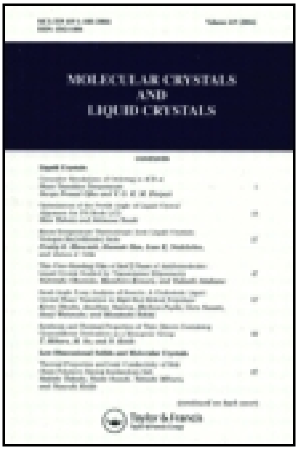

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Modeling of Hole Transport in Poly[2-Methoxy-5-(2′-Ethylhexyloxy)-p-Phenylene Vinylene] Doped with Polar Additives

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The theoretical model of the hole mobility in poly[2-methoxy-5-(2′-ethylhexyloxy)-p-phenylene vinylene] doped with a photochromic polar additive is proposed. Our model involves description of the on-chain charge carrier states, charge carrier thermalization, and inter-chain hopping. While the on-chain states are calculated by means of quantum mechanical methods, the semi-classical Marcus approach is used for the description of inter-chain hopping. The dependence of the mobility on several parameters of the model is studied. The results predict the possibility to construct an efficient optoelectronic switch based on a polymer doped with a photochromic polar additive.

Keywords: charge transport; conjugated polymers; marcus theory; monte carlo modeling; photochromism

INTRODUCTION

Conjugated polymers, like poly[2-methoxy-5-(2′-ethylhexyloxy)-p-phenylene vinylene] (MEH–PPV), attract considerable scientific attention for their potential applications in molecular optoelectronic

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devices. Their semiconducting properties can be utilized in the construction of gas sensors, solar cells, field-effect transistors, electroluminescent diodes, etc. [1–3]. For the efficient function of these devices the charge carrier transport plays an important role [4]. Thus, the mechanisms of conductivity in organic materials are currently intensively studied.

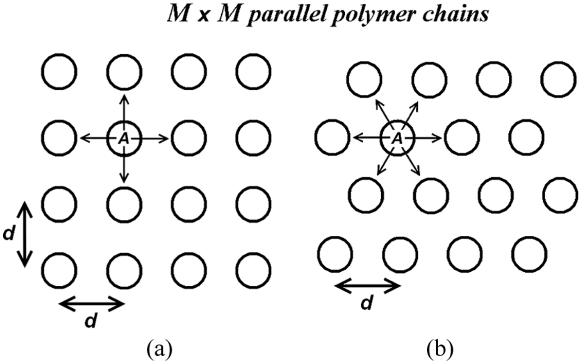
Charge carrier transport in polymeric materials consists of charge moving through the chain (molecular wire) and of inter-chain hopping [5]. The charge transport along the poly(p-phenylene vinylene] (PPV) chain was theoretically described by Grozema *et al.* [6,7] using tight-binding approximation model. They have found that on-chain charge carrier mobility is governed by the structural (torsional) disorder of the main chain, giving rise to a distribution of transfer integrals between the polymer repeating units. It is known that the main chain transport of conjugated macromolecules may be strongly influenced by attaching polar side groups or by admixing polar additives [8–10]. In our previous paper [11], we have studied photoswitching of the on-chain hole transport in MEH–PPV doped with the photochromic additive 6-nitro-1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indoline]. Upon irradiation with light of an appropriate wavelength, this molecule undergoes a ring-opening reaction from the closed form of spiropyran (SP) to the open merocyanine form (MR) [12]. The reversible SP ↔ MR reaction is accompanied by a charge redistribution resulting in a significant increase of the dipole moment of the molecule. We have found, that the introduction of polar species results in a broadening of the distribution of charge carrier site energies (energetic disorder), and consequently decrease of the on-chain hole mobility. The aim of this paper is to continue the theoretical studies of this molecular system and put forward the theoretical model of the photo-induced modulation of the inter-chain hole transport.

