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Relaxation kinetics of photogenerated charged excitations in conjugated polymer crystals

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Abstract. The recombination kinetics of photoinjected charge carriers in quasi-one-dimensional conducting polymers is studied. The dynamics of the correlated pair of photoexcitations is considered within the model of one-dimensional diffusion of quasiparticles in segments of a polymer chain confined by defects (traps). The main characteristics of the dynamics of a recombining pair (distribution function and survival probability in a confined segment, and the averaged survival probability in a polymer chain with random trap distribution) are calculated. The results obtained are associated with the observed characteristics, such as transient photocurrent decay, kinetics of photoinduced changes in optical absorption (or reflectivity) and delayed fluorescence caused by charge carrier recombination. It is shown that the influence of the defects leads to acceleration of the photocurrent decay, namely, the usual power-law dependence $\propto t^{-1/2}$ describing the geminate recombination kinetics in an infinite chain, at times $\simeq (10\pi^2 Wc^2)^{-1}$ (W is the diffusion rate, c is the trap concentration), is changed to a faster exponential-like dependence $\propto t^{1/6} \exp(-t^{1/3})$. In contrast, it is shown that the photoinduced absorption decay is slowed down due to trapping of photoexcitations by defects. The delayed fluorescence decay caused by recombination of photoexcitations also obeys an exponential-like dependence, $\propto t^{-1/2} \exp(-t^{1/3})$, unlike the case of an infinite chain, when delayed fluorescence decay follows a power-law dependence $\propto t^{-3/2}$. The theoretical results are compared with the experimental data on relaxation kinetics of photoexcitations in *trans*-polyacetylene and restrictions on the model are considered.

1. Introduction

The prediction of the existence of soliton-like excitations in conjugated polymer crystals of *trans*-polyacetylene (*trans*-(CH)_x) put forward about ten years ago [1] was a strong catalyst to stimulate interest in investigations of charge and energy transport processes in conducting polymers. Since that time a great wealth of information, both experimental and theoretical, concerning the spectral, transport and magnetic properties of elementary excitations in conducting polymers, particularly in the simplest one, *trans*-(CH)_x, has been obtained (see review articles and monographs [2]). In studies of the charge carrier nature in conjugated polymer structures, investigation of photogenerated excitations plays an important role because of the possibility of excluding the influence of an undesirable interaction of solitonic excitations with outside dopant. In the pioneering work of Su and Schrieffer [3] it has been shown that photoinjection of an electron-hole (e-h) pair leads to its fast thermalization (of the order of the inverse optical phonon frequency, or 10⁻¹³ s) with subsequent conversion to a pair of charged topological defects (kinks), i.e. to a soliton-antisoliton pair (S⁺-S⁻). These solitonic excitations occupy the level in the middle of the gap and they are characterized by the reverse spin-charge relations. The

subsequent evolution of the $S^+ - S^-$ pair can be described in terms of random walks (or diffusion), caused by the interactions of the kinks with thermally excited phonons or by soliton Brownian motion [4].

Studying the soliton dynamics, in particular, using time-resolved experiments on photoconductivity, photoinduced absorption, bleaching and reflection, combined with the spectral investigations, is a powerful source of information on the nature and dynamics of elementary excitations in *trans*-(CH)_x. An application of the time-resolved technique is especially informative under one-dimensional excitation motion, because in this case, in contrast to the three-dimensional case, exact results for a number of model systems can be obtained. Note that the kinetics of transport processes in one-dimensional systems is essentially different from that for two- or three-dimensional ones; for example, trapping and recombination 'constants' in one-dimensional systems are time dependent [5]. Thus, a comparison of the theoretical curves with the experimental data allows us to make a conclusion about the possibility of applying different models to describe soliton dynamics in *trans*-(CH)_x and other conjugated polymers.

A significant influence is exerted on charge carrier transport in *trans*-(CH)_x by defects (chain order breaking, outside impurities, *cis* segments, sp³ hybridized carbon atoms, chain ends, etc). For example, Vardeny *et al* [6] have shown that excess impurities and imperfections in a polymer chain of *trans*-(CH)_x, which appeared in a sample kept in an evacuated ampoule for one year, drastically changed the observed kinetics of transient photoinduced bleaching. This role of defects is especially important in quasi-one-dimensional structures (including *trans*-(CH)_x) because the charge carriers are 'locked' in the chain segments (cages) confined by the defects. The kinetics of transient photocurrent [7, 8], photoinduced bleaching [6, 9] and reflectivity [10] are considerably different from the predictions of the quasi-one-dimensional geminate recombination theory [11], the differences being associated with charge carrier trapping by defects (impurities).

