Novel Sulfonium Salts as Thermal and Photoinitiators for Epoxide and Acrylate Polymerizations

Eiji Takahashi,[1] Fumio Sanda,[2] Takeshi Endo[3]

[1]*Specialty Polymers Research Dept. R&D Laboratory for High-Performance Materials, Nippon Soda Co. Ltd., 12-54, Goi Minamikaigan, Ichihara, Chiba 290-0045, Japan*
[2]*Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan*
[3]*Department of Polymer Science and Engineering, Yamagata University, 4-3-16 Jonan Yonezawa, Yamagata 992-8510, Japan*

ABSTRACT: Novel sulfonium salts, 1-naphthylmethyl-, cinnamyl-, 9-fluorenyl tetramethylene sulfonium hexafluoroantimonates, and dimethylsulfonium hexafluoroantimonates, were synthesized by the reaction of tetrahydrothiophene and dimethylsulfide with the corresponding bromides or chloride, followed by anion exchange with $KSbF_6$. These sulfonium salts polymerized epoxy monomers at a temperature lower than previously reported for benzyltetramethylenesulfonium hexafluoroantimonate. They initiated radical photopolymerization as well as cationic polymerization. The photopolymerization was accelerated by the addition of aromatic compounds such as *p*-methoxyphenol, 4-methoxy-1-naphthol, 2-ethyl-9,10-dimethoxyanthracene, *N*-ethylcarbazole, and phenothiazine as photosensitizers. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 589–597, 2004

Key words: initiators; photopolymerization; cationic polymerization; radical polymerization; FTIR

INTRODUCTION

Onium salts[1] have been widely developed as cationic photoinitiators. Triarylsulfonium[2–6] and diaryliodonium[7–9] salts developed by Crivello et al. have especially attracted much attention in the fields of UV curable coatings, printings, adhesives, release papers, holography, and resists. We have demonstrated that several sulfonium,[10–15] phosphonium,[16] and pyridinium salts[17–21] serve as thermally latent cationic initiators, which show no activity at ambient temperature but rapidly polymerize epoxide monomers at elevated temperatures. These cationic thermal or photoinitiators have been modified and developed independently to meet end-users' requirements. The aromatic sulfonium and iodonium salts show high activity as cationic photoinitiators, but show lower activity as thermal cationic initiators. On the contrary, the aliphatic sulfonium and pyridinium salts serving as thermal cationic initiators hardly show photoactivity. Though the rates of cationic photopolymerization are slower than those of radical photopolymerization, the former is superior to the latter in thin film curing owing to no influence of oxygen. Radical photopolymerization is preferable because it is free from influence of humidity and basic compounds. Hybrid curing systems consisting of epoxides and acrylates are of importance for coatings, printings, and adhesives. However, there are few initiator systems applicable to both cationic and radical polymerization.

This article presents novel 1-naphthylmethyl-, cinnamyl-, and 9-fluorenyl sulfonium initiators, which show (1) higher activity than previously reported benzyl sulfonium type initiators, (2) cationic and radical photoactivities simultaneously, and (3) higher photoactivity in the presence of a sensitizer.

EXPERIMENTAL

Materials

Commercially available extra-pure-grade cinnamyl bromide, 1-naphthylmethyl chloride, 9-bromofluorene, tetrahydrothiophene, dimethylsulfide, potassium hexafluoroantimonate, *p*-methoxyphenol (MP), 2-ethyl-9,10-dimethoxyanthracene (EDMA), *N*-ethylcarbazole (EC), 4-methoxy-1-naphthol (MNT), phenothiazine (PT), ethyl 4-(dimethylamino)benzoate (DMAB), *N,N'*-diphenyl-1,4-phenylenediamine (DPPDA), benzophenone (BP), triphenylsulfonium hexafluoroantimonate [TPS; melting point (mp): 177–178°C, λ_{max} = 235 nm, ϵ = 18,600 (data of a reagent supplier)], and solvents were used without further purification. 3,4-Epoxycyclohexylmethyl-3,4-epoxycy-
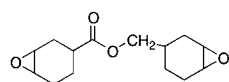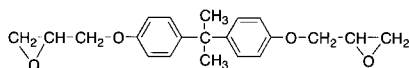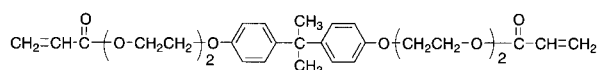
UVR-6110

YD-128

M-210

Scheme 1

clohexylcarboxylate (UVR-6110, epoxy equiv = 136) was obtained from Union Carbide Corp. Bisphenol A diglycidyl ether (YD-128, epoxy equiv = 186) was obtained from Tohto Kasei Corp. Diacryloxy ethoxylated bisphenol A (M-210) was obtained from Toagosei Co., Ltd. Benzyl tetramethylenesulfonium hexafluoroantimonate [λ_{max} = 262 nm, ϵ_{max} = 300 (c = 43.0 mg/L, ethanol)] (**4a**), 4-nitrobenzyl tetramethylenesulfonium hexafluoroantimonate [λ_{max} = 258 nm, ϵ_{max} = 11,200 (c = 46.6 mg/L, ethanol)] (**4b**) and 4-methoxybenzyl tetramethylenesulfonium hexafluoroantimonate [λ_{max} = 239 nm, ϵ_{max} = 14,100 (c = 46.4 mg/L, ethanol)] (**4c**) were synthesized according to the previously reported methods.[22–23]

