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Modelling of charge carrier transport in conjugated polymers doped by polar additives[*]

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A theoretical model of the inter-chain charge carrier transport in poly[2-methoxy-5-(2′-ethylhexyloxy)-*p*-phenylene vinylene] doped with a photochromic polar additive is put forward. The model attributes to each polymer chain a set of charge states, in which charge carriers thermalize. These on-chain states are calculated by solving the Schrödinger equation with a tight binding Hamiltonian. The inter-chain transfer rates are determined using the Marcus formula. The model describes the effect of polar additives on charge carrier transport. The presence of the additives results in a decrease of charge mobility, because of the increase of the local energy disorder. A decrease of the inter-chain mobility by up to several orders of magnitude is found if the width of the local energy disorder is doubled. This finding confirms the possibility of constructing an optoelectrical switch based on a polymer doped with a photochromic polar additive.

Key words: *conjugated polymers; charge carrier transport; molecular electronics; Monte Carlo modeling*

1. Introduction

Inter-chain charge carrier transport in conjugated polymers is commonly considered as hopping within a geometrically and energetically disordered system. A classical model of charge transport in disordered organic solids was developed by Bässler [1]. The model describes conjugated segments of the polymer chains as sites with Gaus-

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sian distribution of energies reflecting an energy (diagonal) disorder. The jump rates among these sites are described by means of the Miller–Abrahams relation [2]. This relation is appropriate if the polaronic effects can be neglected but simultaneously the electron–phonon coupling is strong enough to ensure charge carrier thermalization. The inter-site coupling parameters are decomposed to site specific randomized ones. Consequently, the model considers a Gaussian geometric (off-diagonal) disorder with some correlation. The charge carrier motion is then solved numerically using a Monte Carlo simulation technique. A similar model was also used by Fishchuk et al. [3, 4] for an analytical solution of the charge carrier transport. If the polaronic effects cannot be neglected, it seems that the Marcus theory [5, 6] better describes the charge carrier transport.

The motivation of our paper is the verification of the idea to construct an optoelectrical switch based on a conjugated polymer doped with a polar photochromic additive, which significantly changes its dipole moment during its photochromic conversion. In our previous paper [7], we 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 (spiropyran (SP)) to the open form (merocyanine (MR)) [8]. A reversible SP $\longleftrightarrow$ MR transformation is accompanied by a charge redistribution, resulting in a significant increase in the dipole moment of the molecule. It was found that the introduction of polar species results in a broadening of the distribution of the local charge carrier site energies (local energy disorder), and consequently leads to a decrease in the on-chain hole mobility. The aim of this paper is to extend the model, taking into account the inter-chain charge carrier transport.

Unlike Bässler and Fishchuk [1, 3, 4], we seek a more realistic description of the polymer charge carrier states participating in the transport. Charge carrier transport in conjugated polymers involves both the on-chain motion through the conjugated chain segments and hops either between two adjacent polymer chains or between two segments of a chain separated by a conjugation break. Thus, our model considers the conjugated polymer chains (or chain segments) as one-dimensional disordered rods, possessing many charge carrier states, instead of the point one state sites. The on-chain transfer integrals are randomized by the torsional disorder of the polymer chain. Simultaneously, the site energy disorder coming from the intermolecular interaction of the charge carrier with dispersed polar species is introduced. Thus, we separate the one-dimensional on-chain motion from the essentially two-dimensional inter-chain hopping, which is investigated in this paper. Since MEH–PPV is a hole-transporting material, only the hole transport is considered.

Although conjugated polymer repeat units can be treated as elementary localization sites possessing specific energies ε_n, their mutual interaction, resulting in energy level splitting, is typically stronger than the disorder of these site energies. While the on-chain transfer integrals between adjacent phenylene and vinylene units in MEH

–PPV are as high as 1.3 eV, the standard deviation $\sigma(\varepsilon_n)$ of the local site energy distribution can hardly exceed 0.4 eV, even in the case of a highly doped polymer. Moreover, due to the long-range character of the Coulombic interaction, adjacent site energies are highly correlated, and the difference of their values rarely exceeds 0.3 eV if these sites describe the repeat units of the same type. Consequently, the charge carrier states become delocalized on the conjugated chain segments. Such a system allows semi-coherent charge carrier motion, limited by the chain disorder. The segment charge carrier states can be described by a tight-binding Hamiltonian and calculated using a numerical solution of the Schrödinger equation.

The typical distance between repeat units located on different chains can be estimated from the envelope of the van der Waals atomic spheres to be about 7 to 10 Å in MEH–PPV. Thus, the inter-chain transfer integrals are several orders of magnitude smaller than the on-chain ones. For this reason, the charge carrier transport occurs mainly by hopping between states localized on the conjugated segments. The charge carrier thermalization, which occurs typically in times of several picoseconds, leads to a complete decoherence of the charge motion between any subsequent hops. Therefore, unlike the on-chain transport, it is appropriate to describe the inter-chain transport by means of quasi-classical master equations. Because the MEH–PPV conformation is rather soft, the presence of any additional charge carrier on the chain segment leads to the conformation distortion and polaron formation. For this reason, the inter-chain hopping is studied using Marcus charge transfer theory [5, 6]. Because the inter-chain transport is much slower than the on-chain motion, the slow inter-chain motion acts as a bottleneck determining the macroscopic charge carrier mobility, if the frequency of the external electric field is not too high.

