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The photocurrent in a one-dimensional single-crystal polymer

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Abstract. We show that the photocurrents seen in a single crystal polymer can be interpreted as being due to two different species. Electrons are initially excited by a field assisted mechanism, though not by the Onsager process. Since the drift velocity is comparable to the thermal velocity, the trapping is faster at higher fields. Polarons responsible for a transit signal are not significantly trapped, but are scattered and exhibit a $(1/T)$ dependence of the mobility at low temperatures, with the mobility saturating at room temperature and elevated field. This account differs from that of the original authors. The pathway leading to polaron formation remains unresolved.

1. Introduction

Molecularly doped polymers are used as transport layers in xerographic applications (Borsenberger 1992, Kanemitsu 1992). The chief technical interest lies in the transport of carriers across the full thickness of a polymer sheet. Under favourable conditions, this transport gives rise to a quite definite transit signal, which can be used to characterize the carrier mobility. However, a typical current response to a short light pulse consists of a sharp rise (a few nanoseconds risetime) followed by a quasi exponential decay (decay time about 50 ns), with the transit signal appearing as a shoulder on top of this decay, as shown in figure 1. Signals of this general form have also been observed in commercial polymer samples not specifically doped, though usually on a longer time scale (Kryszewski *et al* 1968, Mizutani and Ieda 1979).

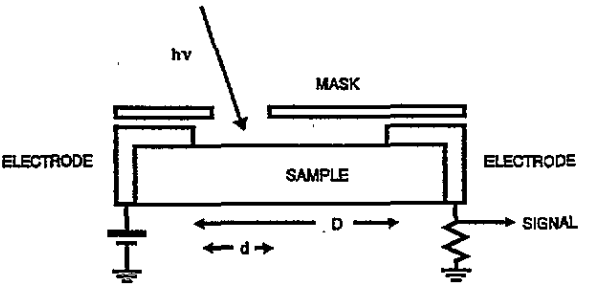

Figure 1. A schematic photocurrent response, showing the main peak followed by a carrier transit signal.

In order to operate transit time devices satisfactorily, it is clear that the main current peak should be reduced in size if this is possible. We require first of all an understanding

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of its origins, but this aspect seems to have been somewhat neglected. A comparable and reasonably complete set of data has recently been published for an undoped material (Fisher and Willock 1992a, Fisher 1992, 1994). The polymer (acronym PDATS) is well characterized and forms good single crystals. The authors gave an analysis of both the current peak and the transit signal. The purpose of the present communication is to suggest that certain parts of their analysis are unsatisfactory, and to propose alternative explanations.

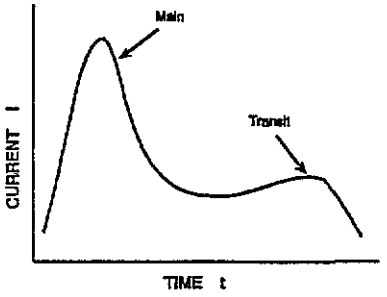

Figure 2. A schematic diagram of the experimental set up (Fisher and Willock 1992a). The sample has electrodes at its ends, which are extended over the top face. The separation between the edges is D. A light pulse illuminates a slit of width d.

2. Preliminary remarks

The experimental arrangement used by Fisher and Willock (1992a) is shown schematically in figure 2. The sample is a thin polymer single crystal equipped with end electrodes connected to non-contacting top electrodes. The separation between the edges of the top electrodes is D, about 300 μm. Illumination is provided through a slit of width 60 μm adjacent to the edge of one electrode, which has a voltage V applied. The other electrode is earthed. Carriers are generated using a short pulse of strongly absorbed laser light. Variants of this basic system have included overall illumination and the ingenious use of an intermediate sensing electrode (Fisher 1992).

