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# Carrier range on conjugated polymers as molecular wires. Example: polydiacetylene, 4BCMU

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# Abstract

The crystalline polydiacetylene 4BCMU is studied using a photocharge collection technique following a 6 ns pulse of UV irradiation. From these studies it is shown, by two separate routes, that with blocking electrodes the single crystal polydiacetylene is a unity gain photoconductor. This entails that the distance of travel of a photocarrier on the polymer backbone of 100% polydiacetylene single crystals is much greater than the 2.5 µm length of the individual polymer chains that form the crystal and equal to the crystal length of up to several millimetres. Furthermore this knowledge of the photocarrier range enables the absolute determination of the photocarrier generation efficiency. Such information is crucial to the interpretation of other photoconduction experiments. © 1999 Elsevier Science B.V. All rights reserved.

# 1. Introduction

Diacetylene single crystals may in certain circumstances polymerise topochemically to produce highly perfect and macroscopic single crystal polymers. A number of diacetylenes have been studied since their re-discovery by Wegner [1]. They have excited interest as model systems in which to study photoconduction [2–4] in conjugated polymers because:

(a) They present no difficulties of interpretation generally associated with transport properties on polymers due to complex tertiary structures and complex topological transport pathways, and (b) They offer the prospect of a highly one-dimensional system, with a covalently bonded semiconductor along the unique chain direction of the crystal and a Van der Waals bonded molecular crystal in the other directions.

In this work the polydiacetylene, PDA 4BCMU, with the side group

$$\mathbf{R}_1 = \mathbf{R}_2 = -(\mathbf{CH}_2)_4 - \mathbf{OCO} - \mathbf{NH} - \mathbf{CH}_2 - \mathbf{COOC}_4 \mathbf{H}_9$$

is of interest because:

(a) It is soluble in common solvents allowing measurement of the polymer chain lengths by conventional polymer chemistry methods [5].

(b) It is polymerised by gamma irradiation and is thermally stable. The polymer content within a monomer crystal matrix may thus be controlled with a suitable gamma dose [5] and will be stable thereafter for the purposes of further experiment on isolated chains in a monomer matrix.

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Both of these properties have been used in two recent studies of the charge transport properties of poly 4BCMU as conjugated molecular wires.

(i) It has recently proved possible in unique experiments to measure the carrier transport along isolated polymer chains in solution by observation of transient photocurrents [6].

(ii) A study of electron transport on well-defined chain extended and isolated polymer chains has been carried out making use of the controllable nature of the polymer content of the 4BCMU monomer crystals [7].

For both of these studies it is necessary to know the carrier generation efficiency of poly 4BCMU in order to interpret the measurements. To find this quantity is the object of the present work.

#### 2. Measurement

With any photoconduction measurement, it is the case that several microscopic quantities may combine to produce the macroscopic quantity measured; the most directly measured quantity in the case of a transient photocurrent is the initial current amplitude,  $I_{\rm P}$ . In that case  $I_{\rm P}$  is determined by the product of two microscopic quantities; the number of carriers produced,  $\{\eta\phi\}N_{\rm PH}$ , where the quantum efficiency for carrier production is given by  $\{\eta\phi\}$  and their drift velocity,  $v_{\rm D}$ . Thus

$$I_{\rm P} = e\{\eta\phi\}N_{\rm PH}\frac{v_{\rm D}}{d}.$$
 (1e)

The quantum efficiency is written as the product of the quantum efficiency,  $\eta$ , for primary pair creation and the probability,  $\phi(E)$ , that the carrier pair escape geminate recombination, a field-dependent quantity.  $N_{\rm PH}$  is the number of photons absorbed and d is the electrode separation.

In measurements of DC photocurrents (or integrated photocharge,  $Q_{\rm PH}$  after a light pulse) the carrier range before recombination will be combined with the number of carriers produced:

$$Q_{\rm PH} = e\{\eta\phi\}N_{\rm PH}\frac{s}{d}, \quad s < d, \qquad (2a)$$

or

$$Q_{\rm PH} = e\{\eta\phi\}N_{\rm PH}, \quad s > d.$$
<sup>(2b)</sup>

Here, the quantity *s* represents the carrier range before recombination. The situation where s < d is the case of variable photoconductive gain (=s/d) and the case where s > d is the unity gain case when the electrodes are non-injecting as is the case in these experiments.

