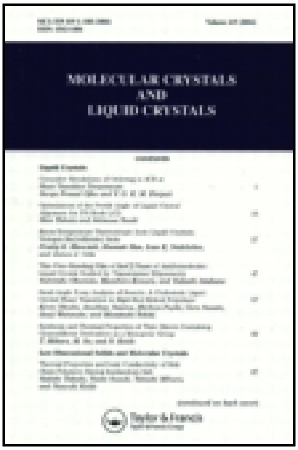

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The Role of the Initial Charge Separation in the Geminate Pair Recombination in Disordered Molecular Systems

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The Role of the Initial Charge Separation in the Geminate Pair Recombination in Disordered Molecular Systems

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Geminate charge pair recombination in sensitised photoconducting polymers was investigated by means of Monte – Carlo simulations. It was found that the initial charge separation distance and the hole recombination rate in the charge transfer (CT) complex, formed between a matrix molecule and a sensitiser, are the main parameters determining the initial part of the recombination kinetics. By comparing the simulation results to the experimentally observed kinetics of sensitised carbazolyl-containing polymers, it has been concluded that part of the charge pairs remain at the CT complexes and recombine exponentially. For the rest, the holes are separated from the CT complexes and cause much slower nonexponential decay. The time scale for the hole hopping steps was estimated to be of the order of 10÷50ps. A model of dynamical scattering of the mobile charges by sensitiser molecules at the initial stage of charge separation is suggested to explain faster recombination at high concentration of the sensitiser.

Keywords: photogeneration; geminate recombination; sensitisation; Monte-Carlo simulation

1. INTRODUCTION

According to the present understanding of charge photogeneration in organic sensitised photoconductors at least two steps can be distinguished in this complex process. Immediately after the light quantum absorption, a bound electron – hole pair is generated.[1–3] This step is very fast and proceeds on the subpicosecond/picosecond time scale while the second step, which describes the subsequent charge separation by overcoming the Coulomb barrier, is much slower.[2,4,5] The latter process is quite adequately described by the Onsager[6] theory, however, the

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initial step of the charge pair photogeneration is not completely clear yet. It is accepted that the low energy charge transfer (CT) states of the chromophore – sensitiser complexes, responsible for the longest wavelength absorption, play an essential role in the first step of the separation process.[2] In the present understanding, the mean transfer distance characterising the first step is not well defined and usually considered as a fitting parameter for describing the subsequent events of the charge transfer. In general, this initial electron – hole separation distance is a distribution function rather than a sharp value, due to the disordered arrangement of the molecules in the system under consideration.

Currently there are two well-developed models describing the distribution of initial electron – hole separation distances. (a) Photocurrent measurements[7] and results of field induced fluorescence quenching experiments[8–10] are explained by assuming fixed initial separation of several tens of Ångströms, i. e. the initial separation distribution function is supposed to be $\delta(r\text{-}r_M)$, where $r_M \approx 30$ Å. As it has been shown by Mozumder,[11] a wide (either exponential or Gaussian) initial distribution with the mean value of several tens of Ångströms provides sufficient agreement with the experimental data of free carrier photogeneration. (b) The other concept denies the assumption of an initial separation at larger distances than the CT complex size, suggesting that the absorbed light quantum creates the electron – hole pair initially separated only inside the CT complex.[12–14] The further separation is then possible because of the disordered arrangement of the molecules leading to a range of state energies on the neighbouring monomers for the mobile charge (hole).[12] However, the hole state energy distribution required for this model is too broad to fit the experimental data of geminate recombination. It also does not allow to explain the observed values for the quantum yield of free carrier generation at reasonable values of the external electric field. Thus, to understand the possible distribution of the initial charge separation and to define the influence of this distribution on the geminate pair recombination (GPR) kinetics on a short time scale, the discussion of this problem based on the Monte-Carlo approach is presented in this paper. The analysis given has been stimulated by the experimental data of sensitised carbazolyl-containing (Cz) compounds;[2] it is, therefore, restricted to a specific range of parameters.

The GPR is related to the second step of the photogeneration process. The initial condition of the GPR process can be attributed to a set of independent charge pairs for which the separation distances r_0 between the hole and the electron are described by an initial separation distribution function $n_0(r_0)$, which denotes the probability of the charge carrier (in most cases, the hole) to be separated by the distance r_0 from the opposite charge, which is localised on the sensitiser involved in the CT complex formation. The recombination process can be divided into two stages. The first stage corresponds to a diffusive motion of the molecular polaron in the polymer framework within the Coulomb attraction field of the counter-ion and it ends by the formation of the excited CT state, corresponding to the hole and the electron both localised on the same CT complex. The second stage corresponds to the CT state relaxation. Thus, the recombination time is limited by the time of diffusive approach of the mobile charge to the immobile one and by the relaxation time of the CT state. It should be noted that most of the well developed Monte Carlo simulation models[12,13,15–18] ignore that the electron – hole recombination rate in the CT complex is finite. On the short time scale this may become a decisive factor however.

Our consideration will focus on sensitised charge carrier generation in photosensitive polymers. According to the experimental time-resolved measurements, either the charge carrier density or the fluorescence intensity dependence on time is well described by a power law on the long time scale.[13,15–17] Such behaviour is attributed to a diffusive motion of a charge carriers through the disordered molecular network.[19–22] Two types of disorder are generally accepted. The polaron state energy disorder (diagonal disorder – DD) is caused by an inhomogeneous distribution of local polarisation interactions with the neighbouring monomer units in the polymer chain, while fluctuations in the intermolecular distance and in the mutual orientation of molecules create spatial disorder (off-diagonal disorder – OD) which modulates transition probabilities. DD, which is reflected in the inhomogeneous broadening of the absorption spectrum, was obtained to be of the order of 0.1eV, in the case of poly-N-vinylcarbazole (PVCz) polymer.[23] A similar value was obtained from the measurements of thermostimulated emission.[24] OD has not been taken into account in most of the models applied to this problem so far. The chain structure of the polymer branch is obviously lost in polymer films. Therefore, models based on a cubic lattice, with the DD included, have mainly been used to describe polymer films.

The principle differences of the simulation model presented in this paper from the Monte Carlo models used so far are the inclusion of the CT complex properties, heterogeneity of the CT states (resulting in both initially nonseparated and separated charge pairs), and inclusion of disorder into the simulation while describing the GPR on the short time scale. The current paper is arranged as follows. The second section is devoted to a detailed description of the Monte Carlo approach. In the third and fourth sections the simulation results are presented. The third section describes the results obtained under the assumption of an *infinite* recombination rate of the CT complex. The regular lattice model (no disorder) is considered firstly, which helps to understand more complex model with DD and OD included which will be considered later. The discussion about the influence of the sensitiser on the charge photogeneration distance and, thus, on the recombination kinetics, is also presented. The fourth section is devoted to the more complex problem of the *finite* CT complex recombination rate. Next section gives a survey of the presented concept of the GPR and compares the simulation results with the experimental data and the last section presents the conclusions.

