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A Novel Imaging System by Dye-Sensitized Photooxidation of Oxazole Groups Attached to a Polymer Backbone. 3. Effect of the Sensitizer on Photooxidation in Thin Films

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ABSTRACT: Oxazole rings attached to a copolymer backbone, which was composed of 2-[3-(methacryloyloxy)-propyl]-4,5-diphenyl-1,3-oxazole and *N*-isopropylacrylamide, were transformed efficiently to the corresponding *N,N*-dibenzoylcarboxamide derivatives in a thin film by photooxidation using various dyes as photosensitizers. This photoinduced transformation was found to be applicable to a panchromatic photoresist with positive tone by development with an aqueous solution of amines to dissolve the exposed areas of the film. The photooxidation had the quantum efficiency for generation of singlet oxygen in the range 0.2–0.7 depending upon the sensitizers used in the system. The conversion showed a maximal value when the average distance between the oxazole rings and sensitizer molecules was about 30 Å.

Introduction

Singlet oxygen possessing a relatively long lifetime has attracted considerable attention as a reactive species in many chemical and biological phenomena.[1] Many triplet sensitizers for singlet oxygen have been reported, and the photochemical processes involved have been extensively investigated.[2] These experiments, however, have been predominantly conducted in solution, and in the solid state little is known about the singlet oxygen behavior and the characteristics of sensitizers.[3]

Applications of singlet oxygen to interesting photoimaging processes were reported by Carre[4] and Breslow.[5] These are based on the reaction between singlet oxygen and either olefins possessing an allylic hydrogen or 2,5-diphenyl-3,4-benzofuran. A radical initiator is generated in both systems, and preimaging parts are subsequently exposed to the ultraviolet light, resulting in photopolymerization.

We reported previously that the oxazole rings attached to a copolymer (*p*-OxM-*co*-IPA), which was composed of 2-[3-(methacryloyloxy)propyl]-4,5-diphenyl-1,3-oxazole and *N*-isopropylacrylamide, were converted efficiently to the corresponding *N,N*-dibenzoylcarboxamide derivatives by photooxidation using *meso*-tetraphenylporphine (TPP) as a photosensitizer in a thin film, and this photoinduced transformation in the copolymer was found to be applicable to a positive working photoresist by development with an aqueous solution of amine to dissolve the exposed areas of the film (Scheme II).[6] Therefore, if triplet sensitizers with different excited-state energies can produce singlet oxygen similarly in the solid state with the aid of diffusion of the atmospheric oxygen molecules, it is possible to form an image by light with a wide range of wavelengths because the wavelength of a class of efficient triplet sensitizers ranges from 250 to 700 nm.[2]

This work deals with panchromatic photoimaging based on the photooxidation of oxazole groups attached to a polymer backbone by several dye sensitizers. Pertinent photophysical and photochemical properties are also reported such as the efficiency for generation of singlet oxygen and its diffusion behavior in the polymer matrix.

Experimental Section

Materials. 2-Methyl-4,5-diphenyl-1,3-oxazole used as a starting material was prepared directly from 2-acetoxy-2-phenylacetophenone by a standard oxazole synthesis.[7]

Tetrahydropyranyl Ether of 1-Hydroxy-2-iodoethane. To a solution of 1-hydroxy-2-iodoethane (25.0 g, 0.20 mol) in THF (150 mL) were added 3,4-dihydro-2*H*-pyran (17.0 g, 0.20 mol) and *p*-toluenesulfonic acid (0.5 g, 2.63 mmol). The mixture was stirred for 1 h at room temperature, and then the solvent was removed until about a 30-mL portion remained, followed by addition of water (100 mL). The solution was extracted twice with diethyl ether. The organic layers were combined, washed twice with saturated aqueous $NaHCO_3$ and NaCl solutions, respectively, and dried over $MgSO_4$. Following filtration, the solvent was removed by evaporation and the residual oil was dissolved in acetone (300 mL). To this solution was added NaI (50.0 g, 0.34 mol), and the mixture was stirred at room temperature for 22 h. The excess NaI was removed by filtration, the solvent was removed under vacuum until about a 50-mL portion remained, and to the residue was added diethyl ether. The solution was washed twice with water, a 5 wt % $Na_2S_2O_3$ solution, and a 10 wt % aqueous NaCl solution, respectively, and dried over $MgSO_4$. The solvent was removed under vacuum, leaving tetrahydropyranyl ether of 1-hydroxy-2-iodoethane (37.5 g, 73%) as a light yellow oil.

