# Photo-Cross-Linking Reaction of Benzophenone-Containing Polyimide and Its Model Compounds

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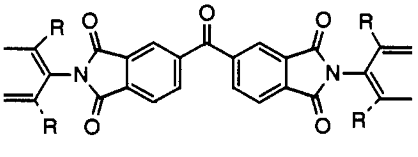
The quantum yield for the photo-cross-linking reaction of the polyimide-containing benzophenones as well as alkyl-substituted diphenylmethane structures in the main chain was determined to be $2.0 \times 10^{-3}$ at room temperature from gel permeation chromatography measurements. The Arrhenius plot of the quantum yields for the cross-linking is linear without any break near the $T_g$ of the polymer and gives an apparent activation energy of 2.4 kcal $mol^{-1}$. From the change in the IR spectra, the key process of photo-cross-linking was determined to be hydrogen abstraction by the triple benzophenone moiety from the pendant ethyl groups and subsequent combination of the radicals produced. The rate constant for the hydrogen abstraction from ethylbenzene by the triplet excited state of the model bisimides is about an order of magnitude smaller than that by triple benzophenone. This difference is thought to be due to the different contribution of n-$\pi$* excited triplet state between model bisimide and benzophenone.

## Introduction

Recently, polyimides have been used in microelectronic device applications such as passivation coating, $\alpha$-particle barriers, and interlayer dielectrics in the manufacture of integrated circuits. They withstand high temperatures during the manufacture and the use of microelectronic devices. However, a number of processing steps are required when a polyimide film is patterned by using the usual photoresist process. So photosensitive polyimide, which can be patterned themselves through a few steps with light, becomes desirable.

Photosensitive polyimides are classified into two groups according to their chemical structures: The first class comprises those polymers that are polyimide precursors (poly(amic acids)) having photosensitive groups that are cured into polyimides after exposure to light and development. Negative type examples are poly(amic acids) esterified with photosensitive vinyl or allyl alcohol, developed by Rubner et al.[1-3] Yoda et al.[4] have reported the development of photosensitive tertiary amine salts of poly(amic acid). A positive type example is nitrobenzyl ester of poly(amic acid).[5] But the images of these materials are subject to distortion due to shrinking during the imidization after the exposure and the development. A second class of photosensitive polyimides is solvent-soluble photoimaginable polyimides, which are expected to be storage-stable and nonshrinking. Moore and Dasheff reported a positive type photosensitive polyimide which is prepared from maleic anhydride dimer.[6] Pfeifer and Rohde[7] reported negative type ones that are full imidized and solvent-soluble benzophenone-containing polyimides with structural unit I. The substituents R and R′ stand for hydrogens or aliphatic groups, which make these polyimides soluble.



Reiser et al.[8] have investigated the reactivity and the mechanism for the photo-cross-linking of this benzophenone-containing polyimide by using gel dose and other methods. Scaiano et al.[9] have measured the phosphorescence spectra of a benzophenone-containing model bisimide. The photoreactions of benzophenone have been widely studied in various chemical systems. We are interested in photochemistry in polymer solids and have already reported the photoreaction of benzophenone in various polymer solids such as poly(methyl methacrylate) and other acrylic polymers,[10-12] polystyrene, polycarbonate,[13] and poly(vinyl alcohol).[14] We have also clarified that the main-chain scission and cross-linking of aromatic polymers occurred simultaneously during the photodegradation of poly(ether sulfone) (PESF), and the reactions are strongly affected by the change in the motion of polymers at glass transition temperature, $T_g$, or sub-glass transition temperature, $T_\beta$.[15]

This paper is concerned with the machanism for the photoreactions of polyimide, PI(BTDA/DEDPM), prepared from benzophenonetetracarboxylic dianhydride (BTDA) and bis(4-amino-3-ethylphenyl)methane (DEDPM), and of its model compound, M(BTDA/DMA), prepared from BTDA and 2,4-dimethylaniline (DMA) and benzophenone (BP).

## Experimental Section

**Materials.** PI(BTDA/DEDPM) was supplied by Mitsubishi

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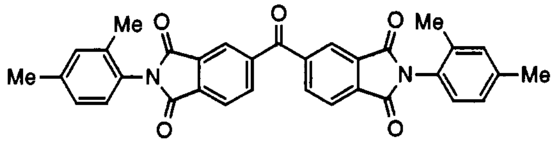
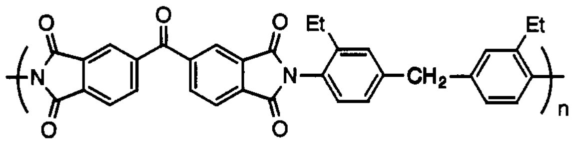


**M(BTDA/DMA)**



**PI(BTDA/DEDPM)**

Kasei Co. Ltd. and used as received. The absolute weight-average molecular weight, $M_w$, of the polymer was measured to be 5.1 × $10^4$ with a light-scattering photometer (Union Giken LS-601), and $T_g$ was determined to be 225 °C by a differential scanning calorimetry (DSC, Du Pont, Model 990) measurement. Polyimide film samples were prepared by the solvent cast method from dichloromethane and dried at 120 °C for 24 h. Benzophenone was purified by recrystallization from ethanol. All solvents for the photoreactions were distilled before use.

**Preparation of M(BTDA/DMA).** Benzophenonetetracarboxylic dianhydride (BTDA, 2.00 g, 6.21 mmol) and 2,4-dimethylaniline (DMA, 1.51 g, 12.46 mmol) in *N,N'*-dimethylacetamide (DMAc, 50 mL) were stirred for 2 h under nitrogen atmosphere and refluxed for an additional hour. The product was purified by flash column chromatography (Silica gel C-300, eluent ethyl acetate:hexane = 1:4) and was identified by IR (Jasco Model IR-G) and NMR (JOEL GX-400) spectra. IR (KBr) 1780, 1720, 1510, 1375, 1105, and 725 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 2.18 (s, 6 H, *o*-Me), 2.3 (s, 6 H, *p*-Me), and 7–7.2 and 8–8.2 (m, 10 H, Ar).

