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# Excited Triplet State of Carbazole Chromophore and the Triplet Energy Migration in Poly[(carbazolylethyl methacrylate)-*co*-(methyl methacrylate)] Film

**Shinzaburo Ito,* Hideaki Katayama, and Masahide Yamamoto***

*Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan.* *Received December 2, 1987*

ABSTRACT: Triplet excimer formation and energy migration among carbazole chromophores in poly[(carbazolylethyl methacrylate)-*co*-(methyl methacrylate)] film were investigated by measuring phosphorescence. The use of the copolymer gave a polymer matrix with a high chromophore concentration but with uniform distribution of the carbazole moiety. Three triplet species were observed depending on the concentration of chromophore: monomer ($^3M^*$), shallow trap ($^3T^*$), and triplet excimer ($^3E^*$). Triplet energy migration occurs at concentrations higher than 0.9 mol $L^{-1}$, where the average distance of chromophore is about 1.2 nm. This energy transport brings a drastic change in the spectra from $^3M^*$ to $^3E^*$. Pulsed excitation gave a clear rise of sensitized phosphorescence from a triplet energy acceptor, 1,4-dibromonaphthalene. The diffusion coefficient of triplet energy ($D$) was found to be on the order of $10^{-9}$ cm$^2$ s$^{-1}$ by evaluation from the rise time. Concentration dependence of $D$ indicated that the energy hopping takes place with the electron-exchange mechanism.

## Introduction

Photophysical processes of the carbazole chromophore have been the center of much attention from the fundamental as well as the application standpoint. Many workers have investigated the electronically excited states and their dissipation processes in poly(vinylcarbazole) and its dimeric model compounds.[1-10] In the triplet state as well as in the singlet state, the carbazole chromophore is said to form the excimer that is an excited dimer between an excited chromophore and a ground-state one.[11]

Compared with the singlet state, the knowledge on the triplet state is poor, because of the weak phosphorescence emission from the triplet state. But a large part of the excited energy dissipates to the ground state via the triplet state, and the fraction often exceeds a half of the excited chromophores. Thus, the triplet state is important when discussing the photofunctional properties of polymer solids.

Triplet-state behavior of many aromatic molecules besides the carbazole chromophore has been studied, e.g., naphthalene and phenanthrene.[12-14] The data obtained on these polymer systems indicate that there are two critical factors deciding the behavior of excited states in polymers, where the chromophores are fixed in a matrix at an extremely high concentration.[15-22] The first factor is trap-site formation. In a glassy solvent, the phosphorescence spectra from polymers often shift to the red side about a few nanometers; it is said to be a shallow trap formed between two neighboring chromophores on the polymer chain. Some polymer films show broad and red-shifted spectra, which are much like the fluorescence spectra of a singlet excimer. This was assigned to a triplet excimer, which acts as a deep trap of triplet energy. The second factor is migration of triplet energy. By triplet energy migration, an efficient energy flow occurs from donor molecules to a small amount of acceptor molecules or trap sites, which is called "sensitization". These two primary factors should be understood when discussing the photophysical processes in polymer systems.

After the detailed studies by Klöpffer et al.,[11] poly(vinylcarbazole) and its analogous polymers were widely investigated by using the time-resolved spectroscopic technique.[23-26] Especially, Burkhart et al. showed the existence of several triplet species in poly(vinylcarbazole) film and studied their behavior in a wide range of temperature.[23] Another effective approach has been carried out by modifying the chemical structure of polymers whose pendant chromophores were linked to the polymer chain in a form so as not to satisfy Hirayama's $n = 3$ rule.[27-30] These polymer structures weaken the interaction between chromophores and make the excited species simpler than those of poly(vinylcarbazole).

Copolymerized samples containing various amounts of the chromophoric monomer in a spectroscopically inert comonomer give another variation for the study of photophysics in polymer systems. Concentration dependence is an important factor to be scrutinized for the excimer formation and energy transfer processes. Both the phenomena result from the interaction of chromophores, that is, they are mainly governed by the distance of separation. However, in polymeric systems, homopolymers impose a fixed and vague local concentration. By the use of a series of copolymers prepared from a similar kind of methacrylate monomer, we can observe the nature of triplet states in the polymer solid as a function of the chromophore concentration. The investigation in this system will give an insight into the triplet state behavior in a wide range from an isolated chromophore to the highly concentrated systems where many interchromophoric processes take place.

