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(22) The calculated value of Λ_S is increased if the $1/e^2$ decay time is used in eq 3–7 instead of the $1/e$ decay time. However, these values agree within the error bars in Figure 4 which are based on the uncertainty in τ_s.
(23) These results were the same for the various copolymers with higher mole fractions (Table I). For the lower anthracene mole fraction copolymers, it is not possible to achieve a sufficiently high anthracene concentration to reach the plateau region of Figure 4.
(24) Analysis of complex fluorescence decay from using a six-bit transient recorder (Tektronix 7912) presents deconvolution difficulties.

Photochemistry in Polymer Solids. 3. Kinetics for Nonexponential Decay of Benzophenone Phosphorescence in Acrylic and Methacrylic Polymers

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ABSTRACT: The laser-pulse-excited phosphorescence of benzophenone molecularly dispersed in poly(methyl methacrylate) (PMMA), poly(isopropyl methacrylate) (PIPMA), and poly(methyl acrylate) (PMA) decays nonexponentially for the temperature range $T_\beta < T < T_g$, while it decays single-exponentially for both $T < T_\beta$ and $T > T_g$ of each polymer. The kinetics for the nonexponential decay of benzophenone triplet in these polymer matrices at 80–433 K are given by using the diffusion-controlled rate coefficient with a time-dependent transition term for the dynamic quenching process of benzophenone triplet by side-chain ester groups of the matrix polymers. The resulting kinetic parameters, namely the reciprocal lifetime ($1/\tau$), a factor characteristic of the deviation from single-exponential decay (C), and the diffusion coefficient of interacting groups (D), reflect molecular motion at the glass transition (T_g) and other secondary transitions ($T_{\alpha'}$ and T_β) of the matrix polymers.

Introduction

The photochemistry and photophysics of chromophores molecularly dispersed in polymer matrices have been studied extensively from both fundamental and practical points of view.[1–3] A typical phenomenon encountered in the study of photoprocesses in polymer solids is that reactions expected to be unimolecular in model systems are frequently not first order[4–7] and that phosphorescence of the chromophores in polymer or organic solids sometimes decays non-single-exponentially.[8–13] The phenomenon has been attributed to several isomeric species,[4,5,9] to heterogeneity of free volume distribution in the matrix,[6] to influence of triplet–triplet (T–T) annihilation,[11] or to the existence of intermolecular energy transfer to acceptor molecule[8,10] or to matrices.[12,13]

The measurement of temperature dependence of these rate processes is very important since the photochemical and photophysical processes are strongly affected by molecular motion, glass transition, and other secondary transition processes of polymer matrices. In our previous papers, the phosphorescence of benzophenone in poly(methyl methacrylate)[12] and in other acrylic polymers[13] has been shown to decay single-exponentially at temperatures, T, both lower than the β-transition temperature, T_β, corresponding to the onset of ester side-group rotation of matrix polymer, and higher than the glass transition temperature, T_g. But the decay curves have markedly deviated from an exponential type in the temperature range between T_β and T_g, and the deviation was suggested to be caused by the intermolecular quenching of the benzophenone triplet by ester groups in the side chain of these polymers.

On the other hand, the concept of diffusion-controlled reaction has been established for many years[14,15] and has been applied to very fast polymer–polymer reactions in solution.[16–19] The influence of a time-dependent term in the expression of diffusion flux expected for the very early stage of reaction where steady-state concentration is not yet attained has been discussed by several authors,[14,20–23] but a clear experimental presentation of the influence of the transient term has not been reported so far for the rate process in dilute solution due to the experimental difficulty of detecting the very early stage of the reaction. Viscous liquid, micellar,[24] and solid systems[25] are supposed to be rather convenient for detection of the transient term.

The present paper is concerned with the kinetics of the nonexponential decay of benzophenone phosphorescence in poly(methyl methacrylate) (PMMA), poly(isopropyl methacrylate) (PIPMA), and poly(methyl acrylate) (PMA) at 80–433 K, based on the application of a concept of a diffusion-controlled reaction with a time-dependent rate coefficient to the dynamic quenching process in solid state.