**Photoirradiation.** Photoirradiation of sample polymer films was carried out with a 250-W ultrahigh-pressure mercury lamp (USH-102D) through an interference filter (Toshiba, KL-38, transparent between 350 and 400 nm) under a nitrogen atmosphere at various temperatures. For the photoreaction of M(BTDA/DMA) or benzophenone in solution, a 450-W high-pressure mercury lamp (Ushio UM-452) was used with a combination of Pyrex glass and a glass filter (Toshiba UV-36A, transparent between 300 and 400 nm). Actinometry was carried out with a photometer (Ushio, UIT101). The incident light intensity was about 2.5 × $10^{-9}$ einsteins $cm^{-2}$ $s^{-1}$ for the samples used for the GPC measurements and was about 1.0 × $10^{-7}$ einsteins $cm^{-2}$ $s^{-1}$ for the samples for the measurements of IR spectra and gel fraction.

**Analysis of Photoirradiated Samples.** The changes in the molecular weight distribution of PI(BTDA/DEDPM) during photoirradiation were measured by a HPLC (Jasco BIP) with a GPC column (Shodex AD-80M) using dichloromethane as an eluent. Calibration for the molecular weight was carried out by using monodisperse polystyrene standards. The changes in the concentration of M(BTDA/DEDPM) during photoirradiation were measured by a HPLC with a column of Finepac Sil 60 (Jasco), using chloroform and tetrachloromethane as a mixed eluent. The changes in the concentration of benzophenone were measured by a vapor-phase chromatography (Yanaco GC, OV-1).

**Measurements of Phosphorescence Decay.** The decay of benzophenone phosphorescence was measured by using a pulsed nitrogen laser (Avco C950B), monochromator (Jasco CT10), photomultiplier (HTV R1464), and transient-time converter (Riken Denshi TCG 8000) as described in previous papers.[10-14]

**Measurements of Emission and Excitation Spectra.** The emission and excitation spectra of PI(BTDA/DEDPM) and M(BTDA/DMA) were measured with a fluorescence spectrophotometer (Hitachi Model 850).

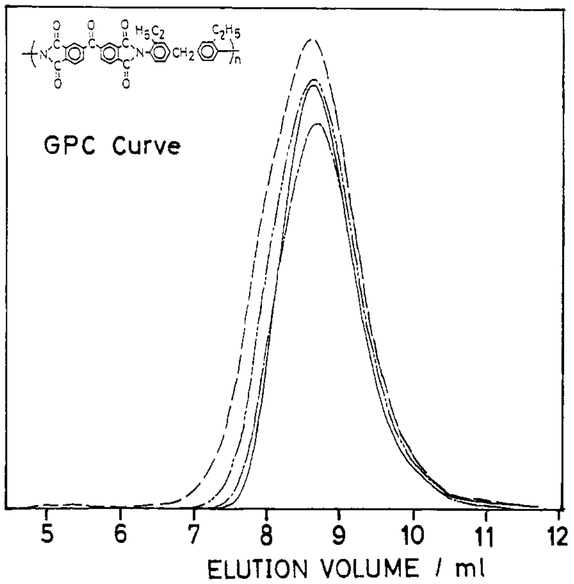


Figure 1. Change in the GPC curves for PI(BTDA/DEDPM) during photoirradiation at room temperature. Irradiation times: 0 (—), 5 (-·-), 10 (-··-), and 20 min (---).

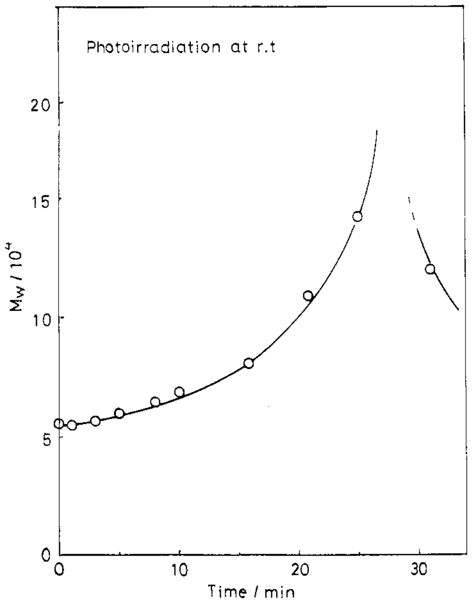


Figure 2. Change in $M_w$ of PI(BTDA/DEDPM) during photoirradiation at room temperature.

## Results and Discussion

**Photoreaction of PI(BTDA/DEDPM).** A typical change in the molecular weight distribution obtained from the GPC measurement of PI(BTDA/DEDPM) during photoirradiation of 365-nm light at room temperature is shown in Figure 1. The amount of higher molecular weight portion increased without the decrease in lower molecular weight portion during the photoirradiation. This means that the cross-linking reaction occurs during photoirradiation, whereas the main-chain scission does not occur. Weight-average molecular weights, $M_w$, were calculated from the GPC measurements, and the change in $M_w$ during photoirradiation at room temperature is shown in Figure 2. According to David's theory[16,17] based on the Saito's integro-differential equation,[18] the change in $M_w$ of a randomly cross-linked polymer during irradiation satisfies the following equation:

$$M_w = M_{w_0}/(1 - 2u_{w_0}x) \qquad (1)$$

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[16] Saito, O. *Statistical Theories of Crosslinking in The Radiation Chemistry of Macromolecules*; Dole, M., Ed.; Academic Press: New York, 1972; Vol. 1.

[17] David, C.; Baeyen-Volant, D. *Eur. Polym. J.* **1978**, *14*, 29.

