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ON PHOTOGENERATION OF CHARGE CARRIERS IN POLYMERS

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Abstract The experimental data on the photoconductivity of poly(arylene vinylenes) and polydiacetylene are discussed and show that separation of $e-h$ pairs in conjugated polymers is connected with delocalization of charges and with their 1-D motion. The probability of escaping of geminate recombination is speculated to be limited by availability of sinks which prevent the geminate recombination. It permits to account for unusual photocurrent on voltage and photocurrent on intensity dependencies observed.

INTRODUCTION

Organic conjugated polymers as photo semiconductors have two features if compared with molecular solids: (*) delocalization of charge carriers along the system of conjugated bonds and (**) quasi-one-dimensional character of movement of carriers. For polymers which are not available in the form of single crystals the point (**) takes place only within micro regions with proper stacking of molecular chain what is usually the case. Both features leads the classic Onsager model of the separation of electron-hole pair primarily produced by photoexcitation to fail. Electron delocalization length (l_{del}) may well be comparable with Onsager radius or with thermalization length. One-D character of motion prevents escaping of electrons from geminate recombination (in low electrical field) even at the $e-h$ distances which are much longer than Onsager radius.

In the present talk the experimental data which include dependencies of the photocurrent on the voltage, intensity of excitation, and magnetic field strength published

previously¹⁻⁴ are discussed. The results have shown that the magnitude of l_{del} to be of the order of tens Å for polydiacetylene single crystal (PTS) and for poly(arylene vinylenes) films. High values of l_{del} permit to suggest the existence of delocalized charge transfer states where electron and hole are situated on the neighbor parallel chains. Separation of e-h pairs in low electrical fields in polymers is a result of diffusive one-dimensional motion of charges from the points of their origin to sinks. The role of the latter may be played by traps and recombination centers, electrons (or holes) from different pairs, failures of 1-dimensionality or, only in perfect 1-D systems, electrodes. Recombination of an electron (or hole) with a hole (or electron) from different pairs leads to appearance of free carriers. That feature of quasi-1-D polymers reveals itself in the dependence of the photo current on the intensity of excitation I at high enough intensities of the type $i_{ph} \sim I^{2/3}$ instead of $i_{ph} \sim I^{1/2}$ what is usual for 3-D systems.

PHOTOGENERATION OF CHARGES IN POLYMERS

Bulk photoconductivity of polydiacetylene-bis(toluene sulfonate) (PTS) single crystals was excited within the range $3 > h\nu > 1.0$ eV. The ratio of the charge carrier mobilities along and across the polymer fibers (\vec{b} axes) was 50 to 100. Silver paste electrodes were applied to the crystal edges so that the electric field E was directed parallel or perpendicular to the polymeric fibers. The experimental details are described elsewhere¹⁻². Photoconductivity of other polymers (poly(*p*-phenylene vinylene) (PPV) and two derivatives, poly(1,4-phenyl-1,2-dimethoxyphenyl vinylene) (DMOP-PPV) and poly(2-phenyl-1,4-phenylene vinylene) (PPPV)) was studied in³⁻⁴. The samples of the polymers were in the form of thin unoriented films and surface electrodes were applied. Features of the photogeneration of free charge carriers in quasi-1-D system are considered below.

(1) Quantum yield of free carriers in 1-D system was expected to be strongly electrical field dependent⁵

$$\varphi \sim E/E_0 \exp(-r_0/r) \quad (1)$$

Here $E_0 = e/\epsilon r^2$, r is a thermalization length of charge carriers and $r_0 = e^2/\epsilon kT$ is Onsager radius. However Eq. (1) is valid only for pure 1-D system. If trapping or/and recombination of carriers in the bulk of the quasi-1-D sample is taken into account φ becomes field independent at low fields¹⁻² (traps act as an effective field $E_{eff} = 4kT/eL$, where L is a diffusion length):

$$\varphi \sim \frac{1}{L} \left[\left(\frac{\alpha}{4} \right)^2 + 1 \right]^{1/2}, \quad \alpha = \frac{e E L}{k_B T} \quad (2)$$

This expression for quantum yield is obtained in¹⁻² by solving the steady state equation in 1-D for total density of charge carriers. Here E is an electrical field strength and $L = \frac{2 D^{1/2}}{(k'N + k''n)^{1/2}}$ is a diffusion length of an electron along the molecular chain direction before it gets trapped or recombines with free charge; N and n are the densities of traps and free charges and k' , k'' are appropriate rate constants respectively.

Comparison with experimental results obtained for PTS¹ and PPPV³ was possible if plots of $\varphi \sim i_{ph}/E$ vs E were considered. For polydiacetylene the best fit was obtained by Eq.(2) with $L = 1600 \text{ \AA}$, and for PPPV with $L = 520 \text{ \AA}$. In the latter case in connection with random distribution of 1-D regions with respect to the direction of the external field E an effective average electric field $E_{av} = 0.4 E$ was taken into account.