DESCRIPTION OF THE CHARGE TRANSPORT MODEL AND BASIC STRATEGY OF CALCULATION

The MEH–PPV is amorphous material consisting of disordered polymer chains. Although without polar species dispersed in the polymer the individual repeating units possess charge carrier site energies given essentially by their chemical structure (i.e., phenylene and vinylene), the structural disorder of a polymer chain induces random distribution of the energies of the on-chain energetic states, in which the charge carrier can be found. Since the polymer chains are twisted and kinked and possess many chemical defects, the mutual positions of the chain are also highly disordered. If the polymer is doped by polar species, the site energies of individual repeating units change and form a random Gaussian distribution. This energetic disorder of the site energies broadens the energetic distribution of the on-chain charge carrier states.

It is hardly possible to describe the charge carrier transport completely from the first principles. Our model is aimed at description of the influence of the energetic disorder on the charge carrier mobility. For these reasons, the energetic structure of charge carrier chain states is described on quite good level, while the description of the mutual arrangement of the polymer chains is simplified. The simplified polymer structure is schematically described by an array of equidistantly placed parallel polymer chains of a given length N (see Fig. 1). Two polymer chain alignments, see Figures 1 (a) and (b), considering four or six nearest neighboring chains, respectively, are studied. The additive molecules are randomly placed among these chains without further specifications of their positions and orientations. Each polymer chain is characterized by the set of its eigenstates, in which a charge carrier is localized. No correlation among chains is assumed. Only the hops between nearest neighbor chains are taken into account.

Since MEH–PPV main chain is conjugated, it is possible to assume that on-chain charge motion is faster than the inter-chain one. This fact enables us to separate the intra- and inter-chain hole transport. The interactions between moving charge carriers and polymer chain result in the fast energy relaxation of the moving charge carriers and the loss of the coherence. For these reasons, the inter-chain



(a) (b)

FIGURE 1 Two polymer chain alignments considered in the inter-chain hole mobility modeling. The possible charge carrier hops from a given chain A are denoted by arrows.

charge carrier motion can be considered as semi-classical hoping among the charge carrier chain states. Thus, the charge transfer rates $\nu_{A\to B}$ between the neighboring chains A and B can be calculated using Marcus theory.

Determination of the $\nu_{A\to B}$ values makes possible to write the master equation describing the charge carrier motion in the form

$$\frac{dP_A(t)}{dt} = \sum_B \nu_{A\to B} P_B(t), \tag{1}$$

where $P_A(t)$ and $P_B(t)$ are the probabilities of finding the given charge carrier on the chains A and B, respectively, in time t. At $t = 0$ the charge carrier is assumed to be localized on a single chain, i.e., $P_0(t = 0) = 1$ and all other P_A are equal zero. It is important to select this initial localization of the charge carrier with regard to the distribution of thermal equilibrium probabilities. Once the time evolution of $P_A(t)$ is determined, the mean-square displacement $\Delta^2(t)$ of the charge carrier in the direction perpendicular to the chain segments can be calculated as

$$\Delta^2(t) = \sum_A i_A^2 d^2 P_A(t), \tag{2}$$

with d being inter-chain distance and $i_A d$ the projection of the distance of the chains "A" and "0" to the direction of the electric field. This quantity was averaged over at least 100 different Monte Carlo realizations of the disordered polymer chains to achieve numerical stability. The mean-square displacement $\Delta^2(t)$ is related to the frequency-dependent charge carrier mobility by the Kubo formula [13]

$$\mu(\omega) = \frac{-e\omega^2}{2kT} \mathrm{Re}\left[\int_0^\infty \Delta^2(t)\exp(-i\omega t)dt\right], \tag{3}$$

where e is the elementary charge, k is the Boltzmann constant, T is the temperature, and $\omega = 2\pi f$ is the radian frequency of the external field.

