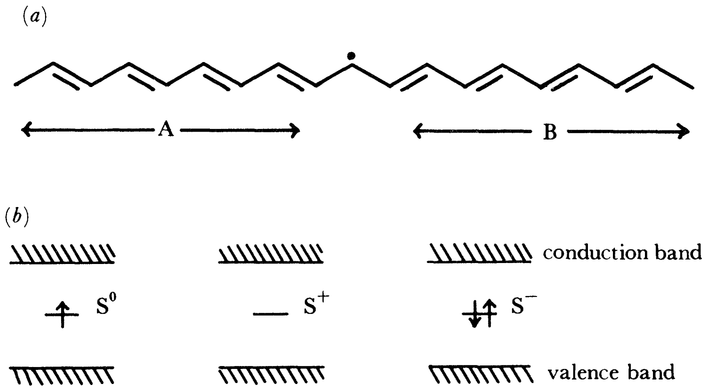


FIGURE 5. (*a*) Bond alternation defect on *trans*-polyacetylene. Note that A and B phases are degenerate. (*b*) Neutral and charged mid-gap soliton levels.

The soliton defect can only be created on long conjugated sequences. Topological considerations require that they be created in pairs, so that a sequence of greater than 30 carbon bonds would be required to observe well separated and mobile soliton defects. We note that this condition is not satisfied in Durham polyacetylene, although it probably is for Shirakawa polyacetylene.

(*c*) *Polaron and bipolaron defects*

The soliton defect developed in the previous section for *trans*-polyacetylene is a topological defect that separates two inequivalent, though in this case, degenerate regions of the polymer chain. For *cis*-polyacetylene, and for the other polymers discussed here, the two regions that are separated by this defect are no longer degenerate. This is illustrated in figure 6*a* for a chain of poly(paraphenylene), for which the defect separates the benzenoid (low energy) and quinonoid (high energy) regions. Thus single defects would move rapidly to the chain end, to reduce the extent of the high-energy phase. However, defect pairs are calculated to be stable defects when charged, either singly to form a polaron, or doubly to form a bipolaron. Figure 6*a* shows schematically a positively charged polaron defect.

The combination of two mid-gap soliton states to form the polaron defect results in the formation of a 'bonding' state and an 'antibonding' state symmetrically separated from mid-gap. Campbell & Bishop (1981) have found exact solutions by using the continuum model applied to the soliton defect by Takayama *et al.* (1980). They find for *trans*-polyacetylene that the two levels are separated by $\pm\Delta/\sqrt{2}$ from mid-gap, when the optical gap is 2Δ. The energy level scheme for these defects is shown in figure 6*b*. The neutral polaron–exciton state has two electrons on it (and decays radiatively to restore the undistorted chain), the positive polaron has one, and the positive bipolaron zero electrons.

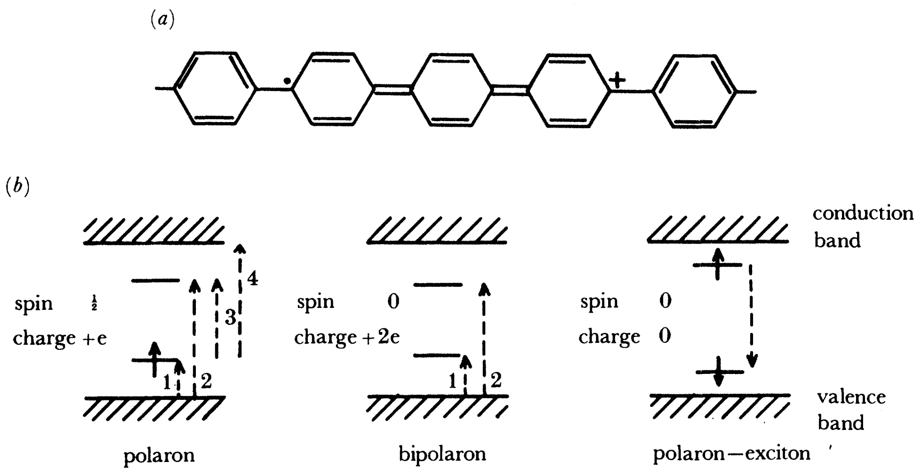


FIGURE 6. (*a*) Schematic representation of a positively charged polaron defect on a poly(paraphenylene) chain, showing the quinonoid structure within the defect. (*b*) Energy level scheme for positively charged polaron and bipolaron defects and the neutral polaron–exciton (shown here as a singlet). Possible optical transitions are indicated.

