On the mobility of charge carriers in polydiacetylene crystals

1991 J. Phys.: Condens. Matter 3 3841

(http://iopscience.iop.org/0953-8984/3/21/016)

J. Phys.: Condens. Matter 3 (1991) 3841–3847. Printed in the UK

COMMENT

On the mobility of charge carriers in polydiacetylene crystals

E L Frankevich
The Institute of Energy Problems of Chemical Physics, Academy of Sciences, Moscow 334, USSR

Received 15 January 1991

Abstract. Discussion of the possible origin of the extremely high mobility of charge carriers in polydiacetylene crystals claimed by Donovan and Wilson is continued. The following new statements are taken into consideration:

(i) the nature of a laser-pulse-induced prompt photocurrent,
(ii) the effect of the random recombination on the yield of free carriers in a 1D system and
(iii) the occurrence of the magnetic field effect on the photoconductivity.

Conclusions are consistent with a normal mobility of about 3 $cm^2 V^{-1} s^{-1}$.

Recently a paper by Donovan and Wilson (1990) has appeared in which an analysis of experiments devoted to the behaviour of photogenerated charges in polydiacetylene toluene sulphonate single crystals (PDATS) was carried out. These workers in their previous papers (see, e.g., Donovan and Wilson 1981, Donovan *et al* 1986) have come to the conclusion that an extremely high mobility of carriers (greater than 2×10^5 $cm^2 V^{-1} s^{-1}$) whose velocity v_d saturates at the velocity of sound at fields as low as 1 V cm^{-1} exists.

Here we continue the discussion of the features of the photoconductivity of PDATS taking into account facts which have not been considered by Donovan and Wilson. These, we believe, permit us to account for the results published without using the hypothesis of an extremely high mobility of carriers in PDATS.

(i) The main arguments of Donovan and Wilson are based on the comparison of the amplitude I_p of the pulse photocurrent excited by a 20 ps laser pulse and a charge Q_m collected subsequently at the electrodes:

$$I_p = e\eta\varphi N v_d/d \tag{1}$$

$$Q_m = e\eta\varphi N s/d. \tag{2}$$

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 that a carrier travels along the field direction before recombination and d is the electrode separation.

0953-8984/91/213841 + 07 $03.50

As $I_p/Q_m = v_d/s$ and Donovan and Wilson believe that $s = d$, equations (1) and (2) seem to permit an estimation of the absolute value of carrier velocity using the experimental values of I_p and Q_m. The result is $v_d = 3 \times 10^5$ cm s^{-1}.

We believe, however, that it is necessary to consider the possibility of another origin of the pulse photocurrent; in the creation of the photocurrent through the sample, not only free charge carriers but all the charges which have been produced by photo-excitation take part. In such a case, equation (1) may well appear to be invalid. In fact it is known that the total yield of charges in molecular solids is much higher than a free-charge-carrier yield. Most of the charges recombine geminately but, during their lifetime before geminate recombination, charges are shifted by an external electrical field and pairs become polarized. The polarization process reveals itself in the current through the sample. The current caused by polarization flows in the same direction as that due to free carriers. However, at the end of the pair lifetime the current changes its direction (flows backwards), subtracting its contribution from the charge transferred through the sample. As detailed calculation shows, the backward current is distributed in time and often cannot be seen against the background of free-carrier current (Yakovlev and Lukin 1985).

In essence the current caused by geminate pairs is a polarization current. Its existence was noted experimentally in the paper by Frankevich and Balabanov (1965) when they studied pulse electron ionization of paraffin layers. Here they advanced the very principle of geminate electrical conductivity. Radiation-induced non-steady-state conductivity of dielectric materials is almost completely caused by charges which belong to geminate pairs, their lifetime often being very long (seconds or longer) owing to the trapping of charges by defects (Frankevich and Yakovlev 1974). A calculation of the kinetics of the polarization current is available (Yakovlev and Lukin 1985, Novikov and Yakovlev 1985). It was shown that the current $i(0)$ at $t = 0$ (at the moment of the excitation pulse) can be expresed exactly by the formula

$$i(0) = eN(0)\mu E \tag{3}$$

where $N(0)$ is the total number of pairs generated. If the probability of the dissociation of pairs is assumed to be zero, then in the limit of low fields the integral of the current is shown to be zero. The kinetics of the current are very sensitive to the initial distribution of charge separations in pairs as well as to the electrical field strength.

