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CHARGE CARRIER PHOTOGENERATION IN POLYMERS CONTAINING CARBAZOLE GROUPS. INFLUENCE OF EXCIMER-FORMING SITES

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Abstract A new model of the charge carrier photogeneration including energy trapping in excimer-forming sites has been proposed for amorphous and crystalline poly(N-vinylcarbazole). The Onsager model with Gaussian distribution of electron-hole pairs represents a suitable description of the photogeneration process in plasma-polymerized poly(N-vinylcarbazole) and in poly(N-(2-propinyl)carbazole).

INTRODUCTION

It was found that in poly(N-vinylcarbazole) (PVCA) the field dependence of photogeneration efficiency is in agreement with predictions based on the Onsager theory.[1–6] According to that model,[7,8] a photon generates a Coulomb field-bound electron-hole (e–h) pair (CT state), which subsequently thermally dissociates into free carriers under combined effects of Coulomb attraction and of the external electric field. It is usually assumed that all e–h pairs are separated by the same distance r_o. Separation distances r_o have been reported to be 2.2–3.0 nm[1,2,8] for PVCA. However, the problem is that for the excitation to the first singlet state (3.5 eV) the energy of the CT state recalculated from r_o is 4.4 eV, i.e. an energy higher than excitation energy, which is physically unrealistic. On the basis of our measurements of the dependences of photogeneration efficiency on electric field and on temperature in both amorphous and crystalline PVCA (a-PVCA and c-PVCA, respectively) a new photogeneration model, which includes the excimer formation and energy trapping, was elaborated. To confirm the role of excimers in the photogeneration process we studied these dependences in plasma-polymerized PVCA (p-PVCA) and in poly(N-(2-propinyl)carbazole) (PPCA).

EXPERIMENTAL

Films of a-PVCA, c-PVCA (crystallinity 76%) and PPCA were prepared by casting as described in our previous papers.[8,9] Films of p-PVCA were deposited in a system[8] consisting of two parallel electrodes (glow discharge frequency 40 Hz, power 9 W). The thicknesses of the polymeric films ranged from 0.5 to 2 μm. The measurements of photogeneration efficiencies were carried out using the emission-limited photoinduced discharge technique.[8,10] The light-induced discharge rates were corrected for the penetration depth of light, the dark discharge and the rest surface charge.

RESULTS AND DISCUSSION

The conventional Onsager model was found to fail at high electric fields ($F > 10^8$ V m^{-1}) in all polymers under investigation (for example in c-PVCA, see Figure 1 — curve 1). The electric field dependences of photogeneration efficiency η could be explained by the Onsager model with the distribution of electron-hole pairs given by Gaussian function. Thus, the photogeneration efficiency is expressed as

$$\eta(\alpha, F, T) = \frac{\eta_{o\alpha}}{\pi^{1/2}\alpha^3} \int 4r^2 \exp(-\frac{r^2}{\alpha^2}) f(r, F, T) \mathrm{d}r \qquad (1)$$

where $f(r, F, T)$ is the dissociation probability given by the Onsager formula[7] and α is the parameter of the distribution of CT states. The both field and temperature dependences of η could be fitted by this model using the same parameters for PPCA and p-PVCA only (Figure 2). Using this model we could not fit temperature dependences for both a-PVCA and c-PVCA (inset in Figure 1). A different model had to be taken into account (see Figure 3). It is supposed that photoexcited carbazole chromophores rapidly lose their energy (in 10^{-12} – 10^{-13}s) via internal conversion and drop to the first excited singlet state. It is known that the monomer fluorescence in solid PVCA is strongly quenched and only excimer fluorescence is usually observed.[11] Therefore we assume that the bound e–h pairs are formed after energy trapping from excimer-forming active sites e^* with a rate constant k_1, independent of the electric field. Of course, the excimers may be deactivated radiatively or nonradiatively (rate constants k_{fg} and k_{ng}, respectively). The rate constant of free carriers generation k_d is assumed to be field-dependent and is given

