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On the Photogeneration of Charge Carriers in Quasi-One-Dimensional Semiconductors: Polydiacetylene

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Experimental data are presented showing that recombination of free carriers occurs in the bulk of mm size samples of PDA-TS single crystals under steady-state excitation. The results, combined with the shape of the photocurrent i dependence on field strength, E, lead to the following conclusions: 1) the quantum yield of free carriers φ does not depend on the field strength at $E < 10^3$ V/cm but increases at higher E; 2) φ depends also on the diffusion length L of free carriers before recombination in the bulk of the crystal: $\varphi \sim L^{-1}$. The latter accounts for the unusual type of i dependence on I, $i \sim I^m$ where m varies with the intensity of the light I in the range $1 \geq m \geq 2/3$. The properties of geminate diffusive pairs of charges of opposite signs are responsible for the photogeneration of free carriers. These pairs are as large as $L \cong 10^{-5}$ cm which is much higher than Onsager's radius r_c. The diffusive pairs are responsible also for the magnetic field effect on the photocurrent observed.

1. INTRODUCTION

Polymer crystals of diacetylene are a subject of general interest because of their quasi-one-dimensionality: the mobility of charge carriers along the chains (crystal axis b) is considerably higher than that in the transverse direction, $\mu_\parallel/\mu_\perp > 10^2$.[1–3] Polydiacetylene *-bis* (toluenesulfonate) (PDA-TS) crystals of a few millimeters in size may be produced relatively easily and this explains why these crystals are so popular among workers in the field. The first investigations of the nature of the photoprocesses in the PDA-TS were done more than ten years ago,[1–3] however, the mechanism of the photogeneration of free charge carriers is not absolutely clear. Blum and Baessler[4] (hereafter -BB) extensively listed the problems involved and we need not reproduce them in detail here. In this paper we would like to concentrate on some of the main problems of charge carrier photogeneration and transport in PDA-TS which still need clarification. These problems raise a number of issues upon which our research will focus. These questions are:

1. What is the main way in which charge carriers in mm size samples recombine? Do they recombine in the volume of the crystal[5,6] or do they reach the electrodes?[4,7-11] (The answer to this question will determine the validity of the second problem.)
2. Does the high mobility of charge carriers along the chains, ($\mu_{\parallel} \geq 2 \times 10^5$ cm^2/V.s) and the saturation of drift velocity in low electrical fields really exist, as was proposed by Donovan and Wilson (hereafter-DW)? See, for example, Reference 7.
3. What is the anisotropy of the quantum yield of free charge carriers with respect to the mutual orientation of the polarization of the exciting light and the polymer chain?
4. Is it possible to use Onsager's 1D or 3D model to describe the separation of charges in PDA-TS?
5. What is the nature of the intermediate states formed in the process of charge carrier generation?

These issues have stimulated us to reinvestigate the mechanism of photogeneration of charge carriers in PDA-TS crystals. In addition to the traditional experiments on photoconductivity we used magnetic field effect measurements which were intended to determine the participation of pairs of paramagnetic species in the photoprocesses (see, for example, References 12,13).

2. EXPERIMENTAL

The diacetylene-bis(toluenesulfonate) single crystals grown from solution in acetone were cleaved preliminarily, mechanically treated, polymerized at 70°C for not less than 25 hours, and fastened to quartz substrates with an isolating sealing compound. The d.c. bulk conductivity was measured using silver paste electrodes, while the surface conductivity was measured using evaporated aluminum electrodes. All measurements were performed in a vacuum of $\sim 10^{-5}$ Torr. The photoconductivity was excited by the light of an incandescent lamp which passed through a water filter, either glass filters or a monochromator, and a polarizer. Two excitation ranges were used: first, "blue" light with the quantum energy $3.5 > h\nu > 2.1$ eV producing the excitation of π-system of the polymer, and second, "red" light with $1.3 < h\nu < 1.9$ eV, which was insufficient for such excitation. The maximum light intensity in the two ranges was $\sim 5 \times 10^{-3}$ and $\sim 5 \times 10^{-2}$ W/cm^2, respectively. The incidence of light was normal to the crystal plane (100) and perpendicular to the polymeric axis b. A magnetic field with a strength of $H < 3$ kOe was created by an electromagnet. The sample temperature was varied from 260 to 350K.

All the crystals investigated were photoconducting in both spectral ranges used, the excitation spectrum of the photocurrent being similar to that described in references 5,9,14. The temperature dependence of the photoconductivity was of the Arrhenius type with an activation energy of $E \cong 0.06$ eV and the peak on the $i(T)$ curve described in References 4 and 11 was not obtained. The mobility ratio for the electric field applied along or across the polymer chains $\mu_{\parallel}/\mu_{\perp}$ was obtained from the ratio of photocurrents $i_{\parallel}/i_{\perp}$ which were measured on the same crystal with

the surface or bulk electrodes at equal electrical field strength E in the linear region of the current-voltage characteristics. In this way, we were able to avoid the errors connected with the dependence of the yield φ on E for $E \parallel b$. In the crystals studied in this work, the mobility ratio was $\mu_{\parallel}/\mu_{\perp} = 50-100$. It should be emphasized that the characteristics of photocurrent were the same for the excitation in the two ("red" and "blue") spectral ranges except for the quantum yield of free carriers.

3. RESULTS AND DISCUSSION

3.1. Character of the decay of charge carriers

To understand the major pathway for recombination of charge carriers in PDA-TS crystals we have performed some simple experiments in addition to those published previously. In all cases, at low light intensities, the equation for the photocurrent may be written as

$$i = en\mu E = eI\varphi\tau\mu E, \tag{1}$$

where n is the concentration of charge carriers, τ is the carrier lifetime, I is the light intensity absorbed by a crystal in quanta/cm^3., and φ is the quantum yield of free charge carriers per quantum absorbed. We assume that a uniform distribution of light occurs in the excited volume. Taking into account non-uniformity of the distribution does not alter our conclusions. If the lifetime τ is determined by a linear recombination of carriers in the bulk of the crystal (τ_r), equation (1) is valid and can be rewritten as

$$i_2 = eI\varphi\tau_r\mu E. \tag{2}$$

When the τ value is determined by the transit of carriers to the electrodes ($\tau_t = d/\mu E$), equation (1) is transformed to

$$i_3 = eI\varphi d, \tag{3}$$

where d is the distance between the electrodes.

