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Polydiacetylenes: Prototype One-Dimensional Semiconductors [and Discussion]

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Polydiacetylenes: prototype one-dimensional semiconductors

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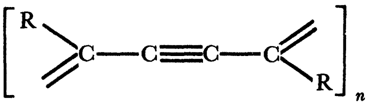
Polydiacetylenes (PDAs) are conjugated polymers with the general structure



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which can be obtained as macroscopic crystals consisting of fully extended polymer chains. The factors that control the solid-state polymerization of disubstituted diacetylenes and the perfection of the resultant polymer crystals are discussed. The presence of large substituent groups leads to weak interchain coupling so that PDAs are quasi-one-dimensional materials.

Optical spectroscopy has shown that the strong dichroism of PDA crystals results from an excitonic excited state lying about 0.5 eV below the interband transition. The latter is weakly absorbing but can be observed by electro-modulation spectroscopy.

Thermal and photogeneration of free carriers is inhibited by the large band gap (greater than 2 eV), the weak interband absorption and the high probability of geminate recombination. The dependence of photocurrents on applied field is adequately described by the Onsager theory of geminate recombination in one dimension. This leads to the conclusion that carrier drift velocities are saturated even for low applied fields. In addition, photocurrent decay displays anomalous behaviour. Both phenomena have been attributed to scattering by defects, which leads to the failure of linear response theory in one dimension.

Even for imperfect samples with high trap densities the carrier motion is still accurately described by a one-dimensional diffusive model. This predicts unusual field and temperature dependencies in the decay of photocurrents that have been confirmed experimentally.

1. INTRODUCTION

Polymeric materials exhibit a wide range of morphologies. While this has resulted in an equally wide spectrum of mechanical properties, which have proved technologically useful, it has hindered progress in elucidating the microscopic properties of the individual molecules. This problem has been highlighted by the difficulties encountered in the attempts to provide microscopic models for the macroscopic properties of electrically conductive polymers such as polyacetylene. Further discussion of this topic is given in the contributions of Professor Heeger and Dr Friend (this symposium) and many recent review articles; see, for example, Baeriswyl *et al.* (1982); Wegner (1981*a*).

In principle, if polymer single crystals were available the correlation of theory and experiment would be much easier. Since the discovery of microscopic crystals of chain folded polymer in the late 1950s, the production of large crystals containing chain-extended polymer has been pursued by many research groups. As this goal seemed unlikely with the use of preformed polymer molecules, routes involving simultaneous crystallization and polymerization were

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considered together with the use of preformed lattices. The latter method, solid-state polymerization, was extensively studied (Morawetz 1966) with little apparent success. This was primarily because the conditions that must be fulfilled for a solid-state polymerization to occur and to proceed to a single crystal product are extremely stringent. Thus, although the reactivity of disubstituted diacetylenes has been known for one hundred years by the coloration that occurs on heating or u.v.-irradiation, the true nature of the process was not elucidated until fifteen years ago. Then, Wegner (1969) showed that the product could, for certain diacetylene compounds, be the sought-after chain-extended polymer crystal.

Since then the polydiacetylenes (PDAs) have attracted considerable attention. Subsequent studies have probed both the solid-state reaction and the physical properties of the resultant polymers. Wider discussions of this work can be found in recent review articles (Bloor 1982, 1984; Huntsman 1983; Wegner 1981 *b*; Baughman & Chance 1978). PDA single crystals contain conjugated polymer chains with the structure shown schematically in figure 1. The ordering of these polymer chains in the crystals is revealed by the strong dichroism observed at visible wavelengths. When viewed in light polarized parallel to the chain direction the crystals have a metallic lustre, while for perpendicular polarization they have the appearance of a tinted glass. X-ray and electron-microscope studies have shown that the best crystals contain very few lattice defects (Dudley *et al.* 1982; Read & Young 1984). The large groups R in figure 1, normally required for the production of polymer crystals, result in large interchain spacing of typically 1 nm. This reduces interchain coupling and makes PDA the best quasi-one-dimensional material available.

Despite this, progress in understanding the basic physical properties has been slow, for two distinct reasons. First, even with single crystals some measurements are not straightforward. In particular, studies of electrical conductivity have been hampered by the difficulty encountered in making ohmic contacts to reactive materials. Second, many new phenomena have been discovered that have required the development of theoretical models appropriate for the physics of a quasi-one-dimensional material.

As our understanding of PDAs deepens it is important to relate this knowledge to work on other conjugated polymers with less perfect morphologies. It is, therefore, important to study PDA samples with a range of morphologies to see how their physical properties are affected by sample morphology. PDAs can be obtained with many different and characterizable morphologies and studies of such samples are rapidly expanding.

In the following paper, §2 will cover the polymerization process and sample morphology; §3, the optical properties of PDAs and §4, studies of photoconductivity in PDAs.

2. Diacetylene polymerization and morphology

The solid-state polymerization of a disubstituted diacetylene is shown schematically in figure 1. Initially the monomer molecules form linear arrays that are converted into a single polymer chain by a concerted reaction. This reaction may be initiated thermally or by ultraviolet or ionizing radiation. In exceptional cases the reaction can proceed under shear of the crystal lattice. Hydrostatic pressure can influence the polymerization rate, thus enabling polymerization to occur in crystals with negligible reactivity at ambient pressure.

Several criteria must be satisfied if solid-state polymerization is to occur and for the product to retain the perfection of the initial monomer crystal. It must be possible for a reaction to occur

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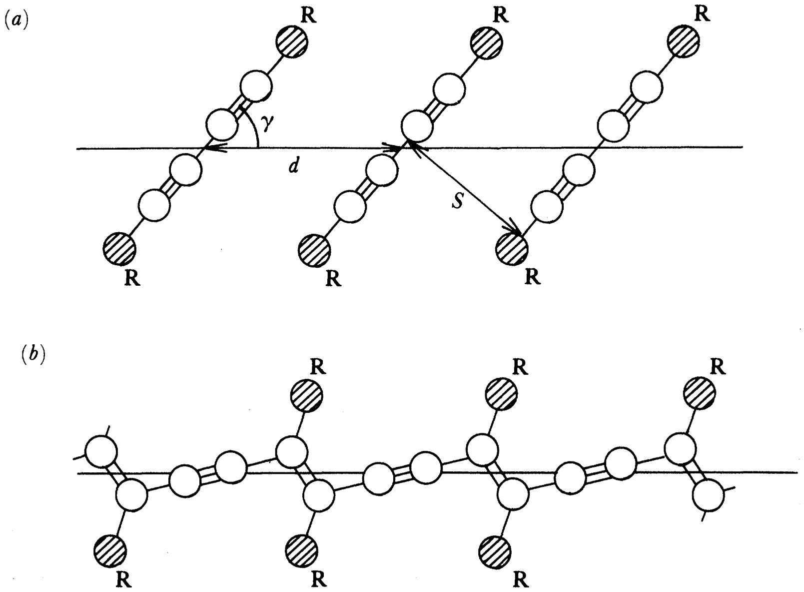

Figure 1. Schematic representation of solid-state polymerization of diacetylenes; (*a*) monomer array and (*b*) resulting conjugated polymer. The monomer molecules may be asymmetric (R, R′).

in the monomer crystal. Two criteria for this have been considered. The simpler of the two is that of Schmidt (1967), based on observations of the lattice packing in a number of different reactive organic crystals. This states that the carbon atoms that are bonded as a result of the reaction must be separated by less than 0.4 nm in the crystal lattice. If their separation is larger than this critical value a reaction is not possible. An alternative criterion was proposed by Baughman (1974), who considered the molecular motion of the reacting monomers. The model was simplified by treating the diacetylene unit as a rigid rod, the substituent groups as small units (which did not affect the motion) and restricting the motion to the plane containing all the monomer molecules. Baughman calculated the root-mean-square motion during polymerization in two cases; (*a*) where the centres of the monomers remain on a common axis during polymerization and (*b*) where the orientation of the monomers remained constant and polymerization proceeds by shearing of the monomer stack.