by the relation $k_d(r, F, T) \times \tau_{CT} = f(r, F, T)$, where τ_{CT} is the lifetime of the e–h pair state with the radius r. The best fit of the experimental data was obtained assuming Gaussian distribution of the CT states. Then, the photogeneration efficiency is expressed as

$$\eta(\beta, F, T) = \frac{\eta_{o\beta}}{\pi^{1/2}\beta^3} \int 4r^2 \exp\left(-\frac{r^2}{\beta^2}\right) \frac{f(r, F, T)}{A + f(r, F, T)}\, dr \qquad (2)$$

where $A = (k_{fg} + k_{ng})/k_1$, $\eta_{o\beta}$ is the yield of the excimers active in the photogeneration process, β is the distribution parameter of CT states.

Full lines 3 in Figure 1 calculated using this model with parameters given in the Table I represent the best theoretical fit. It should be stressed that both the field and temperature dependences of photogeneration efficiency can be described by this model using the same parameters A, β and $\eta_{o\beta}$. The most probable separation distances determined to be 0.5 and 0.6 nm in c-PVCA for the 355 and 254 nm

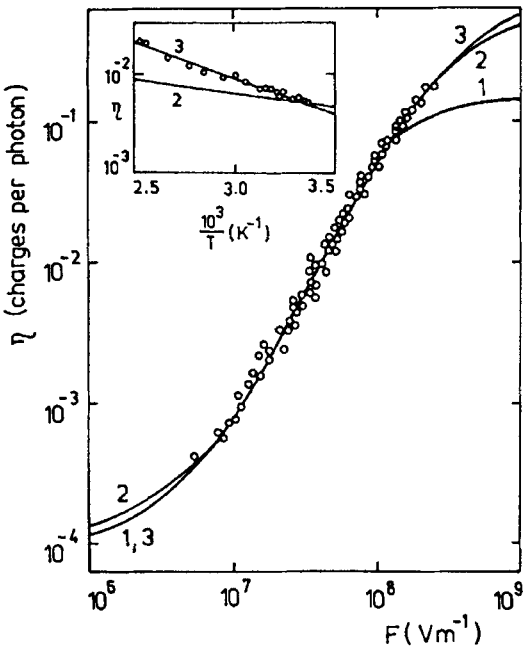

FIGURE 1 Dependences of the photogeneration efficiency on electric field (T = 296 K) and on temperature ($F = 3 \times 10^7$ Vm^{-1}, inset) in c-PVCA for 254 nm irradiation. Lines 1, 2 were calculated using the Onsager theory with distribution δ-function and Gaussian function, respectively, lines 3 were calculated using the proposed model with the parameters given in Table I.

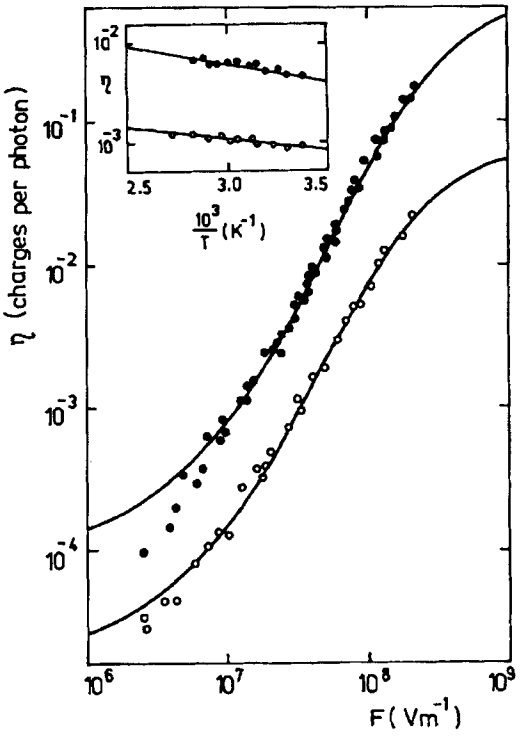

FIGURE 2 Dependences of the photogeneration efficiency on electric field (T = 296 K) and on temperature ($F = 3\times10^7$ Vm^{-1}, inset) in p-PVCA (○) and PPCA (●) for 254 nm irradiation. Full lines were calculated using the Onsager theory with the Gaussian distribution function and the parameters given in Table I.