## Experimental Section

**Materials and Sample Preparation.** The monomer, 2-(9-carbazolyl)ethyl methacrylate (CzEMA), was synthesized by es-

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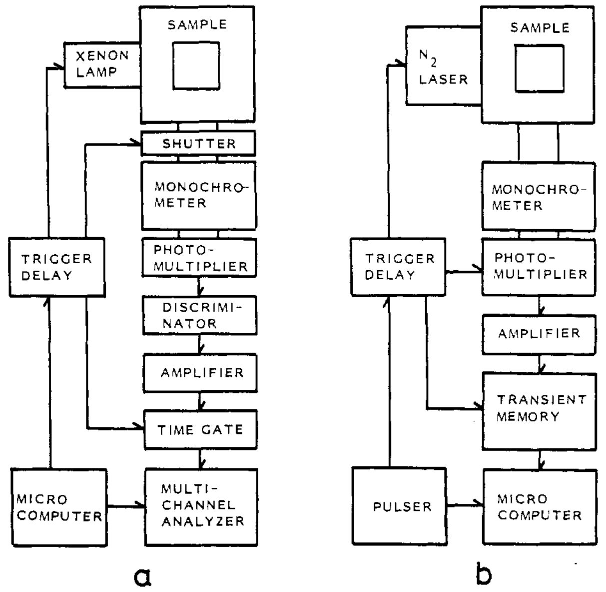

**Figure 1.** Schematic diagrams of the apparatus for measuring phosphorescence decay and time-resolved spectra: (a) photon counting system for the millisecond time range; (b) $N_2$ laser system for the microsecond time range.

terification of methacryloyl chloride with 9-(2-hydroxyethyl)carbazole. Methyl methacrylate (MMA) (Tokyo Chemical Industry Co., Ltd.) was distilled under reduced pressure before use. Weighed quantities of these monomers were dissolved in purified DMF containing azoisobutyronitrile as an initiator and polymerized at 60 °C. The obtained copolymer, P(CzEMA-*co*-MMA), was purified by repeated reprecipitation and dried in vacuo. Film was cast in a quartz cell from degassed solutions of the copolymer (0.5–1 wt %) in methylene chloride (Dojindo Laboratories, spectrophotometric grade). The solvent was gradually removed by vacuum distillation. Obtained film was dried in vacuo for a day and then sealed under $10^{-5}$ mmHg. 1,4-Dibromonaphthalene (DBN) (Kantou Chemical Industry Co., Ltd.) was recrystallized from methanol several times. DBN-doped film was cast from the solution of the copolymer and DBN, whose concentration was determined by the absorbance at 295 nm ($\epsilon$ = 10 200 L mol$^{-1}$ cm$^{-1}$). Poly(methyl methacrylate) (PMMA) (Nakarai Chemicals, Ltd.) was used as received. The PMMA film prepared without any chromophores and dopants gave no observable emission under the experimental conditions. 9-Ethylcarbazole and 9-phenylcarbazole (Tokyo Chemical Industry Co., Ltd.) were purified by recrystallization. 2-Methyltetrahydrofuran (MTHF) (Aldrich Chemical Co., Inc.) which was used as a rigid glass at 77 K, purified by vacuum distillation after preliminary distillation over sodium metal.

**Measurements.** Spectroscopic measurements were carried out for the degassed film. Phosphorescence spectra in a photostationary condition were measured with a Hitachi 850 spectrofluorophotometer fitted with a phosphorescence attachment. Phosphorescence decay and time-resolved phosphorescence spectra were measured with a phosphorimeter assembled in our laboratory. The spectral response was calibrated according to a standard tungsten lamp. Figure 1 shows a block diagram of the setup.

Two distinct systems were used. For the measurement in the millisecond time range, the delayed emission from the sample film after excitation by a Xe flash lamp (EG&G, FX198UV) was converted into an electrical pulse train by a photon counting unit (Hamamatsu, C-1050) with a photomultiplier (Hamamatsu, R649) (Figure 1a). The signals are accumulated 100–2000 times on a multichannel analyzer (Norland Co., IT-5300) and then analyzed by a microcomputer. The second system was used for measurement in the microsecond range (Figure 1b). A nitrogen laser (NDC Co., JH-500) was used as an excitation light source, and phosphorescence decay was detected by a gated-photomultiplier (Hamamatsu, R1333). The electric signals were digitized and accumulated on a transient memory (Kawasaki Electronica, MR-50E). The sample cell was set in a quartz Dewar. The temperature was controlled by liquid nitrogen or precooled nitrogen gas.

**Table I**
**Composition, Average Distance between Cz Residues, and $M_w$ for P(CzEMA-*co*-MMA) Film**

| Cz concn, mol L$^{-1}$ | Cz content, mol % | dist,[a] nm | $10^{-3}M_w$ |
|---|---|---|---|
| 0.14 | 1.2 | 2.28 | 87 |
| 0.49 | 4.4 | 1.50 | 100 |
| 0.95 | 9.2 | 1.20 | 100 |
| 1.44 | 15.3 | 1.05 | 104 |
| 1.91 | 22.1 | 0.95 | 104 |
| 2.42 | 31.1 | 0.88 | 113 |
| 2.91 | 41.9 | 0.82 | 110 |

[a] Calculated by $R = n^{-(1/3)}$, where $n$ is the average number of Cz per unit volume.