Measurements

mps were measured with a Mettler FP62. NMR, IR, and ultraviolet–visibility (UV–vis) spectra were measured with Bruker AMX-400, Nicolet MAGNA 760 FTIR, and Hitachi U-4000, respectively. Differential scanning calorimetry (DSC) was carried out with a Rigaku Inc. Thermo plus DSC 8230 at a heating rate of 10°C/min under a flow of N_2 gas (sample amount, 5 mg).

Real-time FTIR measurement

The UV-induced reaction rates of the epoxy monomer (absorption at 790 cm^{-1}) and acrylate monomer (absorption at 1635 cm^{-1}) were estimated with a Nicolet MAGNA 760 FTIR spectrometer equipped with a reflection-type optical apparatus and a spot-cure-type UV lamp (SP5-250U, UV lamp; UXM-Q256BY, Ushio Inc.), at a sampling rate of 70 ms/scan with a resolu-

tion of 8 cm^{-1}. The film of epoxy formulation was prepared on a tin plate coated by a bar coater. The film thickness was 10 μm. The light intensity at the sample surface was 50 mW/cm^2, which was measured by a Ushio Inc. Uni meter UIT-101 radiometer equipped with a Ushio Inc. UVD-S365 detector head at a wavelength band of 310–390 nm.

Computer simulation

The heat of formation of sulfonium salts and carbocations was calculated by Fujitsu Ltd. CAChe 4.5 MOPAC with PM3 Hamiltonian.
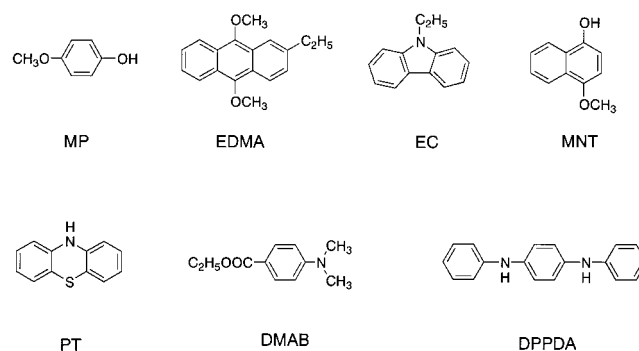
Synthesis of initiators

1-Naphthylmethyldimethylsulfonium hexafluoroantimonate (**1a**)

1-Naphthylmethyl chloride (17.7 g, 0.1 mol) was dissolved in dimethylsulfide (20 mL), and the resulting mixture was stirred at room temperature for 20 days. After that, it was poured into distilled water (100 mL) and washed with toluene (30 mL). Potassium hexafluoroantimonate (27.5 g, 0.1 mol) was added to the aqueous layer to precipitate a white powder. It was collected by filtration, washed with distilled water successively, and dried at 40°C.
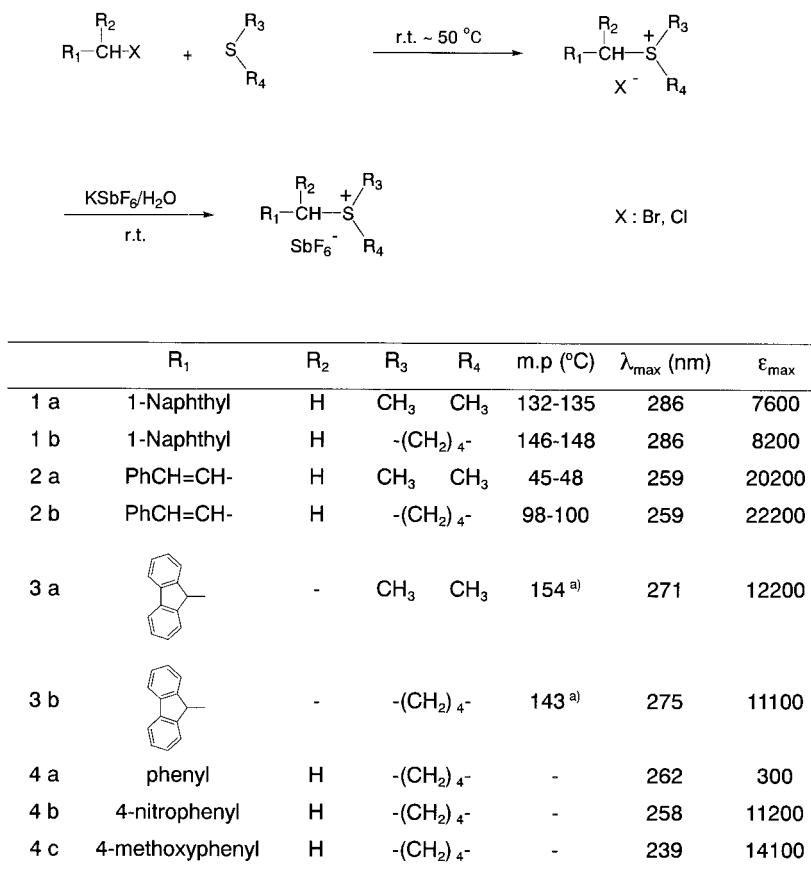Yield, 30%; mp, 132–135°C. IR (KBr, cm^{-1}): 3036, 1515, 1433, 803, 777, 656, ^{1}H-NMR (DMSO-d$_6$): δ 2.88 (s, 6H), 5.14 (s, 2H), 7.58–7.75 (m, 4H), 8.03–8.12 (m, 2H), 8.39 (d, J = 8.7 Hz, 1H). ANAL. calcd for $C_{13}H_{15}F_6SSb$: C: 35.56, H: 3.44, S: 7.30. Found: C: 35.35, H: 3.62, S: 7.28. UV spectrum (c = 42.4 mg/L, ethanol): λ_{max} = 286 nm (ϵ_{max} = 7600).