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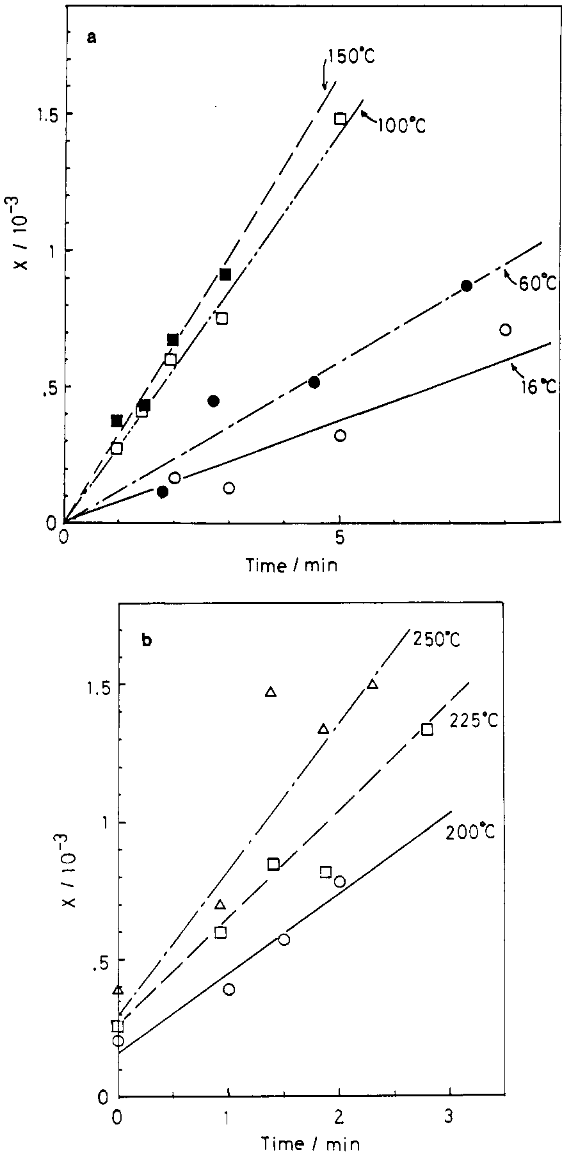

**Figure 3.** (a) Cross-linking density, $x$, vs irradiation time at various temperatures: 16 (○), 60 (●), 100 (□), and 150 °C (■). (b) Cross-linking density, $x$, vs irradiation time at various temperatures: 200 (○), 225 (□), and 250 °C (△).

where $M_{w_0}$ and $u_{w_0}$ are the weight-average molecular weight and the weight-average degree of polymerization before irradiation, respectively, and $x$ is the cross-linking density, i.e., the number of crosslinks per a monomer unit. Figure 3 shows the change in the cross-linking densities of PI(BTDA/DEDPM) during photoirradiation at various temperatures calculated from eq 1. From the slope of the straight line in Figure 3, the quantum yield for cross-linking, $\Phi_{GPC}$, was determined to be 2.0 × $10^{-3}$ at room temperature. The quantum yield for cross-linking can also be determined by the gel dose, $D_g$, by using eq 2, where

$$\Phi_{gel} = 1/(2.303 m \epsilon M_w D_g) \qquad (2)$$

$M_{w_0}$ is the weight-average molecular weight before photoirradiation, $m$ is the molarity, and $\epsilon$ is the molar extinction coefficient at irradiation wave length (365 nm).[19] We measured the gel dose, $D_g$, to be 4.5 × $10^{-6}$ einsteins cm$^{-2}$. By use of this value together with $m$ = 3.0 mol L$^{-1}$, $\epsilon$ = 1.79 × $10^2$ L mol$^{-1}$ cm$^{-1}$, and $M_{w_0}$ = 5.1 × $10^4$, the quantum yield for the cross-linking of PI(BTDA/DEDPM) at room temperature, $\Phi_{gel}$, was obtained to be 3.5 × $10^{-3}$. The molecular weights of PI(BTDA/DEDPM) calculated from GPC measurements might be different from the intrinsic values because the monodisperse polystyrene samples were used as standards for $M_w$. On the other hand, the cross-linking densities obtained from gel fraction would be larger than the intrinsic values because it is affected by the physical entanglements[20] as well as by the chemical crosslinkings. Recently, Reiser et al.[8] reported that the quantum yield for the photo-cross-linking of polyimide consisting of BTDA and 4,4′-diamino-3,3′,5,5′-tetraethyldiphenylmethane is 0.027 measured from gel dose. The difference between the present result (0.0035) and theirs (0.027) is greater than expected from the difference in the number of ethyl groups. Solid-state reactions are often affected by the residual solvent in polymers. We prepared two kinds of PI(BTDA/DEDPM) films. One is a film cast with $N,N'$-dimethylformamide (DMF, bp 150 °C) followed by drying at 155 °C for 20 h, whose $T_g$ was determined to be 185 °C from DSC measurements. The other is a film cast with dichloromethane (bp 39 °C) followed by drying at 120 °C for 20 h, whose $T_g$ was measured to be 225 °C in agreement with the intrinsic value of the $T_g$ for PI(BTDA/DEDPM). The decrease in the $T_g$ for the film cast with DMF is supposedly due to the effect of the residual solvent. The quantum yields, $\Phi_{GPC}$, for the photo-cross-linking of PI(BTDA/DEDPM) at room temperature, which were cast from DMF and from dichloromethane, were measured to be 4.8 × $10^{-3}$ and 2.0 × $10^{-3}$, respectively. Although there is no information about the method used by Reiser et al.[8] for the preparation of their films, the difference between our results and theirs might also be explained by the effect of the residual solvent.