IR (neat): 2940, 2860, 1350, 1200, 1120, 1020 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.6–4.7 (m, 1H, –OCHO–), 3.2–4.1 (m, 6H, –OCH_2, ICH_2) 1.6–2.0 (m, 6H, –CH_2–).

2-(3-Hydroxypropyl)-4,5-diphenyl-1,3-oxazole. This compound was prepared according to the literature.[8a] To a solution of diisopropylamine (1.10 g, 10.9 mmol) in THF (10 mL) at 0 °C was added a 1.6 M hexane solution of *n*-BuLi (7.0 mL, 11.2 mmol), and the mixture was stirred for 30 min at 0 °C. After cooling to −78 °C, a solution of 2-methyl-4,5-diphenyl-1,3-oxazole (2.60 g, 11.1 mmol) in THF (25 mL) was added over a period of 1 h, followed by stirring for 30 min at −78 °C. Then a solution of tetrahydropyranyl ether of 1-hydroxy-2-iodoethane (2.80 g, 10.9 mmol) in THF (12 mL) was added. The mixture was spontaneously warmed to room temperature and stirred for 4 h. After quenching with a small amount of water, the solvent was removed under vacuum and the residue was dissolved in ethyl acetate (100 mL). The solution was then washed three times with water and once with a saturated aqueous NaCl solution and dried over

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$MgSO_4$. Following filtration, the solvent was removed under vacuum and the residual compound was dissolved in a MeOH–AcOH mixture (1:1; 100 mL). The solution was stirred at 60 °C for 8 h, and the solvent was removed under vacuum, leaving a light yellow oil. Column chromatography using ether–hexane (4:1) as eluent and recrystallization from hexane gave 2-(3-hydroxypropyl)-4,5-diphenyl-1,3-oxazole (1.88 g, 62%) as a white solid.

IR (KBr): 3350, 3050, 3020, 1600, 1560, 1500, 760 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.2–7.7 (m, 10H, aromatic), 3.81 (t, 2H, $-CH_2O-$), 2.98 (t, 2H, oxazole–CH_2–), 2.71 (s, 1H, –OH), 2.11 (tt, 2H, $-CH_2-$).

Monomer. 2-[3-(Methacryloyloxy)propyl]-4,5-diphenyl-1,3-oxazole (OxM). To a solution of 2-(3-hydroxypropyl)-4,5-diphenyl-1,3-oxazole (0.53 g, 1.90 mmol) and triethylamine (0.41 g, 4.40 mmol) in benzene (7 mL) on an ice–water bath was added dropwise a solution of methacryloyl chloride (0.41 g, 4.05 mmol) in benzene (6 mL) over a period of 30 min. The mixture was stirred at room temperature for 12 h. The solution was washed three times with an aqueous 2 N Na_2CO_3 solution, an aqueous 2 N HCl solution, and water, respectively, and dried over $MgSO_4$. Following filtration, the solvent was removed under vacuum until about a 5-mL portion remained. The residue was chromatographed on silica gel using benzene as eluent, giving 2-[3-(methacryloyloxy)propyl]-4,5-diphenyl-1,3-oxazole (0.52 g, 79%) as a light yellow oil.

IR (neat): 3050, 2960, 2930, 1720, 1440, 1320, 1295, 1160 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.2–7.8 (m, 10H, aromatic), 6.12 (d, 1H, $=CH$), 5.65 (d, 1H, $=CH$), 4.33 (t, 2H, $-OCH_2-$), 3.01 (t, 2H, oxazole–CH_2–), 2.31 (tt, 2H, $-CH_2-$), 1.93 (s, 3H, CH_3).

Polymerization. Copolymerization of 2-[3-(methacryloyloxy)propyl]-4,5-diphenyl-1,3-oxazole (OxM) with *N*-isopropylacrylamide (IPA) was performed according to our previous paper.[6] Composition of the copolymer was determined by means of UV spectra. The copolymer contained a 6 mol % OxM unit. The molecular weight of this copolymer was 1.3×10^5, which was determined by a laser light-scattering method (KMX-6; solvent, methanol).

