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LETTER TO THE EDITOR

The field-independent early-time drift velocity of carriers in polydiacetylenes: solitary-wave acoustic polaron or dispersive trap-limited transport in 1D?

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Abstract. Current controversy concerning the nature of the motion of charge carriers in polydiacetylene single crystals is examined. New results using picosecond time-resolved photocurrents are able to distinguish whether the observed saturated drift velocity is due to the motion of a solitary-wave acoustic polaron or a carrier moving in a distribution of traps and barriers, and indicate the former case. The relevance of the Onsager geminate recombination theory in these materials is also demonstrated unequivocally.

The current debate on the nature of charge-carrier motion in polydiacetylene toluene sulphonate, PDATS, is resolved in this letter using the results of pulsed photoconduction experiments with a temporal resolution of 35 ps. The various sides of the debate are set out before we describe what are in principle simple measurements to resolve the issue.

The observation that one needs to explain is the fact that photocreated carriers are found to move with a drift velocity of around the velocity of sound independently of electric field for times less than 50 ns (Donovan and Wilson 1981a, Donovan *et al* 1986). This experimental observation holds true down to fields of 100 V m^{-1} and thus entails an ultra-high low-field mobility, $\mu_0 > 2 \times 10^5$ cm^2 V^{-1} s^{-1}.

There are two current explanations of this experimental fact which are as follows.

(i) What is observed is the motion of free carriers, before any initial trapping event, travelling as solitary-wave acoustic polarons, SWAPS (Wilson 1983).

It has been demonstrated that in 1D an excess electron in the conduction band will give rise to an acoustic deformation of the polymer backbone irrespective of the strength of the electron–acoustic-phonon deformation potential (Whitfield and Shaw 1976). This deformation will move with the carrier thus limiting its velocity to the speed of sound. The SWAP, because of this limitation on its velocity, will not be scattered by usual single-phonon processes and so requires second-order processes in order to produce scattering and these processes are weak (Wilson 1983, Gogolin 1988). Hence, the SWAP will be expected to have a high low-field mobility. In this model the observed value of the saturated drift velocity and the ultra-high mobility are natural consequences of the 1D nature of the system (Wilson 1985).

(ii) An alternative view is that the carriers trap in a time much shorter than that resolved by any experiment and the observed motion is always that of a trap-limited

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carrier crossing a distribution of trap depths and barrier heights (Blum and Bassler 1988). Such dispersive trap-limited transport has been theoretically described by Movaghar *et al* (1984b) for 1D systems where departures from the usual Scher and Montroll theory (1975) are observed. The theory predicts that as the carriers travel through this system of obstacles sampling the trap distribution, the average drift velocity, $\langle v_d \rangle$, will evolve with time and follow a power law of the form

$$\langle v_d \rangle \simeq t^{-\alpha} \tag{1}$$

where α is some parameter less than 1 involving the trap distribution. Furthermore the theory predicts that the field dependence of $\langle v_d \rangle$ varies with electric field as

$$\langle v_d \rangle \simeq E^{1-\alpha}. \tag{2}$$

At times greater than 10 μs, the current is seen to follow a power law decay over six orders of magnitude in time (Movaghar *et al* 1984a), as expected from equation (1), where $\alpha = 0.85$. Clearly then one expects $\langle v_d \rangle$ to vary as $E^{0.15}$, a dependence that may be said to be practically independent of field. This then is used to explain the observation of the saturated drift velocity while not addressing the actual value of the saturated velocity (an accident), nor the ultra-high drift mobility which may be considered unusual for a trap-limited motion. Furthermore, and crucial to what follows, it is a requirement that this theory, and all it entails for the time dependence of the drift velocity, holds true at the shortest times where such a trap-limited velocity occurs.

Both models above have in common the view that photocarrier generation is field dependent, being linear in field at low fields and becoming superlinear at higher fields. This dependence, the supporters of views (i) and (ii) maintain, is due to the Onsager mechanism of geminate recombination, and in fact describes the probability of a photocreated electron–hole pair separating in an applied field and thus giving rise to a photocurrent (Donovan and Wilson 1981b, Seiferfeld *et al* 1983). The process is well described theoretically and expected to occur in the uniquely one-dimensional PDAS, and in its three-dimensional version in a wide range of molecular crystals exemplified by anthracene.

(iii) A third view currently being propounded claims that the carrier generation rate is not field dependent and that the voltage dependence of the photocurrents observed is due to a drift velocity linear in field. This iconoclastic viewpoint derives from the claimed observation by Moses *et al* (1987) of a carrier transit (sweep-out) demonstrating a field-dependent velocity. If this were the case then there would be no need to invoke the Onsager mechanism and moreover it would not be supported by the facts.

