

ANTHRACENE-SENSITIZED PHOTOLYSIS OF ONIUM TETRAKIS(PENTAFLUOROPHENYL)BORATE CATIONIC PHOTOINITIATORS

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Abstract – Sensitized photolysis of two onium borates (diphenyliodonium and dimethylphenacylsulfonium tetrakis(pentafluorophenyl)borate, **1a** and **2a**, respectively) and cationic photopolymerization of an epoxy monomer by the photolysis were investigated. The onium borates were sensitized by the excited singlet of the anthracenes (non-substituted-, 9-methyl-, and 9,10-dimethylantracene) and generated acid by decomposing themselves. The quantum yields of photobleaching of the anthracenes (ϕ_{AH}) and acid generation (ϕ_{acid}) by the onium borates were the same order as those of the corresponding onium salts in aerated solutions (methanol and acetonitrile) and in argon (Ar) saturated acetonitrile. However, in the photolysis of the iodonium borate **1a** in Ar saturated MeOH, ϕ_{acid} was much higher than the corresponding ϕ_{AH} . The acid generated by the photolysis of the onium borates initiated cationic polymerization of an epoxy monomer. The values of both rate of polymerization (R_p) and degree of conversion on the photopolymerization for the iodonium borate **1a** were higher than those of the sulfonium borate **2a**. In the photopolymerization for the iodonium borate **1a**, both the R_p value and the degree of conversion increased upon the addition of glycerol as a hydrogen donor. It is suggested that the increase of both values may be caused with the increase of ϕ_{acid} by addition of glycerol.

INTRODUCTION

Cationic photopolymerization is a technology used in many fields: UV-curing, photolithography, photo-imaging applications. Onium salts are a typical cationic photoinitiator. They decompose after absorbing light, generate acid, and initiate cationic polymerization of an epoxy monomer.¹ In particular, diaryliodonium,²⁻¹⁵ triarylsulfonium,⁶⁻²⁰ and phenacylsulfonium²¹⁻²⁴ salts are important onium salts for photopolymerization of an epoxy monomer. Since most of these onium salts themselves absorb light significantly only below *ca* 300 nm, technologically useful spectral response requires that photolysis of the onium salts are spectrally sensitized. Therefore, sensitized photolysis^{5-14,16,17} as well as direct photolysis^{2-5,14,15,17-20,22-24} of the onium salts have been investigated.

Recently, Priou *et al.* reports that the diaryliodonium tetrakis(pentafluorophenyl)borates serve as an efficient photoinitiator for cationic polymerization of epoxy monomers.^{25,26} The iodonium borates have higher reactivity and solubility for epoxy monomers, and less toxicity than the corresponding onium salts. However, photosensitization of the iodonium borates has not been investigated.

We have investigated the sensitized radical polymerization of acrylate monomers with the other onium borates.^{27,28} In the present paper, we report sensitized photolysis of new

dimethylphenacylsulfonium borate as well as the iodonium borate by anthracenes as a sensitizer and cationic photopolymerization of an epoxy monomer by the photolysis.

MATERIALS AND METHODS

Materials. Acetonitrile (MeCN), methanol (MeOH) (Merck, spectral grade), hexane (Merck, HPLC grade), cyclohexanone, dichloromethane, and diethyl ether (Kanto Chemical Co., Inc.) were used as received. Anthracene (**An**), 9-methylantracene (**MAN**), 9,10-dimethylantracene (**DMAN**), diphenyliodonium hexafluorophosphate (**1d**), dimethylphenacylsulfonium tetrafluoroborate (**2e**), and acridine were obtained from Tokyo Chemical Industries Co., Ltd. Decane, biphenyl, iodobenzene, 2-, 3-, and 4-iodobiphenyl, dimethylsulfide, acetophenone, and pentafluorobenzene were obtained from Tokyo Chemical Industries Co., Ltd. as authentic samples of photoproducts. 3,4-Epoxy-cyclohexylmethyl-3',4'-epoxycyclohexane carboxylate (ERL-4221, Union Carbide Chemical and Plastics Co. Inc.), lithium tetrakis(pentafluorophenyl)borate (Tosoh Akzo Co.), and sodium tetraphenylborate (Wako Pure Chemical Ind., Ltd.) were purchased. Crystal violet lactone (CVL), poly(methylmethacrylate) (PMMA, $M_w=996,000$), and poly(vinylalcohol) (PVA, 99% hydrolyzed, $M_w=124,000\sim 186,000$) were obtained from Aldrich Chemical Co., Inc. Diphenyliodonium tetrakis(pentafluorophenyl) borate (**1a**),²⁵ dimethylphenacylsulfonium bromide,²² dimethylphenacylsulfonium butyltriphenylborate (**2c**),²⁷ and

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dimethylphenacylsulfonium hexafluorophosphate (**2d**)²² were prepared according to the reported procedure. The preparations of dimethylphenacylsulfonium tetrakis(pentafluorophenyl)borate (**2a**) and dimethylphenacylsulfonium tetraphenylborate (**2b**) are carried out as follows:

Dimethylphenacylsulfoniumtetrakis(pentafluorophenyl)borate (2a). 5.30 g (*i.e.*, 20.3 mmol) of dimethylphenacylsulfonium bromide²² was dissolved in 100 mL of water in a 300 mL Erlenmeyer flask. 13.93 g (*i.e.*, 20.3 mmol) of lithium tetrakis(pentafluorophenyl)borate dissolved in 100 mL of water was added dropwise. The mixture was left to stand for 30 min with stirring and then filtered. The residual product was washed with water and then dried in the dark over night in *vacuo*. 14.45 g of dimethylphenacylsulfonium tetrakis(pentafluorophenyl)borate (**2a**) was obtained (with a yield of 83 %, mp 202-204°C (*dec.*)). ¹H NMR (DMSO-*d*₆) δ 2.97 (s, 6H, Me₂S⁺), 5.43 (s, 2H, COCH₂), 7.60-7.69 (m, 2H, *m*-PhCO), 7.75-7.82 (m, 1H, *p*-PhCO), 8.00-8.08 (m, 2H, *o*-PhCO); ¹³C NMR (DMSO-*d*₆) δ 24.82 (s, Me₂S⁺), 53.03 (s, COCH₂), 123.5 (sm, C₆F₅B⁻), 128.49 (s, *o*-PhCO), 128.98 (s, *m*-PhCO), 133.76 (s, *ipso*-PhCO), 134.86 (s, *p*-PhCO), 136.07 (dm, J_{C-F} = 238 Hz, C₆F₅B⁻), 137.52 (dm, J_{C-F} = 246 Hz, C₆F₅B⁻), 147.40 (dm, J_{C-F} = 240 Hz, C₆F₅B⁻), 191.05 (s, C=O); IR (KBr) 1678 (C=O), 1645, 1514, 1466, 1277, 1211, 1086, 980, 775, 756, 685, 661 cm⁻¹. Anal. Calcd. for C₃₄H₁₃BF₂₀OS: C, 47.46; H, 1.523. Found: C, 47.46; H, 1.50.