Sensitizers. We employed the following dyes as sensitizers in this study (Scheme I): *meso*-tetraphenylporphine (TPP), methylene blue (MB), tetrakis(3,4-dimethoxyphenyl)porphine (H_2TMPP), a zinc complex (ZnTMPP), a *meso*-diphenyltetrabenzoporphine zinc complex (ZnPTBP), and 3,3′-carbonylbis-[7-(diethylamino)coumarin] (KCD). H_2TMPP, ZnTMPP, ZnPTBP, and KCD were kindly gifted by Dr. M. Yasuike of Toyo Ink Manufacturing Co., Ltd.

Reactivity of Photosensitizers. A 5 wt % solution of OxM copolymer in chloroform or ethanol containing a 10 mol % dye based on the oxazole unit as a sensitizer was spin-coated on a quartz plate to yield a film with an appropriate thickness, and the thin film was dried for 20 min at 80 °C. The resulting film was then exposed for several minutes to monochromatic light from an irradiator (Jasco CRM-FA). The irradiation was carried out in such a way that the transmittance of the exposed light ranges from 75 to 90%. The ability of sensitizers was evaluated by estimating a conversion of the oxazole groups to the *N*,*N*-dibenzoylcarboxamide derivatives and the quantum yield of this process. The conversion was spectroscopically determined from the absorbance of the oxazole ring (λ_{max} = 290 nm) before and after photoirradiation.

The limiting quantum yields of photooxidation were determined from the decrease in the concentration of the oxazole groups and the absorbed light energy according to the procedure reported previously for the limonene photooxidation in organic solution.[2d] The energy absorbed by the sensitizer was estimated from the differences between the incident and the transmitted light energy, which was measured with a photosensor (Advantest Model TQ-8210). Then the irradiation was stopped, keeping the consumption of the oxazole units below 15% of the initial concentration. Double reciprocal plots of the concentration of oxazole versus the quantum yield of the oxazole photooxidation gave a straight line where the limiting quantum yields could be calculated from the intercepts at the *y* axis.

Sensitivity Determination. A thin film was prepared in the same way, and the relationship between the film thickness and the absorbance due to the oxazole moiety was obtained to make a calibration line. The sensitivity was measured in the following way. When TPP was used as a sensitizer, the thin film was exposed to light at 410 nm with 0.38 mW/cm², which was isolated from a 500-W high-pressure mercury lamp by the use of a combination of a glass filter (Toshiba UV-39) and an interference filter (Toshiba KL-40). When ZnPTBP was used, it was exposed to monochromatic light at 659 nm with an intensity of 2.4 mW/cm² from the irradiator. The development was performed by dipping the exposed film in a 5 wt % aqueous solution of 2-aminoethanol for 5 min, followed by rinsing with water. Then, the thickness of the residual film was measured by UV spectra.

Scheme I. Triplet Sensitizers Used in This Work

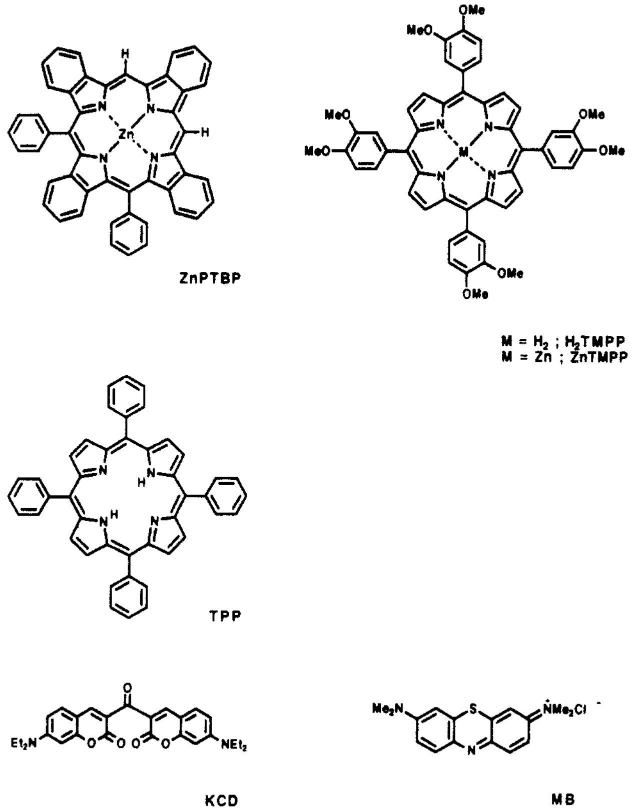


Table I. Absorption Properties of Sensitizers[a]

sensitizer[b]	λ_{max} in polymer (nm)	λ_{max} in solvent (nm)
TPP	420	420
ZnTMPP	431	427
H_2TMPP	428	425
ZnPTBP	436	431
KCD	461	460
MB	663	664[c]

[a] UV spectra were measured in a thin film of *p*-OxM-*co*-IPA or in $CHCl_3$. [b] See Scheme I for the structures of the sensitizers. [c] In H_2O.