In our previous work [12–14] some preliminary results concerning the dynamics of quasiparticles in one-dimensional structures with traps have been obtained. In the present work these results will be used to calculate the observed characteristics of photoexcitations in conjugated polymer crystals, particularly *trans*-(CH)_x: transient photocurrent decay, photoinduced changes in optical absorption and the kinetics of delayed fluorescence caused by soliton–soliton recombination.

2. Dynamics of a correlated pair in a confined polymer segment

Let us first consider the simplest problem of geminate recombination of a correlated pair of quasiparticles on an infinite ideal chain. In the case of diffusion motion the equation for the distribution function describing the relative position of quasiparticles in the chain at the moment t is written as

$$\partial g(x, t) / \partial t = 2W \partial^2 g(x, t) / \partial x^2 \quad (1)$$

$$g(x, 0) = \delta(x - x_0) \quad (2)$$

$$g(0, t) = 0 \quad (3)$$

where W is the quasiparticle diffusion rate, initial condition (2) describes the separation of quasiparticles by the distance x_0 at the moment $t = 0$, and boundary condition (3) corresponds to the instant of recombination when quasiparticles occupy the same cell.

To calculate the escape probability $\mathcal{E}(t)$ by the moment t one has to integrate the distribution function $g(x, t)$ over all the possible positions of quasiparticles in a chain:

$$\mathcal{E}(t) = \int_0^\infty dx g(x, t). \quad (4)$$

Substituting the solution of (1)–(3) into the definition (4) one obtains for the escape probability for a correlated pair in an infinite chain

$$\mathcal{E}(t) = \text{erf}\{x_0/[2(2Wt)^{1/2}]\} \quad (5)$$

that is

$$\mathcal{E}(t) = x_0/(2\pi Wt)^{1/2} \quad x_0/(Wt)^{1/2} \ll 1. \quad (5a)$$

Equation (5) was verified for the initial (picosecond) stages of charge carrier geminate recombination (mainly in *trans*-(CH)_x) in a number of experiments on time-resolved photoconductivity [7, 8, 15–17], photoinduced bleaching [6–9] and reflectivity [10].

Note that, in the case of one-dimensional motion, all the charge carriers decay inevitably due to recombination, i.e. $\mathcal{E}(\infty) = 0$, in contrast to three-dimensional systems where $\mathcal{E}(\infty)$ has a constant limit [5].

We consider now the dynamics of a correlated pair in a segment of a polymer chain confined by defects (traps). According to different estimations the defect concentration in *trans*-(CH)_x lies in the range 10^{-2} – 10^{-4} per carbon atom [7], i.e. soliton motion takes place in confined chains of 100–10 000 unit cells.

Hereafter we will assume a random trap distribution. We will suppose that defects play the role of infinitely deep traps, solitons being trapped immediately on reaching them; in other words, the motion of pairs in each segment can be regarded as independent (a more detailed description of the model is given in [18]). Thus, in the case of soliton diffusion the equation for the distribution function for a pair of quasiparticles in a segment consisting of n cells (host polymer molecules) has the form

$$\frac{\partial g_n(x, y, t)}{\partial t} = W \frac{\partial^2 g_n(x, y, t)}{\partial x^2} + W \frac{\partial^2 g_n(x, y, t)}{\partial y^2} \quad (6)$$

with coordinates of the particles, x and y , being counted off from the left and right ends of the chain respectively. Boundary conditions describe the immediate recombination of quasiparticles that occupy the same cell

$$g_n(x, y, t) = 0 \quad x + y = n \quad (7)$$

and the trapping of quasiparticles at chain ends

$$g_n(0, y, t) = g_n(x, 0, t) = 0. \quad (8)$$

Assuming particles to be divided after photoinjection by distance x_0 , an initial condition is written in the form

$$g_n(x, y, t = 0) = \delta(x + y - n + x_0). \quad (9)$$

Solution of the problem (6)–(9) has the form (for details see [13])

$$g_n(x, y, t) = \frac{4}{\pi n} \sqrt{2} \sum_{m=1}^{\infty} \sum_{l=1}^{\infty} \exp\left(-\frac{\pi^2}{n^2}(m^2 + l^2)Wt\right) \sin\left(\pi l \frac{x}{n}\right) \times \sin\left(\pi m \frac{y}{n}\right) \frac{(-1)^m - (-1)^l}{m^2 - l^2} \left[l \sin\left(\pi m \frac{x_0}{n}\right) + m \sin\left(\pi l \frac{x_0}{n}\right)\right]. \quad (10)$$