2. MODEL APPROACH FOR MONTE-CARLO SIMULATION

For describing the GPR, the initial charge separation, being several orders of magnitude faster than the recombination, may be considered as an instantaneous event, setting the initial conditions for the GPR process: a distribution $n_0(r_0)$ of charge pairs with random separation distances r_0. A single ("geminate") charge pair is taken into account and the interaction between the charge carriers of different pairs is neglected.

The recombination time of a charge pair separated by the distance r_0 is a sum of the diffusion-limited charge carrier approach time and the CT state recombination (relaxation) time. The diffusive approach time is related to the mean hopping rate k, reflecting the bulk system properties, while the CT state relaxation rate k_{CT} is the internal property of the CT complex.

The starting arrangement of the system under consideration is a cubic lattice framework with a lattice constant a (see Figure 1). The non-correlated OD is taken into account by deflecting each site randomly from the original cubic lattice site. As the simplest case, the deflection Δr is assumed to be distributed by a Gaussian function with the dispersion σ_{od}^2 (the distribution function is related to a particular cubic lattice site and the deflection is defined by $\Delta r^2 = \Delta x^2 + \Delta y^2 + \Delta z^2$) The DD accounts for the energy difference between that of a particular site i, ε_i, and the mean value for all sites of the lattice. The site energies ε_i are also supposed to be distributed by a Gaussian function with dispersion σ_{dd}^2 .

In the carbazolyl based photosensitive polymers (for instance, poly-N-vinylcarbazole (PVCz) or poly-N-epoxypropylcarbazole (PEPCz) sensitised with trinitrofluorenone (TNF) or tetracyanobenzene (TCNB)) both charge carriers, electrons and holes, are mobile: holes can move through the carbazolyl chromophores while electrons move through the sensitiser molecules in the limit of high concentration of sensitiser. Thus, two types of the sites are suggested to be present in the lattice: hole sites (probability to find the hole site in the lattice is denoted by p_h) for the hole transport and electron sites (the electron site probability $p_{CT} = 1 - p_h$) for the electron transport. Thus, the hole sites correspond to the native polymer chromophores, while the electron sites are attributed to the sensitiser molecules. Since the sensitiser molecules are bound in the CT complexes,

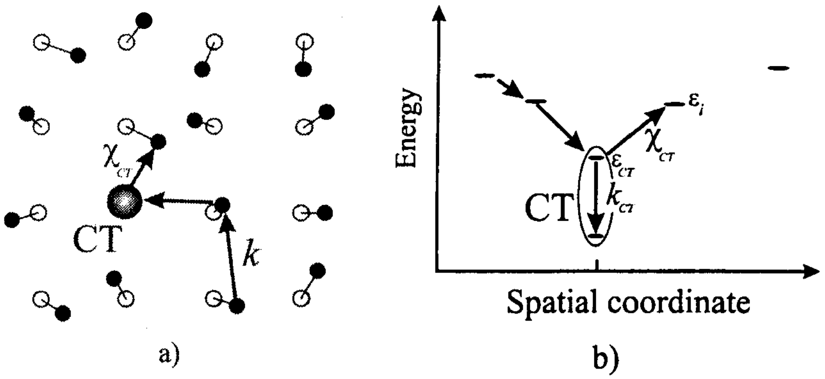

FIGURE 1 Geminate pair recombination (GPR) model. a) Disordered lattice model. Open circles correspond to the square lattice sites; solid circles correspond to the hole sites (H- sites), while the large sphere indicates the CT complex as one site. χ_{CT} is the hole escape rate from the CT complex, k is the mean rate of the hole transfer between any two H sites in the regular lattice. b) GPR model in the view of energy vs. spatial coordinate; k_{CT} indicates the CT complex recombination rate and ε_{CT} denotes the hole energy on the CT complex

the electron sites correspond to the entire CT complexes. Thus, we denote the hole sites as H-sites and the electron sites as CT sites.

The hole is restricted to be situated only on H sites. For the recombination event to be taken into consideration, the hole is also allowed to jump to the CT site if the electron is currently present at this particular CT site. Then either the recombination may occur with the rate constant k_{CT}, or the hole may escape from the CT site to the rest of the volume with the rate constant χ_{CT}. The recombination rate of the CT state k_{CT} is an intrinsic parameter of a particular chromophore-senstiser complex, while the corresponding escape rate χ_{CT} results from the charge hopping between the CT site and its neighbouring H site on the lattice. The latter value is determined by the difference of the site energies (ΔE) for the mobile charge situated on the CT site, ε_{CT}, and at the neighbouring H site, ε_i, (including the energy of Coulomb interaction.), i. e. $\chi_{CT} \propto k \exp(-\Delta E/k_B T)$, where T is the temperature and k_B is the Boltzmann constant. According to this model, the CT sites, that are formed as molecular complex of the electron-donating and the electron-accepting moieties, are strongly perturbed sites in comparison with the regular H sites and this difference is determined by the site energy value for the hole ε_{CT}.

The total energy of the charge at a particular site depends on the distance to its counter-charge, and on the value of the diagonal disorder of this site ε_i. Thus, the energy for the hole situated on the site i is defined as follows:

$$E_i = -\frac{q}{|\mathbf{r_i} - \mathbf{r_e}|} + \varepsilon_i, \tag{1}$$

where $q = \dfrac{e^2}{4\pi\varepsilon\varepsilon_0}$, $\mathbf{r_e}$ is the electron coordinate on the lattice (the OD also including). The probability per unit time of the jump of the charge carrier to a particular site depends on the energy difference between the sites under consideration and the distance between them. The jump rate is assumed to be of the Miller – Abrahams type:[25]

$$\nu_{ij} = \nu_0 \exp(-2\gamma|\mathrm{r_i} - \mathrm{r_j}|)k_{ij}(\Delta U) \tag{2}$$

where ν_0 is a frequency prefactor, γ is a wavefunction overlap factor of particular chromophores,

$$k_{ij}(\Delta U) = \begin{cases} \exp\left(\frac{\Delta E}{kT}\right) & \Delta E < 0; \\ 1 & \Delta E > 0, \end{cases} \tag{3}$$
$$\Delta E = E_i - E_j.$$

Then the normalised probability of the jump $i \to j$ is given by

$$P_{ij} = \frac{\nu_{ij}}{\sum\limits_{m \neq i} \nu_{im}}, \tag{4}$$

where the denominator accounts for all possible final sites for the charge carrier. The time of the jump is obtained by:

$$t_i = \frac{x^e}{\sum\limits_{l \neq i} \nu_{il}}, \tag{5}$$

where x^e is a random number of the exponential distribution. The final position is selected randomly according to the uniform random number generation, taking into account the probabilities of all possible jumps.