Dimethylphenacylsulfonium tetraphenylborate (2b). 10.91 g (*i.e.*, 41.8 mmol) of dimethylphenacylsulfonium bromide²² was dissolved in 300 mL of water in a 1000 mL Erlenmeyer flask. 13.00 g (*i.e.*, 38.0 mmol) of sodium tetraphenylborate dissolved in 300 mL of water was added dropwise. The mixture was left to stand for 30 min with stirring and then filtered. The residual product was washed with water and extracted with 200 mL of dichloromethane. The extract was dried over sodium sulfate and then evaporated. To crystallize the residue from dichloromethane-diethylether, 17.97 g of dimethylphenacylsulfonium tetraphenylborate (**2b**) was obtained (with a yield of 94 %, mp 161-163°C (*dec.*)). ¹H NMR (DMSO-*d*₆) δ 2.93 (s, 6H, Me₂S⁺), 5.39 (s, 2H, COCH₂), 6.74-6.84 (m, 4H, *p*-PhB⁻), 6.87-6.97 (m, 8H, *m*-PhB⁻), 7.12-7.24 (m, 8H, *o*-PhB⁻), 7.56-7.67 (m, 2H, *m*-PhCO), 7.73-7.81 (m, 1H, *p*-PhCO), 7.97-8.05 (m, 2H, *o*-PhCO); ¹³C NMR (DMSO-*d*₆) δ 24.59 (s, Me₂S⁺), 52.80 (s, COCH₂), 121.20 (s, *p*-PhB⁻), 124.96 (s, *o*-PhB⁻), 128.26 (s, *o*-PhCO), 128.81 (s, *m*-PhCO), 133.48 (s, *ipso*-PhCO), 134.71 (s, *p*-PhCO), 135.20 (s, *m*-PhB⁻), 162.98 (q, J_{C-F} = 49.5 Hz, *ipso*-PhB⁻), 190.80 (s, C=O); IR (KBr) 3052, 2999, 1680 (C=O), 1597, 1580, 1480, 1451, 1428, 1325, 1300, 1210, 1184, 1155, 989, 738, 709, 687, 607 cm⁻¹. Anal. Calcd. for C₃₄H₃₃BOS: C, 81.59; H, 6.645. Found: C, 81.62; H, 6.63.

Instruments. IR spectra were recorded on a Perkin Elmer 1720 Fourier transform infrared spectrometer except the real-time Fourier transform infrared (RT-FTIR) spectroscopy. ¹H and ¹³C NMR spectra were measured using a JEOL JMN-GSX270 NMR spectrometer (270 and 67.8 MHz, respectively). Chemical shifts are in ppm with tetramethylsilane as the internal standard. Absorption and fluorescence spectra were recorded on a Jasco V-530 UV/VIS spectrophotometer and a Jasco FP-770F spectrofluorometer, respectively. Fluorescence decays were

measured by a time-corrected single photon counting apparatus (Horiba, NAES-550) equipped with a nitrogen lamp; the emissions were monitored through a cutoff filter (Hoya, L-42) to minimize the scattering. Reduction potential of the onium compounds was measured by cyclic voltammetry on a CV-50W voltammetric analyzer (BAS Inc.). All measurements of the reduction potentials were carried out with a scan rate of 100 mV/s in dry acetonitrile under Ar at room temperature. Platinum-inlay electrode was used as the working electrode along with a platinum auxiliary electrode and a Ag / AgClO₄ reference electrode. The electrolyte was 0.1 M tetrabutylammonium perchlorate in dry acetonitrile. The electrode was calibrated with ferrocene using its known reduction value (0.06 V vs Ag/Ag⁺)²⁹ and converted to the value relative to SCE by the addition of 0.337 V. The reduction potential (*E*_{red}) of the onium compounds stands for peak potential (*E*_{peak}).

Photopolymerization of epoxy monomer. Kinetic study of photopolymerization of an epoxy monomer was analyzed by the real time Fourier transform infrared (RT-FTIR) spectroscopy.³⁰⁻³³ A sample solution was prepared by mixing cyclohexanone (8 g), ERL-4221 (0.5 g), PMMA (0.5 g), the onium compounds as an initiator (6.5 × 10⁻⁵ mol), and the anthracenes as a sensitizer (6.5 × 10⁻⁵ mol). The photopolymerizable film was prepared by coating the sample solution onto a stainless steel plate (mesh # 600) using a spin coater (Mitsui Seiki Co., with 500 rpm for 5 s) and by drying it at 50°C for 10 min in an oven. Thickness of the photopolymerizable against was measured by a surface profile measuring system (Veeco Instruments Inc., Dektak 3030) and was found to be *ca* 10 μm. If there was need to protect the photopolymerizable film against oxygen, the photopolymerizable film was coated with PVA (thickness = 2 μm). The coated plate was placed into an IR spectrometer (Nicolet, Magna 560 FTIR spectrometer) equipped with a liquid nitrogen cooled MCT detector and attached with a grazing angle accessory (Graseby-Specac Co., 19650 series). The plate was irradiated by UV light (365 nm) from a high pressure mercury lamp (Ushio Inc., UXM-200YA) after passing through an U-360 ultraviolet filter. Incident angles of the IR beam and the UV light were 60° and 90° onto the plate, respectively. The UV light intensity at the plate position was measured by an optical power meter (Ushio Inc., UTI-150 Unimeter) and was found to be 960 W/m². IR spectra were recorded at the rate of 120 spectra/min with resolution of 4 cm⁻¹ and were processed using an OMNIC rapid scan software version 2.0 from Nicolet. All photopolymerization experiments have been carried out in the presence of air.

Determination of quantum yields of photobleaching of the anthracenes (φ_{AH}) and acid generation (φ_{acid}). Sample solution (0.3 mL) containing the anthracenes and the onium compounds was irradiated in a 1 mm × 10 mm × 40 mm quartz cuvette. The light intensity at the cuvette position was 3.2 × 10⁻⁹ einstein cm⁻² s⁻¹. Photobleaching by reduction of acridine was used as an actinometer (φ = 0.032 in aerated MeOH at 25°C).³⁴ The quantum yields of photobleaching of the anthracenes (**An**, **MAAn**, and **DMAAn**) were determined by monitoring the change in the absorption maximum at 356, 365, and 375 nm of the absorption spectra, respectively. The photobleaching was run below 10% conversion at the absorption maximum.