To begin with, we would like to dispose of three peripheral points. Firstly, the main feature resembles the pyroelectric signal seen in many insulating polymers (Andress *et al* 1977, Wintle and Turło 1980). However, we can rule out this possibility since there is no evidence of any return signal when the light is cut off, and because the response is non-linear, showing a narrowing for higher electric field or for lower light intensity (a fuller discussion of this behaviour is given below). It follows that this feature is indeed due to charge motion as was assumed, and not simply to thermally driven dipolar reorientation or to differential thermal expansion of an existing distribution of trapped charge. The second point is to ask what happens when a carrier leaves the main part of the sample and arrives underneath one of the top electrodes. In this region, the voltage will hardly differ from the electrode voltage. The Ramo–Shockley theorem (see De Visschere 1990, Kim *et al* 1991) can be applied to this location, just as it has been implicitly used for the rest of the sample. Since the local field is small, the current induced in the measuring electrode can be ignored, even if geometric constraints force the carrier to drift to the end of the sample before it is discharged. (An alternative way of seeing this is to realise that a carrier

close to the electrode will have induced a surface charge of almost equal magnitude on the electrode.) The statement '... the slower carriers are also traversing the electrode gap and then discharging, rather than travelling under the electrodes' (Fisher and Willock 1992a, p 2530) cannot therefore be substantiated.

The final question is the role of space charge. The transit peak can under suitable conditions resemble the space charge limited current (SCLC) peak observed in planar geometry (Helfrich and Mark 1962, Many and Rakavy 1962, Morrison and Edelson 1962). At high illumination, the amount of charge in motion may be sufficient to perturb the electric field. The criterion $Q < CV$, where Q is the charge and C the capacitance, is used to determine the regime in which space charge has little effect. We caution that this perhaps cannot be applied to the essentially surface electrode arrangement shown in figure 2, because the capacitance is not well known, and also because the SCLC responses for this geometry differ considerably from the planar case, both in the steady state (Geurst 1966) and under transient conditions (Chapman and Wintle 1982, Pépin 1992). The experimental procedure adopted was to keep the light intensity low enough to avoid changes in the signal shape at a given voltage, and this seems to be a satisfactory empirical test for the lack of space charge effects.

3. The main peak

The main peak is essentially symmetric with respect to the applied voltage, and exhibits the same time dependence no matter whether the illumination is at either end of the sample or restricted to a centrally located slit (Fisher and Willock 1992a, figures 4 and 6). Exactly the same form of response was found when the illumination was uniform over the whole sample (Fisher 1992, figures 6–12). These authors assert that the signal may be 'dominated by the drift and discharge of the electrons at their nearest electrode' (i.e. the anode) when V is positive. However, the observations are not consistent with their suggestion, because of the symmetry. The obvious interpretation is that the featureless decay reflects carrier trapping with a fixed time constant τ. There is a 6:1 ratio in the response between excitation at the end and central excitation. This ratio is larger than the effective ratio of 2.2:1 between the mean fields at these two positions (Fisher 1994). Since the mean displacement per carrier ($\mu E\tau$) would have the same 2.2:1 ratio, the enhanced signal is consistent with the field dependent carrier yield discussed in the next paragraph. Here, μ is the carrier mobility and E the electric field.

The experimental work by itself does not give the sign of the carriers involved, though it is likely that they are electrons, mainly because the positive charge seems to move on a much slower timescale (Fisher 1994). At constant integrated light flux and fixed geometry, the size of the peak increased sharply with field (Fisher 1992, figure 12). Though the data are a little sparse, it is easy to show that they do not obey the Onsager relation for geminate recombination because the curve of peak current I versus field E is linear as expected, but the intercept is negative. If we take the previous suggestion that the carrier displacement is proportional to E, then the carrier yield should be proportional to $1/E$. Using (I/E) as a measure of this yield, the Onsager plot now gives a positive intercept, but a slope that is an order of magnitude too high. On the other hand, a Poole–Frenkel plot of $\ln(I)$ versus $E^{1/2}$ gives a line of slope 2.6×10^{-3} (m $V^{-1})^{-1/2}$, though with some scatter. We have allowed for the fact that the effective field is higher than the average field. This slope is about twice the slope of 1.2×10^{-3} (m $V^{-1})^{-1/2}$ expected for the one-dimensional Poole–Frenkel model for a material having a dielectric constant of six, and almost an order of

magnitude too high compared with a typical three-dimensional model (Hartke 1968). The correponding plot using (I/E) gives a slope of 1.4×10^{-3} (m $V^{-1})^{-1/2}$, with a factor of two in uncertainty. This is correct for the one-dimensional model, though still too high for the three-dimensional model. One should view this rough agreement with some scepticism, since the apparent yield taken over most of the sample (a span of 230 μm) is only about twice that drawn from the end alone (a span of 30 μm). However, this last observation by itself confirms the strongly field dependent nature of the carrier production.

