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Visible Light Polymerization of Acrylate Using Dialkylphenacylsulfonium Butyltriphenylborate Initiators: Effect of the Reduction Potential of the Sulfonium Cation on the Polymerization

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ABSTRACT: Visible light polymerization of an acrylate in poly(methyl methacrylate) (PMMA) film using a series of dialkylphenacylsulfonium butyltriphenylborate initiators was investigated. When 3,3′-carbonylbis(7-diethylaminocoumarin) (**KCD**) was used as a sensitizer, the rates of polymerization (R_p) and the degrees of conversion increased with increasing the reduction potential of the sulfonium cations of the sulfonium borates. They also increased with decreasing lowest unoccupied molecular orbital (LUMO) energy level for the same cations. The photoreaction between the sulfonium borates and **KCD** was discussed.

Introduction

In recent years, visible light polymerization is becoming increasingly important in the field of applications such as laser direct imaging,[1,2] holography,[3] and stereolithography.[4] Since photoinitiators extremely affect the photosensitivity of photopolymerizable materials and require not only high photosensitivity but also exhibiting adequate solubility and high storage stability, a large number of studies of photoinitiators have been instigated. Several excellent reviews[5−7] of those studies are available and some efficient visible light photoinitiators[8−17] have been proposed.

Recently, we reported that dimethylphenacylsulfonium butyltriphenylborate (**SB1a**) serves as a more efficient initiator for radical photopolymerization of an acrylate in solutions than the analogous sulfonium salt and ammonium borate.[18,19] However, photopolymerization in the field of the applications is generally carried out in polymer films or resins. Moreover, to obtain optimum photosensitivity, photoinitiators often require one to control the photosensitivity.

In this paper, we report a series of dialkylphenacylsulfonium butyltriphenylborate initiators and visible light polymerization of an acrylate in poly(methyl methacrylate) (PMMA) film using the initiators. We present that the rate of polymerization can be controlled by varying intentionally the reduction potentials of the sulfonium cation of the initiators. In this study, 3,3′-carbonylbis(7-diethylaminocoumarin) (**KCD**) was used as a sensitizer, since it has strong absorption in visible region[20] and serves as an efficient sensitizer.[21−25] Figure 1 shows the structures of **KCD**, the sulfonium borates, and the related initiators used.

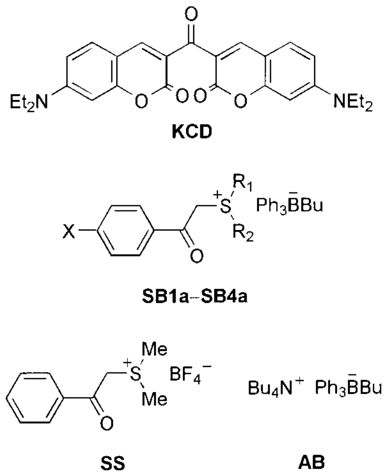

Figure 1. Structure of sensitizer (**KCD**) and initiators used.

Experimental Section

IR spectra were recorded on a Jasco FT/IR-300E Fourier transform infrared spectrometer except for real time Fourier transform infrared (RT−FTIR) spectroscopy investigations. ^{1}H and ^{13}C NMR spectra were measured using a JEOL JMN-GSX270 NMR spectrometer. (270 and 67.5 MHz, respectively). Chemical shifts are in ppm with tetramethylsilane as an internal standard. Absorption and fluorescence emission spectra were recorded on a Jasco V-530 UV/VIS spectrophotometer and a Jasco FP-770F spectrofluorometer, respectively. Reduction and oxidation peak potentials of the initiators were measured by cyclic voltammetry on a CV-50W voltammetric analyzer (BAS Inc.) with a scan rate of 100 mV/s in dry acetonitrile under argon at room temperature. A platinum-inlay electrode was used as a working electrode along with a platinum auxiliary electrode and an Ag/AgClO$_4$ reference electrode. The electrolyte was 0.1 M tetrabutylammonium perchlorate in dry acetonitrile. An electrode was calibrated with ferrocene using its known reduction value (0.06 V vs Ag/

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Table 1. Properties of the Dialkylphenacylsulfonium Butyltriphenylborates

initiator	R_1	R_2	X	mp (dec) (°C)	E_{red} (V vs SCE)	solubility (wt %) acetone	MEK[a]	EtOAc[b]	AmOAc[c]
SB1a	Me	Me	H	143−145	−1.01	>50	>50	28	1.4
SB1b	Me	Me	CN	137−139	−0.90	42	48	6.9	0.5
SB1c	Me	Me	Br	151−153	−0.97	>50	>50	14	1.1
SB1d	Me	Me	Cl	140−142	−0.98	>50	>50	14	1.2
SB1e	Me	Me	F	150−152	−1.00	47	39	4.0	0.4
SB1f	Me	Me	Ph	155−157	−1.01	31	42	2.4	1.0
SB1g	Me	Me	Me	141−143	−1.04	>50	>50	30	2.5
SB1h	Me	Me	MeO	155−156	−1.05	>50	>50	18	0.9
SB2a	Me	Et	H	116−118	−1.09	>50	>50	38	3.2
SB3a	Et	Et	H	80−82	−1.14	>50	>50	>50	>20
SB4a	-$(CH_2)_4$-		H	155−157	−1.12	25	24	0.5	0.1

[a] 2-Butanone. [b] Ethyl acetate. [c] Isoamyl acetate.