DETERMINATION OF THE ON-CHAIN CHARGE CARRIER STATES

In order to calculate the hole states, the polymer chains are modeled as sequences of N sites corresponding to the repeating units. The length N corresponds to the average distance between chemical defects breaking the conjugation rather than the real polymer chain length. For simplicity, all polymer chains in our model possess the same length N. The hole states on such a chain can be described within the tight-binding approximation by the Hamiltonian

$$H = \sum_{n=1}^{N} \left[\varepsilon_n a_n^+ a_n - b_{n,n+1}\left(a_{n+1}^+ a_n + a_n^+ a_{n+1}\right)\right], \tag{4}$$

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. The distribution of transfer integrals $b_{n,n+1}$ was calculated according to Grozema *et al.* model [6]. In the materials without polar or ionic species, the site energies ε_n are essentially equal to the ionization potentials of the isolated polymer repeating units and can be calculated using standard quantum chemical methods. In the polymer doped by polar species, the site energies can be calculated within the frozen orbital approximation

$$\varepsilon_n = \varepsilon_n^{(0)} + < HOMO| \sum_i \Delta\phi_i |HOMO >, \tag{5}$$

where $\varepsilon_n^{(0)}$ is the site energy of an isolated repeating unit and $\Delta\phi_i$ are the electrostatic potentials describing the charge–dipole interactions of a hole localized at highest occupied molecular orbital $|HOMO>$ with all surrounding polar species. Since the positions and orientations of the additive with respect to the polymer chain are essentially random, the effect results in the broadening of the distribution of transport states. The most important parameter of this distribution is its half-width, proportional to the standard deviation $\sigma(\varepsilon)$ of the site energies from its average value. Another very important characteristics of this distribution influencing the charge transport is the site to site energy correlation, which effectively reduces $\sigma(\varepsilon)$. The correlation coefficient between the ε_n values corresponding to the nearest neighboring centers is in the modeled case 0.97. There is a strong correlation between up to about tenth nearest neighboring sites. This fact can be explained by the long-range character of the charge–dipole interactions.

In order to estimate the change of $\sigma(\varepsilon)$ during the spiropyran photochromic reaction, the equilibrium molecular conformations of SP and MR were calculated by means of the Hartree-Fock (HF) method. It was found, that the reaction SP $\leftrightarrow$ MR is accompanied by a redistribution of the atomic charges, and consequently by a change of the dipole moment from 5.5 D (SP form) to $11 \div 12$ D (MR form). While the value obtained for SP is close to reality, the dipole moment of MR is probably underestimated since the polar environment increases the zwitterionic character of MR. Bletz *et al.* [14] reported the dipole moment of MR measured in a polar environment to amount to $15 \div 20$ D.

The electrostatic potential $\Delta\phi_i$ was calculated for several different mutual positions and orientations of the MEH–PPV oligomer and an SP/MR additive molecule by the HF method. For each position the distance between the chain and additive was determined on the basis of the van der Waals atomic radii. The HOMO orbital of MEH–PPV as well as HOMO orbitals of its oligomers of any length are localized along the main chain. For this reason, it is enough to calculate electrostatic potentials $\Delta\phi_i$ only along the main chain approximated by a line going through C=C bonds of vinylenes and crossing phenylenes through their centers. After statistical evaluation of the calculated electrostatic potentials $\Delta\phi_i$, the standard deviations $\sigma_{SP}(\varepsilon) = 0.08\,\mathrm{eV}$ and $\sigma_{MR} = 0.14\,\mathrm{eV}$ of the site energies in MEH–PPV oligomer in the vicinity of a SP and MR molecule, respectively, were determined. These values provide the estimate of the broadening of the site energy distribution caused by *an individual* randomly placed and oriented additive molecule (taken as a non-point dipole). Thus, the calculation gives the ratio $r = \sigma_{MR}(\varepsilon)/\sigma_{SP}(\varepsilon)$ of the standard deviations of the ε_n distributions for MR and SP around 1.75 (the estimate for point dipoles 11.9 and 5.5 D yields the ratio equal to 2.16). However, it is possible to expect that the real broadening of the site-energy distribution is for MR even higher than the calculated one because of its above-mentioned increased zwitterionic character due to polar environment. Taking into account both effects one can expect at least two-fold increase of the energetic disorder during the SP → MR photochemical reaction.

