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LETTER TO THE EDITOR

On the mechanism of photogeneration of charge carriers in polydiacetylene crystals

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Abstract. Experimental data are presented which give evidence about the short free path before recombination of free charge carriers in single crystals of polydiacetylene-toluene-sulphonate (PDA TS). The free path is shown to be much shorter than the millimetre-size electrode spacing. The recombination of carriers occurs via traps (of Shockly–Read type) or, at higher intensities, bimolecularly. The results obtained do not allow us to consider as substantiated the literature data on high (up to $10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) mobility of carriers in PDA TS, and on the validity of one-dimensional diffusive theory of charge-pair separation as applied to PDA TS. All these data critically depend on the assumption of the absence of recombination.

Single crystals of polydiacetylene-bis(toluenesulphonate) (PDA TS) are the subject of interest because of the high anisotropy of the charge carrier mobility: $\mu_{\parallel}/\mu_{\perp} = 10^2\text{--}10^3$, where μ_{\parallel} is the mobility along the polymer chains and μ_{\perp} is that in the transverse direction (see, for example, [1] and the references cited therein). Due to the anisotropy PDA TS crystals can be used as model objects for studying the features of photogeneration and transport of charge carriers in quasi-one-dimensional systems. Physical, electrical and optical properties of PDA TS crystals were investigated by different groups, and the data obtained are basically similar. However, interpretations of the data vary significantly, resulting in a difference of elementary characteristics of charge carriers and schemes for carrier photogeneration. Thus, the mobility values was estimated from experimental data as $\mu_{\parallel} \geq 2 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and the drift velocity of charge carriers was supposed to saturate at $2.2 \times 10^5 \text{ cm s}^{-1}$ at the field strength $E \geq 1 \text{ V cm}^{-1}$ [2, 3]. On the other hand, values $\mu_{\parallel} \leq 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ have been reported [4–6]. The mechanism of the separation of primary electron–hole pairs generated under the action of light is not clear either. The experimental results were regarded as a proof of the validity of application of the 1D version of the diffusion model of the separation of pairs [7, 8]. According to this model, the probability φ of free-carrier generation depends on the electrical field strength E as

$$\varphi_{1D}(a, E) = (Eea^2/r_c kT) \exp(-r_c/a) \quad (1)$$

where a is the initial electron–hole separation and r_c is the Onsager radius (see, for example, [9]). On the other hand the same experimental data were interpreted in the

frames of other models of charge separation where φ is constant at low electrical fields as though it were due to the 3D character of the separation [9, 10].

These different models are based on the same experimental results and originate from different interpretations of current–voltage characteristics of PDA TS crystals. Evidently, in any model of linear response the photocurrent density j may be written as

$$j = en\mu E = eI\varphi\tau\mu E \quad (2)$$

where n is the concentration of charge carriers, τ is the carrier lifetime, I is the light intensity absorbed by a crystal in quanta $\text{cm}^{-3} \text{s}^{-1}$, which is assumed to be low enough to prevent bimolecular recombination, φ is the quantum yield of free charge carriers per quantum absorbed, and e is the electron charge. We assume that a uniform distribution of light occurs in the excited volume. Taking into account the non-uniformity of the distribution does not alter our conclusions. Two different cases may be considered. In the first one the lifetime t is determined by a monomolecular recombination of carriers in the bulk of the crystal ($\tau = \tau_{\text{mr}}$), and equation (2) can be rewritten as

$$j_1 = eI\varphi\tau_{\text{mr}}\mu E. \quad (3)$$

In the second case τ is determined by the transit time of carriers to the electrodes ($\tau = d/\mu E$), and equation (2) is transformed into

$$j_2 = eI\varphi d \quad (4)$$

where d is the distance between the electrodes. Authors of many publications follow Donovan and Wilson's hypothesis [2, 3] assuming that free transit of carriers to electrodes takes place and equation (4) is valid. In such a case the basic conclusion is that the dependence of quantum yield on E is similar to that of the photocurrent. This, in turn, is essential for the understanding of features of the 1D process of carrier generation. Donovan and Wilson's conclusion that recombination of any kind is not the dominating process of carrier disappearance in the bulk of PDA TS crystals was based on the results of their experiment when regular artificial cuts of a polymer sample were made. The cuts were supposed to work as carrier recombination centres; however, it is not evident that they do exactly in this way. High mobility values and saturation of drift mobility in low electrical fields are based on the applicability of the equation (4) too.