Note that the similar problem of annihilation of uncorrelated pairs in non-ideal one-dimensional structures was considered by Gaididei *et al* [12].

To characterize the kinetics of a recombining pair diffusing in a confined segment of length n we introduce the value

$$\Omega_n(t) = \frac{1}{\sqrt{2}} \int_0^n dx \int_0^{n-x} dy g_n(x, y, t) \quad (11)$$

defining the probability for the pair to survive by the moment t (at the initial moment $\Omega_n(t=0) = n - x_0$). Note that in the case of a finite segment, survival probability $\Omega_n(t)$ is different from the escape probability $\mathcal{E}_n(t)$ and is related to it by the obvious relation

$$\Omega_n(t) = \mathcal{E}_n(t) - T_n(t) \quad (12)$$

where $T_n(t)$ is the probability for the quasiparticles in the pair to be trapped.

Inserting equation (10) into equation (11) one obtains [13]

$$\Omega_n(t) = \left(\frac{2}{\pi}\right)^3 n \sum_{m=1}^{\infty} \sum_{l=1}^{\infty} \exp\left(-\frac{\pi^2}{n^2}(m^2 + l^2)Wt\right) \frac{[1 - (-1)^l][1 + (-1)^m] m}{(m^2 - l^2)^2} \frac{1}{l} \times \left[l \sin\left(\pi m \frac{x_0}{n}\right) + m \sin\left(\pi l \frac{x_0}{n}\right)\right] \quad (13)$$

that is

$$\Omega_n(t) = n \operatorname{erf}\{x_0/[2(2Wt)^{1/2}]\} \quad x_0 \ll n \quad (Wt)^{1/2}/n \ll 1 \quad (13a)$$

$$\Omega_n(t) \propto x_0 \exp(-5\pi^2 Wt/n^2) \quad 5\pi^2 Wt/n^2 \gg 1. \quad (13b)$$

It follows from equation (13a), for times when the diffusion length $(Wt)^{1/2}$ is much less than the segment length n , and $n \gg x_0$, that the dependence for survival probability up to a normalization factor is described by equation (5) obtained for an infinite chain; it means that particles do not ‘feel’ the segment ends. The influence of the confinement of particle motion begins to manifest itself for times $\sim (Wt)^{1/2}/n \leq 1$, when the diffusion length becomes comparable with that of the segment. For such times the dependence (13a) describing the geminate recombination kinetics on an infinite chain changes to the exponential one (13b).

In obtaining (13a) we used a condition $x_0 \ll n$. The value of x_0 is expected to be of the order of some cell units [19]. In [6–10, 15, 16] it was assumed explicitly that $x_0 = 1$. Generally, the initial separation x of particles in the pair (at the moment of photoinjection) is characterized by the distribution function $\varphi(x)$; for the sake of simplicity hereafter we will restrict ourselves to the case of δ -function initial distribution, equation (9), i.e. $\varphi(x) = \delta(x - x_0)$, where $x_0 \ll n$.

Let us calculate the photoinjected pair density decay kinetics $\rho(t)$ in quasi-one-dimensional structures with defects that play the role of infinitely deep traps. Averaging $\Omega_n(t)$ over a Poisson distribution of lengths of segments confined between two traps one obtains

$$\rho(t) = c^2 \int_{x_0}^{\infty} dn \Omega_n(t) \exp(-cn) \quad (14)$$

with c being the trap concentration. The appearance of the value of x_0 in the lower limit of integration in (14) corresponds to the condition that an e-h pair with initial separation x_0 can be created only in segments of length $n > x_0$. Having inserted equation (13) into equation (14) one has