2. Charge states

2.1. Model

The conjugated polymer chain segments are modelled as sequences of N sites corresponding to the repeat units, alternating phenylenes and vinylenes. The hole states on such a chain can be described within the tight-binding approximation by the Hamiltonian

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

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 on-chain transfer integral between the sites n and $n+1$. The distribution of transfer integrals $b_{n,n+1}$ is calculated according to the model of Grozema et al. [9].

In the absence of a polar additive, the site energies ε_n are essentially equal to the ionization potentials of the isolated polymer repeat units and can be calculated using standard quantum chemical methods. For materials doped by polar species, it was found that within the frozen orbital approximation, the local site energies are given by the formula [10]

$$\varepsilon_n = \varepsilon_n^{(0)} + < \mathrm{HOMO} \,|\sum_i \Delta\varphi_i \,|\, \mathrm{HOMO} > \tag{2}$$

where $\varepsilon_n^{(0)}$ is the site energy of an isolated repeat unit and $\Delta\varphi_i$ are the electrostatic potentials describing the charge–dipole interactions of a hole located at the highest occupied molecular orbital |HOMO> of this unit with all surrounding polar species. Note that the |HOMO> orbitals are located on the phenylenes and vinylenes forming the main polymer chain, and not on their aliphatic substituents. Since the sizes of individual repeat units as well as additive molecules are much smaller than the distance of the additive molecules from the main chain, it is possible to treat them as points. Because the positions and orientations of the additive molecules with respect to the polymer chain are essentially random, their common effect results in the broadening of the distribution of local site energies ε_n. The most important parameter of this distribution is its half-width, proportional to the standard deviation $\sigma(\varepsilon_n)$ of the site energies from its average value. It should be remarked that we define $\sigma(\varepsilon_n)$ as just the standard deviation of the distribution of the second term on the right side of Eq. (2), regardless of the different values $\varepsilon_n^{(0)}$ of phenylenes and vinylenes. Another very important characteristic of this distribution, influencing the charge transport, is the site to site energy correlation, which effectively reduces $\sigma(\varepsilon_n)$. There is a strong correlation between sites that are no more than about ten sites apart from each other. This fact can be explained by the long-range character of the charge–dipole interactions. It was shown in our previous paper [7] that the additive photochromic reaction SP $\longleftrightarrow$ MR is accompanied by a significant change in the dipole moment resulting in ca. twofold change in the standard deviation $\sigma(\varepsilon_n)$ of the polymer chain local site energies.

Using the Hamiltonian (1) with the molecular parameters ε_n and $b_{n,n+1}$ and taking the stationary states $|\varphi_i\rangle$ as superpositions of states $|n\rangle$ located at individual sites

$$|\varphi_i\rangle = \sum_{n=1}^{N} c_{i,n} \,|n\rangle \tag{3}$$

the time-independent Schrödinger equation can be solved

$$H|\varphi_i\rangle = E_i|\varphi_i\rangle \tag{4}$$

This approach leads to the same time evolution of the wave function

$$|\psi(t)\rangle = \sum_{i=1}^{N} k_i \mathrm{e}^{-iE_i t/\hbar} |\varphi_i\rangle \tag{5}$$

where the time-independent coefficients k_i can be found from the initial conditions, as an alternative approach based on the direct numerical integration of the time-dependent Schrödinger equation, performed in our previous paper [7]. However, the solution of the eigenstate problem provides also the charge carrier states $|\varphi_i\rangle$ and their energies E_i.

2.2. Results and discussion

The on-chain hole states were calculated for polymer chains (conjugated segments) consisting of 180 phenylene vinylene units, i.e. $N = 360$ centres. This length was suggested by Grozema et al. [9] as an effective conjugation length, at which the calculated on-chain hole mobility reproduces the experimental mobility measured for MEH–PPV by the microwave technique.

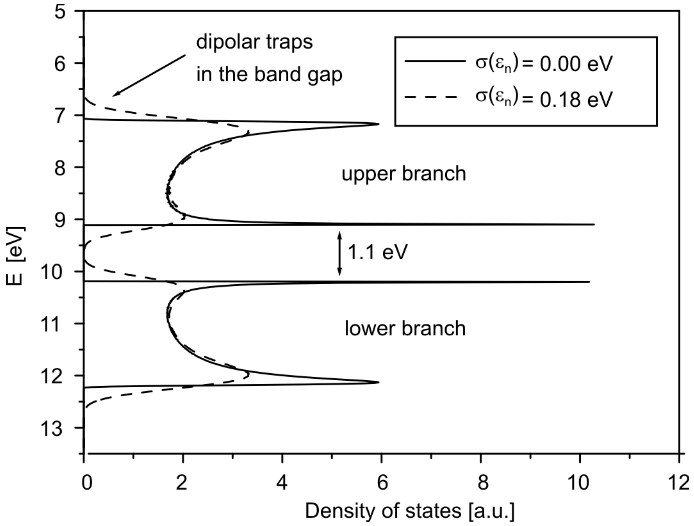


Fig. 1. Diagram of the MEH–PPV valence band consisting of two branches. The value of the local energy disorder is indicated by the standard deviation $\sigma(\varepsilon)$. Solid lines corresponds to the pristine polymer, dashed lines to the polymer doped with a polar additive