The lifetime of the pair is equal to the sum of the jump times until the hole is captured by the CT site, $\sum\limits_i t_i$, and the CT state recombination time k_{CT}^{-1}. An ensemble of 10^4 recombination events of independent charge pairs are calculated, and, by summing up all the results, the pair density dependence on time $n_0(r,t)$ is obtained. Geminate pair recombination kinetics is obtained by integration of the pair density function $n_0\ (r,\ t)$ over the spatial coordinate: $n(t) = \int n_0(r,t)dr$ The time scale of the total process is attributed to the mean hole jump rate k in the regular lattice in the absence of the disorder (both DD and OD) and of the sensitiser with the countercharge on it, according to the following definition: $k = \sum_{l \neq i} \nu_{il}$. Thus, the normalised (dimensionless) jump time between any two H sites is defined as $\tau_i = kt_i$ and correspondingly the mean recombination time of the CT site as $\tau_{CT} = k / k_{CT}$. Then, the time scale turns out to be independent of the frequency prefactor ν_0. Distances of the model system are normalised to the lattice constant a while the initial number of charge pairs is normalised to one: $n(t = 0) = 1$.

The range of parameters used in calculations refers to those typical of PEPCz films, sensitised with TNF,[2] i.e. the cubic lattice constant a= 0.68 nm is equal to the mean distance between Cz chromophores while the permitivity of the system is suggested to be $\varepsilon = 3$.[26] The wave function overlap parameter $2\gamma a = 10$ was suggested to be the same as the one used by Ries and Bässler.[18]

3. GPR FOR AN "INFINITE RATE" OF CT COMPLEX RECOMBINATION

In this case the hole recombines immediately when it occupies the CT site, while the escape probability is zero. This approach is identical to the models ignoring the CT complexes. We start from this simplification to estimate the influence of the initial charge separation distance and of the disorder. In the model approach, the infinite CT complex recombination rate corresponds to the case of $k_{CT}^{-1} = 0$. Then the duration of the GPR process is determined by the diffusion limited hole approach time to the CT site, which is dependent on the initial separation and on the bulk system properties, i.e. on the degree of disorder.

3.1 The regular lattice approximation

As the first step of simulations, the regular lattice with neither the DD nor the OD is considered. For comparison three types of the initial charge pair distributions are suggested: the delta function $n_d(r) = \delta\,(r\text{-}r_M)$, the Gaussian function $n_g(r) = \frac{1}{\sigma_r\sqrt{2\pi}} \exp\left(-\frac{(r - r_M)^2}{2\sigma_r^2}\right)$ and the exponential function $n_e(r) = \frac{1}{r_M} \exp\left(-\frac{r}{r_M}\right)$, where r_M is the mean separation distance of the charge pairs and σ_r is the width of the Gaussian distribution. In the regular lattice approximation, the distributions are assumed to be isotropic for all directions in the lattice. The continuous space distributions determined above were adopted to

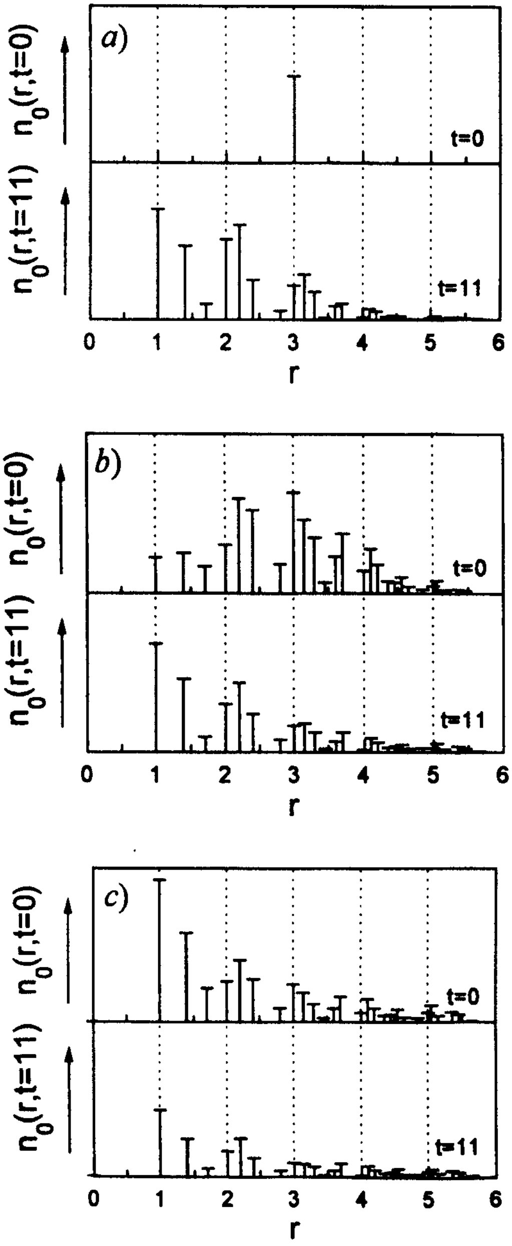

FIGURE 2 The distribution of the electron – hole separation distance at the initial moment and at t=11 in the case of $n_0(r)=n_d(r)$ (δ- type distribution), $n_0(r) = n_g(r)$ (Gaussian distribution), $n_0(r)= n_e(r)$ (exponential distribution). The mean initial separation distance $r_M= 3$ was assumed in all cases

the discrete lattice model by assuming that the hole, positioned continuously according to such continuous functions, is shifted to occupy the nearest lattice site. The mean separation distance in all cases of the distributions was set to be the same and equal to $r_M = 3$. The initial distributions and the evolution of these distributions in time are presented in Figure 2. It is seen that information of the initial distribution is already lost on a relatively short time scale: at $t > 10$ jumps all the initial distributions become qualitatively similar.

