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Fast Charge Transport in Nanocomposite Polymer Materials Containing J-Aggregates

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Charge transport in polymers containing J-aggregates of cyanine dyes serving as fast transport channels is considered. Shape of photocurrent transient depends on initial spatial distribution of carriers. If carriers are homogeneously generated at the electrode surface, then at the initial stage current raises reflecting carrier collection to fast channels and corresponding rate constant is determined by channel density.

Keywords: charge carrier transport; composite materials; J-aggregates

1 INTRODUCTION

Under proper treatment some organic polymers (polyimides and others) doped with cyanine dyes demonstrate formation of highly ordered J-aggregates of dye molecules in the bulk of the polymer matrix. J-aggregates usually contain many molecules of a dye and may be considered as nanocrystals. Such composite polymer materials demonstrate intense narrow band electroluminescence (attributed to J-aggregates) that can be exploited in electronic organic devices [1].

Experimental data on the positions of transport energy levels in polymers, dye molecules, and J-aggregates suggest that both isolated dye molecules and J-aggregates should serve as traps for electrons and holes, and yet hopping mobilities of both kinds of carriers are

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much greater (by the order of magnitude) in nanocomposite material in comparison with undoped polymer [1,2]; polymer matrices doped with non-aggregated dyes do not demonstrate increase in carrier mobility. This observation suggests that in thin (100–200 nm) transport layers J-aggregates provide channels connecting the opposite electrodes and carriers could travel from one electrode to another without need to enter into the polymer matrix. Very long thread-like structures of J-aggregates have been directly visualized in supercooled water solutions of cyanine dyes [3]. Motion of carriers inside regular quasi-crystalline channels with reduced energetic disorder naturally explains high mobilities of carriers in composite materials.

The simplest model of the composite material should be a quasi-crystalline cylindrical channel with radius b between two electrodes surrounded by disordered polymer matrix. We used the model of dipolar glass [4] to describe disordered polar polymer serving as a source of residual energetic disorder $U(\mathbf{r})$ inside the transport channel. Sites of the channel carry no dipole moment and all energy fluctuations at these sites are due to contributions of the surrounding dipolar matrix (see Fig. 1). To model difference in positions of energy levels in the dipolar matrix and J-aggregate a constant value Δ was subtracted from the energy of every site inside the channel. Every basic cell with linear size L contains one channel, so the surface density of channels is $1/L^2$ (in simulation we used $L = 50a$, where $a \approx 1\,\text{nm}$ is lattice scale).

2 MONTE CARLO SIMULATION OF TOF CURRENTS

Monte Carlo (MC) simulation of time-of-flight (TOF) current transients demonstrates that in nanocomposite material carrier mobility μ becomes greater and for weak electric field E the usual Poole-Frenkel dependence

$$\mu \propto \exp(\gamma E^{1/2}) \tag{1}$$

takes place with coefficient γ having the same magnitude as in the case of undoped matrix (see Fig. 2). Simulation reveals a characteristic feature of the transient in the case of homogeneous carrier generation at the electrode surface: for small time current raises with time (after initial sharp decrease, associated with energetic relaxation), which reflects collection of carriers to fast transport channels (see Fig. 3).

Simulation results suggest that two conditions are necessary for realization of fast transport: first, aggregates should have quasi-crystalline structure that provides reduced energetic disorder inside channels; second, transport energy levels in aggregates have to be