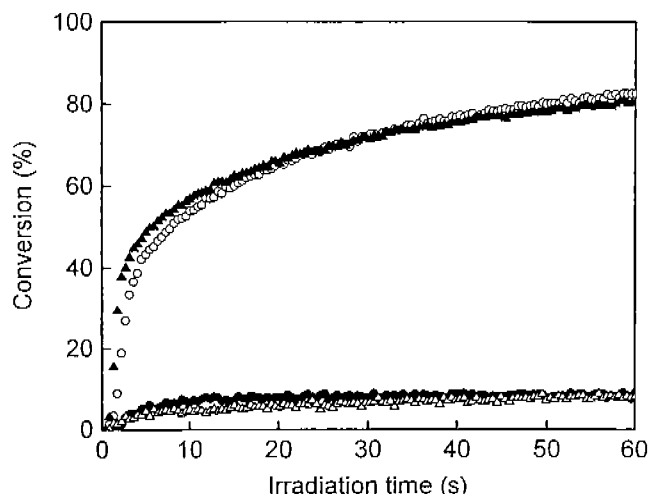


Figure 1. **MAN**-sensitized polymerization profiles of an epoxy monomer (ERL-4221) in a PMMA film recorded by RT-FTIR spectroscopy exposed to the 365 nm irradiation for comparing the diphenyliodonium compounds with different counteranions: **1a** (○: $\text{B}(\text{C}_6\text{F}_5)_4^-$), **1b** (●: BPh_4^-), **1c** (△: BPh_3Bu^-), **1d** (▲: PF_6^-). $[\text{MAN}] = [\text{initiator}] = 7.7 \times 10^{-2} \text{ M}$ in the mixture of ERL-4221 and PMMA (w/w = 1/1). Light intensity = 960 W/m^2 .

The quantum yield of acid generation was determined by titration with CVL as an acid indicator. MeOH solutions of hydrochloric acid were used to prepare a standard curve of absorbance at 600 nm of CVL ($\epsilon_{600} = 25200 \text{ M}^{-1} \text{ cm}^{-1}$ in MeOH). 0.2 mL portion of the irradiated sample solution containing the anthracenes and the onium compounds was added to 2 mL of 0.5 mM CVL in MeOH. The absorbance at 600 nm increased by irradiating the sample solution, and acid concentration was determined by the standard curve.

Analysis of photoproducts. Sample solution (2 mL) containing the anthracenes and the onium compounds was irradiated in a 1 mm × 10 mm × 40 mm quartz cuvette. The light intensity at the cuvette position was 80 W/m^2 . 0.3 mL portion of the irradiated sample solution was washed by 1.5 mL of 1 M NaCl solution and then extracted by 0.5 mL of hexane. The hexane extract was analyzed by a GC and a GC/MS. GC measurements were carried out on a Hewlett-Packard (HP) 5890 series II gas chromatograph with a 15 m × 0.53 mm ID × 1.5 μm film thickness DB-5 column (J & W Scientific) and a flame ionization detector. GC/MS spectra were measured on a HP 5970 mass selective detector coupled with a HP 5890 series II GC with a 30 m × 0.25 mm ID × 0.25 μm film thickness DB-5 column (J & W Scientific). Authentic samples of the photoproducts were used to obtain response ratio, which was used in quantification of the samples against decane as an internal standard.

RESULTS AND DISCUSSION

Photopolymerization of epoxy monomer with the onium borates

The epoxy monomer, ERL-4221 was used as a typical

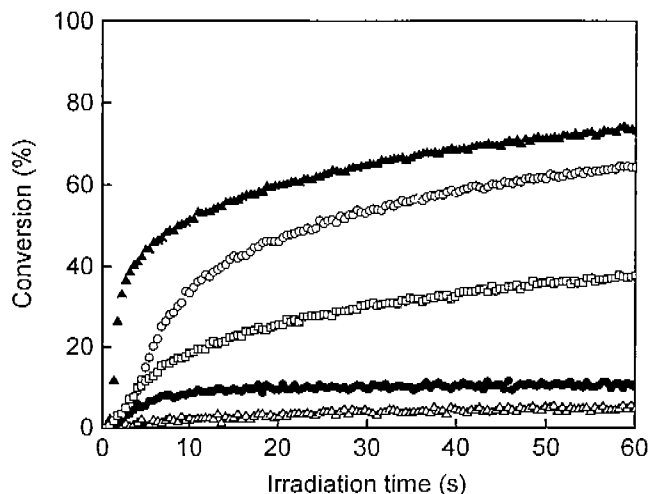


Figure 2. **MAN**-sensitized polymerization profiles of an epoxy monomer (ERL-4221) in a PMMA film recorded by RT-FTIR spectroscopy exposed to the 365 nm irradiation for comparing the dimethylphenacylsulfonium compounds with different counteranions: **2a** (○: $\text{B}(\text{C}_6\text{F}_5)_4^-$), **2b** (●: BPh_4^-), **2c** (△: BPh_3Bu^-), **2d** (▲: PF_6^-), **2e** (□: BF_4^-). $[\text{MAN}] = [\text{initiator}] = 7.7 \times 10^{-2} \text{ M}$ in the mixture of ERL-4221 and PMMA (w/w = 1/1). Light intensity = 960 W/m^2 .

cycloaliphatic difunctional epoxide. Three anthracenes, **An**, **MAN**, and **DMan** were selected as sensitizers, since it is known that these anthracenes have strong absorption in ultraviolet region and sensitize several onium salts.^{5-12,14,16,17} The cationic photopolymerization of the epoxy monomer was studied by the real time Fourier transform infrared (RT-FTIR) spectroscopy.^{32,33} By simultaneously irradiating the photopolymerizable film containing the epoxy monomer with UV light and recording its IR spectrum, the changes in the IR absorption bands of the epoxy monomer undergoing photopolymerization can be monitored as a function of time. The epoxy monomer shows the absorption band at 790 cm^{-1} corresponding to the C-H bond stretching vibration of an epoxy group.³² Hence progress of the photopolymerization can be followed by the decrease of the absorption band. Degree of conversion of the epoxy monomer at any time during the UV irradiation can be obtained by calculating the peak height under the specific absorption band from the equation:

$$\text{Degree of conversion} = \frac{A_0 - A_t}{A_0} \times 100 (\%)$$

where A_0 and A_t are the absorbance levels at 790 cm^{-1} based on an epoxy group in the photopolymerizable film before and after UV irradiation during time t , respectively. From the kinetic curves, one can evaluate how many epoxy groups have polymerized, and thus determine both the actual rate of polymerization (R_p) at a given time:

$$R_p = [\text{M}]_0 \frac{A_{t1} - A_{t2}}{A_0 (t_2 - t_1)}$$

Table 1. Rate of polymerization (R_p) and degree of conversion of an epoxy monomer (ERL-4221) in a PMMA film containing the onium compounds on the sensitized polymerization.^a

Sensitizer	Initiator		R_p ($10^2 M/s$)	Conversion ^b (%)	
	Cation	Anion			
MAN	1a	Ph ₂ I ⁺	B(C ₆ F ₅) ₄ ⁻	80	83
	1b	Ph ₂ I ⁺	BPh ₄ ⁻	6.4	9
	1c	Ph ₂ I ⁺	BPh ₃ Bu ⁻	4.2	8
	1d	Ph ₂ I ⁺	PF ₆ ⁻	120	81
	2a	Me ₂ S ⁺ CH ₂ COPh	B(C ₆ F ₅) ₄ ⁻	24	65
	2b	Me ₂ S ⁺ CH ₂ COPh	BPh ₄ ⁻	5.7	10
	2c	Me ₂ S ⁺ CH ₂ COPh	BPh ₃ Bu ⁻	1.3	5
	2d	Me ₂ S ⁺ CH ₂ COPh	PF ₆ ⁻	110	73
	2e	Me ₂ S ⁺ CH ₂ COPh	PF ₄ ⁻	13	37
AN	1a	Ph ₂ I ⁺	B(C ₆ F ₅) ₄ ⁻	75	74
	1b	Me ₂ S ⁺ CH ₂ COPh	B(C ₆ F ₅) ₄ ⁻	10	58
DMAN	1a	Ph ₂ I ⁺	B(C ₆ F ₅) ₄ ⁻	82	75
	1b	Me ₂ S ⁺ CH ₂ COPh	B(C ₆ F ₅) ₄ ⁻	23	65

^a[Sensitizer] = [initiator] = $7.7 \times 10^{-2} M$ in the mixture of ERL-4221 and PMMA (w/w = 1/1). Light intensity = 960 W/m².

