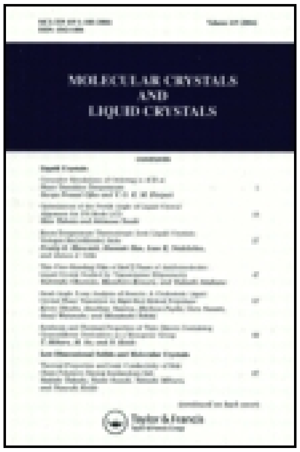

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Geminate Pair Recombination in Sensitized Polymers (Monte-Carlo simulations)

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Dynamics of the geminate charge pair recombination in the sensitized poly-N-epoxypropylcarbazole films was described by the Monte-Carlo simulations. The model was based on the assumption of a very fast charge separation over several carbazolyls and further slow recombination governed by the diffusive motion of the hole on an energetically and structurally irregular lattice. Both diagonal and off-diagonal disorder are taken into account by analyzing the experimental data. It is concluded that for the poly-N-epoxypropylcarbazole polymer sensitized with trinitrofluorenone the initial separations of the charge pairs are distributed exponentially with the mean value of 5 lattice constants and the widths of the diagonal and off-diagonal disorders are $0.04eV$ and 0.3 times the lattice constant, respectively.

Keywords: sensitized polymers; geminate recombination; photogeneration

INTRODUCTION

Photoconductivity of the sensitized polymeric compounds is observed under the excitation of the low energy charge transfer (CT) states of the polymer-sensitizer complex, however the mechanism of further charge separation in such systems is unclear so far. The main idea of the current understanding is based on the assumption that the loosely bound ion pair with the separation distance of several nanometers is created via thermalization of the higher excited CT state, what is similar to the autoionization - thermalization charge pair generation model [1-3,4]. However, recent transient absorption and transient anisotropy studies of PVK solutions [5] and films [6], doped with the tetracyanobenzene (TCNB) imply a negligible impact of the excess thermalization energy on the charge separation.

A coulombically bound charge pair is the outcome of the initial photogeneration stage. Dissociation of the bound pair is usually described by means of the Onsager theory [7]. According to this theoretical approach, the probability of the pair dissociation is mainly governed by the radius of the initial charge separation, which in general has to be distributed. In most cases the δ- distribution function is assumed, but according to Mozumder's calculations [8], exponential or Gaussian distributions provide the closest correspondence with the experimental data.

Diffusion of the charges in the potential well plays the decisive role in the recombination kinetics [9-11]. The Monte Carlo simulations [12] indicate an importance of the energy and structural disorder for the geminate pair recombination (GPR). Ries and Bässler [12] took into account the diagonal disorder in their model, and the disorder distribution value of 0.01-0.1eV was estimated. However, their investigations were confined to the very long time limits while the GPR dynamics in the short time scale was not considered.

Here the GPR simulations using the Monte-Carlo approach and a comparison of the results with the absorption pump-probe spectroscopy data for poly-N-epoxypropylcarbazole (PEPCz) are presented [13]. Initial charge pair separation distribution and both energy and spatial disorder are taken into consideration.

MONTE CARLO SIMULATION MODEL

The initial state of the recombination process is the set of charge pairs, characterized by the distribution of the initial charge pair separation distances. The GPR process is determined by the diffusive motion of a molecular polaron in the Coulomb attraction field of the counterion.

We followed basic principles of the Monte Carlo simulations of Ries and Bässler [12], but some modifications are additionally suggested. The simulation was carried out on a cubic lattice with a lattice constant a. The spatial (off-diagonal) disorder was included by deflecting each site randomly from its original crystalline position. In the spherical co-ordinate system the deflection is distributed by a Gaussian function with dispersion σ_{off}^2. An intrinsic energetic (diagonal) disorder ε_i accounts for the difference between the self - energy of site i and the mean value of all site energies. The latter is also characterized by a Gaussian function with distribution σ_ε^2.

The cubic lattice constant was assumed to be $a = 0.68$ nm which is equal to the mean distance between carbazolyl (Cz) chromophores in the solid PEPCz, the dielectric permitivity of the system $\varepsilon = 3$ [14] and the wave function overlap parameter $2\gamma a = 10$ [12]. Other parameters, such as the frequency prefactor ν_0 for the transition rate, the initial charge pair distribution and its mean distance, values of the diagonal and off-diagonal disorder, were obtained from the best fit with the experimental data.

The simulation results are normalized as follows: 1) the time scale is related to the hole jump time in the absence of the disorder, the sensitizer and the counterion; 2) distances are normalized to the lattice constant a; 3) the initial charge pair density equals to 1.

