Modelling of the dependence of charge transport in organic layer, containing crystallites, on the layer morphology

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A Monte Carlo simulation of the charge carrier mobility in a polymer layer with a thickness of about 100 nm, containing both nanosized crystallites and disordered (amorphous) regions, has been carried out. The mobility has a maximum at a certain energy depth of crystallites. The mobility increases along with an increase in the fraction of crystallites and can exceed its value for the case of disordered material by several orders of magnitude..

Keywords: disordered polymers, thin polymer layer morphology.

Being used in such electronic devices as light-emitting diodes, photovoltaic elements, field-effect transistors, etc., organic (specifically, polymer) semiconductors attract much research attention. Charge transport, which is characterized primarily by carrier mobility, is one of the key physical processes forming the basis for operation of electronic devices. An active semiconductor layer in such devices normally takes the form of a thin (approximately 100 nm) film that, in addition to spatially averaged disorder parameters (e.g., energy distribution of hopping centers), may have certain morphological features. Specifically, films fabricated under different conditions may feature amorphous, polycrystalline, or crystalline aggregated phases. Macromolecules in a disordered polymer are oriented fairly chaotically (amorphous phase), but may be relatively ordered and form aggregated nanoscale regions with a reduced energy disorder; in what follows, we refer to these regions as crystallites. Conflicting data have been reported on the influence of morphology of organic semiconductors on the carrier mobility. An enhanced overlap of wave functions (due to closer packing of molecules in the crystalline aggregated phase compared to the amorphous phase) in such semi-crystalline polymers as poly(3-hexylthiophene) (P3HT) translates into an increase in mobility in crystallites relative to the amorphous-phase mobility [1,2]. In contrast, grain boundaries in polycrystalline materials, which may act as traps or barriers depending on the position of their average energy relative to the energy of crystalline domains, interfere with charge transport [2,3]. At the same time, it was reported that, depending on the structure of molecules of π-conjugated low-molecular compounds (e.g., perylene bisimides), crystallites may both enhance and reduce the carrier mobility relative to the one in an amorphous film [4].

The aim of the present study is to perform a Monte Carlo (MC) simulation of the carrier mobility in thin two-phase organic layers as a function of the layer morphology and temperature. As in [5], the studied material in the model is constructed from point hopping centers that form a simple cubic lattice. A certain fraction of sites V corresponds to the crystallite phase. The algorithm for generation of a two-phase structure imitates the natural process of crystallite growth from an amorphous phase. In contrast to [5], „seed" crystallites are distributed randomly in space, just as the crystallite sizes (average value $\langle l \rangle$). Crystallites in the shape of parallelepipeds are separated by amorphous-phase states (Fig. 1); the minimum distance between crystallites is a (lattice constant). The energy distribution of cubic lattice sites (from which both crystallites and the amorphous phase are constructed) is, in accordance with the Gaussian disorder model [6], a sum of two Gaussian distributions:

$$g(E) = a^{-3}\left[\frac{1-V}{\sqrt{2\pi\sigma_1^2}}\exp\left(-\frac{E^2}{2\sigma_1^2}\right)\right.$$

$$\left. + \frac{V}{\sqrt{2\pi\sigma_2^2}}\exp\left(-\frac{(E-E_t)^2}{2\sigma_2^2}\right)\right]. \qquad (1)$$

The upper and lower Gaussians with standard deviations σ_1 and $\sigma_2 < \sigma_1$ correspond to states of amorphous and crystallite phase, respectively (in what follows, they are referred to as states $G1$ and $G2$). States $G2$ also have a certain σ_2 energy spread due to the structural disorder [2]. Energy shift $E_t < 0$ of the lower Gaussian, which may exceed considerably both thermal energy kT and σ_1 [2], is attributable to a more compact structure of crystallites. In contrast to the models used recently in [3,5], the amorphous phase is dominant in the present case, $V < 0.4$ (the highest values of $0.4-0.5$ for P3HT were reported in [2]). Just as in earlier studies [6–8], the random walk of a carrier over lattice sites is simulated in accordance with the Gaussian disorder model. Hopping rates are calculated using the well-known Miller−Abrahams model [6] with the localization radii of wave functions for $G1$ and $G2$
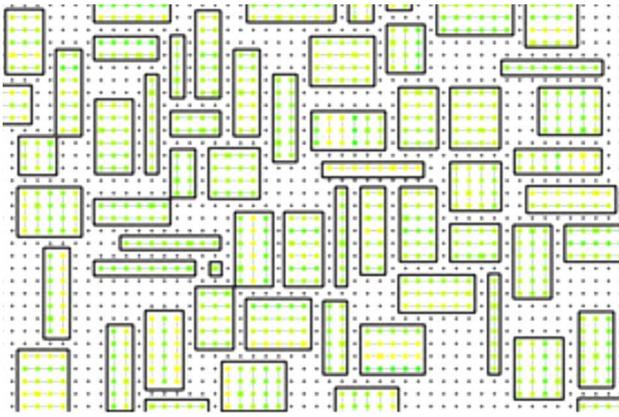
Figure 1. Example section of the modeled structure (model $M1$). Rectangles denote crystallites.