Ag^+)[26] and converted to that relative to SCE by the addition of 0.337 V.

Acetonitrile, hexane, and methanol were used as received (Merck, HPLC analytical grade). Dichloromethane, pentane, acetone, 2-butanone (MEK), ethyl acetate (EtOAc), isoamyl acetate (AmOAc), and cyclohexanone were purchased from Kanto Chemical Co., Inc (reagent grade). Tetrabutylammonium perchlorate, tetrabutylammonium tetrafluoroborate, dimethylphenacylsulfonium tetrafluoroborate (**SS**), biphenyl, acetophenone, and 1-phenyl-1-hexanone were obtained from Tokyo Chemical Industries Co., Ltd. Pentaerythritol triacrylate (PE3A) was received from Kyoeisha Yushi Chemical Industry Ltd. Poly(methyl methacrylate) (PMMA, $M_w = 996\,000$), poly(vinyl alcohol) (PVA, 99% hydrolyzed, $M_w = 124\,000-186\,000$), and triphenylborane were purchased from Aldrich. 3,3′-Carbonylbis(7-diethylaminocoumarin) (**KCD**, Acros Chemicals) was used after being recrystallized from ethanol. Lithium butyltriphenylborate[27] and phenacylsulfonium butyltriphenylborates (**SB1a**−**SB4a**)[18,28,53] were prepared according to the reported procedure.

Real Time FTIR Study. A sample solution was prepared by mixing cyclohexanone (16 g), PE3A (1.0 g), PMMA (1.0 g), **KCD** (0.020 g), and the initiator (1.2×10^{-4} mol). The photosensitive plate was prepared by coating the sample solution onto a grained stainless steel plate (mesh # 600) using a spin coater (Mitsui Seiki Co., model SP30W, with 500 rpm for 5 s and 1500 rpm for 20 s) and by drying it at 60 °C for 10 min in an oven. The thickness of the photopolymerizable film on the plate was measured by a surface profile measuring system (Veeco Instruments Inc., Dektak 3030) and was found to be 1.5 μm. The plate was further coated with 1 μm of PVA as an oxygen barrier layer. 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 435 nm light from a high-pressure mercury lamp (Ushio Inc. UXM-200YA) after the light had passed through an band-pass filter and a neutral density filter (ND-1) while the IR spectra were measured. Incident angles of the UV light and the IR beam of the IR spectrometer were 90° and 60° onto the plate, respectively. The intensity of the UV light at the plate position was measured by an optical power meter (Advantest Inc., model TQ8210) and was found to be 1.6 mW/m^2 (at 435 nm). IR spectra were recorded at the rate of 120 spectra/min with a resolution of 4 cm^{-1} and were processed using OMNIC rapid scan software, version 2.0 (Nicolet). All the RT−FTIR experiments was carried out under ambient atmosphere.

Photosensitivity Measurement. A plate for photosensitivity measurement was prepared in the identical materials and manner as the RT−FTIR study. The plate was exposed to the light (488 nm) of an argon-ion laser (Lexel model 95) with varying scanning speed at a constant laser power. The laser scanning was carried out using a laser scanning kit model LK3001 (General Scanning Inc.). The laser beam was adjusted to be focused at every point on the surface of the plate (the diameter and the incident power of the laser beam at the focused position were 28 μm and 120 mW/cm^2, respectively). The exposed plate was rinsed in tap water to remove PVA film and then developed in toluene at 20 °C. The line width of the residual film after the development was measured by the surface profile measuring system.

Laser Flash Photolysis. Nanosecond laser flash photolysis was carried out on a setup described in a previous paper[19] using the third harmonic of a Q-switched Nd:YAG laser as the excitation source. The sample solution in a quartz cuvette of 10 × 10 × 40 mm was purged with argon gas before the experiment. The samples were excited with a 10 mm optical path by 355 nm pulses (pulse width 6 ns fwhm; 15 mJ/pulse).

Photoproduct Analysis. A sample solution was prepared by mixing cyclohexanone (16 g), PE3A (1.0 g), **KCD** (0.020 g), and the initiator (1.2×10^{-4} mol). A sample plate was prepared by coating the sample solution onto a glass plate and dried to produce a 1.5 μm thickness film, followed by applying PVA of 1 μm. The plate was exposed to the light (435 nm) with 1.6 mW/cm^2 for 120 s. A 0.01 g portion of the film exposed on the plate was extracted by 1 mL of hexane. The hexane extract containing photoproducts was analyzed by a GC/MS. GC/MS spectra were measured on a HP 5970 mass selective detector coupled with a HP 5890 series II GC with a DB-5 column (J & W Scientific, 30 m × 0.25 mm i.d. × 0.25 μm film thickness).

Computational Molecular Orbital Calculation. All calculations were performed using a semiempirical molecular orbital calculation program, AM1[31,32] (in MOPAC version 6.01[33]), on a Fujitsu S-4/10 computer with an ANCHOR II software (Fujitsu). The sulfonium cations and the sulfonium radicals were calculated by the restricted Hartree−Fock (RHF) and the unrestricted Hartree−Fock (UHF) methods, respectively. The geometry of the cations and the radicals was completely optimized in all internal coordinates using the keyword EF and GNORM = 0.01. Each bond energy in the sulfonium radicals was evaluated as a two-center energy using the keyword ENPART.

