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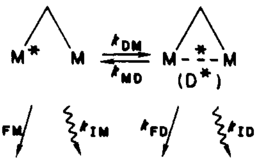
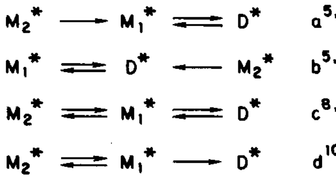
An Explanation of the Existence of Three Decay Constants in a Singlet Monomer–Excimer System

Recently, many reports concerning intramolecular excimer formation in polymer systems have been published, as nanosecond or picosecond time-resolved transient techniques have been developed. In particular, it has become of major interest lately that the conventional kinetic scheme of Birks[1,2] and Klöpffer[3,4] may not be applicable to some polymer systems. Although there should be only two decay constants in a monomer–excimer fluorecence system, the decay curves of some polymers have been found to be fit better by a linear combination of three exponentials. These results were reported for copolymers of 1-vinylnaphthalene (1VN) and methyl methacrylate (MMA),[5] copolymers of acenaphthylene and MMA,[6] P1VN, P2VN, and poly(1-naphthyl methacrylate) (PNMA)[7] by Phillips et al., PNMA[8] and dicarbazolylpropane (DCzP)[9] by Guillet et al., P2VN,[10,11] bis(2-naphthylethyl) ether,[10] and bis(1-naphtylmethyl) ether[12] by De Schryver et al., and P1VN by Gupta et al.[13] If there are three decay constants in these systems, there is a need to examine photophysically the kinetics of intramolecular excimer formation, because the existence of three decay constants corresponds to the existence of three excited states.

Scheme I



Scheme II



The conventional model used to describe the kinetics of excimer formation is shown in Scheme I, which was obtained by Birks for an intermolecular excimer system and then uncritically applied to the intramolecular excimer system. In Scheme I, k_{FM} and k_{FD} are the rate constants for the radiative deactivation of monomer and excimer state, respectively, k_{IM} and k_{ID} are those for the nonradiative deactivation, and k_{DM} and k_{MD} are those for excimer formation and dissociation. According to Scheme I, the response function of each fluorescence after pulse excitation is as follows: if [D*] is zero at $t = 0$

$$I_M(t) = A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t)$$

$$I_D(t) = A_3\{\exp(-\lambda_1 t) - \exp(-\lambda_2 t)\}$$

$$\lambda_2 > \lambda_1 > 0$$

Phillips et al.,[5,6] Guillet et al.,[8,9] and De Schryver et al.[10] recognized the need for appropriate kinetics and proposed new models, which are summarized in Scheme II. M_1 and M_2 represent the different conformers. The excimer can be formed only from the M_1 conformer by internal rotation (Scheme IIa,c,d), while Scheme IIb proposes that excimer also can be formed from the M_2 conformer by long-range interaction. The existence of a conformer that cannot form an excimer also was proposed by Goldenberg et al.[14]

However, the discrete two-state model does not seem to be the most appropriate for explaining this problem, because more than two conformers exist in various proportions (e.g., in *meso*-2,4-di(2-naphthyl)pentane, the fractions of tg$^-$, g$^+$t, and tt conformers are 0.49, 0.49, and 0.02[15]).

We think that these experimental data should be divided into three groups corresponding to a dimer model, a homopolymer, and a copolymer. The inherent complexity of polymer systems (namely, the existence of several configurations and many conformations, the distribution of polymer molecular weight, and photophysical processes such as energy migration and excimer formation between nonadjacent chromophores) makes it very difficult to elucidate this problem. The values of the time constants of oligomers are particularly dependent on the degree of polymerization. For instance, the lifetime of a monomer singlet is ca. 3 ns in the dimer, while it is only 1 ns in the octamer of oligostyrenes.[16] Accordingly, the decay curves may be multicomponent when the sequence length of chromophores in copolymers is in the oligomer region and has some complicated distribution. Therefore, if we consider this problem of three decay constants in relation to conformation, the dimer model is most suitable for exact examination.

We think that two explanations are possible for the case where three decay constants exist in a monomer–excimer

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fluorescence system. One concerns a "second excimer". A second excimer is supposed to have a partially overlapped sandwich structure of two aromatic rings and shows its emission peak in the middle of the monomer and the normal excimer peaks. The second excimer phenomenon has already been reported for naphthyl rings by Itagaki et al.,[17-19] De Schryver et al.,[10-12] and Nakahira et al.,[20] for anthryl rings by Mataga et al.[21] and Itoh et al.,[22] and for carbazolyl rings by many authors.[23] In the polymer system, the conformation of a second excimer is confirmed experimentally to be different from that of a normal excimer.[24]

Although Gupta et al.[13] apparently assigned the third excited component to the second excimer, they did not propose a kinetic scheme. So far, the only examples with three decay constants in a bi- or polychromophoric system are naphthyl and carbazolyl rings, and these rings can overlap partially. Then it is likely that the third excited component is due to second excimer emission.