Our first experiments compared the photocurrents for the 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 $h\nu > 2{,}1$ eV polarized along the b-axis for which the crystal has an absorption coefficient $\alpha_{\parallel} > 10^5$ cm^{-1}.[1] Since the excitation conditions and the electrical field E are the same for both samples, and measurements are done of the photoconductivity when the behavior is Ohmic, 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. Alternatively, the ratio would be equal to d_1/d_2 for carriers recombining at electrodes (see equations (2) and (3)). The experiment shows that linear recombination of carriers in the bulk of the crystal takes place (Figure 2).

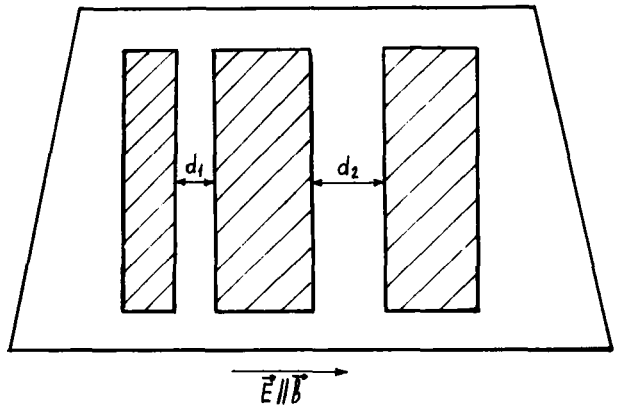

FIGURE 1 Crystals of PDA-TS with three surface electrodes forming different gaps d_1 and d_2.

In a different kind of experiment we compared the current-voltage dependence obtained for the same sample at different light intensities. An increase of light intensity usually changes the character of $i(I)$ curves in that they become sublinear instead of linear. This results from a transition from monomolecular to bimolecular recombination (in the latter case the recombination of carriers obviously occurs in the bulk of the crystal). Thus, for high intensities for any mechanism of carrier

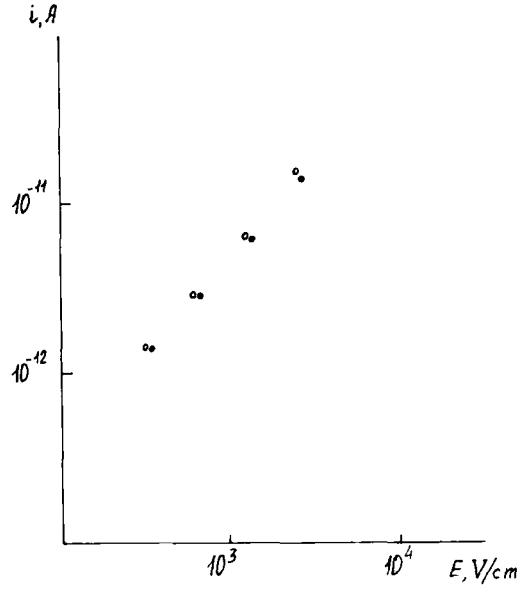

FIGURE 2 Dependences of the photocurrent on electrical field strength E obtained for samples with the gap $d_1 = 0.25$ mm (open circles) and $d_2 = 0.7$ mm (full circles) shown in Figure 1. Excitation by the light with $h\nu \geq 2.1$ eV polarized along the chain. $E \parallel b$.

recombination the equation for the photocurrent is

$$i_4 = e(I\varphi/k)^{1/2}\,\mu E, \tag{4}$$

where k is the rate constant of the bimolecular recombination. Comparing the dependence of the ratio of photocurrents measured at high and low intensities with those predicted by equations (2)–(4) one can come to the following conclusions concerning the character of carrier recombination: if it occurs in the bulk of the crystal then $(i_4/i_2)^2 \sim \varphi^{-1}(E)_i$ and if it occurs at the electrodes then $(i_4/i_3)^2 \sim E^2\varphi^{-1}(E)$. Under the experimental conditions we were unable to get $i \sim I^{0.5}$ dependences even at high intensities. (The explanation for this effect can be found in Section 3.3). However, it is possible to estimate the tendency of the voltage dependences 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 as shown in Figures 3a and 3b (solid curves). The results of the estimations which have been done for the ratio of photocurrents corresponding to the $i \sim I^{0.85}$ and to the $i \sim I^{1.0}$ dependences are shown in the same figures. (The details will be published elsewhere).[15] One can see that the experimental data (triangles in Figure 3c) correspond to the dashed curve on Figure 3a and at the same time are quite different from the dashed-dotted curves.

Thus, our results agree with those of Siddiqui[5,6] (hereafter-S) that the charge carriers recombine mainly in the bulk of the crystal being trapped by the recombination centers (Shockley-Read type recombination). This, in turn, proves that for conductivity directed along the polymeric chains the quantum yield φ does not depend on the electrical field at $E < 10^3$ V/cm since the photocurrent has a linear dependence on the field due to carrier velocity rise (Figure 4). Therefore, it follows that the 1D version of Onsager's model is not applicable for this field's range. Moreover, DW's conclusions about the giant carrier's mobility and about the saturation of carrier's drift velocity[7] are not valid, since they assumed the recombination of carriers at electrodes.

