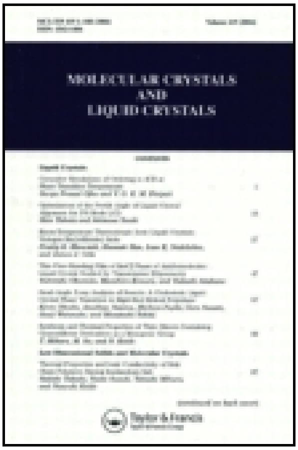

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ELECTRON DELOCALIZATION LENGTH IN ORGANIC SEMICONDUCTORS AND MAGNETIC FIELD EFFECT

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Abstract New method is suggested and applied for an estimation of the delocalization length of charge carriers in photoconductive polymers based on the magnetic field effect (MFE) on the photoconductivity (PC). The method was applied to photoconductive polymers PTS, PPV, PPPV, DMOP-PPV and has permitted to estimate delocalization lengths as large as 60 Å. It makes questionable the usage of Onsager's model of charge separation for conjugated polymers (CP).

INTRODUCTION

The MFE on the PC is associated with the dependence of the geminate charge carrier recombination on the spin state of the e-h pair[1]. A scheme of charge carrier photogeneration illustrating the role of the spin state is shown in Fig.1. Under the action of light, the e-h pairs are formed in the spin state that was possessed by the system prior to its excitation. The hyperfine interaction (HFI) in one or both pair members mixes the singlet (S) and triplet (T) states, the degree of mixing being dependent on the external magnetic field strength H. Fig. 1 shows

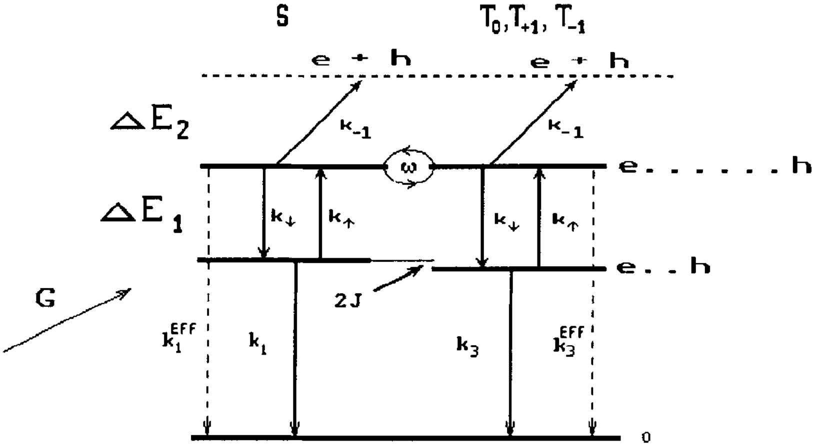

FIGURE 1 A scheme of energy transitions between different regions of the evolution of the e-h pair. Broken line shows an energy level of free charges. Levels (e.....h) and (e + h) may coincide ($\Delta E_2 = 0$).

the mixing as intersystem crossing between S and T states occurring at the frequency $\omega(H)$. The experimentally observed relative changes in the photocurrent as a function of H, $\Delta i_{ph}/i_{ph} = [(i_{ph}(H)-I_{ph}(0)]/i_{ph}(0)$ have the shape of stepwise curves. This indicates that spin evolution takes place in the states without exchange interaction (EI). EI is responsible for the "selection" of the spin state during a short but close enough approach of pair particles and this determines the different values of the rate constants k_1^{eff} and k_3^{eff}. Since the MFE is studied by measurement i_{ph} which is proportional to the free carrier density, then upon the spin "checking" in the EI region, a probability of the pair redissociation should attain a considerable value. One can distinguish three main regions of the e-h pair evolution: (i) EI region (e..h); (ii) spin evolution in the absence of the EI (e.....h); (iii) free charge carrier (e + h). Since the process of charge separation takes place inside the Coulomb well each of these regions is associated with certain energy of Coulomb interaction. An opportunity to determine activation energies of transitions between corresponding states of the pair, ΔE_1 and ΔE_2, is connected with the measurement of the temperature dependence of the MFE on the PC. The spatial distribution of the regions and wave functions of e and h are shown schematically in the Fig.2.