To test these hypotheses, experiments measuring the time-resolved photocurrent after a 20 ps laser pulse and the total charge transferred to the electrodes as a result of the photocharge created by one of these laser pulses were carried out.

Typical results of these two measurements are shown in figures 1(*a*) and 1(*b*). Figure 2 shows the electric field dependence of the peak photocurrent, I_p, and total charge transferred per pulse, Q_m, as a function of electric field. To obtain the required time resolution for the result of figure 1(*a*), the Auston switch electrode geometry was used (Auston *et al* 1980). To achieve this geometry, the sample was mounted on an alumina substrate the underside of which had an evaporated gold electrode acting as a ground plane. Onto the surface of the crystal was evaporated a strip of gold with a 140 μm gap in it, the width of this strip chosen such that the line and ground plane presented a 50 Ω

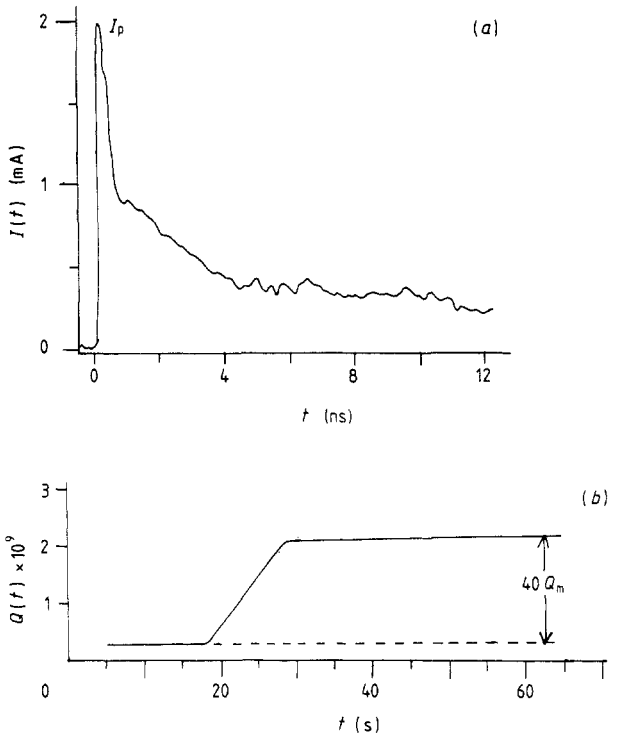

Figure 1. (*a*) The photocurrent induced by a 20 ps light pulse from a frequency-tripled, passively mode-locked Nd YAG laser, $h\nu = 3.5$ eV. The signal was collected on a boxcar system as a series of points each with a gate-width of 25 ps. The sample was furnished with 50 Ω strip-line electrodes with a gap of 140 μm which constituted the sample in the Auston switch arrangement with 100 V across the gap. (*b*) Total charge transferred to the electrodes, Q_m, as a result of 40 of those light pulses on the same sample with the same field.

transmission line which was completed when the sample in the gap was rendered conducting by the light pulse. The signal shown is the result of a collection of points on a boxcar system with a gatewidth of 25 ps. Figure 1(*b*) is the result of 40 consecutive laser pulses.

The photocurrent I_p is given by

$$I_p = e\eta\varphi N v_d / d. \tag{3}$$

The charge transferred per pulse, Q_m, is given by

$$Q_m = e\eta\varphi N s / d. \tag{4}$$

Here: e is the electron charge; η is the quantum efficiency for carrier pair creation; φ is the probability that these pairs escape geminate recombination; N is the total number of photons absorbed; s is the distance a carrier travels before recombination; d is the electrode separation.

Independent experiments on PDATS have shown that $s = d$ (Donovan and Wilson 1981a, Donovan *et al* 1986). Thus the ratio $I_p/Q_m = v_d/d$. These are the same steps as followed in previous studies leading to the deduction of a saturated drift velocity and a probability of escaping geminate recombination that is linear in electric field, E.

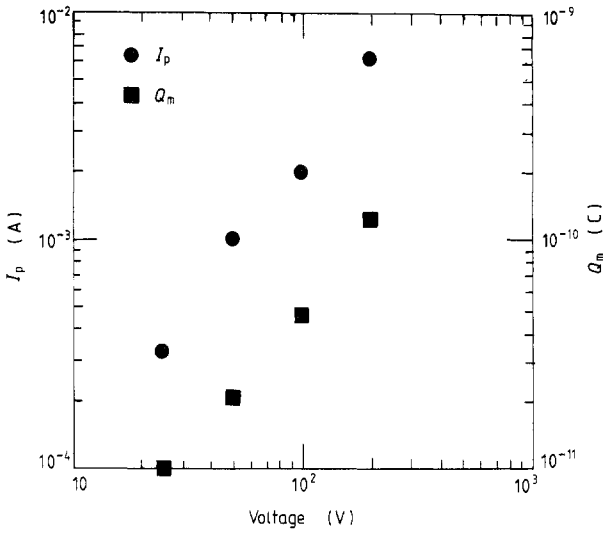

Figure 2. The voltage dependence of I_p and Q_m, typical examples of which are shown in figure 1.

