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Review

Synthesis and material and electronic properties of conjugated polymers

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Conjugated polymers such as polyacetylene are semiconductors, and can be chemically doped to give very high values of conductivity (up to 150 000 S cm^{-1}). The semiconducting properties are due to delocalization of the π electron system formed along the polymer chain, and this general class of materials shows many desirable semiconductor properties for electrical and optical applications. There are considerable challenges to find synthetic routes to allow processing of the polymer to the forms required for applications, and many of the recent important advances in the field are due to improvements in this area.

1. Introduction

Organic materials are not usually recognized for their ability to conduct electronic charge, and the traditional roles for polymers in the field of electronics has been as insulators. Generally, organic materials, which contain mostly saturated bonds, are excellent insulators because bonding orbitals are tightly-bound to form localized covalent bonds, and there is little overlap between the molecular wavefunctions on adjacent bonds, however, organic materials which possess extended π-electron systems behave very differently; within the molecular unit there can be very substantial delocalization of the p_z orbitals to form π-electron molecular orbitals. Conjugated polymers are of this type, with the p_z orbitals at each site along the polymer chain delocalized to form a π-electron system along the chain. Overlap of adjacent p_z orbitals is highly directional, and it is the character of molecular conductors of this type that conduction is highly anisotropic. For conjugated polymers, delocalization is along the chain axis, and interactions in the transverse directions are weak. Low-dimensionality in the electronic structure is a key distinguishing feature between organic semiconductors and inorganic semiconductors such as silicon. As we discuss in Section 3, this has profound consequences for the electronic processes that determine semiconductor behaviour, and much of the interest in conjugated polymers lies in the novel semiconductor physics that they exemplify.

Polyenes are the simplest conjugated structures, and are found in several biological materials. A widespread structural type consists of an alternating copolymer of acetylene and methylacetylene, i.e. $-(-CH{=}CH{-}CH{=}C(CH_3)-)-_n$; thus, the polyene where $n = 5$ is a functional part of the visual pigment rhodopsin, and that with $n = 10$ is found in the yellow pigment β-carotene. The simplest polymer of this type is polyacetylene, $-(-CH-)-_n$ and interest by Lennard-Jones in the π electron structure data back more than 50 years [1]. As the length of the conjugated sequence is increased the energy gap between the filled π and empty π^* states falls, though in the long chain limit the gap remains finite, for reasons discussed in Section 3 first appreciated by Longuet-Higgins [2], and takes a value of about 1.5 eV. Polyacetylene has served as the prototypical conjugated polymer; the simplicity of its structure has allowed theoretical modelling, and recently there has been a ready supply of polymer in a form suitable for a range of experiments. The polymer can exist in several isomeric forms and the trans-transoidal isomer, usually referred to as 'trans', which is the thermodynamically stable isomer at room temperature, is shown in Fig. 1.

The obvious route to polyacetylene is addition polymerization of acetylene, and this route allowed the preparation of the polymer in powder form [3]. Berets and Smith [4] showed that at a pressure of 6.7×10^8 Pa, the polyacetylene powder could be formed into silvery discs which showed semiconducting properties with an electrical conductivity which was increased on exposure to volatile oxidizing agents and reduced by exposure to ammonia. The first major stimulus to a more widely based study of the physics of polyacetylene came with the observation, in Shirakawa's laboratory, that the polymerization could be accomplished at the interface between a solution of a Ziegler-Natta initiator and gaseous acetylene [5]. Polyacetylene produced by this technique is obtained in morphologies varying from an isotropic fibrilla mat of low density through to a highly anisotropic dense material [6–8]. Heeger and MacDiarmid showed that these could be chemically doped with electron acceptors such as AsF_5 and iodine, or electron donors such as sodium, to give

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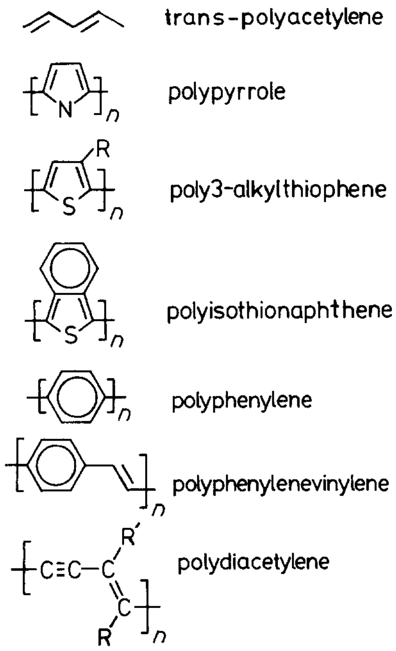

Figure 1 Various conjugated polymers.

values of conductivity up to 1000 S cm^{-1} at room temperature [9]. This value of conductivity is high, and just about in the range of metallic behaviour. This was the first demonstration of metallic behaviour within the intramolecular π-electron system along the polymer chain, and the significance of these results was quickly picked up by many other groups worldwide.

The behaviour of the conductivity with both acceptor and donor dopants is suggestive of the conventional substitutional p and n doping of a semiconductor. The appropriate sign for the thermopower is indeed observed [10]. Doping, of course, is not substitutional; the dopant species reside alongside the polymer chain and there is a charge transfer reaction akin to the intercalation chemistry known for graphite and other layer structure materials [11, 12]. Very high concentrations of dopants can be taken up by the polymer, and the high, metallic values of conductivity are usually measured on samples with molar fractions of dopants in the range 1 to 20% per carbon atom. These high values of dopant concentration cause large structural changes, and though there is some tendency to form ordered 'intercalation' structures [13, 14], there is usually a high level of disorder in the doped phase. This must limit the value of the metallic conductivity, indeed the conductivity values, though metallic at room temperature, fall at lower temperatures, in contrast to the behaviour expected from a metal, and this is generally attributed to disorder, both at the microscopic level and also at the macroscopic scale, in the contact between crystallites or fibrils in the sample.