3.2. Anisotropy of quantum yield of free charge carriers

The dependence of the free carrier's yield φ on the mutual orientation of the electric field vector of the exciting light wave and the direction of molecular chains in PDA-TS crystals has been only briefly discussed in the literature. Thus, in one of the first papers on photoconductivity of PDA-TS[16] it was concluded that for the excitation within the spectral range $h\nu < 1.75$ eV the yield $\varphi_\parallel$ for light polarized along the b-axis is more than one order of magnitude higher than that for light polarized across the chains: $\varphi_\parallel/\varphi_\perp > 10$. One can conclude from the results published by S[6] that $\varphi_\parallel/\varphi_\perp = 1$ for $h\nu = 1.9$ eV. However, we have done some additional measurements of anisotropy of the yield in PDA-TS crystals. In our work we compared the values of steady-state photocurrents excited by light of the same intensity which was polarized either along or across the polymeric chain, the dependences of the absorption and reflection cofficients on polarization having been taken into account. (The absorption coefficients for "red" light were measured directly and the values

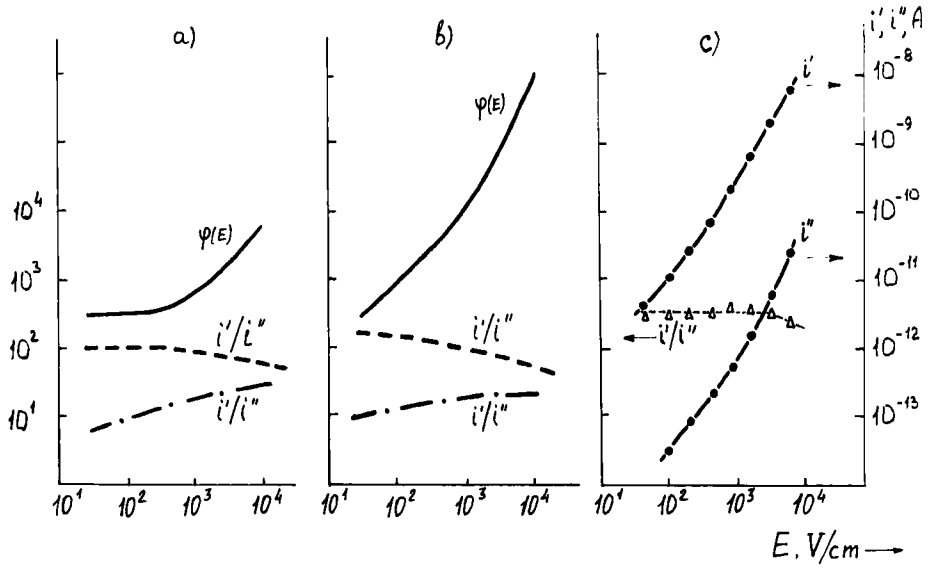

FIGURE 3 Comparison of current-voltage dependences obtained for different mechanisms of generation and recombination of charge carriers in PDA-TS. Photocurrents i' and i'' are used generated in the bulk of the sample when excited by light of high and low intensities ($i' \sim I^{0.85}$, $i'' \sim I^{1.0}$). (a) Dependences of the ratio i'/i'' on E calculated for the case when $\varphi(E)$ curve shown by a solid line is valid. Dashed-line curve is calculated for bulk recombination, dashed-dotted curve—for electrode recombination; (b) the same as (a), but other $\varphi(E)$ dependence shown by solid line is used; (c) triangles show experimental data on the ratio of i'/i''; i' and i'' versus E curves are shown by full circles. The curve drawn through triangles resembles the dashed-line curve on the Figure 3a. All curves except i' and i'' on Figure 3c arbitrarily shifted in vertical direction.

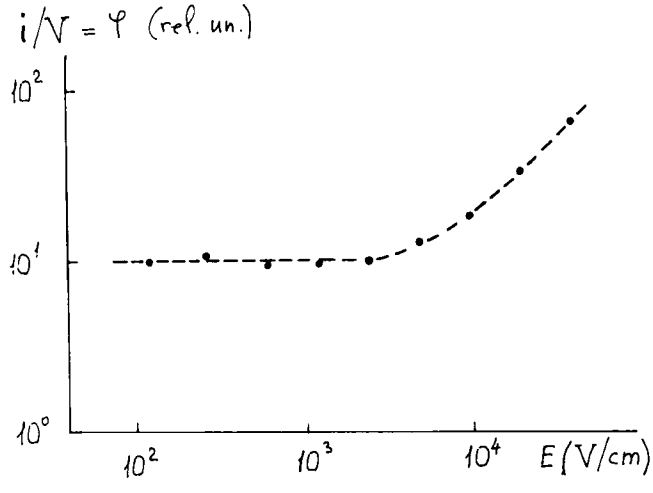

FIGURE 4 The dependence of the quantum yield φ of free charge carriers on the electrical field strength E. $E \| b$. Dashed curve was calculated from Equation (9) for L = 1600A. Circles—experimental data obtained for bulk samples. Excitation: $h\nu < 1.9$ eV, I = 50 mW/cm^2.

obtained coincide with those published elsewhere). Our experiments lead us to conclude that for light with photon energy $h\nu < 1.9$ eV the charge carriers are produced mostly by the interchain generation as we got $\varphi_\perp/\varphi_\parallel = 5$. This result agrees with the data obtained by others working with oriented polyconjugated systems (see, for example, references 17–20). The results may be attributed to a higher recombination rate of electron-hole pairs created in one chain as compared to that of electrons and holes from the neighboring chains. An increase in the quantum energy leads to a significant increase of the relative contribution of $\varphi_\parallel$ as compared with $\varphi_\perp$ which agrees with the predictions of Danielsen,[19] and Gartstein and Zakhidov.[20] For $h\nu \geq 2.1$ eV we have obtained $\varphi_\parallel/\varphi_\perp > 1$. At these energies the molecular excitons are also formed[1-3] and the values $\varphi_\parallel/\varphi_\perp \geq 1$ can be explained only if we assume that a direct ionization occurs simultaneously with a large contribution of $\varphi_\parallel$. It should be noted that in steady-state photoconductivity only the quantum yields depend on the quantum energy. This suggests that the photogeneration of free carriers in both excitation regions proceeds through similar excited states. We assume that the states are formed as a result of a hop of electron excited by light to the next chain. When an electron is initially excited in the chain direction, there is still a probability of interchain hopping during its diffusive motion back to the parent positive ion, and the same excited interchain state may be created. The longer the distance of initial intrachain electron-hole separation, the higher the probability is of forming an interchain excited state.

