Sensitivity and Sensitization Mechanism of Halomethylated Polystyrene to Near UV Region

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Synopsis

Bromo- and chloromethylated polystyrene (BCMS) prepared for an X-ray resist was sensitized to near UV region by addition of some sensitizers. Among them, 2, 4-diisopentylthioxanthone (DITX) and Michler's ketone were found to be efficient sensitizers for BCMS and related polymers under irradiation with a high pressure mercury lamp. To investigate the sensitization mechanism, IR and UV spectra were measured with the BCMS/DITX system under light irradiation. From the results, together with those of oxygen and radical scavenging effects on sensitivity of the polymer, it was suggested that hydrogen abstraction of the triplet state of DITX from the polymer induces photocrosslinking between the polymer chains.

INTRODUCTION

In recent microlithography such as in producing microelectronic devices, resist materials (which is used as image carriers) are required to show high resolution and high sensitivity to electron-beam radiation, X-ray radiation, and/or UV radiation, as well as high resistance to dry etching.[1-3] As an electron-beam resist with high resistance to dry etching, chloromethylated polystyrene (CMS) was developed recently.[4] Considering the strong correlation between chemical processes of polymers induced by X-ray radiation and those by electron-beam radiation,[1,3] polystyrenes and/or CMS can be modified to exhibit desirable characteristics to X-ray radiation.

Actually, two of the present authors have recently synthesized some bromo- and chloromethylated polystyrenes (BCMSs) (Fig. 1), and have found that BCMS exhibits high sensitivity and high resolution as an X-ray resist.[5] Because these polymers do not absorb light longer than 250 nm, BCMS itself can not be used as a photopolymer.

Under these circumstances, we have undertaken the sensitization of BCMS to near UV region by the addition of some sensitizers, and investigated the characteristics of BCMS/sensitizer systems.

To get insight into the mechanism of photocrosslinking of BCMS/sensitizer systems, IR and UV spectra of BCMS/2, 4-diisopentylthioxanthone (DITX) have been measured with thin films of the sample under UV light irradiation, and compared with the results obtained by X-ray radiation. Furthermore, oxygen effect on the sensitizer, DITX, has also been investigated for the *p*-xylene solution from the results of UV absorption spectra.

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$$-(CH_2-CH)_l-(CH_2-CH)_m-$$

$$l : m = 55 : 45$$

$$-(CH_2-CH)_l-(CH_2-CH)_m-(CH_2-CH)_n-$$
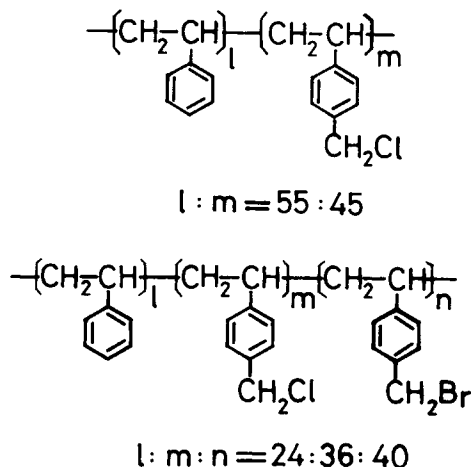
$$l : m : n = 24 : 36 : 40$$

Fig. 1. Chemical structures of chloromethylated polystyrene (CMS) (the top) and bromo- and chloromethylated polystyrene (BCMS) (the bottom).

EXPERIMENTAL

Materials

DITX (Toshin Kayacure) and Michler's ketone [4, 4'-bis-(dimethyl-amino)benzophenone] (MK) (British Drug Houses) used as sensitizers were purified by repeated recrystallization from ethanol three times. DITX was further purified by vacuum sublimation. Other sensitizers employed were used as supplied. Ethanol and p-xylene (Kanto G. R. grade) used as solvents were purified by fractional distillation. CMS and BCMS (Fig. 1) were supplied from Toyo Soda Co., and polymethylstyrene (PMS), from Japan Synthetic Rubber Co. These are used without further purification.

Photosensitive compositions were prepared by dissolving 1 g of sensitizer (i.e., DITX, etc.) and 10 g of polymer into 100 mL of p-xylene. These were spin-coated on Si wafers and prebaked at 80–120°C for 15–25 min.