1-Naphthylmethyltetramethylenesulfonium hexafluoroantimonate (**1b**)

The title compound was synthesized by the reaction of 1-naphthylmethyl chloride and tetrahydrothiophene at 50°C for 24 h in a manner similar to **1a**.

MP   EDMA   EC   MNT

PT   DMAB   DPPDA

Scheme 2

	R_1	R_2	R_3	R_4	m.p (°C)	λ_{max} (nm)	ε_{max}
1 a	1-Naphthyl	H	CH_3	CH_3	132-135	286	7600
1 b	1-Naphthyl	H	$-(CH_2)_4-$		146-148	286	8200
2 a	PhCH=CH-	H	CH_3	CH_3	45-48	259	20200
2 b	PhCH=CH-	H	$-(CH_2)_4-$		98-100	259	22200
3 a		-	CH_3	CH_3	154 [a]	271	12200
3 b		-	$-(CH_2)_4-$		143 [a]	275	11100
4 a	phenyl	H	$-(CH_2)_4-$		-	262	300
4 b	4-nitrophenyl	H	$-(CH_2)_4-$		-	258	11200
4 c	4-methoxyphenyl	H	$-(CH_2)_4-$		-	239	14100

a) decomposition

Scheme 3

Yield, 37%; mp, 146–148°C. IR (KBr, cm^{-1}): 1514, 1426, 804, 779, 662. ^{1}H-NMR (DMSO-d$_6$): δ 2.16–2.28 (m, 2H), δ 2.39–2.50 (m, 2H), 3.35–3.55 (m, 4H), 5.02 (s, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.67 (t, J = 7.8 Hz, 1H), 7.75 (t, J = 7.3 Hz, 1H), 7.81 (d, J = 6.9 Hz, 1H), 8.04–8.13 (m, 2H), 8.47 (d, J = 8.3 Hz, 1H). ANAL. calcd for C$_{15}$H$_{17}$F$_6$SSb: C: 35.74, H: 3.68, S: 6.89. Found: C: 38.82, H: 3.89, S: 6.86. UV spectrum: λ_{max} = 286 nm, ε_{max} = 8200 (c = 45.8 mg/L, ethanol).

Yield, 79%; mp, 45–48°C. IR (KBr, cm^{-1}): 1648, 1429, 1248, 979, 758, 660. ^{1}H-NMR (DMSO-d$_6$): δ 2.84 (s, 6H), 4.20 (d, J = 7.8 Hz, 2H), 6.32–6.41 (m, 1H), 6.87 (d, J = 15.6 Hz, 1H), 7.35 (t, J = 6.9 Hz, 1H), 7.40 (t, J = 6.9 Hz, 2H), 7.57 (d, J = 7.3 Hz, 2H). ANAL. calcd for C$_{11}$H$_{15}$F$_6$SSb: C: 31.83, H: 3.64, S: 7.73. Found: C: 31.69, H: 3.99, S: 7.69. UV spectrum: λ_{max} = 259 nm, ε_{max} = 20,200 (c = 41.2 mg/L, ethanol).

Cinnamyldimethylsulfonium hexafluoroantimonate (2a)

2a was synthesized by the reaction of cinnamyl bromide and dimethylsulfide at room temperature for 24 h in a manner similar to **1a**.