Results and Discussion

Properties of the Sulfonium Borates. Table 1 shows the several properties of dialkylphenacylsulfonium butyltriphenylborates **SB1a**−**SB4a**. The electrochemical reduction potentials for these sulfonium borates were all irreversible, and the peak potentials (E_{red}) are provided in the table.

SB1a−**SB1h** had melting points from 137 to 157 °C and were stable at 25 °C over six months. Hence, it is assumed that the substituent X does not affect the thermal stability of these sulfonium borates. However, it was observed that the E_{red} values of the sulfonium borates were influenced by the substituent X. Figure 2 shows Hammett's plots for the E_{red} value and the lowest unoccupied molecular orbital (LUMO) energy level of the sulfonium cations of **SB1a**−**SB1h**.

It is reported that the E_{red} value of several sulfonium salts varied with the substituent on their sulfur

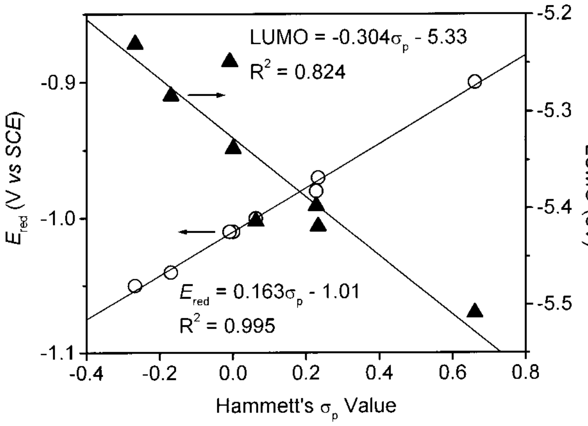


Figure 2. Plots of the reduction potential (E_{red}) and the lowest unoccupied molecular orbital (LUMO) energy level of the sulfonium cations of **SB1a**–**Sb1h** as a function of the Hammett σ_p value.

atoms.[34–38] Also, it is known that the LUMO energy level of sulfonium cations can be estimated by a semiempirical molecular orbital calculation such as AM1[36–38] or PM3.[39,40] It is evident that Hammett's σ_p value increases with increasing E_{red} value and with decreasing LUMO energy level of the sulfonium cations. Namely, an increase in the electron-withdrawing ability of the substitutent X produces the more positive E_{red} value. As described in the following section, we shall show that the E_{red} value and the LUMO energy level of the sulfonium cations influenced the photopolymerization of an acrylate.

On the other hand, the thermal stability of the sulfonium borates is significantly affected by the alkyl groups R_1 and R_2 on their sulfur atoms. **SB1a** having two methyl groups was stable in the solid state at 25 °C over 6 months as shown in a previous paper.[19] However, **SB2a** having a methyl group and an ethyl group was less stable than **SB1a** and turned yellow under the same condition within 6 months. **SB3a** having two ethyl groups was even more unstable and turned brown due to decomposition within a few months. Conversely, **SB4a** was more stable than **SB1a**. The thermal stability would be a little higher in **SB4a** compared to **SB1a** because of the formation of a rigid structure, since the tetramethylene group on the sulfur atom of **SB4a** is not able to exhibit free rotation.

To confirm the influence of the alkyl groups R_1 and R_2 on the thermal stability of the sulfonium borates, gelation of a polymerizable composition containing the sulfonium borates was examined. When a composition consisting of cyclohexanone, PE3A, and **SB1a** was kept at 50 °C in the dark, its viscosity increased, and gelation of trace amounts of the PE3A was observed after 2 weeks under this condition. Gelation for **SB2a** was observed after 1 week. In the case of **SB3a**, gelation of large amounts of PE3A occurred within 2 days. However, gelation of **SB4a** did not occur even after 2 weeks.

It seems that these thermal stabilities reflected the decomposition at the melting points. Both the thermal stability and the melting point of the sulfonium borates decrease in the order **SB4a** > **SB1a** > **SB2a** > **SB3a**. However, this order was different from that of the E_{red} value. Hence, the thermal stability would come from the steric repulsion of the two alkyl groups between R_1 and R_2 rather than an electron-transfer reaction from the borate anions to the sulfonium cations such as diphenyliodonium butyltriphenylborate.[19,41]

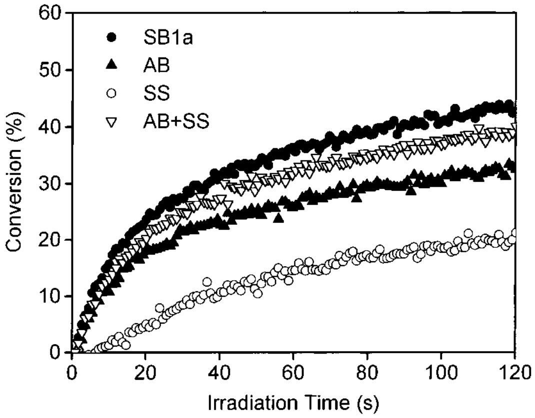


Figure 3. Photopolymerization profiles of PE3A in a PMMA film recorded by RT–FTIR. Key: **SB1a** (●); **AB** (▲); **SS** (○); equimolar mixture of **AB** and **SS** (▽). $[\text{PE3A}]_0 = 2.0$ M, $[\textbf{KCD}]_0 = 2.6 \times 10^{-2}$ M, and $[\text{initiator}]_0 = 7.1 \times 10^{-2}$ M in the PMMA film. Light intensity = 1.6 mW/cm² (435 nm).