From figure 2 we see that the ratio I_p/Q_m is independent of field even for times of the order of 100 ps. Further, and most important, the calculated velocity is $v_d = 6 \times 10^3\ m\ s^{-1}$. Since I_p is resolution limited, this velocity is an underestimate of the short-time velocity of these carriers. However, it is reasonable to take the current at the start of the slow decay at 300 ps and use this to find the drift velocity of these carriers. The drift velocity found at 300 ps is $3.0 \times 10^3\ m\ s^{-1}$ and is thus, again, an acoustic velocity. The fast peak seen in figure 1(*a*) is explained elsewhere (Donovan and Wilson 1986, 1989) as being due to hot electrons, and a full analysis of this is also to appear elsewhere. The remaining current at 300 ps after this fast peak gives a velocity identical with that deduced using a slower resolution of 10 ns in earlier experiments.

We begin the discussion of the three models in the light of these results by observing that the data of figure 2 show Q_m to be slightly superlinear in field. This is as expected for a 1D system at the high fields used where geminate recombination dominates the generation of photocarriers. For Q_m can but measure that generation and this is the most straightforward and simple method of so doing. Furthermore the field dependence of I_p is identical to the field dependence of the generation rate and thereby shows that the drift velocity is field independent. The shape of the current transient is independent of field and the velocity at 300 ps also remains field independent at the SWAP velocity. Model (iii) stands clearly then in contradiction to the facts, and the view of the work of Moses *et al* (1987) remains contrary to these and similar results from this and other groups (Donovan and Wilson 1981b, Seiferfeld *et al* 1983). The 'pseudo-transit' observed by that group is a phenomenon whose origin cannot be explained in terms of sweep-out of carriers across a gap of defined length, as the Auston switch electrode geometry in highly anisotropic media such as PDATS does not allow such a definition (Donovan and Wilson 1989). An alternative understanding of the transients they observe should be sought.

An explanation of the result of Moses *et al* (1987) is provided if bimolecular recombination is occurring under their experimental conditions. In that circumstance, the rate

of decay of the photocurrent after the light pulse is given by βn, where β is the bimolecular recombination coefficient and n the carrier density. With increasing electric field, n will increase due to the Onsager mechanism. At high enough fields such that the carriers recombine in a time $(\beta\eta)^{-1}$ less than the 2 ns gate-width of their boxcar system, a triangular transient, which they claim as sweep-out due to carrier drift across the gap, would be observed. There is no reason to suppose that this is not happening and as an explanation of their results it would fit in with all other known data, something their preferred explanation does not do.

The present authors have tried to reproduce the result of Moses *et al* (1987) with superior resolution but have failed, seeing instead a featureless decay independent of electrode separation. An analysis of the fields produced by surface electrodes would predict such a decay (Donovan and Wilson 1989). The fact that the fast peak seen in figure 1(*a*) is independent of temperature (Moses *et al* 1987) has also been used in support of the idea that geminate recombination plays no role. The current authors had previously made this experimental observation and noted that the Onsager theory could be adjusted to account for this in a simple fashion (Donovan and Wilson 1986). We now turn our attention to model (ii) and how these results impinge upon it.

The proponents of an explanation involving dispersive transport (Movaghar 1987, 1988) require the velocity to vary as $t^{-0.85}$. Hence, on going from 10 ns to 300 ps the velocity should increase by a factor of 20, which is clearly not what is observed. On the other hand, one would expect the SWAP velocity to be independent of time subsequent to its formation and prior to trapping as is observed. The experiment then clearly indicates that the SWAP explanation is correct and that dispersive transport has not begun to occur until after 10 ns, and indeed the authors would hold that it is not seen until the microsecond time regime and beyond (Donovan and Wilson 1985, Movaghar *et al* 1984a).

Full details of the initial fast-current transient are not germane to this letter and the conclusions made here. They will be the subject of a future paper. The beauty of this experiment is its simplicity—in that the current, which is the product of a charge and a velocity, can be deconvolved after a second and independent measurement of that charge. To do this relies on the fact that there is no recombination of charge, and novel and elegant experiments described elsewhere (Donovan and Wilson 1981a, Donovan *et al* 1985) demonstrate that this proviso holds. Such a deconvolution of charge and velocity is not possible for systems such as polyacetylene where the effects of recombination cannot be known.

In summary, three alternative views of photocarrier creation and motion have been mooted and here it is established that model (i) correctly describes the situation. That is that carriers move at around the velocity of sound with an ultra-high mobility as SWAPS and the efficiency of their photogeneration is field dependent.

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