Figure 1 shows a diagram of the valence band of the pristine and doped polymer. The valence band of the pristine polymer is split into two branches, which correspond to two types of repeat units, phenylenes and vinylenes, in the main chain. The 1.1 eV gap between these two branches is equal to the difference between phenylene and vinylene ionization potentials (local site energies ε_n). An increasing local energy disorder $\sigma(\varepsilon_n)$ leads to the broadening of the originally sharp valence band edge and formation of the tail states in the gap. These states, owing to their relatively low density and consequently weak connectivity, behave as shallow hole traps. Furthermore, the valence states in the doped polymer are less delocalized along the polymer chain than the states in the pristine polymer, which limits inter-chain hopping.

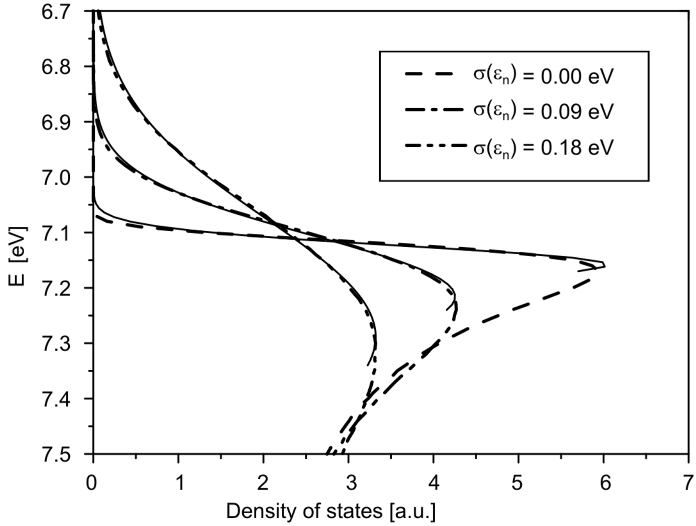


Fig. 2. Detailed drawing of the band edge for various values of the local site energy disorder $\sigma(\varepsilon)$. Solid lines show the fitting of the band edge slope by a Gaussian curve

Figure 2 displays a detailed drawing of the band edge region for various local energy disorders $\sigma(\varepsilon_n) = 0.00$, 0.09, and 0.18 eV. Tiny lines show that the band edge slope can be well fitted by a Gaussian curve. The fitted standard deviations $\sigma(E_i)$ of hole state energies E_i are listed in Table 1. Note that due to the transfer integral disorder there is also a small non-zero standard deviation $\sigma(E_i)$ of hole state energies for the pristine polymer, which possesses no local energy disorder ($\sigma(\varepsilon_n) = 0$).

Table 1. Centres $E_{\max}$ of the peaks and standard deviations $\sigma(E_i)$ of the Gaussian fits of the density of states on the valence band edge slope calculated for various values of the local site energy disorder $\sigma(\varepsilon_n)$ at 293 K. All values are given in eV

$\sigma(\varepsilon_n)$	$E_{\max}$	$\sigma(E_i)$
0.000	7.158	0.034
0.045	7.179	0.061
0.090	7.216	0.110
0.135	7.250	0.161
0.180	7.289	0.215

It should be pointed out that our model takes into account only the highest molecular orbitals (HOMO) of individual repeat units. Thus, the band diagram of a real polymer should consist of more mutually overlapped bands. However, only the charge carrier states near the valence band edge can participate in charge carrier transport.

Since the transfer integrals between lower orbitals of phenylene and vinylene are much smaller than the transfer integrals between HOMOs, lower orbitals do not contribute to the density of states near the band edge. Hence, for our purpose it is sufficient to calculate only the highest occupied band.

3. Charge carrier transport

3.1. Model

The description of the charge carrier transport in polymers is complicated, due to the absence of any well-ordered crystal structure typical of molecular single crystals and crystalline inorganic semiconductors. Our inter-chain hopping model assumes a simplified three-dimensional polymer structure, schematically depicted in Fig. 3.