Subsequently, the total effect of *all* additive molecules with a given dipole moment m on the site energy distribution was calculated. Randomly oriented additive molecules, modeled here as point dipoles, were randomly placed in the vicinity of the chain. It was assumed that no additive molecule can be placed at the distance shorter than 10 Å from the chain (this value was estimated from the chemical structures of MEH–PPV and SP/MR). On the other hand, the influence of the additive molecules distant more than 50 Å from the polymer chain was neglected. The concentration of the additive was taken to be $c = 1 \times 10^{-4}\,\text{Å}^{-3}$. Then, for each repeating unit, the energetic disorder was calculated as a sum of Coulombic electrostatic potentials from all additive molecules. The energetic disorder of ε_n was calculated according to this model for several values of the dipole moment of the additive m. For a typical value of $m = 12$ D the standard deviation of the ε_n distribution is 0.18 eV. Since the mutual interaction of the additive molecules is neglected, the standard deviation of the ε_n distribution is proportional to the dipole moment m of the additive and to the square root of the additive concentration c. Note that this model of the ε_n distribution does not take into account the polarization effects of the reaction field of the dipoles.

Using the Hamiltonian (4) the time-independent Schrödinger equation can be written in the form

$$H|\varphi_i\rangle = E_i|\varphi_i\rangle. \tag{6}$$

The stationary states $|\phi_i\rangle$, are taken as superpositions of states $|n\rangle$ located at individual sites

$$|\varphi_i\rangle = \sum_{n=1}^{N} c_{i,n}|n\rangle. \tag{7}$$

Solution of the eigenstate problem yields the hole states $|\phi_i\rangle$ together with their energies E_i. Thus, the energy spectrum of the density of states of the valence band and the extent of the delocalization of the charge carrier states $|\phi_i\rangle$ along the polymer chain can be determined. An increasing energetic disorder $\sigma(\varepsilon_n)$ leads to the broadening of the originally sharp valence band edge and the formation of the tail states in the gap (see Fig. 2). These states, with their relatively low density and weak connectivity, behave as hole traps. Moreover, the energetic disorder increases localization of the charge carrier states and consequently decreases their connectivity.

INTER-CHAIN HOPPING

The inter-chain transfer is slow in comparison with the charge carrier thermalization, which occurs typically in times of several picoseconds. Thus, it is possible to expect full charge carrier thermalization over all states of the given chain A between two subsequent inter-chain hops. Therefore, our model assumes the following steps of the inter-chain charge carrier transport: charge carrier moving to any possible state on the chain A, charge carrier thermalization over all its possible states on the chain A, and finally charge carrier hop to any possible state on one of the nearest neighboring chains B.

Generally, fermions thermalize to the Fermi-Dirac distribution. However, under usual experimental conditions it is very improbable that there is more than one free charge carrier on a given conjugated chain segment. Hence, it is possible to consider thermalization to the

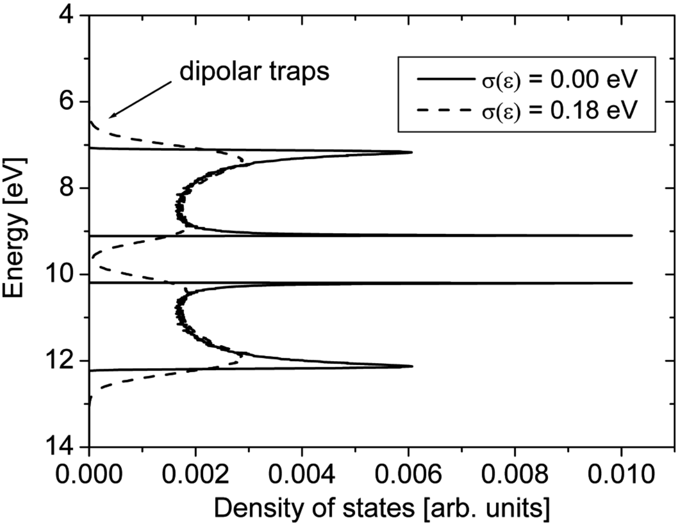


FIGURE 2 Diagram of the polymer valence band calculated for the as prepared polymer (no energetic disorder) and the polymer doped by polar species (energetic disorder $\sigma(\varepsilon) = 0.18\,\text{eV}$).

