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ment and surface, (2) the fraction of polymer segments directly attached to the surface, (3) the concentration of displacer, and (4) the molecular sizes of the preadsorbed polymer and displacer. We can ignore factor 2 because of the constant total fraction of adsorbed SM copolymer segments in the entire range studied, as described in the previous paper.[8] Also, we need not take into account the molecular size of a preadsorbed polymer chain since we use only one molecular weight for PS.

The displacement of PS by PMMA[1,2] as well as by PEO[4] strongly depended on the size of a displacer polymer chain. Namely, a large chain of a displacer molecule could completely replace the preadsorbed chain at the lower concentration in comparison with a small displacer polymer. In this experiment, however, the result of displacement adsorption shows the reverse tendency; i.e., the smallest SM75 copolymer chain behaves as the best displacer.

Of course, factor 1, corresponding to the difference in surface–polymer segment interaction strength between methyl methacrylate–silanol and styrene–silanol, should be dominant for the displacement adsorption. Since the concentration of the SM copolymer giving the constant remaining amount of PS molecules preadsorbed agrees with that giving the plateau adsorbed amount of SM copolymer for individual adsorption, factor 3 is also attributed to the displacement adsorption of PS by the SM copolymer.

## Conclusions

Competitive and displacement adsorption of PS by SM copolymers onto the silica surface exhibits some markedly different behaviors from that of different chemical homopolymers. SM copolymers preferentially adsorb and replace PS. A SM copolymer higher in styrene content shows a better preferential adsorption and behaves as a better displacer, regardless of the smaller chain. The preferential adsorption behavior of SM copolymer over PS chains is well correlated with the magnitude of the plateau adsorbed amounts in the adsorption isotherms for the individual adsorption of the SM copolymers.

**Registry No.** PS, 9003-53-6; PMMA, 9011-14-7; SM (copolymer), 25034-86-0; Aerosil 130, 7631-86-9.

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# Trap-Site Formation and Trap-Controlled Triplet Energy Migration in Phenanthrene Copolymer Films

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

*Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan.*
*Received August 24, 1988;*
*Revised Manuscript Received November 8, 1988*

ABSTRACT: Triplet spectroscopy and energy migration among phenanthrene chromophores in poly[(9-phenanthrylmethyl methacrylate)-*co*-(methyl methacrylate)] film were investigated. The copolymerization of a chromophoric monomer with a photophysically inert monomer provides a polymer system having high chromophore concentrations in a uniform distribution. At temperatures below 150 K, the phenanthryl moieties did not form a deep trap such as a triplet excimer, but they formed a shallow trap with diverse energy levels which were reflected in the phosphorescence spectra as red shifts which depended on the concentration of the chromophore and on the film temperature. The energy migration process was observed by the rise of sensitized emission from a triplet energy acceptor, 1,4-dibromonaphthalene, after pulsed excitation of a phenanthrene chromophore. The average rise time showed a marked temperature dependence. This indicates that the migration occurs with iterative trapping–detrapping processes at the trap sites and is enhanced by thermal activation. This system gives a typical example of trap-controlled photophysics of the triplet state.

## Introduction

Electronically excited states of polymers with pendant aromatic chromophores have been widely investigated.[1] Most of the work in this field has been carried out on the singlet state, because fluorescence is usually intense and easily detectable by steady-state and time-resolved spectroscopic techniques. However, the triplet state has not been studied as much as the singlet state, owing to some experimental difficulties, although it is important from the fundamental as well as application standpoints. A large portion of the excitation energy, often exceeding 50%, dissipates to the ground state via the triplet state. In connection with photofunctional materials, the polymer solid is an important system and its photophysical processes should be clarified in detail. Many photochemical reactions involving triplet states have been utilized for so-called photosensitive polymers, and "triplet sensitizers" are often used. However, in many cases the primary processes have not been fully understood, because of experimental difficulties such as weak emission due to efficient nonradiative deactivation.

In condensed phases such as polymer matrices, excited chromophores are often involved in various interchromophoric processes, including energy migration and excimer

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formation. In the triplet state, the energy migration process occurs by a short-range interaction involving a coupling of the molecular orbital of each chromophore.[2] This means that effective energy transport arises only in concentrated matrices. As a result many experiments on triplet energy transfer have been conducted in a polymer matrix doped highly with a low molecular weight chromophore.[3,4] Such high concentrations can cause aggregation or crystallization of chromophores, which complicates the interpretation of energy transfer data.[5] In a previous paper, we reported the triplet-state behavior of the carbazole chromophore in copolymer films.[6] Random copolymers were prepared from the chromophoric monomer and a spectroscopically inert monomer and gave a polymer sample with highly concentrated chromophores in a statistical distribution. This method of copolymerization has been widely utilized and provides an important experimental variable in the study of polymer photophysics.[7-13]

Phenanthrene is another chromophore whose intrinsic photophysical properties are well-known.[14,15] Besides its unimolecular properties, some interesting data relating to its bimolecular interaction have been reported. In rigid dimers the phenanthrene chromophores showed only weak interaction, even with a face-to-face arrangement of the aromatic rings.[16-18] However, Aikawa et al. reported triplet excimer formation in fluid solutions of phenanthrene.[19] Furthermore, phenanthryl groups linked by a flexible methylene chain showed a broad absorption band in laser photolysis.[20,21] These facts suggest that the phenanthrene chromophore can form an intramolecular triplet excimer in solution. The existence of triplet excimers has been the subject of lively discussion.[22-26]

In the current study, the copolymerization method was applied to the phenanthrene chromophore, and the triplet-state behavior and energy-transport mechanism in the polymer solid were investigated.

