Macromolecules **1998,** *31,* 6022−6029

Onium Butyltriphenylborates as Donor−Acceptor Initiators for Sensitized Photopolymerizations of Vinyl Monomer

Yasumasa Toba and Yoshiharu Usui*

Graduate School of Science and Engineering, Ibaraki University, 2-1-1, Bunkyo, Mito, Ibaraki 310, Japan

Maksudul M. Alam and Osamu Ito

Institute for Chemical Reaction Science, Tohoku University, Katahira, Aoba-ku, Sendai, 980-8577, Japan

Received January 30, 1998; Revised Manuscript Received June 10, 1998

ABSTRACT: Donor−acceptor initiators, onium butyltriphenylborates (DPIB, DMPSB) containing both an onium cation (electron-accepting radical generator) and a borate anion (electron-donating radical generator) within the same compound were able to be sensitized by two aromatic ketones (2-chlorothioxanthone and Michler's ketone) to initiate polymerization of tetrahydrofurfuryl acrylate monomer. The photopolymerization efficiency of the onium butyltriphenylborates was higher than that of the onium salts (DPI, DMPS) or the borate compound (TBAB). The photoinitiation processes between the photosensitizers and the initiators have been investigated by laser flash photolysis. It has been clarified that two kinds of radical species are generated by a photoinduced electron-transfer mechanism.

Introduction

Photopolymerization is widely used in the areas of radiation curing and imaging technologies, e.g. photoresists, laser imaging, holography and stereography, etc. The development of materials in the field of photopolymerization requires researchers to discover more efficient photoinitiator systems. A large number of studies have been made on photoinitiator systems. The initiator systems based on sensitized electron-transfer reactions are well-known; the systems are either electron-accepting initiator/electron-donating photosensitizer or electron-donating initiator/electron-accepting photosensitizer.[1]

Particular onium salts such as diaryliodonium,[2−6] triarylsulfonium[3−8] and dialkylphenacylsulfonium[9] salts are typical electron-accepting initiators, which are reduced by electron-donating photosensitizer, e.g. Michler's ketone,[10] thioxanthones,[10−14] based on a photoinduced electron-transfer mechanism.

On the other hand, some kinds of borate compounds (e.g. alkyltriarylborates) are typical electron-donating initiators and are oxidized by electron-accepting photosensitizers such as cyanine dye cation,[15−17] fluorones,[18−20] benzophenone derivatives,[21,22] and chromophore ammonium.[23] Recently, the three component photoinitiator systems (sensitizers/onium salts/borate compounds) could also be found in the proceedings[24] and the patent applications[25,26] by Neckers et al.

The onium salts or the borate compounds are decomposed as a result of photoreduction or photooxidation, respectively, generating free radicals, which in turn initiate polymerization of vinyl monomers (e.g., acrylates, mathacrylates). Although an anion radical (or cation radical) of the photosensitizers is formed at the same time, the radical of the photosensitizers is generally too reactive to initiate polymerization.

Recently, we reported in a short communication[27] that the onium borates act as efficient photoinitiators and are able to satisfy the requirement in the field of photopolymerization. Some of the onium borates are also found in symposium proceedings[28] and patent applications[29−32] to be efficient photoinitiators. The present paper deals with characterization of the onium borates, the efficiency of the onium borates for photopolymerization with an acrylate monomer, and the mechanism of the photoinitiation process between the onium borates and aromatic ketones as photosensitizers (Figure 1).

Experimental Section

NMR spectra were measured using a JEOL JMN-GSX270 NMR spectrometer. Chemical shifts are in ppm with tetramethylsilane as the internal standard. Absorption spectra and fluorescence spectra were recorded on a Jasco V-530 UV/vis spectrophotometer and a Jasco FP-770F spectrofluorometer, respectively. Redox potentials of initiators were measured by cyclic voltammetry on a CV-50W voltammetric analyzer (BAS Inc.) by the standard procedure.[33] All the measurements were carried out with a scan rate of 100 mV/s in dry acetonitrile under argon at room temperature. Platinum-inlay electrodes were used as the working electrode along with a platinum auxiliary electrode and a $Ag/AgClO_4$ 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)[34] and converted to those relative to SCE by the addition of 0.337 V. The redox potential, E_{red} and E_{ox} values of the initiators and the photosensitizers show the peak potential (E_p) for the initiators and the thermodynamic potential ($E_{1/2}$) for the photosensitizers, respectively.

Acetonitrile and dicholoromethane were used as received (Merck, HPLC grade). Diphenyliodonium hexafluorophosphate (DPI) and dimethylphenacylsulfonium tetrafluoroborate (DMPS) were obtained from Tokyo Chemical Industries Co., Ltd.. Tetrahydrofurfuryl acrylate (THFA, Osaka Organic Chemical Industry Ltd.) was distillated before use. The photosensitizers, 2-chlorothioxanthone (CTX, Tokyo Chemical Industries Co., Ltd.) and Michler's ketone (MK, Aldrich) were used after being recrystallized from ethanol. Lithium butyltriphenylborate,[35] tetrabutylammonium butyltriphenylborate (TBAB),[19] dimethylphenacylsulfonium bromide,[36] diphenyliodonium butyltriphenylborate (DPIB),[27] and dimethylphena-

S0024-9297(98)00131-4 CCC: $15.00

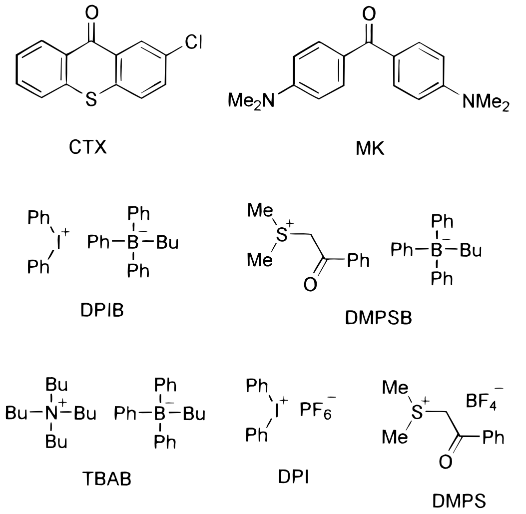


Figure 1. Structure of sensitizers and initiators.

cylsulfonium butyltriphenylborate (DMPSB)[27] were prepared and isolated according to the reported procedure.

Photopolymerization. The rates of polymerization (R_p) were measured with IR spectroscopy by the methods described previously.[27,37] Sample solution was prepared by mixing the initiator, the photosensitizer, THFA, and solvent. The solution was flushed with argon and immediately filled in a KBr solution cell and sealed. The KBr cell containing the solution was placed into an IR spectrometer (Jasco IR-700 infrared spectrometer), by fixing at 810 cm^{-1} where the acrylic double bond exhibits sharp and distinct absorption. The cell was irradiated by light (365 nm) from a high-pressure mercury lamp (Ushio Inc. USH-500D) after passing through a HA-30 heat absorbing filter and an U-360 ultraviolet filter. The light intensity at the cell position measured using an optical power meter (Ushio Inc. UTI-150 Unimeter) was found to be 1.6 mW/cm^2.