3.3. Some features of generation of charge carriers due to the quasi-one-dimensionality of the system

As we have stated previously (Section 3.1) measuring the dependence of the photocurrent on the exciting light intensity we were not able to reproduce the exponent $m = 0.5$ in the dependence $i \sim I^m$ which has been reported by S in Reference 6. Rather we found that $i(I)$ curves could be described by the relation $i \sim I^m$ with $m \geq 0.7$ even at the highest I values (see Figure 5). An attempt to reproduce S's results using similar quantum energy, light intensities and other experimental conditions gave us photocurrent values similar to those obtained in Reference 6 but m was equal to 0.7. It should be noted that the experimental i versus I dependence found by Lochner *et al.*[21] for high intensities corresponds better to $m = 0.7$ than to $m = 0.5$. It is important that the exponent m remains constant, when the light intensity is varied by a factor of 10–100 to higher intensities (see Figure 5). The dashed line in Figure 5 represents the expected behavior of m in the region of $m = 2/3$ for the usual i versus I dependence controlled by the competition of bi- and monomolecular recombination processes (where $0.5 \leq m \leq 1$ within a wide intensity range) described by Equations (2) and (4). A decrease in the light intensity by several orders of magnitude below the level indicated in Figure 5 results in photocurrent values comparable with the dark current; at these intensities m is equal to unity.

To rationalize such a "strange" exponent in the i versus I curves we have to consider some feature of quasi-one-dimensional systems. In those systems the charge carriers arising from electron-hole pairs cannot be regarded as free even when

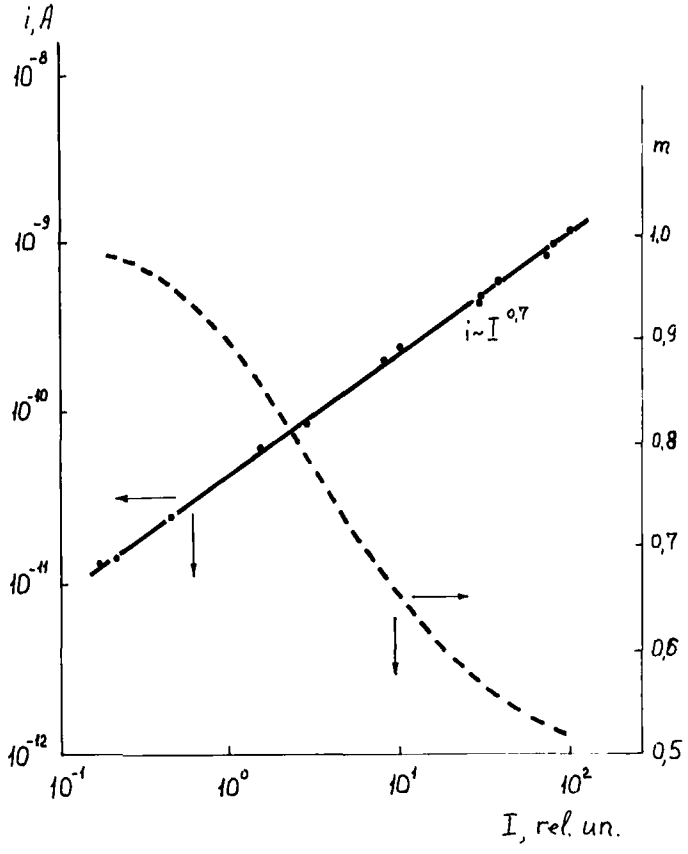

FIGURE 5 Dependence of the photocurrent i on light intensity I in PDA-TS crystal (solid curve). $E \div b$. $E = 2.7 \times 10^4$ V/cm. Excitation by Ar laser, light polarized along the chain, $\lambda = 448$ nm, $I_{max} = 50$ mW/cm^2. Bulk conductivity. Dashed curve is a dependence of the exponent m on I calculated for the competition between mono- and bimolecular recombination of carriers with φ being independent of n.

separated by a distance exceeding $r_c = e^2/\epsilon kT$, because in the absence of an external electric field, diffusion in these systems unavoidably leads to the geminate recombination. In this case the carrier recombines with the same partner from which it moved apart, even if the Coulomb attraction is negligible. But carriers which suffer geminate recombination do not contribute to the steady-state photoconductivity, so that the yield of free carriers in pure one-dimensional systems is zero. A non-zero yield may occur only in the presence of non-geminate recombination processes, e.g., via the recombination centers, at electrodes, at the meeting of carriers from different pairs. In such a case, the yield of free carriers should be a function of the recombination rate. It is a feature of a quasi-one-dimensional system.

We would like to mention that the quasi-one-dimensional approach to the geminate recombination may be valid when $\mu_\parallel/\mu_\perp \geq (L/r_c)^2$, where L is the diffusion length of the carrier prior to the nongeminate recombination. That means that

during its diffusive motion (mostly along the chains) electrons travel in the transverse direction at a distance of less than r_c. Obviously, electrons can hop to the next chain during their diffusion along the chains (see Figure 6). The motion of electrons should occur in the potential well which may be described as $U = e/\epsilon \sqrt{x^2 + l^2}$ where x and l are the distances from electron to parent ion in the longitudinal and transverse directions. If a charge carrier returns during its diffusive motion to an ellipsoid whose dimensions are determined by the Onsager's radius (one obtains ellipsoid because of the anisotropy of the permitivity ϵ[22]), then it has a high probability of being attracted to the parent ion and to recombine with it geminately. In such a case the charge carrier can not be considered as having been a free one. A high probability of geminate recombination follows from the low values of quantum yield. We assume that the mobility of carriers along the polymer chain is about its macroscopic value $\mu_\parallel = 0.1-10$ cm^2/V.s (see, for example, Reference 1 and Sec. 3.1) and we have measured that $\mu_\parallel/\mu_\perp = 10^2$.