Results and Discussion

Photooxidation of Oxazole Rings Attached to *p*-OxM-*co*-IPA. We attempted to apply a series of triplet sensitizers (Scheme I) to the photooxidation of the oxazole groups attached to a copolymer of OxM with an IPA (*p*-OxM-*co*-IPA) backbone. Table I summarizes the absorption properties of the dyes in solution and in polymer. It is clearly observed that the absorption of the dyes in a thin film of *p*-OxM-*co*-IPA is very similar to that in solution, suggesting that there is no specific interaction between the dyes and the matrix polymer, and the dye molecules are homogeneously dispersed in the matrix. Those dyes having triplet energies greater than 94.1 kJ/mol, which is an energy gap between singlet and triplet oxygen molecules, and possessing high quantum yields for triplet formation have been reported to be effective sensitizers for the generation of singlet oxygen in organic solutions.[2]

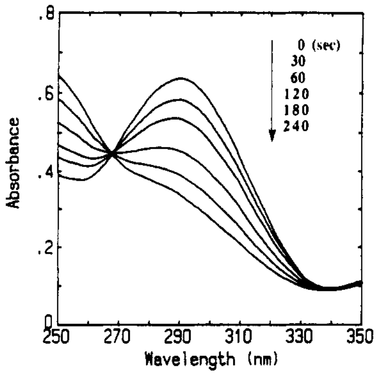


Figure 1. Spectral change of a thin film of *p*-OxM-*co*-IPA doped with 10 mol % TPP based on the oxazole units upon exposure to visible light.

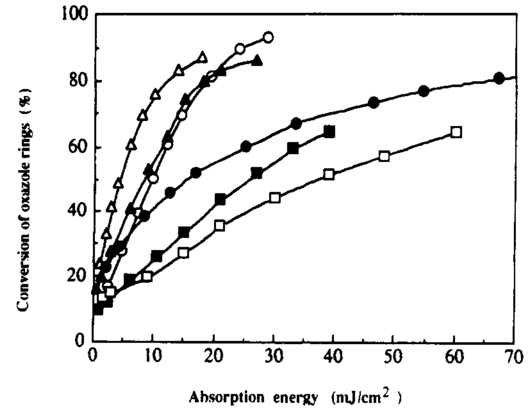


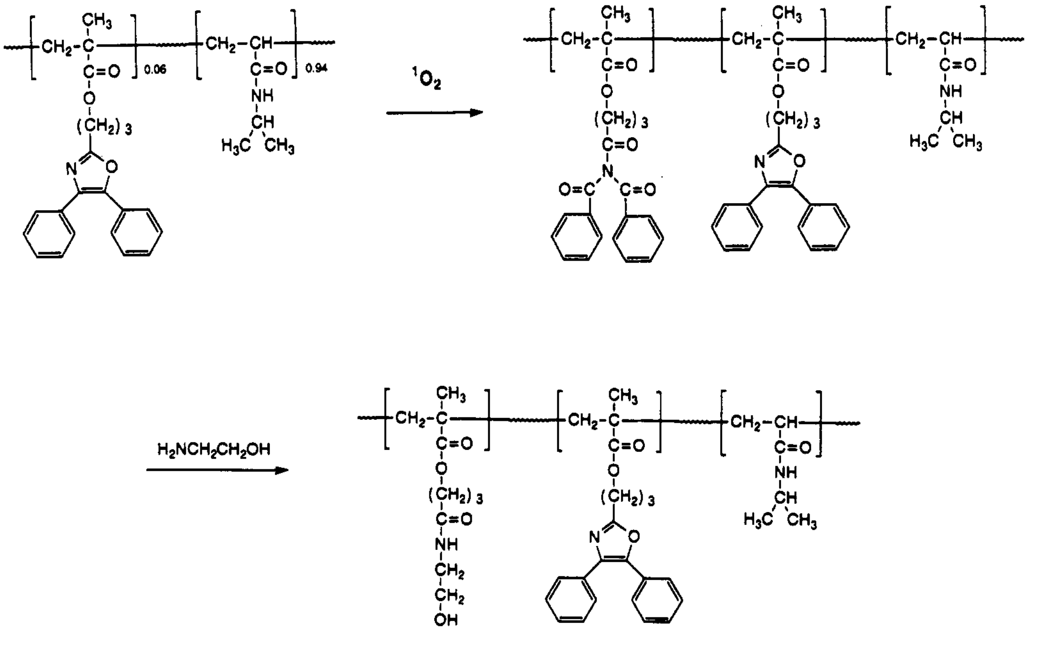
Figure 2. Conversion curves for photooxidation of the oxazole rings attached to *p*-OxM-*co*-IPA doped with 10 mol % dyes based on the oxazole units upon exposure to visible light: (△) ZnTMPP (irradiation wavelength; 588 nm); (○) MB (636 nm); (▲) TPP (659 nm); (●) ZnPTBP (598 nm); (■) KCD (505 nm); (□) H_2-TMPP (584 nm).