The solubility of the sulfonium borates was examined, since generally photoinitiators are used and dissolved in solvents such as ketones or esters. Their solubility in several solvents is listed in Table 1. These solvents were typical ketones and esters and sometimes used in industry. The solubility in the ketones was higher than that in the esters. It seems that an increase in the hydrophobicity of the solvent decreases the solubility. The poor solubility for **SB4a** would be derived from the rigid structure. Though **SB3a** showed excellent solubility, it has the disadvantage of thermal instability.

Effect of the Reduction Potential of the Sulfonium Cation on Photopolymerization Kinetics. Photopolymerization kinetics of an acrylate in a PMMA film were measured by real time Fourier transform infrared (RT–FTIR) spectroscopy.[29,30] PE3A and PMMA were used, since they are a typical multi-functional acrylate monomer and a binder polymer, respectively. The rate of polymerization (R_p) can be calculated from the decrease of the absorption band at the 810 cm^{-1} based on the acrylate double bond.[29,30] Since the sulfonium borates hardly absorb light at 435 nm, no photolysis of the sulfonium borates themselves would take place by this wavelength.

Figure 3 shows the photopolymerization profiles of PE3A in a PMMA film for a comparison of **SB1a** with the related initiators (**AB** and **SS**). It is evident that both the R_p value and the degree of conversion for **SB1a** were higher than those for **AB** or **SS**. Namely, the relative efficiency of **SB1a** as an initiator is higher than that of **AB** or **SS**. It is interesting to note that the relative efficiency of the mixture of **AB** and **SS** was lower than that of **SB1a**. In the case of the mixture, an ion exchange reaction between **AB** and **SS** may occur to form **SB1a** and tetrabutylammonium tetrafluoroborate. When an equimolar mixture of **SB1a** and tetrabutylammonium tetrafluoroborate was used, its mixture gave the same photopolymerization profile as the equimolar mixture of **AB** and **SS**. Thus, it has been clarified that tetrabutylammonium tetrafluoroborate inhibited the photopolymerization.

Figure 4 shows the influence of the para-substituent on the phenacyl groups of the sulfonium borates on the photopolymerization. It was observed that both the R_p values and the degrees of conversion increased in the order **SB1b** > **SB1a** > **SB1h**. Table 2 summarizes the R_p values and the degrees of conversion. As shown in

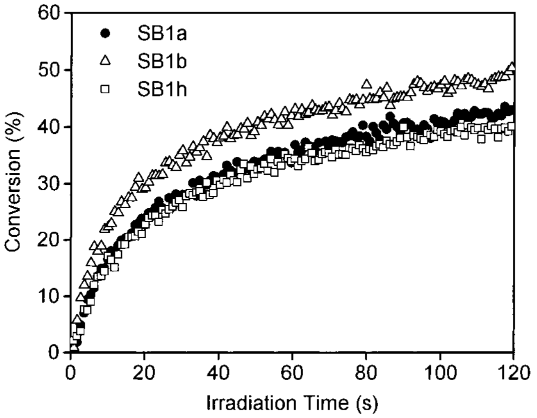


Figure 4. Influence of the *p*-substituent on the phenacyl group of the sulfonium borates on the photopolymerization of PE3A in a PMMA film. Key: **SB1a** (●, H); **SB1b** (△, CN); **SB1h** (□, MeO). $[\text{PE3A}]_0 = 2.0$ M, $[\mathbf{KCD}]_0 = 2.6 \times 10^{-2}$ M, and $[\text{initiator}]_0 = 7.1 \times 10^{-2}$ M in the PMMA film. Light intensity = 1.6 mW/cm^2 (435 nm).

Table 2. Rate of Polymerization (R_p) and Degree of Conversion on the Photopolymerization of PE3A in a PMMA Film by the Sulfonium Borate−KCD Photoinitiator Systems[a]

initiator	R_p (10^3 M/s)	conversion[b] (%)
SB1a	1.10	43
SB1b	1.76	50
SB1c	1.47	46
SB1d	1.21	45
SB1e	1.09	43
SB1f	1.22	43
SB1g	1.02	42
SB1h	1.07	40
SB2a	1.01	43
SB3a	1.01	43
SB4a	1.03	42
AB	0.80	33
SS	0.10	20
AB + **SS**[c]	0.93	39

[a] $[\text{PE3A}]_0 = 2.0$ M, $[\mathbf{KCD}]_0 = 3.8 \times 10^{-2}$ M, and $[\text{initiator}]_0 = 6.0 \times 10^{-2}$ M in the PMMA film. Light intensity = 1.6 mW/cm^2 (435 nm). [b] Degree of conversion at 120 s after light irradiation. [c] Equimolar mixture of **AB** and **SS**.

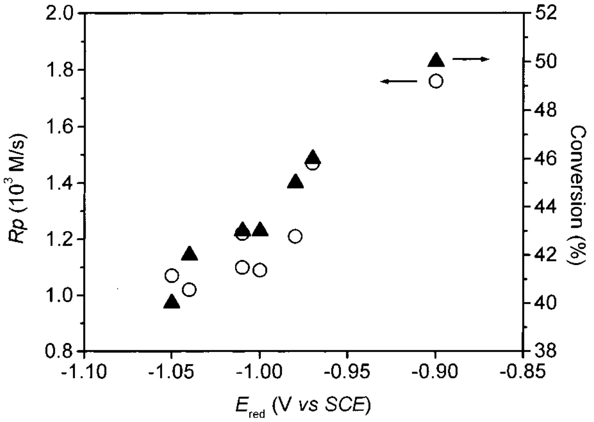


Figure 5. Dependence of the rate of polymerization (R_p) and the degree of conversion on the reduction potential (E_{red}) of the sulfonium cations of **SB1a**−**SB1h**.