irradiation, respectively, indicate the formation of e–h pairs on the nearest neighbouring carbazole units. In the measured range of electric field the greatest photogeneration efficiency was observed in amorphous films. Crystallinity led to reduced photogeneration efficiency probably due to shorter separation distances. The experimental data obtained with p-PVCA and PPCA could not be fitted by this model. The formation of excimer sites is restricted in PPCA due to the rigid main chain and in p-PVCA due to the crosslinked structure formed during plasma polymerization under the conditions used. Lower values of η in both PPCA and p-PVCA in comparison with a-PVCA suggest that the restriction of molecular motion leads to a decrease in photogeneration efficiency.

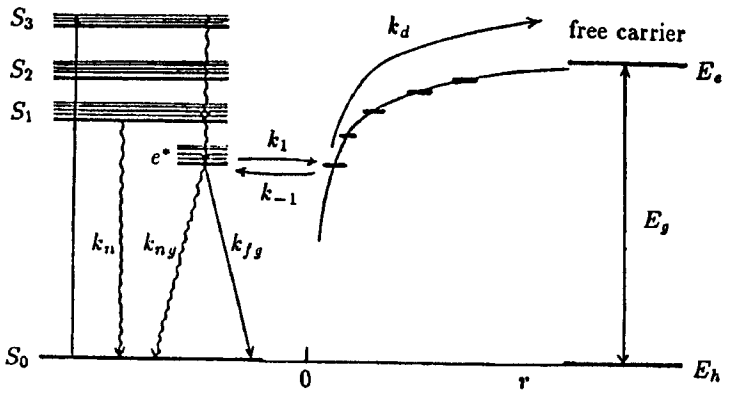

FIGURE 3 A schematic view of charge carrier photogeneration according to the proposed model for a-PVCA and c-PVCA.

TABLE I Parameters obtained from experimental data using different theoretical models: the Onsager model with distribution δ-function (r_o, η_o) and Gaussian function $(\alpha, \eta_{o\alpha})$, and the proposed model $(\beta, A, \eta_{o\beta})$.

Polymer	λ_{exc} (nm)	r_o (nm)	η_o	α (nm)	$\eta_{o\alpha}$	β (nm)	A	$\eta_{o\beta}$
a-PVCA	254	2.9	0.14*	1.60	0.48*	0.8	5×10^{-3}	0.44
($\varepsilon_r = 3.0$)	355	2.6	0.17*	1.30	0.95*	0.6	7×10^{-4}	0.87
c-PVCA	254	2.5	0.15*	1.25	0.82*	0.6	1×10^{-3}	0.80
($\varepsilon_r = 3.0$)	355	2.4	0.15*	1.20	0.83*	0.5	2×10^{-4}	1.00
p-PVCA	254	2.6	0.02	1.40	0.08	–	–	–
($\varepsilon_r = 3.0$)	355	2.6	0.01	1.40	0.04	–	–	–
PPCA	254	2.2	0.24	1.15	0.94	–	–	–
($\varepsilon_r = 3.2$)	355	1.8	0.12	0.85	0.94	–	–	–

* Only electric field dependences could be fitted by the respective model.

CONCLUSIONS

The Onsager model with the Gaussian distribution of CT states gives a good description of the charge carrier photogeneration in p-PVCA and PPCA only. The fast energy trapping in excimer-forming sites plays an important role in the photogeneration process in a-PVCA and c-PVCA. Using the new model including energy trapping, shorter separation distances of e–h pairs were obtained which indicates their formation on adjacent carbazole units.

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