Experimental Section

Materials. Benzophenone and benzoyl peroxide were purified by recrystallization from ethanol solution. The monomers of methyl methacrylate, isopropyl methacrylate, and methyl acrylate were distilled under reduced pressure and stored in a dark refrigerator.

Sample Preparation. The purge of oxygen is important in the study of triplet lifetimes even in solid matrices. Solutions of benzophenone (2×10^{-3} M) and benzoyl peroxide (1×10^{-3} M) in methyl methacrylate or other monomers were evacuated by several freeze–pump–thaw cycles under a high-vacuum system, sealed in a cylindrical Pyrex cell with a diameter of 10 mm, polymerized at 70 °C for 120 h, and postcured at a temperature above T_g of each polymer for 20 h. In cases of PMMA and PIPMA, the sealed rod samples were annealed by cooling from 130 °C at a rate of 0.2 °C/min. The resulting rod samples in the sealed cell were used for the phosphorescence measurements.

Measurements of Phosphorescence Decay. A pulsed nitrogen laser (Avco C950B) with a pulse width of 10 ns as an exciting light at 337 nm, cryostat (Oxford DN704), monochromator (Jasco CT10), photomultiplier (HTV R1464), transient time

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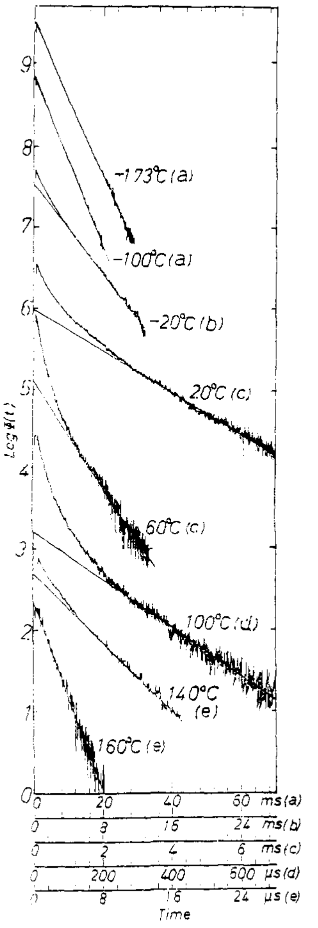

Figure 1. Semilogarithmic decay curves of benzophenone phosphorescence in PMMA excited by 10-ns nitrogen laser pulse at 337 nm. Temperatures and symbols for time scales are given beside the curves.

converter (Riken Denshi TCG8000), and desk-top computer (YHP 9825T) were used for measuring the decay and transient spectra of benzophenone phosphorescence. The apparatus is almost the same as that previously used for the triplet probe study of intermacromolecular reactions[18] and covers the time range 10^{-8}–10^{3} s. The details of the measurements have been given elsewhere.[13]

Temperature Dependence of Decay Curves of Benzophenone Phosphorescence

Typical decay curves at various temperatures of benzophenone phosphorescence at 450 nm in PMMA rod samples excited by a 10-ns nitrogen laser pulse at 337 nm are visualized in Figure 1. The phosphorescence intensity, $\Phi(t)$, decreases single-exponentially at temperatures lower than the β-transition temperature, T_β, corresponding to ester side-group rotation ($T_\beta = -30$ °C for PMMA).[26] When the temperature becomes higher than T_β, a deviation from a straight line in semilogarithmic decay of $\Phi(t)$ is observed. The deviation increases with increasing temperature until the temperature reaches the T_g of the matrix polymer, and then the deviation becomes less marked and disappears at 160 °C. The decay rate of phosphorescence for $T > T_g$ is more than 10^3 times faster than that for $T < T_\beta$. Similar temperature dependence of decay curves (deviation from a single-exponential for $T_\beta < T < T_g$) has also been observed for benzophenone phosphorescence in PIPMA and PMA, as was already shown in Figures 2 and 3 of the previous paper.[13]

The transient spectra of $\Phi(t)$ for PMMA rod samples at 20 °C with typical peaks of benzophenone phosphorescence at both $t = 0$ and $t = 3$ ms (Figure 2) show that the decay curves in Figure 1 reflect only the change in concentration of excited-triplet-state benzophenone. The possibility of the nonlinear part of log $\Phi(t)$ being due to residual monomer that might have existed in the rod sample was eliminated by the fact that the same decay profile was also observed at 20 °C for the benzophenone phosphorescence in the PMMA film sample that contained no residual monomer.[12]

