Initial spatial distribution of geminate charge carriers photogenerated in doped conjugated polymers

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A B S T R A C T

A diffusion model of the charge carrier photogeneration in doped conjugated polymers is suggested. A dissociation of a vibrationally relaxed exciton into a Coulombically bound geminate pair of charges occurs at a charge transfer center which consists of a conjugated segment of a polymer chain and a nearby dopant molecule. A photogenerated hole executes one-dimensional diffusion motion along the conjugated segment in the on-chain potential well formed by the Coulomb and external electric fields. Holes are assumed to become localized in trapping sites. It is shown that the spatial distribution of trapped holes is determined mainly by effective temperature of pretrapped holes and external electric field. The model is consistent with experimental data on photoconduction of a copolymer of a phenyl-substituted poly-phenylenevinylene doped with trinitrofluorenone, which have been reported by Weiter et al. (2004). Effective temperature of holes is evaluated at about 1200 K.

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1. Introduction

The mechanism of charge carrier photogeneration in conjugated polymers is a subject of discussion for last three decades. A quantitative understanding of kinetics of primary stages of charge generation and separation following light absorption in polymers is important for improving the performance of organic solar cells and for development of new materials for organic optoelectronic devices.

It has been established that the photogeneration of free charge carriers in conjugated polymers, as well as in organic molecular crystals, is a multi-step process [1–4]. At first, absorption of light leads to creation of excitons, neutral electronically excited states of conjugated segments of polymer chains. One of the pathways of the non-radiative exciton decay is dissociation into a Coulombically bound pair of geminate charges of opposite signs, electron and hole (also called the charge transfer state, or the geminate polaron pair). It is assumed that geminate charges are rapidly trapped in localized states. Further dissociation of geminate charges to free charge carriers occurs by thermally activated jumps of holes from one localized state to another in the joint Coulomb and external electric fields. This latter stage can be described in the Onsager diffusion model [5], or it can be studied by the Monte Carlo simulation [6–10]. The geminate trapped charges have an

initial distribution of separation distances that determines the quantum yield of free charge carriers. The basic challenge is to understand what parameters determine the initial spatial distribution of geminate charges formed as a result of exciton dissociation. The goal of the present study is to find the initial spatial distribution of trapped charges produced by exciton dissociation on a charge transfer center, which consists of a conjugated segment of a polymer chain and an adjacent dopant molecule (electron acceptor) or a deep electron trap. Among the systems which have been investigated, the study of conjugated polymers doped with electron acceptors is of fundamental importance for the following reasons.

If the electron affinity of dopant molecules is large enough, dissociation of the vibrationally relaxed excitons becomes possible even at small excess photon energies [1]. This allows one to use experimental data on the photo-induced luminescence of the doped polymer for the simulation of the electron transfer from long-lived vibrationally cold excitons to dopant molecules. The study of the photoionization mechanism in doped polymers may be useful in understanding photoionization of pristine polymers, in which the concentration of unindentified impurities acting as electron scavengers (electron traps) has been estimated to be of the order of 0.1% [11]. In addition, conjugated polymers doped by insignificant amount of electron acceptors can be considered as a bridge to the bulk heterojunction layer in organic solar cells consisting of a polymer/acceptor blend with a high electron acceptor concentration.

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Arkhipov, Emelianova and Bässler [12] have suggested a quantum–mechanical model of the dopant-assisted carrier photogeneration. In their model [12], it is assumed that a hole is delocalized within the conjugated segment, in which it has been generated. The hole can escape from the on-chain potential well of the Coulomb field by thermally activated jumps. Menšik et al. [13,14] have modified the model [12] to describe photoionization in pristine polymers. They have assumed that exciton dissociation proceeds as an inter-chain electron transfer taking place in a location where two polymer chains approach each other in space. According to the model [12], the motion of a hole within the conjugated segment is considered as a transition between two states separated by the on-chain potential barrier: an initial delocalized state and a state located beyond the top of the potential barrier formed by the joint Coulomb and external electric fields. However, in polymers with low dielectric constant $\varepsilon \approx 3$ the characteristic width Δb of the on-chain potential barrier can be rather large: $\Delta b > 10$ nm at the strength of the external electric field $F < 10^5$ V/cm. It is apparent that a character of the motion of holes on the scale of 10 nm along the polymer chain determines the spatial distribution of trapped holes. On the other hand, the time resolved electrodeless methods of measurements, developed in the recent years, have revealed a fast on-chain transport in many conjugated polymers with the initial mobility of holes of 0.1–1 $cm^2\,V^{-1}\,s^{-1}$ followed by slower interchain transport [4,15,16]. Such a value of mobility is close to that of electrons and holes in molecular crystals, like the anthracene crystal, in which a mean free path of charges is assumed to be of the order of the lattice constant. This suggests the diffusion type of motion on the scale of 10 nm. So, for the problem of the exciton dissociation on a charge transfer center it is of interest to consider a diffusion intrachain motion of holes corresponding to the limiting case of small mean free paths.