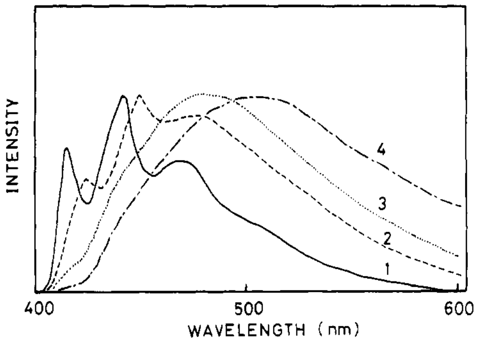

**Figure 2.** Phosphorescence spectra of P(CzEMA-*co*-MMA) film at 77 K: (1) 0.14; (2) 0.95; (3) 1.44; (4) 2.42.

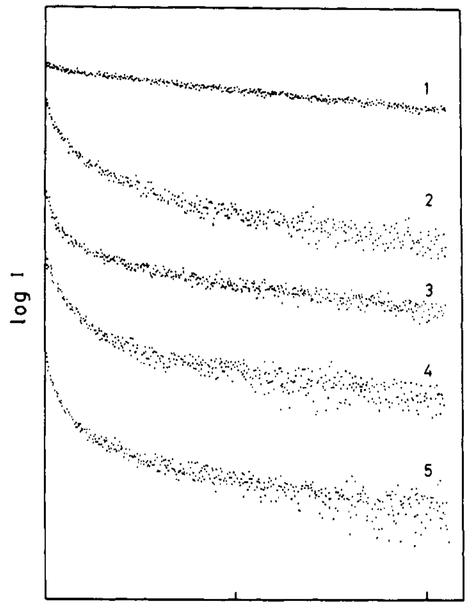

**Figure 3.** Phosphorescence decay curves of P(CzEMA-*co*-MMA) film observed at 440 nm for (1) and (2) and at 480 nm for (3)–(5): (1) 0.49; (2) 0.95; (3) 1.44; (4) 1.91; (5) 2.42.

## Results and Discussion

Table I shows the characteristics for the copolymers having various compositions. In this table, the mean distance between carbazole chromophores was evaluated from the density of the film. Each sample is hereafter referred to by the concentration (mol L$^{-1}$) of carbazole chromophores in the polymer matrix.

Figure 2 shows the phosphorescence spectra at 77 K. Samples 0.14 and 0.49 show spectra similar to those of the monomeric model compound, 9-ethylcarbazole (EtCz)

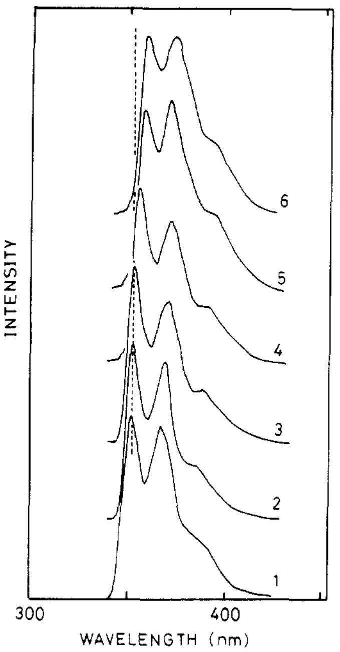

**Figure 4.** Fluorescence spectra of P(CzEMA-*co*-MMA) film at 77 K: (1) 0.14; (2) 0.49; (3) 0.95; (4) 1.44; (5) 1.91; (6) 2.42.

doped in PMMA at a dilute concentration: $2 \times 10^{-3}$ mol $L^{-1}$. In these film samples, there is no evidence of triplet traps or excimer which would be formed by the interaction between carbazole moieties. The decay curves for these samples are fitted with a single exponential function, as shown in Figure 3.

In this copolymer, the carbazole chromophores behave like isolated ones up to a fairly high concentration, compared with the doped system, i.e., EtCz in polystyrene film.[23d] It is worth noting that the copolymerization method enables the uniform dispersion of chromophores even at such high concentrations and prevents microcrystallization of carbazole moieties in the polymer matrix. In sample 0.95, the band shape of the spectra is similar to that of sample 0.49, but the wavelength clearly shifted to a longer wavelength of about 10 nm. The decay curve also changed to show multiexponential behavior. The spectrum, which shifts to the longer wavelength but holds the vibrational structure of the monomer emission, often appears in homopolymers in glassy solutions or in polymer blend film.[15c,18,21,25a] The excited state is considered to be stabilized by a mutual interaction of chromophores, but the interaction energy is smaller than the vibrational energy of the chromophore. In this sample, 0.95, the interaction between chromophores is not strong enough to change the spectrum to excimeric broad emission. We call this emissive species "shallow trap" $^3T^*$ and distinguish it from triplet excimer $^3E^*$. The next sample 1.44 already shows broad emission in the longer wavelength range. As mentioned later, we assigned this species to the triplet excimer. The wavelength gradually shifts to a longer wavelength with the increase of concentration of chromophore. In the singlet state, it is known that the carbazole chromophore forms two distinct excimers, namely, sandwichlike excimer and partial overlap excimer (second excimer).[2,3] However, the triplet excimer is not so simple; the species probably has continuous energy levels corresponding to the interaction energies determined by the various configuration of two carbazole chromophores. This property in the triplet state is also seen in the decay profile. The phosphorescence decay curves from these samples show noticeable deviation from simple exponential behavior. Here, it should be noted that the intensity of excitation light is too weak to cause triplet–triplet annihilation, which is not the reason for the nonexponential behavior.