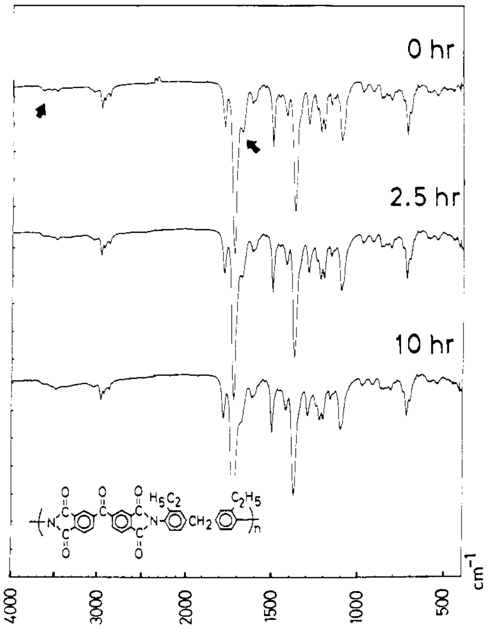

**Figure 4.** Change in IR spectra of PI(BTDA/DEDPM) during photoirradiation at room temperature.

To investigate what reaction occurs chemically during photoirradiation, the changes in IR spectra for the polymers cast on KBr disks were monitored as shown in Figure 4. A strong band at 1720 cm$^{-1}$ is a carbonyl absorption including both the imide carbonyl and benzophenone carbonyl. A weak absorption at 1780 cm$^{-1}$ corresponds to the carbonyl group of a five-membered imide ring.[21] The

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[19] Reiser, A.; Pitts, E. *J. Photogr. Sci.* **1981**, *29*, 187.

[20] Mita, I.; Horie, K.; Masuda, M. *Polym. Bull.* **1981**, *4*, 369.

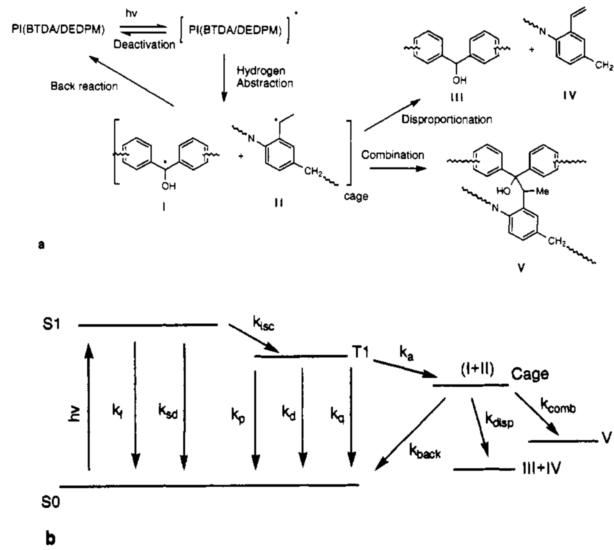

**Figure 5.** (a) Chemical scheme for the photoreaction of PI(BTDA/DEDPM). (b) Photophysical and photochemical processes for the photoreactions of PI(BTDA/DEDPM) and the model compounds.

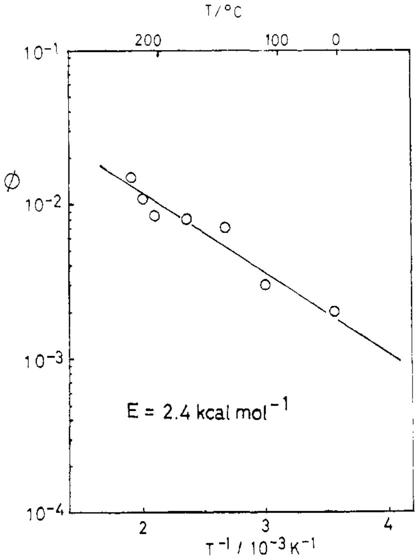

**Figure 6.** Arrhenius plots of quantum yields for the photo-cross-linking of PI(BTDA/DEDPM) from room temperature to 250 °C.

change in the intensity of these two bands during photoirradiation was not observed, while many photochemical reactions of phthalimide and related aromatic imide compounds in solution have been already reported.[22] That is thought to be due to the relatively small reactivity of the imide carbonyl group compared to the benzophenone carbonyl. A weak absorption at 1680 cm$^{-1}$ was observed only for benzophenone-containing polyimide and is not observed in other polyimides.[23] Thus, this peak was assigned to benzophenone carbonyl absorption. The intensity of this peak decreased during photoirradiation and became a shoulder after a 10-h photoirradiation. The broad absorption at 3500 cm$^{-1}$ corresponding to a hydroxyl group also increased during photoirradiation. From the changes in the IR spectra and based on the mechanism for the photoreaction of benzophenone in poly(vinyl alcohol),[14] the photo-cross-linking reaction of PI(BTDA/DEDPM) is proposed to proceed via the scheme shown in Figure 5a: (1) An excited triplet-state benzophenone moiety is formed via singlet state by the absorption of a photon. (2) A part of the excited benzophenone is deactivated back to the ground state. (3) The excited triplet-state benzophenone moiety abstracts a hydrogen atom from an ethyl group of a neighboring polymer chain, resulting in two radicals, a ketyl radical (I) and a benzyl radical (II). (4) The benzyl radical abstracts the hydrogen of ketyl radical to reproduce the starting carbonyl and ethyl groups. (5) Some radicals disproportionate to give benzhydrol groups (III) and styryl groups (IV) on the polymer backbone. (6) Two radicals I and II combine with each other to form a cross-link (V).