Figure 1 shows the spectral change of a thin polymer film (about 1.5 μm) doped with 10 mol % of TPP based on the oxazole units. The exposure of the thin film to the 569-nm light with 0.4 mW/cm^2 which was absorbed only by the Q-band of TPP led very quickly to photooxidation of the oxazole rings in the polymer (Scheme II). This suggests that very rapid quenching of the excited dye by triplet oxygen takes place in the film to generate singlet oxygen as a result of permeation of the atmospheric oxygen molecules into the polymer layer, and the singlet oxygen thus produced reacts with the oxazole acceptor to form the corresponding *N*,*N*-dibenzoylcarboxamide derivative, as Wasserman and co-workers reported on 2,4,5-trisubstituted oxazole compounds in solution.[8] When other dyes such as MB, H_2TMPP, ZnTMPP, ZnPTBP, and KCD were used as triplet sensitizers instead of TPP, it was similarly found that the absorption of the oxazole ring (λ_{max} = 290 nm) decreased with a slight consumption of the dyes. This finding enables us to construct panchromatic photoresists which give clear relief images with positive tone with sensitivity in a wide range of wavelength by the use of several dye molecules with various excited-state energies.

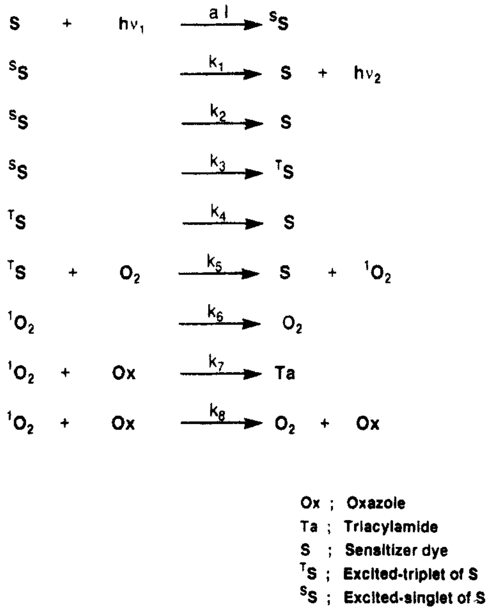
Figure 2 shows the conversion curves for the photooxidation of the films of *p*-OxM-*co*-IPA with about 1 μm thickness, in which a 10 mol % dye was doped on the basis of the oxazole units. The irradiation was carried out at an appropriate wavelength, at which these dyes had similar transmittance ranging from 75 to 90%. The consumption of the oxazole groups was plotted as a function of the absorption energy in order to compare the ability of the dyes for the singlet oxygen generation. The conversion of oxazole to the *N*,*N*-dibenzoylcarboxamide derivative was evaluated spectroscopically. As shown in the figure, the transformation of the oxazole groups into *N*,*N*-dibenzoylcarboxamide derivatives occurred with any dye used in this study. This means that these dyes act efficiently as triplet sensitizers, resulting in the generation of singlet oxygen. We showed previously that about 80% conversion of the oxazole groups was enough to remove the exposed part in an aqueous amine solution, making an image of positive tone in the thicker films. The mechanism of this photoimaging is shown in Scheme II.[6] Most of the dyes used in this study were capable of converting the oxazole groups to *N*,*N*-dibenzoylcarboxamide derivatives in well above 80% yields so that they can form an image. Particularly, TPP, ZnTMPP, and MB generate singlet oxygen more effectively in the polymer layer. On the other hand, the conversion for KCD and H_2TMPP did not go up to 80%, but this is due to insufficient irradiation energy.