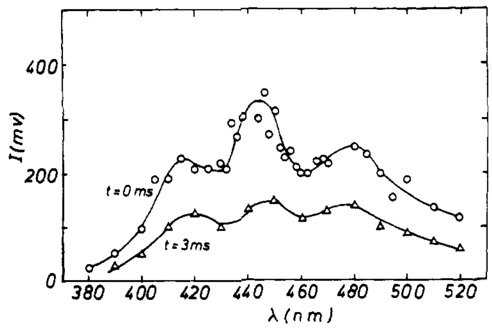

Figure 2. Transient spectra of benzophenone phosphorescence in PMMA at 20 °C immediately after the pulse excitation (○) and after 3 ms (△).

Bräuchle et al.[27] have reported that no irreversible hydrogen abstraction by benzophenone from PMMA occurs from the lowest nπ^* or $\pi\pi^*$ triplet state, though hydrogen abstraction from a higher nπ^* triplet state (two-photon process) proceeds. Our measurements of benzophenone disappearance in PMMA films under stationary-state irradiation with a high-pressure mercury lamp at 20 °C[28] gave the apparent quantum yield $Y_{\mathrm{app}} = 0.012$ for an incident light intensity of $I = 7.0 \times 10^{-9}$ einstein/(cm^2 s) and $Y_{\mathrm{app}} = 0.023$ for $I = 2.4 \times 10^{-8}$ einstein/(cm^2 s). Thus, in the present case with single short-pulse (10 ns) irradiation, hydrogen abstraction is not suggested to be the main pathway for the deactivation of a benzophenone triplet which causes the deviation of decay curves from single-exponential.

Quenching of the benzophenone triplet by a side-chain ester group in acrylic and methacrylic polymers has been suggested as the cause of the deviation from a single-exponential decay.[12] Since the deviation is not observed at temperatures below T_β of each polymer where no rotation of ester side group occurs, this quenching is not suggested to be of static character like a Perrin–Dexter–Ermolaev type[8] but is supposed to be a dynamic one due to collision between the functional groups and energy transfer with a certain amount of activation energy. The model quenching rate constant of benzophenone triplet by methyl acetate in acetonitrile solution was measured to be 3.9×10^3 M^{-1} s^{-1} at 30 °C.[13] This order of magnitude for the quenching rate constant in nonviscous solution is reasonable for an uphill-type endothermic triplet energy-transfer mechanism.[29] The triplet energy level, E_T, for PMMA has been suggested to be 297–301 kJ[30,31] compared with an E_T for benzophenone of 283 kJ.[32] The possibility of nonexponential decay due to triplet–triplet annihilation[11] can be eliminated in the present case, since exponential decay is observed at temperatures above T_g.

It is noteworthy that the triplet decay curves at room temperature of various chromophores in PMMA observed in the literature[11,12,33,34] can be divided into two groups according to the E_T of the chromophores as is shown in Table I. Non-single-exponential phosphorescence decay has been observed for chromophores with an E_T not much smaller than the E_T of PMMA, while single-exponential phosphorescence or T–T absorption decay is obtained for chromophores with much lower triplet energy levels. These results also support the occurrence of dynamic quenching

Table I
Type of Triplet Decay Curves and Triplet Energies, E_T, for Various Chromophores Dispersed in PMMA at Room Temperature

chromophore	type of triplet decay	E_T,[35] kJ/mol	ref
fluorene	non-single-exponential	284	11
benzophenone	non-single-exponential	283	12
triphenylene	non-single-exponential	278	11
naphthalene	non-single-exponential	255	11
coronene	single-exponential	228	11
pyrene	single-exponential	202	33
anthracene	single-exponential	179	34

for excited-triplet-state chromophores by matrix PMMA due to an endothermic triplet energy-transfer mechanism.