**Effect of Reaction Temperature in Photo-Cross-Linking.** We also measured the change in the cross-linking densities during photoirradiation at higher temperatures shown in Figure 3. PI(BTDA/DEDPM) does not cross-link without photoirradiation at temperatures from room temperature to 150 °C but it cross-links thermally above 200 °C. The cross-linking densities at zero photoirradiation time for various photoirradiation temperatures in Figure 3b were obtained for the films heated to the temperature and cooled again without photoirradiation. This process took about 30 min, which was longer than the photoirradiation time. Therefore the thermo-cross-linking of the polymers during photoirradiation was regarded to be negligible compared with the thermo-cross-linking during heating and cooling process before and after the photoirradiation. Therefore the cross-linking densities are composed by both photo-cross-linking during photoirradiation and by thermal cross-linking during the heating and cooling process. Accordingly, the slopes in Figure 3b reflect the true rates of photo-cross-linking, and the quantum yields for the photo-cross-linking can be obtained from the slopes. The Arrhenius plot of the quantum yield for photo-cross-linking is shown in Figure 6. The apparent activation energy, $E$, for the photo-cross-linking of PI(BTDA/DEDPM) was determined to be 2.4 kcal mol$^{-1}$, which is rather small compared to those for other polymers we have investigated.[15] No change in apparent activation energies was found from room temperature to 250 °C in Figure 6, though $T_g$ of this polymer was measured to be 225 °C. This shows a marked contrast to the case of the degradation of poly(ether sulfone) (PESF),[15] where a break in the Arrhenius plot of the quantum yields for photo-cross-linking was observed at a temperature 50 °C lower than the $T_g$. The mechanism of photo-cross-linking of PESF was proposed as the intermolecular attack of an aryl radical produced by the photocleavage of a sulfone group on another polymer chain. The change in the activation energy for the photoreaction of PESF reflects the change of molecular motion of the polymer. In the case of PI(BTDA/DEDPM), however, the molecular motion necessary for the combination of the geminate ketyl and benzyl radicals (Figure 5a) is of local character, and this local motion is not supposed to be affected much by $T_g$.

**Effect of Oxygen Quenching.** Molecules in the excited triplet state are usually quenched rapidly by oxygen, and the quenching rate is controlled by a diffusion process. But since the rate of diffusion of oxygen in polymers is smaller than that in solution, the quenching rate constant in solid is also considered to be small. So, photoreaction of PI(BTDA/DEDPM) unde air was carried out and the quantum yield for photo-cross-linking under air was determined to be 1.2 × 10$^{-3}$. The comparison of this value with the result under nitrogen (2.0 × 10$^{-3}$) shows a small

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[21] Tanaka, S. *Yuki kagobutu no Kozo Kettei Ho*, Sangyo Tosho: Tokyo, 1979; p 95.

[22] Coyle, J. D. *Synthetic Organic Photochemistry*; Horspool, W. H., Ed.; Plenum Press: New York, 1984; p 259.

[23] Din-Hart, R. A.; Wright, W. W. *Macromol. Chem.* **1971**, *143*, 189.

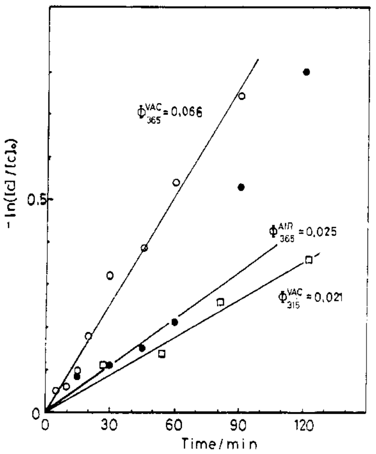

**Figure 7.** First-order plots of the decrease in the M(BTDA/DMA) concentration, [C], during the photoirradiation of 365 nm (○) and 315 nm (□) light under vacuum, and 365 nm under air (●).

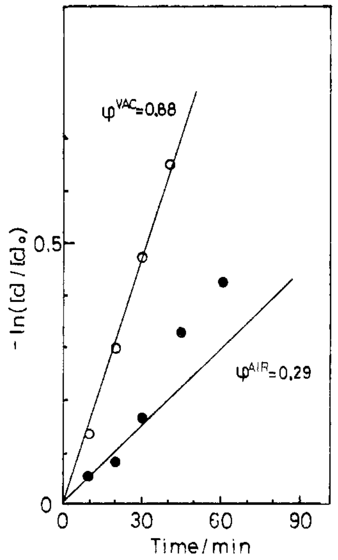

**Figure 8.** First-order plots of the decrease in benzophenone concentration during 365-nm irradiation under vacuum (○) and under air (●).

effect of oxygen quenching due to the slow diffusion of oxygen in polymer solid, which is consistent with the result by Reiser et al.[8]

**Comparison of the Reaction of the Model Bisimide, M(BTDA/DMA), with That of BP.** To examine the influence of the imide structure of PI(BTDA/DEDPM) on the reactivity of a benzophenone carbonyl group, a model bisimide, M(BTDA/DEDPM), was prepared and its photoreaction in ethylbenzene solution was compared to that of benzophenone, BP. The carbonyl groups of these compounds are expected to abstract benzyl hydrogen of ethylbenzene to produce ketyl radical and benzyl radical. These radicals may react in various ways, for example, combination with each other, further hydrogen abstraction from solvent, and so on,[24] but the rates for the disappearance of the models follow the first-order plot, which are shown in Figure 7. The quantum yields $\Phi^{vac}$ and $\Phi^{air}$ for the disappearance of M(BTDA/DMA) were 0.066 and 0.025 under vacuum and air, respectively. Those for BP under vacuum and air were also obtained in the same way to be 0.88 and 0.29, respectively (Figure 8). Photophysical and photochemical process for the photoreactions of M(BTDA/DMA) and BP as well as PI(BTDA/DEDPM) are illustrated in Figure 5b. The quantum yields, Φ, for the consumption of M(BTDA/DMA) during photoirradiation are given eq 3, by using $\Phi^{isc}$, $\Phi^{abst}$, and $\Phi^{trans}$ as the quantum