Figure 5, the R_p values and the degrees of conversion depend on the E_{red} values of the sulfonium cations. A similar observation is reflected in the LUMO energy levels of the sulfonium cations as shown in Figure 6. It is clarified that the more positive the E_{red} values and the lower the LUMO energy levels, the higher the R_p value and the degree of conversion. On the other hand, both the R_p values and the degrees of conversion for **SB2a**−**SB4a** were lower than for **SB1a**, since the E_{red} values of these sulfonium cations were more negative than that of **SB1a**.

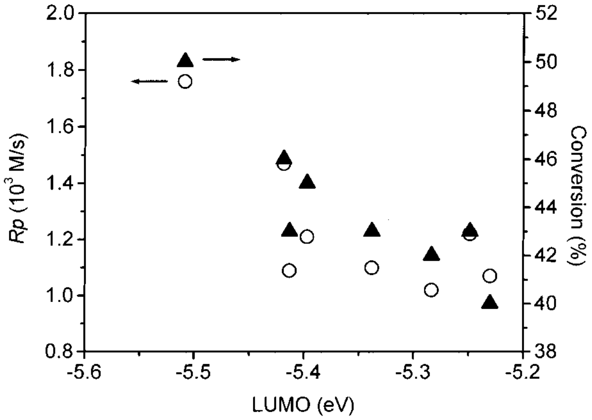


Figure 6. Dependence of the rate of polymerization (R_p) and the degree of conversion on the lowest unoccupied molecular orbital (LUMO) energy level of the sulfonium cations of **SB1a**−**SB1h**.

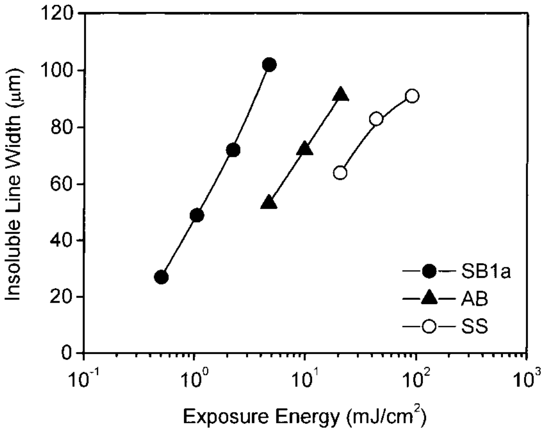


Figure 7. Sensitivity curves of the photopolymerizable film containing the initiators and **KCD** for argon-ion laser light. Key: **SB1a** (●); **AB** (▲); **SS** (○). $[\text{PE3A}]_0 = 2.0$ M, $[\mathbf{KCD}]_0 = 2.6 \times 10^{-2}$ M, and $[\text{initiator}]_0 = 7.1 \times 10^{-2}$ M in the PMMA film. Light intensity = 1.6 mW/cm^2 (488 nm).

Sensitivity of the Photopolymerizable Film onto Argon Ion Laser. The sensitivity measurement of the photopolymerizable film was carried out by scanning the light (488 nm) of an argon-ion laser. The film used was the same as the RT−FTIR study. Irradiation was kept at a constant intensity of the light with varying scanning speed at this wavelength. Figure 7 shows the characteristic curves of the photopolymerizable films containing the initiators and **KCD**. The sensitivity of the photopolymerizable film containing **SB1a** was 4.5-fold higher than that of the related ammonium borate **AB** and 12-fold higher than that of the sulfonium salt **SS** at the insoluble line width of 65 μm. This order of the sensitivity agrees with that of the R_p value in the RT−FTIR study.

Figure 8 shows the dependence of laser incident power on the sensitivity of the photopolymerizable film containing **SB1a** and **KCD**. The sensitivity was not dependent on the laser incident power in the range 1.9×10^5 to 8.4×10^6 mW/cm^2.

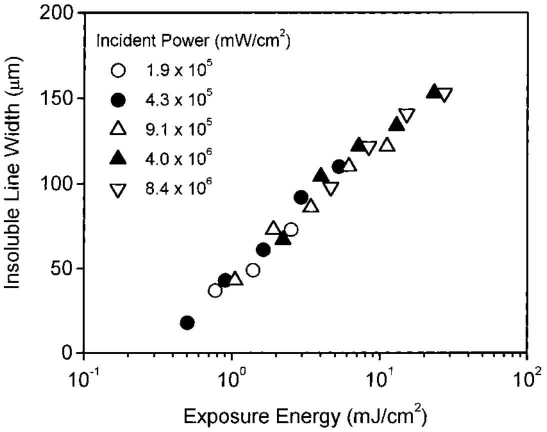


Figure 8. Dependence of laser incident power on the sensitivity of the photopolymerizable film containing **SB1a** and **KCD**. $[\mathrm{PE3A}]_0 = 2.0$ M, $[\mathbf{KCD}]_0 = 2.6 \times 10^{-2}$ M, and $[\mathrm{initiator}]_0 = 7.1 \times 10^{-2}$ M in the PMMA film. Light intensity = 1.6 mW/cm² (488 nm).