The failure of the yield of the main peak to obey the Onsager relation is somewhat surprising, since the fields are in the range where other organic materials give good correlations (Chance and Braun 1973, Borsenberger *et al* 1978). A possible explanation is that, in the system under consideration, the carriers are shed from an excited state of the absorbing centre, with negligible incipient ionization and thus with no meaningful thermalization length r_0. This would be consistent with the relatively low quantum energy employed. The somewhat better agreement between the yield and the one-dimensional Poole–Frenkel model, as opposed to the three-dimensional scheme, is perhaps an indication that the free carriers move preferentially along the polymer chains.

The temperature dependence of the main peak height has been studied (Fisher and Willock 1992b, figure 5). Again, the data are rather sparse and scattered, but by making the assumption of an Arrhenius activation behaviour, we obtain energies of 13 meV (weighted average), or 19 meV (300–150 K) and 5 meV (150–100 K). Given that the field lowering is 38 meV, we obtain excitation energies of 51, 57 and 43 meV respectively. Clearly, there may be some question as to the validity of a Poole–Frenkel model for a shallow state with strong field depression. It is possible that the weakening of the temperature dependence at low temperature is due to a tunelling process masked at the higher temperatures.

We are now in a position to discuss the narrowing of the signal at high field (Fisher and Willock 1992a, figure 13). These authors suggested that sweep-out of the charge was responsible for the narrowing, presumably because of the faster drift speed. This cannot be the case for two reasons, as follows. Some asymmetry ought to should be seen between the signals for positive and negative applied voltage at the same field in longer samples, but this does not occur. In addition, the yields are inconsistent. The charge passed in the external circuit is proportional to $(d/2D)L\eta$, where d is the width of the illuminated slit (15 μm), D the sample length (also 15 μm, given the isolating effect of the intermediate wire electrode), L the integrated light flux and η the quantum efficiency for carrier production. The last is of course field dependent. The measured charges are in the ratio 2:1 (broad:narrow). The light fluxes are in the ratio (22:1) and the efficiencies are about 1:4, so the expected ratio would be 6:1 if all the released charge were collected. The broad peak could be reduced to the observed value if the average displacement of the charge were about one-third of $d/2$, i.e. about 2.5 μm, but this would imply a sharp increase in the mean displacement for fields in the vicinity of 1 MV m^{-1}. The evidence (Fisher and Willock 1992b, figure 5) suggests that there is no such rapid change.

An alternative explanation for the narrowing is that it is due to a smooth transition from a low-field region in which the drift velocity is less than the thermal velocity to a high-field region where the reverse is the case. The time constant for trapping will be of order $(1/\sigma v_{th} n_t)$ in the first case, and $(1/\sigma \mu E n_t)$ in the second. Here, v_{th} is the thermal velocity, σ the capture cross-section and n_t the trap density. The transition will occur when $v_{th} = \mu E$. Since most insulating polymers have wide conduction and valence bands, the effective mass of an electron in the conduction band differs little from the free electron mass, and v_{th} is of the order of 10^5 m s^{-1}. The transition thus implies a mobility of 0.1 m^2 V^{-1} s^{-1}, which is a reasonable value for a conduction band electron.

The original suggestion by Fisher and Willock of a fast sweep-out is also somewhat inconsistent with their proposition that the real carriers responsible for transit time signals are separate entities, which they identify as solitary wave acoustic polarons (SWAPs).