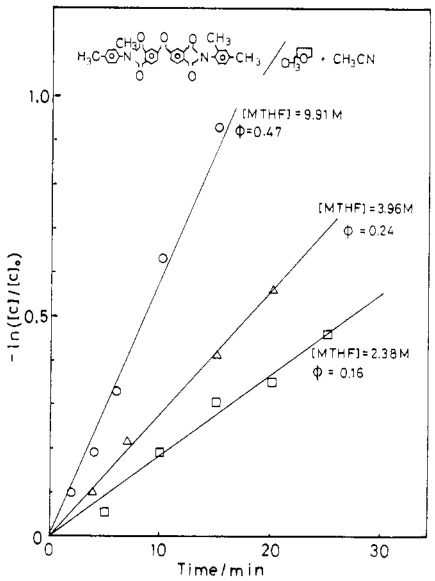

**Figure 9.** First-order plots of the decrease in the M(BTDA/DMA) in the mixed solvents of MTHF and AcCN under vacuum. [MTHF] = 9.91 (○), 3.96 (△), and 2.38 mol L$^{-1}$ (□).

$$\Phi = \Phi^{isc}\Phi^{abst}\Phi^{trans} \tag{3}$$

yields for the intersystem crossing, hydrogen abstraction, and the chemical transformation of the chromophores, respectively (Figure 5b). Each of the quantum yields is expressed by the elementary rate constants, which are shown in eqs 4–6,

$$\Phi^{isc} = \frac{k_{isc}}{k_f + k_{sd} + k_{isc}} \tag{4}$$

$$\Phi^{abst} = \frac{k_a^{EB}[EB]}{k_p + k_d + k_a^{EB}[EB] + k_d^{EB}[EB] + k_q[O_2]} \tag{5}$$

$$\Phi^{trans} = \frac{k_{com} + k_{disp}}{k_{com} + k_{disp} + k_{back}} \tag{6}$$

where $k_{isc}$, $k_f$, $k_{sd}$, $k_p$, $k_d$, $k_a^{EB}$, $k_d^{EB}$, and $k_q$ are the rate constants for the intersystem crossing from the excited singlet state to the triplet state, fluorescence, nonradiative deactivation from the excited singlet state, phosphorescence, nonradiative deactivation from the triplet state, hydrogen abstraction from ethylbenzene, quenching by ethylbenzene, and quenching by oxygen, respectively. The [EB] and [$O_2$] stand for the concentrations of ethylbenzene and of oxygen. The $k_{com}$, $k_{disp}$, and $k_{back}$ are the rate constants for combination, disproportionation, and back reaction between geminate ketyl and benzyl radicals inside the solvent cage.

The value of $\Phi^{isc}$ for benzophenone is known to be unity,[25] and the quantum yield for the consumption of benzophenone, $\Phi^{vac}$, is already determined to be 0.88. This means that the ratio of back reaction is relatively small in this system. To determine the value of $\Phi^{isc}\Phi^{trans}$ for M(BTDA/DMA), the quantum yields for the disappearance of M(BTDA/DMA) in the mixed solvent of aceto-

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[24] Dedinas, J. *J. Phys. Chem.* **1971**, *75*, 181.

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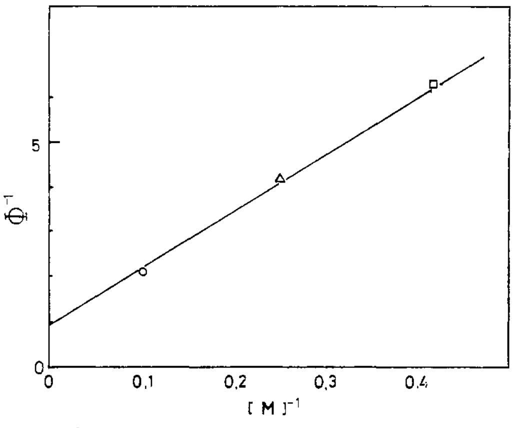

**Figure 10.** Stern–Volmer plots of the quantum yields, $\Phi$, for disappearance of M(BTDA/DMA) in the mixed solvents of MTHF and AcCN under vacuum.

nitrile (AcCN) and 2-methyltetrahydrofuran (MTHF) were measured (Figure 9). In this system, the rate constants for the quenching by the solvents are negligibly small compared with that for the hydrogen abstraction from MTHF,[25,26] and the term of the oxygen quenching is eliminated. Therefore, the quantum yield for the consumption of the model compound under vacuum, $\Phi^{vac}$, is given by eq 7, where $k_a{}^M$ is the rate constant for the hydrogen abstraction from MTHF. The Stern–Volmer relationship, eq 8, is derived from eq 7, where $\Phi^{isc}\Phi^{trans}$ is

$$\Phi^{vac} = \Phi^{isc}\frac{k_a{}^M[\mathrm{MTHF}]}{k_p + k_d + k_a{}^M[\mathrm{MTHF}]}\Phi^{trans} \tag{7}$$

$$\frac{1}{\Phi^{vac}} = \frac{1}{K} + \frac{k_p + k_d}{Kk_a{}^M[\mathrm{MTHF}]} \tag{8}$$

replaced by a constant $K$, since both of the quantum yields $\Phi^{isc}$ and $\Phi^{trans}$ can be regarded to be constant in this experimental condition (Figure 10). Figure 10 shows a straight line for the Stern–Volmer plots, and from the intercept of the line, $K$ was ascertained to be unity for M(BTDA/DMA). Consequently, by using $K = 1$, eqs 3–6 are replaced by eqs 9 and 10 under vacuum and air, respectively.

$$\Phi^{vac} = \frac{k_a{}^{EB}[\mathrm{EB}]}{k_p + k_d + k_a{}^{EB}[\mathrm{EB}] + k_d{}^{EB}[\mathrm{EB}]} \tag{9}$$

$$\Phi^{air} = \frac{k_a{}^{EB}[\mathrm{EB}]}{k_p + k_d + k_a{}^{EB}[\mathrm{EB}] + k_d{}^{EB}[\mathrm{EB}] + k_q[\mathrm{O_2}]} \tag{10}$$