These criteria have been compared with crystallographic data by plotting limiting contours for lattice packing and reactivity with the use of monomer separation and orientation data (d and γ of figure 1) as variables. Such plots show that Schmidt's criteria describes adequately the behaviour of diacetylenes (Bloor 1982, 1983). Figure 2*a* illustrates the ranges of d and γ required for reaction of the extreme carbon atoms of mono-, di- and triacetylenes. The broken curves show the upper limits set by Schmidt's criterion while the solid curve is a lower limit set by the close packing of the acetylenic monomers, i.e. S of figure 1 is equal to 0.34 nm. Figure 2*b* shows the crystallographic data for reactive and unreactive diacetylenes, which indicates the utility of Schmidt's criterion. It is interesting to note that d and γ values appropriate for the 1,6-polymerization of a triacetylene appear improbable. Experimentally triacetylenes have been observed to react as if they were diacetylenes (Kiji *et al.* 1973). In contrast, diacetylenes with d and γ values close to those for a 1,2-reaction still polymerize by a 1,4-reaction.

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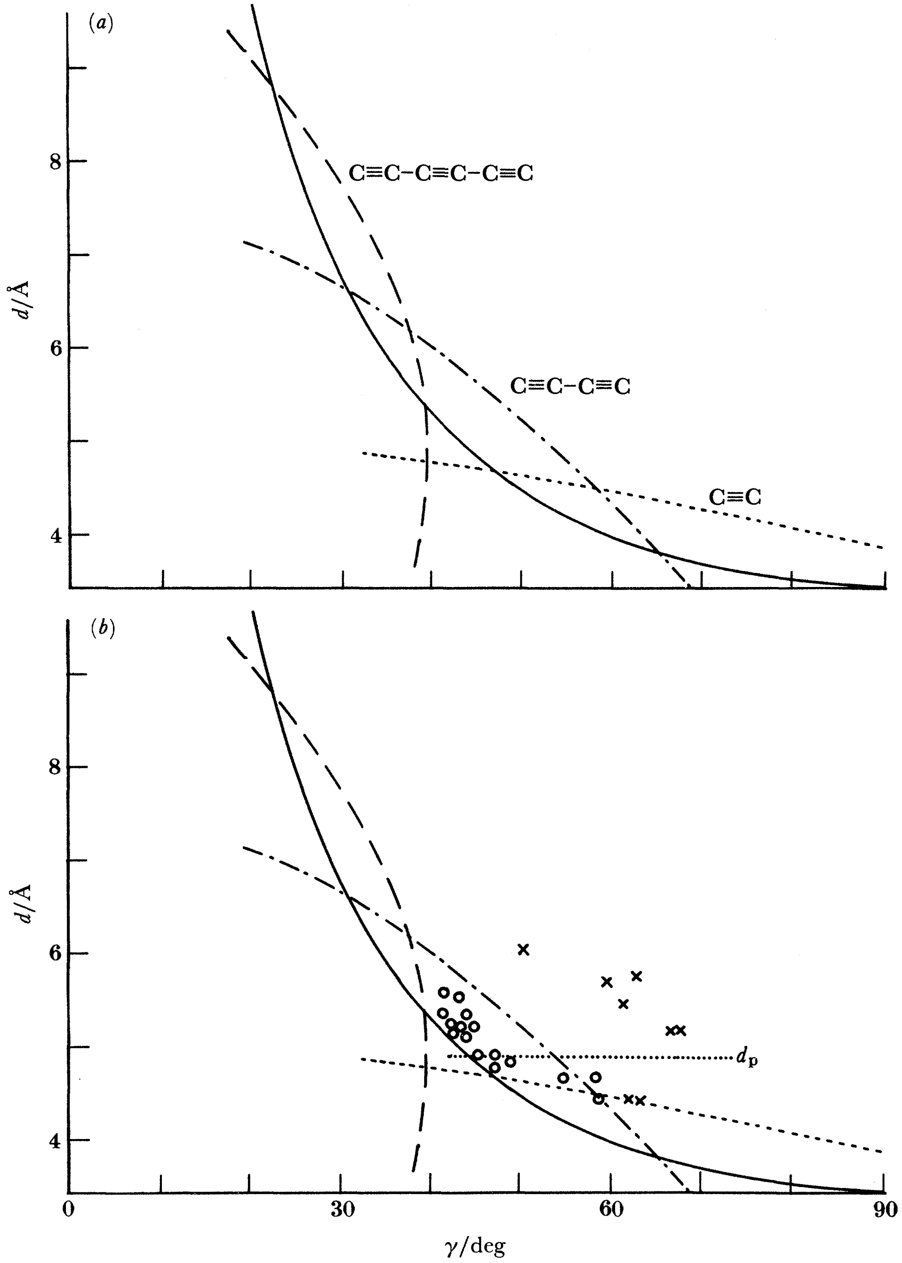

FIGURE 2. Monomer packing requirements for solid-state reactivity; (*a*) boundaries for reaction of mono-, di- and tri-acetylenes; (*b*) data for reactive (○) and unreactive (×) diacetylenes. (1 Å = 10^{-10} m = 10^{-1} nm.)

The criterion discussed above dictates that the 1,4-reaction is topochemical in nature, i.e. the reaction path is controlled by the topology of the monomer lattice. For the reaction to lead to a single crystal product the lattice must control the reaction throughout the polymerization. This may not be the case if the heat of reaction destroys the crystal lattice because the reaction, though initiated in the crystal, actually proceeds in a disordered phase (see, for example, Steinbach & Wegner 1977). A further condition is that the product is topotactic, i.e. has an orientation fixed relative to the monomer lattice structure. This can be stated alternatively as

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the need for a unique polymerization direction. If several possible directions occur the product is not a single crystal (see, for example, Bloor & Stevens 1977). Even if all these conditions are satisfied the product is often a fibrous bundle of microcrystallites rather than a single crystal. Thus it is necessary for the polymerizing crystal to remain in a single phase, i.e. to behave as a solid solution of polymer in the monomer matrix (Kaiser *et al.* 1972; Baughman 1974).