Photoreaction Mechanism between the Sulfonium Borate and KCD. It is important to consider the mechanism of photoinitiation process between initiators and sensitizer to clarify the details of the photopolymerization. The free energy change (ΔG_{et}) on a photoinduced electron-transfer reaction is given by the Rehm–Weller equation (eq 1),[42] where $E_{\mathrm{ox}}(\mathrm{D/D^{+\bullet}})$ is the oxidation

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

potential of the donor, $E_{\mathrm{red}}(\mathrm{A^{-\bullet}/A})$ is the reduction potential of the acceptor, E is the excited energy of the sensitizer, and $Ze^2/\epsilon\alpha$ is the Coulombic energy, which is the free energy gained by bringing the two radical ions formed to an encounter distance α in a solvent with dielectric constant ϵ. In a previous paper,[19] we clarified that the photoreaction between **SB1a** and the aromatic diketones is based on a photoinduced electron transfer (PET). To obtain the free energy changes $\Delta G^{\mathrm{S,T}}$ (suffixes S and T stand for singlet and triplet, respectively) between the sulfonium borates and the excited state of **KCD**, we approximated eq 1 to eq 2 and eq 3 as follows:

$$\Delta G^{\mathrm{S,T}} = E_{\mathrm{ox}}(\mathbf{KCD}/\mathbf{KCD}^{+\bullet}) - E_{\mathrm{red}}(\mathrm{Sul^{\bullet}/Sul^{+}}) - E^{\mathrm{S,T}} \quad (2)$$

$$\Delta G^{\mathrm{S,T}} = E_{\mathrm{ox}}(\mathrm{Bo^{-}/Bo^{\bullet}}) - E_{\mathrm{red}}(\mathbf{KCD}^{-\bullet}/\mathbf{KCD}) - E^{\mathrm{S,T}} \quad (3)$$

Here, $E_{\mathrm{ox}}(\mathbf{KCD}/\mathbf{KCD}^{+\bullet})$ and $E_{\mathrm{red}}(\mathbf{KCD}^{-\bullet}/\mathbf{KCD})$ are the oxidation (1.03 V vs SCE[43]) and reduction (−1.23 V vs SCE[43]) potentials of **KCD**. $E_{\mathrm{red}}(\mathrm{Sul^{\bullet}/Sul^{+}})$ and $E_{\mathrm{ox}}(\mathrm{Bo^{-}/Bo^{\bullet}})$ are the reduction potentials of the sulfonium cation and the oxidation potentials of the borate anion of the sulfonium borates, respectively. $E^{\mathrm{S,T}}$ combines the excitation energies of **KCD** ($E^{\mathrm{S}} = 59.6$ kcal/mol;[43] $E^{\mathrm{T}} = 50.8$ kcal/mol[20]). Table 3 summarizes the ΔG^{S} and ΔG^{T} values. Both the ΔG^{S} and ΔG^{T} values for the PET processes from the excited states of **KCD** (**KCD***) to the sulfonium cation are slightly more negative than those from the borate anion to **KCD***. It is considered that the former processes occur more readily than the latter processes.

It is reported that the quantum yields of the fluorescence and the intersystem crossing of **KCD** are 0.0064[43] and 0.92,[20] respectively. Namely, the quantum yield of the intersystem crossing is ca. 144-fold greater than that of the fluorescence. It is also reported[43] that the lifetime of the excited singlet state and triplet state of **KCD** are 0.41 ns and 5.9 μs, respectively. The lifetime of the triplet state of **KCD** (^{3}**KCD**) is 1.2×10^4 fold longer than that of the excited singlet state of **KCD** (^{1}**KCD***). Hence, it seems that the initiators in Table 3 react with ^{3}**KCD** rather than ^{1}**KCD***. In fact, no quenching of the fluorescence of **KCD** was observed in solutions such as ethyl acetate, methanol, dichloromethane. However, it is possible slightly that the initiators react with ^{1}**KCD*** as well as ^{3}**KCD**, since the concentration of the initiators in the film is higher than that in solution. It is known that ^{1}**KCD*** was quenched by 3,3′,4,4′-tetrakis(*tert*-butyldioxycarbonyl)benzophenone[44,45] or 2,2′-bis(2-chlorophenyl)-4,4′,5,5′-tetraphenyl-1,1′-bi-1*H*-imidazole[46] in a PMMA film. Also, no evidence of ground-state complex formation was obtained for **KCD** with the initiators in these solutions and in a PMMA film.

We attempted to confirm the reaction ^{3}**KCD** with the initiators using the laser flash photolysis technique. The quenching rate constant ($k_{\mathrm{q}}^{\mathrm{T}}$) of ^{3}**KCD** by the initiators is estimated as shown in eq 4, where [initiator] is the

$$k_{\mathrm{obs}} = k_0 + k_{\mathrm{q}}^{\mathrm{T}}[\mathrm{initiator}] \quad (4)$$

concentration of the initiators, k_{obs} and k_0 are the decay rate constant of the transient absorption of ^{3}**KCD** in the presence and absence of the initiator, respectively. It is reported that transient absorption bands of ^{3}**KCD** appear at 520[22,23] and 725 nm.[25] In the laser flash photolysis study, it was observed that ^{3}**KCD** showed the same transient absorption bands and was quenched by **SB1a**, **SS**, and **AB**. The $k_{\mathrm{q}}^{\mathrm{T}}$ values are presented in Table 3. Since the $k_{\mathrm{q}}^{\mathrm{T}}$ value for **SB1a** was *ca.* 13-fold higher than for **AB** and was the same as for **SS**, the PET from ^{3}**KCD** to dimethylphenacylsulfonium cation occurs more easily than that from butyltriphenylborate anion to ^{3}**KCD**.