It is therefore necessary for the experimentalist who wishes to find the quantum efficiency for carrier production, to be able to unfold these quantities. In this paper integrated photocharge measurements, after a 6 ns duration UV laser pulse are reported and the unfolding of the carrier range and photocarrier generation efficiency achieved by two independent methods.

### 2.1. Line cutting

The first of these methods involves the experimentally controlled reduction of the carrier range by introducing a line of recombination centres at a shallow cut on the surface across the centre of the crystal perpendicular to the chains. If the carriers were travelling a distance d before (the unity gain case) they will now travel to the cut, a distance d/2with a resultant decrease in the measured photocharge by a factor 2. If on the other hand they were travelling a distance  $s \ll d$  then the majority of carriers will not arrive at the cut and the photocharge will remain unchanged. In this latter case further equispaced cuts can be made until the intercut separation  $s_n < s$  when the photocharge will begin to fall [8]. This technique works in principle in these quasi one-dimensional crystals as the opportunity to diffuse into the sample and around the cut is not afforded. Also with the cut being shallow there is a bulk dark current that continues to flow, thus maintaining the field.

This method has been used previously on two other polydiacetylene single crystals with very different effects representing each of the above scenarios. It was originally used on PTS-6 where one cut across the centre was demonstrated to halve the photocharge collected. Further cuts that divided the crystal into quarters and then eighths were seen to be followed by further factor-two reductions in the measured photocharge [8]. This result was interpreted to show that the photocharge had originally been traversing the entire crystal ~ 3 mm in length. With this conclusion, using Eq. (2b), a value for the

quantum efficiency for carrier generation was found. While such an interpretation was contentious, leading as it did to conclusions elsewhere in the reported data of a drift velocity saturated with field, it received strong support when the polymer crystal of another diacetylene, the carbazole derivative, DCH was studied. This crystal showed a marked reduction in quantum efficiency for carrier generation as compared with PTS-6 when the assumption was made that the carriers traversed the whole DCH crystal length as in PTS-6 and Eq. (2b) was asserted in order to arrive at the quantum efficiency. However, it was then established that in the case of DCH the presence of a single cut across the centre of the crystal had no effect on the magnitude of the measured photocharge. Indeed, it was ultimately necessary to resort to e-beam microscopy techniques to achieve a set of 'cuts' close enough together ( $s_n < s$ ) to affect the magnitude of the photocharge [9]. The implication of these experiments was that the carrier range was of order,  $s = 70 \ \mu m$  on PDADCH. Given such a range, the generation efficiencies of PDADCH using Eq. (2a) and PTS-6 using Eq. (2b) were comparable in magnitude. This demonstrates that the 'line cutting' experiment is indeed valid and the results will depend on the carrier range on the particular diacetylene chain and not on some arbitrary and capricious disruption of the electric field that leads fortuitously to the observed (and otherwise explained) results. This line cutting technique is used here to establish the carrier range on poly 4BCMU.

#### 2.2. Photoconductive gain

As can be seen by an inspection of Eqs. (2a) and (2b) it is possible to determine whether a unity gain situation exists by varying the electrode separation, *d*. In the case of variable gain, Eq. (2a), the photocharge will increase as  $d^{-1}$  whereas for unity gain when  $s \equiv d$ , the photocharge is independent of *d*. By measuring the photocharge on a number of different samples where *d* is varied we may hope to establish which of Eq. (2a) or Eq. (2b) applies.

## 3. Experimental

4BCMU monomer crystals are grown from acetone solution and subsequently polymerised to 100% polymer using a Co<sup>60</sup> gamma source and a dose of 10 Mrad. The crystals were contacted with electrodes using two techniques:

(i) The crystals on a clean quartz substrate were contacted with *bulk electrodes* by evaporating Al on the end faces of the crystal and contacting this with a water-based silver paste. The water-based paste was used in order to avoid destroying the crystals which are soluble in organic solvents. The silver paste was in turn contacted by acetone-based silver paste which dried hard and wires were attached using the acetone-based silver paste. By this means a robust sample with electrodes and wires is constructed.

(ii) Al stripline *surface electrodes* with a gap of 250  $\mu$ m were evaporated on the surface of the crystal such as to apply an electric field in the chain direction.