However, a fourth decay component was reported in the poly(vinylcarbazole) fluorescence system, which has been generally confirmed to have second excimer. This emitting component was described as a "relaxed monomer" in pulse radiolysis studies (time resolution 10 ps) by Tagawa et al.[25] or as a third excimer in laser photolysis work by Roberts et al.[26] Itaya et al.[27] observed a third decay of 60 ps in poly(*N*-vinyl-5*H*-benzo[*b*]carbazole) by picosecond laser photolysis (time resolution 30 ps), in spite of the absence of monomer fluorescence. These facts suggest that the fluorescence of "two" excited states decays with "three" decay constants while that of "three" excited states decays with "four" decay constants. We think that this is sufficient reason to propose another interpretation.

The presentation of another explanation for these experimental results is the purpose of this short communication. We think that these results might be caused by the relaxation process of the nonequilibrium state, because the time scale of fluorescence measurements (nano- or picosecond) is supposed to be comparable with the relaxation time of internal rotation. The spin-lattice relaxation times of the main-chain $-CH_2-$ segment in poly(alkyl methacrylate) $\{-(CH_2C(CH_3)(COOR))_n-\}$ change from 0.23 ns (R = Me) to 0.66 ns (R = *t*-Bu).[28] This indicates that the relaxation time of internal rotation seems to be in the nano- or subnanosecond range, and that the more bulky the side-chain chromophores are, the longer the relaxation time is.

Any compound at thermal equilibrium consists of molecules having an equilibrium distribution of conformations before excitation. If one of the molecules with a conformation ready to change to the excimer conformation is excited, it turns immediately to excimer. If another molecule with a conformation far from the excimer conformation is excited, the excited side-chain ring changes its conformation during the lifetime of the excited state through the Markov process and finally turns to excimer or emits the monomer fluorescence before forming excimer. Accordingly, the two-state model as shown in Scheme II is only one of the approximations concerning conformational change.

The nonequilibrium process induced by the conformational change of side-chain chromophores can be treated theoretically by two different methods. One is the approach involving the stochastic process and will be published elsewhere in a full paper. The other, discussed in this paper, is based on the model that the formation of excimer is encounter controlled. When molecules or functional groups initially distributed at random encounter each other by a diffusion process, a transient phenomenon appears at the beginning, and this nonequilibrium effect can be expressed by substituting the time-dependent term into the rate constant. In our case, the rate constant for excimer formation, k_{DM}, can be expressed by

$$k_{DM} = A + B/t^{1/2} \quad (A \text{ and } B \text{ are constants}) \qquad (1)$$

Equation 1 is based on the Einstein-Smoluchowski diffusion theory.[29] For the case of a bimolecular encounter, A and B are, respectively, $4\pi N_A DpR/1000$ and $4N_A p^2R^2(\pi D)^{1/2}/1000$ (D = diffusion coefficient, R = interaction radii, N_A = Avogadro's number, and p = reaction probability per collision). However, in our case where the encounter of the chromophores is achieved only through internal rotations, it is not easy to discuss the details of the constants A and B. For the moment, only the relation containing $1/t^{1/2}$ is important.

We now examine how the monomer and excimer fluorescence will decay if k_{DM} depends on time under Birks kinetics (Scheme I). In order to avoid complexity of calculation, we neglect the dissociation of the excimer, which is confirmed experimentally at room temperature for polystyrene and its model dimer.[16,30] Under the condition that $k_{MD} = 0$, the following rate equations are obtained from Scheme I.

$$d[M^*]/dt = I_0 - (k_M + A + B/t^{1/2})[M^*]$$

$$d[D^*]/dt = (A + B/t^{1/2})[M^*] - k_D[D^*] \qquad (2)$$

where

$$k_M = k_{FM} + k_{IM}$$

$$k_D = k_{FD} + k_{ID}$$

In the case of pulse excitation, I_0 is supposed to be represented by a δ function. Then by solving eq 2 with the initial condition that $[D^*] = 0$ at $t = 0$, we obtain

$$I_M(t) = k_{FM}[M^*]_0 \exp\{-(k_M + A)t - 2Bt^{1/2}\} \qquad (3a)$$

$$I_D(t) = k_{FD}[M^*]_0[(A/a)(\exp(-k_Dt) - \exp\{-(k_M + A)t - 2Bt^{1/2}\}) + 2B \exp(B^2/a) \exp(-k_Dt)\{(1 - A/a)/a^{1/2}\}\{\text{Erfc } (B/a^{1/2}) - \text{Erfc } (B/a^{1/2} + (at)^{1/2})\}] \qquad (3b)$$

$$a = k_M + A - k_D$$

In the case that k_{MD} cannot be neglected, the response function of monomer fluorescence can be expressed by

$$I_M(t) = |P_1| \exp(-\alpha t - \beta t^{1/2}) + |P_2| \exp(-\gamma t) \qquad (4)$$

where α, β, and γ are composed of rate constants shown in Scheme I.