MEASUREMENTS

Photosensitive layer on a Si wafer was irradiated with a 250 W high pressure mercury lamp (Ushio USH-250D) equipped with a Mikasa manipulator Model MA-5. After developing with 2-ethoxyethanol/isopentylacetate (58 : 42 for BCMS, 65 : 35 for CMS) and with 1-acetoxy-2-ethoxyethane for PMS, and rinsing with 2-propanol followed by post-baking at 80–90°C for 10–15 min, residual film thickness t, was measured with an interferometer (Nikon surface finish microscope). Compared with the initial film thickness, t_0 ($\simeq 0.5$ μm), gel fraction (i.e., t/t_0) was determined as a function of irradiated incident energy of the high pressure mercury lamp in the wavelengths shorter than 430 nm to give characteristic curves. Sensitivity of photosensitive materials was defined to be the incident energy at which the gel formation initiates (D_g^i) and/or the gel fraction reaches to 0.5 ($D_g^{0.5}$).

Spectral sensitivity of the photosensitive materials were measured with a Narumi RM23 spectrophotometer equipped with a 450 W medium pressure
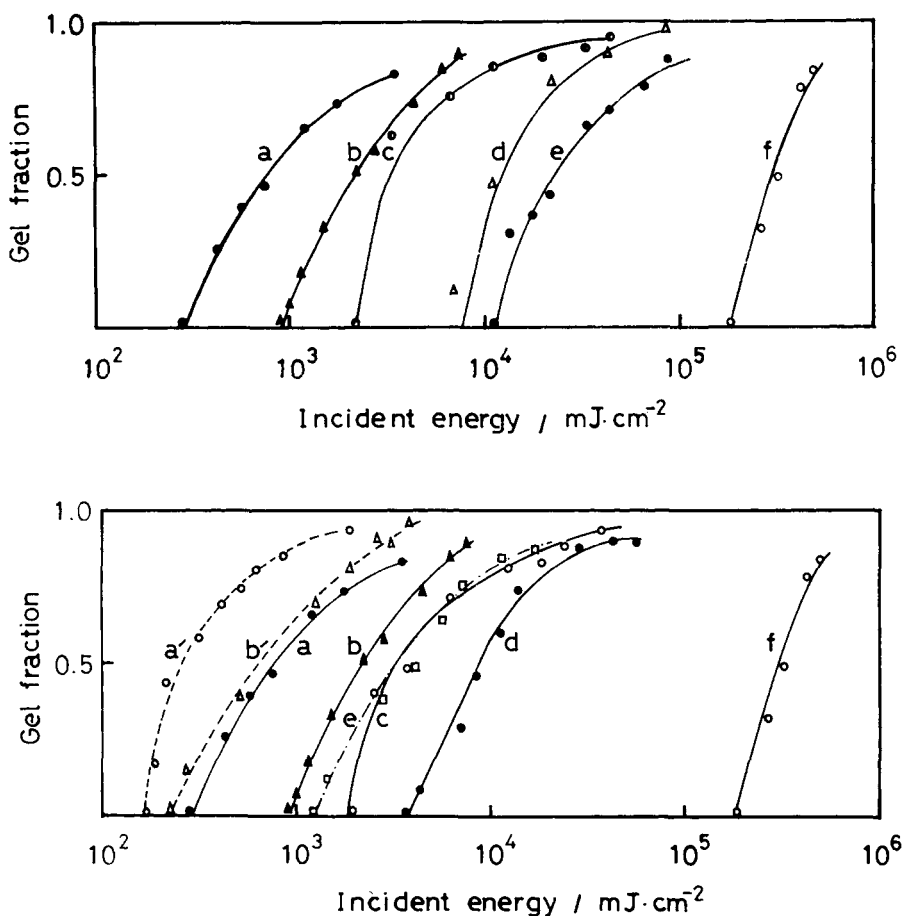
Fig. 2. (A). Characteristic curves for BCMS/sensitizer systems in air. Sensitizer: (a) MK; (b) DITX; (c) DABA; (d) MNQ; (e) CHBA; (f) none. (B). Characteristic curves for some polymer/sensitizer systems: (a) BCMS/MK in air; (a′) BCMS/MK in N$_2$; (b) BCMS/DITX in air; (b′) BCMS/DITX in N$_2$; (c) PMS/DITX in air; (d) CMS/DITX in air; (e) BCMS/DITX/HQ in air; (f) BCMS in air.