It is the monomer end-groups that determine whether these criteria are satisfied. The end-group interactions play a major part in determining lattice packing, particularly if they are large. Large, strongly interacting groups produce stacks of monomers closely spaced in one direction but well separated laterally. Three examples of end-groups are shown in figure 3.

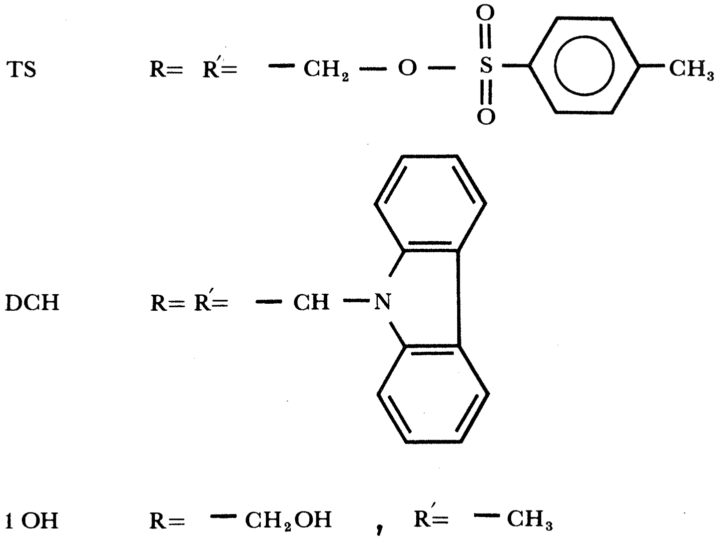

FIGURE 3. Chemical structures of end-groups of TS, DCH and 1 OH diacetylenes.

Figure 4 shows the *ac* lattice plane of the bis-toluene sulphonate (TS) polymer, polymer chains are oriented along the *b* axis. This is an example of monomer end-groups with strong dipolar interactions. The end-groups also determine the lateral interactions of the polymer and monomer lattice. The balance of inter- and intrastack interactions is critical but has received little attention to date. The dimensional changes during polymerization can be large, as shown in figure 2*b*. The dotted line (d_p) shows the repeat unit spacing in PDA polymer crystals, which is markedly different from the monomer spacing. TS is a typical example having an overall lattice contraction on polymerization of 5%. The interstack interaction is strong enough to distribute the strain throughout the lattice during polymerization. The smooth conversion to polymer is reflected by continuous changes in the physical properties of the crystals during polymerization (Bloor 1983).

An example where weak interstack interaction leads to break-up of the polymer is 1-hydroxy-2,4-hexadiyne (1 OH). The monomer crystal structure is shown in figure 5 (Fisher *et al.* 1978). Monomers are arranged in a herringbone structure with a backbone of hydrogen bonds. The monomers are closely packed and polymerize along the *a* axis because of the hydrogen bonding. Interactions between these groups are through weaker van der Waals forces. During polymerization the crystal cleaves along these weakly bonded interfaces, producing a fibrous product.

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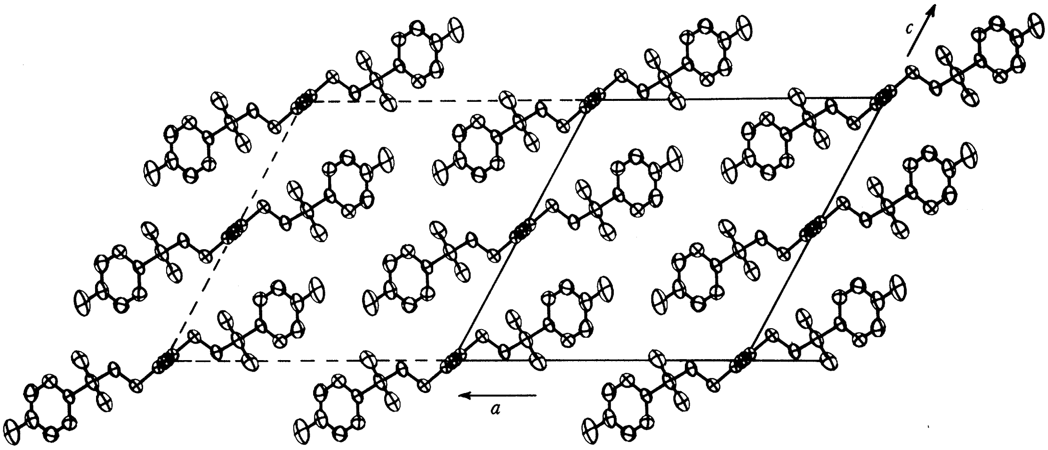

Figure 4. Projection of the crystal structure of TS polymer at 300 K viewed along the *b* axis.

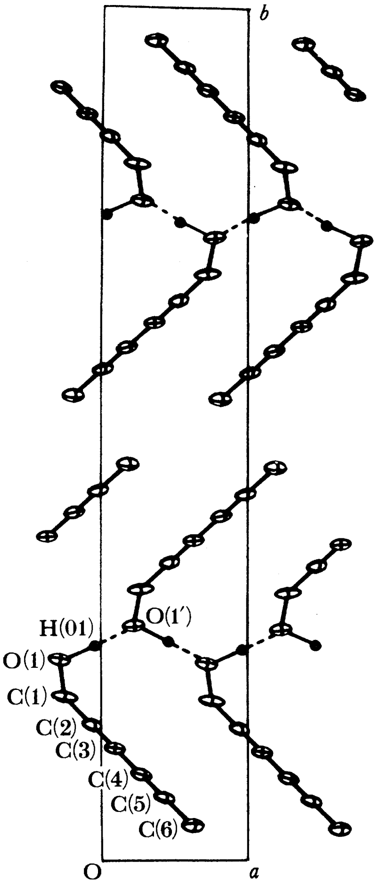

Figure 5. Structure of 1 OH monomer crystal at 100 K (after Fisher *et al.* 1978).

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The mechanism of polymerization has been exhaustively studied and a range of radical intermediates identified in crystals irradiated with ultraviolet light at low temperatures (Bubeck *et al.* 1980). The polymerization kinetics have also attracted considerable attention. Neither of these topics will be discussed here. Further details can be found in the reviews of Bloor (1982, 1983); Bässler (1984) and Sixl (1984).

The perfection that can be attained in PDA crystals has been demonstrated by X-ray topography of TS crystals (Dudley *et al.* 1982). The defect density of the polymer crystal is identical with that of the monomer and can be as low as a few dislocations per square centimeter in carefully grown crystals. Even under conditions of rapid growth and rapid polymerization the density of defects can be low. DCH crystals grown rapidly from solution and polymerized in the electron microscope show very few dislocations (Read & Young 1984).

The range of morphologies observed in PDAs is indicated in table 1. Examples of perfect, chain-extended and imperfect, chain-extended polymer have been given above. Less ordered samples can be obtained by the mechanical working of single crystals; such materials have been characterized by using electron microscopic and spectroscopic techniques (Young *et al.* 1981; Batchelder *et al.* 1981). Less well characterized polymer can be obtained by recrystallization from solution (Young *et al.* 1979). Recently the properties of polymer solutions, melts, glasses and aggregates have attracted attention (Patel *et al.* 1979; Casalnuovo *et al.* 1984; Muller *et al.* 1984; Rughooputh *et al.* 1984). Such samples are highly disordered but the details of the structure are currently a matter for debate. Recrystallization of the more soluble PDAs from solution leads to spherulitic, hedritic and crystal morphologies similar to those found in conventional polymers.