The possibility for a charge carrier to have a free transit through the millimetre-size crystal looks strange in such an imperfect system (typically, in PDA TS the single-crystal conjugation length does not exceed 1000 \AA [11]). At the same time the process of carrier density decay in the crystal is one of the key points for understanding the photogeneration mechanism. This situation stimulated us to run a simple experiment providing additional information about the process of disappearance of charge carriers in PDA TS crystals.

In this experiment we compared the photocurrents for samples differing only by the gap between the electrodes. To do this we evaporated three Al electrodes on the surface of the same crystal (figure 1) and measured the surface photoconductivity excited by light with $h\nu \geq 2.1 \text{ eV}$ polarised along the b axis, for which the crystal has an absorption coefficient $\alpha \geq 10^5 \text{ cm}^{-1}$ [1]. The penetration depth of the light was very small ($\approx 200 \text{ \AA}$) thus permitting all free charge carriers produced by the light to take part in the photoconductivity between electrodes. In the experiments the electrical field was parallel to the polymer chains. Measurements were done in a vacuum of about 10^{-5} Torr to avoid the photo-oxidation of the surface [12]. An incandescent lamp combined with the monochromator or glass filters and with the polariser was used for excitation of crystals. The DC photocurrent was measured by an electrometric amplifier.

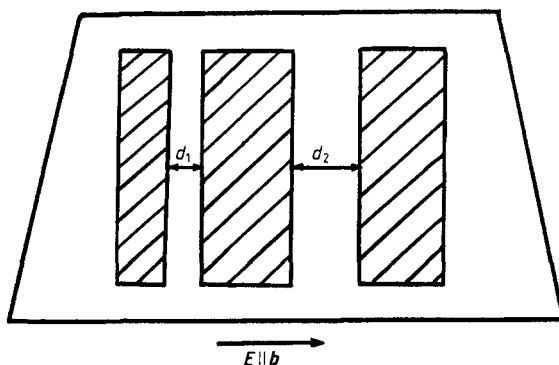


Figure 1. Crystals of PDA TS with three surface electrodes forming different gaps d_1 and d_2 .

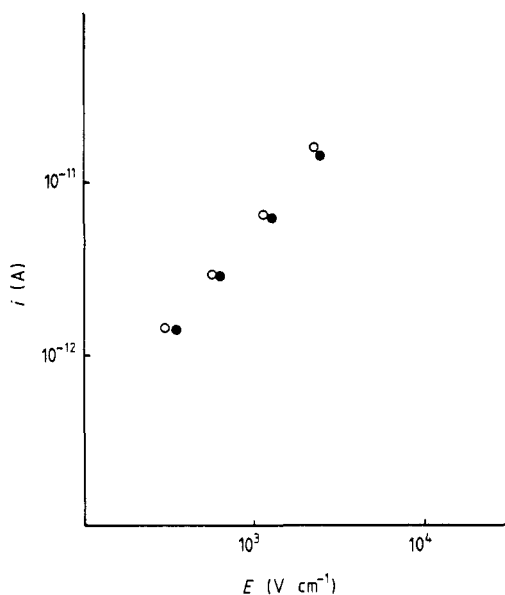


Figure 2. Dependences of the photocurrent on electrical field strength E obtained for samples with the gap $d_1 = 0.25$ mm (open circles) and $d_2 = 0.7$ mm (full circles) shown in figure 1. Excitation by the light with $h\nu \geq 2.1$ eV polarised along the chain.