mercury lamp. UV absorption spectra of the BCMS/DITX system in p-xylene (a cell of 1 cm light path length being used) and on a quartz plate (sample thickness is ~ 1 μm) were measured with a Hitachi 200-20 recording spectrophotometer. IR spectra of ~ 20 μm thick films of BCMS/DITX, which were prepared on and stripped off from a Sn plate, were measured with a Hitachi 295-10 infrared spectrophotometer. Degassed solutions were prepared by freeze–pump–thaw cycles under background pressure of 5×10^{-5} Torr.

RESULTS AND DISCUSSION

Characteristic Curves for BCMS Systems

Figure 2 shows the characteristic curves measured with some BCMS/sensitizer systems. Preliminary experiments revealed that addition of 10 wt % of

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TABLE I

Sensitivity of Some BCMS/Sensitizer Systems under Irradiation with a
High Pressure Mercury Lamp

Sensitizer	Atmosphere	Content (wt %)	D_g^i (mJ/cm^2)	$D_g^{0.5}$ (mJ/cm^2)	Relative sensitivity
none	Air	—	107,000	232,000	1
CHBA[a]	Air	10	8,910	17,800	13
MNQ[b]	Air	15	8,190	9,800	24
DABA[c]	Air	10	1,780	2,500	93
DITX	Air	10	930	2,260	103
	N$_2$	10	236	645	360
DITX/HQ[d]	Air	10	1,230	3,580	65
MK	Air	10	377	587	395
	N$_2$	10	167	263	882

[a] 11-Chloro-6-hydroxybenzanthrone.
[b] 2-Methyl-1,4-naphthoquinone.
[c] p-Dimethylaminobenzaldehyde.
[d] p-Dihydroxybenzene (hydroquinone).

DITX, MK, 11-chloro-6-hydroxybenzanthrone (CHBA), and p-dimethyl-aminobenzaldehyde (DABA), and 15 wt % of 2-methyl-1,4-naphthoquinone (MNQ) makes each sensitizer/BCMS system most sensitive to UV light irradiation by a high pressure mercury lamp. Sensitivities (D_g^i and $D_g^{0.5}$) of the systems are listed in Table I. Sensitivity of BCMS itself is low (2.3×10^5 mJ/cm^2), and BCMS is not practically insolubilized by a high pressure mercury lamp. By the addition of DITX and MK, BCMS markedly enhances its sensitivity (~ 100 and ~ 400 times, respectively). Figure 3 shows a spectral sensitivity of the BCMS/DITX system compared with that of BCMS itself. While BCMS is sensitive only to the light shorter than 280 nm, BCMS/DITX extends its spectral region to 405 nm, revealing that optical sensitization has taken place in the BCMS/DITX system.

By flushing nitrogen gas under light irradiation, sensitivity of both the BCMS/DITX and BCMS/MK systems further increases as much as 3.5 and 2.2 times, respectively, compared with the corresponding aerated samples [Fig. 2(B) and Table I]. This result together with desensitization by p-dihydroxy-benzene (hydroquinone) (HQ) for the BCMS/DITX system (Table I) clearly suggests that, in BCMS/DITX, BCMS is sensitized through radical inter-mediate(s) originated from DITX.