Kinetics for Nonexponential Decay due to Dynamic Quenching in Polymer Solids

The decay process of triplet benzophenone (^{3}BP*) produced by a laser-pulse irradiation in polymer matrices having an ester side group can be given by eq 1 and 2 based on the results in the preceding section

$$^3\mathrm{BP}^* \xrightarrow{k_0} \mathrm{BP} \qquad (1)$$

$$^3\mathrm{BP}^* + [\mathrm{Q}] \xrightarrow{k_q} \mathrm{BP} + [\mathrm{Q}] \qquad (2)$$

where $k_0 = k_{PT} + k_{IT}$ is the rate constant for spontaneous deactivation consisting of phosphorescence (k_{PT}) and nonradiative deactivation (k_{IT}) processes, [Q] is the concentration of the ester carbonyl group in the polymer side chain, and k_q is the quenching rate coefficient of benzophenone triplet by the ester side group. As the diffusion process of an ester carbonyl group approaching triplet benzophenone is limited by the side-chain rotation and the local segmental motion of the polymer chain, the bimolecular rate coefficient, k_q, is expressed by eq 3[14]

$$k_q = \frac{4\pi RDN}{1 + 4\pi RDN/k}\left\{1 + \frac{R}{(1 + 4\pi RDN/k)(\pi Dt)^{1/2}}\right\} \qquad (3)$$

where D is the sum of the diffusion coefficient for the carbonyl group in benzophenone and that for ester carbonyl group, R is the reaction radius between the two groups, k is the intrinsic (chemical) rate constant that would pertain if the equilibrium concentration of the quenching group were maintained, and N is the Avogadro number divided by 10^3. When k_q is controlled by the diffusion process of the two groups ($k \gg 4\pi RDN$), eq 3 is reduced to eq 4

$$k_q = 4\pi RDN(1 + R/(\pi Dt)^{1/2}) = A + B/t^{1/2} \qquad (4)$$

with

$$A = 4\pi RDN$$
$$B = 4R^2(\pi D)^{1/2}N$$

and the rate coefficient k_q includes a time-dependent term that is important at the very early stage of reaction where the steady-state diffusive flux of the quenching group is not yet attained.

As the decay rate of benzophenone triplet is given by eq 5

$$-\mathrm{d}[^3\mathrm{BP}^*]/\mathrm{d}t = (k_0 + k_q[\mathrm{Q}])[^3\mathrm{BP}^*] = (k_0 + A[\mathrm{Q}] + B[\mathrm{Q}]t^{-1/2})[^3\mathrm{BP}^*] \qquad (5)$$

we get

$$[^3\mathrm{BP}^*] = [^3\mathrm{BP}^*]_0 \exp\{-(k_0 + A[\mathrm{Q}])t - 2B[\mathrm{Q}]t^{1/2}\} \qquad (6)$$

for the concentration of benzophenone triplet, [^{3}BP*], at time t, where [^{3}BP*]$_0$ is the initial concentration of benzophenone triplet. The phosphorescence intensity, $\Phi(t)$, is proportional to k_{PT}[^{3}BP*], so we get finally

$$\ln \Phi(t) = -(k_0 + A[\mathrm{Q}])t - 2B[\mathrm{Q}]t^{1/2} = -(t/\tau) - C(t/\tau)^{1/2} \qquad (7)$$

where

$$1/\tau = k_0 + A[\mathrm{Q}] = k_0 + 4\pi RDN[\mathrm{Q}] \qquad (8)$$

$$C = 2B[\mathrm{Q}]\tau^{1/2} \qquad (9)$$

$$B = C\tau^{-1/2}/(2[\mathrm{Q}]) = 4R^2(\pi D)^{1/2}N \qquad (10)$$

Thus the curve fitting for experimental phosphorescence decay exemplified in Figure 1 with eq 7 by the least-squares method will determine the values of τ and C for every curve. This provides the basis for an estimation of kinetic parameters such as rate constant for spontaneous deactivation of benzophenone triplet (k_0), quenching radius (R), and the diffusion coefficient for the benzophenone carbonyl and an ester carbonyl group (D).

