

Photocationic and Radical Polymerizations by Novel *N*-Phenacylammonium Salts

Eiji Takahashi,¹ Fumio Sanda,² Takeshi Endo³

¹Specialty Polymers Research Department, R & D Laboratory for High-Performance Materials, Nippon Soda Co. Ltd. 12-54, Goi Minamikaigan, Ichihara, Chiba 290-0045, Japan

²Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan

³Department of Polymer Science and Engineering, Faculty of Engineering, Yamagata University, 4-3-16 Jonan Yonezawa, Yamagata 992-8510, Japan

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ABSTRACT: Novel *N*-phenacylammonium salts [*N*-(α -benzoylbenzyl)-, *N*-(1-benzoylethyl)-, *N*-phenacyl-, pyrazinium, 3-bromoquinolinium, benzothiazolium, or *p*-cyanopyridinium hexafluoroantimonates] were synthesized by the reaction of α -benzoylbenzyl bromide, 2-bromopropiophenone or phenacylbromide, and the corresponding *N*-hetero aromatic compound, followed by anion exchange with KSbF_6 . These *N*-phenacylammonium salts showed higher activity than pre-

viously reported *N*-benzyl-2-cyanopyridinium hexafluoroantimonate in the photopolymerization of epoxides. Further, these *N*-phenacylammonium salts served as photoradical and thermal cationic initiators as well as photocationic initiators. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3470–3476, 2004

Key words: initiator; photopolymerization; radical polymerization; cationic polymerization; ammonium salts

INTRODUCTION

Epoxy resins are widely used in electronics, automobile, and construction industries as thermosetting resins. Latent initiators are gaining importance in these industrial applications. Aromatic sulfonium^{1–5} and iodonium salts^{6–8} have been widely developed as photocationic initiators, and used in UV curable coatings, printings, adhesives, release paper, holography, and resists. Pyridinium salts such as *N*-alkoxy-2-methylpyridinium salts^{9,10} by Yagci et al. and *N*-Phenacylammonium salts¹¹ by Crivello can be also applicable to the same purposes. However, these ammonium salts may not be expected to show high photoactivity, because they generate amino compounds, with higher basicity, by photoirradiation. We have demonstrated that several pyridinium salts^{12–16} such as *N*-benzylpyridinium salt serve as thermally latent cationic initiators, which show no activity at ambient temperature but rapidly polymerize epoxide monomers at elevated temperature. Further, we have also demonstrated that aromatic ketones, such as thioxanthone derivatives, accelerate the photoactivity of these pyridinium salts.¹⁷ Ammonium salts such as pyridinium salts also polymerize epoxy monomers, but the photoactivity is lower than aromatic sulfonium^{1–5} and iodonium salts.^{6–8} Recently, hybrid curing systems,

consisting of epoxides and acrylates, have been important for coatings, printings, and adhesives. Therefore, it is desirable to develop initiators applicable to both cationic and radical polymerizations. This article describes novel *N*-phenacylammonium type initiators, which show (1) the same photoactivity as triphenylsulfonium type initiators, (2) photocationic and radical activities simultaneously, (3) the same thermal activity as previously reported for benzylpyridinium type initiators, and (4) higher thermal activity in the polymerization of peroxides.

EXPERIMENTAL

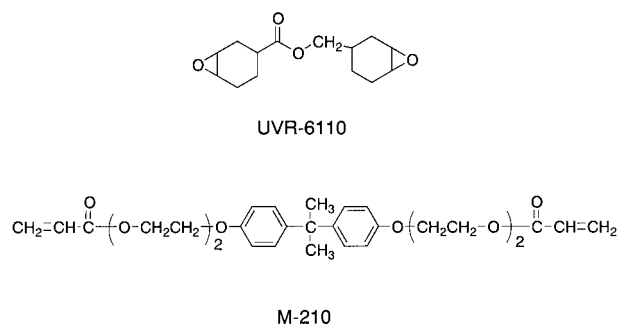
Materials

Commercially available extra pure grade α -benzoylbenzylbromide, 2-bromopropiophenone, phenacylbromide, pyridine, 4-cyanopyridine, pyrazine, 3-bromoquinoline, benzothiazole, benzophenone (BP), 2-ethyl-9,10-dimethoxyanthracene (EDMA), 2,2-dimethoxy-2-phenylacetophenone (DMPA), triphenylsulfonium hexafluoroantimonate (TPS), KSbF_6 , and solvents were used without further purification. 3,4-Epoxycyclohexylmethyl-3,4-epoxycyclohexylcarboxylate (UVR-6110, epoxy equiv = 136) were obtained from Union Carbide Corp. Diacryloxy ethoxylated bisphenol A (M-210) was obtained from Toagosei Co., Ltd.