SIMULATION RESULTS

Regular Lattice Approximation. Initial Charge Separation Distribution

As the first step of our simulations, in order to understand the impact of the initial charge separation distribution, we calculated the GPR kinetics for the regular lattice without either diagonal or off-diagonal disorder. Three types of the initial distribution of the charge separation radius were used: δ- function, Gaussian function and exponential function, that are characterized by the mean separation radius r_0 (and the distribution width σ_r in the Gaussian case). For the qualitative estimation of the influence of the distribution function on the recombination kinetics, the mean separation radius for all the distributions was set the same with $r_0 = 4a$.

The calculated hole density kinetics is presented in Fig. 1. The initial part of the kinetics for Gaussian and delta functions is almost flat. Due to the absence of the electron-hole pairs with the minimal separation distance the recombination is delayed by the diffusion limited approach time. Later the recombination is quite fast and during ca. 60 jump times most of the carriers recombine. Kinetic curves obtained with Gaussian and δ- function distributions differ only qualitatively – the recombination starts earlier and lasts longer in case of the Gaussian distribution.

The exponential distribution of the charge pair separation leads to the fast recombination at the very initial time moment. The initial part of the kinetics is exponential with the decay rate being equal to the inverse single jump-time, while in the course of time the recombination process becomes diffusion limited and its rate decreases.

Only the exponential distribution leads to the calculation results qualitatively similar to the experimental kinetics, thus, only the exponential distribution was used in the following consideration.

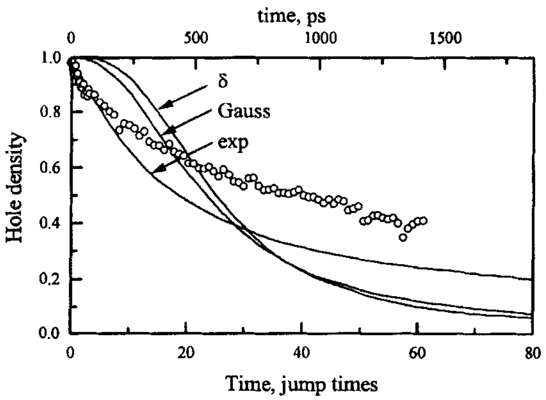
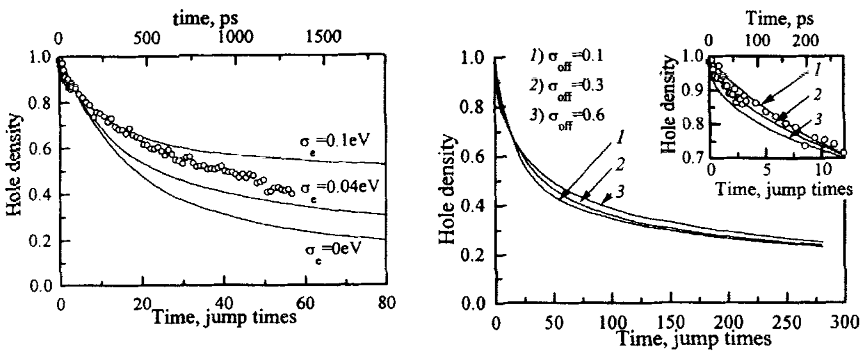


FIGURE 1 Calculated GPR kinetics (solid lines) for: δ, Gaussian (σ_r=1) and exponential initial separation radius distributions. The mean initial separation for all distributions r_0=4a; disorder parameters σ_ε=0; σ_{off}=0. Circles show the experimental kinetics for PEPK+0.5%TNF film.

Disordered Lattice Model

The simulation results for various widths of the diagonal disorder (off-diagonal disorder is absent) and comparison with the experimental data are shown in Fig. 2a. An initial exponential part of the kinetics, which responses to the nearest neighbour pair recombination, does not depend on the diagonal disorder. The width of the diagonal disorder σ_ε influences mainly the recombination rate in the long time scale: the wider disorder leads to the slower recombination kinetics. The closest agreement with the experimental data was obtained with $\sigma_\varepsilon = 0.04eV$.



a) b)

FIGURE 2 Calculated GPR kinetics (solid lines) for various widths of diagonal (a) and off-diagonal (b) disorder with the initial part emphasized in the insert. Distribution of the thermalization radius is exponential ($r_0=5a$); Parameters: a) $\sigma_{off}=0$, σ_e is varied; b) $\sigma_e=0.04eV$, σ_{off} is varied. Experimental kinetics of PEPK+0.5%TNF film (circles).

The off-diagonal disorder was also taken into account during the simulation. The mean square deviation σ_{off} is expressed in units of the lattice constant. The off-diagonal disorder (Fig. 2b) influences mainly the initial part of the kinetics. The off-diagonal disorder induces distribution of the jump rates and nonexponentiality of the initial recombination. The disorder increases the recombination rate at the very initial time and slows down this rate later, but it almost has no influence on the long time scale kinetics. Perfect agreement of the experimental and calculated kinetics was obtained for the exponential initial pair distribution with $r_0=5a$ and disorder parameters $\sigma_e= 0.04$ eV and $\sigma_{off}=0.3$ (Fig. 3).