Steady-State Photolysis. Sample solution (2 mL) was irradiated in a 1 cm quartz cuvette purged with argon. The light intensity at the cuvette position was 8 mW/cm^2. The irradiated solution was analyzed by GC or GC/MS. GC measurements were carried out on a Hewlett-Packard (HP) 5890 series II gas chromatograph with a 15 m × 0.53 mm i.d. × 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 i.d. × 0.25 μm film thickness DB-5 column (J & W Scientific).

Laser Flash Photolysis. The laser flash photolysis apparatus was standard design with a Q-switched Nd:YAG laser (Quanta-Ray, GCR-130, fwhm 6 ns) as the excitation source.[38] The sample solutions were photolyzed with light from the third harmonic generator (THG, 355 nm, ca. 10 mJ/pulse). The time profiles were measured using a photomultiplier system. The transient absorption spectra were recorded with a multichannel photodiode system. The sample solutions were contained in a 1 cm × 1 cm × 4 cm quartz cuvette and were deaerated using argon gas.

Results and Discussion

Characterization of the Onium Borates. The absorption spectrum of DPIB in MeCN was equal to the additive spectrum obtained from the spectra of DPI and TBAB in MeCN (a polar solvent). In CH_2Cl_2 (a less polar solvent), DPIB exhibits a weak extended absorption tail in the 320−450 nm region and enhanced absorptivity. The absorptivity of DPIB in CH_2Cl_2 was stronger than that of the additive spectrum obtained from those of DPI and TBAB in CH_2Cl_2 (Figure 2).

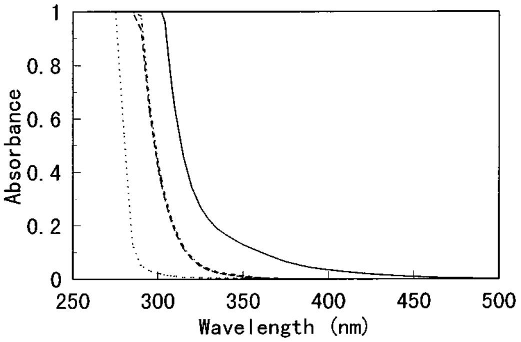


Figure 2. Absorption spectra of 1.0 mM DPIB (solid), DPI (dash), and TBAB (dotted) in CH_2Cl_2 and the additive spectrum of DPI and TBAB (dot−dash).

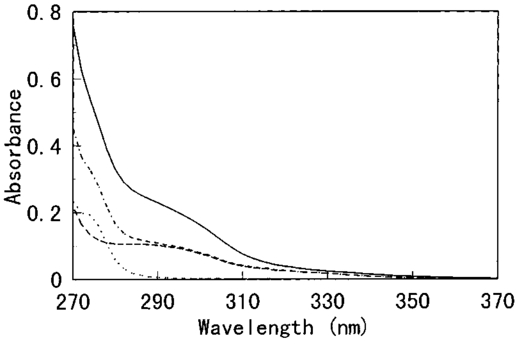


Figure 3. Absorption spectra of 0.1 mM DMPSB (solid), DMPS (dash), and TBAB (dotted) in CH_2Cl_2 and the additive spectrum of DMPS and TBAB (dot−dash).

The extended absorption tail and the enhanced absorptivity observed for DPIB in CH_2Cl_2 can be attributed to an ion-pair charge transfer (IPCT) transition from butyltriphenylborate anion to the diphenyliodonium cation. On the other hand, DMPSB did not exhibit an extended absorption tail like DPIB in CH_2Cl_2; however, the absorptivity of DMPSB was greater than that of the additive spectrum obtained from the spectra of DMPS and TBAB in CH_2Cl_2 (Figure 3). Furthermore, in the ^1H NMR spectra of both DPIB and DMPSB, the signal shape of the spectra in MeCN-d_3 and DMSO-d_6 was more sharp than that of in acetone-d_6 and in $CDCl_3$. We suppose that the onium borates, DPIB and DMPSB exist primarily as weak solvated ion pair in polar solvents and as IPCT complex in less polar solvents (eq 1).

$$(\mathrm{On^+\,Bo^-})_{\mathrm{CT}} \xrightarrow{+\,\mathrm{MeCN}} \mathrm{On^+_s\,Bo^-_s} \qquad (1)$$

IPCT complex solvated ion pair
in less-polar solvents in polar solvents
(*e.g.*, CH_2Cl_2) (*e.g.*, MeCN)

$\mathrm{On^+}$: $\mathrm{Ph_2I^+}$ or $\mathrm{Me_2S^+CH_2COPh}$
$\mathrm{Bo^-}$: $\mathrm{^-BPh_3Bu}$

DPIB in the solid state was stable below 5 °C for over 6 months, but it became unstable above 40 °C, turning brown after a few months in the dark by gradual decomposition. In contrast, DMPSB in the solid state was stable above 40 °C for over 6 months. Since DPIB is stronger IPCT complex than DMPSB both in a less polar solvent and the solid state, a decomposition by a redox reaction of DPIB itself more readily would occur than one with DMPSB. We infer that the redox reaction from the butyltriphenylborate anion to its countercation of the onium borates in the ground state would occur

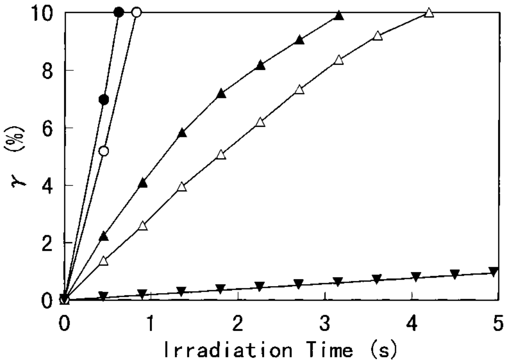


Figure 4. Influence of initiators (1.4×10^{-2} M) on the CTX (5.8×10^{-3} M) sensitized photopolymerization of THFA (9.2×10^{-1} M) in MeCN solutions. Key: DPIB (●); DMPSB (○); TBAB (▲); DPI (△); DMPS (▼). Light intensity = 1.6 mW/cm^2 (365 nm).

more easily in DPIB than in DMPSB, because the reduction potential of diphenyliodonium cation (−0.64 V vs SCE)[14] is higher than that of dimethylphenacylsulfonium cation (−1.01 V vs SCE).