As for the formation of soliton defects in *trans*-polyacetylene, these polaron and bipolaron defect states are formed in preference to occupation of band states during chemical doping, as discussed by Bredas *et al.* (1982*b*). For one charge added to a single chain a polaron is formed. If a second charge is added it is energetically favourable to form a bipolaron. This prediction, that bipolarons which are, as solitons, spinless when charged, provides an explanation for the absence of magnetic properties of heavily doped polyparaphenylene (Peo *et al.* 1981).

4. PHYSICAL PROPERTIES

(*a*) *Durham polyacetylene*

The Durham route to polyacetylene described in §2(*a*) gives a material with a very different morphology to Shirakawa polyacetylene, with a lower conjugation length along the chain that is too short to support mobile soliton defects. Comparison between Shirakawa and Durham materials therefore enables us to distinguish between those phenomena that are specific to long conjugated sequences, such as mobile spins on neutral solitons, and those properties that may also be described by polaron or bipolaron defects.

(i) *Undoped polyacetylene*

As discussed in §2(*a*) the transformation from the precursor polymer to polyacetylene may be taken first to a *cis*-rich polymer, which may subsequently be isomerized to the *trans*-isomer. E.s.r. measurements show the appearance of localized spins in a concentration of a few hundred per million during the isomerization reaction. The e.s.r. line is broad, with a width of *ca.* 0.8 mT, and is close to gaussian in form. It shows a slight increase in width on cooling to 4.2 K to a value of *ca.* 1.2 mT. These localized spins have a line shape due to inhomogenous broadening. The electrical conductivity is at a low level in the *cis*-rich phase after transformation (under $10^{-13}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at 300 K), rising only after isomerization to a value of *ca.* $10^{-7}\ \Omega^{-1}\ \mathrm{cm}^{-1}$. The nature of the spins generated during isomerization is very different from those observed in Shirakawa polyacetylene. In this material, the spins also appear during isomerization, but show a line width of *ca.* 0.1 mT at room temperature, due to motional narrowing. This is thought to be consistent with the introduction of mobile soliton defects during isomerization (Weinberger *et al.* 1980).

As undoped materials Shirakawa and Durham polyacetylene are semiconductors with transport properties characteristic of hopping conduction between localized states. The *trans*-isomer from the Shirakawa route has a room temperature conductivity of *ca.* $10^{-5}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ (Epstein *et al.* 1981). The conductivity for both Durham and Shirakawa materials is not simply activated, having a weaker temperature dependence, which empirically obeys the relation

$$\sigma = \sigma_0 \exp\{-(T_0/T)^{\frac{1}{4}}\}.$$

This $T^{\frac{1}{4}}$ temperature dependence is well known in amorphous semiconductors and is characteristic of Mott's model of variable range hopping (v.r.h.) (Mott & Davis 1979). Data for the two types of polyacetylene are shown in figure 7*a*. The $T^{\frac{1}{4}}$ temperature dependence is not sufficient to demonstrate that the conduction process is v.r.h., but it may be reasonably concluded that conduction does involve hopping between localized states in three dimensions. If the v.r.h. model is followed, the constant T_0 is related to the density of states at the Fermi energy, $N(E_\mathrm{F})$ and the (assumed) exponential decay length of the localized wavefunctions, α^{-1}, through the equation

$$T_0 = 16\alpha^3/k_\mathrm{B}\,N(E_\mathrm{F}).$$

Values for T_0 of *ca.* 2×10^{9} K and 2×10^{10} K are obtained for the Durham and Shirakawa materials respectively. However, transport processes unique to soliton-containing materials have been proposed by Kivelson (1981, 1982). Although solitons as topological defects cannot hop between chains, if both charged and neutral solitons are present, then hopping of the charge between a neutral and a charged soliton on adjacent chains is possible, and Kivelson has developed a semi-empirical model for many of the transport properties. A satisfactory fit to the d.c. transport data shown in figure 7*a* ($\sigma = \sigma_0\ T^{13.7}$) is obtained for Shirakawa, but not Durham, material.