TABLE 1. MORPHOLOGIES OBSERVED FOR POLYDIACETYLENES

single crystals	planar, fully extended chains
fibrillated polymer residual polymer Langmuir–Blodgett films inclusion compounds	imperfect, fully extended chains
recrystallized polymer	imperfect, planar chains (folded?)
polymer solutions, melts worked polymer aggregated polymer	non-planar, non-extended chains (random coil?)

3. OPTICAL PROPERTIES

Spectroscopic investigations provide the most direct way of probing the electronic energy levels of materials. As noted in §1, PDA crystals display striking optical properties. Initial studies of the reflection spectra of TS crystals suggested that the high and structured reflectivity could be interpreted in terms of an interband transition in a one-dimensional semiconductor (Reimer *et al.* 1976; Bloor 1976). This case is shown in figure 6*a*. The strong bond alternation in the PDA backbone will lead to a band gap larger than that for a bond-alternated polyacetylene chain (Whangbo *et al.* 1979). The absence of energy dispersion for lateral directions leads to maxima in the density of states at the band edges, resulting in an inverse square root van Hove singularity at the gap energy. The occurrence of features with this profile led to the assignment to an interband transition.

Subsequent studies of line shapes (Bloor & Preston 1977) and photoconduction (Lochner

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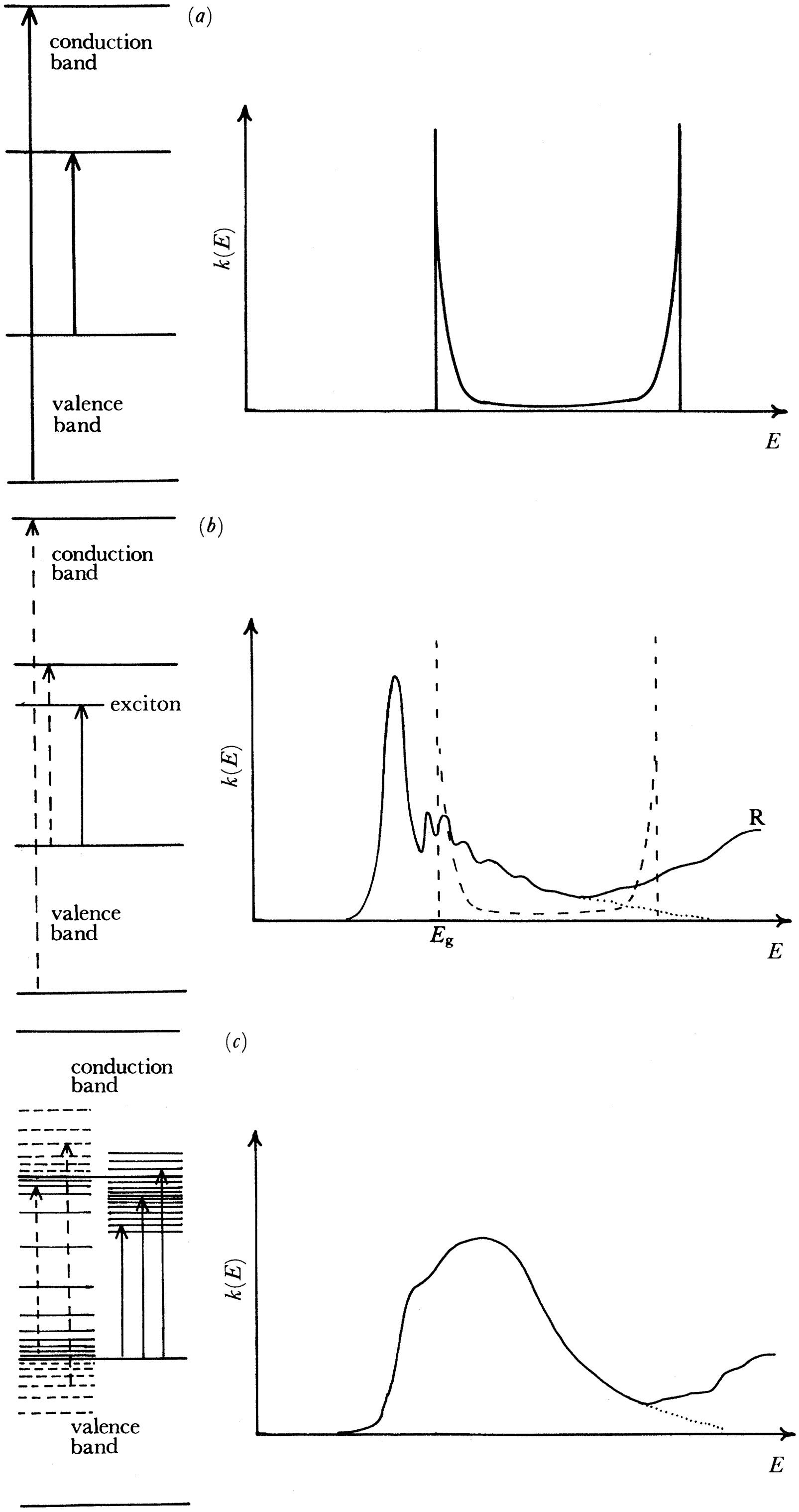

FIGURE 6. Optical spectra and energy levels of PDAs (*a*) in the Hückel approximation, (*b*) with Coulomb interaction and (*c*) as (*b*) but for an imperfect material.

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et al. 1978) suggested that this was not the case. The absence of a photoconduction edge indicated that the main optical excitation produced a neutral species, an exciton. A typical result is shown in figure 7 (Lochner *et al.* 1978). The occurrence of an exciton is predicted if Coulomb interactions are included in the hamiltonian for the polymer chain (Pugh 1973; Cade & Young 1979). This situation is shown in figure 6*b*. The exciton is split off from the band edge and steals most of the oscillator strength from the interband transition. Electron–phonon interaction gives a finite line width and phonon side bands that swamp the weakened interband transitions, while at high energies the spectrum is dominated by side-group absorptions. The exciton model accords well with experimental spectra as shown in figure 8.