Photopolymerization. Two aromatic ketones, CTX and MK, were selected as photosensitizers, because they have strong absorption in ultraviolet region and are important not only in fundamental studies but also for industrial uses. THFA was chosen to dissolve large amount of the initiators. The rate of polymerization (R_p) was measured by observing IR spectra before and after the irradiation. The absorbance levels at 810 cm^{-1} were used for the calculations of γ (acrylic double bond conversion),

$$\gamma = (A_0 - A_t)/A_0 \quad (2)$$

where A_0 and A_t are the absorbance levels at 810 cm^{-1} before and after the irradiation, respectively. The R_p values were obtained from the slope (γ/t) of the linear part of the time−γ curve (eq 3) below a 10% decreasing of γ. [THFA]$_0$ is the molar concentration of THFA before light exposure.

$$R_p = [\mathrm{THFA}]_0(\Delta\gamma/\Delta t) \quad (3)$$

The time dependence of photopolymerization of THFA in MeCN in the presence of CTX and several initiators is shown in Figure 4.

These findings clearly showed that the efficiency of the onium borates (DPIB and DMPSB) as an initiator is much higher than that of TBAB, DPI, or DMPS in the cases of CTX. Namely, the R_p value increases in the order DPIB > DMPSB > TBAB > DPI $\gg$ DMPS. Table 1 summarizes the results of photopolymerization of THFA using several initiators with the photosensitizer. In the cases of MK as a photosensitizer, the R_p values were less than the cases of CTX. Although the efficiency of MK as a photosensitizer was less than that of CTX so far as using the onium borates; the R_p values with MK were in the same order as those with CTX. The efficiency of the onium borates is also much higher than that of TBAB, DPI, or DMPS in the case of MK.

The R_p values in CH$_2$Cl$_2$ were increased compared with those in MeCN. These solvent effects on the R_p values were more pronounced in the case of MK than CTX. But, the efficiency of the initiators in CH$_2$Cl$_2$ was in the same order as that in MeCN. The solvent effects on the R_p values would be affected by the differential degree of dissociation in each initiators as shown in eq 1. We shall return to this point later.

Table 1. Rate of Sensitized Polymerization (R_p) of THFA Using Several Initiators[a]

sensitizer	initiator	R_p (M s^{-1}) in MeCN	R_p (M s^{-1}) in CH$_2$Cl$_2$
CTX	DPIB	15	17
	DMPSB	11	17
	TBAB	4.0	11
	DPI	2.2	5.1
	DMPS	0.26	*b*
MK	DPIB	5.1	16
	DMPSB	4.6	15
	TBAB	0.58	0.69
	DPI	0.21	0.26
	DMPS	0.062	*b*

[a] Light intensity = 1.6 mW/cm^2 (365 nm); [THFA]$_0$ = 9.2×10^{-1} M; [initiator]$_0$ = 1.4×10^{-2} M; [CTX]$_0$ = 5.8×10^{-3} M; [MK]$_0$ = 8.2×10^{-4} M. [b] Not detected because the solubility of DMPS was poor.

Neckers and co-workers recently reported the photopolymerization of iodonium borates themselves, which act as photoinitiators, without photosensitizers.[28] The photopolymerization in the report was similar to that using the combination of phenyl-4-octyloxyphenyliodonium hexafluoroantimonate (OPPI) and tetramethylammonium triphenylbutylborate as photoinitiator.[24] We also attempted to polymerize using the initiators (DPIB, DMPSB, DPI, TBAB, DMPS) without photosensitizers (CTX, MK), but we could not observe polymerization in any our experimental conditions, because the photopolymerizable compositions hardly absorb light at 365 nm without photosensitizers. We think that there is little that the onium borates themselves do to initiate photopolymerization under the conditions.

Steady-State Photolysis Study. It is important to consider the mechanism of photoinitiation process between the onium borates and the photosensitizer to clarify the details of the photopolymerization. No evidence of ground-state complex formation was obtained for CTX and MK with the initiators in both MeCN and CH$_2$Cl$_2$.

While the apparent spectra of CTX in an argon-saturated MeCN solution containing DPIB showed no appreciable change with light irradiation (Figure 5a), the spectra of the solution containing DPI (Figure 5b) or TBAB (Figure 5c) clearly showed bleaching of CTX with light irradiation. The spectral change in the solution containing TBAB was less than that in the solution containing DPI. In the case of DMPSB, we observed the same result as DPIB.

From the irradiated solution of CTX/DPIB system, iodobenzene and biphenyl were detected by GC. It is suggested that both diphenyliodonium cation and butyltriphenylborate are decomposed.[2,11−14,19] Thus, in the case of CTX/DPIB system, CTX promotes decomposition of DPIB without being changed itself. On the other hand, CTX reacts with DPI or TBAB irreversibly. In the case of the irradiated solution of CTX/DMPSB system, dimethyl sulfide was detected instead of iodobenzene.

In addition, we obtained the similar results from the other systems, i.e., CH$_2$Cl$_2$ as a solvent and MK as a photosensitizer. Moreover, the fluorescence of CTX and MK was not quenched by the initiators in both MeCN and CH$_2$Cl$_2$; thus, we would expect decomposition of the initiators occurs via triplet state of CTX and MK.

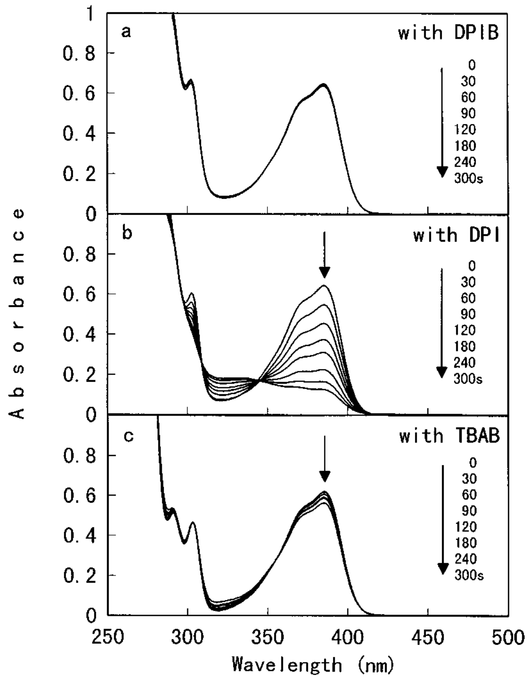


Figure 5. Absorption spectral changes of 0.1 mM CTX by irradiation in argon-saturated MeCN solution containing 0.1 mM initiators: (a) DBIB; (b) DPI; (c) TBAB. Light intensity = 8.0 mW/cm^2 (365 nm).