First, we examine the excimer formation of a dimer model compound. It is controlled only by conformational change and is not contaminated by the energy migration process. There is no other paper than that of Ng and Guillet[9] which deals with excimer formation in a dimer model. They reported that the monomer fluorescence of dicarbazolylpropane decays according to

$$I_M(t) = -0.09 \exp(-t/15 \text{ ps}) + 0.06 \exp(-t/5.7 \text{ ns}) + 0.006 \exp(-t/30 \text{ ns}) \qquad (5)$$

This empirical equation involves some problems, because the first exponential term accounts for less than 1% of the second term at $t = 0.1$ ns and becomes much smaller for $t > 0.1$ ns, while the time resolution of these measurements is supposed to be not less than 0.1 ns. However, having no alternative, we first tried to reexamine this multicom-

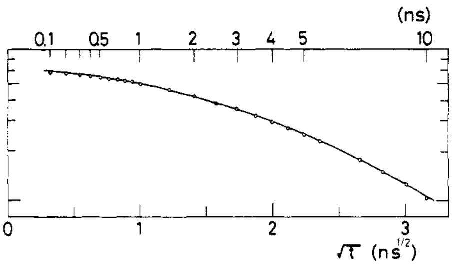

Figure 1. Replot by the pattern of $\exp(-\alpha t - \beta t^{1/2})$ for $-0.09 \exp(-t/15 \text{ ps}) + 0.06 \exp(-t/5.7 \text{ ns})$ (eq 5). The circles show the sum of the values of the first and second terms of eq 5, and the solid line indicates the replot curve by a least-squares method $\{(0.062 \exp(-t/6.1 \text{ ns} - (t/550 \text{ ns})^{1/2})\}$.

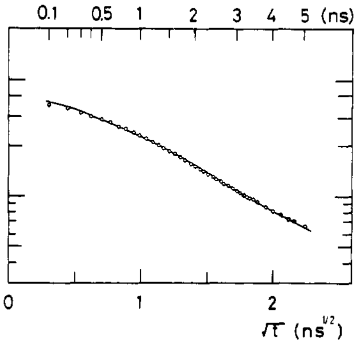

Figure 2. Replot by the pattern of $\exp(-\alpha t -\text{n}\ \beta t^{1/2})$ for $0.29 \exp(-t/1.6 \text{ ns}) + 0.079 \exp(-t/12.6 \text{ ns})$ (eq 6). The circles show the sum of the values of the first and second terms of eq 6, and the solid line indicates the replot curve by a least-squares method $\{0.446 \exp(-t/6.5 \text{ ns} - (t/3.5 \text{ ns})^{1/2})\}$.

ponent decay curve. After summing the values of the first and second terms of eq 5 from 0.1 to 10 ns at intervals of 0.1 ns, we tried to fit these calculated values to eq 4 by using a least-squares method. Figure 1 shows the calculated sums of the first two terms in eq 5 fitted by the pattern of $\exp(-\alpha t - \beta t^{1/2})$. The good fitting indicates that the existence of three decay constants in a monomer–excimer system would be explained by introducing a time-dependent term (eq 1) into k_{DM}.

Phillips et al.[7] obtained an empirical equation for the monomeric fluorescence decay curve of P1VN as follows.

$$I_M(t) = 0.290 \exp(-t/1.6 \text{ ns}) + 0.079 \exp(-t/12.6 \text{ ns}) + 0.029 \exp(-t/39.1 \text{ ns}) \quad (6)$$

We again tried to fit the sum of the first two terms from 0.1 to 5 ns by the pattern of $\exp(-\alpha t - \beta t^{1/2})$ in the same way as was mentioned for DCzP. Good fitting was obtained, as is shown in Figure 2. The excimer in a dimer model is formed only by conformational change of an excited side-chain chromophore, but the formation of intramolecular excimer in polymer systems can be accomplished also by another mechanism, i.e., a singlet energy migration along the polymer chain to the preformed excimer conformation site.[31,32] This good fitting may indicate that the nonequilibrium effect is not influenced by the process of singlet energy migration through the side-chain chromophores. Thus the existence of three decay constants in polymer systems also can be explained by the time-dependent term. At least it is sometimes true that the decay according to $\exp(-\alpha t - \beta t^{1/2})$ term apparently looks like dual exponentials.

It would be possible to suppose from the above that the deviation from the Birks scheme (Scheme I) is due to such nonequilibrium process. The measurement of the fluorescence decay curve with higher accuracy will give information on the nonequilibrium transient term. We believe that the development of time resolution techniques for measuring intramolecular excimer formation will make it possible to investigate the dynamics of internal rotation.

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Registry No. DCzP, 25837-66-5; P1VN, 25135-12-0.

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