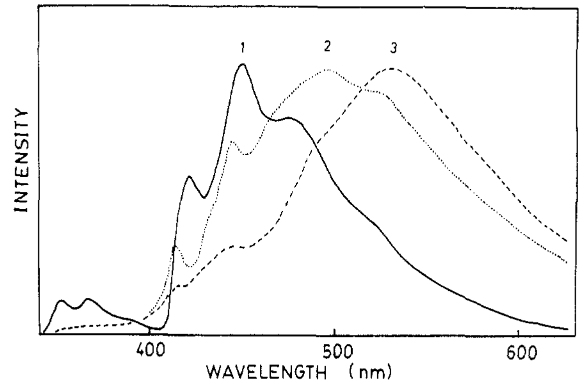

**Figure 5.** Phosphorescence spectra at three different temperatures for P(CzEMA-*co*-MMA) 0.95 film: (1) 77 K; (2) 143 K; (3) 298 K.

Previously, we reported that the homopolymer, poly(CzEMA) film, whose concentration of carbazole moiety is 4.4 mol $L^{-1}$, gives no singlet excimer emission even in the neat film.[30] However, careful observation of the fluorescence spectra at 77 K indicates that the emission band slightly shifts to a longer wavelength of about 5 nm. This singlet behavior is similar to the triplet shallow trap, as mentioned above. Thus, the fluorescence spectra for the copolymer film were measured at 77 K, as shown in Figure 4. The spectrum of 0.95 slightly shifted to the red side, and a further wavelength shift occurred with the increase in concentration. This shows that the shallow trap in the singlet state is closely related to the triplet excimer, since both the fluorescence and the phosphorescence spectra begin to shift in the same sample, 0.95. This means that the stabilization energy in the singlet state is still weak even for the geometrical arrangement of the triplet excimer. It is not necessary for the triplet excimer to take a strict arrangement of two chromophores, compared with the singlet one. This probably comes from the loose potential curve for the triplet state with respect to the geometrical arrangement of two chromophores. Chandra et al.[31] made theoretical calculations for the triplet excimer of naphthalene. They predicted that the steric configuration of the triplet excimer is significantly different from a sandwich-parallel geometry favored by the singlet excimer.

Temperature dependence of phosphorescence spectra gives us further information on the triplet state. In samples 0.14 and 0.49, there is no change with the increase in temperature, except for the broadening of the vibrational band. However, the sample having the critical concentration, 0.95, shows marked changes with temperature. Figure 5 shows the phosphorescence spectra measured at various temperatures. As described previously, the spectrum observed at 77 K mainly consists of the shallow trap emission. A slight increase in temperature gives a quite different spectrum; the monomer emission at 413 nm and broad excimer emission at around 500 nm appear in place of the shallow trap emission. This means that the energy on the shallow trap dissipates by the following two pathways. One is that the excitation energy is thermally detrapped and returns to the mobile monomer state. The other is that the shallow trap is further stabilized by thermal rearrangement of two carbazole rings and varies to the triplet excimer. Since the increase in temperature accelerates the rearrangement process, the maxima of excimer emission gradually shifts to the longer wavelength

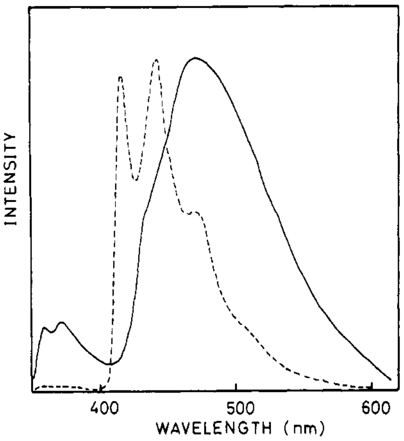

**Figure 6.** Phosphorescence spectra of 9-phenylcarbazole doped in poly(carbonate) film at 77 K: (---) 0.5 mol/L; (—) 2.0 mol/L.

range. A similar shift was previously observed at 77 K as the concentration dependence of excimer emission. The excited monomer state is considered to be a mobile state of the triplet energy, then it is ultimately trapped at the deep trap, excimer, after repeated migration. At higher temperatures, the latter way becomes the main route of the dissipation processes even in the low-concentration sample, 0.95. The reason for the drastic change between 77 and 140 K is not clear at present. It may be related to the side-chain motion of PMMA, since the relaxation of the methoxy group occurs at about 120 K. In this sample, 0.95, all emissive species in the triplet state can be seen as a function of temperature. The average distance of carbazole chromophores is calculated to be ca. 1.2 nm, which agrees with the quenching radius for the triplet state, obtained by the conventional Perrin plot.[32,33] This means that the radius is also applicable to the energy migration process, since the triplet energy migration takes place by the same electron-exchange mechanism. The polymer matrix does not have so many trap sites, but the trap emission is efficiently sensitized by the energy flow from the monomer state. It is noteworthy that there is a critical concentration at around 0.9 mol $L^{-1}$, at which the triplet behavior in the polymer matrix markedly varies.