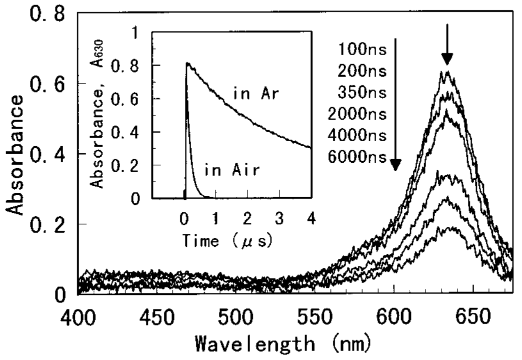


Figure 6. Transient absorption spectra obtained by the laser flash photolysis (355 nm) of 0.1 mM CTX in an argon-saturated MeCN solution. Inset: Decay profile of triplet state of CTX at 630 nm in argon-saturated and air-saturated MeCN solutions.

Laser Flash Photolysis Study. To prove the photoreactions between the photosensitizer and the initiators, nanosecond laser flash photolysis studies were performed. In the laser flash photolysis of deaerated MeCN solution containing 0.1 mM CTX, a transient absorption band appeared at 630 nm immediarely after the laser pulse excitation (Figure 6). Since the absorption band was readily quenched by oxygen (Figure 6, inset), the absorption band would be assigned to the triplet state of CTX (^{3}CTX) and was in good accordance with the reports.[11,12,46] Decay profiles of the absorption band showed first-order decay kinetics. In CH_2Cl_2 solution containing 0.1 mM CTX, a transient absorption band appeared at 620 nm.

In the laser flash photolysis of the solution containing CTX with DPI in MeCN, the absorption band of ^{3}CTX disappeared within a few microseconds (Figure 7). The decay rate of the absorption band increases with concentration of DPI. Each decay was confirmed to obey first-order kinetics by the good linearity in the time-scale region (Figure 7, inset). A very weak new absorption band was appeared at 420 nm which exhibits a long lifetime (>50 μs). It is expected that the new absorption band is due to the cation radical of CTX (CTX$^{+\bullet}$).[11,12] The quenching rate of ^{3}CTX increased with increasing of the concentration of DPI; however, the rise rate of the absorption band was little varied with increasing of the concentration of DPI. Anyhow, it is certain that the photoreaction between CTX and diphenyliodonium cation of DPI is based on a photoinduced electron-transfer reaction.[11,12] This is conformed by the fact that the free energy change (ΔG^T) between ^{3}CTX and DPI shows a negative value. The quenching rate of ^{3}CTX with DPI in MeCN is over 100 times faster than that with DMPS.

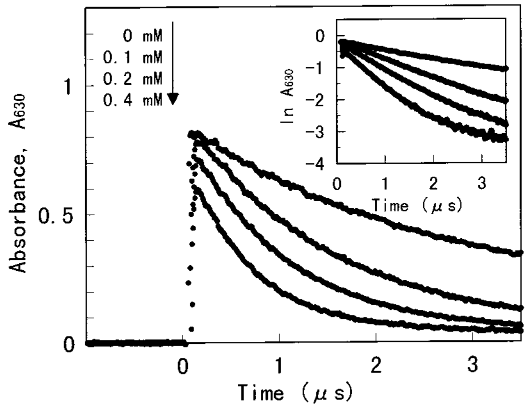


Figure 7. Decay profiles of triplet CTX at 630 nm in argon-saturated MeCN solution containing DPI ([CTX] = 0.1 mM; [DPI] = 0, 0.1, 0.2, and 0.4 mM). Inset: First-order decay analysis of the transient intensity.

Table 2. Quenching Rate Constants (k_q) of Triplet Sensitizers by Initiators

	10^{-9} k_q (M^{-1} s^{-1})		
	CTX		MK
initiator	in MeCN[a]	in CH_2Cl_2[b]	in MeCN[a]
DPIB	8.3	4.4	7.0
DMPSB	5.1	4.0	6.2
TBAB	3.0	3.0	
DPI	2.1	2.5	7.0
DMPS	1.4	*c*	7.4

[a] DPIB and DMPSB exist as weak solvated ion pairs of the onium cations and butyltriphenylborate anion in MeCN. [b] DPIB and DMPSB exist as IPCT complexes of the onium cations and butyltriphenylborate anion in CH_2Cl_2. [c] Not detected because the solubility of DMPS was poor.

The quenching rate constants (k_q) for the photoinduced electron-transfer reactions between the triplet state of the photosensitizer and the initiators are summarized in Table 2. The k_q values were obtained by linear fittings as shown in Figure 8.

In the case of CTX with TBAB in MeCN, it would be expected that a photoinduced electron-transfer reaction occurs between CTX and butyltriphenylborate anion of TBAB. The absorption band of ^{3}CTX disappeared within a few microseconds, and the k_q value for TBAB was about 1.5 times faster than that for DPI. It is reported that the anion radical of thioxanthone exhibits an absorption maximum at 700 nm.[40-42] It seems that the absorption maximum of the anion radical of CTX (CTX$^{-\bullet}$) is the nearly same as that of anion radical of thioxanthone. Although the rise of new absorption band could barely appear around 700 nm, the rise was almost masked by strong absorption of ^{3}CTX. We confirmed

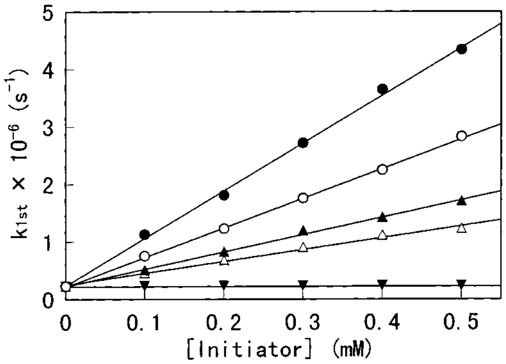


Figure 8. Concentration effects of initiators on pseudo-first-order rate constant in argon-saturated MeCN solutions: DPIB (●); DMPSB (○); TBAB (▲); DPI (△); DMPS (▼). DPIB and DMPSB exist as weak solvated ion pairs of the onium cations and butyltriphenylborate anion in MeCN.

that the very-weak transient absorption band at 700 nm for a long lifetime (>50 μs) is due to $CTX^{-\bullet}$. However, the absorption intensities of both $CTX^{+\bullet}$ and $CTX^{-\bullet}$ are too weak to be quantitatively discussed.