^bDegree of conversion at 60 s after 365 nm light irradiation.

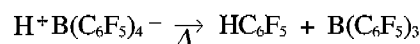
where $[M]_0$ (= 4.7 M) is the concentration of the epoxy monomer in the film before UV light irradiation, and t_2 and t_1 are the times between which the conversion data are collected. A plot of percent conversion versus irradiation time provides a kinetic curve for the photopolymerization. The slope of the initial linear portion of the curve corresponds to the factor $R_p/[M]_0$. This value gives a measure of the relative rates of photopolymerization of the monomer. Irradiation was carried out at 365 nm with the concentration of **MAN** adjusted to absorb *ca* 50 % of the incident light. The onium compounds absorbed less than 3 % of the light at 365 nm. All the anthracenes were ineffective in the absence of the onium compounds.

Fig. 1 shows the **MAN**-sensitized polymerization profiles of the epoxy monomer in a PMMA film for comparing diphenyliodonium compounds with different counteranions. It is known that the iodonium salt **1d** was sensitized by anthracene⁵⁻¹⁴ and initiates cationic photopolymerization of an epoxy monomer.^{6-8,14} We observed that the iodonium borate **1a** also initiates photopolymerization of the epoxy monomer. However, we could not observe to initiate photopolymerization for the iodonium borates **1b** and **1c**, in spite of that both **1b** and **1c** were sensitized by the anthracenes. Since the iodonium borates **1b** and **1c** will not generate reactive cationic species such as an acid, they could not initiate polymerization of the epoxy monomer.

Fig. 2 shows the **MAN**-sensitized polymerization profiles of the epoxy monomer in a PMMA film for comparing dimethylphenacylsulfonium compounds with different counteranions. Crivello *et al.* reported anthracene-sensitized polymerization of an epoxy monomer with the sulfonium salt **2d** and **2e**.²¹ The efficiency of the sulfonium borate **2a** for cationic photopolymerization was better than that of **2e** and worse than that of **2d**. However, we could not also observe to initiate photopolymerization with the sulfonium

borates **2b** and **2c**, in spite of both **2b** and **2c** were sensitized by the anthracenes.

Table 1 summarizes the results of the photopolymerization of the epoxy monomer using several initiators with the anthracenes. The R_p values for the diphenyliodonium compounds are much higher than that for the corresponding dimethylphenacylsulfonium compounds. It is clear that diphenyliodonium cation is a more efficient cationic initiator than dimethylphenacylsulfonium cation. From the influence of different counteranions, the R_p value increases in the order, PF₆⁻ > B(C₆F₅)₄⁻ > BF₄⁻ >> BPh₄⁻, BPh₃Bu⁻. The onium borates **1b**, **1c**, **2b**, and **2c** could not initiate photopolymerization of the epoxy monomer. Namely, both BPh₄⁻ and BPh₃Bu⁻ were ineffective for cationic photopolymerization in contrast to radical photopolymerization.^{27,28} In the cases of using **AN** as a sensitizer, the R_p values were lower than those for **MAN**. In contrast to the cases of using **DMAN**, the R_p values were higher than those for **MAN**. Namely, the R_p value increases in the order, **DMAN** > **MAN** > **AN**. It is reasonable because the order of the R_p value is the same as the order of the quantum yield of acid generation ϕ_{acid} that we shall see later. It is interesting that the generated acid by decomposing the onium borates **1a** and **2a** was disappeared by heating at 100 °C for 10 min. This remarkable result can be explained as follows:



Thus, the generated acid, H⁺ B(C₆F₅)₄⁻ would decompose to pentafluorobenzene and B(C₆F₅)₃ by heating. Though we could not directly detect H⁺ B(C₆F₅)₄⁻, pentafluorobenzene was detected by GC/MS from the irradiated photopolymerizable film containing the onium borate **1a** and **2a** after heating. On the other hand, any acid could not be detected from the film containing the onium borate **1b**, **1c**, **2b**, and **2c**. Hence, the species initiating cationic polymerization would be the generated acid rather than other cationic species. In the cases of the onium salts **1d**, **2d**, and **2e**, generation of acid was observed. In these cases, since the generated acids, H⁺ PF₆⁻ and H⁺ BF₄⁻ are stable, they are not decomposed by heating.

To observe the influence of concentration of the anthracenes on the photopolymerization, photopolymerization was carried out in the range of 2.5×10^{-2} to $1.3 \times 10^{-1} M$ of the anthracenes in the photopolymerizable film. Absorbance of the films showed the range of 0.1 to 0.9 with varying the concentration of the anthracenes. However the R_p values were nearly the same in the range of the concentration studied. In the absence of the anthracenes, photopolymerization did not occur.

To observe the influence of concentration of the onium borates **1a** and **2a**, photopolymerization was carried out in the range of 2.5×10^{-2} to $1.3 \times 10^{-1} M$ of the onium borates in the photopolymerizable film. The R_p values increased with increasing concentration of the onium borates. Fig. 3 shows the R_p values using various concentrations of the onium borates **1a** and **2a**. In Fig. 3,

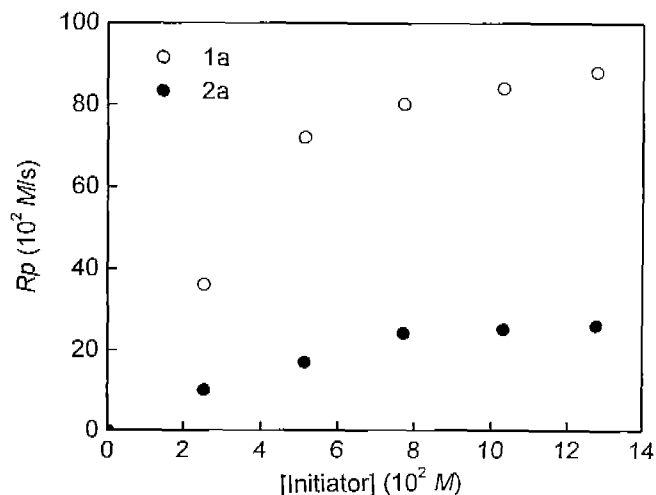


Figure 3. Influence of the concentration of the onium borates **1a** and **2a** on **MAN**-sensitized polymerization of an epoxy monomer (ERL-4221) in a PMMA film: ○: **1a**, ●: **2a**. [**MAN**] = [initiator] = 7.7×10^{-2} M in the mixture of ERL-4221 and PMMA (w/w = 1/1). Light intensity = 960 W/m².

the R_p values for **1a** and **2a** were changed markedly at the concentration of $ca 5 \times 10^{-2}$ and 8×10^{-2} M, respectively. Hence, it is possible that the iodonium borate **1a** is a more efficient initiator than the sulfonium borate **2a**.