Spectroscopic measurements in such concentrated systems are often disturbed by some impurity emission.[13] Careful examination is required for assignment of the broad emission at around 500 nm. As mentioned above, we assigned this species to the triplet excimer. This conclusion is based on the following finding. (1) The excited singlet state of these film specimens clearly gave monomer emission of the carbazole chromophore (see Figure 4). The samples with a carbazole chromophore concentration higher than 0.95 showed a slightly shifted fluorescence spectra, but the band structure was similar to the monomer emission. These film specimens had good migration efficiency for the singlet energy. The excited state after a number of steps still lies in the carbazole chromophore, and not in impurities. (2) Phosphorescence spectra of $^3T^*$ and $^3E^*$ showed marked temperature dependence (see Figure 5). It is difficult to explain these phenomena by some unknown impurity. It seems reasonable to assume that the spectral change comes from thermal rearrangement of the excimer conformation. (3) Many carbazole derivatives give similar excimeric emission, in spite of the different sources and different workers. An example is shown in Figure 6. Figure 6 shows delayed emission of 9-phenylcarbazole doped in poly(carbonate) film. The sample at the concentration of 2.0 mol $L^{-1}$ gave broad phosphoresence and delayed monomer fluorescence at around 360 nm. We checked several carbazole derivatives: some were synthesized, and some were purchased. The gave similar spectra to those shown in Figure 6. Another example is the famous poly(vinylcarbazole) (PVCz). As reported by Klöpffer et al., the film shows broad emission at around 500 nm.[11] In a glassy solvent, the phosphorescence spectrum of the polymer changed to the shallow trap one, and there is no evidence of impurity emission.

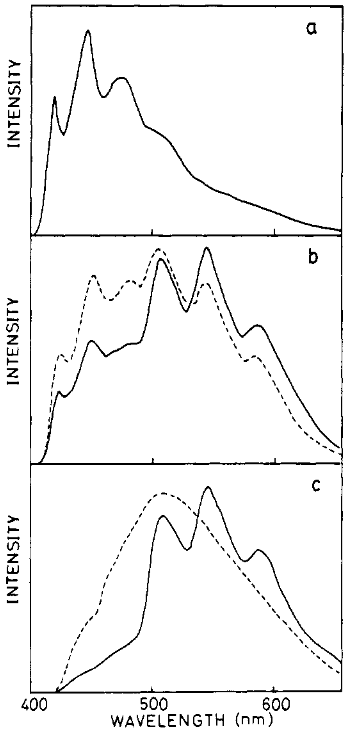

**Figure 7.** Time-resolved phosphorescence spectra of DBN-doped film ([DBN] = 1 × $10^{-3}$ mol $L^{-1}$) at 77 K. Solid lines are total phosphorescence spectra and dashed lines are the spectra observed at the range of 80–400 ms after excitation: (a) 0.49; (b) 0.95; (c) 1.44.

As a summary of the photostationary measurements, the characteristics of each species is briefly noted. The monomer triplet state $^3M^*$ appeared at 413 nm, which acts as a mobile energy. The energy is finally caught by the shallow trap or the excimer if such trap sites exist in the film and energy migration is allowed. The shallow trap $^3T^*$ is a metastable state formed by the interaction of carbazole chromophores. It gives a shifted spectrum with a similar band shape to the monomer emission. Since the stabilization energy is not sufficient, the triplet energy easily returns to the monomer state or changes to the excimer state, by low activation energy. The excimer state, $^3E^*$, is a deep trap and gives broad emission at the long-wavelength range, but the steric geometry is different from that of the singlet excimer. The potential energy probably has a loose curve with respect to the arrangement of chromophores; then the emission spectra gradually shift with the degree of stabilization.

Time-resolved measurements enable us to see the migration behavior of the triplet energy. Figure 7 shows the time-resolved phosphorescence spectra measured by using an appropriate time-gate in the circuit. These samples contain a triplet energy acceptor, DBN, at the concentration of 1 × $10^{-3}$ mol $L^{-1}$. Figure 8 shows the emission properties of DBN in comparison with carbazole emission. Since the energy level of DBN at excited singlet state is higher than that of the carbazole chromophore, carbazole groups can be selectively excited at the wavelength of ca. 330–350 nm. However, the triplet energy, which is seen

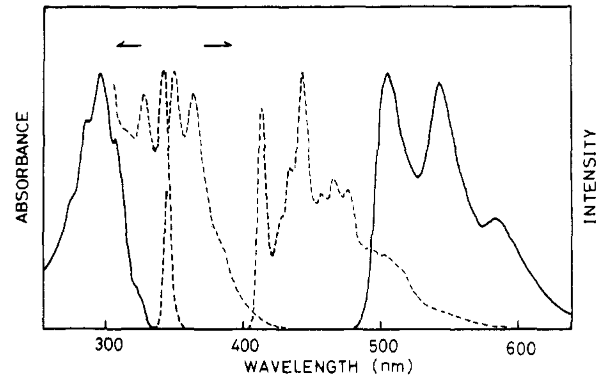

**Figure 8.** Spectroscopic properties of DBN (solid lines) and 9-ethylcarbazole (dashed lines) in MTHF. Phosphorescence spectra were measured in rigid glass at 77 K.