The a.c. conductivities for both materials have been measured up to 10^{5} Hz. Epstein *et al.* (1981) report data for Shirakawa material, and data for Durham material is shown in figure 7*b*.

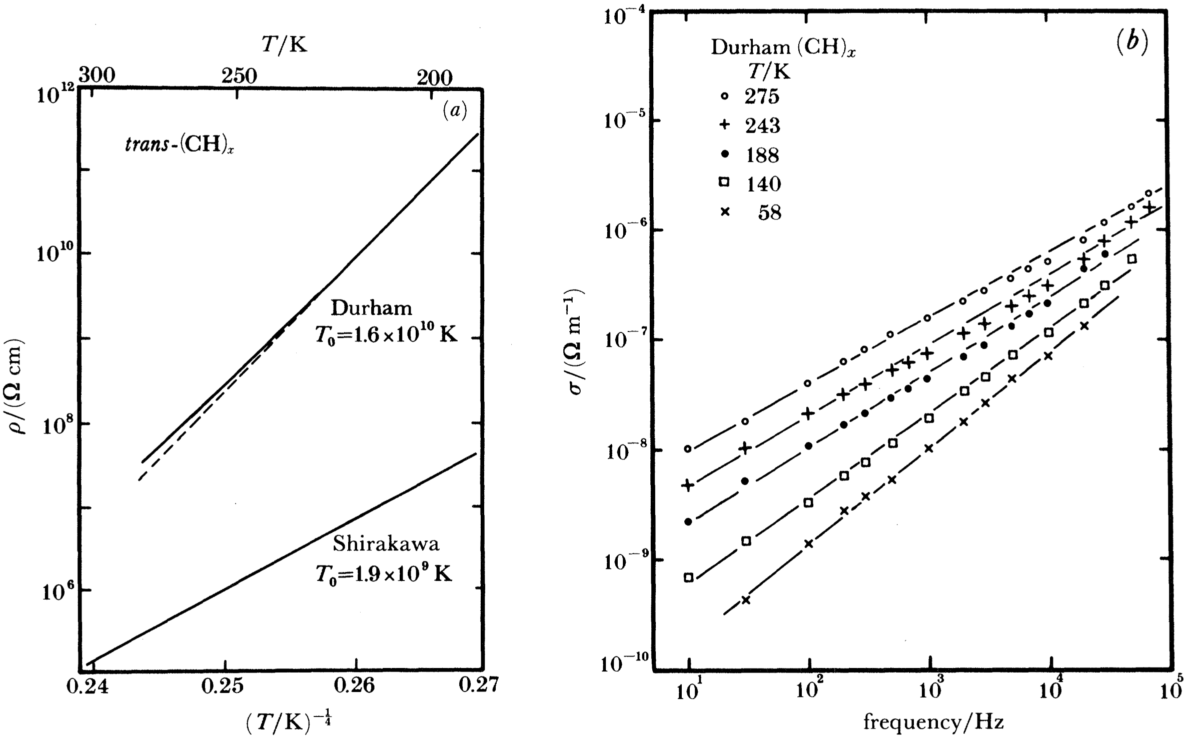


FIGURE 7. (*a*) Resistivity against temperature for Durham- and Shirakawa-route polyacetylene. Data for Shirakawa from Epstein *et al.* (1981). (*b*) A.c. conductivity for Durham-route polyacetylene.

Both show a frequency dependence of the form $\sigma \approx \omega^s$ with $s \approx 0.8$ characteristic of hopping conduction in amorphous semiconductors (Mott & Davis 1979). The temperature dependence of the a.c. conductivity is different for the two materials. The Shirakawa form shows a rather strong dependence that has been modelled both by the Kivelson (1981, 1982) theory and also conventionally (Chroboczek & Summerfield 1983). In contrast the Durham material shows a weakly activated dependence (E_A ≈ 0.15 eV) and can be fitted to a polaron hopping model.