Boltzmann distribution

$$p_i(E_i) = \frac{\exp\left(\frac{-E_i}{kT}\right)}{Z(T)}, \tag{8}$$

where $p_i(E_i)$ is the probability of occupation of the state i at temperature T, E_i is the energy of state i, and $Z(T)$ is partition function over all states of the chain A.

The rate for 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 can be calculated according to semi-classical Marcus relation as

$$\nu_{i\to j} = \frac{J_{ij}^2}{\hbar}\sqrt{\frac{\pi}{\lambda_{ij}kT}}\exp\left[\frac{-\left(E_i - E_j - \lambda_{ij}\right)^2}{4\lambda_{ij}kT}\right], \tag{9}$$

where λ_{ij} is the charge carrier reorganization energy and J_{ij} is the effective charge transfer integral.

The reorganization energy and charge transfer integrals can be in principle calculated using standard quantum chemical methods. However, their values depend on the particular realizations of the spatial and energetic disorder of the polymer chains. For this reason, only

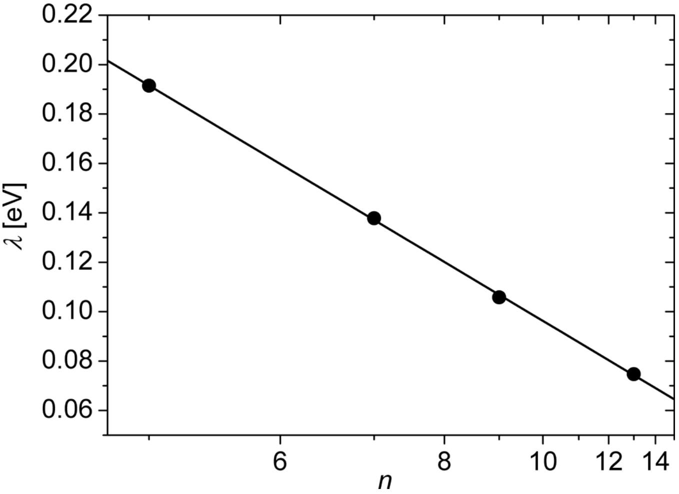


FIGURE 3 Dependence of the hole reorganization energy λ on the length of the oligo(phenylene vinylene). The oligomers were capped by phenyls. The length n indicates the number of phenylene units.

estimation of the typical values of these parameters from the calculations performed for simple model systems was done. Note, that generally the reorganization energy of a hole depends on the initial and final states due to the disorder and different delocalization of the states. However, this dependence was further neglected in our model ($\lambda_{ij} = \lambda$).

The reorganization energy λ can be separated into an inner (molecular) λ_i and outer (solvent) part λ_o. The inner reorganization energy is related to the change in geometry of the molecules induced by the charge transfer. For a hole hopping between two molecules of the same type λ_i is defined by the relation

$$\lambda_i = \left[E^+(g^0) + E^0(g^+)\right] - \left[E^0(g^0) + E^+(g^+)\right], \tag{10}$$

where $E^+(g^0)$ is the total energy of the cation with the equilibrium conformation of the neutral molecule and so on. Figure 3 shows the dependence of λ_i on the reciprocal length of the phenylene vinylene oligomers. Their conformations were optimized using B3LYP/3–21G$^{(*)}$ method [15] and no disorder was taken into account. For short ordered oligomers (about 5 repeating units), λ_i reaches values around 0.2 eV. On the other hand, the linear fit of the data indicates that the value of λ_i tends to zero for long ordered oligomers, for which the hole is highly delocalized. The chain disorder effectively reduces the conjugation and the orbital delocalization. Therefore it is possible to expect greater values of λ_i for disordered chains, than for the ordered chains of the same length. However for longer chain, λ_i can hardly exceed the value 0.2 eV calculated for the ordered phenyl-capped tetramer.

