Excitation Trapping in Dynamically Disordered Polymers

ARTICLE *in* MACROMOLECULES · MARCH 1998

Impact Factor: 5.8 · DOI: 10.1021/ma9715987

Excitation Trapping in Dynamically Disordered Polymers

T. Pálszegi,[†,‡] I. M. Sokolov,[§,∥] and H. F. Kauffmann*[,†]

Institut für Physikalische Chemie, Universität Wien, Währingerstrasse 42, A 1090 Vienna, Austria, Department of Chemical Physics, Faculty of Chemical Technology, Slovak Technical University, Radlinskeho 9, 812 37 Bratislava, Slovakia, Theoretische Polymerphysik, Universität Freiburg, Rheinstrasse 12, D-79104 Freiburg i.Br., Germany, and P. N. Lebedev Physical Institute of Academy of Sciences of Russia, Leninsky Prospect 53, Moscow 117924, Russia

Received October 30, 1997; Revised Manuscript Received February 3, 1998

ABSTRACT: Trapping of migrating incoherent electronic excitation by dynamically disordered substitutional traps in a 1-D polymer chain has been studied analyticaly and by means of Monte Carlo simulations. A closed-form analytical solution to the model is based on the assumption that the temporal changes in the spatial coordinates of the traps, due to conformational motion, can be mimicked by a global Poissonian renewal process of the polymer configuration as a whole. The excitation survival probability $P(t)$ for this model of dynamic disorder hopping (DDH) obeys an Ornstein−Zernike-type integral equation, which can be solved analytically in the short- and long-time limits and numerically in the whole time domain. The DDH results are compared with Monte Carlo simulations using discrete and continuous-time random walks showing a good agreement. The relevance of our theoretical findings has been discussed and connections have been made to observations of migrative excitation trapping in aromatic vinyl polymers, where the traps—in the pair approximation—consist of mobile excimer-forming sites (EFS) triggered by the local conformation of a chain.

1. Introduction

Incoherent electronic excitation energy transport (EET) in a side-chain polymer is generally perceived as a superposition of multistep donor−donor and irreversible, single-step transitions to substitutional traps, both processes being substantially affected by the site density, the site disorder, and the location of the traps, as well as by the dimensionality and the anisotropy of the transport pathways.[1] In many situations, the traps correspond to moieties other than monomeric donor sites, with their positions being fixed along the chain coordinates. On the other hand, an entirely different situation will arise, where one and the same chromophoric site may represent both a donor and a trap state as a stochastic function of time, determined by the thermal equilibrium conditions. The local changes of a chromophore from its donor state to a trap state and back provides an example of a reversible process associated with a change of its self-energy. In particular, for aromatic vinyl polymers in liquid solution, the traps are attributed to dynamic excimer-forming sites (EFS) resulting from typical polymer-inherent conformations composed of distinct pairs of donor chromophores and spatially varying on the time scale of rotational diffusion.[2]

Incoherent migrative excitation trapping along *static* chains containing substitutional traps was extensively studied in the past.[3−11] Contrary to these investigations, much less is known about the *dynamic site disorder regime* of a polymer where the spatial positions of donors (D) and traps (T) become time-dependent on the time scale of EET. In this situation EET can be conceived as a complex knot of energy transport and dynamic molecular processes, where continuous, positional changes of sites alter the preferred migrative pathways and form-up or destroy excimer-forming sites via conformative transitions, i.e., motional pathways of torsional angle rotations (rotational sampling or, more precisely, conformational sampling). The problem of migrational EET superimposed by rotational sampling in an aromatic site polymer was tackled by Fredrickson and Frank.[12] Assuming the rate of rotational sampling to be slow as compared to that of migrational sampling, they have formulated the dynamics in terms of a quasi-static D−D transport separated by conformational breaks (disruptive chains).[12,13] Their treatment led to a typically nonexponential decay law, which was successfully applied to the analysis of transient fluorescence of poly(2-vinylnaphthalene) in dilute solutions and blends.[14] Similar kinetics was studied in distributed, reversible donor−excimer systems along polymer backbones, both in the (predominantly) migrative[15] and in the rotational sampling regime.[16]

The aim of the present work is to analyze EET in the presence of dynamically disordered traps with the help of a dynamic disorder hopping (DDH) method.[17] Originally, the DDH model was used to tackle the problem of charge transport by means of a random walk with global renewals of the lattice, with the objective of calculating the mean-square distance of charge transport.[18] In this approach the method is based on a global description of dynamical disorder, in which the dynamics of the system is modeled by renewals of static disorder configurations in the entire system taking place at random times. The global renewal time τ_{conf} is a model parameter and, in our study, is proportional to the inverse of the rate constant of the local conformational transitions, causing, for example, the EFS formation. Information about the rate of such conformational transitions (i.e., the activation energy of segmental rotation from an Arrhenius functional low) can be extracted by applying our model to fluorescence trapping measurements in aromatic polymers. The flex-

[†] Universität Wien.
[‡] Slovak Technical University.
[§] Universität Freiburg.
[∥] Academy of Sciences of Russia.