We note that there are large differences in the magnetic and electrical properties of these two forms of polyacetylene, and while mobile soliton models are appropriate for the possibly long chain Shirakawa material, the results for Durham material, which should not support soliton defects, are not fitted by soliton models.

(ii) *Chemically doped polyacetylene*

Both Shirakawa and Durham polyacetylene can be doped to give high values of conductivity, although doping of the Durham route material is more difficult on account of the dense morphology. Dopant concentrations of up to 20% iodine can be obtained, but AsF_5 doping, which is initially very rapid, becomes very slow above 0.01 M. At low values of dopant concentration the conductivities for the two materials at room temperature are similar.

The broad e.s.r. line present in undoped Durham material is rapidly removed by exposure to AsF_5 or iodine. For AsF_5, a narrow line, of width 30 μT and intensity equivalent to $10/10^6$

spins, appears in its place, as seen in figure 8. This may be associated with small regions of the sample, which are heavily doped to the 'metallic' régime. In contrast no new spins appear with iodine doping. The loss of magnetic properties is also observed with Shirakawa material for these low doping levels, and this has been interpreted as the appearance of charged soliton states. For the shorter chain Durham material we would have to choose bipolaron defects.

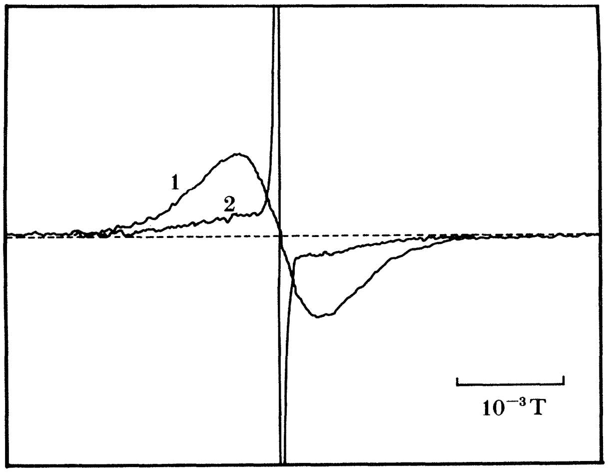


FIGURE 8. E.s.r. spectra for Durham-route polyacetylene, before and after exposure to AsF_5. (1) Undoped; (2) after exposure to 100 Pa AsF_5 for 30 s.

The optical spectrum of doped polyacetylene shows a strong 'mid-gap' band in the near i.r., which has been associated with transitions between the band edges and mid-gap soliton levels (Suzuki *et al.* 1980). This band appears at *ca.* 0.75 eV in Shirkawa material, but is shifted to *ca.* 1 eV for Durham material, as shown in figure 9, both for iodine and AsF_5 doping. The effects of impurity potentials from the dopant species have been considered by Bryant & Glick (1982), who consider that polaron levels in the presence of impurities may also explain this absorption feature.

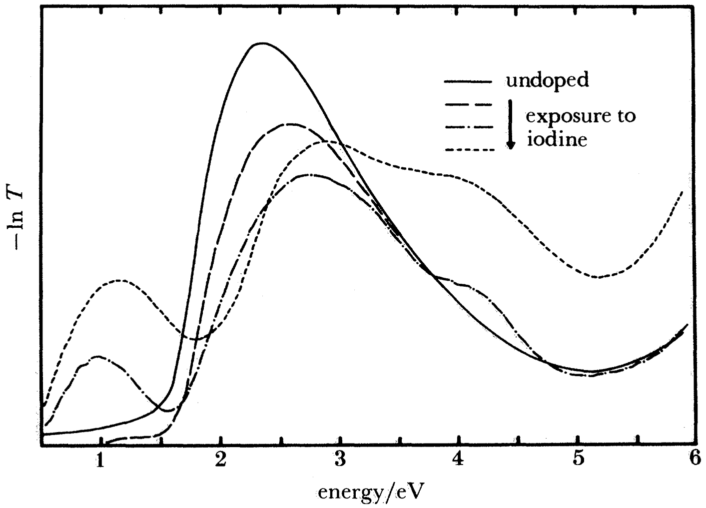


FIGURE 9. Optical absorption for Durham-route polyacetylene, undoped and at various levels of iodine doping. The highest doping level is approximately 0.06 M of I_3^-.