To examine the ability of DITX as a sensitizer, DITX was also added to CMS and PMS; the results are shown in Figure 2(B). CMS and PMS without the sensitizer are not practically insolubilized by the high pressure mercury lamp ($D_g^i > 10^5$ mJ/cm^2). The fact that PMS is effectively sensitized by DITX as well as CMS and BCMS strongly suggests that α-hydrogen abstraction by DITX is the effective photoinitiation step for photocrosslink formation of the polymers under study. This is compared to BCMS irradiated with X-ray where the experimental results[5] strongly suggest that the formation of
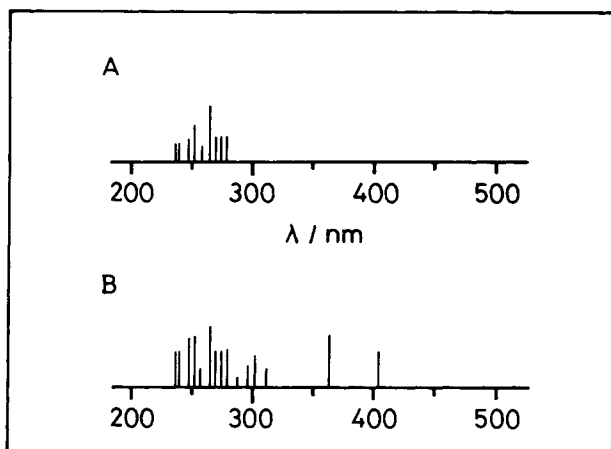
Fig. 3. Spectral sensitivity of (A) BCMS and (B) BCMS/DITX.

halogen (i.e., Cl and Br) radicals by secondary electrons is essential for crosslink formation.

The quantum yield of photocrosslink formation, ϕ, for the BCMS/DITX system was evaluated according to the following equation[6]:

$$2.303 E_g D\phi = rd/\overline{M_W}$$

where E_g is the gel point exposure (einstein/cm^2) and D, the optical density (i.e., absorbance) of the BCMS/DITX film of thickness r and of specific gravity d, and $\overline{M_W}$ is the weight average molecular weight of BCMS (10.8 × 10^4). With the use of UV33 filter, D_g^i was measured. Considering the absorption spectrum of the system and the spectral energy distribution of the mercury lamp, $E_g \times D$ value is evaluated to be 2.8 × 10^{-7} einstein/cm^2 for the film of 1.2 μm thickness, and ϕ is determined to be 0.002 assuming $d \simeq 1$. The low quantum yield for the system may correspond to the weak reaction through hydrogen abstraction.[7,8]

The sensitivity for some polymer/DITX systems is compared in Table II, where to take into account the effect of degree of polymerization ($\overline{DP}$) on the measured sensitivity, reciprocal value of $D_g^i \times \overline{DP}$ is taken as an index of relative sensitivity.[9] In the present case where the substituted benzene groups pertain to the reactivity of hydrogen abstraction, content x of the substituted benzene groups are further included in the estimation of relative sensitivity. The results are listed in Table II. The sensitivity of BCMS increases as more halomethyl groups are introduced. Reactivity of the pendent groups to photocrosslink formation by DITX is estimated to be in the order:$-C_6H_4 \cdot CH_2Br > -C_6H_4 \cdot CH_2Cl > -C_6H_4 \cdot CH_3$.

IR SPECTRA OF THE BCMS / DITX SYSTEM

To investigate the photocrosslinking mechanism of the BCMS/DITX system in detail, IR spectra were measured with the BCMS/DITX films (of

TABLE II
Sensitivity of Some Polymer/DITX Systems under Irradiation with a High Pressure Mercury Lamp

Polymer	$\bar{M}_w^a$ ($\times 10^4$)	$\bar{M}_w/\bar{M}_n^a$	$\bar{DP}^b$	x^c	D_g^i (mJ/cm^2)	$D_g^{0.5}$ (mJ/cm^2)	$D_g^i \cdot \bar{DP}$ ($\times 10^5$)	$D_g^i \cdot \bar{DP} \cdot x$ ($\times 10^5$)
BCMS	10.8	1.18	681	0.76	930	2260	6.2	4.7
BCMS^d	12.2	1.11	768	0.50	1290	3610	9.9	5.0
CMS	13.0	1.14	1040	0.45	3470	8600	36	16
PMS	16.3	1.53	1380	1.00	1930	3610	27	27