In the framework of the proposals made above one can consider the dependence of the quantum yield of free charge carriers φ on recombination conditions.[23] Let us assume that the excitation of carriers by light (i.e. the excitation of geminate pairs) proceeds at a rate g per unit length as a result of an electron hopping to the next chain within a small region whose width is δ at $x = 0$. Trapping of electrons by the recombination centers prevents geminate recombination and effectively produces free charge carriers and thus gives rise to a photoconductivity. The distribution of electron concentration n_o over the coordinate x where x is an electron-

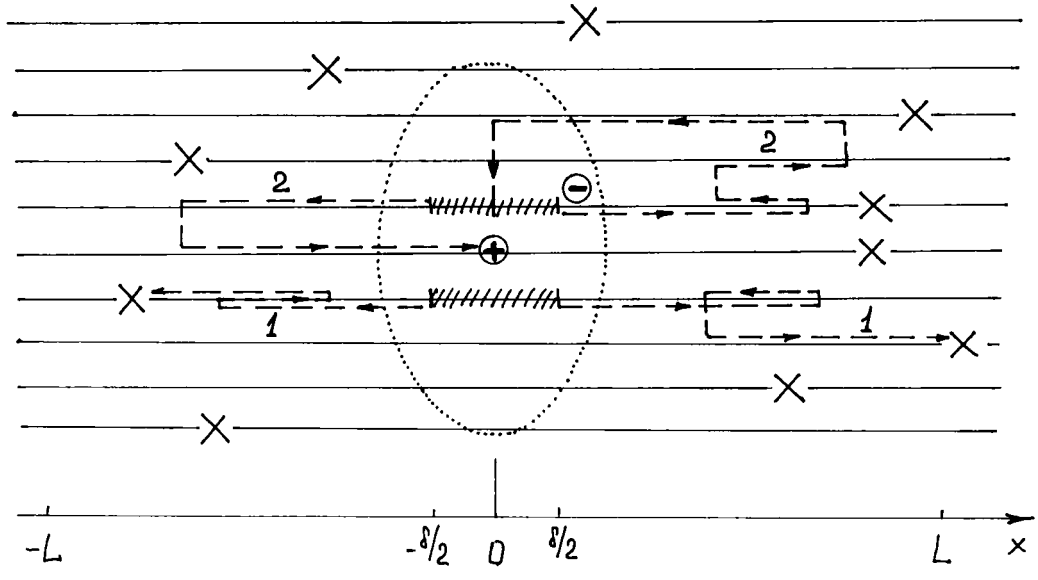

FIGURE 6 Scheme of a motion of charges at the primary separation step in the quasi-one dimensional system. Typical diffusive motions of charges are shown: 1) charge is captured by a recombination center (x) thus escaping from geminate recombination, 2) motion resulting in geminate recombination. In the dashed area $-\delta/2 \leq x \leq \delta/2$, the primary pairs of carriers are produced. Onsager's radius border is shown by dotted line.

parent ion distance, is determined by the solution of a steady-state equation

$$D_{\|} \frac{d^2 n_o}{dx^2} + \mu_{\|} E \frac{dn_o}{dx} - k_1 N n_o - k_2 n_o n = 0 \tag{5}$$

with the next boundary conditions: $n_o = g\tau_{el}$ at $-\delta/2 \leq x < \delta/2$ and $n_o = 0$ at $x \to \infty$. In Equation (5) $D_{\|}$ is the coefficient of longitudinal carrier diffusion, E is the electric field strength, τ_{el} is the charge lifetime in the region δ, N is the concentration of the recombination centers, n is the concentration of free carriers, k_1 and k_2 are the rate constants. The solution of Equation (5) yields that the diffusion flux of charge carriers from the region at $x = 0$ towards the nongeminate recombination centers is described by the expression

$$F = D_{\|} g \tau_{el} L^{-1} f(E) \tag{6}$$

where $f(E) = 3\alpha/4 + [(\alpha/4)^2 + 1]^{1/2}$, $\alpha = eEL/kT$, and

$$L \cong 2[D/(k_1 N + k_2 n)]^{1/2}. \tag{7}$$

L is a diffusion length of electron along the chain before it gets trapped by a recombination center or recombines bimolecularly with free charge. (Equal concentrations of free positive and negative carriers are presumed).

Formula (7) applies to a quasi-one-dimensional system if the frequency of interchain hopping is higher than that of intrachain diffusion between the centers:

$$D_{\|}/l_o^2 = \nu_{\|} = \nu_{\perp} = D_{\perp}/l_1^2 \tag{8}$$

where l_1 is the interchain distance ($l_1 = 7$A) and l_o is a mean distance between recombination centers along one chain ($l_o \cong 1/Nl_1^2$). An inequality (8) means that an electron has a high probability to hop on another chain before meeting a center on its own chain. For $D_{\perp}/D_{\|} = 1/100$ it occurs at $N < (D_{\perp}/D_{\|})^{1/2} l_1^{-3} \cong 3.10^{20}$ cm^{-3}.

Taking into account that only the carriers which avoid geminate recombination are considered as the free ones (that is, contributing to the steady-state photocurrent through the sample), the quantum yield of free carriers (for $\varphi << 1$) is:[23]

$$\varphi' = F/g\delta = D\tau_{el}(\delta L)^{-1} f(E) \tag{9}$$

It is essential that $\varphi' \sim f(E)L^{-1}$; $D\tau_{el}/\delta$ should be considered as a parameter. More exactly, considering in the general case the emptying of a reservoir of carriers at $x = \delta/2$, we have $\varphi = \varphi'/(\varphi' + 1)$. The function $f(E)$ starts from $f = 2$ at $E = 0$ and becomes $f \simeq \alpha$ at $E >> kT/eL$. It has just the same shape as the experimentally revealed $\varphi(E)$ dependence (Figure 4).