Doping of polyacetylene also introduces new absorption bands in the infrared, with new lines appearing at 1400 and 900 cm^{-1}. This is seen for both types of polyacetylene. Data for Durham material are shown in figure 10. Data for Shirakawa material have been reported by Fincher *et al.* (1979). Mele & Rice (1980) have calculated i.r. modes for the soliton defect, which agree with experiment, but Horovitz (1981) has pointed out that these dopant-induced lines are independent of the charge configuration and may arise from other charged defects.

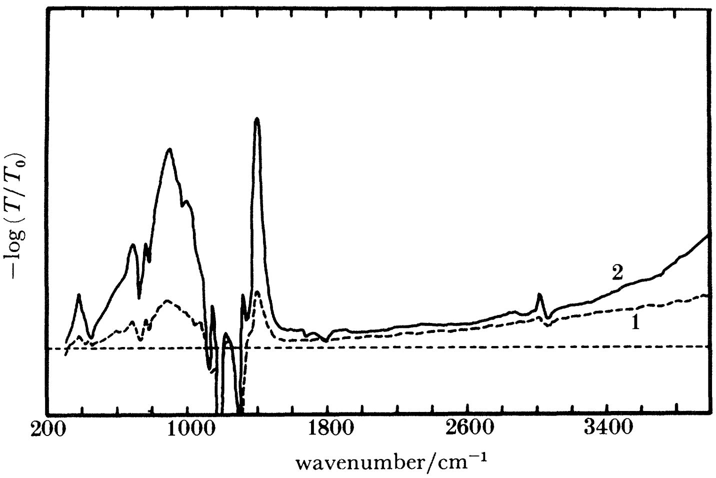
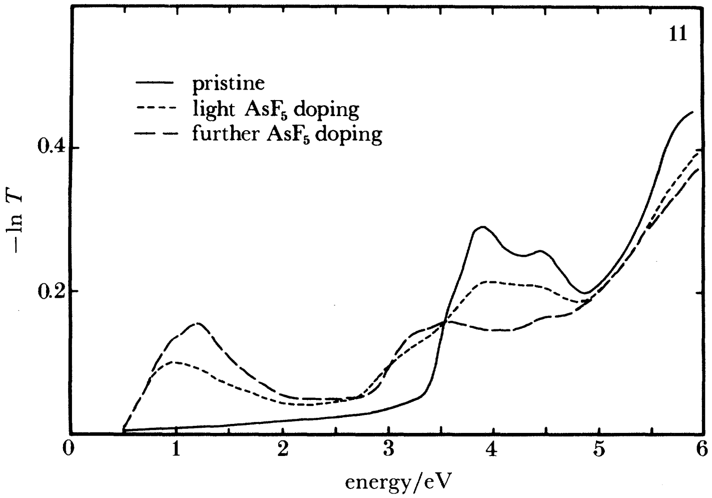


FIGURE 10. Dopant-induced i.r. spectra for Durham-route polyacetylene. 'Soliton' bands at 1400 and 900 cm^{-1} are observed, together with an increased absorption at higher energies. The undoped sample was 75 % *cis*, 25 % *trans*, and contained some fluoroxylene groups. Some *cis–trans* isomerization occurs during doping, as is evident from the loss of *cis* bands at 450 and 740 cm^{-1}. Features between 1100 and 1300 cm^{-1} indicate a further loss of fluoroxylene during doping. T_0, undoped (75 % *cis*, 25 % *trans*); T, after exposure to AsF_5 for (1) 1 min at 0.1 kPa, (2) 4 h at 2.5 kPa.