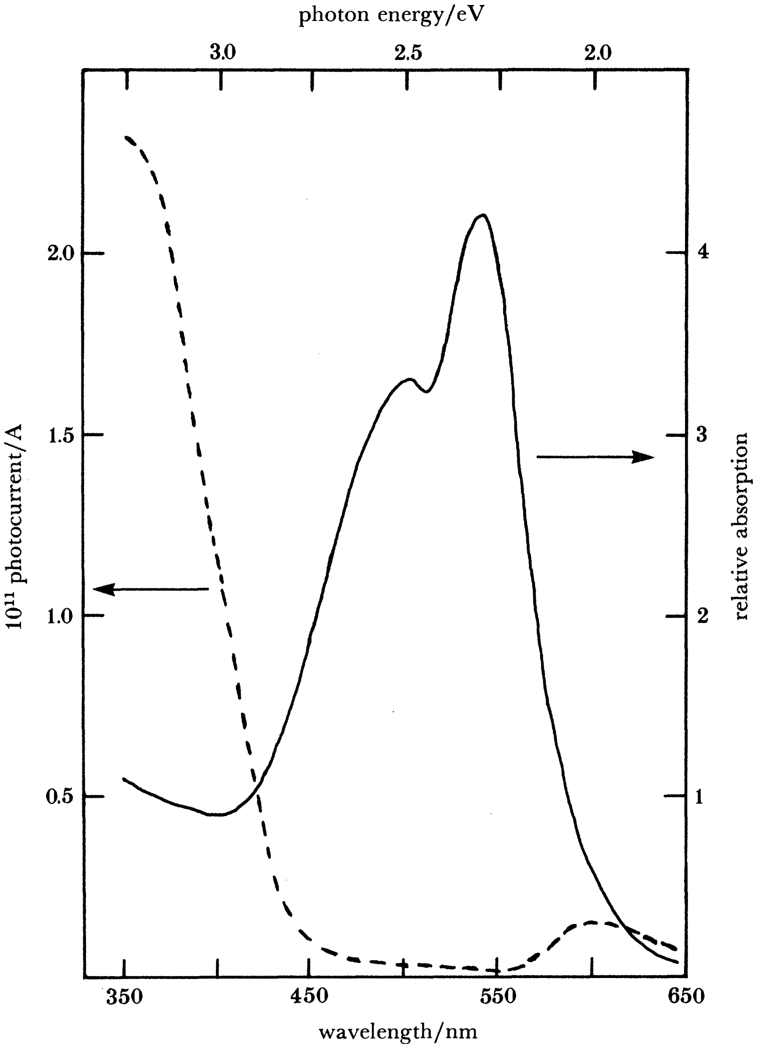

FIGURE 7. Absorption spectrum and photocurrent for the TCDU PDA (after Lochner *et al.* 1978).

This picture has been confirmed by a number of subsequent measurements and calculations. Observations of electro-modulated reflection spectra for TS, DCH and a number of other PDAs have revealed that at low temperatures a strong feature occurs about 0.5 eV above the exciton band (Sebastian & Weiser 1981*a*, *b*). The spectra show a second derivative profile for the

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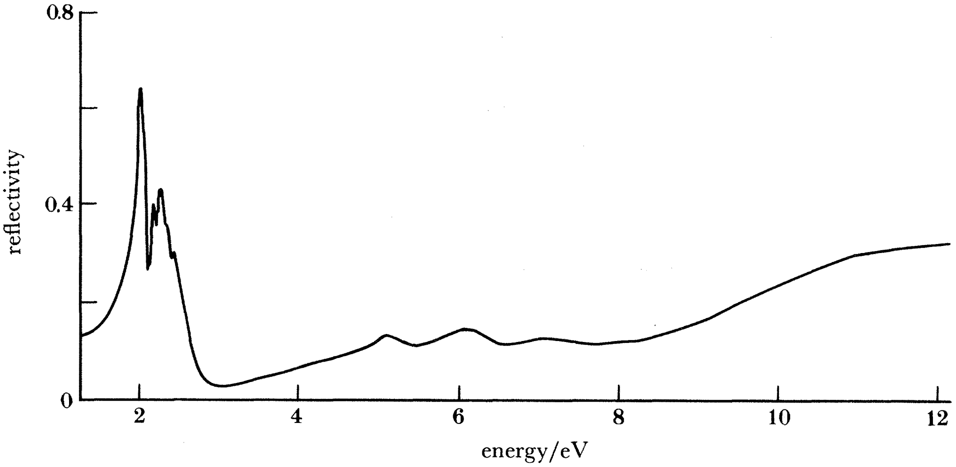

FIGURE 8. Reflection spectrum of TS polymer recorded at 300 K for light polarized parallel to the polymer chains.

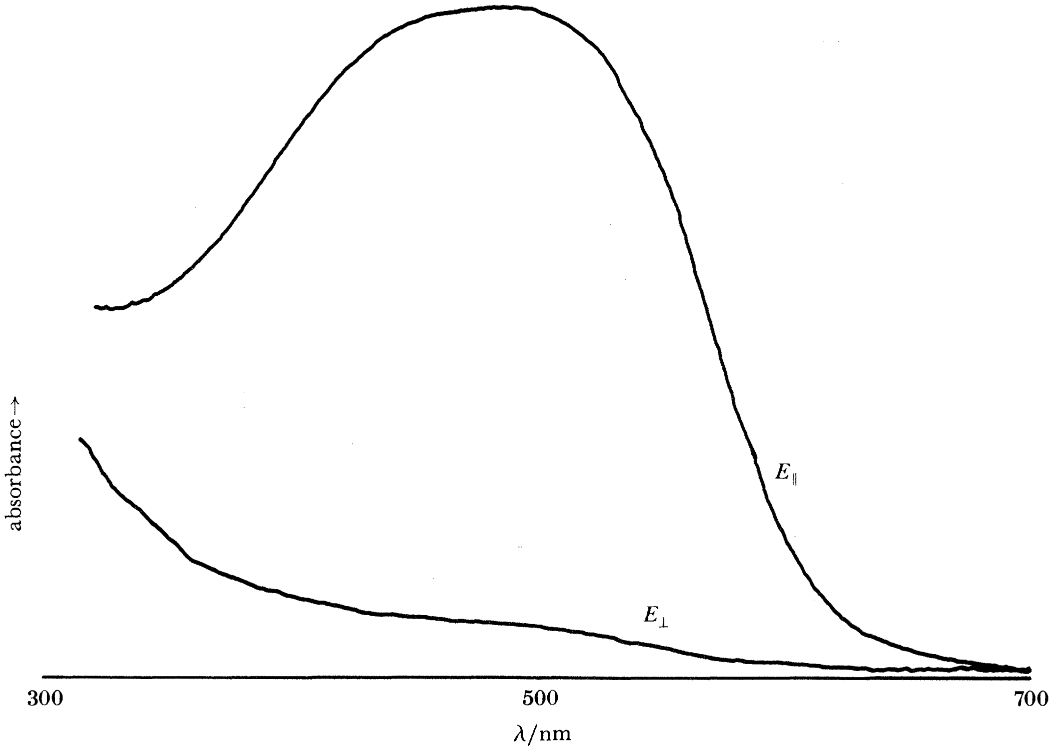

FIGURE 9. Absorption profiles, at 300 K for parallel and perpendicular polarization, of a thin 1 OH polymer film.

exciton and first derivative for the higher lying features, indicating that the latter is the interband transition. Confirmation is provided by the observation of a photoconduction edge in this region (Donovan & Wilson 1981*a*). The excitonic state has been studied by using resonant Raman scattering (Batchelder & Bloor 1982) to provide information about the excited-state potentials and the changes in bond length between ground and excited states.

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These were found to be in good agreement with values deduced for PDAs with the use of polaron formalism (Cade & Movaghar 1983). A theoretical model developed by using an exciton formalism (Suhai 1984) gives exciton energies and ionization potentials in good agreement with experimental values.