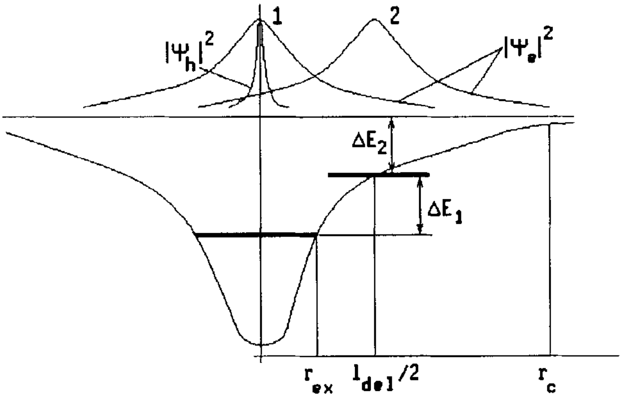

FIGURE 2 Energy and positions of delocalized charges when approaching each other. Two main positions are shown: (1) with maximum EI and (2) with a small EI. r_c is the Onsager radius.

We applied this method to a number of photoconductive CP and have arrived at the conclusion about high values of l_{del} which were as large as 60 Å. As l_{del} has occurred to be comparable with r_c the application of O's model of initial charge separation to CP becomes questionable.

EXPERIMENTAL

Structure of polymers is shown in Fig. 3. Samples of polymers PPPV and DMOP-PPV were prepared by drying the appropriate solutions in chloroform on the quartz support. Dried layers of polymers had molecular masses M = 9000 and 19200 respectively. Surface Al electrodes were deposited by vacuum evaporation. Samples of PPV were prepared in two stages: (i) drying of the water solution of the precursor on Teflon support and (ii) warming up of the layer at 200°C in vacuum for three days. Silver paste electrodes were applied. A Xe lamp was used as a light source and glass filters have cut an appropriate spectral band. DC magnetic field was switched on and off and corresponding changes Δi_{ph} of the i_{ph} were monitored. All the measurements were made on the samples under vacuum in the temperature range from 100 to 350 K.

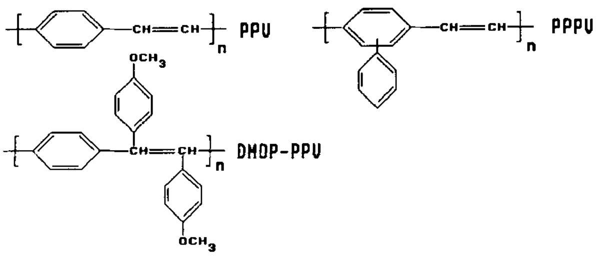

FIGURE 3 Structure of the polymers studied.

RESULTS

Fig.4 shows the plot of the ratio i_{ph}/E (which is proportional to the rate of the free charge carrier production) against the electric field strength E. Temperature dependencies of MFE for three polymers are shown in Fig. 5. The feature of all the curves $\Delta i_{ph}/i_{ph}(T)$ consists in the presence of a maximum at the relatively low T.

DISCUSSION

MFE and Delocalization Length

The general theoretical formula for MFE on the PC (when H ≫ HFI) was derived[2,3] in accordance with transitions shown on the scheme (Fig.1). The only supposition used was that $k_{1,3} \gg k$[illegible]:

$$\Delta i_{ph}/i_{ph} = K/[(1 + Ak_{\spadesuit})(1 + Bk_{-1}) + Bk_{-1}] \qquad (1),$$