The solvent reorganization energy λ_o is often the dominant contributor in solutions [16]. On the other hand, in the solid-state environment the phonon-like modes are sufficiently stiff that local vibronic coupling should dominate [17]. For this reason, we approximate the total reorganization energy λ by the inner reorganization energy λ_i. We estimate its value for real disordered MEH–PPV chain to be between 0.05 and 0.4 eV. These values are consistent with the values determined by Prins *et al.* [18] for similar phenylene-vinylene derivatives.

The transfer integral $J_{\alpha\beta}$ between the corresponding repeating units of adjacent chains (see Fig. 4) was estimated from the energy splitting between HOMOs of two benzene molecules located at the typical interchain distance (Fig. 5). Since we believe that the spatial disorder of the chain alignment does not play a significant role, distribution of $J_{\alpha\beta}$ was taken as a standard normal distribution multiplied by a typical value of $\sigma(J_{\alpha\beta}) = 10^{-4}$ eV. Then, the average absolute value of $J_{\alpha\beta}$ is about 8×10^{-5} eV. Note that $\sigma(J_{\alpha\beta})$ is just a multiplication factor in Marcus formula (9) which can be used to scale the calculated absolute values of mobility.

Using the expansion coefficients $c_{i,\alpha}$ (see Eq. 7) of each chain state i and the transfer integrals $J_{\alpha\beta}$, it is possible to determine the transfer integrals J_{ij} between states i and j located on two different chains

$$J_{ij} = \sum_{\alpha,\beta} c_{i,\alpha} c_{j,\beta} J_{\alpha\beta} \delta_{\alpha\beta}, \tag{11}$$

where α and β are the repeating units of chains A and B, respectively, and $\delta_{\alpha\beta}$ is the Kronecker delta. Unlike transfer integrals $J_{\alpha\beta}$, the

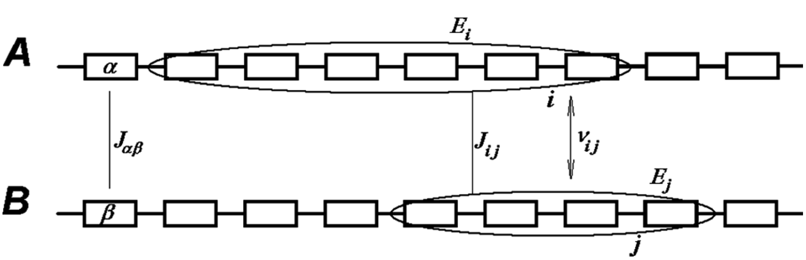


FIGURE 4 Detail of two neighboring polymer chains A and B. Letters α and β denote repeating units, i and j are the charge carrier on-chain states.

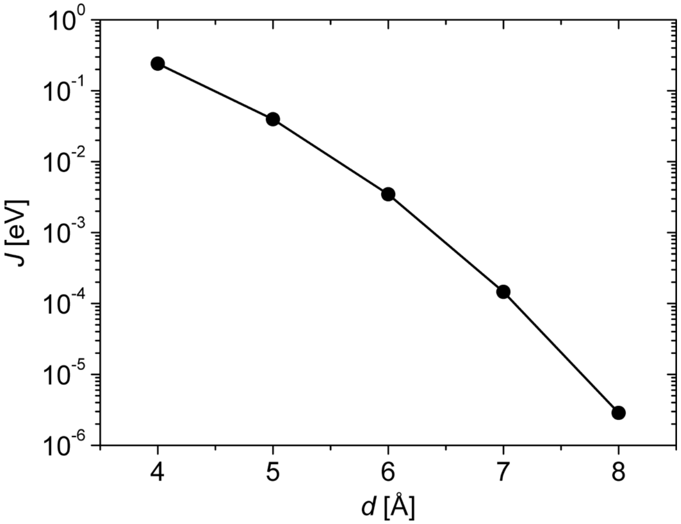


FIGURE 5 Dependence of the hole transfer integral J between two coplanar benzene molecules on the inter-molecular distance calculated by the HF/6-31G* method.