Disorder broadens and shifts the exciton absorption band of PDAs and produces an extended tail of localized states extending into the band gap as shown in figure 6*c*. There are two possible origins of spectral shifts; changes in conjugation length and changes in the environment of extended chains. The latter effects are large because the polymer chains are deformable. Thermal expansion can give shifts of 0.1–0.5 eV for an extended polymer in partly polymerized crystals (Bloor & Hubble 1978), while comparable shifts can be produced by the extension of PDA polymer fibres (Batchelder & Bloor 1978). Thus, broad profiles are expected for imperfect PDAs containing extended chains. The spectrum of a 1 OH polymer film (figure 9) is almost featureless but displays strong dichroism.

4. PHOTOCONDUCTIVITY

The band gap in PDAs is large (2.4 eV or more), so that the density of thermally generated carriers will be low at room temperature. Therefore the dark current is expected to be low if injection of carriers from the electrodes is small. This has been confirmed experimentally (Lochner *et al.* 1976*a*; Siddiqui & Wilson 1979). For DCH with non-injecting electrodes dark currents are in the range 10^{-12}–10^{-14} A, but when alkali or alkaline earth electrodes (which act as electron injectors) are used, currents fall in the range 10^{-5}–10^{-7} A (Spannring & Bassler 1981). For TS polymer crystals, which have been used in most studies of conduction, all electrode materials are non-injecting, probably because surface decomposition produces an insulating (blocking) layer at the electrode. The information that dark current measurements have provided about electrode behaviour is important in the interpretation of photoconductivity.

Studies of photoconduction were first made on single crystal samples with low densities of defects that could trap carriers. This situation is shown schematically in figure 10. A photon incident on a PDA chain will generate a hot electron and hole with some probability η, which will be low because of competition with the stronger exciton absorption. To contribute to the photocurrent the carriers must thermalize at a separation greater than the Coulomb capture distance, r_{th}. For PDAs this is large so that most electron–hole pairs suffer geminate recombination. The theoretical framework for understanding this process was first presented by Onsager (1938). Once a carrier is thermalized with a probability ϕ, it will move under the influence of an applied field with a drift velocity v_{d}. After time τ it encounters a shallow trap from which it escapes into the band after a further time τ_{b}. Finally it will either encounter a deep trap or the electrode where it will eventually recombine.

Photocurrents in PDA crystals are linear in light intensity but become sub-linear at high intensity (Lochner *et al.* 1976*b*). Field dependence is initially linear, becoming approximately quadratic at high fields (Donovan & Wilson 1979; Siddiqui 1980*a*; Seiferheld *et al.* 1983*b*). Typical results for TS and DCH are shown in figure 11. Such behaviour is expected for space-charged limited current with injecting (ohmic) electrodes. This is now known not to be the case for the silver paste electrodes commonly used in the photoconductivity measurements. An alternative explanation is that the voltage dependence of the photocurrent is controlled by

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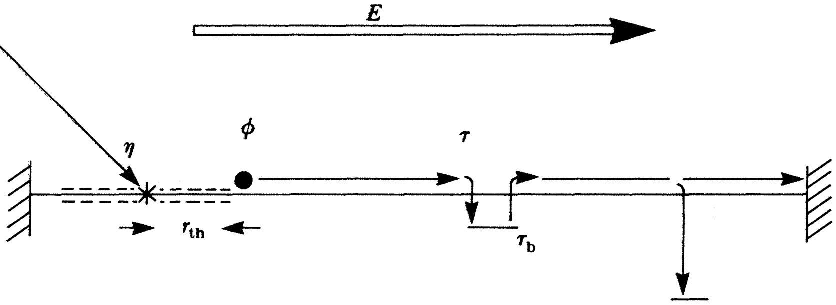

FIGURE 10. Schematic representation of photocarrier generation and motion in a PDA with low defect density (see text for details).

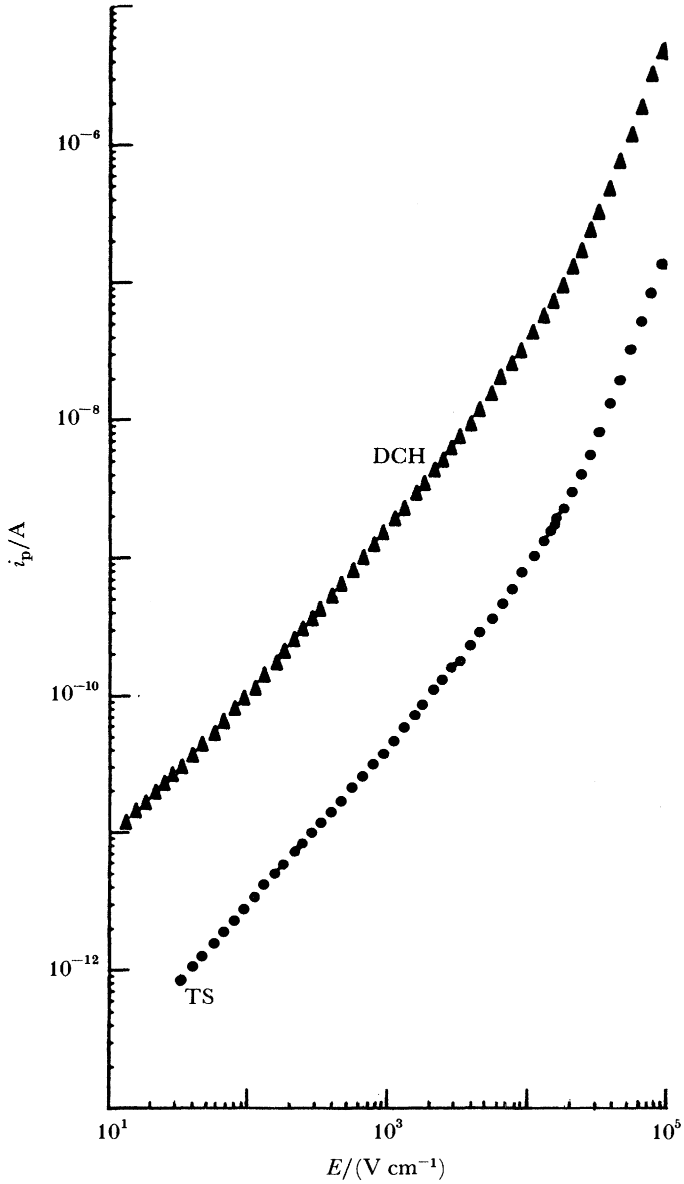

FIGURE 11. Photocurrents for DCH and TS polymer at 300 K (after Seiferheld *et al.* 1983*b*).

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the voltage dependence of the photocarrier generation process. Application of the Onsager model for geminate recombination has been shown to predict field dependence close to that observed experimentally (Donovan & Wilson 1979, 1981 *a*, *b*; Siddiqui 1980*a*, 1984; Seiferheld *et al.* 1983 *b*). At high fields the experimental photocurrent increases, whereas the theory predicts saturation, a difference attributed to ionization of vibrationally excited excitons at high fields.