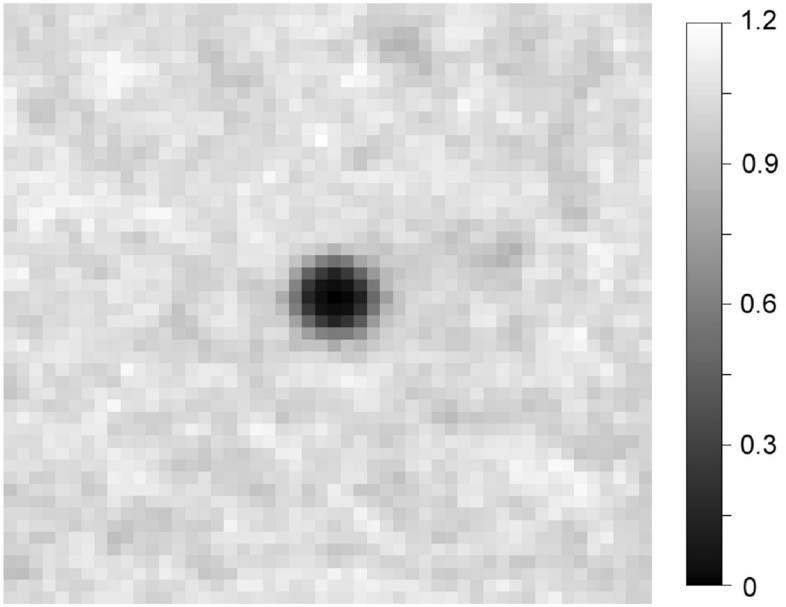

FIGURE 1 Fast channel with $b = 3a$ in dipolar matrix. Distribution of variance $\sigma_l^2 = \langle U^2(\mathbf{r}) \rangle / \sigma^2$ across a cross-section of the basic lattice sample is shown (average is calculated along lines parallel to channel direction), here σ^2 is energy variance in undoped dipolar glass; typically, $\sigma \approx 0.1\,\text{eV}$. Minimal value of σ_l^2 is about 0.1.

located at lower energies in comparison to the transport levels in surrounding matrix, thus serving as effective traps for carriers. Effective trapping is absolutely necessary for realization of fast transport, thus Δ should be large enough (see Figs. 2 and 3, curves for $\Delta/kT = 5$ and $\Delta/kT = 16.7$). Without trapping carriers quickly leave fast channels and get trapped by deeper energetic wells in the surrounding disordered matrix, effective carrier collection does not take place, and photocurrent transient has an ordinary form (Fig. 3, curve for $\Delta/kT = 5$). In materials discussed in [1,2] Δ is large enough ($\Delta \approx 0.5\,\text{eV}$), while preliminary experimental data indicate that formation of J-aggregates does not change mobility of holes in composite materials with small Δ [5].

If carriers are generated in channels, then, naturally, initial raise of the current does not take place. Yet trapping of carriers in channels is still a necessary condition for fast transport: if Δ is too small, carriers quickly diffuse out of channels. In that case initial sharp decrease of current becomes prolonged reflecting spatial relaxation of carriers.