In the case of CTX with DPIB in MeCN, the k_q value for DPIB was evaluated to be 8.3×10^9 M^{-1} s^{-1} and is larger than the sum (5.1×10^9 M^{-1} s^{-1}) of the k_q values for DPI and TBAB. If DPIB is completely dissociated into the free ions (Ph_2I^+ and BPh_3Bu^-) in MeCN, the k_q value for DPIB should be same to the sum of the k_q values for DPI and TBAB, but these are not same in practice. One explanation for the difference of these k_q values may be that each initiator may have a deferential degree of dissociation to each other. Thus, the reacting species of each initiator would be different from each other. Since DPIB would exist primarily as the weak solvated ion pair rather than the free ions in MeCN, where ^3CTX was quenched by the Ph_2I^+ of the ion pair of DPIB, we obtained the results that the k_q value for DPIB differ from the sum of the k_q values for DPI and TBAB. Most of the other results are able to be explained with similar logic. It is noteworthy that the rise of new absorption at 420 nm after the laser pulse and the exceedingly fast decay of the absorption was observed. On the basis of the observation, we think that $CTX^{+\bullet}$ was momentarily formed via the oxidation of ^3CTX by the diphenyliodonium cation of the solvated DPIB ion pair and it immediately reduced by the butyltriphenylborate anion.

In the case of CTX with DMPSB in MeCN, the k_q value for DMPSB was faster than that for TBAB. It is remarkable that the long-lived absorption at 700 nm was completely quenched, in contrast to the case of TBAB. It seems reasonable to suppose that $CTX^{-\bullet}$ formed via the reduction of ^3CTX by butyltriphenylborate anion of the solvated DMPSB ion pair, and it immediately was oxidized by dimethylphenacylsulfonium cation.

In the laser flash photolysis of solutions containing CTX with the initiators in CH_2Cl_2, each k_q value for the initiators in CH_2Cl_2 was the same order as that in MeCN. DMPS was too poorly soluble to CH_2Cl_2 to measure the k_q value. In CH_2Cl_2, ^3CTX would be quenched by the IPCT complexes of the onium borates.

Table 3. Free Energy Changes (ΔG^T) for the Electron Transfer Reaction between Triplet Sensitizers and Initiators[a]

	sensitizer	
	CTX	MK
E^T (eV)	2.61[b]	2.69[e]
E_{ox} (V vs SCE)	1.52[c]	0.87[e]
E_{red} (V vs SCE)	−1.62[d]	−2.48[f]
ΔG^T($^3Sens \rightarrow DPI^+$) (eV)	−0.45	−1.18
ΔG^T($^3Sens \rightarrow DMPS^+$) (eV)	−0.08	−0.81
ΔG^T($Bo^- \rightarrow {}^3Sens$) (eV)	−0.15	0.63

[a] Key: E^T, triplet energy; E_{ox}, oxidation potential; E_{red}, reduction potential; ^{3}Sens; triplet sensitizer; DPI^+, diphenyliodonium; $DMPS^+$, dimethylphenacylsulfonium; Bo^-, butyltriphenylborate; $E_{red}(DPI^+)$ = −0.64,[14] $E_{red}(DMPS^+)$ = −1.01, $E_{ox}(Bo^-)$ = 0.84 (V vs SCE), respectively. [b] Reference 33. [c] Reference 13. [d] Reference 30. [e] Reference 34. [f] Reference 35.

The free energy changes (ΔG^T) for the photoinduced electron-transfer reactions between the excited triplet state of the photosensitizer and the initiators are summarized in Table 3. ΔG^T values are given by the Rehm−Weller equation (eq 4),[39]

$$\Delta G^T = E_{ox}(D/D^{+\bullet}) - E_{red}(A^{-\bullet}/A) - E^T - Ze^2/\epsilon\alpha \quad (4)$$

where $E_{ox}(D/D^{+\bullet})$ is the oxidation potential of the donor, $E_{red}(A^{-\bullet}/A)$ is the reduction potential of the acceptor, E^T is the triplet energy of the photosensitizer, and $Ze^2/\epsilon\alpha$ is the 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. Butyltriphenylborate serves as a donor (E_{ox} = 0.84 V vs SCE). Diphenyliodonium cation (E_{red} = −0.64 V vs SCE)[14] and dimethylphenacylsulfonium cation (E_{red} = −1.01 V vs SCE) serve as acceptors. The photosensitizers (CTX, MK) serve not only as a donor but also as an acceptor to be affected by the properties of the coexisting initiator. In the cases of DPIB and DMPSB, it is expected that a photoinduced electron-transfer reaction will occur between the photosensitizers and either the onium cations or the borate anion of the onium borates.

This brings us to the case of MK. Transient absorption spectra of MK in MeCN are shown in Figure 9 (inset). The spectra had absorption bands at 400, 520, and 740 nm, which were readily quenched by oxygen. The transient absorption bands were identified as the triplet state of MK (^{3}MK) by comparing the spectrum with those of analogous compounds.[47−49] We selected the absorption band at 740 nm to obtain the k_q values for the initiators.

In the case of MK with DPIB in MeCN, the k_q value for DPIB was nearly the same as that for DPI. The time profiles of the transient absorption of ^{3}MK containing DMPSB and the dependence of the pseudo-first-order rate constant on concentration of DMPSB are shown in Figures 9 and 10, respectively. In the case of MK with DMPSB, the absorption band of ^{3}MK disappeared within a few microseconds. The k_q value for DMPSB was longer than that for DPI. We could not observe new absorption because of the strong transient that absorption of ^{3}MK showed in the region 400−800 nm. The k_q value for DMPS in MeCN was the nearly same as that for DPI. Conversely, ^{3}MK was hardly quenched by TBAB. From these facts, it is clear that ^{3}MK is easily oxidized and more difficulty reduced than ^{3}CTX. The best account for its reason can be found in the ΔG^T between ^{3}MK and TBAB (Table 3).

Mechanism. From the above results, the proposed mechanism of photoreaction between the onium borates and the photosensitizers is summarized in Scheme 1.

The triplet state of the photosensitizer (^{3}Sens) are formed via the excited singlet state ($^1Sens^*$) from the ground state (Sens) of the photosensitizer by irradiating

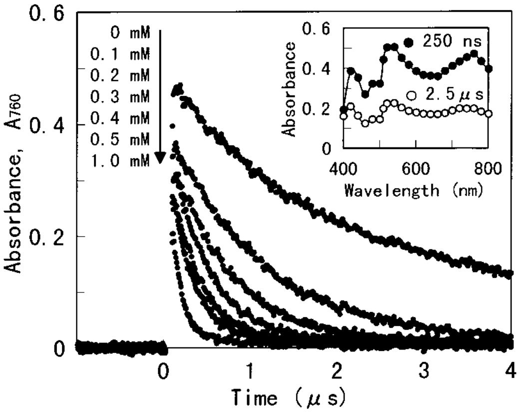


Figure 9. Decay profiles of triplet MK at 760 nm in argon-saturated MeCN solutions containing DMPSB ([MK] = 0.01 mM; [DMPSB] = 0, 0.1, 0.2, 0.3, 0.4, 0.5, and 1 mM, DMPSB exists as a weak solvated ion pair of dimethylphenacylsulfonium cation and butyltriphenylborate anion in MeCN). Inset: Transient absorption spectra obtained by the laser flash photolysis (355 nm) of 0.01 mM MK in argon-saturated MeCN solution.