$$\rho(t) = \left(\frac{2}{\pi}\right)^3 c^2 \sum_{m=1}^{\infty} \sum_{l=1}^{\infty} \frac{[1 - (-1)^l][1 + (-1)^m] m}{(m^2 - l^2)^2} \frac{m}{l} \int_{x_0}^{\infty} dn n \exp\left(-\frac{\pi^2}{n^2}(m^2 + l^2)Wt - cn\right) \\ \times \left[l \sin\left(\pi m \frac{x_0}{n}\right) + m \sin\left(\pi l \frac{x_0}{n}\right)\right] \quad (15)$$

that is

$$\rho(t) = \operatorname{erf}\{x_0/[2(2Wt)^{1/2}]\} \quad (Wt)^{1/2}c \ll 1 \quad (15a)$$

$$\rho(t) = x_0/(2\pi Wt)^{1/2} \quad x_0/(Wt)^{1/2} \ll 1 \quad (15b)$$

$$\rho(t) \propto x_0 c (10\pi^2 c^2 Wt)^{1/6} \exp[-\frac{3}{2}(10\pi^2 c^2 Wt)] \quad 10\pi^2 c^2 Wt \gg 1. \quad (15c)$$

Therefore, the dependence (15b), which is typical for an infinite chain, for times $\simeq (10\pi^2 c^2 W)^{-1}$ is altered by a faster exponential-type dependence (15c). Note that the analogous dependence ($\propto \exp[-\frac{3}{2}(2\pi^2 c^2 Wt)^{1/3}]$) describes the decay of the averaged survival probability of a single particle executing random walks in a chain with random traps [20]. The fivefold difference in the characteristic timescale is caused by the existence of an additional (recombination) channel of particle disappearance in the case of geminate recombination.

Thus, in this section the main characteristics of the dynamics of a recombining pair diffusing in a chain with random traps have been calculated. In the next section the results obtained will be associated with the observables, namely, transient photocurrent, photoinduced absorption (bleaching or reflection) spectroscopy signal and delayed fluorescence caused by charge carrier recombination.

3. Charge carrier recombination kinetics

3.1. Transient photocurrent

To describe the photocurrent kinetics, it is necessary to take into account the influence of the bias field applied to the sample. Let us consider the recombination kinetics of a charge carrier pair in an infinite chain under the presence of electric field E . The relative position of particles in a chain is described by the distribution function $g(x, t)$, obeying the equation of motion

$$\frac{\partial g(x, t)}{\partial t} = 2W \frac{\partial^2 g(x, t)}{\partial x^2} + 2\eta \frac{\partial g(x, t)}{\partial x} \quad (16)$$

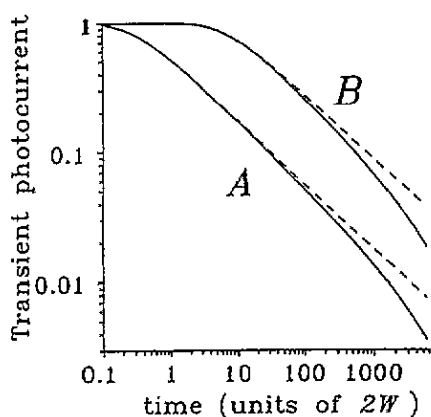


Figure 1. Charge carrier recombination kinetics in an infinite chain in the presence of an electric field, equation (17) (full curves), and without a field, equation (5) (broken curves); $\eta = 0.005$, $x_0 = 1$ (A), 5 (B).

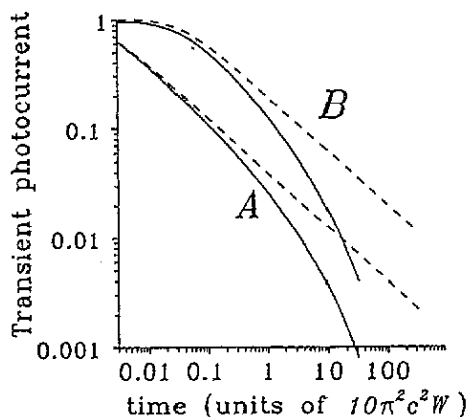


Figure 2. Recombination kinetics of photogenerated charge carriers in a polymer crystal with traps, equation (15) (full curves). Broken curves represent recombination kinetics in an infinite chain, equation (5); $c = 0.01$, $x_0 = 1$ (A), 5 (B).