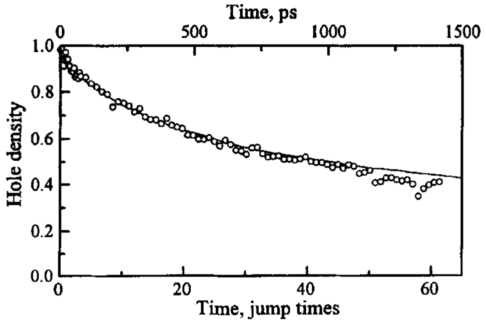


FIGURE 3 Experimental and calculated GPR kinetics: circles - experimental data, solid line - simulation results, obtained with the exponential initial distribution ($r_0=5a$) and disorder parameters $\sigma_e=0.04\text{eV}$, $\sigma_{off}=0.3a$.

DISCUSSION

Gaussian or δ- function distributions theoretically are based on the autoionization and ballistic charge separation model. These distributions were also obtained from the analysis of the voltage and thermal dependences of photoconductivity of sensitized polymers. However, the thermalization model is hardly adequate in case of sensitized polymers, where photoconductivity is observed under excitation to the lowest excite states, therefore, which distribution of pair separation distances should be is not clear so far. On the other hand, the initial distribution changes very rapidly. Only those charge pairs that survive for a long time can overcome the full separation into the free charge carrier states and contribute to the photocurrent. Therefore, photocurrent measurements can hardly be sensitive to the initial distribution. The charge pair recombination dynamics gives more direct and reliable information about the initial separation. The absence of the delay in pair recombination is a direct evidence against the Gaussian or delta function of the initial distribution.

The diagonal disorder makes traps for the hopping hole, therefore it strongly influences the kinetics in a long time scale while it has no influence at the very initial time for the nearest neighbour recombination. The role of the off-diagonal disorder is not very strong. Its influence is mainly limited by the very initial part of the recombination kinetics. The off-diagonal disorder induces distribution of the jump rates resulting in the nonexponentiality of the initial recombination. However, the off-diagonal disorder probably makes no influence on the yield of the free carriers, since it affects only the recombination of holes separated at very small distances.

CONCLUSIONS

The Monte-Carlo simulations have shown that the charge separation and recombination processes can be described by the model allowing for a very fast charge separation over several carbazolyls followed by a slow diffusive recombination. The initial fast separation yields wide distribution of the separation radii for the independent charge pairs. The exponential distribution with the mean radius of 5 lattice constants was found to give the best agreement between the simulated and experimental decay dynamics. The diagonal (site energy) disorder was found to be a very important factor influencing significantly the GPR kinetics by reducing the recombination rate on the long time scale. The off-diagonal (positional) disorder enhances the recombination rate at the very initial time. It comes from the variation of the lifetime of charge pairs separated by minimal distances, and has almost no influence on the long time scale kinetics and, probably, makes no effect on the charge carrier generation efficiency.

References

[1.] M. Yokoyama, A. Matsubara, S. Shimokihara, H. Mikawa, *Polym. J.*, **14**, 73 (1982).

[2.] M. Yokoyama, Y. Endo, A. Matsubara, H. Mikawa, *J. Chem. Phys.*, **75**, 3006 (1981).

[3.] M. Yokoyama, H. Mikawa, *Phot. Sci. Eng.*, **26**, 143 (1982).

[4.] E. A. Silinsh, V. A. Kolesnikov, I. J. Muzikante, D. R. Balode, *Phys. Stat. Sol. (b)*, **113**, 379 (1982).

[5.] H. Miyasaka, T. Moriyama, S. Kotani, R. Muneyasu, A. Itaya, *Chem. Phys. Lett.*, **225**, 315 (1994).

[6.] H. Miyasaka, T. Moriyama, A. Itaya, *J. Phys. Chem.*, **100**, 12609 (1995).

[7.] L. Onsager, *Phys. Rev.*, **54**, 534 (1938).

[8.] A. Mozumder, *J.Chem.Phys.*, **60**, 4305 (1974).

[9.] K.M. Hong, J. Noolandi, *J.Chem.Phys.*, **68**, 5163 (1978).

[10.] K.M. Hong, J. Noolandi, *J.Chem.Phys.*, **68**, 5172 (1978).

[11.] K.M. Hong, J. Noolandi, *J.Chem.Phys.*, **69**, 5026 (1978).

[12.] B. Ries, H. Bässler, *Mol.Electron.*, **3**, 15 (1987).

[13.] A. Ruseckas, V. Gulbinas, V. Sundström, A. Undzenas, L. Valkunas, *J. Phys. Chem B* (to be published).

[14.] V. Gaidelis, A. Girdziusas, A. Undzenas, *Liet. fiz. rink. (Sov. Phys.-Collection)*, , **22**, 72 (1982).