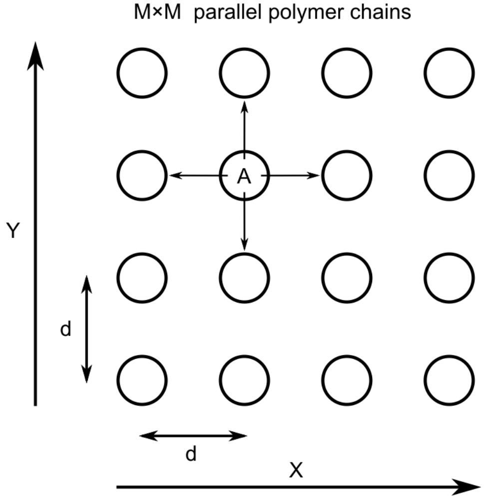


Fig. 3. Simplified polymer chain alignment considered in the inter-chain hole mobility modelling. The possible charge carrier hops from a given chain *A* are denoted by arrows

The polymer chains of a given length *N* form a regular, equidistant matrix. Additive molecules, which are not shown in the figure, are placed randomly among them. While the on-chain motion proceeds in a one-dimensional space, the inter-chain hopping takes place in the two remaining perpendicular directions *X* and *Y*. The geometric (off-diagonal) disorder is introduced by the Gaussian distribution of the transfer integrals $J_{\alpha\beta}$ between the corresponding repeat units of adjacent chains (see Fig. 4). The distribution is centred at zero and its standard deviation is $\sigma(J_{\alpha\beta}) = 10^{-3}$ eV. This value, which just acts as a multiplication factor in the Marcus equation, was set to reproduce the experimental mobility of the pristine MEH–PPV (ca. 10^{-5} cm^2/(V·s) [11]) at room temperature. We believe that the shape of the transfer integral distribution has no significant influence on the results. Each polymer chain possesses disorder in local energies ε_n and on-chain transfer integrals $b_{n,n+1}$ resulting in a unique set of the on-chain charge carrier states, i.e. hole energies E_i and expansion coefficients $c_{i,\alpha}$ (see Eq. 3). No correlation among chains is assumed.

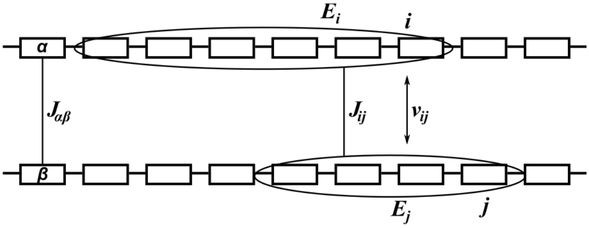


Fig. 4. Two adjacent polymer chains A and B. Letters α and β denote repeating units, i and j are the on-chain hole states

The model considers full charge carrier thermalization over all states of the given chain A between two subsequent hops. Hence, the charge carrier transport consists of the following steps: hole movement to any possible state on the chain A, thermalization of the hole over all its possible states on the chain A, and finally a hop of the hole to any possible state on one of the nearest neighbouring chains B. The more distant hops can be safely omitted due to the negligibly small transfer integrals.

Although fermions generally follow the Fermi–Dirac statistic, under usual experimental conditions it is very improbable that there is more than one free charge carrier on a given conjugated segment. Thus, in the case of one-particle approximation, the position of the Fermi level is not important and a simpler Boltzmann distribution can be used. Hence, if the hole hops to a given chain A, the occupation probability of its state i at temperature T will be

$$p_i\left(E_i\right)=\frac{\exp\left(\frac{-E_i}{kT}\right)}{Z\left(T\right)} \tag{6}$$

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

MEH–PPV chain conformation is relatively soft and undergoes a significant deformation (polaron formation) in the presence of an additive charge. For this reason, using the Marcus concept is more appropriate than using the Miller–Abrahams formula. Hence, the rate of 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 as [6]

$$v_{i\to j}=\frac{J_{ij}^2}{\hbar}\sqrt{\frac{\pi}{\lambda_{ij}kT}}\exp\left(\frac{-\left(E_i-E_j-\lambda_{ij}\right)^2}{4\lambda_{ij}kT}\right) \tag{7}$$

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

The reorganization energy λ_{ij} can be separated into an inner (molecular) and an outer (solvent) part. The solvent reorganization energy is often important in solutions [12]. On the other hand, in the solid state environment the phonon-like modes are sufficiently stiff that local vibronic coupling should dominate [13]. Thus, only the inner reorganization energy is considered. It can be calculated, in principle, using standard quantum chemical methods. However, such a calculation takes too much cpu time to be repeated many thousands times for all considered Monte Carlo realizations of the chain disorder. Therefore, we have roughly estimated its value, from the calculations of short regular oligomers, to be about $\lambda_{ij} = \lambda = 0.4$ eV. This value is consistent with the values determined by Prins et al. [14] for similar phenylene–vinylene derivatives.

The transfer integral J_{ij} between states i and j located on two different chains A and B is determined from the transfer integrals $J_{\alpha\beta}$ between the repeat units α and β using known expansion coefficients $c_{i,\alpha}$ as

$$J_{ij} = \sum_{\alpha,\beta} c_{i,\alpha} c_{j,\beta} J_{\alpha\beta} \delta_{\alpha\beta} \tag{8}$$

where $\delta_{\alpha\beta}$ is the Kronecker delta function, and summation runs through all polymer repeat units. Note that besides the hole energies E_i, the expansion coefficients $c_{i,\alpha}$ are also strongly dependent on the distribution of local site energies ε_n.