S0024-9297(97)01598-2 CCC: $15.00
Published on Web 03/26/1998

ibility and morphology of these polymers is strongly determined by the dynamics and energetics of local chain motions.

In this work (section 2), our central concern is to make use of the DDH method to formulate the excitation survival probability $P(t)$ for a 1-D excitonic chain in the presence of dynamically disordered substitutional traps. Closed form solutions will be worked out, and the accuracy of this description will be checked by continuous as well as discrete time random walk simulations (section 3). Moreover, the possible application of the method to migrative trapping experiments on aromatic vinyl polymers in liquid solution will be considered. In these systems the renewals are determined by the conformational transitions of donor pairs leading to the formation and dissociation of EFS. In section 4 a summary of the results and concluding remarks are presented.

2. DDH Model and Its Solution

In general, conformational and torsional site transitions in a polymer create a pronounced dynamical disordering factor for EET, as these processes make the hopping and trapping rates stochastic in time. For EET among pure donor sites (no traps) the corresponding equation of motion describing the evolution of site excitation probabilities (sometimes called the stochastic master equation) has been solved for site ensembles, whose position and/or orientation is modulated by different types of motional modes (diffusion, rotation, etc.).[19−24]

The master equation characterizing the marginal probability distribution for the *composite stochastic process* of excitation hops (along the chain in a particular conformation) *and* conformational changes (independent of the exciton position) provides another mathematical tool for studying dynamically disordered EET. Depending on the system's complexity, this type of master equation (whose size is given by the number of the chromophore sites times the number of possible chain conformations) can be solved analytically (for short chains, ca. 10 chromophores), by the dynamical Monte Carlo simulation[25] (for several hundreds of chromophores), by the cumulant expansion method (for fast conformational motion[25]), or with the help of the effective medium method of Harrison and Zwanzig[26] (for infinite system[27,28]). Finally, both the resolvent-matrix method of Cáceres and Budde[29] and an integral equation method of Vlad[30] are additional and powerful tools for solving composite stochastic processes.

If the conformational changes take place on the time scale of EET, it is a general experience drawn from such studies that the effect of dynamic disorder, i.e., the time-dependent fluctuations of torsional angles caused by conformational transitions among the site-ensemble in the polymer backbone, makes modeling of EET a difficult enterprise. Only for times shorter than the characteristic time of large amplitude site fluctuations does the static disorder of spatial and energetic site coordinates provide a quite satisfactory basis for the stochastic description of EET.

Setting the features and limitations of the DDH method, the different time domains relevant to the excitation transfer in vinyl polymer chains have to be addressed. In many morphological situations these scales create physical boundary conditions that allow us to tackle the dynamical disorder modulation problem and thus to simplify the EET hopping process. On one hand, it is reasonable to assume that the duration of an elementary, incoherent site-to-site EET between two chromophores is short on the time scale of conformational changes. In this limit, the elementary acts of conformational transitions are assumed to be rare and of short duration.[31] As a consequence, during the relatively long residence time of a conformative state, EET can be considered as evolving in a static structure, and the amount of energy transferred *during* the conformational changes can be neglected. The same factoring is also assumed for the long-range librational relaxations after (and before) the conformational transitions.

On the other hand, the short-range fluctuations of torsional angles are fast on the time scale of the elementary steps of EET and can be included in the excitation transfer rate constants via the Franck−Condon factors, in a way similar to the fast bond vibrations being concealed in the Förster rate constant.[32] Assuming these conditions to be fulfilled on the time scales of exciton and torsional angle dynamics, a simplified picture of EET in disordered aromatic polymers arises: (i) excitation hopping transfer is proceeding, specifically, along those sites whose positions correspond, exclusively, to the conformational minima of the polymer's potential energy, and (ii) the conformational transitions between these stable conformations are sudden and random both in time and in space along the chain. The overall structure of traps is thus dynamically changing so that the initial configuration of the system gets forgotten after some time t. In our DDH approach we model this effect by a renewal of the whole configuration, which is plausible, because the excitation confined between the two traps does not feel whether all other traps are renewed simultaneously or not. It is necessary to mention that the global renewal time τ_{conf} is a model parameter, and our further simulations will show that this quantity does not strongly deviate from the mean lifetime of a trap (EFS). This is why the dynamic disorder in the DDH method is assumed as *global*. This concept is opposite from the *local* dynamic disorder, the latter being a terminology that refers to the pure, local conformational changes at *random times* at *random positions* along the polymer chain.