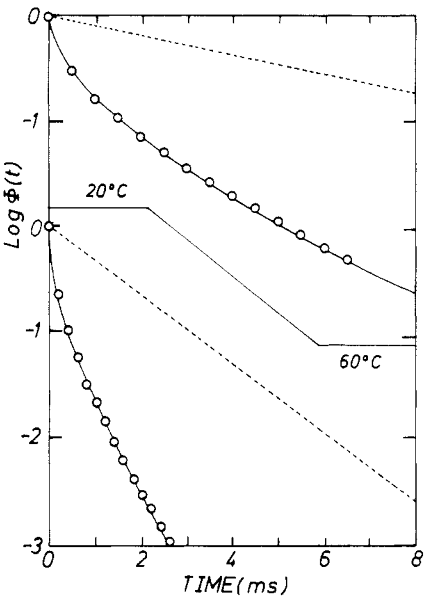

Figure 3. Curve-fitting profiles of experimental decay data (○) with eq 7 for for benzophenone phosphorescence in PMMA at 20 and 60 °C. Solid lines are calculated for $-(t/\tau) - C(t/\tau)^{1/2}$, and dotted lines are those for $-(t/\tau)$.

Kinetic Parameters in Polymer Solids

Typical curve-fitting profiles of the experimental decay data with eq 7 by a nonlinear least-squares method calculated with a YHP 9825T desk-top computer are illustrated in Figure 3. The standard deviation (SD) was 2–3% in normal cases, but sometimes it is greater at temperatures near T_g of the matrix polymer. The temperature dependences of the parameters $1/\tau$ and C, as well as B derived from eq 10 by using [Q] = 11.5 M (PMMA), 10.0 M (PIPMA), 13.4 M (PMA), are summarized in Figure 4 ($1/\tau$ and B) and in Figure 5 (C).

The onset of deviation from single-exponential decay is clearly evident in the abrupt increase in B in Figure 4 and C in Figure 5 at β-transition temperatures, T_β, corresponding to the relaxation of ester sidegroup rotation in the matrix polymers. The values of T_β for each polymer are given in Table II. The kinetic parameter, $1/\tau$, is almost constant over a wide range in the low-temperature region up to a temperature 50–70 °C below each T_g and has the same value for each of the three polymers. The break temperature (T_g minus 50–70 °C) corresponds to the

Table II
Transient Temperatures and Kinetic Parameters for Phosphorescence Decays of Benzophenone in Polymer Matrices

polymer matrix	T_β, °C	$T_{\alpha'}$, °C	T_g, °C	R, Å	k_0 at −193 °C, s^{-1}	D, cm^2/s		E (kJ/mol) for D at			E (kJ/mol) for k
						at $T = T_{\alpha'}$	at $T = T_g$	$T_\beta < T < T_{\alpha'}$	$T_{\alpha'} < T < T_g$	$T > T_g$	
PMMA	−40 (−30 to −10)[26,38]	40 (45–75)[36–38]	110 (105–120)[40]	5.0	2.0×10^2	6.7×10^{-14}	1.5×10^{-12}	29	40	131	
PIPMA	−70	20	80 (81)[40]	5.3	2.0×10^2	7.5×10^{-14}	8.9×10^{-13}	22	36	127	
PMA	−70		10 (5–10)[40]	3.0	2.1×10^2		2.5×10^{-13}		23	145	26

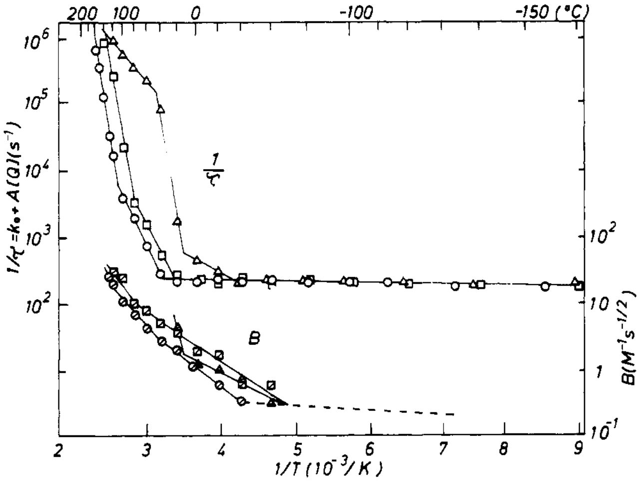

Figure 4. Arrhenius plots of kinetic parameters $1/\tau$ (○, □, △) and B (⊘, ⧄, ▲) for phosphorescence decay of benzophenone in PMMA (○, ⊘), PIPMA (□, ⧄), and PMA (△, ▲).