Measurements

Differential scanning calorimetry (DSC) was measured with a Seiko Instruments Inc. DSC 220 C at a heating rate of 10°C/min under a flow of N_2 gas.

Correspondence to: T. Endo (tendo@poly.yz.yamagata-u.ac.jp).



Scheme 1

Real-time FTIR measurement

UV-induced reaction rates of an 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.) a sampling rate of 70 ms/scan with a resolution of 8 cm^{-1} . An epoxy formulated film was prepared on a tin plate by a bar-coator. The thickness of the film was $10\text{ }\mu\text{m}$. The incident light intensity at the sample surface 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 $310\text{--}390\text{ nm}$.

Analytical instrument

Melting points (mp) were measured with a Mettler FP62. NMR, IR, and UV-vis spectra were measured with Bruker AMX-400, Nicolet MAGNA 760 FTIR, and Hitachi U-4000, respectively.

Computer simulation

The heat of formation with sulfonium salts was calculated by MOPAC of CAChe 4.5 (parameter: PM3) made by Fujitsu Ltd.

Initiators

N-(α -Benzoylbenzyl)benzothiazolium hexafluoroantimonate (**1a**)

α -Benzoylbenzyl bromide (27.5 g, 0.1 mol) and benzothiazole (13.5 g, 0.1 mol) were dissolved in 10 mL of acetonitrile, and the resulting mixture was stirred at 50°C for 2 days. After that, it was poured into 100 mL of distilled water and washed with 30 mL of ethyl acetate. Potassium hexafluoroantimonate (27.5 g, 0.1 mol) was added to the aqueous layer, then white crystalline powder was precipitated. This powder was collected by filtration, washed with distilled water

successively, and dried at 40°C . Yield: 75%. It was further purified by recrystallization from methanol. mp: $199\text{--}201^\circ\text{C}$. IR (KBr, cm^{-1}): 3129, 1677, 1663, 1238, 986, 761, 701, 661. $^1\text{H-NMR}$ (DMSO- d_6): δ 7.55–7.64 (m, 5H), 7.66–7.78 (m, 3H), 7.92 (t, $J = 7.4\text{ Hz}$, 1H), 7.98 (t, $J = 8.0\text{ Hz}$, 1H), 8.19 (d, $J = 7.3\text{ Hz}$, 2H), 8.45 (d, $J = 8.7\text{ Hz}$, 1H), 8.58 (d, $J = 8.3\text{ Hz}$, 1H), 8.66 (s, 1H), 10.22 (s, 1H). Anal. calcd for $\text{C}_{21}\text{H}_{16}\text{ONSF}_6\text{Sb}$. C: 44.55, H: 2.85, N: 2.47, S: 5.67. Found. C: 44.47, H: 2.98, N: 2.52, S: 5.65. UV: $\lambda_{\text{max}} = 264\text{ nm}$ ($\epsilon_{\text{max}} = 8500$).

N-(α -Benzoylbenzyl)-4-cyanopyridinium hexafluoroantimonate (**1b**)