The technique of our DDH approach is related to the method outlined by Hernández-García et al.,[33] where the stochastic master equation was solved in terms of the Green function formalism under inclusion of both global and local renewals of the disorder. In the paper of Plonka et al.[34] the DDH method was applied to calculate the number of the sites visited by a random walker in a renewed environment, a quantity of interest when considering reactivity in relaxing solid state systems.

In the next paragraphs we describe in detail the DDH solution to the migrational excitation trapping problem, where the traps are considered to be substitutional in nature, with a spatial distribution subject to dynamic disorder.

In the first part of our analysis, we assume that each trap occupies one site of a model chain only (this section). In a next step, the effect of the two-site character of EFS traps on migrative trapping will be discussed for the vinyl-aromatic chain (section 3).

To begin, let us consider the donor excitation survival probability $P_s(t)$ in a static array of traps. For a particular realization of a walk the probability F_n that trapping did not occur before the nth step is equal to $(1-p)^{R_n-1}$, where p is the probability that the chromophore visited by migrating excitation is a trap, randomly substituted between donors (trap concentration), and R_n is the number of different chromophores visited by the excitation during n steps. The survival probability $P_s(t)$ is then obtained by averaging F_n over all random walks and all starting points of the exciton. The cumulant expansion expresses this average $P_s(n) = e^{\lambda}\langle e^{-\lambda R_n}\rangle_{stat}$ by a single-exponential function (here $\langle ...\rangle_{stat}$ denotes the average over all random walks and all starting points of electronic excitation on static chromophore system and $\lambda = -ln(1-p)$). The excitation survival probability $P_s(n)$ for a nearest-neighbor random walk of excitation on a static disordered system of donors and substitutional traps after n steps is then given by[35]

$$P_s(n) = e^{\lambda}\exp\left[\sum_{j=1}^{J} K_{j,n}\frac{\lambda^j}{j!}\right] \qquad (1)$$

where $K_{j,n}$ is the jth cumulant of the distribution of the number R_n of chromophores visited in n steps, calculated for all realizations of random walks from all starting points of the exciton. The first cumulant is defined by

$$K_{1,n} \equiv S_n = \langle R_n\rangle_{stat} \qquad (2)$$

where S_n is the mean (average) of R_n. The second cumulant is given by the equation $K_{2,n} \equiv \sigma_n^2 = \langle R_n^2\rangle_{stat} - \langle R_n\rangle_{stat}^2$, where σ_n^2 denotes the variance of R_n. The goodness of the cumulant approach to $P_s(n)$ as a function of the higher order expansion terms and its asymptotic form have been rigorously analyzed by Zumofen and Blumen.[36] In what follows we consider the continuous-time version of the above relations obtainable by replacing the discrete number of steps n through the function n_t^{exc} given by the equation $n_t^{exc} = t/\tau_{exc}$ (see in ref 35); here τ_{exc} is the mean time of the electronic excitation transfer between two donors, $\tau_{exc} = \int_0^\infty t\psi_{exc}(t)\,dt$, where $\psi_{exc}(t)$ is the waiting-time distribution of excitation transfer. We use the index exc for steps of excitation, to distinguish them from the steps of conformational changes. The simple replacement of n by n_t^{exc} in the functions dependent on the number of discrete steps is reasonable for the finite characteristic time τ_{exc} of excitation transfer. The average number of the visited chromophores $S(t)$ is then given by replacing n by n_t^{exc} in eq 2.

For short times the survival probability $P_s(t)$ of an excitation in a static donor−substitutional trap system is given by

$$P_s(t) = \exp(-R(t)) \qquad (3)$$

with $R(t)$ having the following explicit form

$$R(t) \doteq \lambda(S(t) - 1) \qquad (4)$$

and $S(t)$ being the number of different sites visited within the time t (Rosenstock approximation). By comparison of eqs 1 and 3, one readily infers that $R(t)$ represents the first-order approximation to the continual form of the expression $\sum_{j=1}^{J} K_{j,n}(-\lambda^j/j!) - \lambda$. For longer times higher cumulants must be taken into account. In the asymptotic limit the reaction is slowed considerably in comparison with eq 3, which is caused by the Vaks−Balagurov slowing down due to the fluctuation effects.[37,38] We mention that our further considerations are quite general and will hold for any form of $P_s(t)$, until the explicit calculations (eq 9) are performed on the basis of the short-time form of eq 3.

Note that eq 3 does not account for the fluorescence, which, due to its radiative loss term, lowers the survival probability. However, multiplication of $P_s(t)$ by an exponential factor $\exp(-t/\tau_F)$, standing for the natural decay of a chromophore site, can be applied in any stage of the calculation, as long as the trapping process is irreversible.