Efficiency for Generation of $^1O_2$ by Sensitizers. To determine the efficiency for the generation of singlet

Scheme II. Process of This Photoimaging



Scheme III. Kinetics in the Photooxidation



oxygen by the sensitizers, the limiting quantum yields for the photooxidation were estimated from the consumption of the oxazole rings by the method reported by Yasuike et al. for the dye-sensitized photooxidation of (+)-limonene in solutions.[2d] If the dye-sensitized photooxidation of the oxazole rings in the rigid matrix can be described by the simple kinetics shown in Scheme III, we can obtain eq 1 by postulating the photostationary states for [$^1O_2$], [T_S], and [S_S]. Here, T_S and S_S are the first excited triplet and singlet states of photosensitizer S, respectively, and Ox and Ta are the oxazole groups and *N,N*-dibenzoylcarboxamide derivatives which are photooxidation products, respectively.

$$\frac{1}{\Phi(\mathrm{Ox})} = \frac{k_6}{\Phi(^1\mathrm{O}_2)\,k_7}\,\frac{1}{[\mathrm{Ox}]} + \frac{k_7 + k_8}{\Phi(^1\mathrm{O}_2)\,k_7} \qquad (1)$$

Equation 1 means that, if the rate constant k_7 is considerably greater than k_8, the reciprocal of the quantum yield $\Phi(\mathrm{Ox})$ for the dye-sensitized photooxidation of oxazole varies in proportion to the reciprocal of the oxazole concentration, and the limiting quantum yields will be given as the intercept at the y axis.

The double reciprocal plots are illustrated in Figure 3 when the photooxidation was carried out using either TPP or KCD as a sensitizer. Both plots gave straight lines at high concentrations of oxazole rings while at low concentrations the plots deviated from the straight line as clearly seen for the TPP-sensitized photooxidation (○ in Figure 3). This is presumably due to reduction in the collision frequency of singlet oxygen with the oxazole units attached to the polymer. At low concentration of the oxazole units in the system, singlet oxygen molecules produced in the vicinity of the sensitizer molecules must diffuse over a relatively long distance to encounter the oxazole units within the lifetime of the excited state. This situation explicitly results in a lowering of the quantum yield of the photooxidation. The initial assumption in the derivation of eq 1 fails under such a condition where the diffusion of singlet oxygen in the photosensitive layer appreciably affects the quantum yields for the consumption of the oxazole units. The kinetic scheme (Scheme III) may be applicable only to the initial stage of the reaction, since the diffusion of singlet oxygen molecules is not taken into account in this scheme.

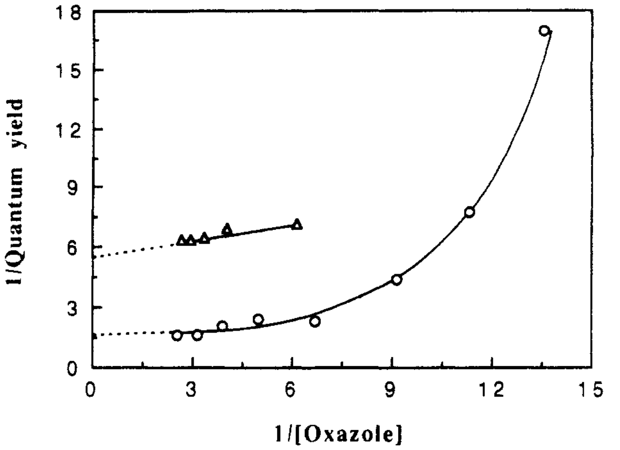


Figure 3. Double reciprocal plots of the oxazole concentration and the quantum yield for the dye-sensitized photooxidation of oxazole using either 10 mol % TPP (○) or KCD (△) based on the oxazole units. Irradiation wavelength: TPP, 659 nm; KCD, 505 nm.

Table II. Efficiency for the Generation of Singlet Oxygen by Various Triplet Sensitizers[a]

sensitizer[b]	efficiency for the generation of $^1O_2$
TPP	0.66
ZnTMPP	0.70
H_2TMPP	0.26
ZnPTBP	0.28
KCD	0.20
MB	0.60

[a] Limiting quantum yield for this photooxidation in a thin film of *p*-OxM-*co*-IPA doped with 10 mol % sensitizer. [b] See Scheme I for the structures of the sensitizers.