Determination of the inter-orbital transfer rates $\nu_{i\to j}$ and the thermalized occupation probability p_i of the initial state makes it possible to calculate the charge transfer rates $\nu_{A\to B}$ between two adjacent chains A and B

$$\nu_{A\to B} = \sum_{\substack{i\in A \\ j\in B}} p_i\left(E_i\right)\nu_{i\to j} \tag{9}$$

where summation runs through all states of the respective chain. Finding the interchain transfer rates $\nu_{A\to B}$ makes it possible to write the master equation describing the hole motion

$$\frac{dP_A(t)}{dt} = \sum_{B} \nu_{A\to B} P_B(t) \tag{10}$$

where $P_A(t)$ and $P_B(t)$ are the probabilities of finding the hole on the chains A and B, respectively, at time t. By analogy to the time-dependent Schrödinger equation for the on-chain motion, the master equation (Eq. (10)) is solved either by means of direct numerical integration, or by using the eigenstates. However, note that the matrix $\boldsymbol{\nu}_{A\to B}$ is not symmetric and its eigenstates are not the stationary states. They involve at least one time-independent eigenstate corresponding to the thermal equilibrium, whereas all other eigenstates decay, due to negative real parts of their respective eigenvalues.

At $t = 0$, the hole is assumed to be localized on a single chain, i.e., $P_0(t = 0) = 1$ and all other P_A are equal to zero. It is important to select this initial hole localization randomly with regard to the thermal equilibrium occupational probabilities $P_A(t\to\infty)$.

Once the time evolution of $P_A(t)$ is found, the mean-square displacement $\Delta^2(t)$ of the hole can be calculated as

$$\Delta^2(t) = \sum_A i_A{}^2 d^2 P_A(t) \tag{11}$$

with d being the interchain distance and the product $i_A d$ being the projection of the distance of the chains A and 0 to the direction of the electric field. This quantity was averaged over 500 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 mobility by the Kubo formula [15]

$$\mu(\omega) = \frac{-e\omega^2}{2kT}\mathrm{Re}\left[\int_0^\infty \Delta^2(t)\exp(-i\omega t)dt\right] \tag{12}$$

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.

3.2. Room temperature results

The modelling of hole mobility presented in this paper was performed with the following parameters: The size of the array of the polymer chains (Fig. 3) was $M = 601$. Each of these chains consisted of $N = 360$ repeat units. The estimated interchain distance was $d = 1$ nm.

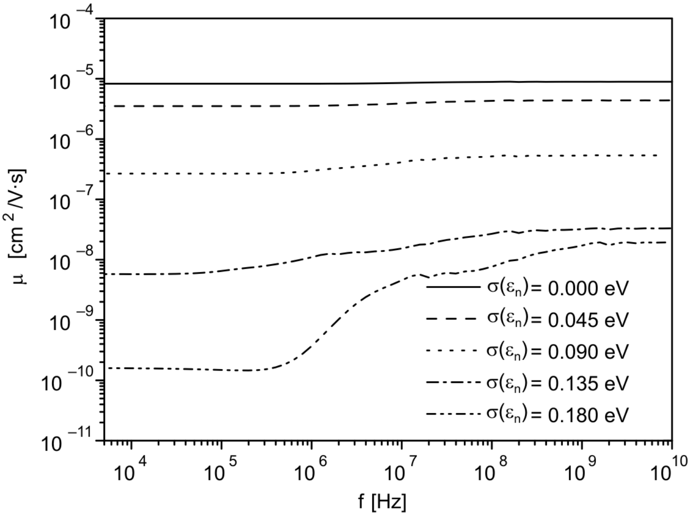
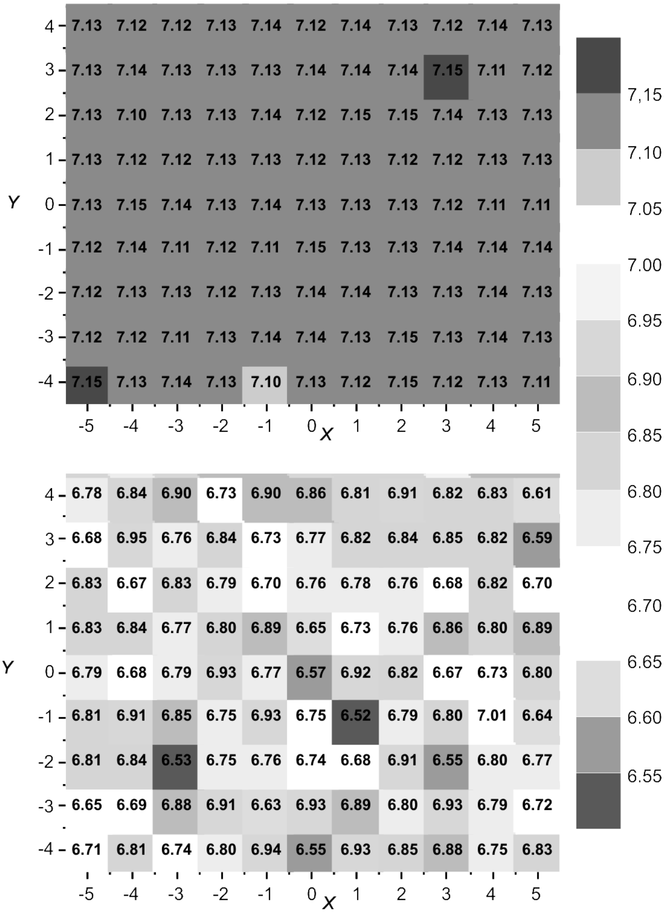