centers defined as $a/5$ and $a/2.5$; thus, jumps involving $G2$ centers proceed at a much higher rate than jumps between $G1$ centers (model $M1$). To obtain data for comparison, calculations were also performed for the case when point $G2$ states are distributed randomly in space and have the same localization radius as $G1$ (i.e., are point defects and do not form crystallites; single-phase amorphous material, model $M0$). The drift mobility is calculated based on the time of carrier transit through a layer averaged over several thousand tests: $\mu = \langle 1/t_{tr} \rangle \cdot (L/F)$, where L is the layer thickness, F is the electric field strength, and t_{tr} is the transit time. In contrast to most earlier studies [1–3,5], the field is applied transverse to a thin layer ($20 \leqslant L \leqslant 100$ nm, the other dimensions are an order of magnitude greater) rather than along it. This is not relevant to transistors, but typical of LED and photovoltaic applications.

The results of calculations demonstrate that the dependence of mobility on the average crystallite size for two-phase systems is fairly weak; crystallite fraction V is a more important parameter. The drift mobility decreases considerably as the layer thickness increases (at least up to $L = 100$ nm). This is apparently attributable to the contribution of diffusion to current. The „true“ mobility characterizing the material was obtained by extrapolating the thickness dependence of drift mobility [7]. Thus, the MC simulation method used in the present study allows one to determine both the drift mobility in thin (less than 100 nm) layers and the „true“ bulk mobility based on the results of calculations for thin layers, thus saving computational resources.

Figure 2 shows the dependences of „true“ mobility on volume fraction V of the crystallite phase at different values of E_t. The mobility is normalized to its value at $V = 0$ (μ_0). The mobility in the two-phase material normally increases with V and may be several orders of magnitude higher than μ_0. In the amorphous material, the mobility increases with V if the average energy of crystallites is not too high. If this is not the case, dependence $\mu(V)$ has a deep minimum at $V < V_* \cong 0.1$. At a given fraction of $G2$

states V, the amorphous material mobility (both „true“ and drift at $L = 100$ nm) goes through a maximum at a certain $E_t = E_t^{\max}$ (Fig. 3, a). The mobility is normalized to the value of μ_0 at $V = 0$ and $T = 298$ K. The same is true for the two-phase system (Fig. 3, b). However, owing to a high rate of jumps within and between crystallites due to a weaker localization of wave functions of $G2$ states, $\mu/\mu_0 > 1$ here throughout the entire examined parameter range.

It is arguable that $E_t^{\max} \approx E_C$, where E_C is the transport level [8], in the amorphous material; thus, $G2$ centers at $E_t \approx E_t^{\max}$ act as „conduction“ states rather than as traps (as is the case at $E_t \ll E_C$ and $V \ll V_*$). At $E_t^{\max} \approx E_C$, the fraction of „conduction“ states grows with V, and the mobility increases; at $E_t \ll E_C$, the mobility decreases until jumps between $G2$ centers at $V > V_*$ start to dominate over thermally activated jumps to states near the transport level. In the case of very deep $G2$ centers, jumps occur only between these centers.

It is unclear how to determine the transport level for the two-phase system (model $M1$) when fraction V is sufficiently high; however, the dependence of average energy E_{av} of occupied states on energy E_t may be analyzed. Calculated data reveal that this energy at a fixed V reaches its maximum $E_{av}^{\max}$ exactly at crystallite depth $E_t^{\max}$ corresponding to the maximum mobility. Thermal activation does not hamper most jumps in this case, and the density of states near both energies E_{av} and E_t is maximized. A carrier easily finds state $G1$ with the same energy near a crystallite and uses it as a „bridge“ between crystallites. Since such transitions do not require any significant thermal activation,
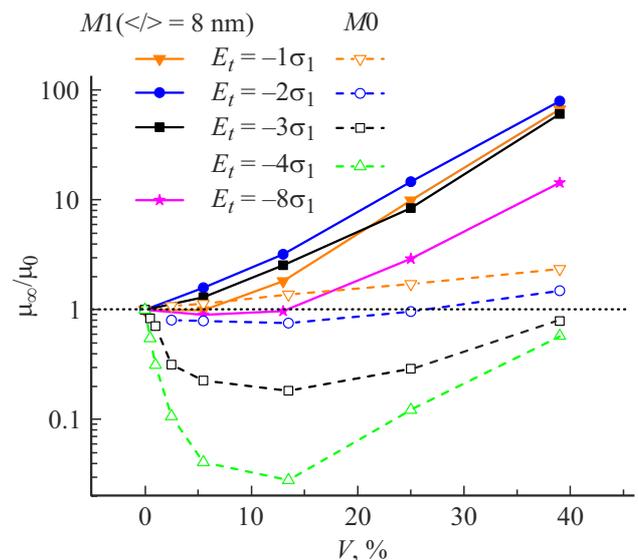