The limiting quantum yields, which reflect the efficiency for the generation of singlet oxygen, for these dyes could be calculated from the intercept of the straight line. The values for TPP and KCD were respectively 0.66 and 0.20. This indicates that TPP is more effective for the generation of active oxygen in the polymer. The limiting quantum yields for the photooxidation could similarly be estimated for other dyes which cover a wide range of spectral response and are summarized in Table II. The quantum yields of dyes in the polymer matrix were generally lower than that in solution, where TPP and ZnPTBP was 0.88[2c] and 0.40,[2d] respectively. It seems likely that the limiting quantum yield strongly depends on the efficiency of the singlet–triplet intersystem crossing of the sensitizer. Namely, the difference in the efficiency for the generation of singlet oxygen observed may be attributed mainly to the quantum yield of the triplet formation. In solution, a nonradiative process frequently dominates the fate of the singlet excited state of a dye, but this process involves the interaction of certain rotamers, which can easily be slowed down in a rigid matrix such as a polymer.[9] Furthermore, the lifetime and the diffusion coefficient of singlet oxygen are regarded to be rarely influenced by the kinds of sensitizers used.

Diffusion of $^1O_2$ in *p*-OxM-*co*-IPA. In the polymer matrix, the mobility of the sensitizer and the oxazole moiety is expected to be very small, and the only mobile reactants involved in the photooxidation are the excited-state oxygen $^1O_2$ and ground-state oxygen O_2 in Scheme III. As discussed previously, the diffusion of the singlet oxygen is a very important process in the photooxidation, so it is essential to evaluate how the diffusion affects the reaction. Figure 4 shows the consumption of the oxazole moieties as a function of the average distance between TPP used as a sensitizer and the oxazole moiety when the film absorbed an energy of 15 mJ/cm^2. The distance was

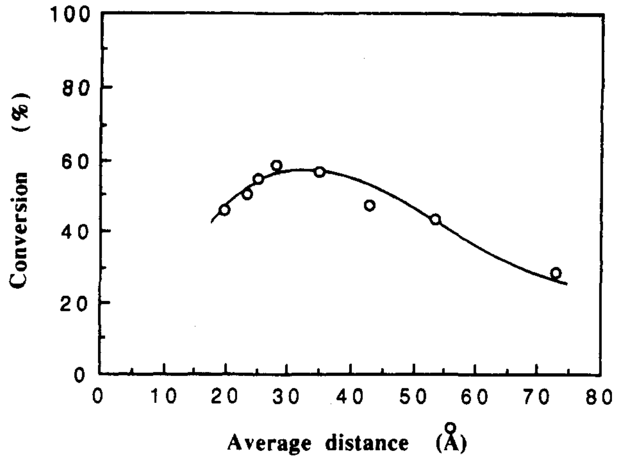


Figure 4. *Efficiency for the photooxidation of the oxazole rings as a function of the average distance between sensitizer TPP and the oxazole moiety. The energy absorbed by the film was kept constant (15 mJ/cm^2).*

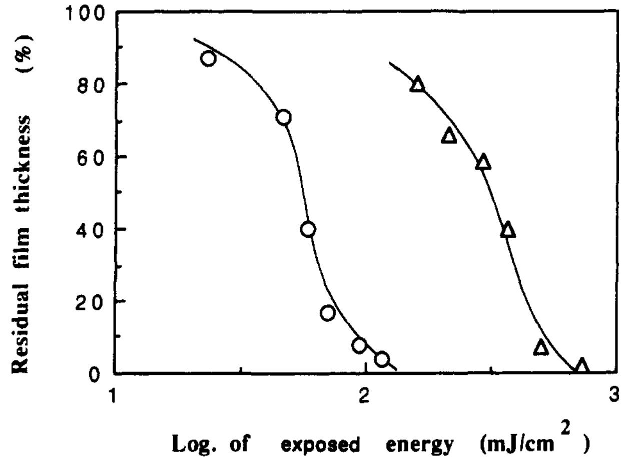


Figure 5. Sensitivity of *p*-OxM-*co*-IPA doped with 2 mol % sensitizer (film thickness, 1.5 μm): (○) TPP, 410-nm light of 0.38 mW/cm^2; (△) ZnPTBP, 632-nm light of 2.4 mW/cm^2.