where $\eta = eEa/2kT$, e is the quasiparticle charge and a is the lattice constant. Substituting the solution of equation (16) into the definition of the survival probability, equation (4), one obtains

$$\mathcal{E}(t, \eta) = \frac{1}{2} \left[\operatorname{erfc} \left(\eta(2Wt)^{1/2} - \frac{x_0}{2(2Wt)^{1/2}} \right) - \exp(2\eta x_0) \operatorname{erfc} \left(\eta(2Wt)^{1/2} + \frac{x_0}{2(2Wt)^{1/2}} \right) \right] \quad (17)$$

that is

$$\mathcal{E}(t, \eta) = \operatorname{erf}\{x_0/[2(2Wt)^{1/2}]\} \quad t \ll t_c \quad (17a)$$

$$\mathcal{E}(t, \eta) = \frac{x_0}{2\pi^{1/2}(Wt)^{3/2}\eta^2} \exp(-\eta^2 Wt) \quad t \gg t_c \quad (17b)$$

where

$$t_c = 1/\eta^2 W. \quad (17c)$$

Thus, the effects associated with the influence of an applied electric field on charge carrier pair dynamics are manifested in the geminate recombination kinetics for times $\simeq t_c$, when the dependence (17a) is altered by the exponential decay law (17b) (see figure 1).

Let us now consider the pair recombination kinetics in the finite segment. Taking into account the applied electric field E leads to the appearance of the term $2\eta(\partial g/\partial y + \partial g/\partial x)$ on the RHS of equation (6). The estimates performed show that the contribution of this term to the values of $\rho(t)$ under low field $\eta \ll c$ has no vital importance for times $t \ll t_c$. Thus, the dependence (15) under the condition $\eta \ll c$ describes the transient photocurrent $I_{PC}(t)$ in quasi-one-dimensional polymeric structures with traps. As follows from equations (15a)–(15c) the photocurrent decay has two characteristic rates: the initial stage of decay of $I_{PC}(t)$ is described by the power-law dependence $\propto t^{-1/2}$ which is changed to the fast exponential-type dependence $\propto t^{1/6} \exp(-t^{1/3})$ caused by the trapping of charge carriers. The alteration of the dependences pointed out in the kinetics of $I_{PC}(t)$ is shown in figure 2.

Note that the dependences (15) and (17) are similar, although the acceleration of the photocurrent fall is due to different reasons. The real reason for the above acceleration can be distinguished by changing the magnitude of the bias field. If the deviations from the $t^{-1/2}$ dependence are associated with charge carrier trapping, the kinetic curve of the transient photocurrent would be unchanged. On the other hand, when the transient photocurrent is changed due to the variation of the magnitude of the electric field applied, the acceleration observed is caused by the influence of the bias field. Estimations show that under low fields (for example, when $\eta = 0.5c$, $c = 0.01$, compare figures 1 and 2) the exponential asymptotics (15c) associated with the trapping effects manifests itself at an earlier time interval than that (17b) caused by the influence of applied electric field.

3.2. Photoinduced absorption

Charge carrier density decay in conducting polymers can be retraced upon the photoinduced changes in optical absorption. These changes are associated with the bleaching of the interband absorption (PB) and with the overall-neutral state that gives rise to a photoinduced absorption (PA) (or photoinduced reflectivity (PR)) peak at $\simeq 1.4$ eV. Although the nature of this neutral excitation is not well understood it was determined that PA (or PR) and PB signals and transient photocurrent decay on the same timescale and are associated with the density of photogenerated excitations (see, for example, Heeger *et al* [2]). But opposite to the case of transient photocurrent the influence of defects on the kinetics of PA manifests itself in the deceleration of the observed signal decay (in this section we will consider the PA signal only, implying all the results can be applied also to the PB and PR signals).

Indeed, the probability for a pair with one immobile carrier to recombine is obviously lower than that for a pair in which both carriers are mobile, and immobile (i.e. trapped) excitations, in contrast to the case of photoconductivity, contribute to the photoinduced absorption signal [7].