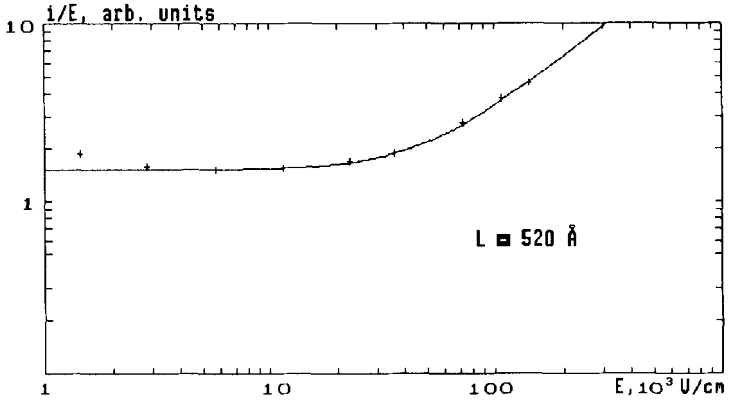

FIGURE 4 The dependence of the ratio i_{ph}/E in a.u. on the E. Wavelengths between 450 and 550 nm. Solid curve is calculated by 1-D formula (4) with L = 520 Å.

where K, A, and B are temperature independent parameters. The possible temperature dependence of the MFE can be connected with rate constants $k_{\spadesuit}$ and k_{-1} which are expected to be activated. Considering diffusion motion of charges one can readily obtain that at mobilities of the order of 10^{-3} to 10^{-4} $cm^2/(V\ s)$ the spin evolution region will be inside the Coulomb well at the intercharge distances less than r_c. It is a reason for an activation character of the rate constant $k_{-1} = k^{o}_{-1}\exp(-\Delta E_2/kT)$. If the mobility of carriers is more than $10^{-1} cm^2/(V\ s)$ the spin evolution takes place outside the r_c and $\Delta E_2 = 0$.

The half sum $[l_{del}(e) + l_{del}(h)]/2$ gives a maximum separation between centers of charges in the EI region. Then an estimation of $l_{del}(e)$ (assuming $l_{del}(h) \approx 0$ and the Coulomb law is valid here) is given by

$$l_{del} = 2e^2/\varepsilon\Delta E_2 \qquad (2).$$

The state where the EI takes place precedes the recombination. One can estimate the radius of this intermediate charge transfer state as

$$r_{ex} \approx e^2/\varepsilon(\Delta E_2+\Delta E_1) \qquad (3).$$

Low limit for l_{del} may be obtained from (3) as $l_{del} > 2r_{ex}$.

The above consideration was applied to the results obtained earlier on the PTS[4] and on the polymers studied here. Using formula (1) and accounting the activation character of k_{-1} and $k_{\spadesuit}$ one can fit the curves shown in Fig.5 with ΔE_1 and ΔE_2 as parameters. One obtained for PTS ΔE_1=0.12 eV, ΔE_2=0; for PPV ΔE_1=0.03 eV, ΔE_2=0.14 eV; for PPPV ΔE_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 only lower limit of $l_{del}>2r_{ex}$. For polyphenylenvinylenes $l_{del} \approx 2e^2/\varepsilon\Delta E_2$ and for $\varepsilon=3$ $l_{del} \cong 60$ 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 (upto hundreds Å) are situated in a perfect order[5] and one can speculate that such an exciton belongs to two parallel chains one of the charges being trapped by some defect on the chain and another delocalized. The size of the exciton may be evaluated by formula (3) which gives values of r_{ex} equal to 35, 27, 20, and 15 Å for PTS, PPV, PPPV, and DMOP-PPV respectively. Values of r_{ex} obtained are quite comparable with electron thermalization length usually used in the O's model of charge separation. This makes us to consider the applicability of the model to CP questionable.