The role played by another alternative type of precursor of free charges should also be mentioned. In molecular solids this may well be the so-called excitons with charge transfer (of the Wannier–Mott type). The polarization current connected with a deformation of the electronic distribution in excitons may be expected. In such a case a positive pulse of the polarization current appears almost instantaneously (10^{-15} s) at the moment of the excitation whereas the backward current subtracts the charge transferred during the lifetime of the exciton. Thus the amplitudes of the positive and backward currents may differ by many orders of magnitude and the backward current may well be lower than the background or noise. In our previous paper (Frankevich *et al* 1990) we have presented experimental results which show that the exchange interaction between electrons and holes takes place at a distance of up to 35 Å, permitting us to suggest the existence of delocalized excited precursors in PDATS.

Thus to describe the amplitude of the photocurrent excited by a short laser pulse the following formulae may be used:

$$I_p = e\eta N v_d \tau_D / d\tau \qquad v_d = \mu E \tag{4}$$

for polarization of pairs or

$$I_p = \eta_{ex} N \alpha E / \tau \tag{5}$$

for polarization of excitons. Here μ is the mobility of charges in pairs, τ_D is the lifetime of the pairs before geminate recombination, α is the polarizability of excitons ($\alpha \approx 4\varepsilon r^3$, where ε is the dielectric constant and r is the exciton radius) and τ is the recording response time. Equations (4) and (5) are valid for $\tau \gg \tau_D$ and $\tau \gg 10^{-15}$ s, respectively. Taking into account equations (4) and (2) instead of equations (1) and (2), one can obtain an I_p/Q_m ratio which does not lead to a high value of v_d:

$$I_p/Q_m = (v_d/s\varphi)(\tau_D/\tau).$$

At $\varphi = 10^{-2}$–10^{-3}, $\tau_D/\tau \leqslant 1$, one obtains a value of v_d two or three orders of magnitude lower than before when equations (1) and (2) are used, even for $s = d$.

A similar conclusion may be arrived at for the case of excitonic nature of precursors when using equations (5) and (2).

(ii) Donovan and Wilson believe that the linear increase in the photocurrent with increasing electrical field strength is due to the $\varphi(E)$-dependence starting from zero field. In fact, according to Haberkorn and Michel-Beyerle (1983) in 1D systems

$$\varphi(E) = (E/E_a) \exp(-r_c/a). \tag{6}$$

Here r_c is the Onsager radius, a is an initial separation of charges in the pair and $E_a = e/\varepsilon a^2$.

The zero yield of free charges in the absence of an external field is a consequence of the 100% return probability of the electron to the point of its origin. However, as pointed out by Frankevich *et al* (1989a, b) the existence of recombination centres in linear chains may prevent the return and in such a case the yield becomes non-zero even at zero field. Taking into consideration the bimolecular recombination of charges from different pairs leads to the same result; in the absence of traps but at a sufficiently high excitation intensity, equation (6) ceases to hold and has to be changed to the formula

$$\varphi(E) = 4[(eEL/4kT)^2 + 1]^{1/2} \exp(-r_c/a). \tag{7}$$

Here L is the diffusion length of carriers before recombination by any means. Thus, at $E \ll kT/eL$, $\varphi \simeq$ constant and the linear increases in I_p and Q_m with increasing field E are not determined by φ but by an increase in the carrier velocity $v_d = \mu E$ and the distance s. Equation (7) is similar to the formula obtained previously by Wilson (1980):

$$\varphi_{1D}(E) = (a/w + eE/kT)(a/r_c) \exp(-r_c/a). \tag{8}$$

Here w is the distance between traps in a 1D chain.

It is worth noting that even in the absence of traps the fact that cross-chain hops of carriers are allowed leads to the same results as trapping and recombination of carriers: the yield of free carriers becomes non-zero at zero field. Effectively an admixture of 3D motion of carriers works.

(iii) An independent estimate of the mobility of charge carriers during the period of their stay in geminate pairs may be made on the basis of the investigation of the magnetic field effect (MFE) on the photocurrent.

Such an effect has been revealed in PDATS (Frankevich *et al* 1989b, c). The effect itself as is well known is connected with the dependence of the geminate recombination rate on the total spin of the electron–hole pair; the recombination rates in singlet and triplet states differ. The external magnetic field influences the degree of mixing of spin

states and thus changes the recombination rate and as a consequence the quantum yield of free carriers and the photoconductivity.

In order to make the MFE possible, certain conditions must be met. In particular the lifetime of the geminate pair must be high enough to permit magnetic-field-induced evolution of the spin state to occur. The lifetime τ_D of the pair depends on the mobility; τ_D is the diffusion time of the carrier before it becomes trapped by recombination centres or hops across the chain:

$$\tau_D \simeq L^2/4D. \tag{9}$$

Here L is the diffusion length of the carrier and D is the diffusion constant of the carrier. The value of L was measured in experiments where the influence of the electrical field on the magnitude of the MFE has been studied (Frankevich *et al* 1989b, c); the MFE disappeared at field strengths $E \geqslant 3 \times 10^3$ V cm^{-1} which has been considered to result from the prevention of geminate recombination by the electrical field. Hence

$$EL \simeq kT/e \tag{10}$$

and at room temperature one can get $L \simeq 1600$ Å. Moreover this feature appears in the photocurrent–voltage plot just at the field of 3×10^3 V cm^{-1}; at higher field strengths the plot becomes superlinear.