The crystals were mounted in a chamber and lead throughs connected the sample to a voltage source and to a coulombmeter. The (100) face of the samples, containing the chain direction, c, was then illuminated by a 6 ns light pulse at 337 nm from a  $N_2$  laser. The wavelength corresponding to a photon energy of 3.68 eV is well above the band gap of polydiacetylenes ( $\sim 2.4 \text{ eV}$ ) [10–12]. The charge, O(t), induced at the electrodes as a function of time was monitored using a chart recorder. O(t) includes a contribution from the dark current,  $\int I_{\rm D} dt$ , that increases linearly with time, and from photocharge created by the laser pulse,  $Q_{\rm PH}$ . It is straightforward to separate these two contributions by running the coulombmeter some time before the laser pulse and continuing sometime afterwards. The initial form of



Fig. 1. The variation of  $Q_{\rm PH}$  with light intensity, demonstrating the linear variation described in Eqs. (2a) and (2b).

Q(t) is a straight line of slope equal to the dark current. The laser pulse induces a sudden increase in Q(t) followed by a gradual return over time to the previously observed slope representing the dark current. Extrapolation allows the excess charge,  $Q_{\rm PH}$ , due to the laser pulse to be determined.

Fig. 1 shows the linear variation of  $Q_{\rm PH}$  with light intensity in accord with the requirements of either Eq. (2a) or Eq. (2b). Fig. 2a and b show the electric field dependence of the collected photocharge,  $Q_{\rm PH}(E)$  normalised to the number of photons absorbed, before and after such a lightly scored cut is made with a scalpel blade across the centre of two samples of poly 4BCMU.  $Q_{\rm PH}(E)$  is linear in field at these fields and the gradient after scoring is approximately half of that measured prior to the cutting.



Fig. 2. (a) The electric field dependence of the photocharge collected (normalised to photons absorbed) after a 6 ns UV pulse before,  $\blacktriangle$ , and after,  $\blacksquare$ , the lightly scored cut has been made. Sample 1, d = 8 mm. (b) The electric field dependence of the photocharge collected (normalised to photons absorbed) after a 6 ns UV pulse before,  $\blacktriangle$ , and after,  $\blacksquare$ , the lightly scored cut has been made. Sample 2, d = 3 mm.



Fig. 3. The electric field dependence of the photocharge collected (normalised to photons absorbed) measured for six different 4BCMU crystals. Some crystals had surface electrodes while others had bulk silver paste electrodes. The electrode gap, d, varies from 250  $\mu$ m for the surface samples (high-field data sets) up to 4 mm. The charge has been normalised to number of photons absorbed.

Shown in Fig. 3, on a log–log plot, is  $Q_{PH}(E)$  vs. *E* normalised to the number of photons absorbed, for six samples. A single line, of slope unity, is fitted through all of the data. The six samples represent data from surface electrode samples and bulk electrode samples with a variation in interelectrode separation, *d*, of a factor 16.

# 4. Discussion

The results of Fig. 3 demonstrate that Eq. (2b) describes the behaviour in poly 4BCMU crystals and that the unity gain case pertains. This observation is further supported independently by the results of Fig. 2 where the photocharge is halved on creating the cuts. This indicates that s > d and with blocking electrodes [8] this implies a unity gain photoconductor.

It is then possible to find the quantum efficiency for photocarrier generation at the wavelength of 337 nm. This is linear in electric field due to the influence of the geminate recombination escape probability,  $\phi(E)$ , and results in a value of  $\eta\phi/E = 4.88 \times 10^{-10}$  mV<sup>-1</sup> ( $\lambda = 337$  nm). This value is in extremely good agreement with the value found previously [8] for the thermally polymerised PDA TS6 where  $\eta\phi/E = 7.1 \times 10^{-10}$  mV<sup>-1</sup> ( $\lambda = 337$  nm).

Such close agreement is itself noteworthy and a further clear demonstration and confirmation of the unity gain situation that pertains in both materials. This is the case as it would require a fortuitous similarity in the carrier range in both materials to achieve agreement if the variable gain scenario applied to either or both of them. That is to say,  $n\phi(E)$ , as determined using the unity gain case of Eq. (2b), is found to be an intrinsic property of the conjugated chain, independent of method of polymerisation, polymer chain sidegroup, size of crystal etc. Furthermore the value is also in close agreement with that found for PDA DCH [10] (where  $n\phi/E =$  $2.45 \times 10^{-10}$  mV<sup>-1</sup> at the same wavelength). This last polydiacetylene being gamma polymerised and with recombination centres such that Eq. (2a) has been used in the determination of  $n\phi/E$ .