The intensity of the PA signal is determined by the relation

$$I_{PA}(t) = \rho(t) + T(t) \quad (18)$$

where $\rho(t)$ corresponds to the part of the charge carriers that survive in the polymer chains (equation (15)), and $T(t)$ to that trapped by defects by the moment t . To determine $T(t)$ let us integrate (6) over all the possible locations of the pair in a chain

$$\partial\Omega_n(t)/\partial t = \mathcal{R}_n(t) + T_n(t) \quad (19)$$

$$\mathcal{R}_n(t) = \int_0^n dy \left. \frac{\partial g_n(x, y, t)}{\partial x} \right|_{x=n-y} \quad (20)$$

$$T_n(t) = \int_0^n dy \left. \frac{\partial g_n(x, y, t)}{\partial x} \right|_{x=0} \quad (21)$$

where equation (20) determines the photoexcitation decay rate due to recombination, and equation (21) that due to trapping. The part of the solitons trapped by the defects in segments of length n and contributed to the photoinduced absorption signal, $T_n(t)$, is determined by the simple balance equation

$$\partial T_n(t)/\partial t = T_n(t) \quad T_n(0) = 0. \quad (22)$$

For the sake of simplicity we did not take into account in (22) the interaction of solitons with the molecules of defects. This interaction will lead to relaxation of excitations to lower-lying energy levels and can easily be taken into account by introducing the soliton lifetime on traps.

Having integrated equation (22) taking account of equations (10) and (20) and then averaging $T_n(t)$ over a random distribution of chain lengths, one obtains

$$T(t) = c^2 \int_{x_0}^{\infty} dn T_n(t) \exp(-cn) \quad (23)$$

$$= \left(\frac{2}{\pi}\right)^3 c^2 \sum_{m=1}^{\infty} \sum_{l=1}^{\infty} \frac{[1 - (-1)^l][1 + (-1)^m] m}{(m^2 + l^2)(l^2 - m^2)} \frac{1}{l} \int_{x_0}^{\infty} dn n$$

$$\times \exp\left(-\frac{\pi^2}{n^2}(m^2 + l^2)Wt - cn\right) \left[l \sin\left(\pi m \frac{x_0}{n}\right) + m \sin\left(\pi l \frac{x_0}{n}\right)\right]. \quad (24)$$

In figure 3 the kinetic curves of photoinduced absorption signal $I_{PA}(t)$ are presented. Deviations from the power-law dependence $\sim t^{-1/2}$ are seen to happen for times $\simeq (10\pi^2 c^2 W)^{-1}$ ($\simeq 100$ ps if $c = 0.01$, $W = 10^{-12}$ s $^{-1}$), which is in agreement with the results of experiments [6, 8].

3.3. Delayed fluorescence

One possible manifestation of charge carrier recombination in conjugated conducting polymer structures can be the existence of delayed fluorescence (DF). The phenomenon of delayed fluorescence consists of the transferring of one excitation (with the help of the energy of another) to a higher (singlet) energy level and its subsequent radiative decay [19]. Note that the delayed fluorescence caused by e-h recombination was observed by Stolzenburg *et al* [21] in polyvinylcarbazole.

Delayed fluorescence kinetics can be calculated on the basis of a balance equation

$$\partial I^{DF}(t)/\partial t = \frac{1}{2}\mathcal{R}(t) - I^{DF}(t)/\tau_s \quad I^{DF}(0) = 0 \quad (25)$$

where the first term on the RHS of equation (25) describes the appearance of the singlet excitation due to $S^+ - S^-$ recombination (the factor 1/2 is connected with the fact that two charge carriers take part in creating one singlet excitation), and the second term corresponds to the radiative decay of singlet excitations (τ_s is the singlet excitation lifetime).

First of all let us consider the case of charge carrier geminate recombination on an infinite chain, when

$$\mathcal{R}_{\infty}(t) = -\partial \mathcal{E}(t)/\partial t \quad (26)$$

where $\mathcal{E}(t)$ is determined by equation (5) and index (∞) corresponds to the case of an infinite ideal chain. Having integrated equation (25) taking into account equations (5) and (26), one has

$$I_{\infty}^{DF}(t) = \exp(-t/\tau_s) \int_0^{Wt} d\tau \tau^{-3/2} \exp(-x_0^2/4\tau + \tau/\tau_s) \quad (27)$$

that is

$$I_{\infty}^{DF}(t) \propto (x_0 \tau_s / 2\pi^{1/2})(Wt)^{-3/2} \quad Wt/x_0^2 \gg 1 \quad (2ia)$$