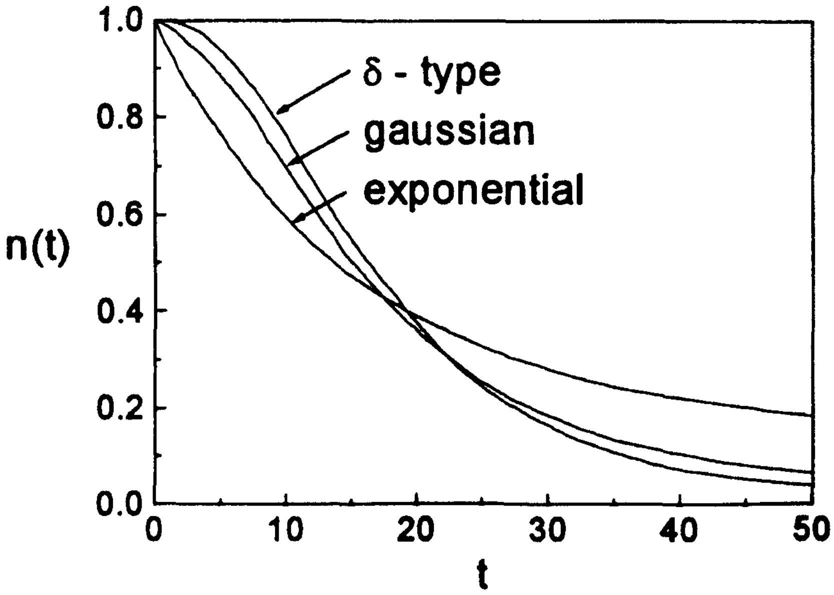

FIGURE 3 GPR kinetics in the regular lattice for the three types of the initial distributions of the charge separation for $k_{CT}^{-1} = 0$

For comparison the GPR kinetics calculated for the above mentioned initial distributions are presented in Figure 3. Kinetics for initial charge separation distributions $n_d(r)$ and $n_g(r)$ are quite similar. There is a very slow recombination at the initial part of the GPR kinetics resulting from the absence of electron-hole pairs separated by the nearest – neighbour lattice site, which causes the time interval (ca 5 jump times) needed for the diffusive approach of the hole to the CT site. After this time lag the recombination kinetics is quite fast and during ca. 40 jump times (t ~ 40) most of the charges are lost by recombination. The rest of the kinetics results from the slow diffusion of surviving pairs that, due to thermal activation, were able to increase their separation distance against the Coulomb potential. Kinetics obtained with Gaussian and delta distributions differ only quantitatively – the recombination starts earlier and runs more smoothly in the case of the wide Gaussian distribution. It is evident that for wider Gaussian distributions these differences will be more distinct.

The initial distribution $n_e(r)$ leads to fast recombination at the very early times. There are many pairs separated only by a single lattice constant, therefore, the very initial recombination part ($t < 1$) is exponential with the decay time being equal to the single-jump time. Later (for $t > 1$), when the nearest – neighbour pairs have already recombined or separated to larger distances, the recombination process becomes diffusion-limited with a decrease in the recombination rate.

The initial separation process is affected by the structural organisation of the polymer environment. Because of the disordered arrangement of hole sites and various kinds of impurities the distribution of initial separation distances is difficult to determine. Moreover, the sensitiser molecules also may be treated as impurities due to their different electrochemical properties. For the fast initial separation as it is assumed, an unrestricted path for the initial hole separation is required. In the model approach, with the CT sites being some kind of impurities (with respect to hole transport) disturbing the native polymer system, interruptions of the paths of charge separation are probable and, thus, redistribution of the mean initial separation distance r_M is to be expected by increasing the amount of sensitisers. Thus it is impossible to obtain the ideal distributions, treated theoretically, in the real sample as used in our case. Any kind of distribution, postulated for the ideal lattice, will be redistributed under the influence of sensitiser molecules. The influence of the sensitiser will be explored in the section "Disordered lattice model".

3.2 Disordered lattice model

Both disorder effects, i.e. the DD and the OD, will consequently be taken into consideration. At first, the case of the DD only, with no OD, will be considered.

According to Bässler,[23]the width of the DD is of the order of 0.1eV for carbazolyl-containing films. Results of the corresponding simulation with the DD included are shown in Figure 4*a*. The very initial part of the kinetics, which is responsible for recombination of the pairs initially separated by the minimal separation distance, is weakly dependent on σ_{dd}. The DD mainly influences the diffusive motion of the charge carrier (the wider disorder slows down the recombination kinetics, see Figure 3 or Figure 4*b* for comparison).

The OD accounts for the differences in distances between molecules and in their orientations resulting in different charge transfer rates. As it is shown in Figure 4*b*, the OD mainly influences the initial part of the kinetics. The OD

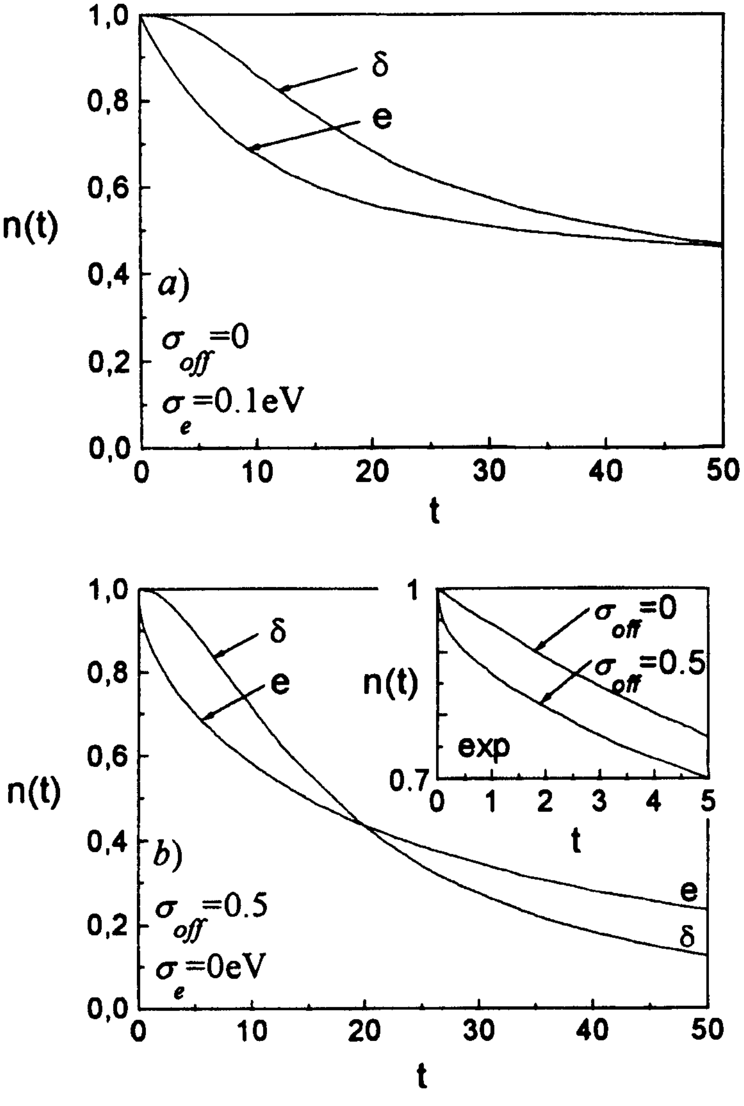

FIGURE 4 GPR kinetics for the exponential and δ – type initial distributions of the charge separation distance in the diagonally (*a*) and off-diagonally (*b*) disordered lattice for k_{CT}^{-1}

reflects the distribution of the jump rates and is responsible for the nonexponentiality of the initial recombination where the nearest neighbour recombination prevails, if one considers the exponential distribution of the initial electron – hole separation. In absence of OD, the recombination rate for all nearest-neighbour pairs is the same. However, in presence of OD the recombination rate of some of the nearest-neighbour pairs is increased, while it may be decreased for the other pairs. The very initial part of recombination kinetics resembles the fastest events of the recombination process. Therefore, the disorder speeds up the recombination rate at the very initial time and slows down this rate slightly later. However, the influence of OD on the kinetics is less important than influence of DD while concerning the delta function distribution of the initial separation due to the absence of the nearest-neighbour pairs at the initial moment.