^{a}Weight average ($\bar{M}_w$) and number average ($\bar{M}_n$) molecular weights determined by gel permeation chromatography.
^{b}Average degree of polymerization.
^{c}Number ratio of methylated or halomethylated phenyl groups to all the pendent groups.
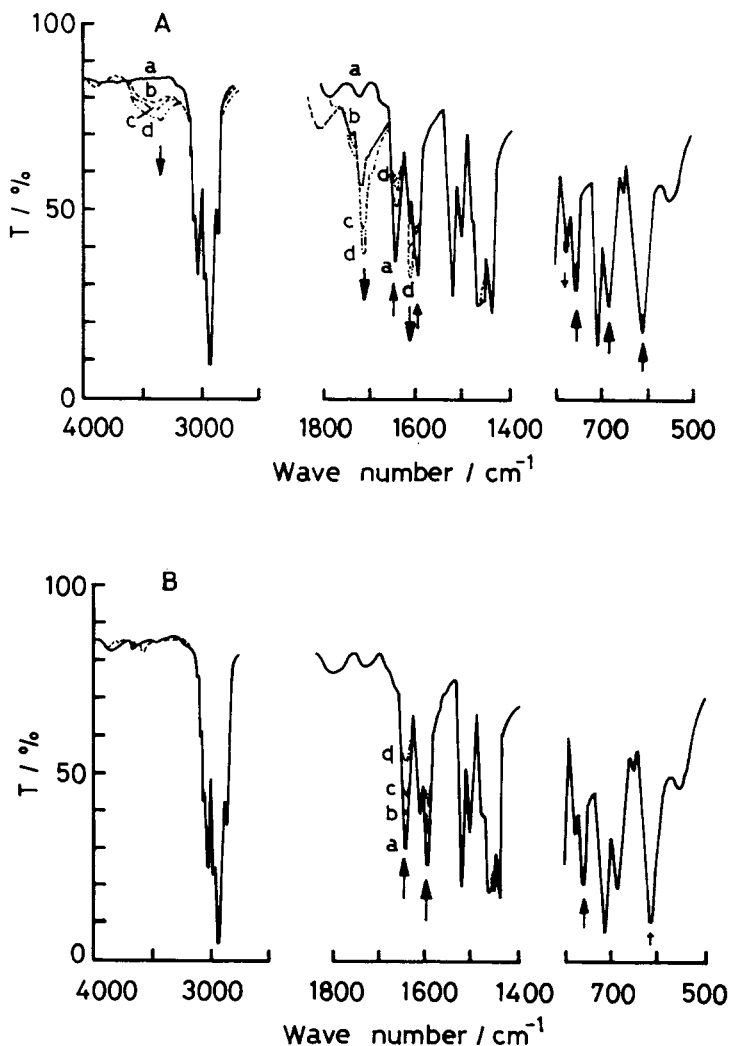^{d}BCMS with $l : m : n = 50 : 22 : 28$ (see Fig. 1).

Fig. 4. (A). IR spectra measured with BCMS/DITX (of 19 μm thickness) in air irradiated for (a) 0, (b) 30, (c) 60, and (d) 90 min. (B). IR spectra measured with BCMS/DITX (of 27 μm thickness) in nitrogen atmosphere irradiated for (a) 0, (b) 15, (c) 30, and (d) 120 min.

~ 20 μm thickness) under irradiation with the high pressure mercury lamp. The results in air and nitrogen atmospheres are shown in Figures 4(A) and 4(B), respectively. In the aerated sample [shown in Fig. 4(A)], as the 1645, 1595, and 750 cm^{-1} bands assigned to DITX[10,11] decrease their intensities, the C—Cl stretching (675 cm^{-1}) and C—Br stretching (610 cm^{-1}) bands[12] of BCMS slightly decrease their intensities, and new bands at ~ 3400, 1710, and 1605 cm^{-1} appear markedly. When the sample is irradiated under flushing nitrogen gas [Fig. 4(B)], decrease in intensity of the DITX bands becomes slower, and intensity change of the C—Cl and C—Br stretching bands of BCMS becomes negligibly small. Furthermore, the broad 3400 cm^{-1} band and sharp 1710 and 1605 cm^{-1} bands do not appear.