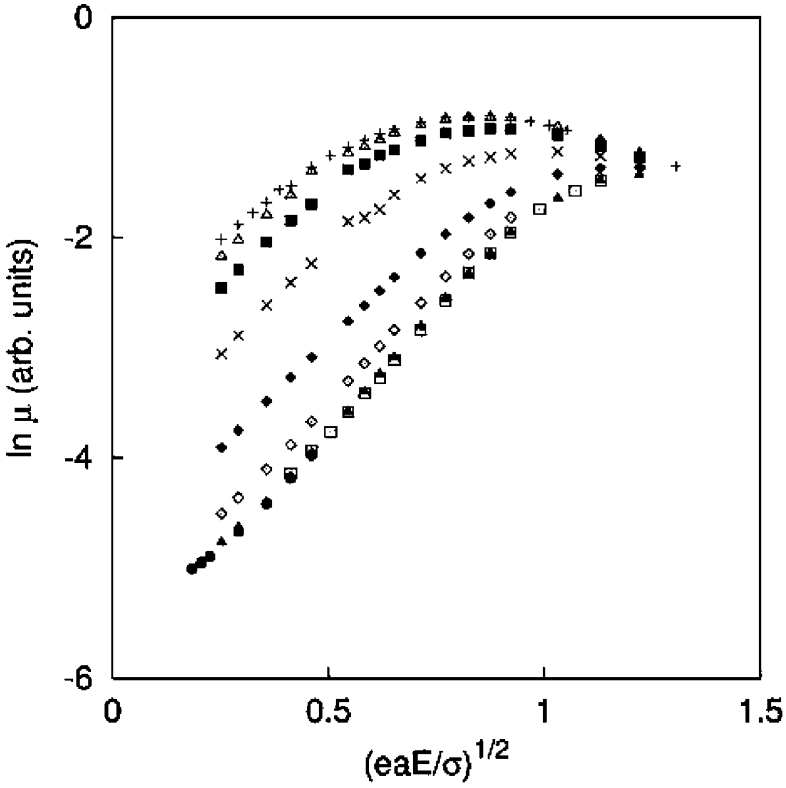

FIGURE 2 Mobility field dependence for MC simulation, $\sigma/kT = 3.9$: dipolar glass (□); composite with $b = 3a$ for different values of Δ/kT: 33.3 (+), 16.7 (△), 10 (■), 8.3 (×), 6.7 (◆), 5 (◇), 0 (●), correspondingly; dipolar glass with "channel" arranged by setting traps with $\Delta/kT = 16.7$ in cylinder domain (▲). If $\sigma = 0.1\,\text{eV}$ and $a = 1\,\text{nm}$, then $eaE/\sigma \approx 1$ at $E = 10^6$ V/cm.

Here fast transport could be realized only in very thin transport layers, in thicker layers mobility curve $\mu(E)$ does not differ from the corresponding curve for the undoped material.

3 CURRENT RELAXATION AT THE INITIAL STAGE

Initial current raise in the case of homogeneous photogeneration may be reasonably well described by a simple model that considers the carrier motion as a superposition of the drift along field direction and 2D transverse diffusion with diffusion coefficient D to the channel serving

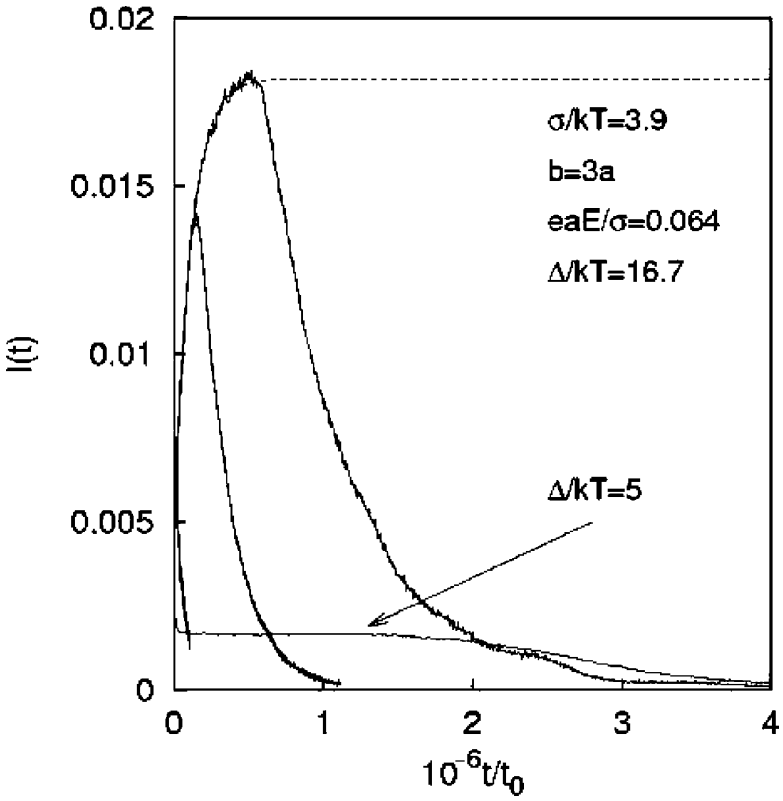

FIGURE 3 Current transients for transport layers with different thickness: 500, 5,000, and 20,000 lattice planes, correspondingly; $1/t_0$ is the hopping frequency. Broken line shows the fit of the transient for 20,000 planes for Eq. (7). The bottom line is the transient for $\Delta/kT = 5$ and 5,000 planes.

as a sink (for simplicity we consider cylinder domain with radius $R \approx L/2$)

$$\frac{\partial c}{\partial r} = D\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right) \tag{2}$$

with boundary conditions $c(b,t) = 0, \partial c/\partial r = 0$ at $r = R$, and initial condition $c(r,0) = c_0, R > r > b$. Usual procedure gives solution with Bessel functions

$$c(r,t) = \sum_{n=0}^{\infty} A_n \exp(-k_n t)\left[J_0(\lambda_n r) - \frac{J_0(\lambda_n b)}{Y_0(\lambda_n b)}Y_0(\lambda_n r)\right], \quad \lambda_n = \sqrt{k_n/D}, \tag{3}$$