In the following section we shall be examining the quantum yield of acid generation ϕ_{acid} , since ϕ_{acid} of the iodonium borate **1a** was higher than 1.0 in Ar saturated MeOH, we expected that the R_p value and the degree of conversion increase in the presence of a hydrogen donor under deaerated condition. To confirm the influence of oxygen and a hydrogen donor, photopolymerization was carried out after covering the photopolymerizable film by coating with PVA as a protect film against oxygen in air and with coexistence of glycerol as a hydrogen donor. Fig. 4 shows the influence of oxygen and a hydrogen donor on the sensitized polymerization. Though both the R_p values with PVA coating were higher than those without PVA coating, each the degree of conversion with PVA coating was the nearly same as those without PVA coating. When **MAN** in the photopolymerizable film is protected against oxygen by coating PVA, **MAN** would be not quenched by oxygen. There is also similar result in a nitrogen-saturated atmosphere and with a laminated polyethylene film by Decker and Moussa²² instead of PVA coating. On the other hand, the R_p value and the degree of conversion in the presence of glycerol were higher than those in the absence of glycerol despite coating with PVA. In the presence of glycerol, ϕ_{acid} may be higher than that without glycerol. It is an interesting result that the R_p value increased by addition of a hydrogen donor.

Photoproducts by sensitized photolysis of the onium borates

It is important to consider the mechanism of photo-

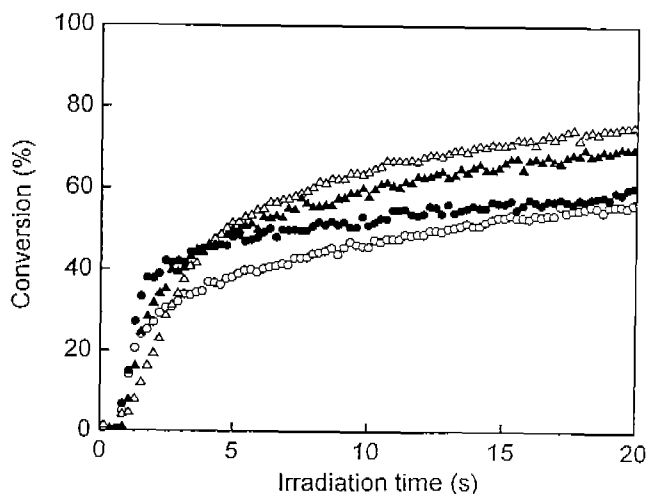


Figure 4. Influence of oxygen and hydrogen donor on **MAN**-sensitized polymerization of an epoxy monomer (ERL-4221) in a PMMA film: ○: without glycerol and no overcoating, ●: without glycerol and overcoating PVA, △: with 1.0 M glycerol and no overcoating, ▲: with 1.0 M glycerol and overcoating PVA. [**MAN**] = [**1a**] = 7.7×10^{-2} M in the mixture of ERL-4221 and PMMA (w/w = 1/1). Thickness of the PVA film = 2 μ m. Light intensity = 960 W/m².

initiation process between an initiator and a sensitizer for to clarify the details of the photopolymerization. It is known that photosensitization of several onium salts by anthracenes occurs by a photoinduced electron transfer reaction in which anthracene is oxidized to form a cation radical and the initiator is reduced to a neutral radical.^{5-14 16 17 21} We investigated that the onium borates **1a** and **2a** showed whether identical behavior such as the onium salts in a photosensitization. No evidence of ground state complex formation was observed for either the anthracenes with the onium compounds in MeOH and MeCN. While the absorption spectra of **MAN** in aerated MeOH containing the onium borates **1a** and **2a** clearly showed bleaching of **MAN** with 365 nm light irradiation as shown in Fig. 5.

In Fig. 5a, four isobestic points appeared at 314, 371, 376, and 390 nm. Analysis of the irradiated solution of **MAN** containing the iodonium borate **1a** by GC/MS indicated iodobenzene as a major photoproduct, and biphenyl, three phenylated anthracene derivatives, and methanolic adduct of **MAN** as minor photoproducts. Though these photoproducts could not be isolated, it was able to identify the photoproducts with authentic samples. From the results of the photolysis of **MAN** in MeCN containing the iodonium borate **1a** or the iodonium salt **1d**, the methanolic adduct was not detected. It is suggested that the photosensitization process of the onium borate **1a** by the anthracenes would be the same as that of the iodonium salt **1d**.⁵ The spectral change in Fig. 5a would be accounted for by consumption of **MAN** and formation of the photoproducts.

On the other hand, from the irradiated solution of **MAN** containing the sulfonium borate **2a**, an isobestic point at 393 nm appeared as shown in Fig. 5b. Dimethylsulfide and

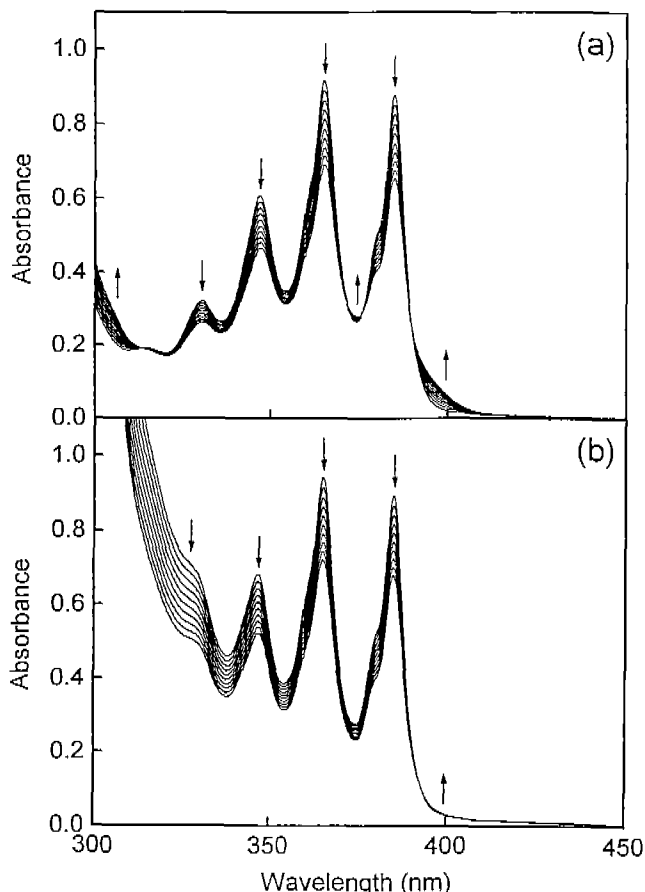


Figure 5. Absorption spectral changes of 1 mM **MAn** in aerated MeOH containing 40 mM of the onium borate **1a** (a) or **2a** (b) in a 1 mm \times 10 mm \times 40 mm quartz cuvette by 365 nm light irradiation.

acetophenone were detected as photoproducts, however, any **MAn** derivatives were not detected. There is a number of reasons for the undetection of **MAn** derivatives. One may be that phenacyl radical is too less reactive to cation radical of **MAn** to form **MAn** derivatives. Another reason may be that **MAn** derivatives were not detected under the GC condition or were not extracted by hexane. Also, we observed the similar results using **An** and **DMAn** instead of **MAn**.