A kinetic equation for the concentration n of free carriers acquires the form

$$\frac{dn}{dt} = g\varphi(n) l_1^{-2} - k_1 N n - k_2 n^2, \tag{10}$$

where the free carrier generation rate term $g\varphi(n)\ l_1^{-2}$ is now concentration dependent. The feature of equation (10) is that the dependence of the steady-state photocurrent on the intensity of excitation is linear at low values of g and tends, as the exciting light intensity increases, to the form $i \sim n \sim g^{2/3}$ instead of the usual law $i \sim g^{1/2}$ (see Figure 5). The generation rate of electrons g is proportional to the light intensity: $g \sim I$. The dependence of the concentration of free carriers n on the field strength E is determined by $f(E)$ and becomes essential only at $E > kT/eL$. Since the photocurrent $i = en\mu E$ at these field strengths, its superlinear dependence on voltage is expected to appear.

One can see that Equation (9) leads to the φ versus E dependence similar to that obtained experimentally if the $L = 1600$Å value is used (dashed curve in Figure 4). It is essential to note that $\varphi(E)$ curve obtained from equation (9) is similar to that proposed by S[6] and BB[4] but now the dissociation of pairs is described neither by the Onsager model[6] nor by a ballistic one[4] but is determined by the process of quasi-one-dimensional diffusion of carriers to recombination centers in the electric field.

3.4. Magnetic field effect on the photoconductivity

One can obtain this effect by switching on the weak d.c. magnetic field H while measuring photoconductivity at room temperatures. The photocurrent increases up to 1–4% in the $H = 100$ Oe, the value of the m.f.e. being independent of the mutual orientation of H and b or E. The dependence of the m.f.e. value, $\Delta i/i = [i(H) - i(0)]/i(0)$, on magnetic field strength H is shown in Figure 7. The lack of influence of the magnetic field on the dark current value indicates that the m.f.e. observed is not due to field-induced variations of the mobility of charge carriers but is due to the increase of quantum yield in the magnetic field.[24] The dependence of the value of m.f.e. on the magnetic field strength (Figure 7) is typical of the

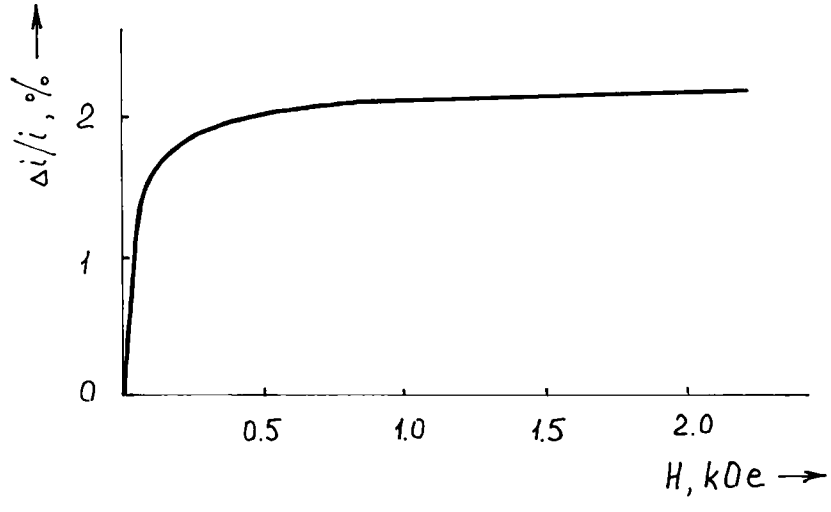

FIGURE 7 Dependence of the m.f.e. value $\Delta i/i$ on the magnetic field strength H.

mechanism of magnetic field effects related to the field-induced variation of steady-state concentration of particles having the spin $\hbar/2$ (electron and hole). These variations are due to the effects of the magnetic field on the total spin evolution of the pairs being formed after the absorption of light but before the creation of free charges. As indicated by the magnitude of halth-saturation field $H_{1/2} = 50$ Oe, the major role in m.f.e. belongs to the hyperfine interaction (HFI).[12,13]

In a zero magnetic field, all four states of the pair are mixed by the HFI—singlet state and three triplet ones. In the high magnetic field $H >> a/g\beta$, (where a is the constant of HFI and β is the Borh's magneton), only the S and T_o states are mixed and T_+ and T_- states remain purely triplet ones and are not occupied. Due to the different values of the rate constants of geminate recombination of singlet and triplet states (k_1 and k_3), any change in the mixing of the states leads to a variation of their total population. The pairs can dissociate into free carriers, the rate constant of the process should be equal to k_{-1} for any state. If we assume that the pairs are created via the singlet channel, the rate of formation of free charge carriers, g, is proportional to pair population: $g = k_{-1} \Sigma_{i=1}^{4} N_i$, and the photocurrent is proportional to the carrier formation rate, $i \sim g$, we obtain the expression for the magnitude of m.f.e. on photocurrent:[24]

$$\frac{\Delta i}{i} = \frac{i(h) - i(0)}{i(0)} = \frac{\Delta N}{N} = \frac{k_3 - k_1}{2k_1 + 2k_3 + 4k_{-1}} \tag{11}$$

It should be noted that magnetosensitivity is possible if the lifetime τ_p of the pair state occurs in the interval $\omega_{HFI}^{-1} < \tau_p < T_1$, where $\omega_{HFI}^{-1} = ag\beta/\hbar$ is the mixing frequency of spin states in the pair ($\omega_{HFI}^{-1} \cong 10^{-9}$ s^{-1}) and T_1 is the time of spin-lattice relaxation ($\sim 10^{-7}$ s). Since it has been found experimentally that $\Delta i/i > 0$, we should assume that $k_3 > k_1$ and thus the triplet geminate pairs recombine at a higher rate than the singlet ones. This may be due to less energy being released during the recombination of triplet pairs, which is determined by the formation of triplet excited states of polydiacetylene with $E_T \cong 1.4$ eV.[25]