We turn now to the *dynamically* disordered case. As mentioned above, we model this dynamical disorder in a system of donors and substitutional traps by global renewals of the system, i.e., by the full change of the whole configuration at traps after some time τ_{conf}.

After a renewal the previous configuration is fully forgotten, and eq 3 is valid again, now for all the particles that have survived during the previous renewal interval. Therefore, given the times of the renewals t_1, t_2, ..., t_n, the survival probability until the time t is

$$P(t) = P_s(t_1)P_s(t_2) \ldots P_s(t_n)\,P_s(t - t_n) \qquad (5)$$

Equation 5 simply states that after each renewal the system's structure is assigned anew and that the memory about the previous state is erased. Multiplying eq 5 by the joint probabilities to have no renewals or, correspondingly, 1, ..., n renewals at the times t_1, t_2, ..., t_n and integrating over the entire set of possible renewal times, one finds then for the mean survival probability in a dynamical system

$$P(t) = P_s(t)\,\Psi_0(t) + \int_0^t P_s(t_1)\,P_s(t - t_1)\,\psi(t_1)\,\Psi_0(t - t_1)\,dt_1 + \ldots + \int_0^t P_s(t_1)\,P_s(t_2) \ldots P_s(t_n)\,P_s(t - t_n)\,\psi(t_1) \times \psi(t_2) \ldots \psi(t_n)\,\Psi_0(t - t_n)\,dt_1\,dt_2 \ldots dt_n + \ldots \qquad (6)$$

where $\psi(t)$ is the waiting-time distribution of the renewal process and $\Psi_0(t) = 1 - \int_0^t \psi_{ren}(t')\,dt'$ is the probability that no renewals occur during the time t. Note that all the integrals in the sum have the structure of multiple convolutions of the functions $f(t) = P_s(t)\,\psi(t)$ with the function $F_0(t) = P_s(t)\,\Psi_0(t)$. The overall sum $P(t) = F_0(t) + \int_0^t f(t_1)\,F_0(t - t_1)\,dt_1 + \ldots$ satisfies then the Ornstein−Zernike-type integral equation, which has been used in different fields of physics (e.g., by Burshtein et al. for static EET; see ref 39 and citations there):

$$P(t) = P_s(t)\,\Psi_0(t) + \int_0^t f(t_1)\langle P(t - t_1)\rangle\,dt_1 \qquad (7)$$

Equation 7 can be easily solved numerically using the explicit forward scheme

$$P_{i+1} = F_{i+1} + h\sum_{j=1}^{i} f_i P_{i-j} \qquad (8)$$

where h is the time step and P_n, f_n, and F_n are the values $P(t)$, $f(t)$, and $F_0(t)$, respectively, taken at $t = nh$.

Now, let $P(t)$ be calculated for the 1-D case. By measurement of the time in units of the mean hopping time of the excitation, the dimensionless time $\mathbf{t}$ coincides then with the average number of steps made up by a random walker, formally: $\mathbf{t} \equiv n_t^{\mathrm{exc}} = t/\tau_{\mathrm{exc}}$. In this situation, one approximately has $S(t) \approx \sqrt{(8/\pi)\mathbf{t}}$ for a one-dimensional transport along the chain and, by neglecting fluctuation effects (refs 37−39), one arrives at $P_s(\mathbf{t}) = \exp(-p\sqrt{(8/\pi)\mathbf{t}})$. This equation is valid for the limit case that only the steps of the excitation along the chain are allowed. On the other hand, the overall square-root t dependence of $S(t)$ is still valid, even if the steps between monomers, which are near each other in the Euclidean space but strongly separated with respect to the chemical distance (along the chain), are possible (provided the chain-conformational changes in 3-D are not too fast). This follows from the fact that the spectral dimension of the self-avoiding walks with bridges in 3-D is approximately 1 (ref 40).

It is also assumed that the mean lifetime of the traps configuration in these units is $\tau_{\mathrm{conf}} = \tau$ so that for a Poissonian renewal process one has $\psi(t) = (1/\tau)\exp(-t/\tau)$ and $\Psi_0(t) = \exp(t/\tau)$, with τ being the mean renewal time. It follows then

$$f(\mathbf{t}) = \frac{F_0(\mathbf{t})}{\tau} = \frac{1}{\tau}\exp\left(-p\sqrt{\frac{8}{\pi}\mathbf{t}} - \frac{\mathbf{t}}{\tau_r}\right) \tag{9}$$

where $\tau_r = \tau_{\mathrm{conf}}/\tau_{\mathrm{exc}}$.