IR spectra of the pure BCMS films were also measured. By irradiating the aerated sample for 3–7 h, the C—Cl and C—Br stretching bands slightly decrease their intensities, and only the 1710 cm^{-1} band appears markedly (~ 3400 and 1605 cm^{-1} bands are not observed), as the 740 cm^{-1} band of BCMS decreases its intensity. In the case of X-ray (Rh, L$_\alpha$ 4.6 Å) irradiation to BCMS,[5] both the C—Cl and C—Br stretching bands decrease their intensities more prominently, and the C—Cl band decreases more than the C—Br band; consequently, the C—Cl bond cleavage caused by secondary electrons is thought to be responsible for crosslinking of BCMS.[5,13] In the case of BCMS/DITX irradiated with the high pressure mercury lamp, only the slight (or negligible) decrease in intensity of the C—Cl and C—Br bands was observed. This may be consistent with the conclusion that the photocrosslinking of BCMS/DITX proceeds through hydrogen abstraction by DITX in the triplet state rather than the C—Cl and C—Br bond cleavage.

The new bands observed at ~ 3400, 1710, and 1605 cm^{-1} appear only when oxygen is present in atmosphere. Considering that sensitivity ($D_g^{0.5}$) in nitrogen is higher than in air, these bands may be originated from reaction(s)
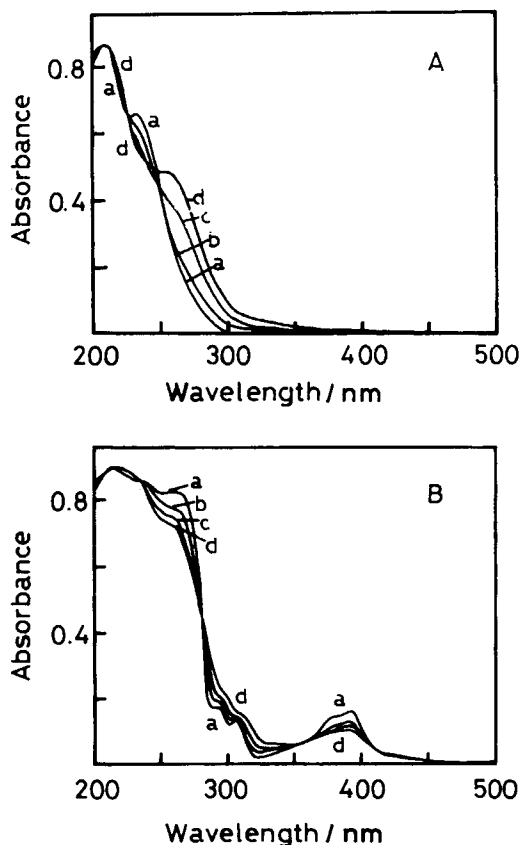

Fig. 5. (A). Near UV absorption spectra measured with BCMS on a quartz plate irradiated with a low pressure mercury lamp for (a) 0, (b) 20, (c) 50, and (d) 90 min. (B). Near UV absorption spectra measured with BCMS/DITX (10 : 3) on a quartz plate irradiated with a high pressure mercury lamp for (a) 0, (b) 5, (c) 15, and (d) 45 min.

which pertains to oxygen and competes with crosslinking. Based on the considerations, the 3400 and 1710 cm^{-1} bands may probably be associated with the formation of hydroperoxide as is suggested for polystyrene[14] and other polymers.[15,16] The 1710 cm^{-1} band may be assigned to the formation of aliphatic ketones.[16]