by the 0–0 band of phosphorescence spectrum, is much lower than that of the carbazole chromophore; that is, DBN is an effective energy acceptor for the triplet energy of the carbazole moiety. Furthermore, DBN has a short lifetime in the triplet state (5 ms) and gives fairly strong phosphorescence. These properties are favorable for an indicator of the energy-transfer process, since it emits phosphorescence quickly after the arrival of triplet energy. As shown in Figure 7a, no sensitized emission from DBN is observed for 0.49. In any time range, the spectra for this sample consist of the mobile $^3M^*$. The concentration of carbazole moiety is too low to carry out efficient migration to DBN. The sample 0.95 showed critical behavior in the photostationary measurement and also in the time resolving. The phosphorescence spectra of this sample show clearly the sensitized emission from DBN in the wavelength range 500–600 nm, as shown by the solid line in Figure 7b. The DBN emission is strong early after the excitation but is still detectable later than 80 ms. This means that the mobile $^3M^*$ remains in that system and continues to migrate into DBN. Here it is again noted that even at the time of a few milliseconds after the excitation, the spectrum consists of the shallow trap emission, and the monomer emission $^3M^*$ cannot be detected. Then the mobile state seen in the later time range comes from the shallow trap by the detrapping process. On the other hand, sample 1.44 shows only excimer emission in the time range later than 80 ms (Figure 7c). Since the migration rate in this sample is fairly fast, the triplet energy is completely caught at an excimer site or at a DBN molecule within a few milliseconds. These acceptor sites act as deep traps for the triplet energy. The time-resolved spectra for the samples having higher concentrations are similar to that for 1.4, except for the longer wavelength of the excimer emission.

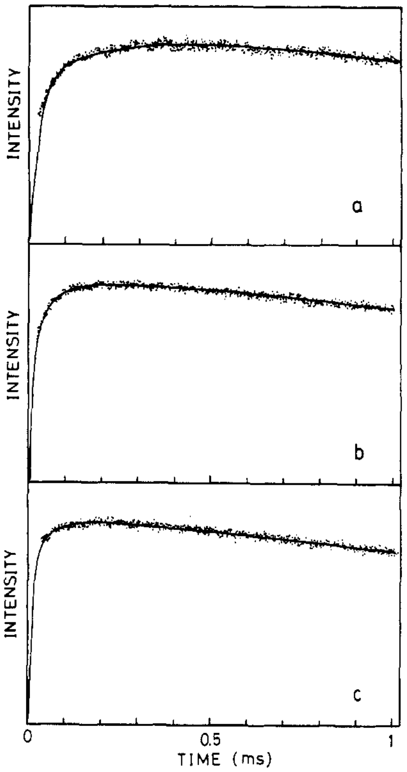

**Figure 9.** Rise and decay curves of phosphorescence from DBN doped in P(CzEMA-*co*-MMA) film at the concentration of 5 × $10^{-3}$ mol/L: (a) 1.91; (b) 2.42; (c) 2.91.

Next, the migration rate of the triplet energy was evaluated by a rise curve analysis for DBN phosphorescence. In general, energy transfer or quenching experiments for triplet state have been analyzed with the Perrin model or Inokuti–Hirayama equation.[32,34] In these models, the decay process is determined by the location of the excited molecule in a matrix. According to these equations, the reaction radius for a given donor–acceptor pair in rigid glasses can be evaluated, but in fluid solution, these processes can be treated with the Stern–Volmer equation, since the interaction radius for triplet reactions is rather small, compared with the length of molecular diffusion. Similarly, if the excitation energy migrates among the chromophores in the polymer matrix, the same treatment as the Stern–Volmer kinetics can be applied for the decay analysis of triplet energy, as a good approximation. Then the kinetic scheme is written by the time-independent rate constants

$$\begin{aligned} {}^3M^* &\rightarrow M_0 && k_M \\ {}^3M^* + E &\rightarrow M_0 + {}^3E^* && k_{EM} \\ {}^3E^* &\rightarrow M_0 && k_E \\ {}^3M^* + A &\rightarrow M_0 + {}^3A^* && k_{AM} \\ {}^3A^* &\rightarrow A && k_A \end{aligned}$$

where $M_0$ and A represent a carbazole moiety and a DBN molecule in the ground state, respectively, and E is an excimer-forming site in the polymer matrix. Here the shallow trap is neglected since it can be treated as a mobile species being in equilibrium with the monomer state. The migration rate constant $k_{mig}$ is given by an average rate for the mobile species in the polymer matrix. Since both E and A are irreversible deep traps for the mobile energy, the rate constant $k_{EM}$ and $k_{AM}$ can be written as

$$k_{EM} = k_{AM} = k_{mig}$$

since both trapping processes are expected to be diffusion-controlled processes between a mobile triplet, $^3M^*$, and a fixed trap site. Under the conditions that the initial concentration of $^3M^*$ takes a constant value and the concentrations for other species are zero at $t = 0$, the decay curve of sensitized emission from DBN is given as follows:

$$\begin{aligned} I_A &= \exp(-k_A t) - \exp[-(k_M + k_{mig}[E] + k_{mig}[A])t] \\ &= \exp(-t/T_1) - \exp(-t/T_2) \end{aligned}$$

where the second term expresses the rise component that will depend on the concentration of the doped DBN molecule. The time constant $T_1$ is known to be 5 ms for DBN, and $T_2$ is approximated by

$$1/T_2 = k_{mig}([E] + [A])$$

since the rate constant $k_M$ is negligibly small compared

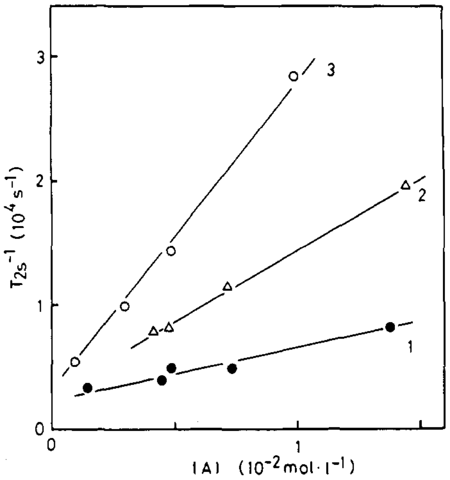

**Figure 10.** Concentration dependence of $T_{2s}$ for different P(CzEMA-*co*-MMA) film: (1) 1.91; (2) 2.42; (3) 2.91.

with the trapping rate. This means that if the rise time is measured as a function of the acceptor concentration, the migration rate constant $k_{mig}$ can be evaluated with the slope of the $1/T_2$ versus [A] plot.

Figure 9 shows the observed rise curves for the samples 1.91, 2.42, and 2.91 with DBN at a concentration of 5 × $10^{-3}$ mol $L^{-1}$. The rise times clearly shorten with the increase of the concentration of carbazole chromophore in spite of the constant value of the DBN concentration. These rise curves cannot be fitted with a single component. To obtain good fit for the observed decay data, it is necessary to use a three-exponential function: one decay time, $T_1$, and two rise times, $T_{2s}$ and $T_{2f}$. Here, the slower and faster rise components are written by $T_{2s}$ and $T_{2f}$, respectively. The faster rise time is less than a few tens microsecond, which is near the limit of time response of the apparatus, since the signals are disturbed during a similar time range by the intense fluorescence and the scattered light of excitation. The $T_{2f}$ seems to be independent of the acceptor concentration. The exact reason for such a fast rise component in this system is not clear at this stage of investigation. It may come from a direct transfer from the excited singlet state to the acceptor DBN; that is, these samples have a good migration efficiency at the singlet state, and the acceptor DBN may act as a weak quencher for the singlet state. Another reason for the fast rise is that a part of the triplet excimer is formed from the singlet trap as described in the previous section, and the excimer emission is observed together with the DBN emission since the wavelengths are located in a similar range.

On the other hand, the slower rate observed as a rise time, $T_{2s}$, clearly depends on the concentration of the acceptor. It is evident that the rise shows a migration process from a mobile carbazole triplet to DBN. In the present work, the $T_{2s}$ is analyzed by the kinetic scheme mentioned above, which predicts that the slope of $1/T_{2s}$ versus [A] gives the migration rate constant $k_{mig}$. Figure 10 shows the plots. The rate constants were found to be 4.1 × $10^5$, 1.2 × $10^6$, and 2.5 × $10^6$ L $mol^{-1}$ $s^{-1}$ for 1.91, 2.42, and 2.91, respectively. We can evaluate the diffusion coefficient $D$ for the triplet energy, by using the following equation:

$$k_{mig} = 4\pi N R_0 D$$

where $N$ is the Avogadro number and $R_0$ is the transfer radius of triplet energy from a carbazole chromophore to DBN. By the quenching experiment for a model system of ethylcarbazole–DBN in rigid glass, the radius $R_0$ was found to be 1.6 nm. Table II shows the $k_{mig}$ and $D$ obtained. These values are much smaller than the diffusion rate of singlet energy in the same polymer matrix: the diffusion coefficient $D$ for the singlet state is larger than that of the triplet by a factor of at least $10^5$. It is worthwhile to note that the lifetime of triplet state is much longer than that of the singlet state. The loss of diffusion length coming from the slow migration rate is sufficiently compensated by the long lifetime.

**Table II**
**Triplet Migration Rate Constants, Triplet Diffusion Coefficients, and Singlet Diffusion Coefficients in P(CzEMA-*co*-MMA) Film**

| Cz concn, mol $L^{-1}$ | $k_{mig}$, L $mol^{-1}$ $s^{-1}$ | $D$(triplet), $cm^2$ $s^{-1}$ | $D$(singlet), $cm^2$ $s^{-1}$ |
|---|---|---|---|
| 1.91 | 4.1 × $10^5$ | 3.4 × $10^{-10}$ | |
| 2.42 | 1.2 × $10^6$ | 9.5 × $10^{-10}$ | 1.1 × $10^{-4}$[c] |
| 2.91 | 2.5 × $10^6$ | 2.1 × $10^{-9}$ | |
| PVCz (glass)[a] | 3.6 × $10^3$ | 3.2 × $10^{-12}$ | |
| PVCz (glass)[b] | 1.2 × $10^4$ | 1.1 × $10^{-11}$ | |

[a] M. Yokoyama et al.[27] [b] A. Itaya et al.[28] [c] S. Ohomori et al., unpublished results.