Assuming the above explicit forms for $P_s(\mathbf{t})$, $\psi(\mathbf{t})$, and $\Psi_0(\mathbf{t})$, one can show that the behavior of $P(\mathbf{t})$ for $t \ll \tau_{\mathrm{conf}}$ obeys a stretched exponential function. On the other hand, at very long times, $t \gg \tau_{\mathrm{conf}}P(\mathbf{t})$ tends to a simple exponential. To show this, one can rewrite eq 6 in the Laplace space

$$P(z) = \frac{F_0(z)}{1 - f(z)} \tag{10}$$

which leads to

$$P(z) = \tau_r\left[\left(\sqrt{2\tau_r}\exp\left(\frac{2p^2\tau_r}{\pi(1+\tau_r z)}\right)\left(\mathrm{erfc}\left(\sqrt{\frac{2p^2\tau_r}{\pi(1+\tau_r z)}}\right) - 1\right) \times \frac{p}{\sqrt{1+\tau_r z}} + 1\right)^{-1}(1+\tau_r z) - 1\right]^{-1} \tag{11}$$

In the asymptotic limit eq 11 yields the exponential form $A\exp(-b\mathbf{t})$ with parameters A and b given by

$$A = \frac{(\sqrt{2\pi}\theta\exp(\theta^2)(\mathrm{erfc}(\theta) - 1) + 2\sqrt{\tau_r})^2}{\tau_r(2\sqrt{\pi}\theta(2\theta^2 + 3)\exp(\theta^2)(\mathrm{erfc}(\theta) - 1) + 4\sqrt{2\tau_r} + 4\theta^2)} \tag{12}$$

and

$$b = A\left[2(\sqrt{\pi}\theta\exp(\theta^2)(\mathrm{erfc}(\theta) - 1) + \sqrt{2\tau_r})^{-1} - \frac{1}{\tau_r}\right] \tag{13}$$

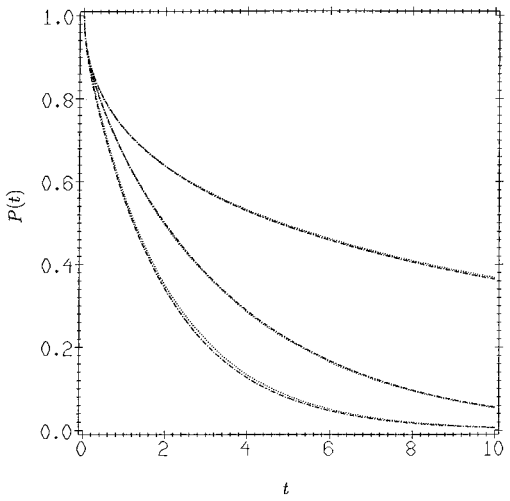

Figure 1. Time dependence of the exciton survival probability $P(t)$, trapped by dynamical one-site traps. $W = 50$ and τ_{conf} had values ∞, 1, and 0.33, respectively, for the curves from the top to the bottom (arbitrary time units) ($p = 0.02$). Numerical solution of eq 7 (dashed−dotted lines) and discrete-time Monte Carlo simulation (dotted lines).

Note that both A and b are functions of τ_r and of the important dimensionless parameter $\theta = p\sqrt{2\tau_r/\pi}$, the mean number of traps among the sites explored during τ_r steps.

In Figure 1 the survival probability $P(t)$ in a 1-D donor−trap system calculated by numerically solving eq 7 has been compared with that obtained in discrete-time Monte Carlo simulations. With regard to the latter technique we hasten to add that no considerable differences between the results of *discrete-time* and *continuous-time* Monte Carlo simulations were detected. In our simulations we have considered a 1-D donor−trap system with nearest-neighbor site-to-site interaction and a constant transition rate W of excitation hops (so the number of excitation steps per unit time is equal to $2W$), and with Poissonian renewals of traps.

The numerical solutions for $W = 50$—expressed in arbitrary time units—and for trap probability $p = 0.02$ are displayed in Figure 1 for different renewal times (dashed, dotted lines). The dotted curves correspond to the result of discrete-time Monte Carlo simulations of the same process. The numerical solution to the Ornstein−Zernike-type integral equation (eq 8) was obtained by setting $h = 0.01$. Note the good agreement between the numerical solution and the simulations for all values of parameters used. The differences between the results (in any case small) could be attributed to the fluctuation effects, i.e., the contribution of higher cumulants in eq 1. Moreover, one readily infers that the influence of the dynamic disorder of trap distribution on $P(t)$ is strong, even if the renewals are relatively rare.