Quantum yield of photobleaching of the anthracenes (ϕ_{-AH}) and acid generation (ϕ_{acid})

We determined the quantum yield of photobleaching of the anthracenes (ϕ_{-AH}) and acid generation (ϕ_{acid}) in the range of 10 ~ 80 mM for the onium compounds. Both ϕ_{-AH} and ϕ_{acid} increased with increasing concentration of the onium compounds and showed constant values when the concentration is higher than *ca* 40 mM. Fig. 6 shows the dependence of ϕ_{-AH} (**MAn**) and ϕ_{acid} on the concentration of the sulfonium borate **2a** in aerated MeOH.

Table 2 summarizes the maximum values of ϕ_{-AH} and ϕ_{acid} in the presence of the onium compounds. Each maximum value of ϕ_{acid} shows in excellent agreement with

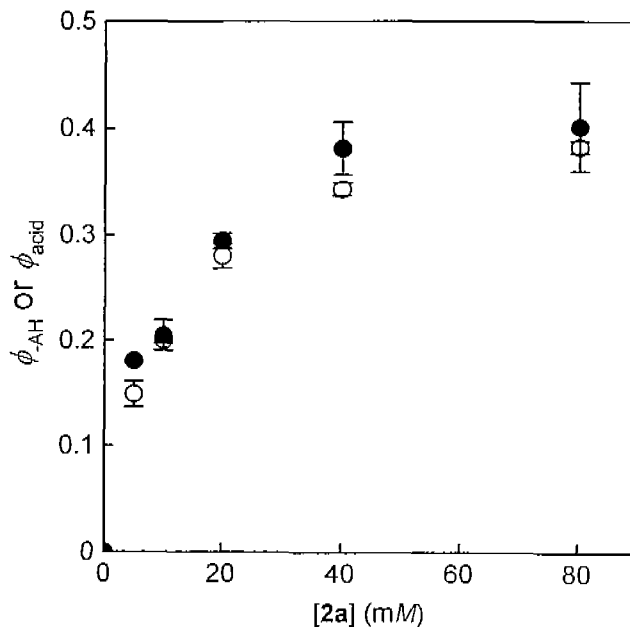


Figure 6. Dependence of ϕ_{-AH} (○) or ϕ_{acid} (●) on the concentration of the sulfonium borate **2a** in aerated MeOH. Sensitizer: **MAn**.

the corresponding value of ϕ_{-AH} except in the cases of Ar saturated MeOH containing the iodonium compound **1a** or **1d**. It is suggested that acid is generated quantitatively by decomposing the onium compounds by the excited singlet of the anthracenes. In the cases of Ar saturated MeOH containing **1a** or **1d**, it is noteworthy that the maximum values of ϕ_{acid} are much higher than those of the corresponding ϕ_{-AH} . These results indicate that the photosensitization of the iodonium compound **1a** or **1b** with **MAn** in Ar saturated MeOH would be mediated by the solvent as a hydrogen donor and would involve a chain reaction. The similar result is reported by Pappas *et al.* on photosensitization of diphenyliodonium salt with benzophenone in MeCN containing 2-propanol as a hydrogen donor.^{6,14} Though a

Table 2. Quantum yield maximum of the photobleaching of the anthracenes (ϕ_{-AH}) and the acid generation (ϕ_{acid}) by the onium compounds.

Sensitizer	Solvent	Initiator	ϕ_{-AH}		ϕ_{acid}		ϕ_{acid}/ϕ_{-AH}	
			Air	Ar	Air	Ar	Air	Ar
MAn	MeOH	1a	0.38	0.45	0.38	2.56	1.0	5.7
		1d	0.31	0.31	0.31	1.35	1.0	4.4
		2a	0.32	0.36	0.32	0.36	1.0	1.0
		2e	0.30	0.32	0.30	0.32	1.0	1.0
		2a	0.35	0.35	0.35	0.55	1.0	1.6
An	MeOH	1a	0.11	0.11	0.11	0.48	1.0	4.4
		2a	0.11	0.11	0.11	0.11	1.0	1.0
		2a	0.45	0.48	0.45	2.86	1.0	6.0
DMAn	MeOH	1a	0.45	0.39	0.45	0.49	1.0	1.3
		2a	0.45	0.39	0.45	0.49	1.0	1.3

Table 3. Relative yield (γ) of the photoproduct by the decomposition of the onium compounds, ratio of γ , ϕ_{-AH} , and ϕ_{acid} .

Sensitizer	Solvent	Initiator	γ^a		γ ratio (Ar/Air)	ϕ_{-AH} ratio (Ar/Air)	ϕ_{acid} ratio (Ar/Air)
			Air	Ar			
MAn	MeOH	1a	4.1	9.8	2.4	1.2	6.7
		1d	1.6	4.4	2.8	1.0	4.4
		2a	0.2	0.16	0.8	1.1	1.1
	MeCN	1a	2.3	3.7	1.6	1.0	1.6
		1d	2.1	3.0	1.4	1.1	2.6
		2a	0.27	0.34	1.3	1.0	1.0
DMan	MeOH	1a	5.3	17.5	3.3	1.1	6.4
		2a	0.24	0.35	1.5	0.9	1.1

^aCalculated by $\gamma = (\text{formation of the photoproduct}) / (\text{consumption of the anthracenes})$. The photoproducts are PhI for **1a** or **1b**, and PhCOCH₃ for **2a**, respectively.

possible mechanism of our cases is different from that of Pappas *et al.* because of using different sensitizers. We shall return to this mechanism later.

In the case of using **An** instead of **MAn**, the maximum values of ϕ_{-AH} and ϕ_{acid} decreased to 0.11. Conversely in the case of using **DMan**, the maximum values of ϕ_{-AH} and ϕ_{acid} increased to *ca* 0.45. One reason would be that each lifetime of the excited singlet of the anthracenes is difference. Table 4 summarizes the fluorescence lifetimes of the anthracenes in the aerated and Ar saturated solvents. Since the anthracenes were quenched by oxygen in the diffusion-controlled limit, the fluorescence lifetimes of the anthracenes in the aerated solvents were less than those in the Ar saturated solvents.