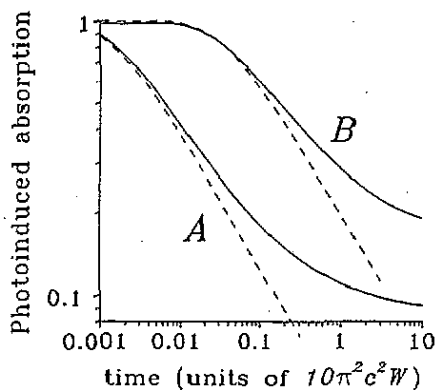


Figure 3. Photoinduced changes in optical absorption in a polymer crystal with traps, equations (18) and (23) (full curves). Broken curves represent recombination kinetics in an infinite chain, equation (5); $c = 0.01$, $x_0 = 1$ (A), 5 (B).

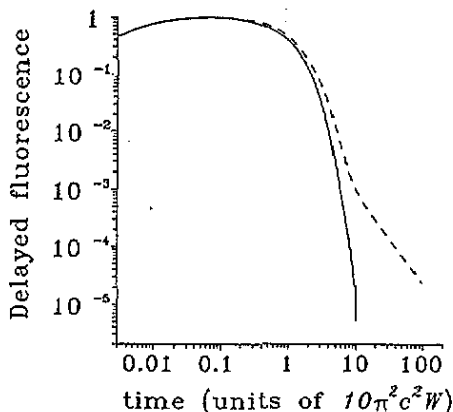


Figure 4. Delayed fluorescence caused by geminate recombination of photoexcitations in a polymer crystal with traps, equation (28) (full curve). The broken curve corresponds to the case of an infinite chain, equation (27); $c = 0.01$, $x_0 = 1$ (A), 5 (B), $10\pi^2c^2W\tau_s = 1$.

i.e. for long times delayed fluorescence decay follows the power-law dependence $\propto t^{-3/2}$. Now we will turn to the polymer crystal model considered here (chain with traps). In this case delayed fluorescence kinetics is determined by averaging the value of $I_n^{\text{DF}}(t)$, which characterizes the probability of creation of a singlet excitation in a finite chain of length n . $I_n^{\text{DF}}(t)$ satisfies the balance equation (25) where $\mathcal{R}_n(t)$ is determined by equation (20). Averaging $I_n^{\text{DF}}(t)$ over the Poisson distribution of segment lengths one has

$$\begin{aligned}
 I^{\text{DF}}(t) &= c^2 \int_{x_0}^{\infty} dn I_n^{\text{DF}}(t) \exp(-cn) \\
 &= \frac{1}{2} \left(\frac{2}{\pi}\right)^3 c^2 \sum_{m=1}^{\infty} \sum_{l=1}^{\infty} \frac{[1 - (-1)^l][1 + (-1)^m]}{(m^2 - l^2)^2} ml \\
 &\quad \times \int_{x_0}^{\infty} dn n \frac{\exp(-t/\tau_s) - \exp[-(\pi^2/n^2)(m^2 + l^2)Wt - cn]}{m^2 + l^2 - n^2/W\pi^2\tau_s} \\
 &\quad \times \left[l \sin\left(\pi m \frac{x_0}{n}\right) + m \sin\left(\pi l \frac{x_0}{n}\right) \right]
 \end{aligned} \tag{28}$$

that is

$$I^{\text{DF}}(t) \propto (x_0 c^3 / \tau_s) (10\pi^2 c^2 W t)^{-1/2} \exp[-\frac{3}{2} 10\pi^2 c^2 W t] \quad 10\pi^2 c^2 W t \gg 1. \tag{28a}$$

At long times delayed fluorescence decay is characterized by the exponential-type dependence $\propto t^{-1/2} \exp[-\frac{3}{2}(10\pi^2 c^2 W t)]$ and follows (with accuracy to a pre-exponential factor) the charge carrier density decay $\rho(t)$. The initial stages of delayed fluorescence decay, as seen from figure 4, are described by the dependence (27), which is typical for geminate recombination on an infinite chain. Note that an analogous effect of the alteration of the power-law dependence $\propto t^{-3/2}$ into the exponential-like one $\propto t^{1/6} \exp(-t^{-1/3})$ was predicted by Onipko and Zozulenko [22] for the kinetics of delayed fluorescence caused by triplet exciton annihilation in quasi-one-dimensional molecular crystals with defects (traps and barriers).