Despite this general agreement there has been considerable controversy concerning the interpretation of the photoconducting data. Thus it has been argued that recombination is important and that the electron mobility is low, of the order 1 $cm^2\,V^{-1}\,s^{-1}$ (Siddiqui 1980*b*). Conversely Donovan & Wilson (1979, 1981 *a*, *b*) have observed carrier transit across the whole of the sample. By measuring d.c. and pulsed photoconductivity they concluded that the drift velocity is essentially field-independent down to the lowest voltages at which photocurrents could be measured. The intrinsic mobility deduced from this result is 20 $m^2\,V^{-1}\,s^{-1}$, an extremely high value.

Movaghar *et al.* (1984*a*) have pointed out that the field independence of the drift velocity follows directly from the fact that field dependence of the photoconductivity is fully contained in that of the carrier generation. They further show that this result can be understood when scattering on the one-dimensional chain is taken into account. Their treatment also explains the difficulties encountered by workers attempting to see carrier transit after pulsed excitation (Chance *et al.* 1976; Reimer & Bassler 1976, 1978) because scattering leads to a $t^{-\alpha}$ decay of photocurrent even for low densities of scattering centres. These results are particular examples of a more general failure of linear response theory in certain one-dimensional problems (Movaghar *et al.* 1984*b*). The experimentally observed decay law leads to the prediction of a very strong dependence of carrier transit times on the defect density.

The problem of carrier motion in one dimension has been considered in a series of papers by Wilson (1980, 1982*a*, *b*, 1983). The model developed is of an acoustic polaron rather than the one normally discussed that involves optic phonons. Solution of the Su–Schrieffer–Heeger hamiltonian with coupling to acoustic phonons leads to the conclusion that such a polaron has a limiting velocity because the polaron mass increases as its energy increases.

As noted above, a moderate increase in defect density is predicted to drastically increase carrier transit times. This has been observed experimentally for fibrous 1 OH polymer samples (Hunt *et al.* 1983), where photocurrent decays lasting several hours at room temperature have been observed. The motion of individual carriers is more complicated, as indicated in figure 12. The initial photocarrier generation process is the same but carriers will be trapped and thermalized several times before falling into a deep trap from which they cannot escape. Some motion will also be possible by hopping between trap levels. Trapped carriers may be subsequently photoexcited back to band-like states. Short chains may act as traps if the probability of tunnelling is low. Recombination can occur at deep traps, particularly where electrons and holes exist on adjacent chain ends. It has been pointed out that a filled trap will provide a Coulomb barrier behind which further carriers can be trapped on adjacent chains (Sworakowski & Ferreira 1984). Strictly, at 0 K, the presence of disorder will localize all states. However, at finite temperature enough delocalization occurs for carrier motion to be observed.

Some of these phenomena have been observed in 1 OH, for example, detrapping of photo-injected carriers by infrared photons that normally produce negligible photocurrent. A treatment in terms of the microscopic processes is, however, too complex and a model of diffusive motion in one dimension has been adopted. This problem has been discussed by Movaghar

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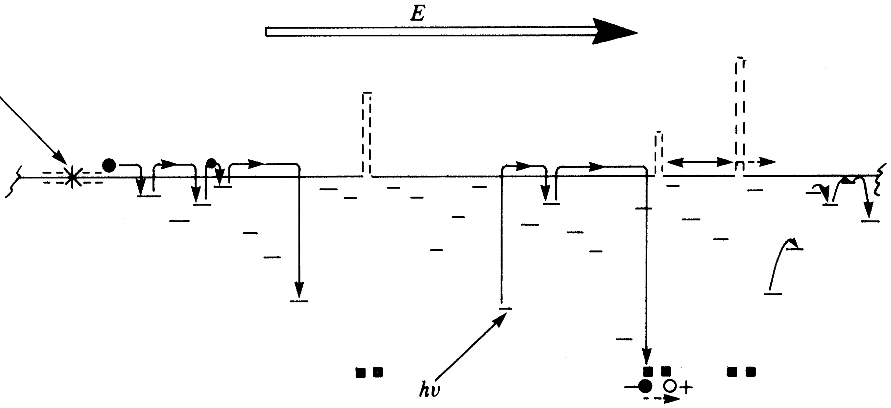

FIGURE 12. Schematic representation of photocarrier generation and motion in a PDA with high defect density (see text for details).

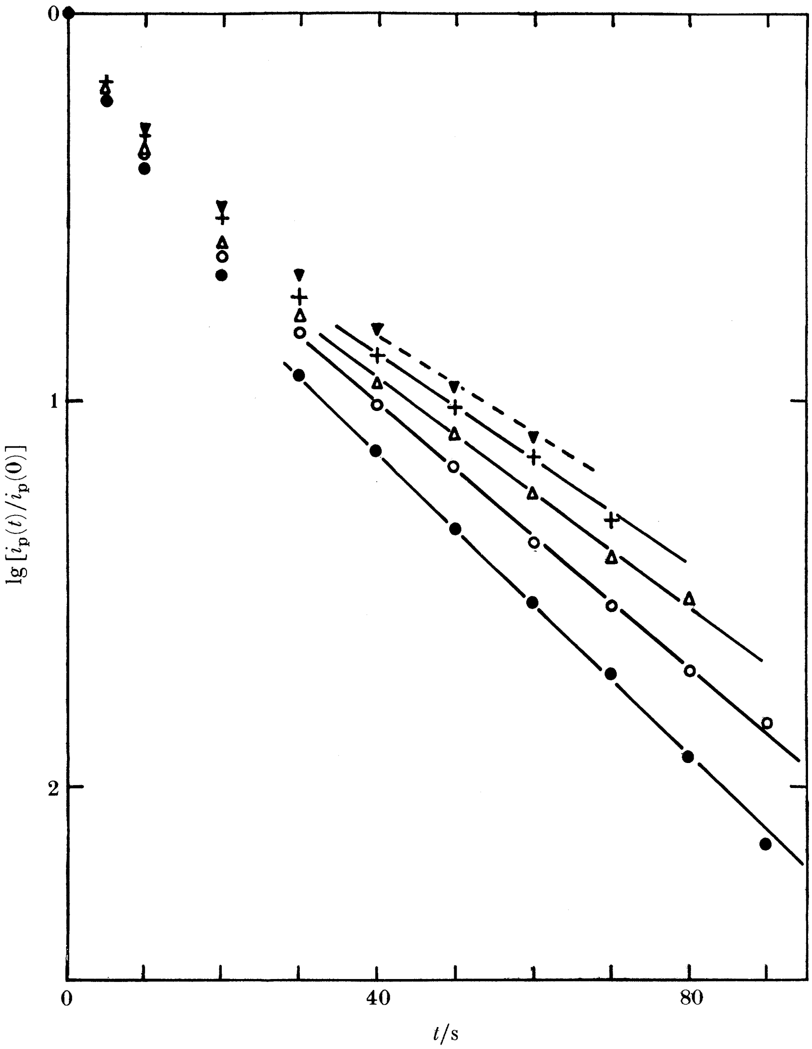

FIGURE 13. Voltage-dependent exponential decay of photocurrents observed in a 1 OH polymer film at 117 K, ▼, 1500 V; +, 1750 V; △, 2000 V; ○, 2200 V; ●, 2500 V.