## Experimental Section

**Materials.** 9-Phenanthrylmethanol was synthesized by reduction of phenanthrene-9-carboxaldehyde (Aldrich Chemical Co.) with sodium borohydride in ethanol. The product was recrystallized from a mixed solvent of hexane and acetone: mp = 152 °C. 9-Phenanthrylmethyl methacrylate (PhMMA) was obtained by esterification of methacryloyl chloride (Tokyo Kasei Kogyo Co., Ltd.) and 9-phenanthrylmethanol. The monomer was purified by several recrystallizations from methanol: mp = 82 °C; IR (KBr) 1720, 1640 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 1.97 (s, 3 H), 5.57 (s, 1 H), 5.70 (s, 2 H), 6.15 (s, 1 H), 7.5–7.9 (m, 6 H), 8.0–8.2 (m, 1 H), 8.5–8.9 (m, 2 H). The data agree fairly with those of ref 7a. Methyl methacrylate (MMA) (Wako Pure Chemical Industries, Ltd.) was purified by distillation under reduced pressure before use. These monomers, PhMMA and MMA, were dissolved in benzene with small amounts of azobis(isobutyronitrile) and polymerized at 60 °C. Obtained copolymers, P(PhMMA-*co*-MMA), were purified by repeated reprecipitation from benzene and methanol and dried in vacuo. 1,4-Dibromonaphthalene (DBN) (Kantou Chemical Industry Co., Ltd.) was used as a triplet energy acceptor and was recrystallized from methanol. 2-Methyltetrahydrofuran (MTHF) was purified by vacuum distillation after preliminary distillation from sodium metal.

**Sample Preparation.** The copolymer was dissolved in dichloromethane or benzene (spectrophotometric grade, Dojindo Laboratories) in a quartz cell and the solution was deaerated by several freeze–thaw cycles to a final pressure of less than 5 × 10$^{-6}$ Torr. Copolymer films were cast in a quartz cell by gradual evaporation of the solvent under reduced pressure. After the film was kept in vacuo for a day, the cell was sealed. DBN doped film was prepared in the same manner by addition of prescribed amounts of DBN to the casting solution.

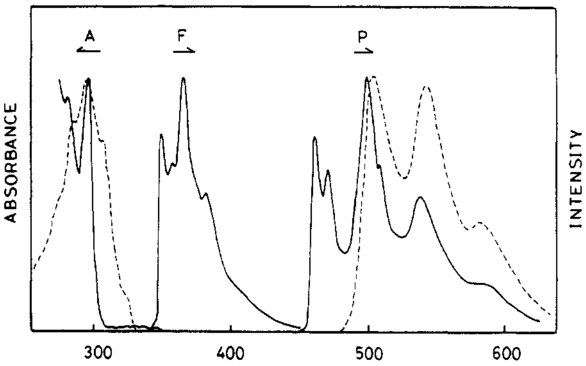

**Figure 1.** Absorption (A), fluorescence (F), and phosphorescence (P) spectra of phenanthrene chromophore (—) and DBN (- - -). A and F were measured in MTHF at 298 K, and P was measured in MTHF glass at 77 K. The excitation wavelengths were 330 nm for phenanthrene and 295 nm for DBN chromophores.

**Table I**
**Composition, Average Distance between Phenanthrene Chromophores, and $M_w$ for P(PhMMA-*co*-MMA) Film**

| Ph concn, mol L$^{-1}$ | Ph content, mol % | $D$,[a] nm | $M_w$,[b] 10$^3$ |
|---|---|---|---|
| 0.09 | 0.78 | 2.63 | 130 |
| 0.42 | 3.76 | 1.58 | 150 |
| 0.85 | 8.18 | 1.25 | 120 |
| 1.27 | 13.1 | 1.09 | 130 |
| 1.67 | 18.6 | 1.00 | 120 |
| 2.05 | 24.7 | 0.93 | 150 |
| 4.31 | 100.0 | 0.73 | 190 |

[a] Calculated by $D = n^{-(1/3)}$, where $n$ is the average number of Ph per unit volume. [b] Determined by GPC calibrated with polystyrene standards.

**Measurements.** Steady-state phosphorescence spectra were obtained with a Model 850 Hitachi spectrofluorophotometer fitted with a phosphorescence attachment. Time-resolved phosphorescence spectra and decay curves were measured with a phosphorimeter assembled in our laboratory. A Xe flash lamp and a nitrogen laser were used as the pulsed excitation light source for the measurements in millisecond and in microsecond time regions, respectively. To avoid damage to the detectors by the intense excitation light, a mechanical shutter and a gated photomultiplier (Hamamatsu, R1333 and C1392) were used. Details of the system have been described elsewhere.[6] The sample cell was immersed in a quartz Dewar. The temperature was regulated by liquid nitrogen or precooled nitrogen gas.