expansion coefficients $c_{i,\alpha}$, and consequently also the transfer integrals J_{ij} are strongly dependent on the chain energetic disorder.

From the charge transfer rates $\nu_{i\to j}$ between two states and the thermalized occupation probability p_i of the initial state the charge transfer rates $\nu_{A\to B}$ between two adjacent chains A and B can be easily calculated

$$\nu_{A\to B} = \sum_{\substack{i\in A\\ j\in B}} p_i(E_i)\nu_{i\to j}, \tag{12}$$

whereas summation goes through all states of the respective chain. Determination of the charge transfer rates $\nu_{A\to B}$ makes possible to solve the master equation (1) and consequently calculate the hole mobility $\mu(\omega)$ according to Kubo formula (3).

RESULTS OF THE MOBILITY MODELING

The frequency-dependent hole mobility in MEH–PPV doped by a polar additive was modeled with the following constants: The size of the array of the polymer chains (Fig. 1) was $M = 601$ chains. Each of these chains consisted of $N = 501$ repeating units (phenylenes and

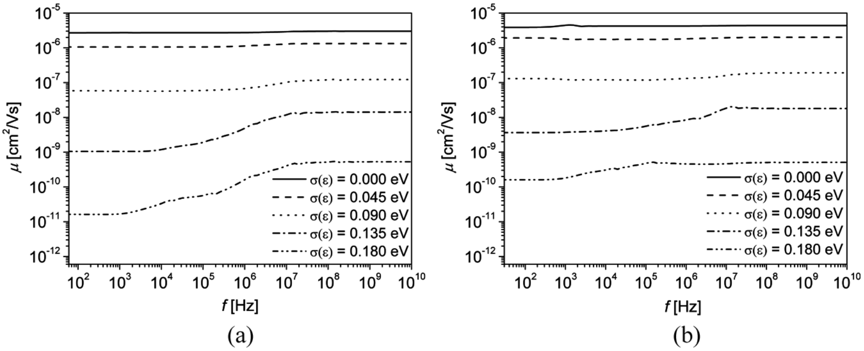


FIGURE 6 Hole mobility $\mu(f)$ calculated for different degrees of the energetic disorder $\sigma(\varepsilon_n)$. The reorganization energy λ was 0.1 eV and the polymer chain alignment with four (a) and six (b) nearest neighboring chains, respectively.

vinylenes). The estimated inter-chain distance $d = 1$ nm. The calculation was done for room temperature. Two different alignments of the polymer chains (Fig. 1) were considered and the dependence of the results on the value of the reorganization energy λ was determined.

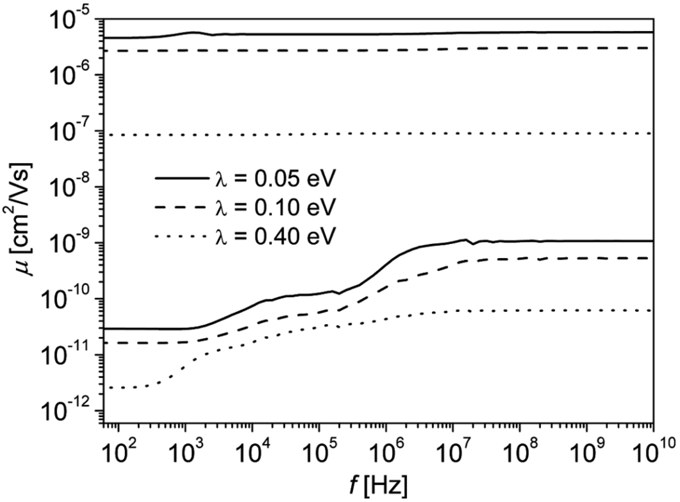


FIGURE 7 Comparison of the hole mobilities $\mu(f)$ calculated for different values of the reorganization energy λ. Upper three curves are calculated for the as prepared polymer (no energetic disorder), lower three curves correspond to the doped polymer ($\sigma(\varepsilon) = 0.18$ eV).