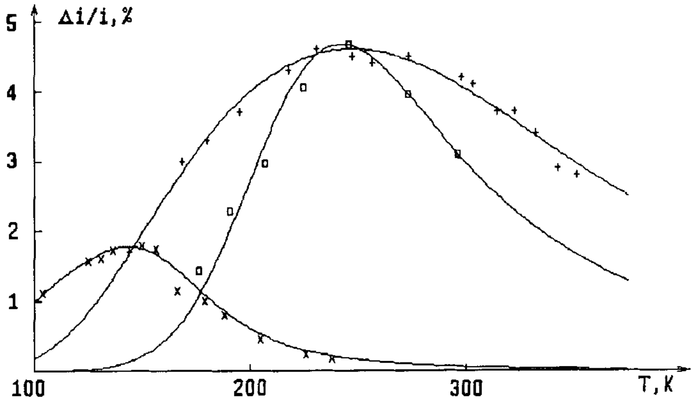

FIGURE 5 Temperature dependence of the MFE. (x) for PPV,(+) for PPPV, (□) for DMOP-PPV. H ≅ 1 kOe. Wavelengths: 475 nm; 450< λ < 550 nm and 450 < λ < 700 nm respectively. Solid curves are calculated by formula (1). See text.

On the Dependence of Free Carrier Yield on Electric Field

It is known[6] that 1-D version of the Onsager's theory anticipates linear dependence of escape probability φ on E. Experimentally dependence of φ on E may be measured as a function of i_{ph}/E on E (see Fig.4). Such an approach is valid only if it was shown that charges recombine in the bulk of the material before they can reach the electrodes[7]. Measurements of the i_{ph} on the samples with different interelectrode gaps have shown that it is the case for the materials studied.

Fig.4 shows the behavior of φ (E) for PPPV. That can be described neither by 1-D nor by 3-D O's models. In the latter case it leads to unreasonable values of parameter r_c. To rationalize the results we suggest that separation of charges occurs within microscopic 1-D regions. This model was suggested earlier[4,8] for PTS and we believe it may be applied to microcrystalline polymer materials as well. The only necessary correction which has to be made is connected with random distribution of 1-D regions with respect to the direction of the E. But we can use the effective electric field $E_{eff} = 0.4$ E acting along the polymer chain in each microcrystal. In such a case 1-D formula[4] is valid:

$$\varphi \sim 1/L\ \{[eE_{eff}L/(4kT)]^2 + 1\}^{1/2} \qquad (4).$$

Here L is a diffusion length, which accounts an irreversible flow of charges from the region of geminate recombination. It gives a good fit for points in Fig.4 if L=520 Å ($L/r_c \cong 3$) is used. This value of L gives the size of the pair in the microcrystalline 1-D region of the polymer.

CONCLUSIONS

The l_{del} of electrons in CP studied is shown to be fairly large and is comparable with r_c. It makes the applicability of 1-D or 3-D O's theory of charge separation questionable.

Delocalized interchain CT exciton is suggested as candidate for the intermediate state in the mechanism of free charge carrier generation.

As a rule the size of the pair exceeds the r_c. Diffusion and drift of carriers in 1-D in the presence of sinks outside the Coulomb well describe the dependence of the yield of free carriers on E satisfactorily.

REFERENCES

1. Ya.B.Zeldovich, A.L.Buchachenko and E.L.Frankevich, Soviet Physics - Uspekhy, 31, 385 (1988).
2. E.L.Frankevich, A.A.Lymarev and I.A.Sokolik, Khimicheskaya Fizika (Chemical Physics), 9, 1361 (1990).
3. E.L.Frankevich, I.A.Sokolik and A.A.Lymarev, Synth. Met., 41-43, 213, (1991).
4. E.L.Frankevich, I.A.Sokolik and A.A.Lymarev, Mol. Cryst. Liq. Cryst., 175, 41 (1989).
5. D.D.C.Bradley, J.Phys.D: Appl.Phys., 20, 1389 (1987).
6. R.Habercorn and M.E.Michel-Beyerle, Chem.Phys.Lett., 23, 128 (1973).
7. E.L.Frankevich, A.A.Lymarev and I.A.Sokolik, J.Phys.: Condens.Matter, 1, 5541 (1989).
8. E.L.Frankevich, A.A.Lymarev and I.A.Sokolik, Chem.Phys.Lett., 159, 113 (1989).