## Results and Discussion

**Trap-Site Formation.** Figure 1 shows the spectroscopic properties of P(PhMMA-*co*-MMA) and DBN: the composition of the phenanthrene unit in the copolymer is only 0.0078. The absorption band of the S$_0$–S$_1$ transition of the phenanthrene chromophore appeared in the wavelength range of 310–350 nm, but this band has a very weak extinction coefficient because of the forbidden $^1$L$_b$ band. This results in a long singlet lifetime (ca. 40 ns) and a small Förster radius for singlet energy migration between phenanthrene chromophores ($R_0$ = 0.87 nm).[27] The quantum efficiency of the triplet formation is reported to be high: ca. 0.8.[28] These facts indicate that much of the excitation energy dissipates to the ground state via the triplet state. On the other hand, the lowest excited singlet of DBN is higher than that of phenanthrene, but the energy of the lowest triplet of DBN is lower than that of phenanthrene. Hence, DBN acts as an effective energy acceptor for the triplet state of the phenanthrene chromophore. Owing to the heavy bromine atoms, DBN gives intense and short-lived phosphorescence. These properties make it quite suitable as a probe of the energy-transfer process.

Table I shows the concentration of phenanthrene

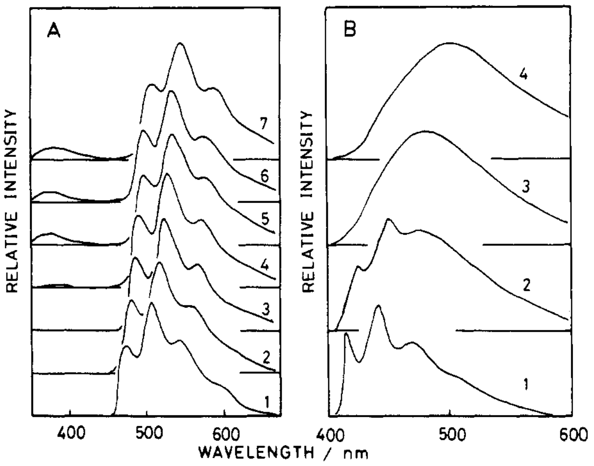

**Figure 2.** (A) Phosphorescence spectra of a P(PhMMA-*co*-MMA) film at 77 K: (1) 0.09, (2) 0.42, (3) 0.85, (4) 1.27, (5) 1.67, (6) 2.05, and (7) 4.31. (B) Phosphorescence spectra of a P(CzEMA-*co*-MMA) film: (1) 0.14, (2) 0.95, (3) 1.44, and (4) 2.42. The samples were excited at 330 nm.

chromophores in each sample film. Concentrations are given in units of moles per liter and were calculated from the film density and the ratio of PhMMA to MMA units in the copolymer. Samples are hereafter referred to by the values of the chromophore concentration in moles per liter. The average separations between chromophores ($D$) and the molecular weights ($M_w$) of the copolymers are also listed in Table I.

Figure 2 shows the phosphorescence spectra of the copolymer films at 77 K. As shown in Figure 1, the low phenanthrene content sample in the MTHF glass gave a phosphorescence spectrum corresponding to the isolated chromophores having no interaction with the neighboring chromophores. The 0–0 band of the triplet state appeared at 461 nm. However, the spectrum for the film of the same sample 0.09 was broadened and shifted slightly to the red. This means that there may be a weak interaction between phenanthrene chromophores even at concentrations as low as 0.09 mol $L^{-1}$. While the maximum wavelength of this band is red-shifted, the leading edge of the 0–0 band is seen at the same position as that in the MTHF glass. The broad band observed in the film probably consists of the overlapping emission from isolated and weakly interacting chromophores. We will refer to the isolated species as the monomer triplet state ($^3M^*$) of phenanthrene. The spectra gradually shifted to longer wavelengths with increasing chromophore concentration, but the band shape remained constant even in the homopolymer of PhMMA. Such shifted phosphorescence spectra have often been seen in glassy solutions of vinyl aromatic polymers.[29-32] The excited triplet state is stabilized by interactions between chromophores, but the interaction energy is not sufficient to change the spectrum to broad excimeric emission. We refer to this stabilized state as the trap ($^3T^*$) and distinguish it from the triplet excimer ($^3E^*$).

This behavior is considerably different from that of the copolymers containing a carbazolyl moiety. Previously, we reported triplet state properties of carbazole chromophores in poly[(9-carbazolylethyl methacrylate)-*co*-(methyl methacrylate)], P(CzEMA-*co*-MMA), film.[6] The concentration dependence of phosphorescence spectra for this copolymer film is shown for comparison in the right-hand side of Figure 2. In this figure, three distinct species, $^3M^*$, $^3T^*$, and $^3E^*$, are noticed, depending on the chromophore concentration. The triplet excimer is clearly observed at concentrations higher than 1 mol $L^{-1}$ as a broad long-wavelength emission.