To close this section, we note that we always supposed the rate constant W of the exciton hops not to be affected by the conformational changes of the chain. In real situations, clearly, more than one local configuration of donors can exist, characterized by different local transport rate constants. In such a case, the characteristic time of excitation migration along conformationally moving chains can be calculated by means of the effective medium approximation (EMA) used in previous work.[29] In those studies the migration of electronic excitation along conformationally moving polymer chains has been described by the effective rate coefficient of

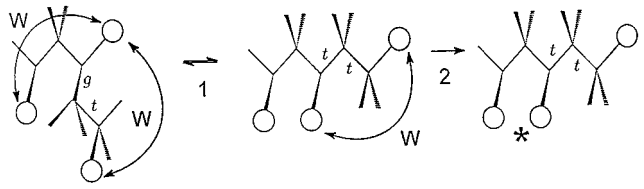

Figure 2. Scheme of a g → t conformational transition of the model chain, causing formation and dissociation of EFS (step 1) and of the excimer (step 2). The excimer is signed by an asterisk and the excitation transfer rate is quoted by *W*.

migration $W_{\text{eff}}(t)$, which is a well-behaved quantity in the migrational trapping case, as well, provided the concentration of EFS is low. The expressions for $\psi_{\text{exc}}(z)$ and for τ_{exc} follow then from $\tau_{\text{exc}} = \int_0^\infty t\psi_{\text{exc}}(t)\,\mathrm{d}t$ and $\psi_{\text{exc}}(z) = 2W_{\text{eff}}(z)/(z + 2W_{\text{eff}}(z))$, as given, e.g., in ref 41. By means of the EMA, both the pure excitonic migration and the trapping process can be described, in the presence of conformational motion.

3. Model Calculations. Poly(2-vinylnaphthalene)

In the present section we will (i) analyze the goodness of the global disorder approximation and (ii) evaluate the differences between the *one-site* and the *two-site* trap model in the DDH approach. A typical two-site trap is depicted in Figure 2, which provides a well-established model for EFS in poly(2-vinylnaphthalene).[14] It is supposed in this concept that g ⇌ *t* conformational transitions lead to the formation and dissociation of EFS, while, simultaneously, these local conformative fluctuations cause the spatial positions of EFS to become time variant.

In the global disorder description of the model (Figure 2) the spatial distribution of traps is renewed according to the waiting-time distribution $\psi(t)$, which can be estimated from the survival probability of the gt local conformation. In our simulation runs the time base for local conformational changes has been generated by exponentially distributed random numbers that rest upon the definitions of gt and tt conformational probabilities as well as the rate constant k_{conf} of the g → t conformational transition, the latter quantity being proportional to the inverse of the characteristic time τ_{conf} for the g ⇌ t conformational transitions.

In Figure 3 the survival probabilities obtained by numerically solving eq 7 have been plotted for different characteristic times τ_{conf} of conformational motion, (i) for global disorder and *single-site traps* (dotted lines, see also Figure 1) and (ii) for *two-site traps* with global renewals (dashed lines) as well as for local disorder (solid lines) obtained by Monte Carlo simulation. The parameters for *W* and *p* have been the same as those in Figure 1, τ_{conf} has been ∞, 1, 0.33, 0.1, and 0.05, respectively, for the patterns from top to bottom. Note that the survival probabilities for local dynamic disorder are somewhat higher than those in the frame of the global disorder approximation (compare the dashed and solid curves!). However, the difference between the two approximations is of minor importance when considering τ_{conf} as a free-fit parameter of the DDH theory.

An interesting conclusion to be drawn from Figure 3 is that the one-site and two-site trap situations give rise to different survival probabilities, even in the static case: compare the dotted line on the top of the figure (one-site traps case) and the overlapping solid and dashed patterns for the two-site traps (static disorder!). As already outlined above, the two-site traps in the present work are referring to EFS (see Figure 2), where the gauche and trans conformations of bonds, in proximity to the two nearest-neighbor chromophores, correspond to the nontrap conformation, while the respective trans and trans conformation corresponds to EFS. The kinetic basis for the different trapping dynamics that arise from one-site and two-site traps, respectively, rests upon the difference in the short-time evolution of the excitation survival probability. This behavior is shown in more detail in Figure 4, where the short-time part of the curves in Figure 3 is reproduced on a larger scale.

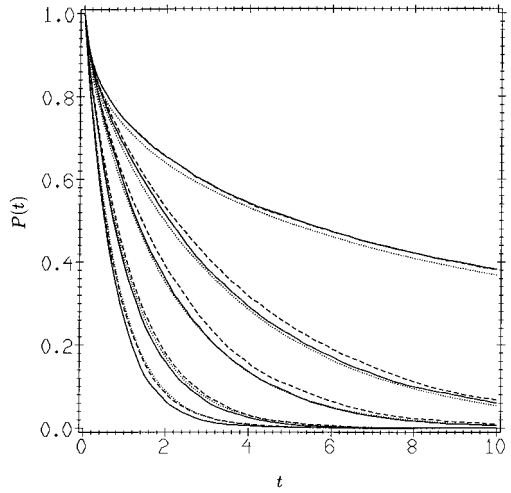

Figure 3. Excitation survival probabilities $P(t)$ for $\tau_{\text{conf}} = \infty$, 1, 0.33, 0.1, and 0.05, respectively, for the bundle of curves, from the top to the bottom (arbitrary time units). Numerical solution to eq 7 (dotted lines), and Monte Carlo simulations with global renewals (dashed lines) and for local disorder (solid lines). *W* and *p* are the same as in Figure 1.