Figure 6a shows the hole mobility determined for the polymer chain alignment with four nearest neighbors and the reorganization energies $\lambda = 0.1$. While the mobility in the polymer with a low degree of the energetic disorder is independent on the frequency, for higher degree of $\sigma(\varepsilon_n)$ there is a certain increase of the mobility with the frequency. The explanation of this effect is based on the fact that at higher external field frequencies each charge carrier oscillates in a small region containing few polymer chains. Also at greater values of $\sigma(\varepsilon_n)$, it may happen that there are rather high transfer rates among such small number of chains. Consequently, the charge carrier will find a path, on which its motion is weakly influenced by the energetic disorder.

The results calculated for different values of the reorganization energy λ (0.05, 0.1, and 0.4 eV, respectively) are shown in Figure 7. It is obvious, that increasing of λ decreases the mobility, but the shape of the curves and the strong dependence on $\sigma(\varepsilon_n)$ remain almost unchanged.

Figure 6b shows the results calculated for the polymer chain alignment with six nearest neighbors and the reorganization energies $\lambda = 0.1$. In this case, the increase of the mobility with the frequency seems to be smaller.

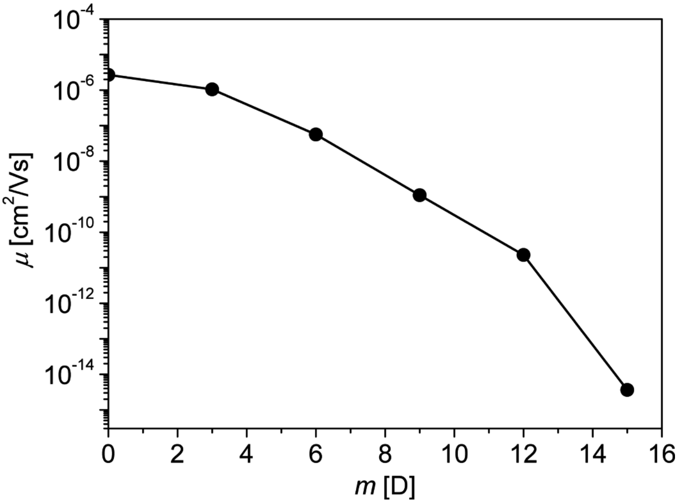


FIGURE 8 Dependence of low-frequency ($f = 100$ Hz) mobility on the additive dipole moment m. The additive concentration is $c = 1 \times 10^{-4}$Å^{-3}, reorganization energy $\lambda = 0.1$ eV, and the polymer chain alignment with four nearest neighboring chains. For dipole moment $m = 12$ D the standard deviation of the energetic distribution is $\sigma(\varepsilon_n) = 0.18$ eV.

In all calculated cases for all frequencies, there is a very strong dependence of the mobility on the energetic disorder $\sigma(\varepsilon_n)$. At low frequencies, the inter-chain mobility decreases by several orders of magnitude, if the standard deviation of the energetic distribution is doubled from $\sigma(\varepsilon_n) = 0.09$ to 0.18 eV (see Fig. 8), while the change of the intra-chain mobility is about five-fold [11]. Such a change of $\sigma(\varepsilon_n)$ can be achieved by the change of the additive dipole moment connected with the photochromic reaction SP → MR at experimentally reasonable additive concentrations. We conclude that our theoretical results predict the possibility to construct an *efficient* optoelectronic switch based on a polymer doped with a photochromic polar additive.

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