Table II
Spectral Shift and Lifetime of Phosphorescence at 77 K

| sample, mol $L^{-1}$ | wavelength, nm | $\Delta E$, kJ/mol | lifetime, s |
|---|---|---|---|
| 0.09[a] | 465 | | 3.8 |
| 0.09 | 471 | 3.3 | 3.0 |
| 0.42 | 479 | 7.6 | 2.5 |
| 0.85 | 483 | 9.7 | 2.1 |
| 1.27 | 488 | 12.2 | 1.8 |
| 1.67 | 494 | 15.2 | 1.7 |
| 2.05 | 497 | 16.6 | 1.5 |
| 4.31 | 505 | 20.5 | 0.76[b] |
| DBN | 506 | 20.9 | 0.0038 |

[a] In MTHF rigid glass. [b] Shorter value in two-exponential curve fitting.

A stabilization energy $\Delta E$ can be determined from the spectral shift of phosphorescence spectra. Table II shows the wavelengths at the center of the first vibrational band. Here, the first bands for the film samples were so broad that they did not split into two peaks as seen in the MTHF glass. The stabilization energy of each film was calculated with reference to 465 nm which is the center of the doublet observed in the rigid glass (Table II). With increasing chromophore concentration, the values increase monotonically and the phosphorescence lifetime decreases. The large stabilization energy of the sample 4.31, PhMMA homopolymer, indicates that the stabilized site acts as a fairly deep trap for the mobile triplet state, $^3M^*$. In fact, the energy trapping process from phenanthrene chromophore to DBN is an exothermic reaction of 20.9 kJ mol$^{-1}$, as shown in Table II. The reaction radius for the transfer was found to be 1.5 nm by using a conventional Perrin plot. This radius is in agreement with the values reported for other exothermic donor–acceptor pairs.[33] It is quite natural for the triplet energy to be caught by the trap having levels nearly equal to that of DBN, at an early stage after the excitation. However, the stabilization energy depends on the concentration of chromophores. For sample films 1.67 and 2.05, the stabilization energies are insufficient to localize the excitation energy at the trap site during the long lifetime; the mobile behavior was clearly shown by the time-resolved spectra shown in Figure 3.

Figure 3A shows the time-resolved phosphorescence spectra for sample 2.05, doped with DBN at a concentration of $5 \times 10^{-3}$ mol $L^{-1}$. DBN emitted a strong sensitized emission immediately after excitation. This emission was still observed at a time later than 80 ms. This point is quite different from the behavior for a P(CzEMA-*co*-MMA) film. For comparison, Figure 3B shows the spectra of a P(CzEMA-*co*-MMA) film in which the carbazole chromophore concentration is 1.91 mol $L^{-1}$. In the later time range, the spectrum consisted of excimer emission, and no sensitized DBN emission was detected. This indicates that the carbazole triplet excitation is trapped at the excimer site immediately after excitation and does not return to the mobile $^3M^*$ state. In contrast to this carbazole polymer, the triplet energy of phenanthrene chromophore migrates for a long period, since there is no excimer site to act as a deep trap. Here it is noteworthy that the film without DBN gave a shifted spectrum of $^3T^*$ even at less than 10 ms, and that the sensitized emission observed at a later time was due to the mobile $^3M^*$ reproduced by detrapping of $^3T^*$.

The phenanthrene and carbazole polymers show two typical types of triplet behavior in condensed matrices corresponding to a trap-controlled system and an excimer-controlled system. To obtain further insight into interactions in the triplet state, experimental data on various

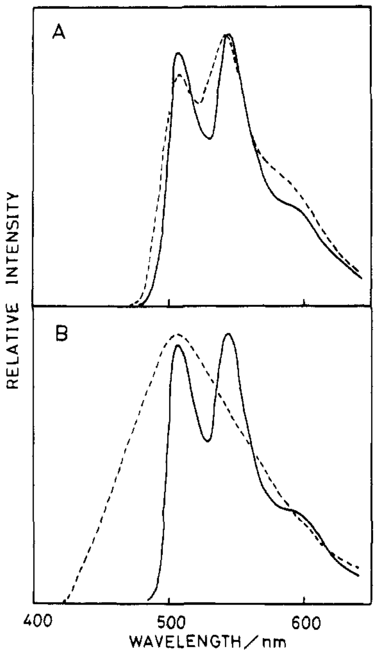

**Figure 3.** Time-resolved phosphorescence spectra of DBN doped film at 77 K ([DBN] = 5 × $10^{-3}$ mol $L^{-1}$): (A) P(PhMMA-*co*-MMA) 2.05 and (B) P(CzEMA-*co*-MMA) 1.91 film. Solid lines are the spectra observed between 1 and 11 ms after pulse excitation ($\lambda_{ex}$ = 320–350 nm) and dashed lines are those observed between 80 and 400 ms.