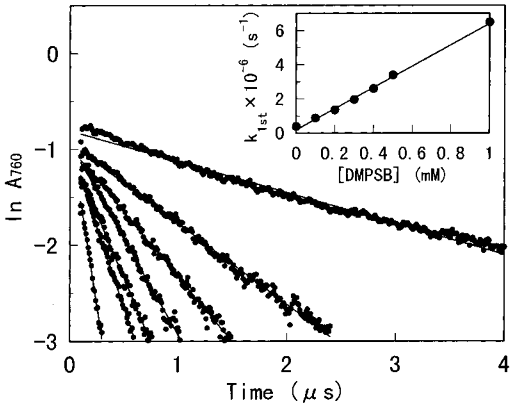


Figure 10. First-order decay analysis to the absorption of triplet MK at 760 nm in argon-saturated MeCN solution containing DMPSB. Inset: Concentration effects of DMPSB on pseudo-first-order rate constant ([MK] = 0.01 mM; [DMPSB] = 0, 0.1, 0.2, 0.3, 0.4, 0.5, and 1 mM, DMPSB exists as a weak solvated ion pair of dimethylphenacylsulfonium cation and butyltriphenylborate anion in MeCN).

Scheme 1. Mechanism for Photoreaction between Triplet Sensitizer and Onium Borates (Sens, CTX or MK; On$^+$, Ph$_2$I$^+$ or Me$_2$S$^+$CH$_2$COPh; Bo$^-$, $^-$BPh$_3$Bu; On•, Ph$_2$I• = PhI + •Ph or Me$_2$S·CH$_2$COPh = Me$_2$S + •CH$_2$COPh; Bo•, •BPh$_3$Bu = BPh$_3$ + •Bu)

$$\mathrm{Sens} \xrightarrow{h\nu} {}^1\mathrm{Sens}^* \xrightarrow{\mathrm{isc}} {}^3\mathrm{Sens} \qquad (5)$$

$$ {}^3\mathrm{Sens} \xrightarrow{k_{\mathrm{Td}}} \mathrm{Sens} \qquad (6)$$

$$ {}^3\mathrm{Sens} + (\mathrm{On}^+\,\mathrm{Bo}^-) \xrightarrow{k_q} (\mathrm{Sens}\cdots\mathrm{On}^+\,\mathrm{Bo}^-)^* \qquad (7)$$

$$(\mathrm{Sens}\cdots\mathrm{On}^+\,\mathrm{Bo}^-)^* \longrightarrow \mathrm{Sens} + (\mathrm{On}^+\,\mathrm{Bo}^-) \qquad (8)$$

$$\longrightarrow \begin{cases} (\mathrm{Sens}^{+\cdot} + \mathrm{On}\cdot + \mathrm{Bo}^-) & (9) \\ \text{or} & \\ (\mathrm{Sens}^{-\cdot} + \mathrm{On}^+ + \mathrm{Bo}\cdot) & (9') \end{cases}$$

$$(\mathrm{Sens}^{+\cdot} + \mathrm{On}\cdot + \mathrm{Bo}^-) \longrightarrow \mathrm{Sens} + \mathrm{On}\cdot + \mathrm{Bo}\cdot \qquad (10)$$

$$(\mathrm{Sens}^{-\cdot} + \mathrm{On}^+ + \mathrm{Bo}\cdot) \longrightarrow \mathrm{Sens} + \mathrm{On}\cdot + \mathrm{Bo}\cdot \qquad (10')$$

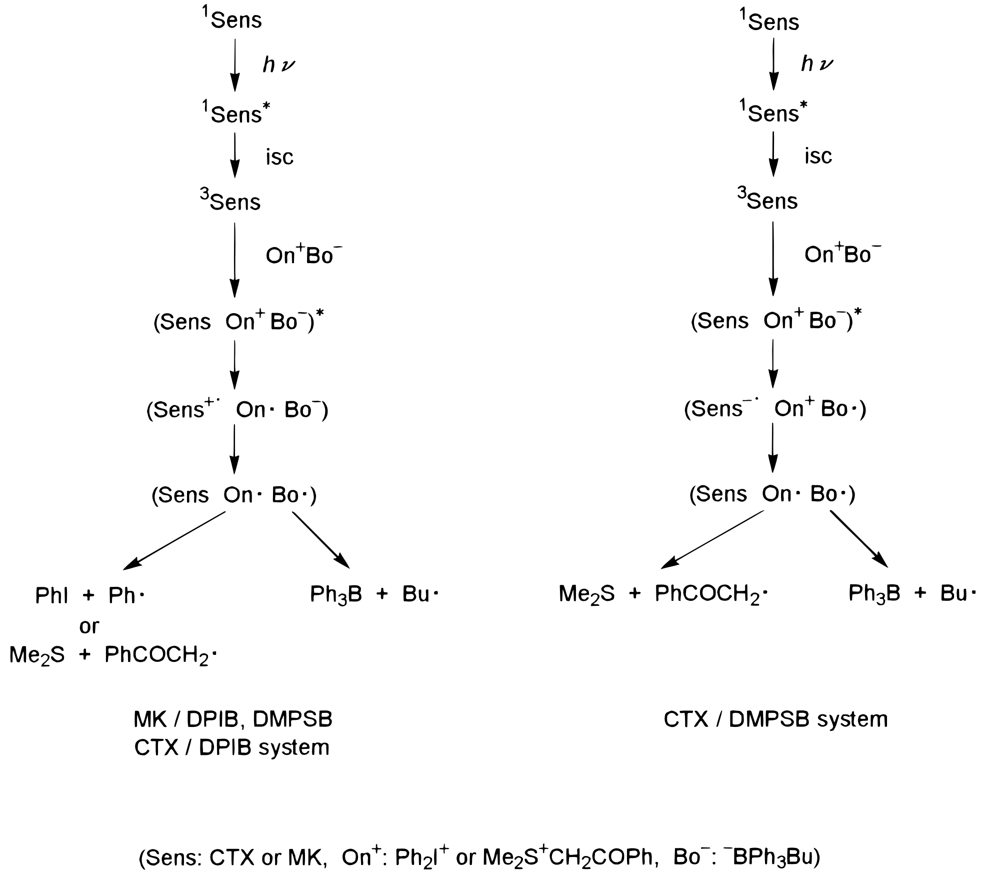
light (process 5). It admits of no refutation from the fact that the fluorescence of CTX and MK was not quenched by the onium borates as well as by DPI, TBAB and DMPS in both MeCN and CH$_2$Cl$_2$. Then, ^{3}Sens returns Sens (process 6), or is quenched by the onium borates and forms the exciplex like (Sens On$^+$ Bo$^-$)* (process 7). As shown in eq 5, ^{3}Sens would be quenched either by the solvated ion pair in MeCN or by the IPCT complex in CH$_2$Cl$_2$ of the onium borates. Process 6 and process 7 are concerted with each other. The quenching rate constants (k_q) of ^{3}Sens by the onium borates may correspond to process 7. Process 7 is followed by nonreactive deactivation (process 8) or electron transfer (either process 9 or 9′). These processes are also concerted each other. Possibility of either process 9 or 9′ would depend on the ΔG^T for the photoinduced electron-transfer reactions between the ^{3}Sens and the initiators. Either the reduction of the cation radical of the photosensitizer (Sens$^{+\bullet}$) by the borate anion (process 10) or the oxidation of the anion radical of the photosensitizer (Sens$^{-\bullet}$) by the onium cation (process 10′) would occur. Then, the onium radicals and the boranyl radical would generate phenyl or phenacyl radical and butyl radical, respectively. Decomposition of the onium and boranyl radicals may occur before process 10 or 10′, because the lifetimes of butyltriphenylboranyl radical[50] and diphenyliodonium radical[5] are both less than the nanosecond time scale. Finally, the generated free radicals initiate polymerization of a vinyl monomer.