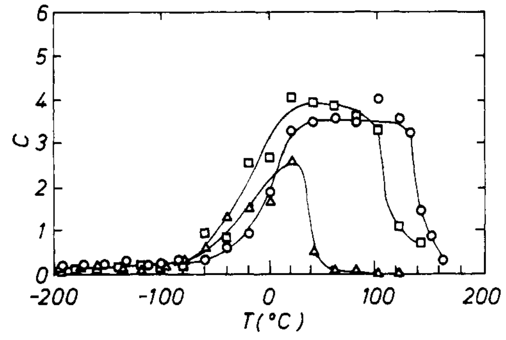

Figure 5. Temperature dependence of kinetic parameter C for phosphorescence decay of benzophenone in PMMA (○), PIPMA (□), and PMA (△).

α'-transition temperature due to a local mode relaxation of the main chain,[36] which was observed at 60 °C[36,37] and 45–75 °C[38] for PMMA. A break at $T_{\alpha'}$ is also observed for the Arrhenius plot of B for PMMA in Figure 4. The glass transition temperature, T_g, is clearly seen as breaks in the Arrhenius plot of $1/\tau$ in Figure 4 (T_g = 110 °C for PMMA, 80 °C for PIPMA, and 10 °C for PMA).

We now discuss the kinetic parameters in various temperature regions. The fact that $1/\tau$ is almost constant for $T < T_{\alpha'}$ and has the same value in the three polymers suggests that $4\pi RDN[\mathrm{Q}] \ll k_0$ in eq 8, resulting in $1/\tau \cong k_0$ in this temperature range. The lifetime, $\tau_0 = 1/k_0$, of benzophenone triplet is 5.0 ± 0.2 ms at 80 K, which is compared to the earlier value of 4.6 ms in PMMA (77 K).[39] τ_0 is 4.0 ± 0.5 ms at room temperature due to a slight increase in the nonradiative deactivation (k_{IT}). We have no information on the parameter A for $T_\beta < T < T_{\alpha'}$, but we know the value of the parameter B. Consequently, by assuming an appropriate value for R, we get an estimation of D from eq 10.

The onset of increase in $1/\tau$ at $T_{\alpha'}$ suggests that $4\pi RDN[\mathrm{Q}]$ becomes larger than k_0 for $T > T_{\alpha'}$. The approximation of

$$1/\tau \cong 4\pi RDN[\mathrm{Q}] \quad \text{for } T > T_{\alpha'} \tag{11}$$

is supported by the fact that activation energy, E, for $1/\tau$ (e.g., 40 kJ/mol for PMMA) is almost twice as large as E for B (21 kJ/mol for PMMA) in the temperature region $T_{\alpha'} < T < T_g$ (Figure 4). Combination of eq 9 and 11 gives

$$C = 4R^{3/2}N^{1/2}[\mathrm{Q}]^{1/2} \tag{12}$$

suggesting that C is constant for $T > T_{\alpha'}$, and the reaction radius R can be determined from eq 12. The average value of R in the range $T_{\alpha'} < T < T_g$ of each polymer is listed in Table II. The constancy of C and hence R is roughly realized in Figure 5 for PMMA and PIPMA in the range $T_{\alpha'} < T < T_g$. The value of about 5 Å for a reaction radius between functional groups is reasonable for the uphill-type triplet energy transfer. The value of R for PMA is indefinite, since the constancy of C was not attained above T_g.

The breaks in Arrhenius plots of $1/\tau$ at T_g are quite natural since the activation energy for D should be changed due to the onset of rapid micro-Brownian motion of polymer main chains. For $T > T_g$, the influence of the transient term in eq 4 on the decay kinetics becomes progressively smaller due to the rapid establishment of a steady-state concentration of the surrounding quenching groups in the rubbery state within the time scale of measurements. This would account for the decrease in C for $T > T_g$ in Figure 5. The increase in $4\pi RDN$ approaching the intrinsic rate constant k would also cause the decrease in C above T_g of each polymer.