There are only a few studies of the OD effects on the charge transport properties. Bässler[27] has concluded that the relative width of the wave functions overlap distribution hardly exceeds 0.3. Thus, it is expected that the OD has a minor effect on the yield of free charge carriers since the OD affects only the recombination of charge pairs initially separated by relatively small distances (by one or two lattice constants), where they have no chances to survive and to be totally separated.

The qualitative shape (either the initial flat part obtained for the delta function distribution of the initial separation, or the exponenial decay obtained for the exponential distribution including the slow tail in the long times) of the GPR kinetic curve turns out to be independent of the intrinsic disorder of the lattice framework, therefore the initial electron – hole separation distribution $n_0(r)$ is a decisive factor on the short time scale.

However, as indicated above, the initial electron – hole separation distribution $n_0(r)$ depends on the concentration of the sensitiser. On this basis it was suggested[28] that the mean separation distance r_M can be reduced by sensitiser molecules acting as scattering centres. Here we will demonstrate how this scattering process may affect the distribution of the initial separation distances.

By modelling the reduction in the hole separation distance caused by the CT sites the following assumptions on the pair separation process are suggested. On the basis of the ballistic pair separation model it is supposed that during its separation a hole moves against the Coulomb potential until it loses its kinetic energy and becomes localised at a particular distance r_0 from a sensitiser molecule. Afterwards a polaron is formed and, thus, the subsequent hole dynamics is well described by a stochastic hopping model. Since the sensitiser molecules have higher electron affinity and holes cannot jump on them, they perturb the hole motion in the initial stage of charge separation. Therefore, it is assumed that the hole is scattered elastically by the CT sites, i.e. the direction of hole transfer is changed randomly if the CT site happens to be on the way of the initial transfer. Upon modelling this initial hole separation, the duration of this process is not considered, because the recombination proceeds on a time scale which is by a

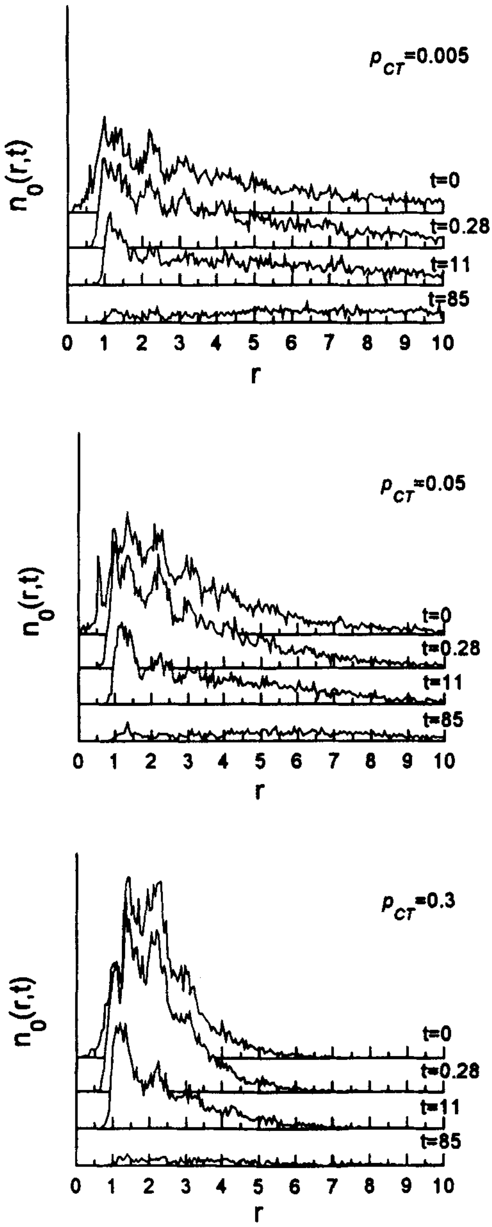

FIGURE 5 The distribution of the electron – hole separation distance and its evolution in time with the charge scattering effect included. Initial distribution in the low limit of sensitiser concentration $n_0(r) = n_e$ (r); σ_{od}= 0.3, ρ_s=2, $k_{CT}^{-1} = 0$

few orders larger than the initial separation time. The scattering efficiency is described by a scattering radius ρ_s, which is a single scattering parameter. The number of scattering events until the polaron formation is determined by the number of scattering centres (p_{CT}), and by the scattering radius ρ_s.

Figure 5 demonstrates the influence of the scattering effect on the shape of the initial separation distribution function as the number of the CT sites increases. An exponential distribution function assumed for initial separation distances[29] due to a multiple scattering of the mobile charge (hole) transforms into a Gaussian with the mean charge separation distance sensitive to the concentration of sensitisers. The mean initial separation distance r_M is reduced from 5 to 2.28 of the lattice constants as the p_{CT} is increased from 0.005 to 0.3. Figure 6 shows the effect of these changes on the GPR kinetics.