On the basis of Scheme 1, the generation of the free radical from the onium borates photosensitized by CTX and MK is assumed as Scheme 2.

In the case of the CTX/DPIB system, CTX$^{+\bullet}$ would be formed by electron transfer from ^{3}CTX to the diphenyliodonium cation of DPIB, and then CTX$^{+\bullet}$ would be immediately reduced by the butyltriphenylborate anion of DPIB and re-form CTX. From the laser flash photolysis study, the rise of transient absorption at 420 nm due to CTX$^{+\bullet}$ after the laser pulse and the exceedingly fast decay of the absorption was observed. In the case of using DPI instead of DPIB, since PF$_6^-$ as a counteranion of diphenyliodonium cation has a difficulty in donating an electron to CTX$^{+\bullet}$, such a fast decay was not observed. Then, diphenyliodonium and butyltriphenylboranyl radicals are formed by a reduction of the diphenyliodonium cation and by an oxidation of the butyltriphenylborate anion, respectively. Subsequently, these radicals immediately give phenyl radical (and iodobenzene) and butyl radical (and triphenylborane), respectively. Accordingly, in coexistence of THFA, the generated phenyl and butyl radicals initiate polymerization of THFA. Since the lifetimes both of butyltriphenylboranyl and diphenyliodonium radical are less than the nanosecond time scale,[50] we could not directly detect the existence of these radicals by our apparatus. As a result, although DPIB decomposed to give the corresponding photoproduct (iodobenzene, etc.), CTX virtually did not decompose. It was found that the spectra of the solution containing CTX with DPIB showed no appreciable change with light irradiation (Figure 5a). Consequently, CTX promotes decomposition of DPIB without being changed itself.

In contrast, in the case of the CTX/DMPSB system, CTX$^{-\bullet}$ would be formed by the electron transfer from

Scheme 2. Proposed Mechanisms for Sensitized Radical-Generation Using Onium Borates



(Sens: CTX or MK, On$^+$: Ph$_2$I$^+$ or Me$_2$S$^+$CH$_2$COPh, Bo$^-$: $^-$BPh$_3$Bu)

the butyltriphenylborate anion of DMPSB to ^{3}CTX, and CTX$^{-\bullet}$ would be immediately oxidized by the dimethylphenacylsulfonium cation of DMPSB and re-forms CTX. From the laser flash photolysis study, the transient absorption at 700 nm due to CTX$^{-\bullet}$ was completely quenched. CTX did not also decompose and the spectra of the solution containing DMPSB showed no appreciable change with light irradiation, despite the fact that photoproducts based on DMPSB were observed. Hence, CTX promotes decomposition of DMPSB without being changed itself. This is supported by the results showing that the k_q value for butyltriphenylborate anion (in the case of TBAB) is over 100 times faster than that for dimethylphenacylsulfonium cation (in the case of DMPS); the ΔG^T between ^{3}CTX and butyltriphenylborate anion ($\Delta G^T = -0.15$ eV) is more negative than that between ^{3}CTX and dimethylphenacylsulfonium cation ($\Delta G^T = -0.08$ eV).

In the case of MK/onium borates (DPIB, DMPSB) systems, we suppose a mechanism similar to that of the CTX/DPIB systems. Since ^{3}MK cannot be reduced by butyltriphenylborate anion, MK$^{+\bullet}$ would form via the oxidation of ^{3}MK by the onium cations of the onium borates, where MK$^{+\bullet}$ would be immediately reduced by butyltriphenylborate anion of the onium borates. Since the oxidation potential of MK is more negative than that of CTX, the ΔG^T values between ^{3}MK and the onium cation are negative enough to photoinduced electron-transfer.

Conclusions

In this paper we have shown useful photoinitiators—the onium borates—for free radical photopolymerizaion. The initiators have a characteristic structure that contains both an onium cation (electron-accepting radical generator) and a borate anion (electron-donating radical generator) within the same compound. Both the cation and anion in the onium borate generate the free radicals on photosensitization with triplet aromatic ketones, and the free radicals initiate polymerizaion of an acrylate monomer. It has been clarified that the photoinitiation process between the onium borates and the aromatic ketones is based on photoinduced electron-transfer reactions.

Acknowledgment. This research was supported in part by a grant from Toyo Ink Mfg. Co., Ltd. We would like to acknowledge here the generosity of these organizations.

Supporting Information Available: Figures showing decay profiles of CTX anion radical with DMPSB and TBAB (2 pages). Ordering and Internet access information is given on any current masthead page.

References and Notes

(1) Monroe, B. M.; Weed, G. C. *Chem. Rev.* **1993**, *93*, 435. Davidson, R. S. *J. Photochem. Photobiol., A: Chem.* **1993**, *73*, 81. Allen, N. S. *J. Photochem. Photobiol., A: Chem.* **1996**, *100*, 101.
(2) Dektar, J. L.; Hacker, N. P. *J. Org. Chem.* **1990**, *55*, 639.
(3) Pappas, S. P.; Gatechair, L. R. Jilek, J. H. *J. Polym. Sci., A: Polym. Chem.* **1984**, *22*, 77.
(4) Pappas, S. P.; Pappas, B. C.; Gatechair, L. R. Jilek, J. H. *Polym. Photochem.* **1984**, *5*, 1.
(5) DeVoe, R. J.; Sahyun, M. R. V.; Schmidt, E.; Serpone, N.; Sharma, D. K. *Can. J. Chem.* **1988**, *66*, 319.
(6) Tilley, M.; Pappas, B.; Pappas, S. P.; Yagci, Y.; Schnabel, W.; Thomas, J. K. *J. Imaging Sci.* **1989**, *33*, 62.