Many other conjugated polymers have now been investigated and a selection of these is shown in Fig. 1. High, metallic conductivities are obtained on doping with many of these polymers, with for example values as high as 5000 S cm^{-1} reported for poly(p-phenylene vinylene) doped with sulphuric acid [15]. Control of the π–π^* gap through modification of the conjugated backbone, or addition of side-groups has been an active area of study, and there is particular interest in finding polymers with bandgaps lower than that of polyacetylene. This particular goal is not easy to achieve, and the only notable success here is the work of the Santa Barbara group with poly(isothionaphthene) for which the gap is as low as 1 eV, and the doped, conducting polymer is transparent in the visible part of the optical spectrum [16].

Whereas conventional polymers are readily processed in solution or in the melt and can be cheaply manipulated into desirable forms, this is not in general possible for conjugated polymers. The delocalized π-electron system makes the molecular chains rigid, with resultant high melting points and low solubilities. The dilemma of a potentially attractive material which can not be processed is not novel in materials science in general or polymer science in particular. Two well established lines of attack on such problems involve either modifying the molecular structure so as to retain the property of interest while rendering the material able to be processed, or carrying out the processing stages with a more tractable precursor which can be converted subsequently to the desired material. Both of these approaches have been successfully applied to the synthesis and processing of most classes of conjugated polymers, and the methods adopted are summarized in Section 2 for the major structural classes.

The semiconductor physics of these polymers has been a major area of interest. There has been considerable theoretical and experimental effort directed towards understanding the way in which charges can be stabilized on the chains, and the nature of the transport processes that can then occur. In contrast to three dimensionally bonded inorganic semiconductors, these materials behave as 'molecular materials', and there is a considerable reorganization of the local π-electron bonding in the vicinity of extra charges added to the chains. This results in self-localization of the added charge, to form, in general polarons, though for the particular symmetry of the trans isomer of polyacetylene, these take the form of bond-alternation defects, or solitons. We review in Section 3 the electrical and optical properties due to charge added through chemical doping, photoexcitation, and through charge injection to form charge accumulation and inversion layers in MISFET (metal–insulator–semiconductor field effect transistor) structures.

2. Materials–synthesis and processing

In this section we discuss in some detail the development of the synthesis and processing techniques for two simple conjugated polymers, polyacetylene and poly(paraphenylene), PPP, by way of illustration of the generally successful methods which have been adopted in this field.

2.1. Polyacetylene

In attempts to circumvent the processing problems associated with polyacetylene produced by the direct route, various precursor routes have been investigated [17] and those developed in Durham [18–20] have proved particularly effective. The steps for this are

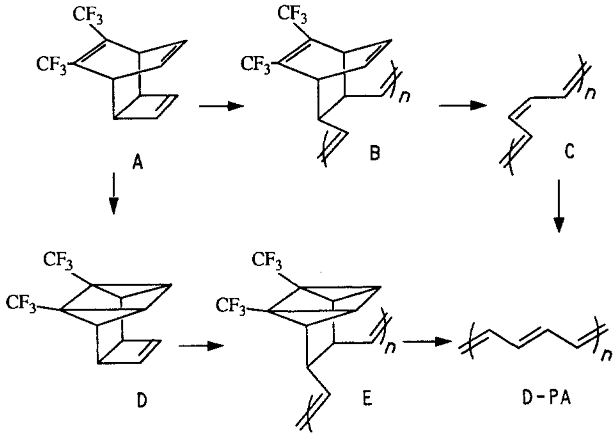

Figure 2 Schematic for the synthesis of Durham polyacetylene.

summarized in Fig. 2, and we refer to the materials produced by this technique as Durham polyacetylene. The monomer A is available in a one step high yield process from commercially available reagents; ring opening metathesis polymerization (ROMP) operates exclusively on the cyclobutene unit to give the polymer B which is soluble and can be characterized by solution-phase methods. The stereochemistry of the backbone vinylene units in B depends on the nature of the ROMP initiator. In most reported work the reactive and fairly non-discriminating WCl_6–Me_4Sn-derived initiator system has been used which gives atactic polymers with random distributions of cis and trans vinylenes; polymer B is therefore expected to have a disordered microstructure and this accounts for its ready solubility. During the last few years the synthesis, characterization and use of well defined metathesis initiators has made spectacular progress and, for example, the initiators M(CH-t-Bu)(NAr)$(O\text{-}t\text{-}Bu)_2$ (where M = W or Mo) allow living ROMP and give samples of B in which the backbone vinylenes are trans [21, 22].