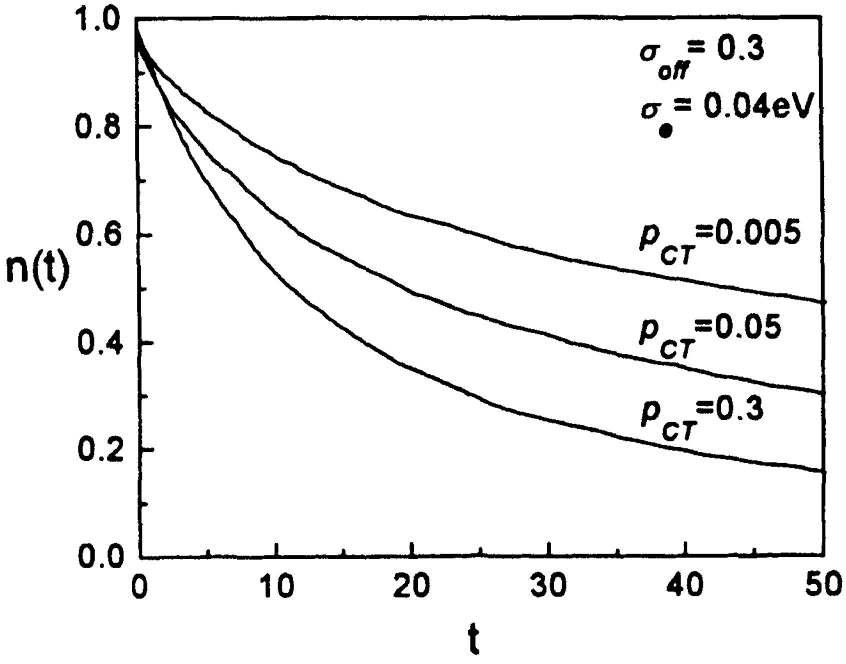

FIGURE 6 GPR kinetics with the charge scattering effect included. Initial distribution in the low limit of sensitiser concentration $n_0(r)= n_e(r)$; $\delta_{dd}= 0.04$eV, $\delta_{od}= 0.3$, $\rho_s=2$, $k_{CT}^{-1} = 0$

The presented model also indicates that the multiple scattering, a Markovian process, produces the final Gaussian-like distribution, irrespective of the initial shape of hole distribution at a high concentration of sensitiser. Thus, the assumption of Gaussian or even delta-type initial distributions, with the mean separation distance exceeding the extension of the CT complex, may be validated by taking into account multiple scattering of the hole by the sensitiser molecules valid, however, only in the limit of high sensitiser concentration.

Thus, the dependence of the GPR kinetics on the sensitiser concentration can be understood resulting from the elastic scattering of the initial movement of the hole, leading to a redistribution of the initial hole separation distance. The set of parameters used to simulate the GPR presented in Figure 6 provides a reasonable value of the yield of free carriers in the presence of the external electric field giving ~0.1 at p_{CT}=0.005 and at $5 \cdot 10^5$ V/cm, which is of the same order as the experimentally obtained values.[30,31] However, the CT complex properties – CT complex recombination and escape rates – must be taken into account to compare the simulation results to the experimentally observed ones on the picosecond time scale.

4. GPR IN THE CASE OF A "FINITE RATE" OF CT COMPLEX RECOMBINATION

The relaxation rate k_{CT} is the intrinsic parameter of the CT state, as well as, the escape rate of the hole from the CT state χ_{CT}, which is related to the difference in the state energies ΔE for the hole situated on the CT complex (ε_{CT}) and that on a neighbouring chromophore. In the case of a low ε_{CT} value in comparison with the neighbouring site energies, when $|\Delta E| \gg kT$, the escape of the hole from the CT site is inconceivable. For the opposite situation corresponding to ε_{CT} large in comparison with that of the neighbouring sites and $|\Delta E| \ll kT$, the competition between the rates k_{CT} and k determines the GPR.

A characteristic distance between the polymer chromophore and the sensitiser molecule in the CT complex for the carbazolyl – containing polymers is $r_{CT} \cong$ 3.5Å, while the lattice constant is two times larger. Rough estimation of the hole energy at the CT site: $\varepsilon_{CT} = q/r_{CT}$, yielding $\Delta E \cong$ 0.7eV in the regular lattice. In this case, the Boltzmann prefactor in eq. 2 is of the order 10^{-13}at room temperature, making hole escape impossible on a short time scale. Thus, when the initial hole transfer across a large distance is ignored, the hole density dependence on time evidently follows the exponential decay function: $n(t) \sim \exp(-k_{CT}t)$. To obtain the nonexponential decay as well as the dependece on p_{CT}, an initial charge separation over a larger distance ($r_M > a$) has to be assumed.

The simulation results for the dependence of the recombination kinetics on the initial separation distance r_0 are presented in Figure 7. It is evident that the kinetics turn out to be independent of the CT complex recombination rate k_{CT} by increasing the mean initial separation distance r_M, when the diffusion limited

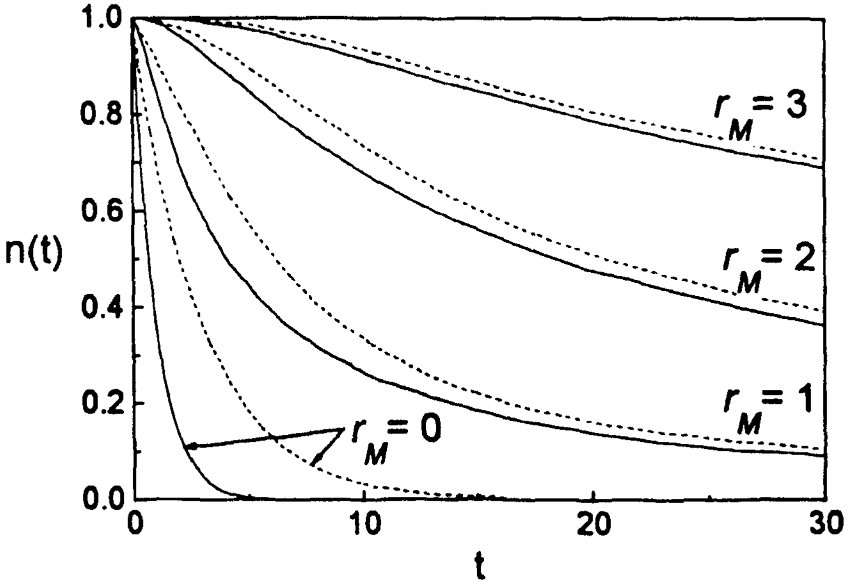

FIGURE 7 GPR kinetics for the different initial separation distances for the CT site recombination rate $k_{CT} = k$ (solid line) and $k_{CT} = k/3$ (dashed line). Initial distribution $n_0(r) = n_d(r)$

approach time becomes dominating. In general, the diffusion limited recombination process is governed by the time – displacement relation: $t_R \sim r_M{}^D$, where D is the dimension of the random walk, while the CT complex recombination time: $t_R \sim k_{CT}{}^{-1}$. Thus, the recombination process is independent of the recombination rate when $r_0 > C\, k_{CT}{}^{-1/D}$ (C is some numerical value). Therefore, the initial separation distance is a decisive parameter for recombination of the initially separated charge pairs across large distances. Moreover, as revealed by the Onsager theory, the quantum yield of free charge carriers is also determined by the mean value of the separation distance r_M. The conclusion drawn from these assumptions ($\chi_{CT} \ll k_{CT}$) is the following: only initially separated pairs may give an input into the photocurrent and, thus, the initial separation distance has to be a dominating parameter for describing the recombination and free charge generation processes.