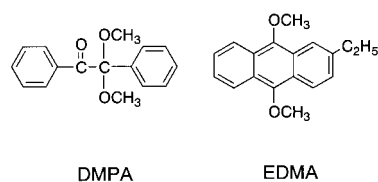
The title compound was synthesized by the reaction of α -benzoylbenzyl bromide and 4-cyanopyridine at 50°C for 4 days in a manner similar to **1a**. Yield: 83%. mp: $179\text{--}180^\circ\text{C}$. IR (KBr, cm^{-1}): 1695, 1640, 1457, 1226, 830, 698, 655. $^1\text{H-NMR}$ (DMSO- d_6): δ 7.52 (t, $J = 3.2\text{ Hz}$, 3H), 7.57 (t, $J = 7.8\text{ Hz}$, 2H), 7.60–7.64 (m, 2H), 7.70 (t, $J = 7.3\text{ Hz}$, 1H), 8.00 (d, $J = 7.8\text{ Hz}$, 2H), 8.37 (s, 1H), 8.73 (d, $J = 6.7\text{ Hz}$, 2H), 9.36 (d, $J = 6.9\text{ Hz}$, 2H). Anal. calcd for $\text{C}_{20}\text{H}_{15}\text{ON}_2\text{F}_6\text{Sb}$. C: 44.89, H: 2.83, N: 5.24. Found. C: 44.69, H: 3.08, N: 5.22. UV: $\lambda_{\text{max}} = 277\text{ nm}$ ($\epsilon_{\text{max}} = 5200$).

N-(α -Benzoylbenzyl) pyrazinium hexafluoroantimonate (**1c**)

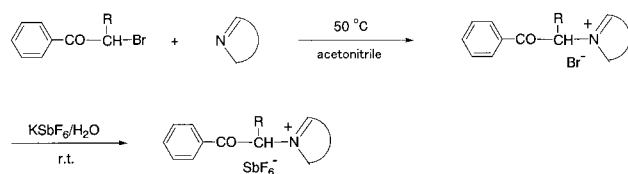
The title compound was synthesized by the reaction of α -benzoylbenzyl bromide and pyrazine at 50°C for 24 h in a manner similar to **1a**. Yield 84%. mp: $162\text{--}164^\circ\text{C}$. IR (KBr, cm^{-1}): 3139, 1701, 1597, 1448, 1257, 691, 625. $^1\text{H-NMR}$ (DMSO- d_6): δ 7.52–7.60 (m, 5H), 7.62–7.67 (m, 2H), 7.70 (t, $J = 7.3\text{ Hz}$, 1H), 8.01 (d, $J = 7.8\text{ Hz}$, 2H), 8.38 (s, 1H), 9.20 (d, $J = 4.6\text{ Hz}$, 2H), 9.63 (d, $J = 4.6\text{ Hz}$, 2H). Anal. calcd for $\text{C}_{18}\text{H}_{15}\text{ON}_2\text{F}_6\text{Sb}$. C: 42.30, H: 2.96, N: 5.48. Found: C: 42.37, H: 3.13, N: 5.44. UV: $\lambda_{\text{max}} = 461\text{ nm}$ ($\epsilon_{\text{max}} = 5800$), $\lambda_{\text{max}} = 395\text{ nm}$ ($\epsilon_{\text{max}} = 4500$), $\lambda_{\text{max}} = 256\text{ nm}$ ($\epsilon_{\text{max}} = 13,200$).

N-(α -Benzoylbenzyl)-3-bromoquinolinium hexafluoroantimonate (**1d**)

The title compound was synthesized by the reaction of α -benzoylbenzyl bromide and 3-bromoquinoline at 50°C for 3 days in a manner similar to **1a**. Yield: 89%. mp: $199\text{--}200^\circ\text{C}$. IR (KBr, cm^{-1}): 1692, 1596, 1518, 1226,



Scheme 2



	R	hetero aromatic compound
1a	Ph	benzothiazole
1b	Ph	4-cyanopyridine
1c	Ph	pyrazine
1d	Ph	3-bromoquinoline
2a	Me	benzothiazole
3a	H	benzothiazole
3b	H	4-cyanopyridine
3c	H	pyridine

Scheme 3

769, 700, 660, $^1\text{H-NMR}$ (acetone- d_6): δ 7.57–7.64 (m, 5H), 7.66–7.71 (m, 2H), 7.75 (t, $J = 7.3$ Hz, 1H), 8.12–8.22 (m, 3H), 8.35 (t, $J = 7.8$ Hz, 1H), 8.50 (d, $J = 8.3$ Hz, 1H), 8.63 (d, $J = 9.2$ Hz, 1H), 8.89 (s, 1H), 9.08 (s, H), 9.83 (s, 1H). Anal. calcd for $\text{C}_{23}\text{H}_{17}\text{ONBrF}_6\text{Sb}$. C: 43.23, H: 2.81, N: 2.20, Br: 12.50. Found. C: 43.05, H: 2.81, N: 2.20, Br: 12.60. UV: $\lambda_{\text{max}} = 327$ nm ($\epsilon_{\text{max}} = 7800$).