One can understand the nature of the magnetosensitive pairs by looking at the dependence of the m.f.e. on the electrical field. This dependence can be seen when $E > 3 \times 10^3$ V/cm and is manifested in a decrease of $\Delta i/i$ in the presence of an electric field oriented parallel to the molecular chains. On the other hand when the orientation of electric field is perpendicular to the chain, the $\Delta i/i$ value remains the same (Figure 8). Note that this effect occurs in the same range of field strength as the effect of electric field on the free carrier yield $\varphi(E)$. According to Equation (11), we assume that the decrease of m.f.e. is due to the electric field induced growth of the pair dissociation rate constant $k_{-1}(E)$. Since $i \sim g4k_{-1}/(2k_1 + 2k_3 + 4k_{-1})$, any further increase in the electric field strength which results in a complete suppression of the m.f.e. ($E > 10^4$ V/cm, $k_{-1}(E) > (k_1 + k_3)$) must simultaneously lead to the yield of free carriers equal to the rate of formation of the magnetosensitive pairs. Therefore, in a high electric field all the magnetosensitive pairs should be dissociated. Experimental results show that in this case the quantum yield of carriers still remains at a low level, which suggests that the formation of magnetosensitive pairs is not primarily a result due to the action of light.

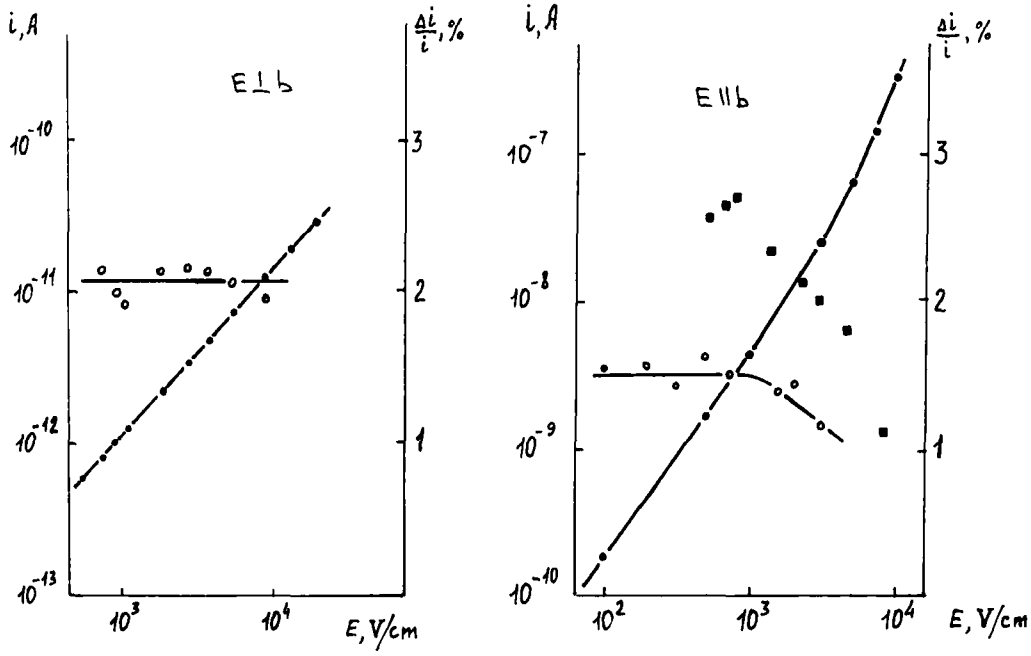

FIGURE 8 Dependences of the photocurrent (full circles) and of the magnetic field effect (open circles) on the electrical field measured for the surface conductivity of the same PDA-TS crystal for $E \perp b$ (left) and $E \parallel b$ (right). Squares – $\Delta i/i$ (E) dependence obtained for other sample with bulk conductivity.

In principle, an alternative explanation of the magnetosensitivity of the photocurrent and $i(E)$ and $\Delta i/i(E)$ dependences could be due to a possible increase in the electrical field strength E, leading to increase in the rate of generation of charge carriers by some nonmagnetosensitive source, i.e. $i = i_M + i_{NM}$. In such a case for $E < 3.10^3$ V/cm there might be a 3D process of carrier generation with the yield being independent of E as was proposed by S.[6] Magnetosensitivity of i_M could be due to the correlated electron-hole pairs (similar to those obtained in molecular crystals[12,13]) formed as a result of the interchain transfer of an electron. (If there is a defect in the conjugation system, the interchain transfer may occur in a direction parallel to the b-axis). This "switching on" of a nonmagnetosensitive 1D generation process proceeding in parallel with the 3D one may cause the superlinearity of current-voltage characteristics, the dependence of φ on E, and the decrease of a m.f.e. obtained for $E > 3.10^3$ V/cm.[6] In our work we did not observe any essential dependence of the characteristics of m.f.e. nor of the photocurrent itself on the excitation wavelength. This suggests that for any quantum energy the generation occurs via one and the same state. This, in turn, directly contradicts to the hypothesis that the photocurrent consists of two components of different nature, i_M and i_{NM}.

Thus, we suggest here that the magnetosensitivity of the photocurrent is a result of a change in the total population of electron-hole pairs when the magnetic field is switched on. Carriers in these pairs are able to diffuse over long distances and

free carriers are generated only when nongeminate recombination occurs. However, as we have shown above, the formation of these pairs must be preceded by the generation of intermediate excited states occurring with the low quantum yield.