UV ABSORPTION SPECTRA OF THE BCMS / DITX SYSTEM

UV absorption spectra of BCMS and BCMS/DITX films on quartz plates were measured under 253.7 nm light irradiation with a low pressure mercury lamp and under longer wavelengths light irradiation with a high pressure mercury lamp, respectively; the results are shown in Figures 5(A) and 5(B). In Figure 5(B), as the 392 nm band of DITX decreases, increase of ~ 300 nm region due to spectral change of BCMS is observed, revealing that BCMS is sensitized by DITX and photocrosslinking has taken place as is actually
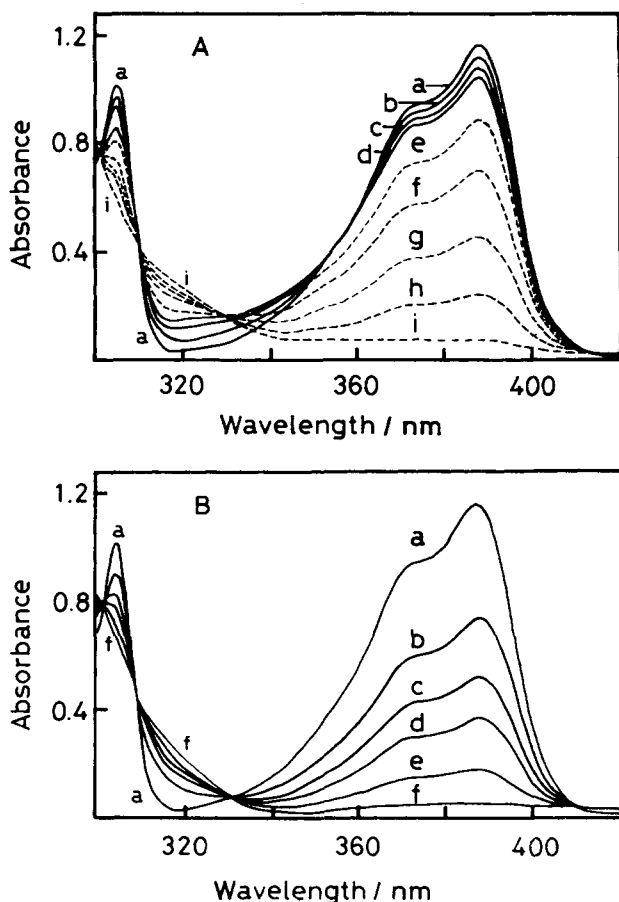
Fig. 6. Near UV absorption spectra measured with (A) aerated and (B) deaerated p-xylene solution of DITX ($1.88 \times 10^{-4}M$). By the use of a UV35 filter, $\lambda > 350$ nm light from a 1 kW high pressure mercury lamp was irradiated on (A) aerated solution for (a) 0, (b) 20, (c) 27.5, (d) 33, (e) 34.5, (f) 35.5, (g) 37, (h) 39, and (i) 42 min, and on (B) deaerated solution for (a) 0, (b) 31, (c) 51, (d) 73, (e) 114, and (f) 224 s.
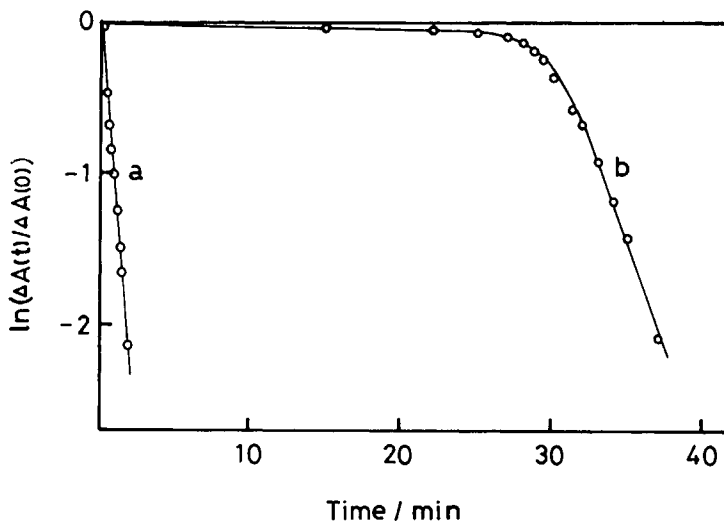
Fig. 7.   Time dependence of absorbance at 388 nm of (a) deaerated and (b) aerated p-xylene solution of DITX irradiated with $\lambda > 350$ nm light.

realized from the fact that the film on quartz plate is insoluble to 2-ethoxyethanol/isopentylacetate solution.

In order to investigate oxygen effect on photochemical initial process of DITX, UV absorption spectra were measured with aerated and deaerated p-xylene solution of DITX under the light ($\lambda > 350$ nm) irradiation. Spectral change is shown in Figure 6, and the absorbance at 388 nm, $\Delta A(t) = A(t) - A(\infty)$, is plotted against irradiation time in Figure 7. In the aerated solution, the 388 nm band decreases very slowly at the initial stage (in the present experiment, within ~ 30 min) of light irradiation with an isosbestic point at 360 nm. This is due to the dissolved oxygen,[8] which quenches the triplet state of DITX, and hence reduces the subsequent reaction, i.e., formation of ketyl radical of DITX by hydrogen abstraction from the solvent. Oxygen also reacts with the ketyl radical to form peroxy radical. These cause slow photoreaction of DITX and slightly different UV spectrum.