Photoreaction and photopolymerization using dimethylphenacylsulfonium salts are reported.[49−52] Nevertheless, the chemistry of the corresponding sulfur radical has not yet been investigated in detail. Since the sulfur radical could not be observed by our laser flash photolysis apparatus, it was investigated by AM1 calculation.[31,32] It is known that several sulfonium cations undergo single electron reductive cleavage due to the σ^* nature of the LUMO.[34−38] When their sulfonium cations are reduced based on a PET, the corresponding sulfur radicals would be generated. Figure 9 shows the LUMO of dimethylphenacylsulfonium cation and the single occupied molecular orbital (SOMO) of the corresponding sulfur radical. The LUMO is localized primarily on the carbon and around the sulfur and is an antibonding σ^* orbital. The SOMO also shows the similar σ^* orbital and predicts that the sulfur−carbon bond cleavage should occur at the sulfur-phenacyl bond rather than at the sulfur-methyl bond as consequence of the single electron reduction.

Bond cleavage is also estimated by the two-center energy[39,40] between the sulfur atom and its neighboring carbon atoms. Table 4 shows the two-center energy of the sulfur−carbon bonds in the sulfur radicals. The two-center energy, which means bond strength, indicates that the sulfur−phenacyl bond (−11.93 eV) cleaves more easily than the sulfur−methyl bond (−13.34 eV) in the sulfur radical. These calculation results also suggest that the phenacyl radical is more easily generated than the methyl radical.

Table 3. Free Energy Changes (ΔG^S and ΔG^T) and Quenching Rate Constants (k_q^T) for the Excited States of KCD with the Initiators[a]

	ΔG^S (kJ/mol)		ΔG^T (kJ/mol)		
initiator	^{1}**KCD*** → Sul$^+$	Bo$^-$ → ^{1}**KCD***	^{3}**KCD** → Sul$^+$	Bo$^-$ → ^{3}**KCD**	k_q^T (M^{-1} s^{-1})[b]
SB1a	−52.1	−49.2	−15.4	−12.5	9.11×10^6
SS	−52.1		−15.4		9.11×10^6
AB		−49.2		−12.5	7.03×10^5

[a] ^{1}**KCD***: excited singlet state of **KCD**. ^{3}**KCD**: triplet state of **KCD**. Sul$^+$: dimethylphenacylsulfonium cation. Bo$^-$: butyltriphenylborate anion. Singlet excitation energy of **KCD** = 59.6 kcal/mol.[43] Triplet energy of **KCD** = 50.8 kcal/mol.[20] [b] Measured in argon-saturated benzonitrile. Excitation wavelength = 355 nm; [**KCD**] = 0.1 mM.

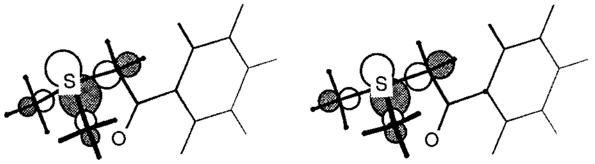


Figure 9. Lowest unoccupied molecular orbital (LUMO) of dimethylphenacylsulfonium cation (left) and single occupied molecular orbital (SOMO) of dimethylphenacylsulfur radical (right) by AM1 calculation.

Table 4. Lowest Unoccupied Molecular Orbital (LUMO) Energy Level of the Sulfonium Cation of the Sulfonium Borates and Two-Center Energy of the Sulfur−Carbon Bonds in the Corresponding Sulfur Radicals[a]

		two-center energy (eV)	
initiator	LUMO (eV)	S−CH$_2$COAr	S−R$_1$, S−R$_2$
SB1a	−5.34	−11.93	−13.34
SB1b	−5.51	−11.43	−13.47
SB1c	−5.42	−11.88	−13.37
SB1d	−5.40	−11.87	−13.37
SB1e	−5.41	−11.87	−13.37
SB1f	−5.25	−11.55	−13.43
SB1g	−5.28	−11.54	−13.42
SB1h	−5.23	−11.54	−13.41
SB2a	−5.27	−11.51	−13.52,[b] −12.56[c]
SB3a	−5.23	−11.51	−12.66
SB4a	−5.16	−11.03	−12.61

[a] Calculated by AM1[31,32] in MOPAC version 6.01.[33] The LUMO energy level and the two-center energy are estimated by RHF and UHF methods, respectively. Ar: phenyl or *p*-substituted phenyl groups. [b] The value based on a S−Me bond. [c] The value based on a S−Et bond.

Evidence for generation of the phenacyl radical was also confirmed by photoproduct analysis. From the irradiated photopolymerizable film containing the **SB1a** and **KCD**, dimethyl sulfide, biphenyl, and 1-phenyl-1-hexanone as major photoproducts and acetophenone as a minor photoproduct were detected. Dimethyl sulfide, 1-phenyl-1-hexanone, and acetophenone would be produced by the butyl and phenacyl radicals generated by the decomposition of **SB1a**. Since biphenyl was detected from the analysis of triphenylborane, it may be produced in the GC analysis.