The time τ_{ev} of the spin evolution is determined by the value of the interaction which causes mixing of the spin states of the pair. In the case of organic solids this is the hyperfine interaction with $H_{HFI} \simeq 30$ G and

$$\tau_{ev} \simeq \hbar/g\beta H_{HFI}. \tag{11}$$

The conditions for the very existence of the MFE are

$$\tau_{ev} \leqslant \tau_D < T_1. \tag{12}$$

Then it follows from equations (9), (11) and (12)

$$D \leqslant L^2 g\beta H_{HFI}/4\hbar = 6 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$$

or

$$\mu = De/kT \leqslant 3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}.$$

Thus the very existence of the MFE gives us a high estimate of the mobility of the charge carriers inside the electron–hole pair within the time interval which is shorter than the spin–lattice relaxation time T_1 ($\simeq 10^{-7}$ s). The mobility is not so high but is of the order of units of square centimetres per volt per second. About the same value resulted from time-of-flight experiments (Moses *et al* 1989).

References

Donovan K J, Freeman P D and Wilson E G 1986 *Electronic Properties of Polymers and Related Compounds (Springer Series in Solid State Sciences 63)* (Berlin: Springer) pp 256–62

Donovan K J and Wilson E G 1981 *Phil. Mag.* B **44** 9

—— 1990 *J. Phys.: Condens. Matter* **2** 1659

Frankevich E L and Balabanov E I 1965 *Fiz. Tverd. Tela* **7** 1667

Frankevich E L, Lymarev A A and Sokolik I A 1990 *Int. Conf. on Science and Technology of Synthetic Metals, Abstracts (Tubingen, 1990)* vol 2 (Tübingen: Gesellschaft Deutscher Cheminer) p 158

Frankevich E L, Sokolik I A and Lymarev A A 1989a *Chem. Phys. Lett.* **59** 113
—— 1989b *Mol. Cryst. Liq. Cryst.* **175** 41
Frankevich E L, Sokolik I A, Lymarev A A, Rakhovskaya T V, Lasareva O L, Vinogradov G A and Schegolikhin A N 1989c *Khim. Fiz.* **8** 1670
Frankevich E L and Yakovlev B S 1974 *Int. J. Radiat. Phys. Chem.* **6** 281
Haberkorn R and Michel-Beyerle M (ed) 1983 *J. Phys. C: Solid State Phys.* **16** 5189
Moses D, Sinclair M, Phillips S and Heeger A J 1989 *Synth. Met.* **28** D675
Novikov G F and Yakovlev B S 1985 *Khim. Visokhih Energii* **19** 282
Wilson E G 1980 *J. Phys. C: Solid State Phys.* **13** 2885
Yakovlev B S and Lukin L V 1985 *Adv. Chem. Phys.* **60** 99

Reply by K J Donovan and E G Wilson

The interpretation of transient photoconductivity measurements on the single-crystal polymer, polydiacetylene toluene sulphonate, PDATS, proposed by Donovan and Wilson (Donovan and Wilson 1981a) has again excited a critical reaction (Frankevich, above) and an attempt to reinterpret the data. This new interpretation, we believe, when examined carefully, brings in its train some unphysical consequences, and it is those that are explored here.

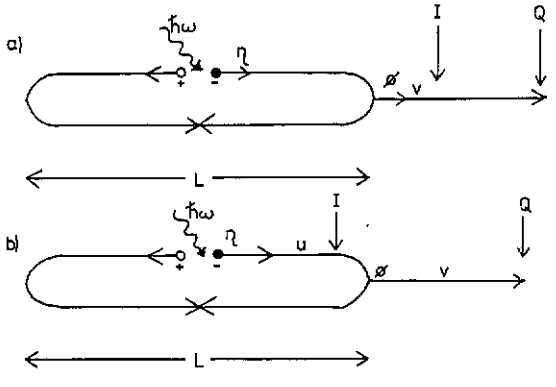

Figure 1. Schematic representation of two alternative views of the origin of transient photocurrents in PDATS as described in the text: (a) depicts the interpretation according to the authors; (b) depicts the interpretation offered by Frankevich.

Figure 1 is a schematic illustration of the essence of the two different interpretations of the experimental facts. It shows electron–hole-pair creation by a light pulse, with quantum efficiency η. A small fraction, Φ, survive geminate recombination and separate, contributing to Q, the charge measured at long times by the electrodes of spacing d. I is the current at the end of the light pulse. (a) is the case of Donovan and Wilson, (b) the case of Frankevich. v and u are the velocities when I is measured. By having the two velocities v and u in case (b) we are allowing for the possibility that different physical mechanisms may determine the velocity before and after separation. L is the mean distance the geminate pair move apart before returning to recombine; T is the time they take to separate to L.