Since B is soluble it can be processed into a variety of forms by standard techniques. Thermal elimination of hexafluoroorthoxylene from samples of the processed precursor polymer B is symmetry allowed and gives rise to C. All the newly formed double bonds in C have cis geometry and at or above room temperature they isomerize to trans polyacetylene, labelled D-PA in Fig. 2. The process from precursor B to D-polyacetylene involves the following steps: a chemical elimination of hexafluoroxylene; the diffusion of the hexafluoroxylene through the sample prior to its evaporation; the cis-to-trans isomerization of the vinylenes; and the crystallization of the polyacetylene chains. These processes overlap in time and space during the formation of D-polyacetylene and together they determine the detailed order and structure of the final polyacetylene sample, thus the protocol adopted (i.e. heating rate, temperature, time, pressure, etc.) for the B to C to D-polyacetylene sequence determines the nature of the sample and hence its properties [23]. A particularly useful aspect of this approach is the ability to orient samples by stretching prior or during conversion to D-polyacetylene [24–26]. One inconvenience of this route is that the precursor polymer has limited shelf life unless stored in a deep freeze, this "problem" can be overcome by adopting the A to D to E to D-polyacetylene sequence shown in Fig. 2. The initial step is a photochemical isomerization, the ROMP from D to E is completely analogous to the A to B process but the conversion of the precursor polymer to D-polyacetylene in this modified route proceeds at a higher temperature since the elimination step requires an initial ground state symmetry forbidden retero 2 + 2 reaction [20].

In summary, by this approach it has been possible to produce solid continuous films of polyacetylene in a range of orders from almost amorphous isotropic, through microcrystalline with varying extents of anisotropy, to highly oriented. The early difficulties encountered in generating high quality samples of polyacetylene in a range of morphologies have therefore been effectively circumvented and manipulation of polyacetylene no longer presents any problems in a well equipped laboratory. One recent development in this approach results from utilization of the well known photooxidative sensitivity of polyenes, and allows high resolution relief patterning [27].

2.2. Poly(para phenylene)

Poly(paraphenylene), PPP, is another simple conjugated polymer, and like polyacetylene it is insoluble and infusible. Attempts to make PPP have an even longer history than polyacetylene were initially motivated by reasons related to its expected high thermal stability and to curiosity concerning the behaviour of a true rigid-rod polymer, rather than any interest in its optical or electrical properties. Since the product is so intractable, early direct syntheses via oxidative coupling of benzene (either chemically or electrochemically) or via catalysed Grignard coupling of paradibromobenzene ran into severe problems of product characterization and processing. Early samples of PPP were, like polyacetylene, obtained as intractable powders; however, despite its unattractive processing properties (only powder compaction was feasible), PPP proved to be thermally and oxidatively stable and worth the attention of synthetic chemists.

Effective processing via a precursor polymer was first achieved by an elegant route, summarized in Fig. 3, established by ICI workers [28, 29]. The

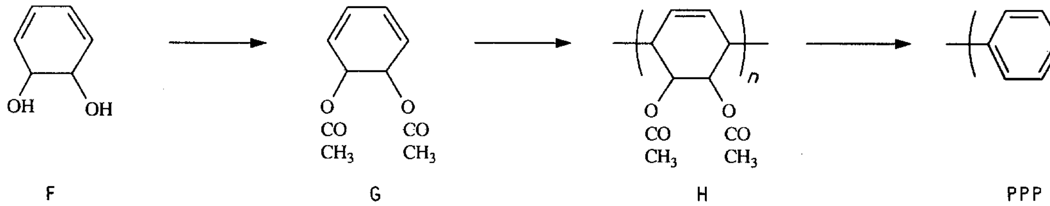

Figure 3 Schematic for the ICI precursor route to polyphenylene.

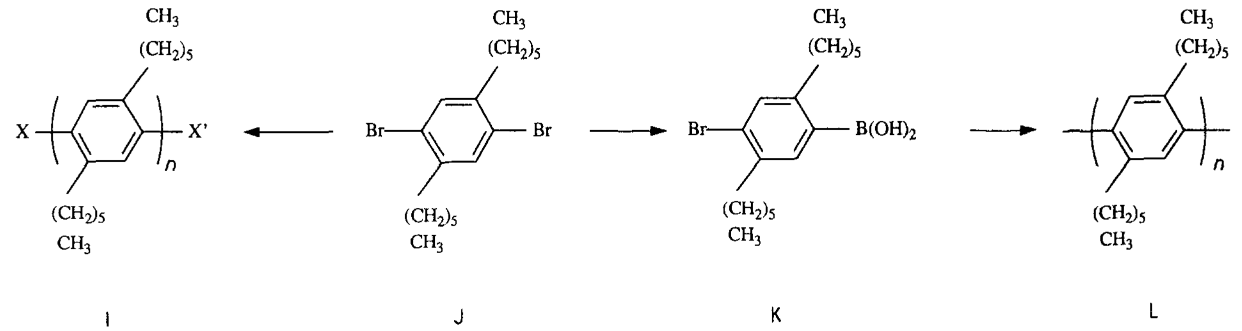

Figure 4 Schematic for routes to structurally homogeneous substituted PPP's.

starting material for this route is obtained via a microbiological oxidation of benzene, the cyclohexadienediol F is esterified to give the monomer G which undergoes free radical initiated polymerization to give a processible precursor polymer H. This polymer is soluble and can be solution processed; heating results in the elimination of methanol and carbondioxide and the formation of PPP. The one minor defect in this route is that the radical polymerization step G to H does not give an exclusively 1, 4 addition polymer and so the material is structurally inhomogeneous [30]. Nevertheless, the routine outlined in Fig. 3 represents the best route to polyphenylene currently available.