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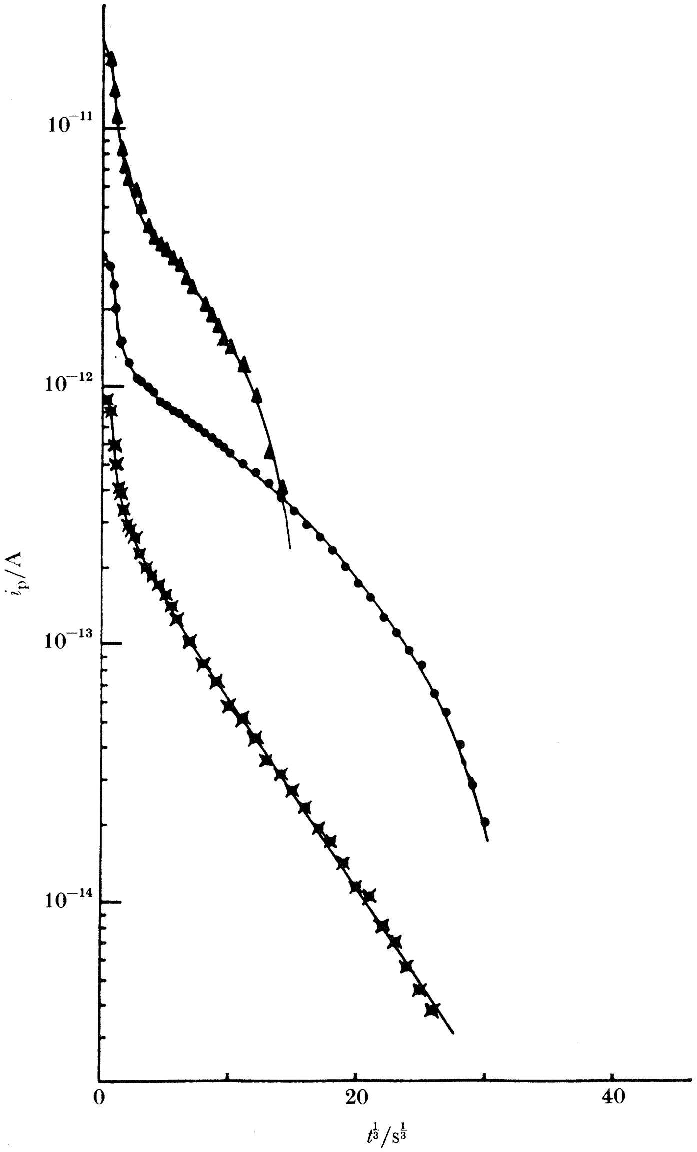

FIGURE 14. Voltage dependence of photocurrent decay in a damaged TS polymer crystal at 300 K (after Seiferheld *et al.* 1983*a*). ▲, 20000 V/cm; ●, 6600 V/cm; ●, 1700 V/cm.

(1980) and an exact analytic solution has been derived in the long time limit when the motion can be described by a constant diffusion coefficient (Movaghar *et al.* 1981, 1984*b*). At high temperatures and low applied fields the full expression can be approximated by an exponential term involving $t^{\frac{1}{3}}$, while at low temperatures and high fields a normal exponential decay will dominate. For 1 OH at room temperature the former dependence is observed (Hunt *et al.* 1983). A proper description of the field and temperature dependence requires numerical evaluation of the full theoretical expression. At room temperature the field independence of the decay and at 117 K the onset of a field-dependent exponential decay are predicted. Both are observed experimentally, the results observed at 117 K are shown in figure 13 (Hunt *et al.* 1984).

An independent demonstration of the one-dimensional diffusion law in PDAs has been given

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by Sieferheld *et al.* (1983*a*) by using TS crystals containing defects introduced by ion bombardment. For such samples the decay behaviour can be switched from a $t^{\frac{1}{3}}$ to a t exponential dependence by increasing the applied field as shown in figure 14.

5. CONCLUSIONS

Progress in understanding the physics of materials with complex morphologies is aided by studies of related single crystals. PDAs have been shown to occur as highly perfect single crystals that can be used to further our knowledge of conjugated polymers. The studies of the optical and electronic properties of PDA crystals have provided critical tests of alternative models of conjugated polymers and revealed new and unexpected behaviour that is a direct consequence of their quasi-one-dimensional structure.

The nature of the electronic excited states in PDAs appears to be well established. The interpretation of photoconductivity data has led to controversy. The conclusion that drift mobility is saturated is currently gaining support. The consequent high intrinsic mobility requires further experimental test. The proposed acoustic-polaron is a concept that also requires further investigation. It should be noted that the alternative view that carrier mobility is low also requires justification for an extended, conjugated system.

The experimental results for imperfect samples are equally striking as is the agreement between this data and the one-dimensional diffusion model. In all these areas there is clearly considerable scope for further experimental and theoretical investigations. The wealth of data already to hand justifies the description of PDAs as prototype one-dimensional semiconductors.

The connection between these studies and those of other conjugated polymers will be made by the investigation of PDA samples with a wider range of morphologies. This is an area currently attracting interest and is likely to become more important in the future.

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Discussion

R. Pethig (*School of Electronic Engineering Science, University College of North Wales, Bangor, U.K.*). It has been mentioned that a mobility value of 20 $m^2\ V^{-1}\ s^{-1}$ can be deduced from some of the measurements. Can Professor Bloor provide more details of this, as the implications of such an enormous mobility value are considerable?

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D. Bloor. The very high mobility deduced for polydiacetylenes is perhaps not unexpected. Similar values have been observed in two-dimensional semiconductor layers and is a consequence of the greatly reduced carrier scattering in two dimensions compared with that in three dimensions. Thus a high mobility might be anticipated in one-dimensional materials for similar reasons. Unfortunately, another effect of low dimensionality is to drastically affect carrier transit through a real sample, i.e. one with chain defects, (Movaghar *et al.* 1984*a*). This means that photocurrent pulses decay monotonically and a simple carrier transit is not observed. There is, therefore, no direct measurement of the carrier mobility in polydiacetylenes.

Also in contrast with inorganic semiconductors polydiacetylenes are not rigid lattice materials. The polymer backbone is readily deformable leading to polaron formation. These would be expected to be relatively massive and of low mobility. Calculations show, however, that optic-mode polarons in polydiacetylenes are not very heavy (Cade & Movaghar 1983). In addition measured deformation potentials suggest that acoustic-mode polarons would be energetically favoured. Wilson (1983) has solved the Su–Schrieffer–Heeger hamiltonian with acoustic phonon coupling. The result is a polaron which cannot scatter from phonons in first order (i.e. has a high intrinsic mobility) but behaves in a relativistic manner; as it becomes more energetic it induces more lattice deformation and becomes more massive. This behaviour is consistent with the experimental observations of a saturated carrier drift velocity down to very low applied fields from which the high mobility is inferred.

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