Fig. 5. Frequency dependence of the hole mobility $\mu(f)$ calculated for various values of the local energy disorder $\sigma(\varepsilon_n)$

The frequency dependent mobility calculated for the different levels of the local energy disorder $\sigma(\varepsilon_n)$ is presented in Fig. 5. While the mobility in the polymer with a low value of the local energy disorder is frequency-independent, for higher values 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 a small number of chains. Consequently, the charge carrier will find a path on which its motion is weakly influenced by the energy disorder. If the external field frequency is low, the charge carrier is surrounded by barriers and cannot follow the oscillating field direction. A typical energy landscape, in which the hole moves, is depicted in Fig. 6.



Y	-5	-4	-3	-2	-1	0	1	2	3	4	5
4	7.13	7.12	7.12	7.13	7.14	7.12	7.14	7.13	7.12	7.14	7.13
3	7.13	7.14	7.13	7.13	7.13	7.14	7.14	7.14	7.15	7.11	7.12
2	7.13	7.10	7.13	7.13	7.14	7.12	7.15	7.15	7.14	7.13	7.13
1	7.13	7.12	7.12	7.13	7.13	7.12	7.13	7.12	7.12	7.13	7.13
0	7.13	7.15	7.14	7.13	7.14	7.13	7.13	7.13	7.12	7.11	7.11
-1	7.12	7.14	7.11	7.12	7.11	7.15	7.13	7.13	7.14	7.14	7.14
-2	7.12	7.13	7.13	7.12	7.13	7.14	7.14	7.13	7.13	7.14	7.13
-3	7.12	7.12	7.11	7.13	7.14	7.14	7.13	7.15	7.13	7.14	7.13
-4	7.15	7.13	7.14	7.13	7.10	7.13	7.12	7.15	7.12	7.13	7.11

Y	-5	-4	-3	-2	-1	0	1	2	3	4	5
4	6.78	6.84	6.90	6.73	6.90	6.86	6.81	6.91	6.82	6.83	6.61
3	6.68	6.95	6.76	6.84	6.73	6.77	6.82	6.84	6.85	6.82	6.59
2	6.83	6.67	6.83	6.79	6.70	6.76	6.78	6.76	6.68	6.82	6.70
1	6.83	6.84	6.77	6.80	6.89	6.65	6.73	6.76	6.86	6.80	6.89
0	6.79	6.68	6.79	6.93	6.77	6.57	6.92	6.82	6.67	6.73	6.80
-1	6.81	6.91	6.85	6.75	6.93	6.75	6.52	6.79	6.80	7.01	6.64
-2	6.81	6.84	6.53	6.75	6.76	6.74	6.68	6.91	6.55	6.80	6.77
-3	6.65	6.69	6.88	6.91	6.63	6.93	6.89	6.80	6.93	6.79	6.72
-4	6.71	6.81	6.74	6.80	6.94	6.55	6.93	6.85	6.88	6.75	6.83

Fig. 6. Map of the average energy (in eV) of the thermalized hole located on particular polymer chains calculated for the pristine (upper, $\sigma(\varepsilon_n) = 0$) and doped (lower, $\sigma(\varepsilon_n) = 0.18$ eV) polymer, respectively. Polymer chains are depicted as grey squares. Coordinates *X* and *Y* show the chain positions.

Polymer chains, aligned perpendicular to the plane, are symbolized by gray squares. The intensity of the gray colour and number indicate an average energy of a hole located on a given chain. Coordinates X and Y show the chain positions. For the pristine polymer (Fig. 6, upper diagram), there are no significant barriers among the chains. On the other hand, for a doped polymer (Fig. 6, lower diagram), there are several rather isolated chains possessing low energy and hence acting as traps. However, if there are more chains with lower energy next to each other, like the pair in the centre of the picture, and the external field frequency is sufficiently high, the charge can oscillate in this small region. A similar phenomenon has been already reported by Hilt et al. [16]. They investigated the charge transport in one-dimensional disordered systems and concluded that the mobility is frequency dependent, if the charges hops over barriers, but it is frequency independent, if the charges hop out of wells.

Figure 5 shows a very significant dependence of the inter-chain hole mobility on the local energy disorder $\sigma(\varepsilon_n)$. At low frequencies, the inter-chain mobility decreases by several orders of magnitude if the standard deviation of the energy distribution is doubled from $\sigma(\varepsilon_n) = 0.09$ to 0.18 eV. 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.