5. DISCUSSION AND COMPARISON TO THE EXPERIMENT

Results of the Monte Carlo simulations presented above point out the sensitivity of the GPR kinetics to the initial distribution of the electron – hole separation. A suggestion of the Gaussian or delta-type distribution can be substantiated by the auto-ionisation and/or ballistic charge separation models.[4,5,32] According to this approach, the excess energy gained from the relaxation during the auto-ionisation of the excited molecule stimulates the mobile charge (the electron or the hole) to sweep away from the generation centre. Thus, a charge pair separated by a particular thermalization distance is created. However, according to the experimental results obtained in PEPCz[2] (as well as in other polymeric photoconductors) the charge separation may be initiated by a low energy quantum of visible light under the excitation of the lowest intermolecular CT states. Thus, the model of the auto-ionisation with a subsequent thermalization as it was mentioned in the Introduction cannot be adequately applied in this case, and as a result the distribution of the charge pair separation distance is hardly predictable *a priori*. However, in the limit of high sensitiser concentration due to multiple scattering of the hole by the sensitiser molecules, the Gaussian distribution becomes a reliable assumption.

Since the initial distribution changes on the nanosecond time scale and only those charge pairs that survive for a long time can be totally separated in to free charge carriers which can contribute to the photocurrent, the photocurrent results have to be rather insensitive to a particular shape of the initial charge pair distribution. On the other hand, the GPR dynamics gives more information on the initial separation of the charge pairs. The fast initial recombination is to be attributed to those charge pairs, which are not separated initially, i.e. to those holes which remain on the CT complexes. Thus, the initial distribution may be represented as a sum of two distribution functions with the peaks corresponding to two different processes: the charge pair separation by short distance r_{CT} and by large distance $r_M > a$. In the other case, by assuming that initially charge pairs are created only within the CT complexes, ε_{CT} has to be postulated to compensate the Coulomb energy so that χ_{CT} is comparable to k. But that is hardly possible due to a strong Coulomb attraction by the electron.

Comparison to the experiment

The course of the experimental kinetics in PEPCz sensitised with TNF are presented in Figure 8. The initial fast recombination and slow tail in the long times reveal the involvement of both separation processes mentioned above. Thus, the initial electron – hole separation distribution can be determined as: $n_0(r)=A_f\delta(r)$ $+A_s f(r)$, where A_f, denotes the "fast" amplitude, and A corresponds to the "slow" amplitude; function $f(r)$ is some distribution function, which has to fulfil the following additional conditions: $f(0) = f(\infty) = 0$. A reasonable shape of the GPR curve can be easily achieved by assuming the simplest approximation of the ini-

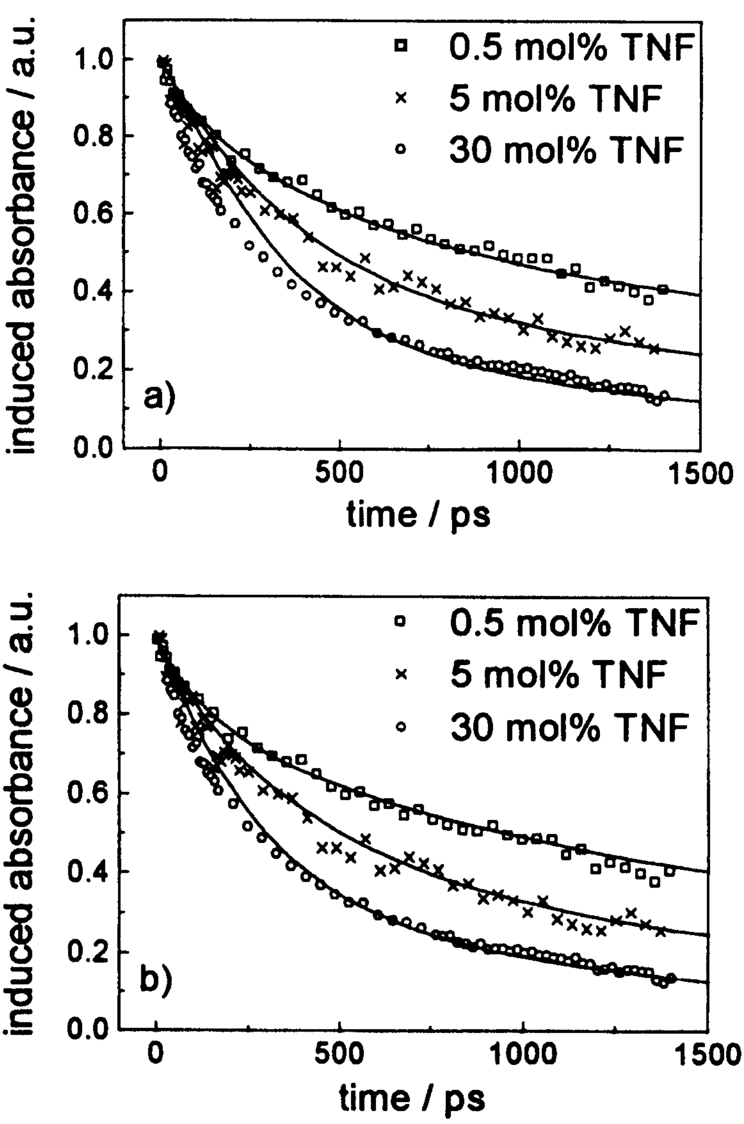

FIGURE 8 Experimental kinetics of the induced absorbance in the PEPCz film sensitized with the different concentrations of TNF (points) and the simulation results (solid lines) by using the initial hole distribution function $n_0(r) = A_f\delta(r) + A_s\delta(r - r_M)$ with the parameters $k_{CT}^{-1} = 150$ ps, $\sigma_{dd} = 0.09$eV, $\sigma_{od} = 0.3$, $A_f = 0.3$, $A_s = 0.7$ and: (a) $k^{-1} = 10$ ps, $r_M = 3.7$, 2.9 and 2.2, for $p_{CT} = 0.005$, 0.05 and 0.3, respectively. (b) $k^{-1} = 50$ ps, $r_M = 2.6$, 1.9 and 1.4, for $p_{CT} = 0.005$, 0.05 and 0.3, respectively

tial electron – hole separation distribution: $n_0(r) = (1 - \eta)\,\delta(r) + \eta\delta(r - r_M)$, where η is the yield of charge pairs separated by $r_0 \geq 1$, as it was already demonstrated.[28] It is evident that this initial distribution is not unique. Similar results may be obtained by assuming different distribution function $f(r)$ for different amplitudes $A_{s,f}$. The density of the CT sites influences only processes that are extended over large distances, therefore, the recombination kinetics dependence on the number of the CT sites may be modelled by taking into account scattering of the hole or phenomenologically modifying the function $f(r)$.[28] Thus, the initial separation of charge pairs is required for explanation of the GPR kinetics, while, the shape of the function $f(r)$ remains hidden by using only the Monte Carlo simulations, expressing only the mean separation distance r_M.