The most important observation to make then. from these results. is that the carrier range in 100% poly 4BCMU is identical to the crystal length which was up to 8 mm in the present experiments. This is the case in spite of the fact that individual chains of length of 2.5  $\mu$ m with a low dispersion [5] make up the 100% crystals. The implication is therefore that for a crystal of 8 mm in length there are more than 3200 individual chains from end to end and the carrier is tunnelling across 3200 chain/chain interruptions. It is to be expected that chain ends produce end states similar to surface states in, for example silicon. Precisely how the chain is terminated and therefore whether these end states are traps or barriers to electron flow is unknown. In any event this chain end seems relatively transparent to carrier transport under the influence of an electric field. The measurement leading to the current conclusion, Q(t), takes place over some tens of seconds. This is in contrast to the transit time across 8 mm if the chains were continuous. Using a velocity of  $2 \times 10^3$  m/s for the carrier on a bare chain [8] gives a transit time of 4  $\mu$ s. To travel a distance of 2.5  $\mu$ m to a chain end however would take 1.25 ns. Clearly there is some slower rate determining step and we may speculate that this is jumping from one chain end to the next. This therefore leaves each chain end jump to be achieved within a time of order 3 ms typically or a tunnelling rate of order  $3 \times 10^2$  Hz. From photoemission experiments the ionisation potential of the polymer is determined to be [13,14],  $I_{\rm P} = 5.4$ 

+ 0.2 eV. With a band gap [11.12.15.16] of 2.4 eV this leaves an electron affinity of A = 3.0 + 0.2 eV. We may take this as the tunneling barrier for electrons tunneling from one chain to the next and an end – end separation of 0.2 nm = a. In order to have a tunneling rate of  $3 \times 10^2$  Hz =  $\nu_0 \exp(-2ka)$ , where  $k = \sqrt{2mA/\hbar}$ , an attempt rate of  $\nu_0 = 1.0 \times$  $10^4$  Hz is required if one takes for *m* the bare electron mass. This is entirely plausible and one may indeed expect the attempt rate for the end-end tunneling to be many orders of magnitude higher and typified by an optic phonon frequency. It is also possible to interpret this ability to cross the sample as a reflection of the close proximity of neighbouring chains in this PDA where in one crystallographic direction there is a chain separation of 0.488 nm. This would then by a similar argument require an attempt rate for perpendicular tunnelling of  $2.5 \times$ 10<sup>11</sup> Hz again an entirely plausible number. This implies in turn that the rate limiting step in determining the time evolution of the charge, Q(t), is not tunneling from one chain end to the next in 100% polymer crystals but tunnelling perpendicular to a parallel chain. With a lack of knowledge of the attempt rates involved this must however remain a speculation.

We have determined from these measurements the quantum efficiency for charge carrier production and shown it to be linear in electric field. Also, we have shown the poly 4BCMU single crystals to be unity gain photoconductors.

# 5. Conclusions

The measurements presented here demonstrate in three independent ways that chain ends in topochemically polymerised single crystal polydiacetylenes do not always act as recombination centres and that the carriers cross the sample:

(i) A line scored halfway across the sample interrupts the carrier path thereby halving the charge collected.

(ii) The charge collected is independent of electrode spacing, indicating a unity gain photoconductor. (iii) Assuming unity gain the same quantum efficiency is arrived at for two different polydiacetylenes where mode of polymerisation and sidegroup are completely different. This shows that the value is an intrinsic property of the conjugated polydiacetylene backbone alone in these particular samples.

It is seen, that with reasonable parameters taken from other experiments it is not implausible that end to end chain-chain tunneling is relatively fast and effective. The precise nature of the chain end will control just how fast the tunneling will be as this will control in detail the tunneling barrier height/trap depth and the end-end separation. A parallel study to be reported elsewhere will show photoconduction measurements in partially polymerised 4BCMU crystals with polymer chains isolated in the monomer matrix [7]. These will again show that photocarriers have an ability to travel further than the isolated chain length. It may be that other mechanisms will need to be invoked in the future to explain the carrier range in these materials with further investigations necessary. The present work is sufficient to demonstrate that the unity gain photoconductor is an adequate description of 4BCMU polydiacetylene single crystals and to thus leave the way open to providing a detailed knowledge of other microscopic parameters when combined with other appropriate experiments. This work is therefore of great value in the study of carrier transport in conjugated polymers.

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