(7) Dektar, J. L.; Hacker, N. P. *J. Am. Chem. Soc.* **1990**, *112*, 6004.
(8) Iu, K.; Kuczynski, J. Fuerniss, S. J.; Thomas, J. K. *J. Am. Chem. Soc.* **1992**, *114*, 4871.
(9) Crivello, J. V.; Lee, J. L. *Macromolecules* **1981**, *14*, 1141.
(10) Timpe, H. J.; Kronfeld, K. P.; Lammel, U.; Fouassier, J. P.; Lougnot, D. J. *J. Photochem. Photobiol., A: Chem.* **1990**, *52*, 111.
(11) Fouassier, J. P.; Burr, D.; Crivello, J. V. *J. Photochem. Photobiol., A: Chem.* **1989**, *49*, 317.
(12) Manivannan, G.; Fouassier, J. P.; Crivello, J. V. *J. Polym. Sci., A: Polym. Chem.* **1992**, *30*, 1999.
(13) Fouassier, J. P.; Burr, D.; Crivello, J. V. *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31*, 677.
(14) Kunze, A.; Müller, U.; Tittes, K.; Fouassier, J. P.; Morlet-Savary, F. *J. Photochem. Photobiol., A: Chem.* **1997**, *110*, 115.
(15) Gottschalk, P.; Neckers, D. C.; Schuster, G. B. U. S. Patent 4,772,530.
(16) Chatterjee, S.; Gottschalk, P.; Davis, P. D.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 2326.
(17) Chatterjee, S.; Davis, P. D.; Gottschalk, P.; Kurz, M. E.; Sauerwein, B.; Yang, X.; Schuster, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 6329.
(18) Polykarpov, A. Y.; Hassoon, S.; Neckers, D. C. *Macromolecules* **1996**, *29*, 8274.
(19) Hassoon, S.; Neckers, D. C. *J. Phys. Chem.* **1995**, *99*, 9416.
(20) Sarker, A. M.; Polykarpov, A. Y.; DeRaaff, A. M.; Marino, T. L.; Neckers, D. C. *J. Polym. Sci., A: Polym. Chem.* **1996**, *34*, 2817.
(21) Hassoon, S.; Sarker, A.; Rodgers, M. A. J.; Neckers, D. C. *J. Am. Chem. Soc.* **1995**, *117*, 11369.
(22) Hassoon, S.; Sarker, A.; Polykarpov, A. Y.; Rodgers, M. A. J.; Neckers, D. C. *J. Phys. Chem.* **1996**, *100*, 12386.
(23) Popielarz, R.; Sarker, A.; Neckers, D. C. *Macromolecules* **1998**, *31*, 951.
(24) Marino, T. L.; DeRaaff, A. M.; Neckers, D. C. *Rad Tech '98 North Am. UV/EB Conf. Proc.* **1996**, 7.
(25) Sarker, A. M.; Hassoon, S. A.; Polykarpov, A. Y.; DeRaaf, A. M.; Marino, T. L.; Neckers, D. C. PCT Int. Appl. WO 97 21,737.
(26) Farid, S. Y.; Moody, R. E. U.S. Patent 4,859,572.
(27) Toba, Y.; Yasuike, M.; Usui, Y. *J. Chem. Soc., Chem. Commun.* **1997**, 675.
(28) Feng, K.; Zang, H.; Neckers, D. C. *Rad Tech 98' North Am. UV/EB Conf. Proc.* **1998**, 215.
(29) Toba, Y.; Yasuike, M.; Yamaguchi, T. U.S. Patent 5,500,453.
(30) Toba, Y.; Yasuike, M.; Yamaguchi, T. *Jpn. Kokai Tokkyo Koho JP* 05, 213, 861.
(31) Okuma, N.; Minami, Y.; Ohbayashi, H.; Noda, M. Jpn. Kokai Tokkyo Koho JP 03,704.
(32) Imahashi, S.; Nakamura, S. Jpn. Kokai Tokkyo Koho JP 02,-1577,760.
(33) Saeva, F. D.; Morgan, B. P. *J. Am. Chem. Soc.* **1984**, *106*, 4121.
(34) Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Non-Aqueous Systems*; Marcel Decker: New York, 1970.
(35) Domico, R. *J. Org. Chem.* **1964**, *29*, 1971.
(36) Böhme, H.; Krause, W. *Chem. Ber.* **1949**, *82*, 426.
(37) Decker, C.; Moussa, K. *Makromol. Chem.* **1988**, *189*, 2381. Decker, C.; Moussa, K. *Macromolecules* **1989**, *22*, 4455. Tanabe, T.; Torres-Filho, A.; Neckers, D. C. *J. Polym. Sci., A: Polym. Chem.* **1995**, *33*, 1691. Sasa, N.; Yamaoka, T. *Chem. Mater.* **1993**, *5*, 1434.
(38) Alam, M. M.; Watanabe, A.; Ito, O. *J. Org. Chem.* **1995**, *60*, 3440.
(39) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.
(40) Aruga, T.; Ito, O.; Matsuda, M. *J. Am. Chem. Soc.* **1979**, *101*, 7585.
(41) Shida, T.; Iwata, S.; Imamura, M. *J. Phys. Chem.* **1974**, *78*, 741.
(42) Handoo, K. L.; Gadru, K. *Tetrahedron. Lett.* **1986**, *27*, 1371.
(43) Allen, N. S.; Catalina, F.; Green, P. N.; Green, W. A. *Eur. Polym. J.* **1985**, *21*, 841.
(44) Sakurai, T.; Utsumi, K.; Ohkita, A.; Nakamura, M.; Inoue, H. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1950.
(45) Fujita, H.; Ohya, H. *Nippon Kagaku Kaishi* **1989**, 195.
(46) Amirzadeh, G.; Schnabel, W. *Makromol. Chem.* **1981**, *182*, 2821.
(47) Abraham, W.; Buchallik, M.; Zhu, Q.; Schnabel, W. *J. Photochem. Photobiol., A: Chem.* **1993**, *71*, 119.
(48) Barnabas, M. V.; Liu, A.; Trifunac, A. D.; Krongauz, V. V.; Chang, C. T. *J. Phys. Chem.* **1992**, *96*, 212.
(49) Hoshino, M.; Kogure, M. *J. Phys. Chem.* **1988**, *92*, 417.
(50) Murphy, S. T.; Zou, C.; Miers, J. B.; Ballew, R. M.; Dlott, D. D.; Schuster, G. B. *J. Phys. Chem.* **1993**, *97*, 13152. Murphy, S.; Schuster, G. B. *J. Phys. Chem.* **1995**, *99*, 511.

MA9801319