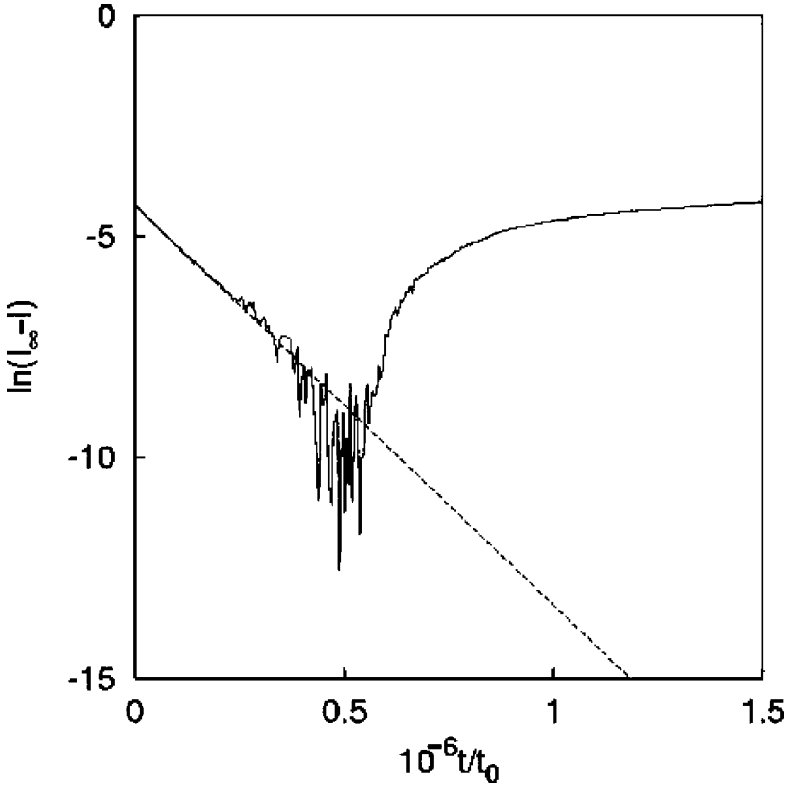

FIGURE 4 Fitting of the transient (Fig. 3; 20,000 planes) for Eq. (7). Best fit (broken line): $k_0 = 9.04 \times 10^{-6}/t_0$.

with eigenvalues λ satisfying equation

$$Y_0(z)J_1(\zeta z) - J_0(z)Y_1(\zeta z) = 0, \quad z = \lambda b, \quad \zeta = R/b. \tag{4}$$

For $\zeta \gg 1$, the only case where the model of isolated transport channel may be applied, the smallest root of Eq. (4) is

$$z_0 \approx \frac{1}{\zeta}\sqrt{\frac{2}{\ln \zeta - \gamma_E}}, \tag{5}$$

where $\gamma_E = 0.5772\ldots$ is Euler constant, and for large n an asymptotic equation is valid

$$z_n \approx \frac{\pi}{\zeta - 1}\left(n + \frac{1}{2}\right), \quad n \gg 1. \tag{6}$$