Cinnamyltetramethylenesulfonium hexafluoroantimonate (2b)

2b was synthesized by the reaction of cinnamyl bromide and tetrahydrothiophene at room temperature for 8 days in a manner similar to **1a**.
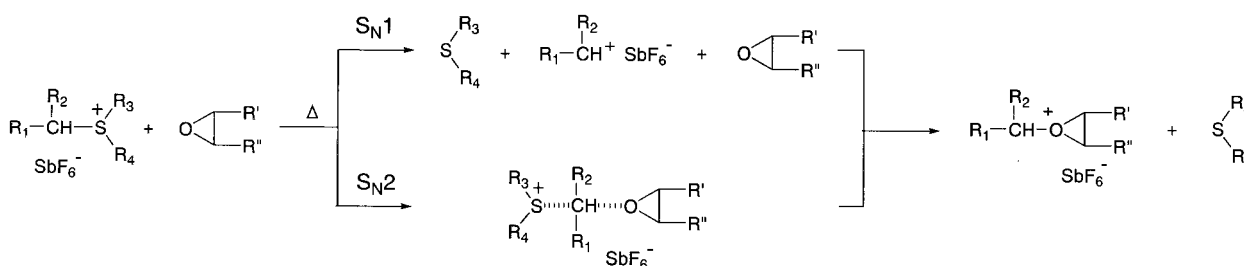
Scheme 4

TABLE I
Thermal Polymerization of Epoxy Monomers
with Sulfonium Salts[a]

Sulfonium salt[b]	UVR-6110		YD-128	
	Temp.[b] (°C)	ΔH^b (J/g)	Temp.[b] (°C)	ΔH^b (J/g)
1a	134	−787	151	−236
1b	129	−781	141	−294
2a	116	−793	126	−412
2b	113	−774	124	−442
3a	114	−805	133	−346
3b	108	−762	129	−172
4a	150	−738	198	−611
4b	163	−707	219	−340
4c	95	−768	109	−404

[a] 0.5 mol % per epoxy group.
[b] Determined by DSC.

Yield, 84%; mp, 98–100°C. IR (KBr, cm^{-1}): 1650, 1493, 1240, 974, 757, 657. ^{1}H-NMR (DMSO-d_6): δ 2.10–2.27 (m, 4H), 3.37–3.54 (m, 4H), 4.14 (d, J = 7.8 Hz, 2H), 6.35–6.44 (m, 1H), 6.94 (d, J = 15.6 Hz, 1H), 7.34 (t, J = 7.3 Hz, 1H), 7.40 (t, J = 6.9 Hz, 2H), 7.54 (d, J = 6.9 Hz, 2H). ANAL. calcd for $C_{13}H_{17}F_6SSb$: C: 35.40, H: 3.88, S: 7.27. Found: C: 35.51, H: 3.97, S: 7.27. UV spectrum: λ_{max} = 259 nm, ϵ_{max} = 22,200 (c = 44.4 mg/L, ethanol).

9-Fluorenyldimethylsulfonium hexafluoroantimonate (3a)

3a was synthesized by the reaction of 9-bromofluorene and dimethylsulfide at room temperature for 24 h in a manner similar to **1a**.
Yield, 56%; mp, 154°C (decomposition). IR (KBr, cm^{-1}): 1606, 1478, 1454, 1429, 1336, 1043, 999, 790, 740, 656, ^{1}H-NMR (DMSO-d_6): δ 2.62 (s, 6H), 6.15 (s, 1H), 7.52 (t, J = 7.3 Hz, 2H), 7.64 (t, J = 7.4 Hz, 2H), 7.84 (d, J = 7.8 Hz, 2H), 8.06 (d, J = 7.8 Hz, 2H). ANAL. calcd for $C_{15}H_{15}F_6SSb$: C: 38.90, H: 3.26, S: 6.92. Found: C: 38.64, H: 3.56, S: 6.94. UV spectrum: λ_{max} = 271 nm, ϵ_{max} = 12,200 (c = 48.0 mg/L, ethanol).

9-Fluorenyltetramethylenesulfonium hexafluoroantimonate (3b)

3b was synthesized by the reaction of 9-bromofluorene and tetrahydrothiophene at 50°C for 10 days in a manner similar to **1a**.
Yield, 60%; mp, 143°C (decomposition). IR (KBr, cm^{-1}): 2948, 1607, 1455, 1422, 784, 741, 660, ^{1}H-NMR (DMSO-d_6): δ 1.83–1.93 (m, 2H), 1.98–2.08 (m, 2H), 3.27–3.35 (m, 2H), 3.48–3.56 (m, 2H), 6.26 (s, 1H), 7.50 (t, J = 7.3 Hz, 2H), 7.64 (t, J = 7.4 Hz, 2H), 7.92 (d, J = 7.8 Hz, 2H), 8.06 (d, J = 7.8 Hz, 2H). ANAL. calcd for $C_{17}H_{17}F_6SSb$: C: 41.74, H: 3.50, S: 6.56. Found: C: 41.45, H: 3.68, S: 6.55. UV spectrum: λ_{max} = 275 nm, ϵ_{max} = 11,100 (c = 43.8 mg/L, ethanol).

RESULTS AND DISCUSSION

Syntheses of initiators

We have previously reported that the initiator activity of benzyl sulfonium salts becomes higher by introduc-

ing electron-donating groups such as the methoxy group into the benzyl group.[23] In this work, novel sulfonium salts were synthesized as shown in Scheme 3, expecting higher thermal and photoactivity. Alkyl chlorides or bromides reacted with sulfides to afford the corresponding sulfonium salts. The exchange of the halogen anion with KSbF$_6$ efficiently proceeded in water to precipitate the corresponding hexafluoroantimonates, whose structures were confirmed by ^{1}H-NMR and IR spectroscopy.