Absorption spectrum of p-xylene solution of the BCMS/DITX system is essentially the same as the one of DITX (in the longer wavelengths than 300 nm). In Figure 8, absorbance at 388 nm of the deaerated solutions of BCMS/DITX with various concentrations of BCMS is plotted against irradiation time. From the slope of the straight line, the relative rate constant k for the photochemical reaction of DITX has been determined: the k value (10^{-2}s^{-1}) is 1.8, 1.5, 1.3, 1.6, and 1.6 for [BCMS]/[DITX] = 0, 10, 30, 60, and 120, respectively. The k value reaches minimum at [BCMS]/[DITX] = $\sim$ 30. Elucidation of the effect needs further study.

The phosphorescence lifetime of 2-methyltetrahydrofuran solution of DITX has been measured at 77 K. The lifetime observed at 460 nm is $\sim$ 160 ms for the deaerated solution. The addition of BCMS does not change the lifetime. This result may also support the hydrogen abstraction mechanism rather than the energy transfer (from DITX in the triplet state to BCMS) mechanism as a plausible photocrosslinking mechanism for the BCMS/DITX system.
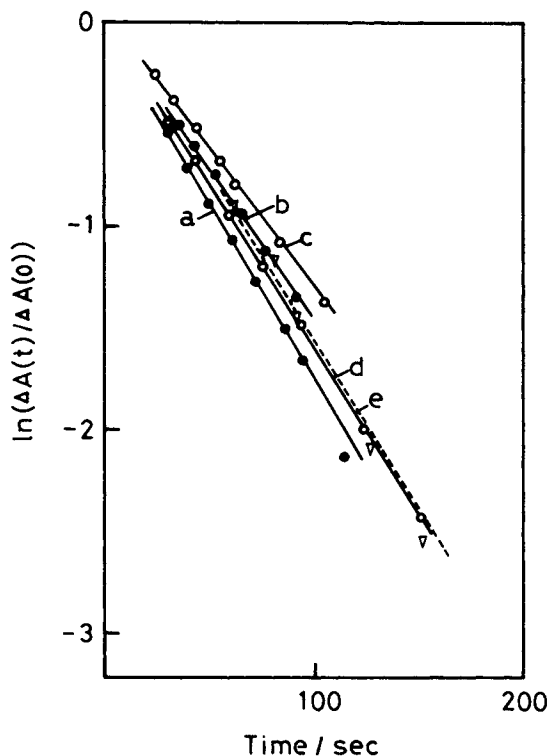
Fig. 8. Time dependence of absorbance at 388 nm of deaerated *p*-xylene solution of BCMS/DITX irradiated with λ > 350 nm light. BCMS/DITX composition in weight is (a) 0 : 1, (b) 10 : 1, (c) 30 : 1, (d) 60 : 1, and (e) 120 : 1.

CONCLUSION

DITX and MK were found to be efficient (as high as 100 and 400 times, respectively) sensitizers for BCMS. In nitrogen atmosphere, BCMS is further sensitized effectively (2–3.5 times), revealing that radical intermediate plays an important role in photosensitization.

Measurement of IR spectra of BCMS/DITX under UV irradiation in nitrogen atmosphere showed that the C—Cl and C—Br stretching band intensities do not decrease appreciably, in contrast to the case of BCMS irradiated with X-ray. This result, together with the fact that PMS is sensitized effectively by DITX, strongly suggests that the C—Cl and C—Br bond cleavage is not essential for photocrosslinking of BCMS. Furthermore, the quantum yield of photocrosslink formation for the BCMS/DITX system is found to be low (0.002), and the phosphorescence lifetime of DITX in 2-methyltetrahydrofuran is unaffected by the addition of BCMS. All the experimental results mentioned above strongly suggest that hydrogen abstraction of DITX in the triplet state is a plausible mechanism for photocrosslinking of the BCMS/DITX system.

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