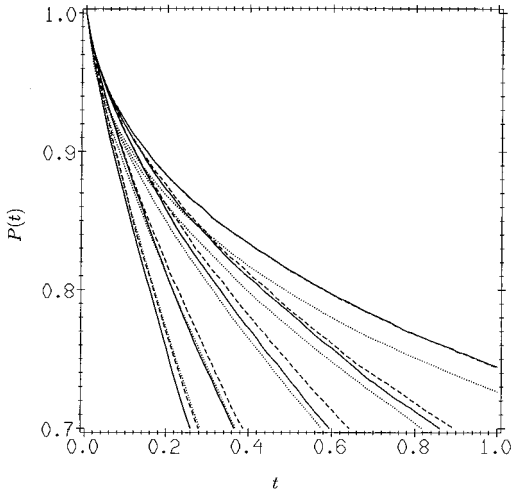

Figure 4. Short-time part of the curves of Figure 3.

The faster decay of $P(t)$ for static one-site traps in comparison with the two-site traps is, presumably, due to the concept of trap-free pathways that are larger in the one-site trap case. Let us consider, e.g., the rather likely situation of a single donor between next-neighbor traps, which leads to a TDT configuration of chromophores. This topological situation corresponds, with the same probability, to a picture of neighboring two-site traps. This is, in particular, true if only tt and gt conformations are possible (see Figure 2); in this regard, the probability of the ttgttt conformation is, quite obviously, the same as a TDT sequence of chromophores.

While the donor between two one-site traps can be excited and, thus, the elementary excitation is trapped in a very short time, the neighboring two-site traps (i.e., neighboring pairs of excimer-forming-sites (EFS)) cannot be excited at all. The same arguments hold when comparing, e.g., two donors between two one-site traps and a conformational sequence, corresponding to a single donor between two two-site traps or, more generally, $m + 1$ and m donors between two one- or two-site traps, respectively. These considerations, quite generally, imply a shorter survival probability of the initial excitation for the one-site traps. Clearly, this effect is significant only in the short-time regime but plays no role in the intermediate-to-asymptotic range of relaxation: the curves for (static) one- and two-trap systems have the same slope for longer times (see Figure 3). For shorter renewal times (compare the curves in Figure 3 or Figure 4, from the top to the bottom) this behavior, subsequently, disappears and the relationship between the one- and the two-site trap situation becomes more complicated. To explain this situation, undoubtedly, a deeper insight into the balance of the elementary donor−donor and donor−trap electronic transfer processes is required.

4. Summary

We have studied excitation trapping of migrating incoherent electronic excitations through dynamically disordered substitutional traps by using a special form of a dynamic disorder hopping (DDH) model with global renewals of the spatial trap configuration. This approach leads to the Ornstein−Zernike-type integral equation for the donor excitation survival probability $P(t)$ along a 1-D chain (eq 7), which can be easily solved numerically.

The results of this treatment have been compared with the results of Monte Carlo simulations taking into account both the experimentally relevant, local configurational changes and two-site traps. The results are in quite satisfactory agreement; they go beyond the qualitative picture and allow some quantitative understanding of how dynamic conformational disorder modulates excitation energy transfer. We have shown that the effect of two-site traps is to increase the decay of the survival probability but does not markedly influence the relaxation behavior at longer times. On the other hand, the global renewal approximation has led to lower survival probabilities than those obtained by simulations in the local renewal regime.

Acknowledgment. This research was supported by the Österreichische Akademie der Wissenschaften (ÖAW), Wien (Ost-West Programm, Grant No. OWP-142), and by the Austrian Science Foundation (Project P11344), which is gratefully acknowledged. T.P. also would like to thank the ÖAW for the tenure of a visitor fellowship and the Slovak Ministry of Education and Science (Research Projects No.1/3201/96 and No.1/4199/97) for support. I.M.S. appreciates the hospitality in the group of H.F.K.