Thermal polymerization

Scheme 4 illustrates the process of cationic polymerization of an epoxide with a benzyl sulfonium salt as a thermally latent initiator as previously reported, wherein the initiation temperature of the polymerization lowers as the stability of the generating carbocation increases.[23] In this work, we employed 1-naphthylmethyl, cinnamyl, and 9-fluorenyl groups instead of benzyl group to enhance the stability of the carbocations.

Thermal polymerization of epoxy monomers, UVR-6110 and YD-128 (Scheme 1), with the sulfonium salts **1a–4c** was examined by DSC. Table I summarizes the maximum temperatures and enthalpy (ΔH) values of exothermic transitions. It was confirmed that the thermal activity of the benzyl sulfonium salts was in proportion to the stability (**4c** > **4a** > **4b**) of the generating benzyl cations. **1a–3b** could sufficiently polymerize the two monomers at the temperatures (UVR-6110: 108–134°C, YD-128: 124–151°C) lower than the nonsubstituted benzyl sulfonium salt **4a** (UVR-6110: 150°C, YD-128: 198°C). Consequently, it can be expected that incorporation of the electron-donating methoxy group into **1a–3b** provides salts with higher activity than the methoxybenzyl sulfonium salt **4c**.

Comparing the polymerization initiation temperatures among the sulfonium salts having the same alkyl moieties, the activity of **1a** decreased more than **2a** and
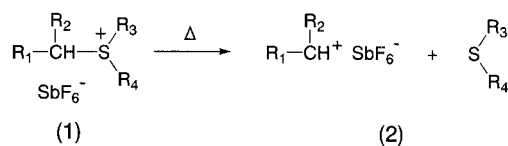

TABLE II
Heat of Formation of the Sulfonium
Salts and Carbocations

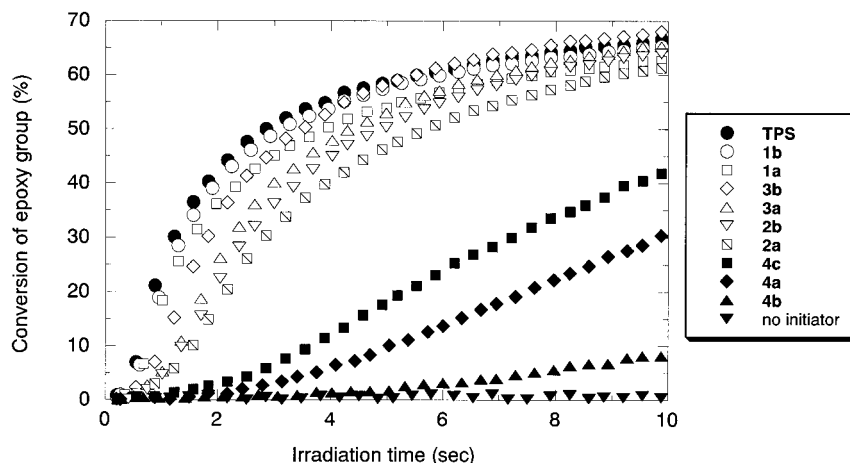| Sulfonium salts	Heat of formation (kcal/mol)		
	(1)	(2)	(2) − (1)
1a	−107.753	−66.138	45.615
2a	−112.993	−80.918	32.075
3a	−85.613	−53.185	32.428

Figure 1 Time-conversion relationships of the epoxy group of UVR-6110 with 0.5 mol % of sulfonium salts under light with an intensity of 50 mW/cm².

3a, and that of **1b** was lower than **2b** and **3b**, presumably reflecting the order of the stability of the generating cations. The tetramethylenesulfonium salts **1b**, **2b**, and **3b** initiated the polymerization at lower temperatures than dimethylsulfonium salts **1a**, **2a**, and **3a**. The cyclohexene oxide based UVR-6110 exhibited lower initiation temperature and larger enthalpy $|\Delta H|$ compared to glycidyl ether based YD128, which confirmed higher polymerizability of UVR-6110 as commonly observed in epoxide polymerization.[9,24]

Table II summarizes the heat of formation of the new sulfonium salts and carbocations simulated by MOPAC, which indicates that the cations are released from **2a** and **3a** more easily than from **1a**. This explains the fact that the former two salts polymerize the monomer at the temperature lower than the latter, as described in Table I.

Photopolymerization

Carbonyl group containing sulfonium salts such as phenacyl sulfonium salts have been examined as photocationic initiators, whose carbonyl groups are incorporated to enhance the photocationic activity.[2,25] On the other hand, benzyl sulfonium salts without carbonyl groups have not been reported as photocationic initiators so far, although they have been widely examined as thermal cationic initiators, presumably because of the low photoactivity.