kinds of chromophores should be accumulated. Detailed studies on cyclophane compounds give important information on the triplet state interaction. As for the phenanthrene chromophore, Schweitzer et al. studied the fluorescence and phosphorescence spectra of [2.2](2,7)-phenanthrenophane in the PMMA matrix;[16] while the fluorescence spectra show typical excimer emission, the phosphorescence shows a red-shifted spectrum with the same vibrational structure as a monomeric phenanthrene compound. This indicates that the triplet state interaction between phenanthrene chromophores is weak even with face-to-face arrangement of the aromatic planes. Chandross et al. also reported the emission spectra for a sandwich pair of phenanthrene prepared by photolytic dissociation of the dimer of 9-(hydroxymethyl)phenanthrene.[17,18] They observed only weak interaction in both singlet and triplet states. These facts as well as our results indicate that the triplet excimer formation is not a major process in our phenanthrene copolymer films.

Studies of the effects of temperature on the phosphorescence spectra afford useful information on triplet-state behavior in a polymer matrix. Thermal deactivation of the triplet state has been studied for various chromophores dispersed in polymer films, and the deactivation rates appear to change discretely at transition temperatures characteristic of the matrix polymer.[34,35] Besides affecting this intramolecular deactivation process, changes in temperature may also change the extent of interaction between chromophores, since the rise in temperature accelerates conformational rearrangements taking place during the excited-state lifetime. In fact, it was shown for the polymers containing carbazole chromophore that the maxima of excimer emission gradually shifts to the longer wavelength range with increasing temperature.[6] Burkhart et al. also reported a marked temperature dependence of the phosphorescence spectra of poly(vinylcarbazole) film.[36] In the present phenanthrene polymers, the results at 77 K indicated that the interaction between chromophores is much weaker than the carbazole chromophore. However, further stabilization occurs at temperatures higher than 77 K, as illustrated in Figure 4.

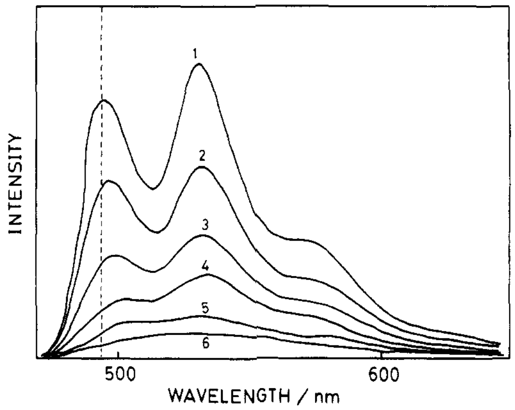

**Figure 4.** Temperature dependence of phosphorescence spectra of a P(PhMMA-*co*-MMA) 1.67 film: (1) 93 K, (2) 103 K, (3) 113 K, (4) 123 K, (5) 133 K, and (6) 143 K; $\lambda_{ex}$ = 330 nm. The broken line shows 494 nm which corresponds to the 0–0 band of phosphorescence at 77 K.

Figure 4 shows the phosphorescence spectra of sample 1.67 at various temperatures. With increasing temperature, the total intensity decreased rapidly, while the vibrational bands were preserved. Each band gradually shifted to lower energy. Above 150 K, the spectra were broadened considerably and their maxima shifted to longer wavelengths than that of the trap-site emission at 77 K. Similar behavior was observed for sample 2.05. These facts may indicate that the thermal stabilization of the trap site converts it to the triplet excimer. However, spectroscopic measurements in concentrated systems often give erroneous results because of impurity emission.[24] As the phosphorescence intensity at high temperature is very weak, careful examination is required before we can conclude that the broad emission comes from the triplet excimer of phenanthrene. At the present stage, it can only be said that the lowest triplet level shifts to the lower energy. This result can be explained by the following two processes: (1) thermal motion of excited chromophore at a shallow trap alters it to a deeper trap site; (2) iterative trapping–detrapping at shallow traps results in a preferential loss of high-energy emission from these trap sites.

**Triplet Energy Migration.** Spectroscopic measurements clearly indicated that this polymer forms a number of trap sites having diverse levels of triplet energy. Lower levels among the trap sites preferentially appear in the phosphorescence spectra as a result of the iterative hopping of triplet energy between the chromophores. The energy transport process in the triplet manifold is also governed by this trap-site formation. The detrapping rate from $^3T^*$ seems to be one of the factors determining the overall rate of migration. This was well confirmed by studies of the temperature dependence of the migration rate. We were able to see the migration rate by monitoring the rise time of sensitized emission of DBN following pulsed excitation.