Improved processability of PPP via structural modification has recently been achieved by workers in Mainz [31]. The routes investigated are summarized in Fig. 4. The monomer J carries two n-hexyl substituents whose function is to enhance the monomer and product solubility at minimum steric cost. Since it was reputedly the most effective route for synthesis of the parent PPP, nickel-catalysed Grignard coupling of the dibromoaryl compound J was initially the route of choice but, in the event, proved to be limited by C–Br bond reduction. This approach gave relatively low molecular weight polymers (I, $n \sim 12$, X and $X' = H$ or Br). Conversion of J to K, and subsequent palladium-catalysed coupling of the parabromoboronic acid was much more effective and gave the soluble substituted PPP L with $n \geqslant 30$.

2.3. Other conjugated polymers

The principles discussed above in relation to polyacetylene and PPP have wide generality in the synthesis and processing of conjugated polymers. This paper is not an appropriate place for a comprehensive review of the considerable achievements of synthetic chemistry during the last decade in generating well characterized materials for study, and there are a multitude of reviews covering this area [6–8]. We briefly list here some of these routes that have produced polymers, shown also in Fig. 1, which have been perceived to be of particular interest.

The Shirakawa route to polyacetylene [5] allowed production of polyacetylene in the form of fibrillar, low density films, and although further processing is difficult these films have been widely used as they are acceptable for many physical measurements. Another class of conjugated polymers which can be formed as thin films onto a substrate are those formed by electrochemical oxidation and simultaneous polymerization of a range of monomers, including pyrrole [32], thiophene [32] and isothionaphthene [16]. These polymers are formed in an oxidized and therefore highly conducting form, and the reversible electrochemistry of doping and dedoping allows use of these polymers as the rechargeable electrodes in secondary batteries [34]. Of these, polypyrrole has been widely investigated and has many useful properties; these include good reversibility and energy storage in battery applications, good long-term stability as a conductor in the oxidized state, and stability in aqueous media. This last property has enabled its use as the electrode material and binder for enzyme systems in biosensors [35].

Of the other precursor routes used to achieve processibility, the use of a sulphonium salt polyelectrolyte as the precursor has been shown to give a range of poly(aromatic vinylene) and poly(heteroaromatic vinylene) materials. Of these, poly(paraphenylene vinylene) is the most extensively studied [36–39]. The addition of side-groups to the polymer chain to achieve solution or melt processibility without loss of conductivity has been extensively investigated, particularly for the family of poly(3-alkyl thiophenes) in which solubility is achieved for alkyl groups of butyl or larger [39–40].

Polydiacetylenes form a major class of conjugated polymers [41], and are generally formed by the solid state polymerization of the monomer. There is a constraint on the selection of the side-groups if the monomer is to be able to transform to the polymer in the solid state, and many of the side groups are relatively bulky, so that the diacetylene chains are well separated. These materials differ from the other conjugated polymers which we have discussed in many ways. Foremost is that the polymer formed by the solid-state polymerization is often obtained as single crystals of very high perfection. The disorder inherent in the other polymers associated with chain entanglement in solution or in the melt is absent.

3. Electronic properties

3.1. Electronic structure and excitations

Polyacetylene has served as the prototype for much of the work in this area. For the modelling of the excitation spectrum the simplest approximation to the electronic structure has been commonly used. In this, the chains are considered in isolation, and the chemical bonding along the chain is described as $sp^2 + p_z$ carbon hybridization, with σ bonding to adjacent

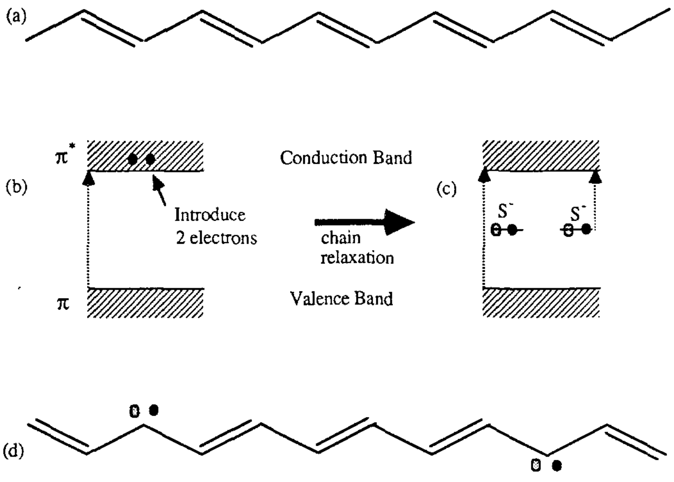

Figure 5 Schematic representation of the formation of a pair of solitons on a polyacetylene chain. (a) shows the undistorted chain and (b) shows the associated band scheme. The interband π–π^* optical transition is shown as a dotted arrow. If two electrons are introduced onto the chain, initially into the conduction band as shown in (b), the chain relaxes to the form shown in (d), with a reversed sense of bond alternation in the centre of the chain separated by two solitons. Associated with the two solitons are non-bonding π states in the gap, created from one (doubly occupied) valence and one (empty) conduction band state. These two states are doubly occupied, as shown in (c), and each carries a negative charge. New optical transitions from the soliton level to the conduction band are indicated with a dotted arrow; the oscillator strength for the interband transition is weakened through the loss of the band states. A complementary picture holds for positive charge, which is accommodated as unoccupied solitons levels.

carbons on the chains and to the hydrogens, and π bonding along the chain due to the singly occupied p_z carbon orbitals. Using Hückel theory for the π electron system, the degree of overlap between p_z orbitals along the chain can be parameterized by the resonance or transfer integral along the chain, $t_{\|}$, and a value of about 3 eV is generally accepted. This degree of overlap is large, giving a full bandwidth for the π band of 12 eV; it is comparable to the values found in inorganic semiconductors and clearly shows that the π electron system is fully delocalized along the polymer chain. The semiconductor energy gap between the filled π and empty π^* states, of about 1.5 eV, is present because the chain is dimerized. Dimerization of the infinite length polyene was shown by Longuet-Higgins and Salem [2] to be driven by the reduction in π electron energy in the presence of the energy gap, which is dependent on the magnitude of the bond length alternation. It is an example of the Peierls instability of the one-dimensional chain to the formation of a superstructure (the dimerized chain) which introduces an energy gap between filled and empty band states [42].