4. Restrictions of the model

In this section we will discuss some restrictions of the model concerned to be taken into account when applying the results obtained to interpret the experimental data.

In the framework of the model used we assumed the excitation motion in different segments of the polymer chain to be independent. This implies the strictly one-dimensional character of excitation motion. In real polymer crystals the interchain hopping probability W_{\perp} associated with the overlap of π -orbitals on adjacent chains generally exists and is evaluated to be less (or much less) than $10^{-2}W_{\parallel}$ (W_{\parallel} is the intrachain hopping probability) [23]. Therefore, at times $\simeq W_{\perp}^{-1}$ the charge carriers that have escaped geminate recombination or trapping leave the home chains (i.e. those in which they were injected) and quasiparticle motion becomes three-dimensional. Besides that, owing to the possibility of tunnelling through defects (or to escape from a trap), charge carriers for times $\gg \tau_{\text{tun}}c$ (τ_{tun} is the probability of tunnelling) move to a neighbouring segment of the same polymeric chain and in the time interval considered quasiparticles will move by jumps on a superlattice formed of the segments (cages) of polymeric chain confined between traps. Note that the analogous process of exciton motion on a superlattice in a one-dimensional molecular crystal of 1,2,4,5-tetrachlorobenzene has been studied in [24]. Thus, the applicability of our results is restricted to an initial time interval during which most of the excitations remain in the segments where they were formed and do not move to the others.

Another very important factor that has an influence on the observed geminate recombination kinetics is the interaction between charge carriers excited on neighbouring chains. According to different estimations the efficiency of charge carrier generation on neighbouring chains is about of 0.01 [17, 25]. Therefore, for times when the photoexcitation density fall may be less than two orders, the contribution of this excitation to the observed kinetics of PC, PA or DF will be dominant.

Therefore, all the factors listed above cause the range of validity of the results obtained to be confined to the initial (subnanosecond) time interval, when using the model of one-dimensional motion of photoexcited pairs in finite segments of a polymer chain is justified.

5. Conclusion

The effect of defects (traps) on the recombination kinetics of photogenerated charge carriers in quasi-one-dimensional conjugated polymer crystals has been studied. In the framework of the model used we assumed that the defects generally present in real polymer crystals divide the polymer chain into segments in which the excitation motion is independent. The dynamics of a geminate pair of photoinjected charge carriers diffusing in the segment is studied. The distribution function and the probability for a pair to survive up to a moment t are calculated.

It is shown that the influence of defects on charge carrier transport and recombination manifests itself in the acceleration of photocurrent decay and in the deceleration of PA (PB or PR) signal. The initial stages of photocurrent decay are shown to be described by the usual inverse square-root law, $\propto t^{-1/2}$, which is characteristic for geminate recombination on an infinite chain. At times $\tau = (10\pi^2c^2W)^{-1} \simeq 1$, when the diffusion length becomes comparable with the average segment length, this dependence is changed to a faster exponential-like dependence $\propto t^{1/6} \exp(-t^{1/3})$, which causes a rapid fall of photocurrent signal. It is shown that charge carrier trapping by defects causes the deceleration of observed PA (PB or PR) signal, because, being trapped, charge carriers, in contrast to the case of

photocurrent, cannot recombine but do contribute to the observed signal. The kinetics of delayed fluorescence caused by the recombination of photoexcitations has been investigated. It is shown that the delayed fluorescence decay follows an exponential-like dependence $\propto t^{-1/2} \exp(-t^{1/3})$, opposite to the case of an infinite chain, when the delayed fluorescence decay obeys the power-law dependence $\propto t^{-3/2}$.

The theoretical curves were compared with the experimental data concerning mainly photoexcitation dynamics in *trans*-(CH)_x. The results obtained are shown to be applicable to a description of photoexcitation relaxation kinetics on the subnanosecond timescale. For longer times the applicability of the model used is restricted owing to the violation of the one-dimensionality of the motion and the necessity to take into account the interaction between charge carriers excited on neighbouring chains.

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