Figure 5 shows the rise and decay curves of DBN phosphorescence at various temperatures. Since the optical arrangement was fixed during the measurements, the relative intensities could be compared. Integration of each curve over time $t$ gives the total intensity of sensitized emission. The total DBN emission intensity and the rate with which this emission grows in increase with increasing temperature. This indicates that the rate of energy migration is accelerated by thermal activation. To quantitatively discuss the migration process, the mean rise time of DBN emission was evaluated from the curves shown in Figure 5. Unfortunately, the rising edges could not be

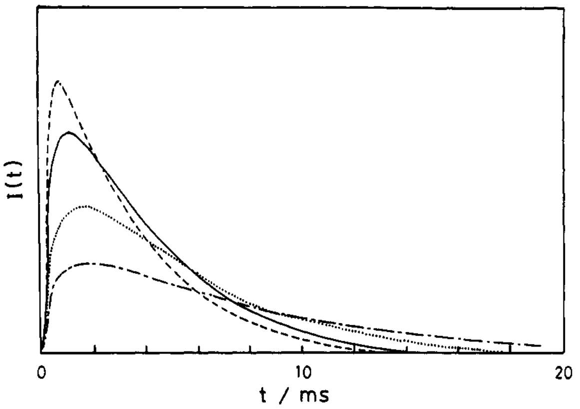

**Figure 5.** Rise and decay curves of sensitized DBN phosphorescence in a P(PhMMA-*co*-MMA) 1.67 film ([DBN] = 8 × $10^{-3}$ mol $L^{-1}$), after pulsed excitation by an $N_2$ laser (337 nm): (-·-) 103 K, (···) 123 K, (—) 143 K, and (---) 163 K.

simulated by a simple exponential function. In polymer systems, emission decays are often not single exponential but are fitted by multiple exponentials or nonexponential functions. Recently, several workers proposed decay functions appropriate for emission from chromophores in polymer matrices.[37-41] However, in our system, the different energy levels within $^3T^*$ give rise to different detrapping rates depending on the trap depth, and this results in the multiple rise times of sensitized emission. The present study intends to clarify the determinant of the energy migration rate. Then, to obtain the average rate of this process, the rise curve was approximated by a sum of two exponential functions and the decay was represented by an exponential function, as follows:

$$I(t) \propto \exp(-t/\tau_A) - [F \exp(-t/\tau_1) + (1 - F) \exp(-t/\tau_2)] \quad (1)$$

where $\tau_A$ is a phosphorescence lifetime of DBN, which was independently measured at each temperature by direct excitation of DBN in a PMMA matrix. The lifetime $\tau_A$ is independent of the copolymer composition at temperatures below 170 K. The observed rise and decay curves were analyzed by an iterative least-squares method. There are three adjustable parameters in eq 1: $\tau_1$, $\tau_2$, and $F$. However, we had to add one more parameter, $C$, to eq 1 in order to obtain a good fit:

$$I(t) \propto (1 + C) \exp(-t/\tau_A) - [F \exp(-t/\tau_1) + (1 - F) \exp(-t/\tau_2)] \quad (2)$$

Parameter $C$ means that a portion of DBN is excited immediately after the excitation; this is probably due to the direct excitation of DBN or one-step transfer from phenanthrene groups located by chance within the active sphere of DBN. An example of the curve fitting is shown in Figure 6. Here, the diverse rates of the migration process are represented by two values, $\tau_1^{-1}$ and $\tau_2^{-1}$. We define the average rate of energy migration as the following weight average:

$$R_{av} = F\tau_1^{-1} + (1 - F)\tau_2^{-1} \quad (3)$$

If the rate obtained from this analysis represents the one for the capturing process of triplet energy by DBN, the rate should give a linear relationship with the acceptor concentration, [DBN]. Figure 7 shows the plots of $R_{av}$ versus [DBN] for sample 1.67 at 153 and 77 K. In the ordinary treatment, the slope of this plot gives an apparent rate constant of the migration.[6] However, we could not obtain the true rate constant in this system, since the rate was not constant and instead varied with the observed time range. Tentatively, the apparent rate constant was calculated from the slope and the values were 4.8 × $10^5$ L $mol^{-1}$ $s^{-1}$ at 153 K and 4.2 × $10^4$ L $mol^{-1}$ $s^{-1}$ at 77 K. The value at 77 K is an order of magnitude smaller than that for P(CzEMA-*co*-MMA) 1.91 film.[6] This probably reflects the trap-controlled mechanism for triplet migration in a P(PhMMA-*co*-MMA) film.

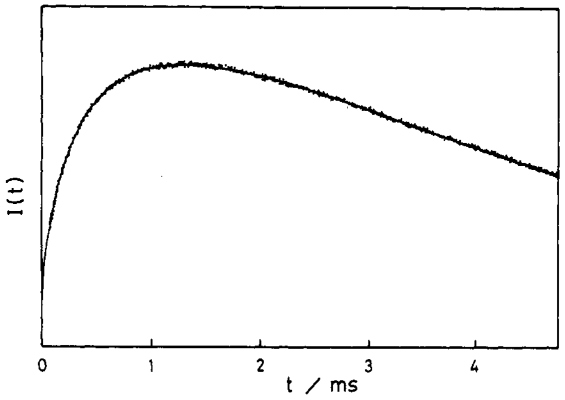

**Figure 6.** Rise and decay curve of sensitized DBN phosphorescence at 133 K. The signals 0–30 μs after pulsed excitation (337 nm) were cut off by a gate circuit to avoid intense scattered light and the fluorescence. The solid line was calculated with the best-fit parameters in eq 2: $\tau_1$ = 0.24 ms, $\tau_2$ = 1.73 ms, $F$ = 0.242, and $C$ = 0.099.