4. The polaronic carriers

In their papers, Fisher and Willock quite rightly concentrated on explaining the nature of the long-range transport process, because this is the more interesting and potentially the more useful feature of the photoexcitation in their material. We can expand on some of their discussion. It is not immediately clear whether the polarons are produced during the excitation process by a separate mechanism, or whether there are two competitive decay channels for the free electrons, one leading to trapping and the other to polaron formation. Separate excitation mechanisms would presumably have different yields as a function of field, while in the other case the polaron concentration would be proportional to the main peak height. Since the curves obtained using a variety of different fields tend to have similar shapes, we have some rather weak evidence favouring competitive capture. However, from amongst the many figures of current response as a function of field, light intensity and temperature that are given in their papers, we are unable to find convincing evidence for either route.

One property of the polaronic carriers that needs clarification is their thermalization (Fisher and Willock 1992b, p 6625). If the polarons are produced by a separate ionization process, then the discussion given by these authors is unexceptionable. However, if they are populated from the general pool of photoexcited carriers, then the the discussion is incorrect because these carriers are produced by a Poole–Frenkel process and are already thermalized.

The other property that requires scrutiny is the question of trapping. Fisher and Willock (1992a, pp 2527, 2530) seem to imply that the decay of the main peak and the dispersion of the transit signals are both due to the same traps, but we believe that their discussion is a little confused on this point. The polaron propagation appears to be governed by an activated process with an activation energy of 58 meV (Fisher and Willock 1992b, figure 11). We wish to point out that if the activated process observed is attributed to trapping, then this implies that there will be on average at least a small number of capture events per carrier transit, in order to establish the dynamic equilibrium between trapped and free polarons, and also that the residence time in the traps is long enough to significantly affect the trapping process, as apparently detected. This in turn implies that there should be a wide distribution of transit times and it follows that there should be no readily identifiable transit signal (Schmidlin 1977, Noolandi 1977), contrary to observation. The same type of criticism can be levelled at variable-range hopping (Pollak 1972) and comparable mechanisms. The original analysis omitted any consideration of the dispersion of arrival times. We conclude that the temperature dependence of the polaronic transport process is unlikely to be due to trapping, and that some scattering controlled mobility must be involved.

Strictly speaking, the data on mean drift velocity v_d (Fisher and Willock 1992b, figures 3 and 9) involve an average over the spatially inhomogeneous field. However, the main part of the drift takes place in a region of slowly varying field, so we can assume that the data refer to the mean field, at least as a first approximation. The velocity is linear at low fields, but at high fields it saturates at an estimated speed of 3600 $m\,s^{-1}$. The temperature and field dependence is represented by 17 data points. Of these, 15 points fit a relation of the form $\mu = cT$, where the constant c has the value 2.5×10^{-6} $m^2\,V^{-1}\,s^{-1}\,K^{-1}$, to within

about 10%. The two exceptions refer to the highest temperatures at the largest field, where saturation begins to take effect. The mobility values are thus of order 5×10^{-4} m^2 V^{-1} s^{-1} over the range 100–300 K, and the temperature dependence suggests some form of impurity scattering (Blatt 1968). This suggestion avoids the problems associated with the trapping model, and seems quite appropriate for polaron motion. In the absence of other evidence as to the nature of the charge–lattice or charge–impurity interaction, we cannot make any further progress in interpreting the high-field, high-temperature saturation of the carrier speed.

5. Summary

We have argued that the signals obtained by photoexcitation of PDATS can be most readily explained by rather different mechanisms from those originally suggested. The main peak seems to be due to field-assisted ionization of an optically excited state, but not the Onsager geminate recombination mechanism. The current flow is due to electrons, and the decay is due to trapping. The high-field narrowing occurs when the drift velocity due to the field exceeds the thermal velocity in the bottom of the conduction band, and a sensible value for the band mobility is deduced. The long-range polaronic transport is due to drift *without trapping but with scattering, possibly due to impurities. The mechanism for the* formation of the polarons remains open, and we have made no attempt to account for the saturation of the polaron drift velocity. It is plain that even with this almost ideal single-crystal system, it is quite difficult to obtain experimental results that are precise enough to make the interpretation unequivocal. This ambiguity in interpreting the measurements at relatively high fields is well known (see e.g. Abkowitz *et al* 1992), while alternative views of the transport processes in this general type of material have recently been discussed by a number of authors (Abkowitz *et al* 1992, Schein 1992, Hirao *et al* 1993).

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