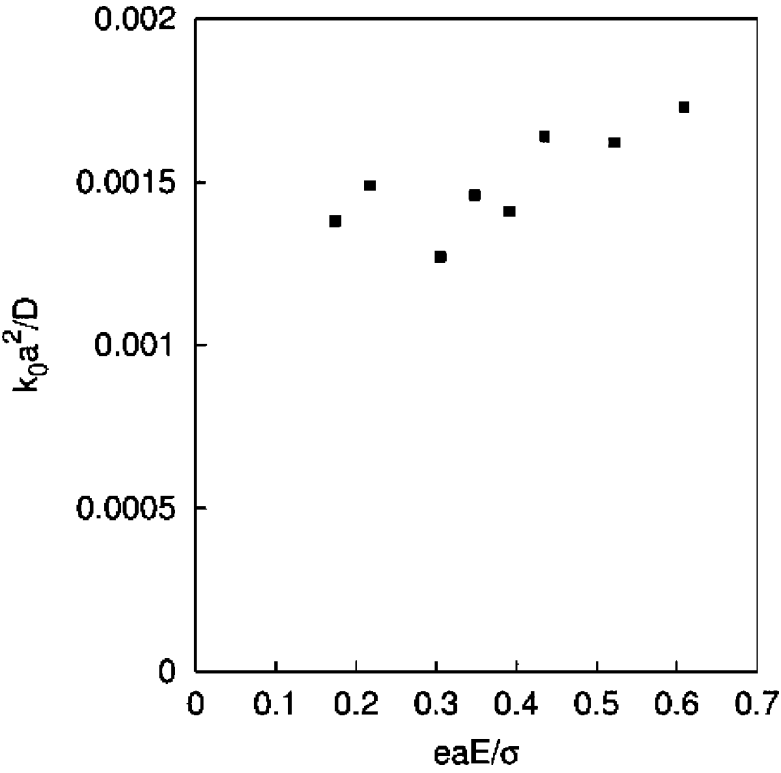

FIGURE 5 Field dependence of the parameter k_0a^2/D in nanocomposite material for $\sigma/kT = 3.9$ and $R/b = 8.33$.

In fact, Eq. (5) has accuracy of 5% even for $\zeta = 3$, and Eq. (6) has the same accuracy even for $n = 1$.

If time is not too small, then only the first term (with smallest eigenvalue) in the sum (3) is important (if $\zeta \gg 1$, then $k_1/k_0 \gg 1$), so total number of carriers in the matrix is $N_m(t) \propto N_m^0 \exp(-k_0 t)$ and for current we have

$$I(t) \propto (N_c^0 + N_m^0)\mu_c - N_m^0(\mu_c - \mu_m)\exp(-k_0 t), \tag{7}$$

here N_c^0 and N_m^0 are initial numbers of carriers in channels and matrix, and μ_c and μ_m are their mobilities, correspondingly. Analysing $I(t)$, we could find k_0 (see Figs. 3 and 4).

This scenario suggests that field dependence of k_0 should reflect that of D and the ratio k_0/D does not depend on E. Computer simulation carried out in close resemblance to that described in [4] proved that this is indeed the case: for $\sigma/kT = 3.9$ and $R/b = 8.33$

$k_0 a^2/D \approx 1.6 \times 10^{-3}$, while Eq. (5) gives $k_0 a^2/D \approx 2 \times 10^{-3}$ (see Fig. 5; it is worth to note that in this field range both D and k_0 grow with field approximately by one order of magnitude). Typically, k_0^{fit} and k_0^{calc} differ by factor of 2–3; we cannot expect better agreement with our crude approach. Exponential term in Eq. (7) develops only if transit time for channels t_{TOF} is large enough, namely $k_0\ t_{\text{TOF}} \geqslant 1$, this leads to a simple estimation for transport layer thickness

$$l \geq \frac{\mu_c}{\mu_m} \frac{eER^2}{kT} \ . \tag{8}$$

For $\mu_c/\mu_m = 10$ and $E = 10^5\,\text{V/cm}$ at room temperature we have $l \geq 1.5$ micron for $R = 20\,\text{nm}$.

The most important result of this consideration is the possibility to estimate typical distance $2R$ between conducting channels knowing k_0 and D. Simulation shows that D may be reasonably well estimated by the Einstein equation $D = kT\mu/e$ from the TOF data. It would be extremely interesting to compare TOF data for channel density with direct visualization of the composite layer surface with the use of AFM: how many visible channels are in fact conducting? Then we could estimate typical current density in a channel and consider an important problem of thermal stability of nanocomposite devices.

4 CONCLUSION

Extensive MC simulation of charge carrier transport in nanocomposite polymer materials has been carried out. Data show that the key feature of the TOF transients in materials with well isolated channels for the case of homogeneous (or, even better, out of channels) carrier generation is an initial raise of photocurrent which reflects collection of carriers to fast channels. At this stage current temporal dependence follows simple exponential law, and the rate constant provides direct information about surface density of conducting channels. Experimental observation of this particular behavior could serve as a reliable test of the model. Proper initial spatial distribution of carriers may be achieved by choosing a suitable photoexcitation wavelength.

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