N-(1-Benzoyl ethyl)benzothiazolium hexafluoroantimonate (**2a**)

The title compound was synthesized by the reaction of 2-bromopropiophenone and benzothiazoline at 50°C for 4 days in a manner similar to **1a**. Yield 74%. mp: 117–119°C. IR (KBr, cm^{-1}): 3112, 1692, 1596, 1450, 1264, 964, 703, 630, $^1\text{H-NMR}$ (DMSO- d_6): δ 2.08 (q, $J = 7.3$ Hz, 3H), 7.41 (q, $J = 7.4$ Hz, 1H), 7.68 (t, $J = 7.8$ Hz, 2H), 7.82 (t, $J = 7.3$ Hz, 1H), 7.86–7.94 (m, 2H), 8.26 (d, $J = 7.8$ Hz, 2H), 8.37 (d, $J = 8.3$ Hz, 1H), 8.58 (d, $J = 8.3$ Hz, 1H), 10.82 (s, 1H). Anal. calcd for

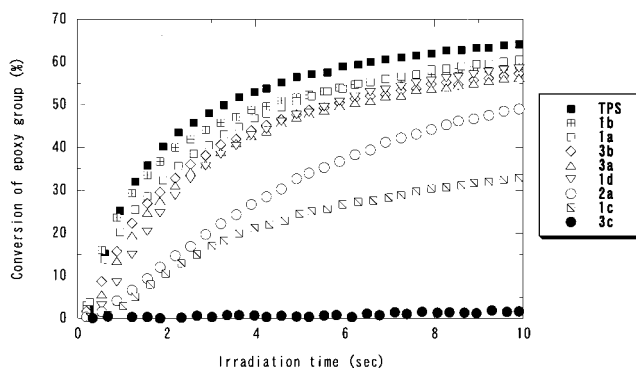


Figure 1 Time-conversion curves of the epoxy group of UVR-6110 with 0.5 mol % of ammonium salts under the light intensity of 100 mW/cm 2 .

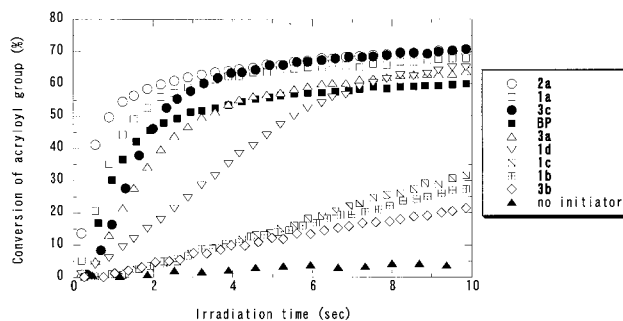


Figure 2 Time-conversion curves of the acryloyl group of M-210 with 0.5 mol % of ammonium salts under the light intensity of 100 mW/cm 2 .

$\text{C}_{16}\text{H}_{14}\text{ONSF}_6\text{Sb}$. C: 38.12, H: 2.80, N: 2.79, S: 6.36. Found. C: 38.39, H: 3.01, N: 2.91, S: 6.37. UV: $\lambda_{\text{max}} = 255$ nm ($\epsilon_{\text{max}} = 12,900$).

N-Phenacylbenzothiazolium hexafluoroantimonate (**3a**)

The title compound was synthesized by the reaction of phenacyl bromide and benzothiazoline at 50°C for 24 h in a manner similar to **1a**. Yield 63%. mp: 168–169°C. IR (KBr, cm^{-1}): 3108, 1692, 1511, 1227, 761, 685, 627, $^1\text{H-NMR}$ (DMSO- d_6): δ 6.73 (s, 2H), 7.65–7.72 (m, 2H), 7.81 (t, $J = 7.4$ Hz, 1H), 7.85–7.94 (m, 2H), 8.12 (d, $J = 8.1$ Hz, 2H), 8.39 (d, $J = 7.8$ Hz, 1H), 8.56 (d, $J = 8.5$ Hz, 1H), 10.56 (s, 1H). Anal. calcd for $\text{C}_{15}\text{H}_{12}\text{ONSF}_6\text{Sb}$. C: 36.76, H: 2.47, N: 2.86, S: 6.54. Found. C: 37.05, H: 2.72, N: 2.87, S: 6.57. UV: $\lambda_{\text{max}} = 255$ nm ($\epsilon_{\text{max}} = 11,700$).