(2) As it is seen from Eq.(2) the quantum yield φ in Q-1-D system is recombination rate dependent: $\varphi = \varphi(n)$. At high intensity the length L becomes small enough and $\varphi \sim n^{1/2}$. In steady state conditions for the density of free charge carriers one can write

$$\frac{dn}{dt} = G \varphi(n) - k'N n - k''n^2 = 0 \quad (3)$$

The feature of Eq.(3) is that the dependence of the steady state photo current on the ionisation rate G is linear at

low values of G and tends (when the light intensity increases) to obey the law $i_{ph} \sim n \sim G^{2/3}$ instead of the usual law $i_{ph} \sim G^{1/2}$, ($G \sim I$). Experimental results (i_{ph} vs I) which confirm the " $2/3$ " law are available elsewhere¹⁻².

(3) Quantum yield ϕ in PTS is polarization dependent¹: for quantum energy $h\nu < 1.9$ eV $\phi_{\perp} / \phi_{\parallel} \approx 5$; for $h\nu > 2.1$ eV $\phi_{\perp} / \phi_{\parallel} \ll 1$. Subscripts \perp and \parallel denote the polarization of light along or normal to the chain direction. We assume that in the \perp -case the initial excited states are formed as a result of hopping of electrons excited by light to the next chain. When an electron is initially excited in the chain direction (\parallel -case) 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 is a distance of initial intrachain electron-hole separation the higher is the probability of forming an interchain excited pair. Unfortunately it is impossible to perform this kind of experiment on nonoriented polymeric films.

(4) As a rule, the process of free-carrier formation due to photoexcitation in molecular crystals and polymers with conjugated bonds characterized by a low mobility of charge carriers is considered within the Onsager model. The alternative model suggests that an electron-hole pair forms a quantum-mechanical system of a Wannier-Mott exciton type in which a delocalized electron possesses of a certain kinetic energy and can exist in various energetic states. The regions of electron-hole exchange interaction in these models are different: in the first model this region is of the size of intermolecular distances (several Å), whereas in the second model it is of the size of an electron orbit radius in the exciton (dozens of Å). Experiments that permit to reveal the role of the exchange interaction distance and thus evaluate the delocalization length of the charge carriers are directly associated with a magnetic field effect on photocurrent.

MAGNETIC FIELD EFFECT ON THE PHOTOCONDUCTIVITY

The magnetic field effect on photoconductivity is associated with the dependence of the geminate charge-carrier recombination on the spin state of electron-hole pairs. Under the action of light, the electron-hole pairs are formed in the spin state that was possessed by the system prior to its excitation (usually in the singlet state). The hyperfine interaction in one or in both pair members mixes the singlet and triplet states, the degree of the mixing being dependent on the external magnetic-field strength H . The experimentally observed relative variations in the photocurrent as a function of H , $\Delta i/i = [(i(H) - i(0))/i(0)]$ for all the samples studied have the form of stepwise curves^{1,6}. This indicates that spin evolution occurs in the states without exchange interaction. However one cannot neglect an important role played by the exchange interaction in the magnetic field effect. The exchange interaction is responsible for the selection of the spin states during a short but close enough approach of the pair particles and this determines the different recombination rate constants for singlet and triplet states of the pair. Since the magnetic field effect is studied by measuring photocurrent variations proportional to the free carrier density, then upon the particle approach and the spin "check" in the region of the exchange interaction dissociation of the pair should take place. Temperature dependence of MFE is caused by the activation character of that dissociation and permits to evaluate important parameters - the activation energies and interchange distance r_{exch} at which the exchange interaction determines the behavior of the pair. Activation energies obtained are ΔE_1 and ΔE_2 , the first one being connected with difference between energies of $e-h$ pair in exchange interaction and spin evolution regions, and the second one connected with an energy of dissociation of the pair in the spin evolution region and production of free charge carriers. The above consideration was applied to PTS single crystal and to other polymers studied³. One obtained for PTS $\Delta E_1 = 0.12$ eV

$\Delta E_2 = 0$; for PPPV $\Delta E_1 = 0.07$ eV, $\Delta E_2 = 0.16$ eV; for DMOP-PPV $\Delta E_1 = \Delta E_2 = 0.15$ eV. For PTS one could evaluate lower limit of $l_{del} > 2r_{exch} \approx 70$ Å. For poly(phenylen vinylenes) $l_{del} \approx 60$ Å. The comparably large value of l_{del} gives us a basis to consider the lowest energy state of the e-h pair as delocalized CT exciton of the Wannier-Mott type. Polymer chains in microscopic scale (to hundreds Å) are situated in a perfect order and one can speculate that such an exciton belongs to two parallel chains one the charges being trapped by some defect on the chain and another delocalized. The size of the exciton may be evaluated from the temperature dependence of MFE which gives values of r_{exc} equal to 35, 27, 20, and 15 Å for PTS, PPV, PPPV, and DMOP-PPV respectively. Values of r_{exc} obtained are quite comparable with electron thermalization length usually used in the Onsager model of charge separation. This makes us to consider the applicability of the model to conjugated polymers questionable.

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