Figure 2. Drift mobility as a function of volume fraction of $G2$ states for two-phase (model $M1$, filled symbols and solid lines) and amorphous (model $M0$, open symbols and dashed lines) materials at different values of average energy E_t of $G2$ states. $T = 298$ K, $\sigma_1 = 2.12kT$, $\sigma_2 = \sigma_1/3$, $eFa = kT$, F is the electric field strength, and $a = 1$ nm.
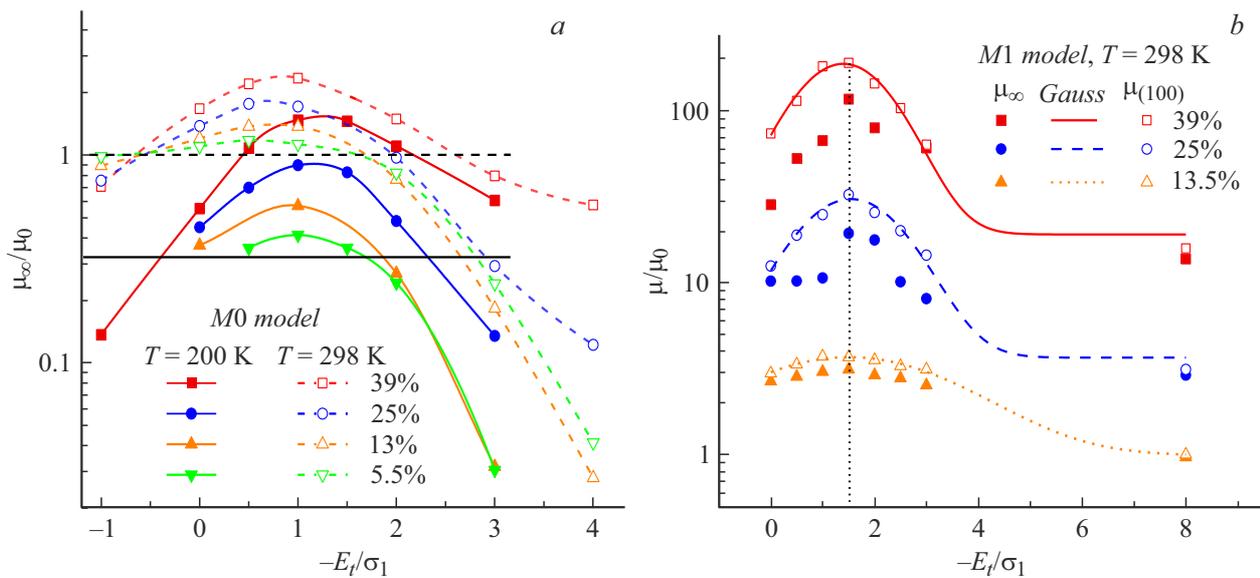
Figure 3. Dependences of mobility on the average depth of $G2$ centers for various fractions V of $G2$ centers. a — Amorphous material (model $M0$), „true" mobility. Horizontal lines denote the mobility values at $V = 0$. b — Two-phase material (model $M1$), „true" mobility (filled symbols) and drift mobility at $L = 100$ nm (open symbols and curves).

the mobility is maximized. If $E_t > E_t^{max}$ ($E_t < E_t^{max}$), thermal activation from states $G1$ to $G2$ (from $G2$ to $G1$) hampers transport. At $E_t \ll E_t^{max}$, thermal activation from states $G2$ to $G1$ is unlikely, and the transport rate is limited by jumps over large distances between crystallites. Therefore, the mobility increases with V (Fig. 2) and depends weakly on temperature due to a low degree of energy disorder of $G2$ states ($\sigma_2 < kT$). Just as in [5], the temperature dependence of mobility in the present study follows the Arrhenius law: $\mu \propto \exp[-E_a/kT]$. At $E_t \approx E_t^{max}$ and room temperature, activation energy E_a is close to $\sigma_1^2/kT = 0.1$ eV; i.e., transport is controlled by thermally activated jumps from the „tail" of $G1$ states [6]. This agrees qualitatively with the data from [2] (from 0.05 to 0.1 eV). Consistent with the calculation results reported in [5], the activation energy at high $|E_t|$ values and low temperatures is low (several meV) and is almost independent of $|E_t|$, since transport is effected via jumps between crystallites.

Thus, dependences of the drift mobility on the volume fraction of the crystallite phase, the average energetic depth and the average size of crystallites, and temperature were determined. The physical mechanisms inducing them were identified. The obtained results explain why crystallization at different molecular structures (under the assumption that E_t depends on them) may trigger both a reduction (the amorphous phase acts as traps at grain boundaries, $E_t \gg E_t^{max}$) and an increase in mobility relative to the amorphous-phase mobility [4] ($E_t \approx E_t^{max}$, amorphous-phase states are involved in conduction). These results allow one to estimate the material structure parameters at which the mobility in a layer of a given material reaches its maximum. This is important for optimization of characteristics of an electronic device containing the indicated active layer.

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Conflict of interest

The authors declare that they have no conflict of interest.

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