This strong coupling between the π electron system and the chain structure has profound consequences for the electronic structure when extra charge is added to the chain, through, for example, chemical doping. This was first modelled by Rice [43] and Su *et al.* [44, 45]. Within the "rigid band" model used for inorganic, crystalline semiconductors, if electrons are added to the semiconductor they are stored in the conduction band. In chemical terms, this amounts to charge storage in antibonding states, and where the semiconductor has a well identified molecular structure a reorganization of the bonding will in general allow accommodation of the added charge in lower energy states. In the case of the trans isomer of polyacetylene the reorganization introduces regions of "phase slip" between regions with opposite senses of bond alternation. These regions have non-bonding character, and have an associated energy level which lies in a one-electron theory at mid-gap. The particular curiosity of these chain excitations is that they are topological in the sense that they separate topologically distinct regions of chain. As such, they possess many of the properties of solitary waves, and are commonly termed as solitons [44, 45].

We illustrate schematically how a pair of added electrons are accommodated on the polymer chain in Fig. 5. Fig. 5a shows the undistorted chain and 5b shows the associated band scheme. The interband π–π^* optical transition is shown as a dotted arrow. As the two electrons are introduced onto the chain, initially into the conduction band as shown in Fig. 5b, the chain relaxes to the form shown in Fig. 5d, with a reversed sense of bond alternation in the centre of the chain separated by two solitons. Associated with the two solitons are non-bonding π states in the gap, created from one (doubly occupied) valence and one (empty) conduction band state. These two states are doubly occupied, as shown in Fig. 5c, and each carries a negative charge. A complementary picture holds for positive charge, which is accommodated as unoccupied solitons levels. The calculations of Su *et al.* [44, 45] showed, very importantly, that the region over which the sense of bond alternation is reversed is quite extended, and with the parameters used for the Hückel modelling of the π bands, the soliton extends over some 14 carbon sites along the chain. This has two important consequences; firstly, it lowers the energy cost for creation of the solitons, and secondly, because the individual carbon displacements are small, the effective mass of the excitation as it moves along the chain is low, of order a few electron masses.

One of the clearest means of demonstrating the change in electronic structure is through measurement of the optical absorption spectrum, particularly in the region below the bandgap [46]. New optical transitions from the soliton level to the conduction band are indicated with a dotted arrow; the oscillator strength for the interband transition is weakened through the loss of the band states. We return to this in the following section when we discuss the optical properties of the polyacetylene MISFET.

In the model adopted by Su *et al.* [44, 45] the electronic structure of the π electrons is described in terms of a Hückel model, with coupling to the lattice through modulation of the resonance integrals with carbon–carbon spacing along the chain. With parameters chosen to get the experimentally measured values for the π band width and the energy gap between the π and π^* bands this provides an excellent working model. There is no explicit consideration of electron–electron interactions, and it has become clear that these are quite strong, with the onsite Coulomb repulsion, U comparable to the full π bandwidth [47–50]. The effect of these Coulomb interactions is to enhance bond dimerisation, and the combined effects of electron–lattice coupling and electron–electron interactions are considered to account for the observed bandgap and dimerisation amplitude.

The second aspect of the Su *et al.* model which has recently been questioned is the validity of treating the polymer chains as independent of one another. Calculations of the electronic structure [51] show that there is significant interaction between the π orbitals on one chain and the hydrogen 1s on an adjacent chain, and that the effect of this is to give the π and π^* bands three-dimensional character near the band edges, with a transverse bandwidth of about 0.5 eV. This level of interchain contact is quite strong, and we characterize polyacetylene as an anisotropic three-dimensional semiconductor. In this respect it is very different from most of the polydiacetylenes in which the chains are commonly 0.6–0.7 nm apart and which can therefore be described as one-dimensional semiconductors. The interchain contact has many important consequences. Firstly, it enables transfer of charge from one chain to another; it is well known that the high levels of conductivity that are attained in the doped polymers are measured in samples in which the chain lengths are very considerably less than the sample dimensions, and therefore in which transport between chains is necessary. Secondly, many of the semiconductor properties, such as photoexcitation of charge pairs which separate to give rise to photoconductivity, require that there is interchain charge transfer [52]. Thirdly, the interchain interactions modify the energetics for the formation of self-localized excitations such as the soliton [51]. In general, self-localization is inhibited, and with the parameters derived from the electronic structure calculation of Vogl and Campbell [49] it seems that the soliton is only marginally stable in three-dimensional polyacetylene. There is much to be explored here, in particular the role of disorder in stabilization of the soliton which are clearly seen in a number of experiments.

3.2. Polyacetylene MISFET

There has been very little work in the past decade on the use of conjugated polymers as the active component in semiconductor device structures. The principal reason for this is the difficulty in processing the polymer to the desired form, and the scope for using Shirakawa polyacetylene in this way is limited [53, 54]. Improvements in the processing of conjugated polymers, through electrochemical deposition during polymerization, and the use of solution-processible poly(3-alkyl thiophenes) has allowed better device fabrication [55–57] and the use of model oligomers which can be deposited by vacuum sublimation has recently been reported [58]. There are also reports of field-induced conductivity measured in MISFET (metal–insulator–semiconductor field effect transistor) structures [59–62].