varied by the concentration of TPP in the polymer film, and the average distance was estimated on the basis of the assumption that TPP is located at the center of a sphere and the oxazole moiety exists at the periphery of the sphere whose volume can be calculated from the concentration of TPP doped in the polymer. The conversion showed a maximal value at a distance of about 30 Å, and it decreased at shorter and longer distances. At distances above 30 Å, the reduction of the conversion may be interpreted in terms of the diffusion of singlet oxygen in the polymer. This suggests that the oxygen permeability of the polymer matrix is a dominant factor in this region. At a distance below 30 Å, the decrease may result from a self-quenching of sensitizer molecules, which leads to suppression of the singlet oxygen generation.

Sensitivity of *p*-OxM-*co*-IPA for Imaging Formation. In practice, the energy required for the formation of an image is important. Figure 5 shows the characteristic curves for the photooxidation of copolymer films with about 1.5 μm thickness, in which either TPP or ZnPTBP was doped. The residual thickness is plotted as a function of the irradiation energy in this figure. A thin film doped with TPP or ZnPTBP was exposed to 410-nm light of 0.38 mW/cm^2 or 632-nm light of 2.4 mW/cm^2, respectively. From this result, it is evident that the photosensitivity of the copolymer containing TPP and ZnPTBP as a sensitizer was about 100 and 500 mJ/cm^2, respectively. It seems that this difference is primarily attributable to the absorbance at the irradiated wavelength and the efficiency of singlet oxygen generation. Another factor may be the reciprocity failure which is induced by the intensity of the irradiated light. Figure 6 shows the conversion of the oxazole groups into *N,N*-dibenzoylcarboxamide derivatives in the thin films (about 1.0 μm) on photoirradiation. The film was exposed to monochromatic light at 569 nm, in which transmittance was above 90%, with an energy of either 0.4 or 4.3 mJ/cm^2. In both cases, the irradiation led to a similar photooxidation of the oxazole rings, indicating that the photosensitivity was independent of the light intensity. On the other hand, when the same experiment was carried out with a sample with a thickness of more than 3 μm, the reciprocity failure was less evident. Thus, the lower the intensity of light, the faster the photooxidation resulted. This implies that the reciprocity failure is dependent on the film thickness. In other words, when high-intensity light is used, an insufficiency of oxygen molecules takes place; that is, the permeability of the atmospheric oxygen into the polymer layer becomes a rate-determining step.

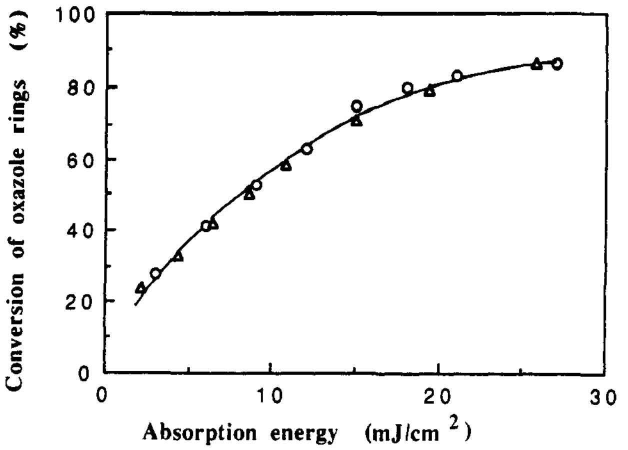


Figure 6. Relationship between the absorbed energy and the conversion of the oxazole groups attached to *p*-OxM-*co*-IPA doped with 10 mol % TPP exposed to 569-nm light of either 0.4 (○) or 4.3 mW/cm^2 (△).

In summary, oxazole rings attached to a copolymer of OxM with IPA were transformed efficiently to the corresponding *N,N*-dibenzoylcarboxamide derivatives in a thin film by photooxidation using many dyes, which include KCD[9] using an Ar$^+$ laser (488 and 514 nm) and ZnPTBP[10] using a He–Ne laser (633 nm) to generate singlet oxygen, and were applicable to the present imaging system. This system enables us to form an image by light of a wide range of wavelengths. The quantum efficiency for the generation of singlet oxygen was in the range of 0.2–0.7, depending upon the sensitizers used in the system. The conversion showed a maximal value when the average distance between the oxazole rings and sensitizer molecules was about 30 Å.

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