The sulfonium salts **1a–3b** newly synthesized in this work are expected as photoinitiators, because the absorption wave lengths are longer than those of the benzyl sulfonium salts **4a–c**, and the molar extinction coefficients (ϵ) are larger than **4a–c** and TPS. The photoactivities of **1–3** were examined along with **4a–c** and
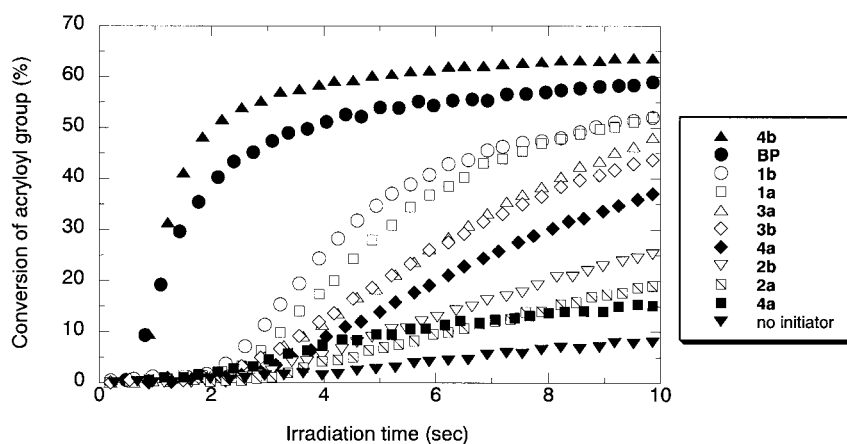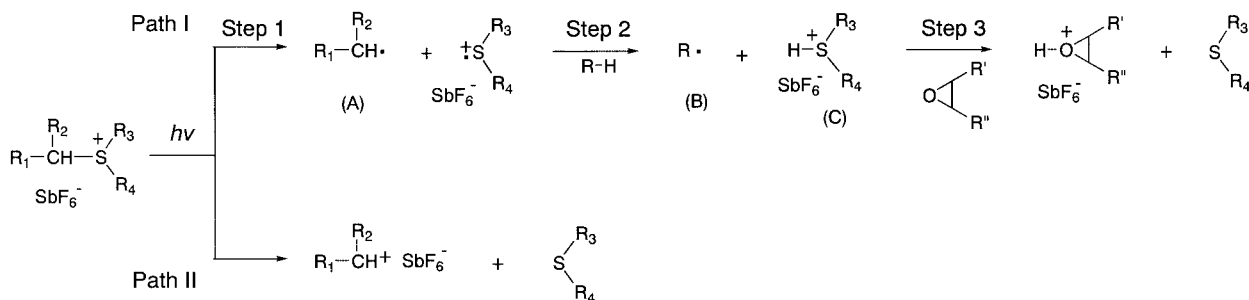

Figure 2 Time-conversion relationships of the epoxy group of M-210 with 0.5 mol % of sulfonium salts under light with an intensity of 50 mW/cm².

Scheme 5

TPS by real-time FTIR spectroscopy under the fixed conditions [25°C, 31% relative humidity (RH)]. The newly synthesized sulfonium salts **1a–3b** could efficiently polymerize the epoxy monomer faster than the benzyl sulfonium salts **4a–4c**, as shown in Figure 1. The naphthylmethyl sulfonium salts **1a** and **1b** especially exhibited the photoactivity almost the same as TPS, practically used as a photocationic hardener.

The tetramethylenesulfonium salts **1b**, **2b**, and **3b** showed photocationic activity higher than the dimethylsulfonium salts **1a**, **2a**, and **3a**. This may be due to the ring-strain of the tetramethylenesulfonium group, resulting in release of tetrahydrothiophene more easily than dimethyl sulfide. The order of photopolymerization rates was **4c** > **4a** > **4b**, which was the same as that of thermal activity, indicating that the photoactivity of the benzyl sulfonium salts was also in proportion to the stability of the generating benzyl cation.

Figure 2 depicts the time-conversion curves in the photoradical polymerization of the bis-acrylate monomer M-210 in the presence of sulfonium salts **1a–4c**. The reaction mixture was coated on a tin plate and

covered with a polyethylene film (thickness 32 μm) to avoid oxygen inhibition. The photoactivity of the newly synthesized sulfonium salts **1a–3b** was in the order of naphthylmethyl type (**1a**, **1b**) > fluorenyl type (**3a**, **3b**) > cinnamyl type (**2a**, **2b**), proportional to the result in the photocationic polymerization. The induction period observed in most cases may be caused by oxygen dissolved in the polymer film. The photoactivity of the 4-nitrobenzyl sulfonium salt **4b** was higher than benzophenone (**BP**: conventional free-radical initiator). The photoactivity of the benzyl-type initiator was in the order of **4b** ≫ **4a** > **4c**, opposite to the thermal activity as described above.