The simulations presented above were carried out by using dimensionless time and space coordinates, thus, for quantitative description of the experimental kinetics (see, for instance Figure 8) the dimensional scales for both variables have to be taken into consideration. The time scale used in our calculations is related to the rate of the hole jumps k in the regular lattice, and the spatial scale was normalised to the lattice constant a, correspondingly. According to Eq. 2, both these scaling factors are not totally independent of each other. Indeed, the rate of the charge transfer between two “nearest neighbours” in the regular lattice

$$\nu_{01} = \nu_0 \exp(-2\gamma a) \qquad (6)$$

contains the spatial scaling factor which determines the strength of the exponential overlap of the wavefunctions of the electron on the corresponding molecules. For estimations, the frequency factor can be set to be the mean vibration frequency according to consideration of the adiabatic transition for small polarons.[33,34] Thus, typical values of ν_0 are of the order of 10^{13} s^{-1}. The exponential factor is also not well defined, therefore, an error in estimating this value can be compensated by applying a correction for the frequency factor. It is evident that due to this exponential factor the hopping rate of the charge between the nearest neighbours (ν_{01}) in the regular lattice is several orders of magnitude smaller than the frequency factor ν_0, leading to an estimation $k \geq 10^{11}$ s^{-1}. Moreover, the space scaling parameter determines the scale of the Coulomb energy (see Eq. 1), however, this scaling factor can be relatively well defined for various structures as a mean interpigment distance in comparison with estimation of the temporal scaling factor.

According to the qualitative analysis of the GPR kinetics presented above the required kinetics at experimentally determined disorder values may be obtained using the initial distribution of the form: $n_0(r) = A_f\delta(r) + A_s\delta(r - r_M)$. Amplitudes A_f and A_s as well as the CT complex relaxation rate k_{CT} are obtained by fitting the experimental data of the GPR kinetics on the short time scale,[2,28] while the long time kinetics results from the diffusion approach of more distant separated charge pairs. This part of the kinetics is sensitive to an actual time scale, k^{-1}, as well as to the mean value of the separation distance r_M. As it is shown in Figure 8, the faster the hopping rate of the charge, the larger is the initial charge separation needed for a good fit with experimental data. By assuming the mean value of the initial separation to be close to that obtained from the photocurrent measurements (~30 Å), the GPR kinetics at the low concentration of the sensitiser as shown in Figure 8 is well described by the following rate scaling parameters: $k^{-1} = 50$ ps at $r_M = 2.6\,a = 18$ Å and $k^{-1} = 10$ ps at $r_M = 3.7\,a = 25$Å, while $k_{CT}^{-1} = 150$ ps was taken in both cases. For the cubic lattice, the hopping rate of the charge between nearest neighbours can be estimated as $\nu_{01} = k / 6$, giving $\nu_{01}^{-1} = 60$ ps and 300 ps for $k^{-1} = 10$ ps and 50 ps, respectively. The recombination kinetics corresponding to the higher concentrations of the sensitiser are modelled by reducing the mean separation distance of the initially separated holes, while the other parameters remain unchanged. It may be explained by the scattering mechanism presented in the section "Disordered lattice model".

7. CONCLUDING REMARKS

The Monte Carlo simulation model presented in this paper extends the previous scope of GPR simulations. The simulation models used so far[12,13,15–18] assume one special site of the lattice to be occupied by the electron. The recombination event is counted when the hole jumps to this site from any neighbouring lattice site in accord with the regular hopping process. However, the CT complex is formed by a sensitiser (where the electron is actually localised) and a particular chromophore being in close contact with the sensitiser. Therefore, the CT complex as a whole with its own recombination rate is included into the lattice framework. Thus, the current model, used in this paper, is more generalised in the sense that it allows the CT complex properties to be included, and it turns into the commonly used Monte Carlo simulation models by assuming the infinite recombination rate of the CT complex. Moreover, the influence of sensitiser is modelled by assuming the elastic scattering of the hole during the initial separation process. The model of course does not include all peculiarities of the real polymer film. The list of the main approximations is outlined below.

Firstly, a particular polymer is not a crystal solid, while the model approach was based on the cubic lattice framework. The additionally included off-diagonal disorder, however, takes into account the randomness of the media, while the Gaussian distribution of the deflections from the cubic lattice sites might be an obvious oversimplification. A more correct approach seems to be the model based on the correlated random set of spheres (molecules and/or chromophores) in a particular volume. The correlative and percolation peculiarities are supposed to modify the charge carrier motion and, therefore, the time behaviour can slightly differ from those obtained here.

Secondly, the diagonal disorder does not depend on the coordinate (x,y,z) in the model under consideration. Due to the randomness of the density of the matter, the width of the diagonal disorder should differ in the vicinity of the sensitiser. Moreover, for the subset of the electron hopping sites (the sensitiser molecules) the disorder type and the corresponding width are unclear. The deep trapping sites, that may be present because of the additional impurities, are also not taken into account.

The following conclusion may be drawn from the simulations and the analysis presented above:

i) The diagonal (site energy) disorder was found to be an important factor, influencing the GPR kinetics as a reduction factor of the recombination rate on the long time scale. On the other hand, the off-diagonal (positional) disorder enhances the recombination rate at the very initial times, corresponding to the charge pair recombination separated at short distances (by one or two lattice constants) and has almost no influence on the long times. However, qualitatively the shape of the kinetics is mainly determined by the initial distribution of the electron – hole separation.

ii) The exponential distribution of the initial electron – hole separation was found to give a qualitative agreement between the simulated and experimental GPR kinetics under the assumption of an infinitely fast recombination of the charges in the sensitiser-carbazolyl complex. A more general approach is based on the assumption of a finite recombination rate in the CT state and on the following initial distribution: $n_0(r)=A_f\delta(r)+A_sf(r)$. The experimental kinetics may be obtained by assuming $f(r) = \delta\,(r - r_M)$, where r_M is the mean long-range separation distance.

iii) Despite the fact that the exact shape of distribution function $f(r)$ cannot be determined from the fitting of the GPR kinetics, the kinetic analysis allows us to determine the charge hopping rate in the lattice framework by introducing an initial charge separation mean value as obtained from other experiments (i.e. photocurrent data).

iv) The gradual increase in the recombination rate by increasing the concentration of the sensitiser is explained by assuming that sensitiser molecules are the hole scattering centres reducing the initial pair separation distance and thus modifying the initial distribution of separation distance $n(r)$. The initial charge separation over several lattice constants is a necessary condition to explain the effect of sensitiser concentration.

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