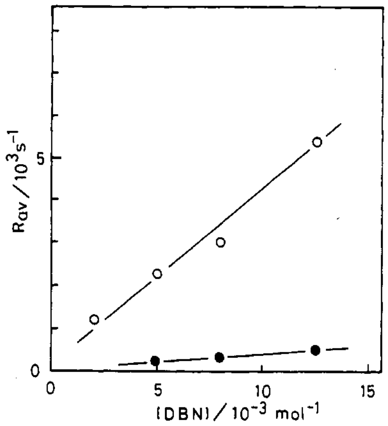

**Figure 7.** Concentration dependence of $R_{av}$ for sample 1.67 of a P(PhMMA-*co*-MMA) film at temperatures (○) 153 K and (●) 77 K.

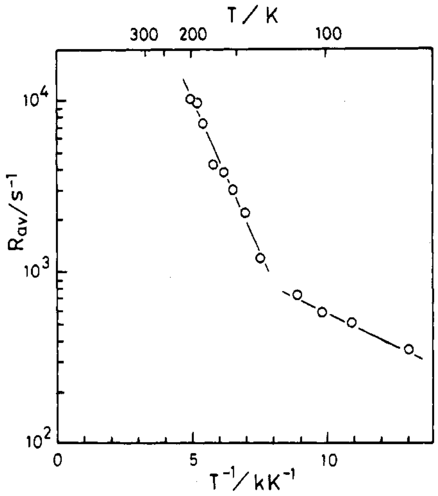

**Figure 8.** Plot of $R_{av}$ against reciprocal temperature for sample 1.67 of a P(PhMMA-*co*-MMA) film ([DBN] = 8 × $10^{-3}$ mol $L^{-1}$).

Figure 8 shows a plot of $R_{av}$ against reciprocal temperature. The migration rate $R_{av}$ rapidly increased with the

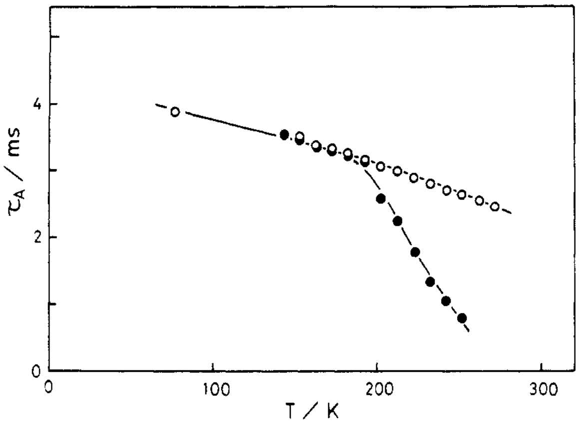

**Figure 9.** Temperature dependence of the lifetime of DBN phosphorescence: (○) for a PMMA film and (●) for sample 1.67 of a P(PhMMA-*co*-MMA) film.

rise of temperature. From Figure 8, the activation energy $E_{\mathrm{mig}}$ for triplet energy migration was estimated to be 1.5 kJ mol$^{-1}$ at a temperature below 120 K and 7.1 kJ mol$^{-1}$ above 120 K. The existence of similar transition temperatures in phosphorescence studies has been reported by Guillet et al.[34,35,39] They measured the temperature dependence of the phosphorescence intensity in several polymer matrices similar to a P(PhMMA-*co*-MMA) film and showed that phosphorescent chromophores are useful probes, indicative of the primary and secondary transition temperatures of the matrix. This behavior may correlate with side-chain motions in PMMA, but the precise origin of the break in the curve in Figure 8 is not clear at present. The result indicates that the energy migration process in this polymer is a thermally activated process, which is characteristic of trap-controlled energy transport. The amorphous polymer P(PhMMA-*co*-MMA) did not exhibit a clear relationship between the activation energy $E_{\mathrm{mig}}$ and the trap depth $\Delta E$ evaluated from the spectral shift (see Table II); the values of $E_{\mathrm{mig}}$ are smaller than $\Delta E$. It should be noted again that the phosphorescence spectra give the lowest level of triplet energy among various trap sites as a result of the iterative migration. On the other hand, the activation energy at a given temperature range is determined by the average depth of trap sites which are able to revert to the monomer state $^3$M* by thermal detrapping and to participate once more in the migration process.

Further increase in the temperature induced another situation for the energy-transfer process as shown in Figure 9. Above 170 K, the lifetime of the sensitized emission of DBN decreased rapidly, while the control experiment for the PMMA film doped with a small amount of DBN showed no such drastic change with the rise in temperature. This effect is similar to the thermal deactivation of DBN triplet and indicates the significant effect of thermal energy on the energy-transfer process. The energy level of DBN as the energy acceptor is sufficiently low only at low temperatures. If thermal activation energy gives a chance to overcome the energy gap between the triplet levels of phenanthrene and DBN moieties, a back-energy-transfer process from DBN to phenanthryl moiety becomes feasible; it is similar to the detrapping from $^3$T* to $^3$M*. When the film temperature is sufficiently high, the energy is captured and released by DBN repeatedly. It should be remembered that the temperature dependence of phosphorescence spectra shows a gradual red shift of $^3$T* with the rise in temperature, because of the motion of chromophores. If the lifetime of the mobile $^3$M* state becomes short compared with the intrinsic lifetime of DBN, the triplet state of DBN seems to be quenched via the back-energy-transfer process. Under these conditions, the thermodynamic equilibrium is attained between the energy levels of the phenanthryl and DBN moieties. Finally, it is worth noting that it is the long lifetime of the phenanthrene triplet state which is responsible for these remarkable thermal effects on energy migration and transfer processes.