In order to understand the nature of these intermediate states, the following considerations have to be taken into account. Since the activation energy of the photocurrent for $E \parallel b$ is very low—about 0.06 eV, it seems natural to suggest that the energy of these states should be about the energy of diffusive electron-hole pairs. On the other hand, the diffusive pairs may exhibit the evolution of their spin states in the magnetic field, but the recombination of pairs, depending on these spin states and determining the magnetic field effect on the photoconductivity, will occur in the region where the electron and hole are coupled by the exchange interaction. If this region was positioned near the center of Coulomb well (where the exchange interaction of localized particles is possible at a distance of r = 5–10Å), the probability of electron escape—after the "check" of spin state and during the time which is less than that of spin-lattice relaxation—should be very low. Indeed, the Coulomb barrier at a distance r = 10Å for ϵ = 4 is estimated at ΔU = 0.4 eV, and the time required for the penetration through this barrier at T = 300K is not less than 10^{-6}s, which considerably exceeds the spin-lattice relaxation time. Moreover, the temperature dependence of photoconductivity is weak and that means that photogeneration does not include any processes in which the activation energies exceed 0.06 eV. On the other hand the m.f.e. itself remains constant in the temperature range between 260 and 350K.

A possible explanation for the photogeneration of carriers in the polydiacetylene crystals is that the primary process involves the formation of an excited delocalized state with the charge transfer. This state could be similar to a one-dimensional Wannier exciton, in the potential of the form $U = e/(x^2 + d^2)^{1/2}\epsilon$. This excited state, comprising an electron-hole pair, has energy levels lying near the energy of a free polaron. In an exciton, the spin-dependent exchange interaction between the electron and hole can occur anywhere in the region of electron delocalization. Therefore, the "check" of spin state in the diffusive pair of particles occurs at a large interparticle distance, where the probability of repeated dissociation of the pair should be higher. Excitons with a charge transfer between the chains are formed in the direct optical transition, as is evidenced by experiments in the spectral range $h\nu \leq 1.9$ eV. For quantum energies above 2.1 eV, their formation appears to be preceded by the appearance of molecular excitons. It is possible that an impurity may serve as the center where the positive charge of the CT exciton is localized. However, we do not yet have definite information on this point.

It should be noted that the hyperfine interaction mechanism of mixing of spin states in pairs requires that there be no averaging of the HFI interaction during the motion of charges in the molecule. The presence of the magnetic field effect indicates that at least one charge in the pair is localized during the pair lifetime $\tau_p < T_1 = 10^{-7}$s. The lifetime of excitons is determined by two factors: first, the spin-dependent electron-hole recombination and, second, the formation of polarons which partly diffuse to recombination centers. The field dependence of the dissociation probability for such linear excitons depends on their size ($r_{ex} \cong 30$A) and may be manifested in the electric field strengths $E > 2kT/er_{ex} = 2/(40 \times 3 \times$

10^{-7}) = 2×10^5 V/cm. The activation energy of photoconductivity is low; its value is determined by the transfer from a CT-exciton to the diffusive pair (which is essentially the pair of polarons) occurring at a distance of about Onsager's radius. In this case the magnetic field effect value should not depend on the temperature which is consistent with our experimental results.

The proposed model can be used to describe the experimental dependencies of the photocurrent on voltage and on light intensity in PDA-TS as well as in any quasi-one-dimensional organic system with $\mu_{\parallel} = 1$ cm^2/V.s and $\mu_{\parallel}/\mu_{\perp} \cong 10^2$. See, for example, the results obtained by Bleier *et al.*,[18] who measured the $i \sim I^{0.8}$ dependence for the delayed photoconductivity of oriented polyacetylene films excited by 25 pS-pulses of laser light. In that and in other work the fast component of photocurrent observed under such excitation for $t < 100$ ps was independent of temperature and linearly dependent on voltage and light intensity.[18,25] This could be interpreted as the result of field induced displacement of hot electrons moving in the area of their delocalization with high mobility and thermalized for longer periods of time in diffusive pairs. Experimentally, this transfer from a CT-exciton to the diffusive polaron pair should look like a transfer from a fast to a delayed component of photocurrent.

CONCLUSIONS

In the introduction a number of questions were brought up which can now be answered combining our present results with other work in the field. The main conclusions concerning the nature of photogeneration and transport of free charge carriers in PDA-TS crystals are:

1. In PDA-TS crystals of mm size, charge carriers recombine in the bulk of the crystal (by Shockley-Read mode) and do not reach the electrodes. This is oposite to the basic hypothesis proposed by DW.[7]
2. Because of the first conclusion, the state of DW about high mobility of carriers and saturation of their drift velocity at low fields seems to be speculative.
3. Neither 3D nor 1D Onsager's models can be used to describe the photogeneration of free carriers in PDA-TS.
4. Charge carriers are produced mostly by interchain generation when light with $h\nu < 1.9$ eV is used: $\varphi_{\perp}/\varphi_{\parallel} = 5$. The results show that an increase in photon energy leads to an increase in the probability of generation of free carriers by light polarized along the chain relative to that caused across the chain.
5. The properties of geminate diffusive pairs of charges of opposite sign are responsible for the photogeneration of free carriers and the magnetic field effect on photoconductivity. These pairs are as large as the diffusion length of the free carriers before recombination and they determine the dependence of the quantum yield of free carriers on electrical field strength and on the recombination rate.
6. The quantum yield of free carriers φ does not change for $E < 3.10^3$ V/cm, and increases with the field strength for higher fields.

7. The quantum yield φ depends on the diffusion length L as $\varphi \sim L^{-1}$. This accounts for the unusual type of dependence of the photocurrent on light intensity, I, $i \sim I^m$, where m varies with the intensity in the range $1 \geq m \geq 2/3$.

8. Speculations about the nature of the initial state of a pair of charges when they are on neighboring chains and still within the Coulomb well must take into account that the free carrier yield is independent of E at low E and that the activation energy (0.06 eV) for free charge generation along the chain is low. A quantum state of the Wannier type may be considered as a candidate for such an interchain state.

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