3.3. Temperature dependence of mobility

Using our model, the temperature dependence of mobility was calculated in the range from 100 K to 600 K. Temperature influences the chain torsional disorder, which determines the on-chain transfer integral $b_{n,n+1}$ distribution, hole thermalization, and transfer rates given by the Marcus formula (Eq. (7)).

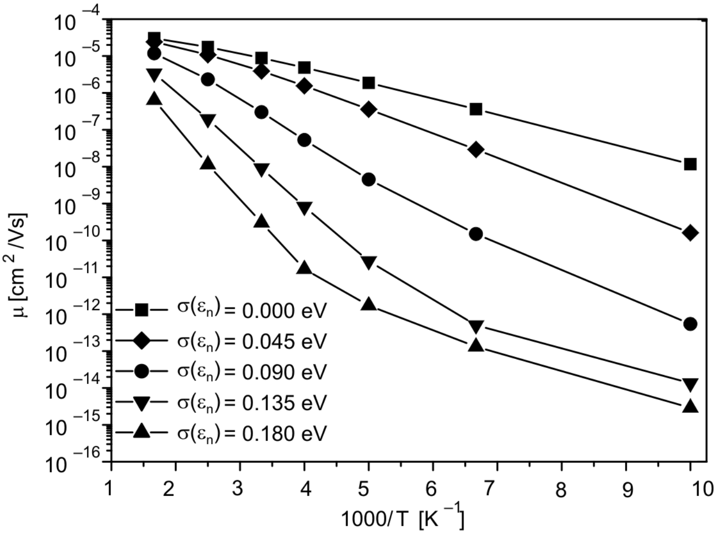


Fig. 7. Arrhenius plot of the temperature dependence of mobility calculated for various values of the local energy disorder $\sigma(\varepsilon_n)$ at the external field frequency 100 kHz. Results obtained for the temperature dependent polymer conformation

Temperature dependence of hole mobility (at 100 kHz) calculated for several values of the local energy disorder $\sigma(\varepsilon_n)$ is shown in Fig. 7. It should be noticed that at low temperatures the chain torsional disorder may be underestimated using the Grozema model [9], due to the relatively greater importance of the conformational mistakes and chemical defects. For this reason, to distinguish the influence of the temperature change of the chain torsional disorder on mobility, the calculation was repeated with the on-chain hole states calculated at room temperature (293 K), i.e., temperature dependence of the chain torsional disorder was in the latter case neglected (frozen conformation results). The results obtained with the temperature-dependent and frozen conformation are compared in Fig. 8. It is obvious that the temperature change of the conformation causes only a slight decrease in the mobility as the temperature increases, which can be explained by a shorter effective conjugation length and thus greater localization of the on-chain hole states at higher temperatures. Thus, possible underestimation of the chain torsional disorder should not significantly affect the results shown in Fig. 7.

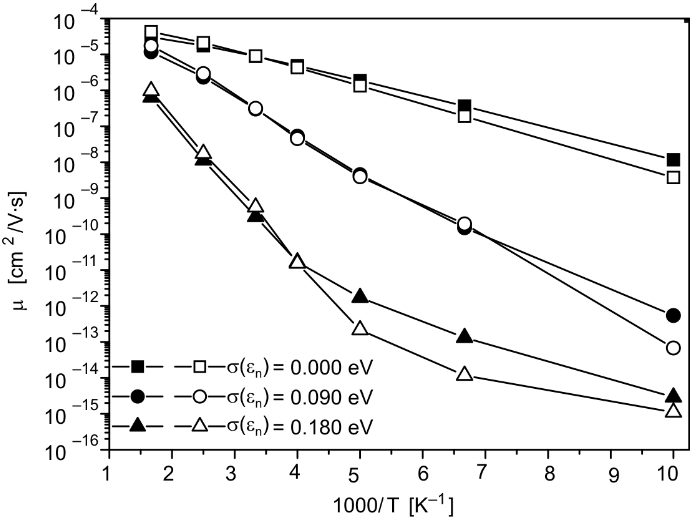


Fig. 8. Mobilities of the temperature dependent polymer conformation (solid symbols) and for the room temperature (frozen) conformation (open symbols). In the latter case, the on-chain hole states were calculated at the constant temperature 293 K, while the mobility modeling was performed at the temperature *T*. The external field frequency was 100 kHz