In the present article, we propose a simple diffusion model for one dimensional (1D) motion of a hole along the conjugated segment, in which the hole is generated as a result of exciton dissociation on a charge transfer center. The model allows us to relate parameters of the intrachain transport of holes to the initial spatial distribution of geminate trapped charges. Below it is assumed that energy of electron transfer from exciton to an acceptor molecule can go to vibrations of the conjugated segment of polymer chain. According to the present notion of the transfer of vibrational energy in polyatomic molecules [17], we take into account that in the conjugated segment the vibrational excitation is not evenly distributed among a large number of intramolecular vibrations, but it can be transferred through the segment by several vibrational states. If the excess vibrational energy is conserved for sufficiently long time within that chain segment, in which a hole has been initially produced, this can result in enhanced effective temperature T_{eff} for intrachain motion of the hole, and hence in an increase of the fraction of holes trapped at large distances from their geminate negative charges localized on the acceptor molecules. So, the second goal of the present study is to estimate T_{eff} and to test the hypothesis that the excess vibrational energy is conserved in the polymer segments for sufficiently long time. For this purpose, the predictions of the developed model are correlated below with the results of measurements of free charge carrier quantum yield η in a copolymer of a phenyl-substituted poly-phenylenevinylene (PhPPV) doped by trinitrofluorenone (TNF), which have been reported previously by Bässler and co-workers [18,19]. It is shown that the field and temperature dependence of η obtained in [18,19] can be fitted by the theory at $T_{eff} \approx 1200 \pm 150$ K. It is concluded that the quantum yield of free charge carriers depends only weakly on intrachain mobility of holes at sufficiently large diffusion lengths.

2. Description of the model

We consider the initial stages of the charge photogeneration induced by absorption of light in the polymer matrix consisting of the array of the conjugated segments with length of $L = 5$–7 nm. After the vibrational relaxation, the electronically excited state S_1 (exciton) generated by optical excitation of polymer is assumed to dissociate at a charge transfer center into a geminate pair of charges consisting of a fast hole (h^+) on the conjugated segment and electron localized in a dopant molecule A (or in a deep trap)

$$S_1 + A \underset{k_{-et}}{\overset{k_{et}}{\rightleftharpoons}} (h^+, A^-) \tag{1}$$

where the brackets indicate that the hole and negatively charged molecule A^- are bound by the Coulomb attraction. The electron transfer from the S_1 state to acceptor molecule A in reaction (1) competes with other non-radiative and radiative pathways of the exciton decay (Fig. 1). We neglect below the reverse reaction in Scheme (1) (i.e. the formation of exciton S_1 due to the return electron transfer from A^- to h^+) because of the assumed large exothermicity of reaction (1). In particular, for the PhPPV film doped with TNF the free energy of direct electron transfer in reaction (1) can be estimated crudely as

$$\Delta E = E_{LUMO}(TNF) - E_{LUMO}(PhPPV) - e^2/(4\pi\varepsilon_0\varepsilon \cdot s) < -1.6\ \text{eV} \tag{2}$$

where $E_{LUMO}(PhPPV) = -2.3$ eV and $E_{LUMO}(TNF) = -3.9$ eV are the LUMO energy levels of PhPPV and, respectively, TNF with respect to the vacuum level [18], e is the elementary charge, ε_0 is permittivity of free space, $\varepsilon \approx 3.5$ is dielectric constant, and s is the distance between the dopant molecule and axis of the conjugated segment. In addition, we assume below that the main pathway of the hole decay is a capture by trapping sites rather than recombination with the ion A^- (Fig. 1). Although the recombination of h^+ and A^- with the formation of the ground electronic state of the chain segment is of course possible, the rate of such the process, as shown in Section 6, is far less than that of the hole trapping. Thus, geminate recombination of charges is assumed to occur only after the trapping of holes.

A hole becomes polaron very quickly remaining on the conjugated segment where it was produced. (We use names holes, fast holes, pretrapped holes, pretrapped charges or pretrapped polarons as synonyms in order to distinguish them from trapped charges.) Fast holes can be captured by traps forming positive trapped charges, also called trapped polarons or trapped holes [20]. Density of traps in the substituted derivative of poly-p-phenylene vinylene was found to be comparable to the density of
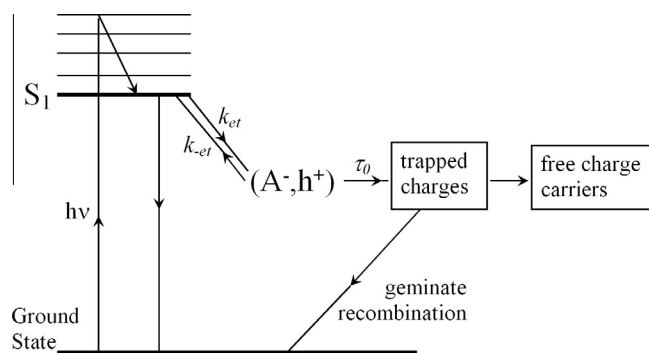

Fig. 1. The processes of light absorption, exciton dissociation on a charge transfer center, trapping of holes, recombination and dissociation of geminate trapped charges into free charge carriers.