A break observed at 40 °C for the Arrhenius plot of $1/\tau$ in PMA is supposed to correspond to the crossover of k_q from a diffusion-controlled to an activation-controlled reaction. Thus, at $T >$ 40 °C for PMA, $k < 4\pi RDN$ holds, and combination of eq 3 and 8 gives

$$1/\tau = k_q[\mathrm{Q}] \cong k[\mathrm{Q}] \tag{13}$$

The activation energy for k was calculated to be 26 kJ/mol from the slope of $1/\tau$ for this region, which gives $k \cong 6 \times 10^3$ M^{-1} s^{-1} at 30 °C as an intrinsic rate constant for the quenching of benzophenone triplet by the ester carbonyl group. This value agrees rather well with the result for the model reaction with methyl acetate in acetonitrile solution ($k = 3.9 \times 10^3$ M^{-1} s^{-1} at 30 °C).[13]

The diffusion coefficient, D, for reacting carbonyl groups was calculated from eq 10 and 11 by using the average value of R given in Table II and is shown against $1/T$ in Figure 6. The breaks corresponding to $T_{\alpha'}$ are observed only for PMMA and PIPMA. It is difficult to say from the present results whether PMA has its α'-transition at −40 °C corresponding to a break in Figure 4. The values of D at T_g and $T_{\alpha'}$ are also given in Table II. It should be noted that D in the present paper is defined as the translational diffusion coefficient for the reacting func-

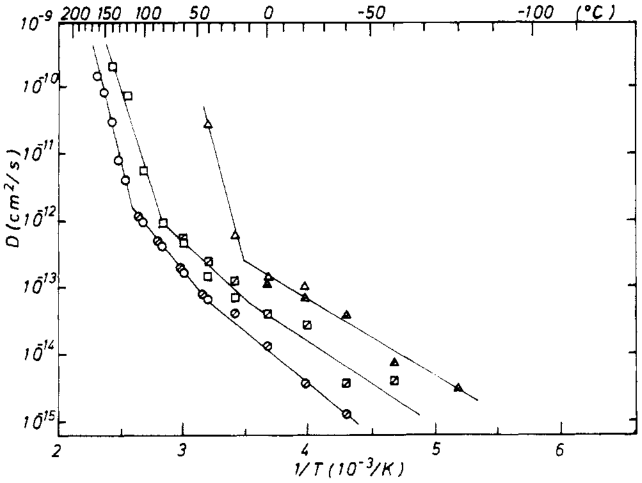

Figure 6. Arrhenius plots of diffusion coefficient D of interacting groups calculated from $1/\tau$ (○, □, △) and B (⊘, ⊠, ▲) for dynamic quenching of benzophenone triplet by side-chain ester groups of PMMA (○, ⊘), PIPMA (□, ⊠), and PMA (△, ▲) as solid matrices.

tional groups but not for the molecule. The diffusion process at temperatures below T_g would be caused by rotation of the benzophenone molecule and segmental motion within a few monomer units of matrix polymers but not by the mass diffusion from a long distance. Nevertheless, the values of D at T_g for PMMA and PIPMA are of the same order of magnitude as the mass diffusion of ethylbenzene in polystyrene at 100 °C (5.6×10^{-13} cm²/s).[41]

In conclusion, the nonexponential decay curves for benzophenone phosphorescence in PMMA, PIPMA, and PMA for the temperature range $T_\beta < T < T_g$ have been analyzed by considering the effect of a time-dependent transient term in the diffusion-controlled intermolecular rate coefficient, k_q, for the quenching of benzophenone triplet by side-chain ester groups of the matrix polymers. The resulting kinetic parameters $1/\tau$, C, and D well reflect molecular motion, glass transition, and other secondary transitions of the matrix polymers.

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Registry No. Benzophenone, 119-61-9; PMMA, 9011-14-7; PIPMA, 26655-94-7; PMA, 9003-21-8.

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