We discuss here some of the results obtained using polyacetylene prepared by the Durham precursor polymer route, shown in Fig. 2. The process step involving the polyacetylene is the preparation of a thin film onto a preprepared substrate. Spin-coating techniques widely used for deposition of photoresists used in lithographic processes for inorganic semiconductors are suitable for this, and the precursor polymer is readily processed in this way from solution in 2-butanone to form films with thicknesses between 20 nm and several μm. As formed the polyacetylene is extrinsically p-doped (10^{16} cm^{-3}). The origin of this doping is not established, though it may result from catalyst residues at chain ends formed during the polymerization to the precursor polymer. It does, however, provide a convenient level of doping for use in unipolar devices, and furthermore the dopants are not mobile on the time scale of the measurements made. An extensive series of measurements has been carried out on a variety of devices [63, 64] and device performance is much improved over earlier work with conjugated polymers, with for example rectification ratios for the aluminium–polyacetylene Schottky barrier of up to 500 000.

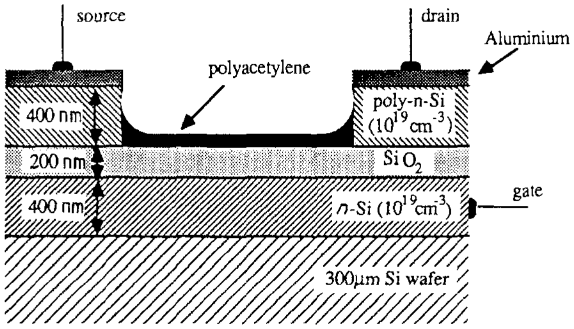

Figure 6 Schematic diagram for a polyacetylene MISFET structure. Dimensions shown are to scale, except the channel width (20 μm) and length (1.5 m).

MISFET structures are fabricated by spin-coating a thin film of Durham precursor polymer onto, usually, the insulator layer of a preprepared structure, followed by thermal conversion to polyacetylene. For the devices discussed here, the insulator used is silicon dioxide, which was grown as native oxide on suitably prepared silicon substrates. For the MISFET structure shown in Fig. 6 no further processing is required. The MISFET structure allows the possibility of band bending at the insulator–semiconductor interface through the Fermi level to produce a surface charge layer which may be the same carrier sign as the majority carriers (accumulation layer) or as the minority carriers (inversion layer). These formation of accumulation, depletion and inversion layers may be demonstrated through the behaviour of the device capacitance with respect to the bias voltage. Demonstration that the charges at the polyacetylene–insulator interface are mobile is made in a MISFET structure, in which source and drain contacts allow measurement of the conductance of the surface charge layer. The MISFET shown in Fig. 6 is constructed with n-silicon source and drain contacts, which are expected to make ohmic contacts to the n-polyacetylene layer. Thus enhanced channel conductance is expected from the formation of an n-type

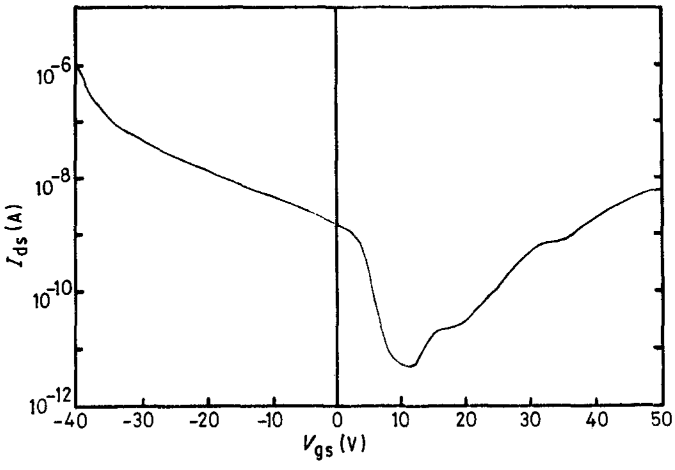

Figure 7 I_{ds} plotted against V_{gs} at constant $V_{ds}/(+10\,V)$ for the polyacetylene MISFET structure shown in Fig. 6.

inversion layer for positive gate voltages. Fig. 7 shows the variation of I_{ds} with V_{gs} at constant V_{ds}. The channel conductance has a minimum at $V_{gs} = +10\,V$ (full depletion) and rises for gate voltages both more positive (inversion layer) and more negative (accumulation layer), with a maximum on–off ratio for this structure of 100 000 ($V_{gs} = -40\,V$ to $V_{gs} = +10\,V$). We see, therefore, the behaviour expected for positive bias, though the strong enhancement of the conductivity for negative bias indicates that the accumulation layer is still able to make good contact to the source and drain electrodes. Carrier mobilities are low, typically $10^{-4}\,cm^2\,V^{-1}\,sec^{-1}$, and similar to those found for photogenerated carriers and the extrinsic carriers in the as-made polyacetylene [65] and it is considered that the mobility-limiting process is the transfer of charge between chains.

As discussed in the previous section, charge is stored in polyacetylene in "soliton" localized states, which have non-bonding p_z "mid-gap" states associated with them. We expect to see, therefore, a modulation in the optical properties of the active semiconductor region of these devices with applied bias voltage. For the MISFET structure we expect a decrease in the device transmission below the band-edge as the device is driven towards accumulation, and new charged solitons are introduced onto the polyacetylene chains at the interface with the insulator.