From the photolyzed solution of **MAn** containing the onium borate **1a** or **2a**, iodobenzene or acetophenone was determined as the major photoproduct by the GC analysis, respectively. The relative yield of these major photoproducts (γ) was estimated as:

$\gamma = \text{formation of PhI [or PhCOCH}_3\text{]} / \text{consumption of the anthracenes}$

The formation of the photoproducts and the consumption of the anthracenes were determined by GC. Each γ value is

summarized in Table 3. In MeOH solution containing the iodonium compound **1a** or **1d**, the γ values in MeOH under Ar saturated condition were higher than those under aerated condition. In contrast, the γ values in MeCN under Ar saturated condition were the nearly same as those under aerated condition. As shown in the ratios of the γ values of the Ar saturated / aerated solution, formation of iodobenzene in MeOH is much higher than that in MeCN under Ar saturated condition. This result supports that ϕ_{acid} for Ar saturated MeOH containing the iodonium compound **1a** or **1d** is much higher than the corresponding ϕ_{-AH} . On the other hand, in the solutions containing the sulfonium borate **2a**, since there is not a difference for the γ values in either Ar saturated or aerated solution, each ratio of the γ values for Ar saturated / aerated solution was close to *ca* 1. The ratio of the γ value roughly agrees with the corresponding ϕ_{acid} and ϕ_{-AH} .

Free energy changes of excited singlet of the anthracene to the onium borates

The free energy change (ΔG_{et}) is given by the Rehm-Weller equation (Eq. 1):³⁵

$$\Delta G_{et} = E_{ox}(D/D^{\bullet+}) - E_{red}(A^{\bullet-}/A) - E - Ze^2/\epsilon\alpha \quad (1)$$

where $E_{ox}(D/D^{\bullet+})$ is oxidation potential of donor; $E_{red}(A^{\bullet-}/A)$ is reduction potential of acceptor; E is excited energy of sensitizer; $Ze^2/\epsilon\alpha$ is Coulombic energy, which is the free energy gained by bringing the radical ions formed to an encounter distance α in a solvent with dielectric constant ϵ . To obtain ΔG^S between the anthracenes and the onium compounds, we approximated Eq. 1 to Eq. 2 as below:

$$\Delta G^S = E_{ox}(AH/AH^{\bullet+}) - E_{ox}(On^{\bullet}/On^+) - E_{00} \quad (2)$$

where $E_{ox}(AH/AH^{\bullet+})$ is the oxidation potential of the anthracenes, $E_{red}(On^{\bullet}/On^+)$ is the reduction potential of the onium cation, and E_{00} is the excited singlet energy of the anthracenes.

The free energy changes (ΔG^S) between the excited singlet of the anthracenes and the onium cation are summarized in Table 4. The anthracenes serve as a donor. Diphenyliodonium

Table 4. Fluorescence lifetime (τ_F), excited singlet energy (E_{00}), oxidation potential (E_{ox}) of the anthracenes and free energy change (ΔG^S) between the excited singlet of the anthracenes and the onium cations.

Sensitizer	τ_F (ns)				E_{00} (kJ/mol)	E_{ox} (V vs SCE)	ΔG^S ^a (kJ/mol)	
	MeOH		MeCN				Ph ₂ I ⁺ ^b	Me ₂ S ⁺ CH ₂ COPh ^c
	Air	Ar	Air	Ar				
An	3.93	5.14	3.64	4.77	316	1.16 ^d	-142	-121
MAn	3.99	5.30	4.99	7.44	308	1.054 ^e	-144	-123
DMan	8.23	15.9	7.80	16.1	297	0.956 ^e	-143	-122

^aCalculated by $\Delta G^S = E_{ox}(AH/AH^{\bullet+}) - E_{red}(On^{\bullet}/On^+) - E_{00}$. $E_{ox}(AH/AH^{\bullet+})$ and $E_{red}(On^{\bullet}/On^+)$ stand for the oxidation potential of the anthracenes and the reduction potential of the onium cations, respectively.

^b $E_{red}(On^{\bullet}/On^+) = -0.64$ (V vs SCE) from Ref. [13]. ^c $E_{red}(On^{\bullet}/On^+) = -0.86$ (V vs SCE). ^dRef. [36]. ^eRef. [37].

Table 5. Stern-Volmer constant (K_{SV}) and fluorescence quenching rate constant (k_q) of the excited singlet of the anthracenes by the onium compounds.

Sensitizer	Solvent	Initiator	$K_{SV}(M^{-1})$		$k_q(10^{-10} M^{-1}s^{-1})^a$			
			Air	Ar	Air		Ar	
MAn	MeOH	1a	56.2	82.9	1.41	(1.18) ^b	1.56	(1.28) ^b
		2a	48.5	72.7	1.22	(1.20) ^b	1.37	(1.21) ^b
	MeCN	1a	110	161	2.20		2.16	
		2a	78.3	120	1.57		1.61	
An	MeOH	1a	50.7	78.5	1.29		1.53	
		2a	50.9	77.0	1.29		1.50	
DMAn	MeOH	1a	103	210	1.25		1.32	
		2a	103	205	1.25		1.29	

^aCalculated by Eq. 3 using K_{SV} and τ_F .

^bCalculated by Eq. 4 using the fluorescence decay rate constant.

cation ($E_{red} = -0.64$ V vs SCE)¹³ and dimethylphenacyl-sulfonium cation ($E_{red} = -1.01$ V vs SCE) serve as an acceptor. ΔG^S for the iodonium cation are lower than those for the sulfonium cation. However, ΔG^S for each anthracene shows the nearly same order each other.

Fluorescence quenching of the anthracenes by the onium borates

The fluorescence of the anthracenes was quenched by the onium compounds. The fluorescence quenching rate constant (k_q) of the excited singlet anthracenes by the onium compounds is estimated by the Stern-Volmer relationship (Eq. 3):

$$I_{F0}/I_F = 1 + K_{SV}[Q] \quad K_{SV} = k_q\tau_0 \quad (3)$$

where I_{F0} and I_F are the fluorescence intensities in the absence and presence of the onium compounds as a quencher Q, respectively; K_{SV} is the Stern-Volmer constant; $[Q]$ is the concentration of the onium compounds; and τ_0 is the fluorescence lifetime in the absence of the onium compounds. Also the fluorescence quenching rate constant (k_q) is estimated by Eq. 4:

$$1/\tau = 1/\tau_0 + k_q[Q] \quad (4)$$

where τ_0 and τ are the fluorescence lifetimes in the absence and presence of the onium compound, respectively; $[Q]$ is the concentration of the onium compounds.