These results are in accord with the photoreaction process, as illustrated in paths I and II, as shown in Scheme 5. In path I, it may be supposed that the carbon–sulfur bond homolytically cleaves by photoirradiation to generate a carbon radical (A) and a sulfonium cation radical (step 1). Subsequently, the cation radical transforms into a sulfonium cation (C) by hydrogen radical abstraction probably from the monomer (step 2). The active species of the radical polymerization seems to be (A) and/or (B), and that of the
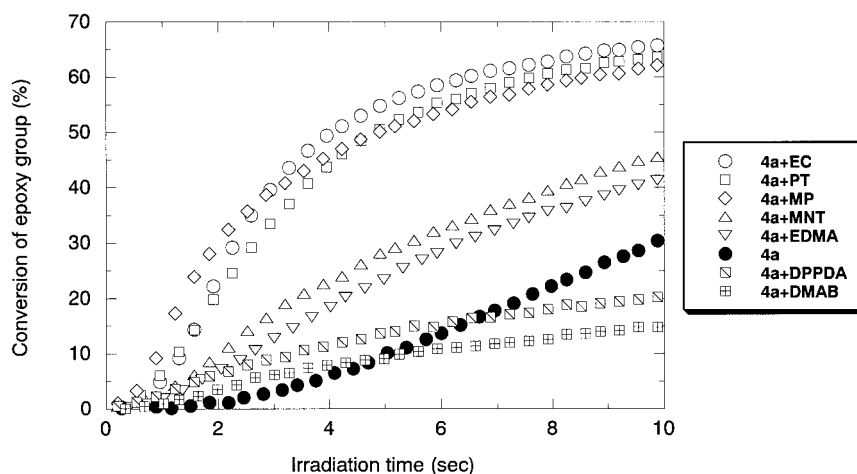

Figure 3 Time-conversion relationships of the epoxy group of UVR-6110 with 0.5 mol % **4a** and 0.5 mol % of sensitizers salts under light with an intensity of 50 mW/cm².
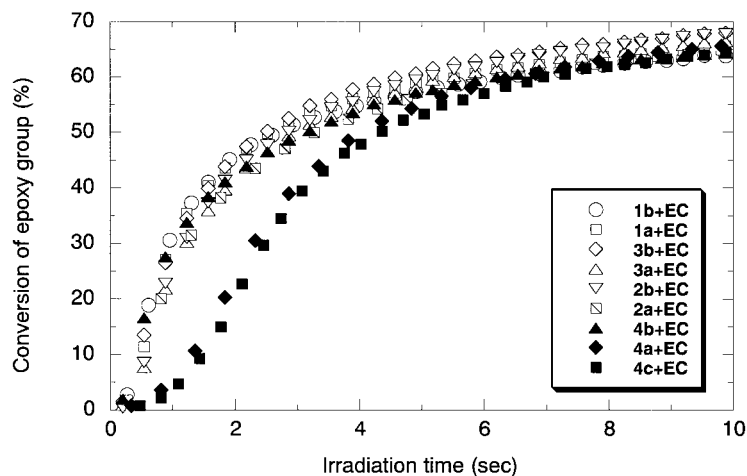
Figure 4 Time-conversion relationships of the epoxy group of UVR-6110 with 0.5 mol % of sulfonium salts and 0.5 mol % of EC under light with an intensity of 50 mW/cm^2.

cationic polymerization seems to be (C). In path II, a carbocation is generated by photoirradiation.

The photocationic activity of the benzyl sulfonium salts was lower as shown in Figure 1, because they have no UV–vis absorption longer than 350 nm. Therefore, we examined several sensitizers, as shown in Scheme 2, to enhance the photocationic initiation activity of the sulfonium salts. Figure 3 depicts the time-conversion curves of the epoxy monomer (UVR-6110) in the presence of the benzylsulfonium salt **4a** and various sensitizers, measured by real-time FTIR spectroscopy. It was confirmed that the sensitizers accelerated the reaction rates in the all cases, compared with the time-conversion relationship in Figure 1. EC, MP, and PT, especially, showed a high sensitization effect. On the other hand, DPPDA and

DMAB accelerated the reaction only at the early stage, indicating that these sensitizers terminated the cationic polymerization at the late stage presumably because of the basicity.

Figure 4 depicts the time-conversion curves of the epoxy monomer (UVR-6110) in the presence of sulfonium salts **1a–4c** and EC as the sensitizer. Sensitization effect by EC was observed in the all sulfonium salts, and the difference between the polymerization rates decreased compared to the cases in the absence of EC. The photoactivity of the 4-nitrobenzyl sulfonium salt **4b** increased particularly among the benzyl-type initiators.

Figure 5 depicts the time-conversion curves of the acrylate monomer (M-210) in the presence of the benzyl sulfonium salt **4a** and various sensitizers. Acceler-
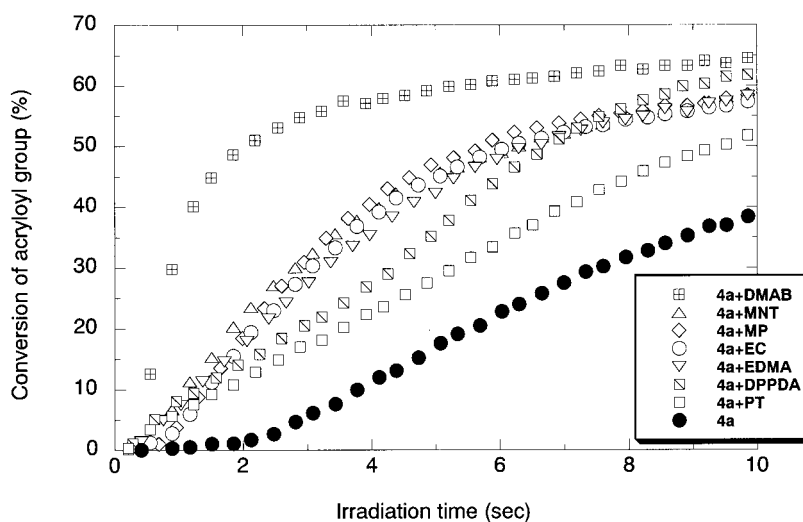