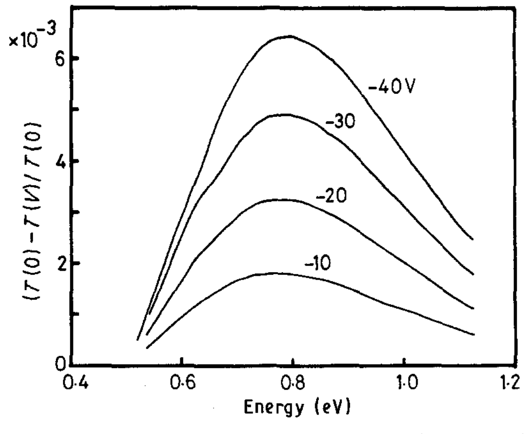

Figure 8 Voltage-modulated optical transmission for a MIS diode, $(T(0) - T(V))/T(0)$ plotted against the photon energy, for various values of V (all negative with respect to the gate).

The electromodulation spectrum between 0.4 and 1.2 eV in Fig. 8 shows that there is a decrease in the transmission through the device for negative bias. The peak value of $\Delta T/T$ is at 0.8 eV, and is attributed to the optical transition between the mid-gap soliton level and the band edges.

3.3. Heavily doped polyacetylene and the metallic state

While the model for self-localized soliton-like excitations given in the previous section provides a good description for the "semiconductor" regime, in which the density of added carriers is low, a different model must be used to describe the highly conducting state that is achieved with heavy chemical doping. This is exemplified in a spectacular fashion by the very high values of conductivity which have been reported recently. Conductivity values reported in the literature showed rather little improvement on the original values reported in 1977 [9], until BASF announced in 1987 that a modification to the standard synthesis due to Shirakawa produced a material with a conductivity when doped with iodine as high as $145\,000\,S\,cm^{-1}$ [66]. This value of conductivity is a factor of 4 lower than copper at room temperature, and when expressed as specific conductivity per unit mass is a factor of 2 larger than that of copper. It is evident that heavily doped polyacetylene is a true metal, and the evidence is now for a phase transition from a soliton-supporting semiconductor to a metallic state at a dopant concentration of about 6% per carbon atom [68]. This dopant concentration is that at which the isolated solitons, each occupying 14 carbon atoms, overlap, but the transition also involves a rearrangement of the "intercalant" structure of the dopant species around the polymer chains. Within the Peierls model, this is the cross-over from the soliton lattice to an incommensurate charge density wave distortion, and it is not immediately clear that the material should be metallic. Mele and Rice [69] show how the Peierls semiconductor gap can be reduced to zero in the presence of disorder and three-dimensional coupling. In view of the conductivity values now obtained, it is unlikely that disorder has an important role, and we must consider that doped polyacetylene is intrinsically metallic, probably as a result of three-dimensional interchain interactions.

A conductivity of 145 000 S cm^{-1} is very high for a material with a concentration of free carriers which is at least an order of magnitude lower than in copper, if a value for the carrier concentration of 0.1 carriers per carbon atom is taken (doping concentrations of up to 10% are reported), then the carrier mobility is about 200 cm^2 V^{-1} sec^{-1} and the estimated mean free path is at least 100 nm. These values are particularly remarkable in a material which contains a considerable amount of disorder [8] and which still shows a conductivity which falls as the temperature is lowered, indicating that carrier scattering is due primarily to impurities and disorder, not by phonons. These results would suggest that the ultimate conductivity which would be achieved in materials where the effects of defects were no longer present may be as much as a factor of 100 larger than that of copper [67]. The reasons for this are quite general: scattering of a free carrier in a one-dimensional metal requires momentum transfer across from $+k_F$ to $-k_F$ or vice versa. If the scattering is achieved with a phonon, then this must have a high frequency; this is particularly the case for hydrocarbon polymer chains for which typical optic mode phonons have energies above 1000 cm^{-1}, and at room temperature in polyacetylene the thermal population of these phonons will be very low. If scattering is due to impurity potentials, then the high q required will only be generated if the impurity is within a few tenths of nanometres of the carrier. Thus, the disorder in the "intercalate layers" of dopant ions may not act as a very efficient scatterer of carriers on the polymer chains [67].

3.4. Other polymers

Most of the conjugated polymers prepared to date do not support isolated bond alternation, or soliton, defects. For these systems there is a preferred sense of bond alternation, so that a defect which switches the sense of bond alternation will move rapidly to reduce the extent of the higher energy phase. This is illustrated schematically in Fig. 9 for the case of a poly(phenylene) chain, for which the aromatic form with long bonds between rings is lower in energy than the quinoid form, however, pairs of bond-alternation defects, which enclose a limited region of quinoid chain, are stabilized if the defect overall has a charge [70, 71] and calculations show that the extent of this quinoid region is of the order of four phenylene rings [72]. The interaction between the two confined mid-gap non-bonding p_z levels gives two levels symmetrically displaced about mid-gap, as shown in Fig. 9. The singly charged defect has also spin $\frac{1}{2}$, and is thus termed as a polaron, i.e. a charge carrying with it a localized "lattice distortion". Accommodation of a second charge on one chain through further charging of the "polaron" state, to give a doubly charged state (generally termed as a bipolaron) is lower in energy than creating a second polaron. For the bipolaron the occupation of the discrete levels within the gap is all empty (charge $+2e$) or all full (charge $-2e$), so as with the charged solitons, these defects are spin zero. The range of optical transitions involving the levels in the gap is now considerable; these are indicated for the positively charged polaron and bipolaron in Fig. 7. Bipolarons show transitions at two energies, from valence band to each of the discrete levels for the positive bipolaron, BP^{++}, whereas there is an extra transition between the two discrete levels for the positive polaron, P^{+}. Also shown in Fig. 9 is the neutral excited state formed following photoexcitation and trapping of the electron–hole pair, which can be termed as a polaron–exciton. It has single occupation of each of the two discrete levels, and in the singlet configuration shown, the transition from upper to lower level is dipole-allowed. This radiative recombination to give luminescence can be an important decay channel for some of the conjugated polymers with larger band-gaps, such as poly(phenylenevinylene). Evidence for charge storage in polarons or bipolarons has been well investigated in several polymers, including poly(phenylenevinylene) [52, 73] and polythiophene [74, 75].