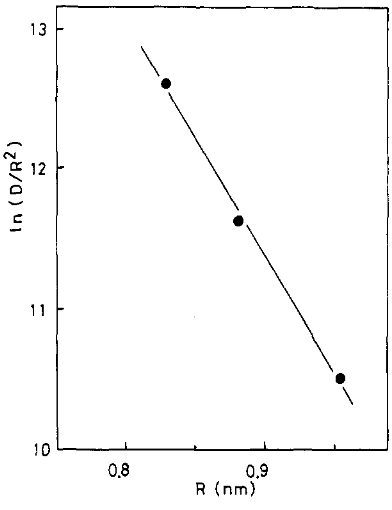

**Figure 11.** Plots of ln ($D/R^2$) as a function of mean distance between carbazole chromophores.

Earlier works for the triplet energy migration along a polymer chain dissolved in rigid glass matrices showed the diffusion coefficient to be on the order of $10^{-12}$–$10^{-13}$ $cm^2$ $s^{-1}$.[27,28] The data obtained in rigid glass with those obtained in polymer film show that the triplet energy in polymer matrices has a migration rate much faster than that in glassy solution. For efficient energy migration of triplet state, a high concentration of the chromophore in polymer matrices is required, since the critical distance of each hopping must be short.

The diffusion coefficient markedly depends on the concentration of chromophore, that is, the average distance $R$ between chromophores. Theoretical prediction for this point is given as follows:

$$D = (1/6)R^2 k_{MM}$$

where $k_{MM}$ is the migration rate constant between carbazole chromophore per unit time. The predominant migration mechanism seems to be Dexter-type transfer, i.e., electron-exchange mechanism.[35] This means that the rate, $k_{MM}$, can be approximated by an exponential function of $R$. Thus, the following relation is given:

$$D/R^2 = K \exp(-2R/L)$$

where $K$ is a constant and $L$ is a value referred to as the Bohr radius. Figure 11 shows the plot of ln ($D/R^2$) versus

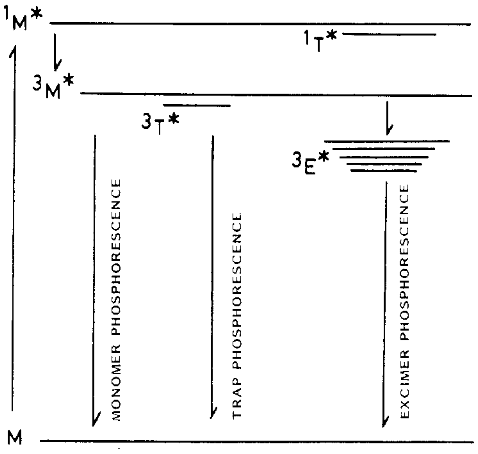

**Figure 12.** Energy level diagram for P(CzEMA-*co*-MMA) film.

*R*. The data give a straight line with the value $L = 0.12$ nm. This result indicates that the hopping of triplet energy is carried out by the electron-exchange mechanism. The polymer system having highly concentrated and dispersed chromophores makes it possible to quantitatively discuss the migration process. Unfortunately, the samples whose concentrations are lower than 1.44 are inadequate for these treatments; the migration length in these samples is not sufficient and one-step transfer to DBN becomes predominant in the range of the acceptor concentration necessary to give observable sensitized emission.

In summary, a schematic drawing of the excited states is shown in Figure 12. The singlet excited state $^1M^*$ in this polymer matrix has no excimers or other deep traps, but there is a shallow trap having a weak interaction energy between chromophores. This trap seems to be correlated with the triplet excimer. The triplet state, however, is considerably complex compared with the singlet state. We have to consider at least three species: monomer, shallow trap, and excimer. Furthermore the energy levels of the excimer become gradually low with the increase in the degree of stabilization. This means that the triplet excimer has fairly continuous energy levels corresponding to the geometrical arrangement. These excimer sites will be formed in the matrix at low probabilities, but the energy migration process efficiently sensitizes the excimer emission. The spectroscopic behavior drastically changes depending on whether the concentrations are above or below a critical concentration: the critical concentration is 0.9 mol $L^{-1}$, at which the migration process begins to occur in the matrix. This value corresponds to the average distance of 1.2 nm. We believe that the diffusion length of the triplet energy is longer than that of singlet energy, if there is neither excimer nor trap site in polymers. Such polymers will give efficient transport matrices for triplet energy, since the lifetime of the excited state is much longer than that of the singlet state.

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**Registry No.** (CzEMA)(MMA) (copolymer), 82729-08-6; DBN, 83-53-4.

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