INFLUENCE OF POLAR ADDITIVES ON THE HOLE MOBILITY IN POLY[(PHENYLENE)VINYLENE] COMPOSITES

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Introduction

Polymer materials are promising candidates for future organic electronic devices for new information technologies and nanoelectronics. Thus, the knowledge of the charge transport mechanism and relations between molecular and macroscopic properties of these materials are very important. Polymers are known to have rather disordered conformations. Therefore, the theoretical description of the charge carrier mobility should take into account disorder. Their properties can be readily modulated by polar additives. A classical model of charge transport in disordered organic solids was developed by Bässler [1]. It was based on charge carrier hopping among sites (point approximation) which are distributed in energy. Grozema et al. [2] found that the on-chain hole motion in poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (MEH–PPV) can be described using a continuous disorder type model, in which the site-to-site charge transfer integrals are randomized by the chain torsional disorder. In our previous paper [3], we have modified this model by introducing the site energy disorder $\sigma(\varepsilon_n)$ resulting from intermolecular interactions of the charge carrier with dispersed polar species. In this paper, the same model is used for the calculation of the on-chain hole states. The finding of the on-chain states density enables the modification of the Bässler hopping model for the description of the charge carrier hopping among the polymer chains. Note, that unlike the Bässler model this modification assumes the quasi-continuum of the charge carrier states on each polymer chain.

On-chain charge carrier states

In order to calculate the on-chain hole states, the polymer chains are modeled as sequences of N sites corresponding to the monomer units. The length N is taken as the average distance between chain defects breaking conjugation length rather than the real polymer chain length. The hole states on such a chain can be described within the tight-binding approximation by the Hamiltonian

$$H = \sum_{n=1}^{N}\left[\varepsilon_n a_n^+ a_n - b_{n,n+1}\left(a_{n+1}^+ a_n + a_n^+ a_{n+1}\right)\right] , \quad (1)$$

where a_n and a_n^+ are the annihilation and creation operators for a hole located at the n-th site, ε_n is the energy of this hole, and $b_{n,n+1}$ is the transfer integral between the sites n and $n+1$. Distributions of both molecular parameters ε_n and $b_{n,n+1}$ are influenced by the random structure of polymer chains and their surrounding, respectively (see Ref. [3] for details).

The density of the states of the valence band (see Fig. 1) was calculated by means of the solution of the time-independent Schrödinger equation using Hamiltonian (1). An increasing energetic disorder $\sigma(\varepsilon_n)$ leads to the broadening of the originally sharp valence band edge and formation of the tail states in the band gap. These states, with their relatively low density and weak connectivity, behave as localized states (for holes in this case).
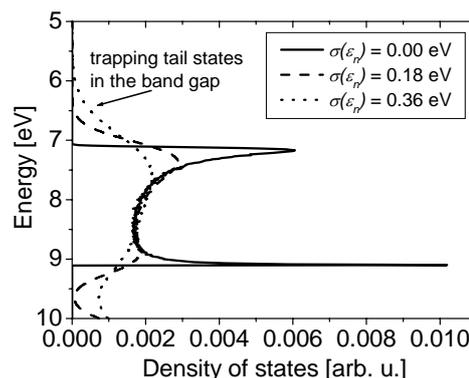

Fig. 1: Density of states in the pure ($\sigma(\varepsilon_n) = 0$ eV) and doped polymer ($\sigma(\varepsilon_n) = 0.18$ and 0.36 eV).

Inter-chain charge carrier hopping

Our inter-chain hopping model assumes a simplified polymer structure schematically depicted in Fig. 2. The polymer chains form a regular lattice; additive

molecules, which are not shown in this figure, are placed randomly in it. While the on-chain motion proceeds in one-dimensional space, the inter-chain hopping takes place in remaining two perpendicular directions. The inter-chain transfer is slow in the comparison with the hole thermalization, which occurs typically in times of several picoseconds. Thus, it is possible to expect full thermalization of the hole between two subsequent inter-chain hops. It means, the model assumes the following steps of the inter-chain hole transport: charge carrier transport to any possible state on the chain A, charge carrier thermalization over all possible states on the chain A, and finally, charge carrier hop to any possible state on one of the nearest neighbor chains B.
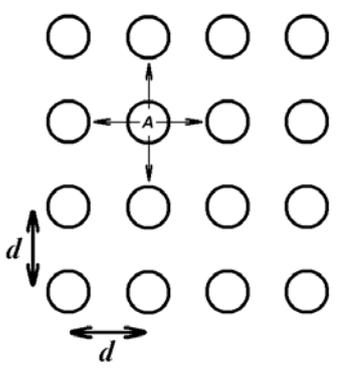

Fig. 2: Simplified polymer chain alignment considered in the hole transport model. Circles represent parallel equidistantly placed polymer chains. Much smaller additive molecules randomly dispersed among them are not shown. The possible charge carrier hops from the chain A are denoted by arrows.

The rate $v_{i \to j}$ for the hole hopping between an initial state i with the energy E_i on the chain A and a final state j with the energy E_j on an adjacent chain B is calculated according to semi-classical Marcus relation [4]. From the charge transfer rate $v_{i \to j}$ between two states i and j and the thermalization occupation probability p_i of the initial state i the charge transfer rates $v_{A \to B}$ between two adjacent chains A and B can be calculated. Determination of the charge transfer rates $v_{A \to B}$ makes possible to solve the master equation describing the hole motion and after Monte Carlo averaging to calculate the hole mobility μ (see Fig. 3).

The obtained results show a very strong dependence of the inter-chain hole mobility on the local energy disorder. Doubling the local energy disorder leads to a decrease in the inter-chain charge carrier mobility by several orders of magnitude. This change is much greater than the change of the on-chain charge mobility [3]. While the mobility in the polymer with the low value of the local energy disorder is frequency-independent, for higher values of the local energy disorder there is some increase of the charge mobility with frequency.
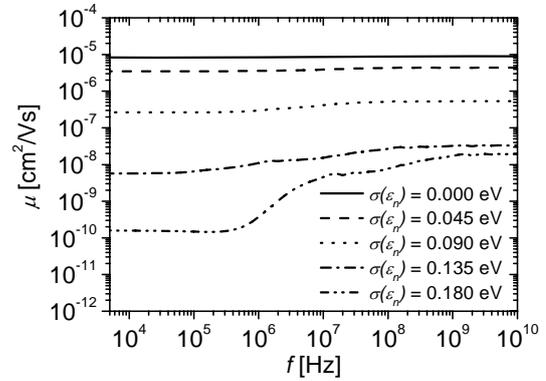

Fig. 3: Frequency dependence of the hole mobility $\mu(f)$ in MEH–PPV doped by a polar additive calculated for various values of the half-width of the local energy disorder $\sigma(\varepsilon)$. Hole reorganization energy was $\lambda = 0.4$ eV.

Acknowledgement

Reference

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