We note that the behaviour with doping of the conductivity, magnetic properties, optical and i.r. spectra of Durham and Shirakawa polyacetylenes are very similar, and are atypical of conventional semiconductor doping. Both materials evidently support defect states that involve a local structural rearrangement around the charge, and have energy levels deep in the π–π^* gap. Our results for Durham material suggest that these unusual properties are not useful in differentiating between soliton and polaron–bipolaron defects.

(*b*) *Poly*(*phenylene sulphide*) (*PPS*)

The appearance of features in the optical absorption spectrum below the π–π^* gap is a characteristic feature of doped conjugated polymers. We have made measurements of the spectra of very thin (100 nm) films of PPS when reversibly doped with AsF_5, before the onset of intrachain cross-linking discussed in § 2 (*c*). The thin films allow rapid, homogeneous doping, and spectra obtained are shown in figure 11. The band gap is at *ca.* 3.9 eV, and on first exposure to AsF_5, features at 0.9 eV and 3.1 eV appear. These may be associated with the two transitions to the polaron levels shown in figure 6*b*. On further doping, a strong feature at 1.2 eV appears, as reported by other workers (Shacklette *et al.* 1981; Clarke *et al.* 1982). These spectra confirm that in spite of the poor conjugation along chains in PPS, chemical doping can produce similar charged defect states to those in other conjugated polymers.



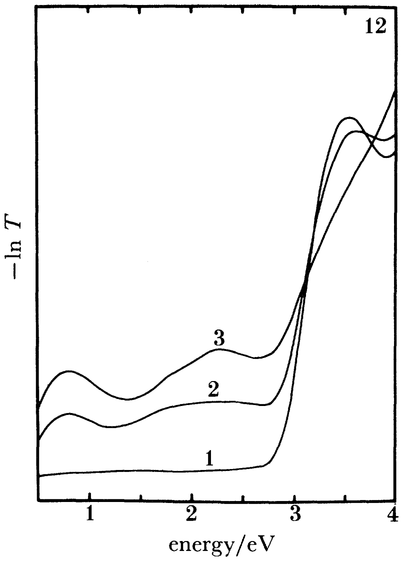


FIGURE 11. Optical absorption spectra for undoped and AsF_5-doped films of PPS. Doping is reversible, and samples could be undoped by compensation with H_2O, NH_3.

FIGURE 12. Optical absorption spectra for PDPV, undoped (1) and after exposure to AsF_5 for 4 h (2) and one month (3).

(c) *Poly(diphenylenediphenylvinylene) (PDPV)*

As PDPV is soluble in, for example, chloroform, it can be easily prepared in thin films, and we have made a study of the optical absorption as a function of AsF_5 doping. Results are shown in figure 12. The absorption peak for the π–π^* transitions is at 3.5 eV, and as doping proceeds, absorption features below the gap appear. The spectrum for the more heavily doped sample shows peaks at 0.8 and 2.3 eV. We expect polaron or bipolaron defects for this polymer, and these two features can be associated with two valence band to bipolaron level transitions shown in figure 6*b*, with the two levels 0.8 eV away from the band edges. The more lightly doped sample shows the 0.8 eV absorption and a broad absorption feature from 1.7 to 2.5 eV. This may be decomposed into a band to upper-level transition at 2.5 eV and the lower to upper level transition at 1.7 eV for a polaron defect. Similar spectra have been reported for lightly doped polypyrrole (Yakushi *et al.* 1983), and for polythiophene (Heeger, this symposium).

PDPV also shows a strong luminescence centred at 2.4 eV when photoexcited in the region of the π–π^* band (Feast *et al.* 1982). This strongly Stokes shifted luminescence (1 eV) can be accounted for within the polaron model if the photoexcited singlet e–h pair relaxes the polymer to form the polaron-exciton level shown in figure 6*b*, which then undergoes a radiative transition from the upper to the lower defect level. For polythiophene, the photoexcited e–h pair may separate and relax to two polaron levels, which give a photoexcited e.s.r. signal (Heeger, this symposium) in contrast to PDPV, for which no photo-induced e.s.r. is seen.

5. CONCLUSION

We have presented experimental work on some polymers prepared by new routes, which allow processibility of the final material. Physical measurements on these polymers provide further evidence in favour of the generalized defect models proposed for this class of material.

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