For figure 1(a) the charge and current per photon absorbed are given by

$$Q = e\eta\Phi \qquad I = e\eta\Phi v/d \qquad I/Q = v/d. \tag{1a}$$

In this interpretation the ratio I/Q is independent of applied field E, over four decades, from 10^2 to 10^6 V m^{-1} (Donovan and Wilson 1981a, b). This simply reflects the field independent velocity, close to the sound velocity, theoretically expected for the SWAP, or Davydov electron soliton, in one dimension (1D) (Gogolin 1988, Davydov 1979, Wilson 1983, 1989). Then the field dependence of Φ, linear at low fields, going superlinear at high fields, is that for geminate escape in 1D (Pope and Swenberg 1982, Seiferfeld *et al* 1983). Moreover, the superlinearity is expected for such escape; it occurs when barrier lowering by the field is significant. L is intrinsic to the chain, a thermalization distance of initially hot carriers; L = 5–10 nm (Donovan and Wilson 1981b).

For the case of figure 1(b) the corresponding equations are

$$Q = e\eta\Phi \qquad I = e\eta u/d \qquad I/Q = u/\Phi d. \tag{1b}$$

The constant ratio of I/Q experimentally found over four decades must then mean that u/Φ is likewise constant. This is the first problem for this view, for we are unaware of any physical reason for Φ having the same field dependence as u over four decades.

Secondly, it follows that u is linear in field at low fields, going superlinear at high fields. This is the second problem, for there is no reason of which we are aware for the velocity u going superlinear.

Thirdly, consider the relation

$$L = uT. \tag{2}$$

This is entailed by the model and holds as u varies by more than four decades (more than four because u goes superlinear at high fields). Suppose in (2) the distance L is independent of field, for whatever reason. Then the time T has to vary by more than four decades. But T is still greater than 10 ns, the duration of the light pulse for which the model applies, at the highest fields and so T must be greater than 100 μs at the lowest fields. We do not find it credible that carriers drift steadily apart for 100 μs, only to return and geminately recombine.

Fourthly, suppose one abandons the assumption that L is independent of field, and supposes instead the other extreme: namely that T is independent of field for whatever reason. Then L increases by more than four decades as the field varies by the same amount. The minimum value of L is 10 nm, for otherwise, model 1(b) is confused with 1(a), where L actually is 10 nm. Thus at the highest field L must increase to more than 100 μm; again, we do not find this credible.

There is a completely independent determination of v by time of flight over distances of 12.5 μm–50 μm that gives the same values as the model of Donovan and Wilson (Donovan *et al* 1985). This result would be inexplicable by the Frankevich view.

We offer here no detailed explanation of the small (2%) magnetic-field effect on the magnitude of the DC photocurrent found by Frankevich (Frankevich *et al* 1989). It does not seem to be unreasonable, however, to assume that Φ is indeed, for the reasons given by Frankevich *et al*, modulated by the magnetic field and that at high E fields Φ becomes superlinear due to an additional source of free carriers unmodulated by magnetic field. This would explain these results. Indeed it has been suggested (Seiferfeld *et al* 1983) that the superlinearity with E field is due to η becoming E-field dependent. Such a process may well be insensitive to magnetic field.

In conclusion, the Donovan and Wilson model of figure 1(a) is simple in its assumptions and consequences. In contrast, that of Frankevich, of figure 1(b), is complex and leads to situations that are physically dubious.

K J Donovan and E G Wilson
Department of Physics
Queen Mary and Westfield College
Mile End Rd
London E1 4NS
UK

References

Davydov A S 1979 *Int. J. Quantum Chem.* **16** 5
Donovan K J, Freeman P D and Wilson E G 1985 *J. Phys. C: Solid State Phys.* **18** L275
Donovan K J and Wilson E G 1981a *Phil. Mag.* B **44** 9
—— 1981b *Phil. Mag.* B **44** 31
Frankevich E L, Sokolik I A and Lymarev A A 1989 *Chem. Phys. Lett.* **59** 113
Gogolin A A 1988 *Phys. Rep.* **157** 348
Pope M and Swenberg C E 1982 *Electronic Processes in Organic Crystals* (Oxford: Oxford University Press) p 689
Seiferfeld U, Ries B and Bassler H 1983 *J. Phys. C: Solid State Phys.* **16** 5189
Wilson E G 1983 *J. Phys. C: Solid State Phys.* **16** 6739
—— 1989 *Syn. Met.* **28** D551