## Summary

Triplet-state properties of phenanthrene chromophore in polymer films are dominated by trap-site formation involving an excited triplet and neighboring ground-state chromophores. The interaction energy was weak at low temperatures and depended on the concentration of the chromophore and the temperature of the matrix. In contrast to the carbazole moiety, the phenanthrene chromophore forms no deep trap such as a triplet excimer, and the triplet energy can migrate for a long period through successive trapping–detrapping processes at the trap sites. The migration process was susceptible to thermal activation due to the long life of the triplet state. This system represents a typical example of trap-controlled triplet photophysics in an amorphous polymer.

**Acknowledgment.** This work was supported by The Kawakami Memorial Foundation and a Grant-in-Aid for Scientific Research (No. 62750814) from the Ministry of Education, Science and Culture of Japan.

**Registry No.** (PhMMA)(MMA) (copolymer), 81565-44-8; DBN, 83-53-4.

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# The Effect of Phase-Transfer Catalysts on Polysilane Formation

**S. Gauthier and D. J. Worsfold***

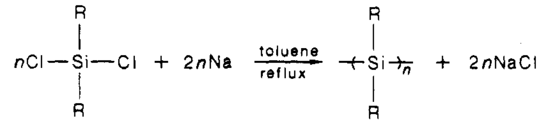
*National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R9.*

*Received August 22, 1988; Revised Manuscript Received November 2, 1988*

ABSTRACT: Polysilanes are most often prepared by a Wurtz-type coupling of organodichlorosilanes with sodium metal in refluxing toluene. The addition of a catalytic amount of crown ether to the reaction mixture was found to increase the rate of disappearance of the monomer with increasing crown ether concentration, suggesting that anionic species are involved in the polymerization mechanism. Higher yields of polymer relative to cyclic material were obtained, and the polymer displays a monomodal distribution. Better reproducibility of the yields and molecular weight of the polymers can be achieved. The presence of cryptand was found to have similar effects although some degradation of the polymer upon continued refluxing of the reaction mixture was observed. Degradation experiments on poly(*n*-hexylmethylsilane) with sodium in refluxing toluene showed that the polymer degraded to cyclics in a few minutes with cryptand but not with crown ether.

## Introduction

Polysilanes display a range of properties such that their usefulness in a variety of applications such as precursors to silicon carbide, photoresists, or photoconductors, is being investigated.[1,2] The polymers are most often prepared by coupling of organodichlorosilanes with sodium metal in refluxing toluene.[3-5]



$$n\mathrm{Cl{-}SiR_2{-}Cl} + 2n\mathrm{Na} \xrightarrow[\text{reflux}]{\text{toluene}} \mathrm{(SiR_2)}_n + 2n\mathrm{NaCl}$$

Unfortunately, the yields in polymer and the reproducibility of the reaction are usually quite poor.[1,2] The mechanism of the polymerization of dichlorides to polysilanes is still uncertain. Indeed, it is even suspected that more than one mechanism may be involved. Although appearing to be a condensation type polymerization, the appearance of high molecular weight material when little dichloride has reacted and in nonstoichiometric reactions argues against this.[6] This type of behavior is usually associated with a chain-growth process, with active radical or ionic chain ends propagating the polymerization. Zeigler has suggested[7,8] that the polymerization of dichlorosilanes with sodium occurs through a radical mechanism. Miller and his co-workers have found that the addition of a small amount of dimethoxyethane or other similar complexing ethers produced an increase in the yield of polymer.[9] Although they had first attributed this effect to the presence of anionic chain propagating species, more recent experiments showed that the addition of small amounts of a nonpolar solvent such as heptane had a similar effect on the polymerization.[1]

It is possible that two different mechanisms are active in these polymerizations and that different reaction conditions promote one mechanism over the other. This could also explain the occurrence of two major peaks in the GPC curves of these polymers. GPC traces for the polymerization of phenylmethyldichlorosilane and *n*-hexylmethyldichlorosilane are shown in Figure 1. The material giving rise to the PI peak has been identified as cyclic pentamers for *n*-hexylmethyldichlorosilane and for phenylmethyldichlorosilane.[6] This cyclic material often represents an appreciable fraction of the products and cannot be transformed into polymer. The curve shows a bimodal distribution (PII and PIII) in the polymeric region. It has been possible to increase the yield in PIII to some extent by conducting the polymerizations at lower stirring speed (lower surface area of sodium metal);[6] nevertheless, the

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