We illustrate the formation of these polaron-like excitations for the case of poly(phenylene vinylene), PPV, which when prepared by the sulphonium salt precursor route [36–38] is available in the form of highly oriented films with high crystallinity. Photoexcitation across the π to π^* bandgap provides a very powerful tool for investigating the energetics and dynamics of both charged and neutral excitations, and in the case of PPV it is possible to see both [52, 73, 76]. Fig. 10 shows the optical absorption and luminescence spectra for this polymer. The band-to-band transition sets in at around 2.5 eV, and the luminescence band appears at energies below this. In every respect these spectra are as expected for a molecular species, and apart from a red-shift are very similar to those measured on model oligomers [76]. The structure seen

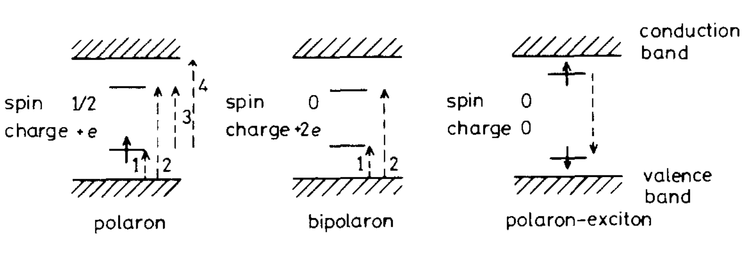

Figure 9 Schematic representation of a positively charged polaron defect on a poly(phenylene) chain, showing the quinoid structure within the defect. Also shown are the energy level schemes for positively charged polaron and bipolaron defects, and the neutral polaron-exciton (shown here as the singlet). Possible optical transitions are indicated.

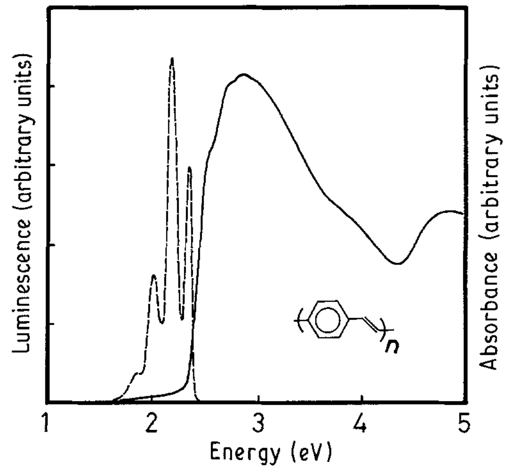

Figure 10 Optical absorption and luminescence spectra for poly(phenylenevinylene). The luminescence was measured at 80 K to resolve the vibrational structure.

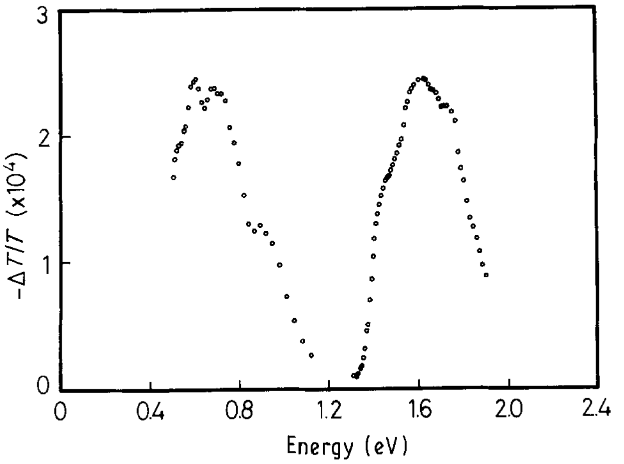

Figure 11 Photoinduced absorption spectrum of PPV at 40 K. Excitation was provided by UV radiation from an Ar^+ ion laser, chopped at 67 Hz. The data show the absorption signal in quadrature (90° phase lag) with the modulated excitation source.

in both the absorption and the emission spectra are due to vibrational coupling to the electronic states, and the luminescence is associated with the radiative decay from the polaron–exciton shown in Fig. 9. These spectra are due to transitions and excitations which are intra-chain, and for which the formation of a neutral excited state, or exciton is expected. If the result of photoexcitation is to be the separation of charges, then inter-chain excitation or charge diffusion is required. For oriented samples of PPV this is best achieved with excitation light polarized perpendicular to the chains [52]. Detection of charged excitations is most easily made through the measurement of photo-induced absorption, and the spectrum due to charged excitations for PPV is shown in Fig. 11. Two absorption bands are seen, peaking at 0.6 and 1.6 eV, and these are associated with optical transitions between the two gap states and the band edges shown for the bipolaron in Fig. 9.

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