References and Notes

(1) Kauffmann, H. F. In *Photochemistry and Photophysics;* Rabek, J. F., Ed.; Chemical Rubber: Boca Raton, FL, 1990; Vol. 2.
(2) Gelles, R.; Frank, C. W. *Macromolecules* **1982**, *15*, 747.
(3) Lakatos-Lindenberg, K.; Hemenger, R. P.; Pearstein, R. M. *J. Chem. Phys.* **1972**, *56*, 4852.
(4) Fitzgibbon, P. D.; Frank, C. W. *Macromolecules* **1982**, *15*, 733.
(5) Parris, P. E. *Phys. Lett.* **1986**, *114A*, 250.
(6) Knochenmuss, R.; Güdel, H. U. *J. Chem. Phys.* **1987**, *86*, 1104.
(7) Fredrickson, G. H.; Andersen, H. C.; Frank, C. W. *Macromolecules* **1983**, *16*, 1456.
(8) Ediger, M. D.; Fayer, M. D. *J. Phys. Chem* **1984**, *88*, 6108.
(9) Byers, J. D.; Friedrich, M. S.; Friesner, R. A.; Webber, S. E. *Macromolecules* **1988**, *21*, 3402.
(10) Mollay, B.; Kauffmann, H. F. *Macromolecules* **1994**, *27*, 5129.
(11) Mollay, B.; Landl, G.; Kauffmann, H. F. *J. Chem. Phys.* **1989**, *91*, 3744.
(12) Fredrickson, G. F.; Frank, C. W. *Macromolecules* **1983**, *16*, 572.
(13) Fitzgibbon, P. D.; Frank, C. W. *Macromolecules* **1982**, *15*, 733.
(14) Tao, W. L.; Frank, C. W. *J. Phys. Chem.* **1989**, *93*, 776.
(15) Kauffmann, H. F.; Mollay, B.; Weixelbaumer, W. D.; Bürbaumer, J.; Riegler, H.; Meisterhofer, M.; Aussenegg, F. R. *J. Chem. Phys.* **1986**, *85*, 3566.
(16) Mollay, B.; Landl, G.; Kauffmann, H. F. *J. Chem. Phys.* **1989**, *91*, 3744.
(17) Pálszegi, T.; Kauffmann, H. F. *J. Luminescence* **1997**, *72−74*, 966.
(18) Druger, S. D.; Ratner, M. A. *Phys. Rev. B* **1988**, *38*, 12589.
(19) Allinger, K.; Blumen, A. *J. Chem. Phys.* **1981**, *75*, 2762.
(20) Knoester, J.; Van Himbergen, J. E. *J. Chem. Phys.* **1984**, *81*, 4380.
(21) Szabo, A. *J. Chem. Phys.* **1984**, *81*, 150.
(22) Fredrickson, G. H. *J. Chem. Phys.* **1988**, *88*, 5291.
(23) Engström, S.; Lindberg, M.; Johansson, L. B.-A. *J. Chem. Phys.* **1992**, *96*, 7528.
(24) Berberan-Santos, M.; Prieto, M. J. E. *J. Chem. Phys* **1988**, *88*, 6341.
(25) Pálszegi, T.; Kauffmann, H. F. *J. Chem. Phys.* **1996**, *105*, 1702.
(26) Harrison, A. K.; Zwanzig, R. *Phys. Rev. A* **1985**, *32*, 1072.
(27) Pálszegi, T.; Rychlý, J.; Melus, M. *Chem. Phys.* **1994**, *186*, 41.
(28) Pálszegi, T.; Rychlý, J.; Melus, M.; Kauffmann, H. F. *Chem. Phys.* **1996**, *203*, 143.
(29) Ceáceres, M. O.; Budde, C. E. *Physica A* **1988**, *153*, 315.
(30) Vlad, M. O. *Phys. Scr.* **1994**, *49*, 389.
(31) Bahar, I.; Erman, B. *Macromolecules* **1987**, *20*, 1368.
(32) Förster, T. *Ann. Phys.* (*Leipzig*) **1948**, *2*, 55.
(33) Hernández-García, E.; Rodríguez, M. A.; San Miguel, M. *Phys. Rev. B* **1989**, *40*, 9056.
(34) Plonka, A.; Paszkiewicz, A. *J. Chem. Phys.* **1992**, *96*, 1128.
(35) Blumen, A.; Klafter J.; Zumofen, G. In *Optical spectroscopy in glasses*; Zschokke, I., Ed.; Reidel Publishing Co.: Dordrecht, The Netherlands, 1986; p 199.
(36) Zumofen, G.; Blumen, A. *Chem. Phys. Lett.* **1982**, *88*, 63.
(37) Balagurov, B. Ya.; Vaks, V. G. *Zh. Eksp. Theor. Phys.* **1973**, *65*, 1939; *Sov. Phys. JETP* **1974**, *38*, 968.
(38) Donsker, M. D.; Varadhan, S. R. S. *Commun. Pure Appl. Math.* **1975**, *28*, 525.
(39) Fedorenko, S. G.; Burshtein, A. I. *J. Chem. Phys.* **1992**, *97*, 8223.
(40) Sokolov, I. M.; Mai, J.; Blumen, A. *Phys. Rev. Lett.*, in press.
(41) Sahimi, M.; Hughes, B. D.; Scriven, L. E.; Davis, H. T. *J. Chem. Phys.* **1983**, *78*, 6849.

MA9715987