We also assume the decomposition of the sulfur radical by AM1 calculation. Figure 10 shows the potential energy change in the bond length between the sulfur atom and the methylene carbon of the phenacyl group in the sulfur radical. The most stable conformer of the sulfur radical has 1.75 Å of the bond length. The conformer at the transition state of the sulfur radical has 3.0 Å of the bond length, because its heat of formation and reaction gradient exhibit the maximum value and a value of zero, respectively. The difference in the heat of formation at these two conformers is estimated to be 20.8 kcal/mol; therefore, it is expected that this sulfur radical is quite stable and that its decomposition is an endothermic reaction with bond dissociation energy over 20.8 kcal/mol. From the above properties, it can be inferred that the sulfur radical has a long lifetime as compared with butyltriphenylboranyl radical. It is known that the boranyl radical decomposes to form butyl radical and triphenylborane in less than 250 fs.[47,48] Thus, the back electron transfer from the boranyl radical to butyltriphenylborate anion would not occur.

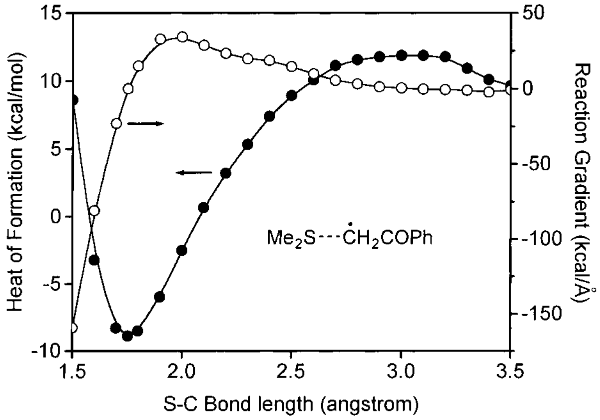
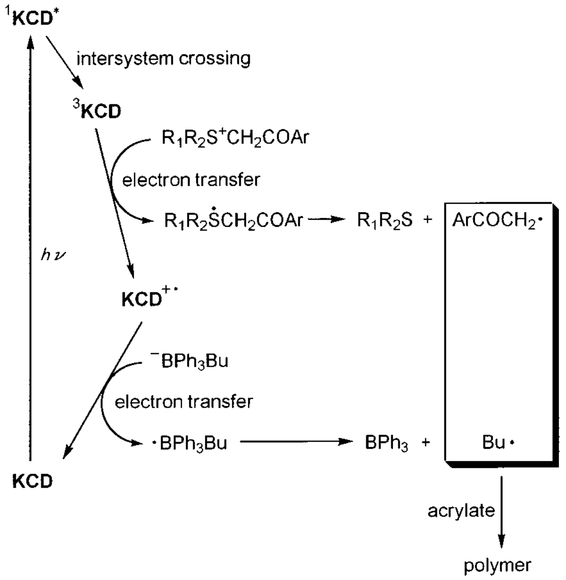


Figure 10. Potential energy change for the generation of the phenacyl radical from dimethylphenacylsulfur radical by AM1 calculation (minimum energy path). The S−C bond length exhibits the distance between the sulfur atom and the methylene carbon of the phenacyl group.

Scheme 1. Proposed Mechanism for Radical Generation from the Sulfonium Borate by KCD Sensitization



From the above results, the proposed mechanism of the photoreaction between the sulfonium borates and **KCD** is depicted in Scheme 1. Namely, first **KCD** absorbs light and transforms into ^{3}**KCD** via ^{1}**KCD*** (process 5). Second, ^{3}**KCD** is oxidized by the sulfonium cation ($R_1R_2S^{+}CH_2COAr$). As a result, the cation radical of **KCD** (**KCD**$^{+\bullet}$) and the corresponding sulfur radical ($R_1R_2S^{\bullet}CH_2COAr$) are generated (process 6). ^{3}**KCD** may be also reduced by the borate anion ($^{-}BPh_3Bu$), and the anion radical of **KCD** (**KCD**$^{-\bullet}$) and the corresponding boranyl radical ($^{\bullet}BPh_3Bu$) are generated (process 7). However, process 6 preferentially occurs over process 7 from the results of the ΔG and k_q^{T} values. Third, **KCD**$^{+\bullet}$ is reduced by the borate anion, **KCD** is re-formed, and the boranyl radical is generated (process 8). The dependence of process 9 upon process 7 is minor. Consequently, the generated sulfur and boranyl radicals decompose to form the phenacyl radical ($ArCOCH_2^{\bullet}$) and the butyl radical ($Bu^{\bullet}$), respectively (processes 10 and 11). Finally, these generated radicals, $ArCOCH_2^{\bullet}$ and $Bu^{\bullet}$, initiate polymerization of an acrylate.

Conclusions

In this paper, we have presented the theory that the initiation efficiency of sulfonium borate initiators for the photopolymerization of an acrylate with a visible light sensitizer is controlled by the reduction potentials of their sulfonium cations. These initiator systems can be applied to visible laser polymerizations in the fields such as laser direct imaging, holography, stereolithography.

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Supporting Information Available: Figures showing plots of the quenching of triplet **KCD** (Figures 1S−3S) and a plot of the dependence of the pseudo-first-order rate constants for quenching on the concentration of the quenchers (Figure 4S). This material is available free of charge via the Internet at http://pubs.acs.org.

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