To determine the rate constant for the hydrogen abstraction from ethylbenzene by the benzophenone triplet, $k_a{}^{EB}$, the lifetime, $\tau$, for the decay of benzophenone phosphorescence under vacuum in the mixed solvent of ethylbenzene and benzene was measured (Figure 11). The Stern–Volmer plot of $\tau^{-1}$ against the concentration of ethylbenzene (Figure 12) fits eq 11,[27] where $\tau_0$ is the lifetime in the absence of ethylbenzene. From the slope in Figure 12, $k_a{}^{EB} + k_d{}^{EB}$ was obtained to be $1.14 \times 10^6$ L mol$^{-1}$ s$^{-1}$, and the lifetime of the benzophenone triplet in bulk ethylbenzene is estimated to be 106 ns by using the concentration of bulk ethylbenzene of 8.18 M. Then from eq 9 together with $\Phi^{vac} = 0.88$, the reciprocal lifetime ($\tau_0{}^{-1} = k_p + k_d = 1.3 \times 10^5$ s$^{-1}$), and $k_p = 2 \times 10^2$ s$^{-1}$,[14] $k_a{}^{EB}$ and $k_d + k_d{}^{EB}[\mathrm{EB}]$ were calculated to be $1.0 \times 10^6$ L mol$^{-1}$ s$^{-1}$ and $1.2 \times 10^6$ s$^{-1}$, respectively. Giering et al.[26] has reported that the rate constant of the hydrogen abstraction from toluene by benzophenone triplet is $1.3 \times 10^5$ L mol$^{-1}$ s$^{-1}$. Considering the difference in the reactivity of the benzyl hydrogen between toluene and ethylbenzene, the value of $k_a{}^{EB}$ obtained in our study ($1.0 \times 10^6$ L mol$^{-1}$ s$^{-1}$) is consistent with the rate of the hydrogen abstraction obtained by Giering et al.

$$\tau^{-1} = \tau_0{}^{-1} + (k_a{}^{EB} + k_d{}^{EB})[\mathrm{EB}] \tag{11}$$

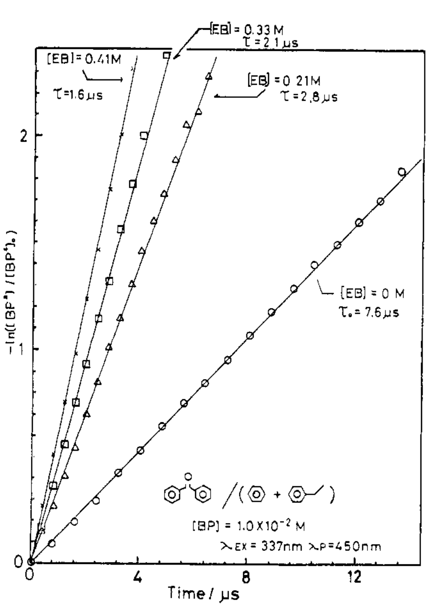

**Figure 11.** First-order plots for the phosphorescence decay of benzophenone in the mixed solvent of benzene and ethylbenzene under vacuum: [EB] = 0 (○), 0.21 (△), 0.33 (□), and 0.41 mol$^{-1}$ L (×).

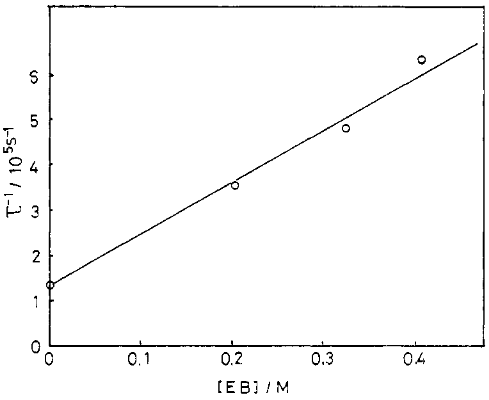

**Figure 12.** Stern–Volmer plots for the quenching of the benzophenone phosphorescence by ethylbenzene in benzene under vacuum.

The rate constant for the oxygen quenching can be obtained by eq 12, which is given by the combination of eqs 9 and 10. By introducing the values of the quantum yield

$$\frac{1}{\Phi^{air}} = \frac{1}{\Phi^{vac}} + \frac{k_q[\mathrm{O_2}]}{k_a{}^{EB}[\mathrm{EB}]} \tag{12}$$

for benzophenone under vacuum ($\Phi^{vac} = 0.88$) and under air ($\Phi^{air} = 0.29$), and the value of $k_a{}^{EB}$ of $1.0 \times 10^6$ L mol$^{-1}$ s$^{-1}$ into eq 12, we obtained $k_q[\mathrm{O_2}]$ to be $1.9 \times 10^7$ s$^{-1}$. The quenching reaction of a triplet-state molecule by oxygen is known to be controlled by a diffusion process, and the value of the rate constant in benzene was obtained by flash

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**Table I. Various Kinetic Parameters for the Photoreactions of M(BTDA/DMA) and Benzophenone in Ethylbenzene**

| | $\Phi^{vac}$ | $\Phi^{air}$ | $K$ | $k_a^{EB}$, $M^{-1}$ $s^{-1}$ | $k_d$ + $k_d^{EB}$, $s^{-1}$ |
|---|---|---|---|---|---|
| benzophenone | 0.88 | 0.29 | 1 | $1.0 \times 10^6$ | $1.2 \times 10^6$ |
| M(BTDA/DMA) | 0.066 | 0.025 | 1 | $9.3 \times 10^4$ | $1.1 \times 10^7$ |

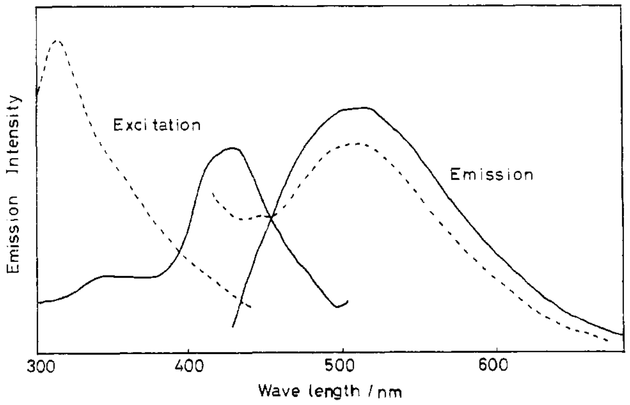

**Figure 13.** Emission (fluorescence) and excitation spectra of PI(BTDA/DEDPM) in film (—) and M(BTDA/DMA) in PMMA (- - -).