The excitation conditions and the electrical field E used were the same for both samples shown in figure 1. Measurements were done in conditions when the photoconductivity was linear with voltage and light intensity. Then the ratio of the photocurrents obtained for different gaps d_1 and d_2 would be equal to unity for carriers recombining in the volume of the crystal (see equation (3)); evidently, $i(d_1)/i(d_2) = j(d_1)/j(d_2)$. Alternatively, the ratio would be equal to d_1/d_2 for carriers recombining at electrodes (see equation (4)). The experiment shows that the ratio is near to unity, and thus we come to the conclusion that linear recombination of carriers in the bulk of the crystal takes place (figure 2).

We verified our conclusion in a different kind of experiment where we compared the current-voltage dependence obtained for the same sample at different light intensities. An increase of intensity usually changes the character of $i(I)$ curves in such a way that they become sublinear instead of linear. This is due to a transition from monomolecular to bimolecular recombination (in the latter case the recombination of carriers obviously

takes place in the bulk of the crystal). Thus, for high intensities for any mechanism of carrier recombination the equation for photocurrent density is

$$i_{\text{HI}} = e(I\varphi/k)^{1/2}\mu E \quad (5)$$

where k is the rate constant of bimolecular recombination. It is possible to estimate the tendency of the voltage dependence of the ratio of photocurrents measured at high and at low ($i \sim I^{1.0}$) light intensities. This can be done for two different dependences of φ on E at low electrical fields predicted by different models of carrier photogeneration: $\varphi \sim E$ (see equation (1)) based on the free carrier transit to electrodes [2, 3], and $\varphi = \text{constant}$ based on the carrier trapping and recombination in the bulk [9, 10]. The estimation shows that the best correlation of the calculated curves with the experimental ones is obtained for the case when φ is independent of E at low electrical fields (i.e. φ is proportional to i/E). This, in turn, is incompatible with the idea of free transit of charge carriers to electrodes.

Thus we conclude that charge carriers recombine in the bulk of the crystal at any light intensities, including low ones when $i \sim I^{1.0}$. According to the conclusion some statement made for PDA TS quasi-1D crystals and regularly reproduced in publications seem to be speculative. These statements are: high mobility of carriers in the direction parallel to polymer chain ($\mu_{\parallel} \geq 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [2, 3]; saturation of carrier drift velocity at low fields $E \geq 1 \text{ cm}^{-1}$ [2, 3]; transit of carriers across the distances up to 1 mm prior to recombination [2, 3]; usability of the 1D diffusive model of charge-pair separation [2-4, 6, 7].

A few additional remarks have to be made. Since the PDA TS single crystal is a quasi-1D system, charge carriers produced by light as a result of an intrachain or of an interchain generation process do not become free even if their initial separation exceeds the Onsager radius. In the absence of an external electrical field the diffusion in a quasi-1D system unavoidably leads to the geminate recombination, i.e. the carrier recombines with the same partner from which it moved apart, even if the Coulomb attraction is negligible. But carriers that suffer geminate recombination do not contribute to the steady-state photoconductivity. A non-zero quantum yield may occur only in the presence of non-geminate recombination process, e.g. via recombination centres, at electrodes, or through the encounters of carriers from different pairs. The absorption of light by PDA TS crystals produces geminate pairs of carriers mostly by interchain generation: the ratio of quantum yields of free carriers produced by light with $h\nu \leq 1.9 \text{ eV}$ polarised along and across polymer chains is $\varphi_{\parallel}/\varphi_{\perp} = \frac{1}{3}$ [13]. The carriers in such a geminate pair most probably are polarons of opposite sign. The distance between charges in these pairs is as large as the diffusion length of free carriers before recombination ($\sim 10^3 \text{ \AA}$, our estimation) and the properties of the pairs determine the dependence of the quantum yield of free carriers on electrical field strength and on the recombination rate. The details will be published elsewhere.

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