We compared our calculated data with the analytical model of hopping mobility proposed by Fishchuk et al. [4]. He suggests, that using Marcus transfer rates at low carrier concentrations leads to the approximate relation

$$\ln(\mu) = -\frac{E_p}{kT} - k_2\left(\frac{\sigma(E_i)}{kT}\right)^2 + \text{const} \tag{13}$$

where $E_p = \lambda/4$ is the polaron activation energy, $\sigma(E_i)$ is the standard deviation of the on-chain hole states, and the coefficient $k_2 = 0.12$. This model was derived with the limitation $\sigma(E_i) << E_p$ and under the assumption of three-dimensional hopping among point centres, each possessing only one energy state. It does not consider any influence of temperature on the molecular conformation. Relation (13) shows that polaron formation eventuate in Arrhenius-type temperature dependence of mobility, while the energy disorder of the charge carrier states is responsible for sub-Arrhenius dependence. Our mobility data calculated for the pristine polymer ($\sigma(\varepsilon_n) = 0$, $\sigma(E_i) = 0.034$ eV) can be fitted using Eq. (13) over the whole temperature range, as is shown in Table 2. The parameters of the fit obtained for the frozen conformation roughly match the expected values $E_p = \lambda/4 = 0.1$ eV and $\sigma(E_i) = 0.034$ eV (see Table 1). On the other hand, mobility calculated for doped polymers cannot be approximated by this relation due to the mobility saturation at low temperatures. Note that in this case $\sigma(E_i)$ (see Table 1) is comparable or higher than the polaron activation energy $E_p = 0.1$ eV and therefore relation (13) cannot be applied.

Table 2. Fitting of the calculated temperature dependence of mobility according to Eq. (13) for the pristine polymer ($\sigma(\varepsilon_n) = 0$). Results obtained for the temperature dependent polymer conformation are compared with the frozen conformation results. All values are given in eV

Conformation	E_p	$\sigma(E_i)$
Temperature dependent	0.062	0.036
Frozen	0.083	0.030

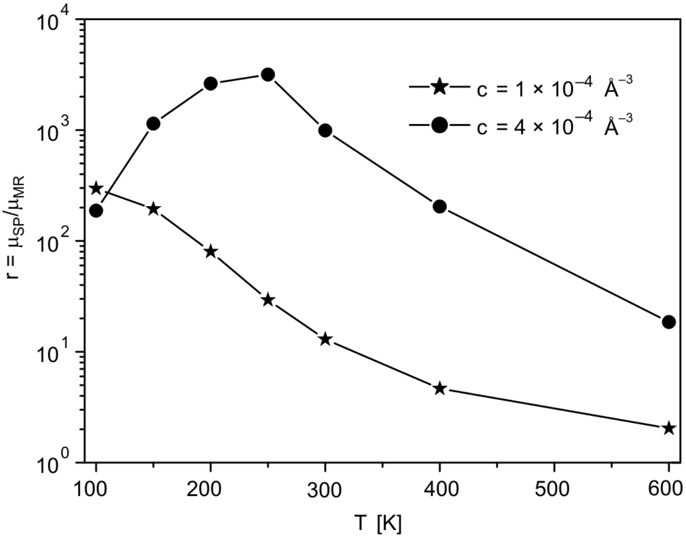


Fig. 9. Temperature dependence of the switching ratio of mobility ($f = 100$ kHz) during the photochromic SP ↔ MR reaction calculated for the low and high additive concentration c

If the reaction field of the dipoles is not taken into account, the MR molecules with the dipole moment 12 D and a high but experimentally achievable concentration $c = 4\times10^{-4}$ Å^{-3} (ca. 20 wt. %) would produce disorder in local energies with the $\sigma(\varepsilon_n) = 0.37$ eV [7]. If the relative permittivity is about 3 (a typical value for organic materials), the dipole reaction field decreases the local energy disorder by about 50 % (see Ref. [17] for details). Thus, the disorder in local energies can be estimated to be about $\sigma(\varepsilon_n) = 0.18$ eV. Because our model neglects mutual interaction of the additive molecules, the local energy disorder is proportional to the additive dipole moment and the square root of the additive concentration c. It follows that SP molecules with dipole moment 6 D and the same concentration cause disorder in local energies for $\sigma(\varepsilon_n) = 0.09$ eV. Figure 9 shows the temperature dependence of the switching ratio $r = \mu_{\mathrm{SP}}/\mu_{\mathrm{MR}}$ of the hole mobilities in the polymer doped by spiropyran and merocyanine, respectively, at low (1×10^{-4} Å^{-3}) and high (4×10^{-4} Å^{-3}) additive concentrations. The switching ratio generally decreases as the temperature increases. However for high concentration, there is a saturation and decrease if the temperature decreases below 250 K. This effect corresponds to the low-temperature saturation of the mobility at high energy disorder (see Fig. 7). Except for the lowest temperatures, the results show a strong dependence of the switching ratio on the additive concentration.

4. Conclusion

The proposed model of the inter-chain hopping predicts a strong dependence of the hole mobility in MEH–PPV on the local energy disorder. Doubling the local energy disorder causes a decrease in the inter-chain hole mobility, by up to several orders of magnitude. These results confirm the possibility of constructing an efficient optoelectrical switch based on a polymer doped with a photochromic polar additive. It should be noted that the magnitudes of the calculated mobilities are relative only; however the scaling does not affect the ratio of the mobilities of the pristine and the doped material. The calculated temperature dependence of the mobility shows essentially Arrhenius type behaviour, with a moderate sub-Arrhenius deviation at a low energy disorder and the low-temperature saturation at a high energy disorder. The switching ratio is significantly dependent on the additive concentration and the temperature.

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