photolysis[28] to be $9 \times 10^8$ L $mol^{-1}$ $s^{-1}$. The difference between the viscosity of benzene (0.64 cP, 20 °C) and that of ethylbenzene (0.666 cP, 20 °C) is very small. Using $k_q[O_2] = 1.9 \times 10^7$ $s^{-1}$ and $k_q = 9 \times 10^8$ L $mol^{-1}$ $s^{-1}$, we calculated the oxygen concentration in ethylbenzene $[O_2]$ to be $2 \times 10^{-2}$ mol $L^{-1}$, which would be a reasonable value.[29]

In case of the photoreaction of M(BTDA/DMA) in ethylbenzene, the values of $k_a^{EB}$ and $k_d + k_d^{EB}[EB]$ were obtained to be $9.3 \times 10^4$ mol $L^{-1}$ $s^{-1}$ and $1.1 \times 10^7$ $s^{-1}$ by using $\Phi^{air}$, $\Phi^{vac}$, and $k_q[O_2]$ obtained above. The kinetic data for the photoreaction of benzophenone and M(BTDA/DMA) in ethylbenzene are summarized in Table I. The differences in the quantum yields between benzophenone and M(BTDA/DMA) are attributed to be the difference in both $k_a^{EB}$ and $k_d^{EB}$ between them.

It is known that the reactivity of a substituted benzophenone is affected by the electronic nature of the substituents, but the decrease in the reactivity cannot be discussed only by the inductive effect of the imide group, because ring substituents produce relatively small inductive effects on hydrogen atom abstraction by n–π* ketone triplet.[30] We have concluded from the study on the fluorescence spectra of various aromatic polyimides that aromatic polyimides form intermolecular charge-transfer (CT) complexes in their excited states.[31] To discuss the reactivity from the view point of the CT nature of polyimide, we measured the emission (fluorescence) and excitation spectra of PI(BTDA/DEDPM) film and M(BTDA/DMA) in ethylbenzene (Figure 13). The fluorescence spectrum of the PI(BTDA/DEDPM) film can be attributed to the emission from the intermolecular CT complex between the imide ring and the diamine moiety as is the case for other polyimides.[31] The fluorescence spectrum of M(BTDA/DMA) in ethylbenzene may also be due to a CT complex. Since the same spectrum was also observed in case of M(BTDA/DMA) dispersed in PMMA, which does not contain aromatic rings, the fluorescence spectrum of M(BTDA/DMA) in ethylbenzene could be attributed to both inter- and intramolecular CT formation. But since the quantum yield for the formation of triplet M(BTDA/DMA) was determined to be unity from our study, the rate of the emission from the excited singlet M(BTDA/DMA) is considered to be negligibly small compared with that of intersystem crossing, i.e., molecules in the excited singlet CT state are usually supposed to undergo intersystem crossing into the excited triplet state. The lowest excited triplet state of M(BTDA/DMA) is considered to be made up by the superposition of the electronic configuration in the excited state of the CT and that in the benzophenone group. So the n–π* nature in the excited state of M(BTDA/DMA) should decrease owing to the increase of the CT nature. For this reason, the $k_a^{EB}$ for M(BTDA/DMA) is thought to be smaller than that of benzophenone. On the other hand, the $k_d + k_d^{EB}[EB]$ of M(BTDA/DMA) is greater than that of benzophenone. This would be caused by the interaction between M(BTDA/DMA) and ethylbenzene due to the intermolecular CT complex. Scaiano et al.[32] have observed the phosphorescence of bisimide consisting of a mole of BTDA and 2 mol of *o*-isopropylaniline in an ethanol:methanol glass at 77 K, whose spectrum is similar to that of the benzophenone triplet. They also reported from the phosphorescence decay in 2-propanol that the bisimide triplet is about an order of magnitude more rapidly quenched than the benzophenone triplet. If the rapid quenching for their bisimide triplet is mainly due to hydrogen abstraction from 2-propanol, the high reactivity in their system might be attributed to the small contribution of CT complex in the excited states.

The quantum yield for disappearance of benzophenone is known to be constant with the change in the excitation wavelength. For M(BTDA/DMA), photoreactions at different wavelengths (365 and 315 nm) were carried out. The quantum yields at 365 and 315 nm were obtained to be 0.066 and 0.021, respectively (Figure 7). The less reactivity at 315-nm excitation would be caused by the absorption of the diamine moiety which does not lead to the hydrogen abstraction.

## Conclusion

The quantum yields for photo-cross-linking of PI(BTDA/DEDPM) were obtained from GPC measurements at various temperatures. The apparent activation energy for the photo-cross-linking of PI(BTDA/DEDPM) was obtained to be 2.4 kcal $mol^{-1}$ from the Arrhenius plot for the quantum yields. Hydrogen abstraction from an ethyl group by a triplet benzophenone moiety and the subsequent radical recombination were determined to be key process in their photo-cross-linking reaction. From the study of model reactions, the chemical reactivity of the benzophenone-containing bisimide with ethylbenzene was shown to be much smaller than that of benzophenone, while the rate of physical quenching by ethylbenzene is higher for the model bisimide than for benzophenone. This change in the reactivity between the bisimide and benzophenone is explained on the basis of the charge transfer nature of the polyimide and model bisimide.

**Registry No.** (BTDA)(DEDPM) (copolymer), 108735-62-2; (BTDA)(DEDPM) (SRU), 108689-66-3; BTDA, 2421-28-5; DMA, 95-68-1; M(BTDA/DMA), 127324-17-8; benzophenone, 119-61-9; ethylbenzene, 100-41-4.

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