Table 5 summarizes the fluorescence quenching rate constants of the excited singlet anthracenes by the onium compounds in the aerated and Ar saturated solutions. Each K_{SV} is different for the anthracenes primarily because of the differences in τ_0 of the anthracenes. Since all the anthracenes are quenched by oxygen, each k_q in aerated solutions showed higher than that in Ar saturated solutions. Fig. 7 shows the Stern-Volmer plots for the fluorescence quenching of MAn by the onium borates 1a and 2a in Ar saturated MeOH. Though all k_q were approximately diffusion-controlled limit,

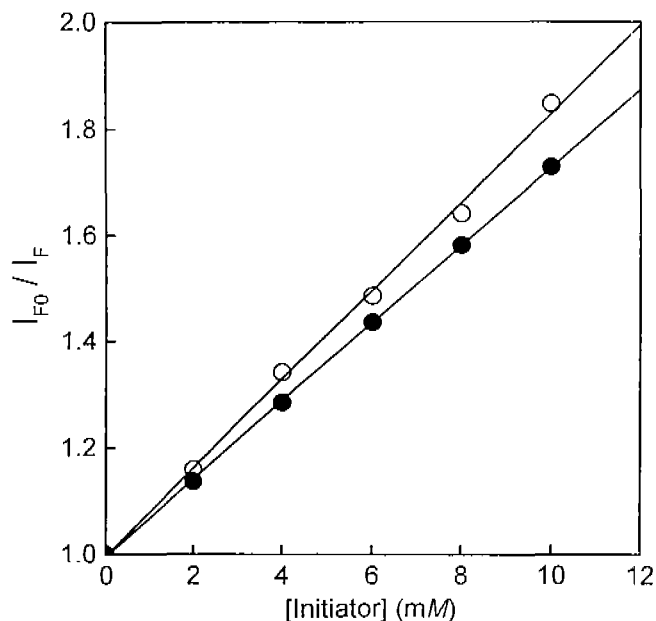
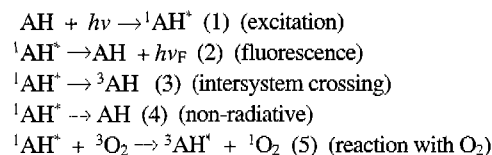


Figure 7. Stern-Volmer plots for the fluorescence quenching of MAn by the onium borates 1a (○) and 2a (●) in Ar saturated MeOH.

k_q in the solutions containing the iodonium borate 1a was higher than that for the sulfonium borate 2a. The iodonium borate 1a serves as a more effective quencher than the sulfonium borate 2a.

Photosensitization mechanism of the onium borates by the anthracenes

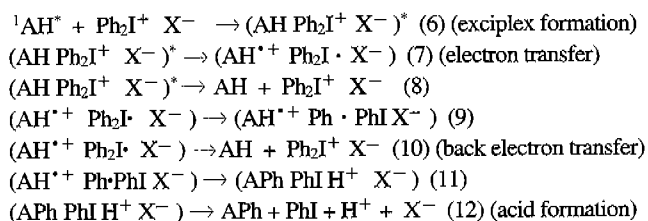
From the above results, the proposed mechanism for the sensitization of the iodonium and sulfonium compounds by the anthracenes is summarized in Scheme 1 ~ Scheme 4. The anthracenes and MeOH were represented as AH and NuH in the schemes, respectively. Processes (1) ~ (5) in Scheme 1 are photophysical processes of the anthracenes and are common for both the iodonium and sulfonium compounds.



Scheme 1.

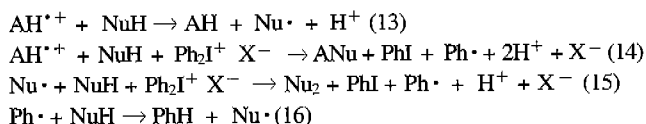
Scheme 2 shows the reaction of the iodonium compounds by the excited singlet of the anthracenes (${}^1AH^*$). Process (9) would be faster than nanosecond time scale. DeVoe *et al.* reported that diphenyliodonium radical was not detected in anthracene-sensitized photolysis of diphenyliodonium salt using picosecond laser flash photolysis technique.⁹ The following processes (9), (10) would occur with high probability in both MeOH and MeCN. It is supported by that the phenylated anthracene derivatives were detected.

This agrees with the result by Deklar and Hacker.⁵



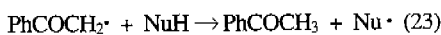
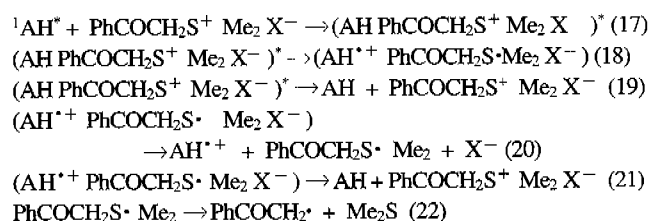
Scheme 2.

Scheme 3 shows the chain reaction of the iodonium compounds in Ar saturated MeOH. NuH stands for MeOH in the scheme. The generated cation radical of the anthracenes (AH^+) by process (12) may partially react with MeOH. It is suggested that the methanolic adducts of the anthracenes were detected by GC/MS and the ϕ_{acid} were higher than the corresponding ϕ_{AH} . Since consumption of the iodonium compounds based on processes as (13)~(16) may occur, the yields of both formation of iodobenzene and ϕ_{acid} are higher than the corresponding ϕ_{AH} . Hence, both the R_p value and the degree of conversion in the presence of glycerol as a hydrogen donor were higher than those in the absence of glycerol. Since we could not isolate the corresponding products as Nu·, ANu and Nu₂, the structure of their products could not be identified. However, the structure of Nu· may be HOCH₂· rather than MeO·, since the bond energy of H-CH₂OH (393 kJ/mol) is lower than that of MeO-H (435 kJ/mol).³⁸ In addition, since acid generation by deprotonation from AH^+ ($\text{AH}^+ \rightarrow \text{AH} + \text{H}^+$) is endothermic,³⁹ this reaction may not occur.



Scheme 3.

Scheme 4 shows the reaction of the sulfonium compounds by the excited singlet of the anthracenes (${}^1\text{AH}^+$). The following processes (17) ~ (19) are similar as processes (6)~(8) in Scheme 2. Since both the yields of formation of acetophenone and ϕ_{acid} are nearly the same as the corresponding ϕ_{AH} , the sulfonium compounds may not react with AH^+ . It is supported by the fact that the phenacylated anthracene derivatives were detected. This namely agrees with the result using triphenylsulfonium salt by Pappas *et al.*^{6,14}



Scheme 4.

CONCLUSIONS

In this paper, we showed the sensitized photolysis of diphenyliodonium and dimethylphenacylsulfonium tetrakis(pentafluorophenyl)borate and cationic photopolymerization of an epoxy monomer by the photolysis. Both of the onium borates were sensitized by the excited singlet of the anthracenes. Under deaerated condition in the presence of a hydrogen donor, both rate of polymerization and degree of conversion increased in the case of using the iodonium borate **1a**. This increasing would be attributable to the high quantum yield of acid generation ($\phi_{\text{acid}} > 1$) under similar condition. We suppose that these findings will be useful for the field of cationic photopolymerization.

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