Figure 5 Time-conversion relationships of the acryloyl group of M-210 with 0.5 mol % **4a** and 0.5 mol % of sensitizers under light with an intensity of 50 mW/cm^2.
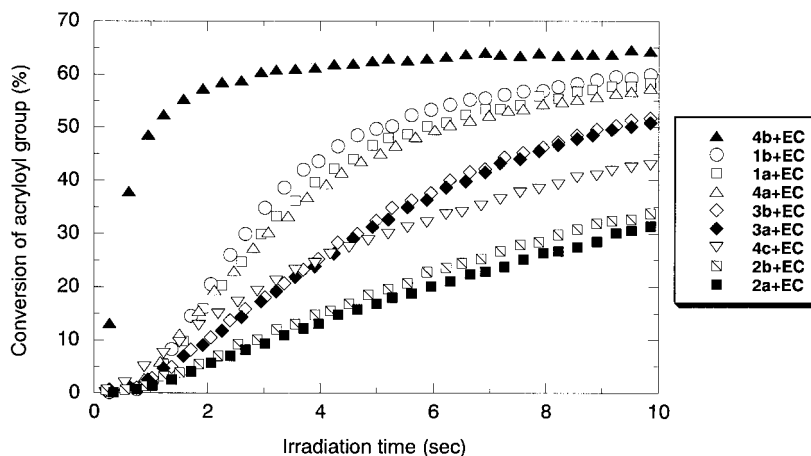
Figure 6 Time-conversion relationships of the acryloyl group of M-210 with 0.5 mol % sulfonium salts and 0.5% of EC under light with an intensity of 50 mW/cm^2.

ation of the radical polymerization was confirmed similarly to the epoxide polymerization as described above. The order of the acrylate polymerization rates differed from that in the epoxide polymerization rates (Fig. 3). DMAB especially showed the higher sensitization effect on the acrylate polymerization, probably because radical polymerization may be not hindered by the amino group.

Figure 6 depicts the time-conversion curves of the acrylate monomer (M-210) in the presence of sulfonium salts **1a–4c** and EC as the sensitizer. Acceleration was also observed in the photoradical polymerization in the all cases similar to the photocationic polymerization.

Scheme 6 illustrates a plausible photosensitizing process under the consideration of the sensitizing mechanism of a sulfonium salt with a sensitizer (PS).[26] An electron may be transferred from the sensitizer to the sulfonium salt to form a radical species and a

sulfide derivative. The sensitizer may be transformed into a cation radical, and subsequently, abstracts hydrogen from the monomer, etc., to generate HSbF$_6$ as the cationic initiating species.

CONCLUSION

In this article, we demonstrated that the novel sulfonium salts having 1-naphthylmethyl, cinnamyl, and 9-fluorenyl groups served as initiators for thermal cationic, photocationic, and photoradical polymerizations of epoxide and acrylate monomers. The photoactivity was increased by aromatic compounds such as MP, EC, and EDMA as the sensitizers. We also revealed that the benzyl sulfonium salts also served as desirable photoinitiators in the presence of the sensitizers. The newly synthesized sulfonium salts have great possibilities as hardeners of thermal and photocuring hybrid systems consisting of cationically po-
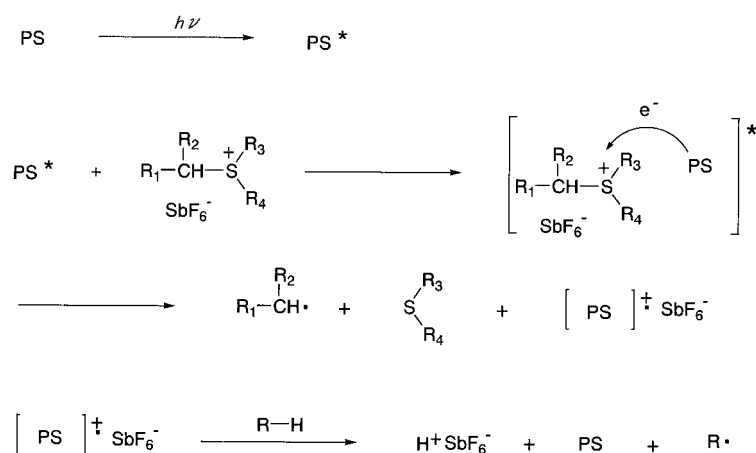
Scheme 6

lymerizable epoxides and radically polymerizable acrylates.

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