N-Phenacyl-4-cyanopyridinium hexafluoroantimonate (**3b**)

The title compound was synthesized by the reaction of phenacyl bromide and 4-cyanopyridine at 50°C for 1 day in a manner similar to **1a**. Yield 81%. mp: 171–172°C. IR (KBr, cm^{-1}): 1710, 1642, 1465, 1346, 1227,

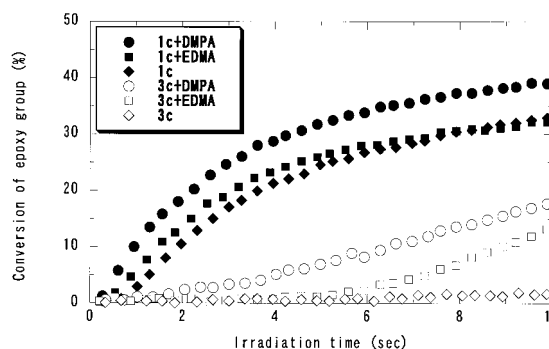


Figure 3 Time-conversion of the epoxy group of UVR-6110 with 0.6 mol % **1c** or **3c** and 0.5 mol % of sensitizers under the light intensity of 100 mW/cm 2 .

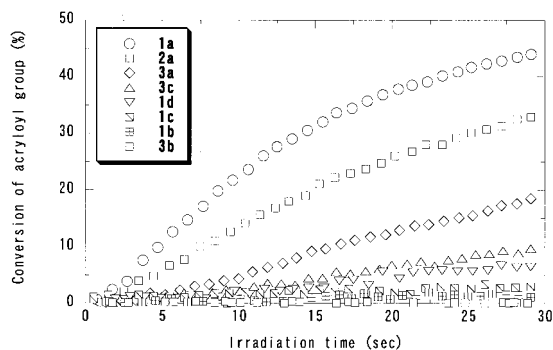


Figure 4 Time-conversion of the epoxy group of UVR-6110 with 0.5 mol % of ammonium salts and 0.5 mol % of EMA using the filter cutting shorter UV light than 387 nm under the light intensity of 100 mW/cm².

993, 766, 661, ¹H-NMR (DMSO-*d*₆): δ 6.53 (s, 2H), 7.68 (t, *J* = 7.8 Hz, 2H), 7.81 (t, *J* = 7.4 Hz, 1H), 8.08 (d, *J* = 7.8 Hz, 2H), 8.80 (d, *J* = 6.9 Hz, 2H), 9.25 (d, *J* = 6.9 Hz, 2H). Anal. calcd for C₁₄H₁₁ON₂F₆Sb. C: 36.63, H: 2.42, N: 6.10. Found. C: 36.70, H: 2.44, N: 6.09. UV: λ_{max} = 483 nm (ε_{max} = 16900), λ_{max} = 253 nm (ε_{max} = 13,500).

N-Phenacyl pyridinium hexafluoroantimonate (**3c**)

The title compound was synthesized by the reaction of phenacyl chloride and pyridine at 50°C for 3 days in a manner similar to **1a**. Yield 91%. mp: 192–194°C. IR (KBr, cm⁻¹): 1705, 1640, 1494, 1346, 1222, 994, 761, 658, ¹H-NMR (DMSO-*d*₆): δ 6.47 (s, 2H), 7.68 (t, *J* = 7.4 Hz, 2H), 7.81 (t, *J* = 7.8 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 2H), 8.27 (t, *J* = 6.9 Hz, 2H), 8.73 (t, *J* = 7.8 Hz, 1H), 8.99 (d, *J* = 5.5 Hz, 2H). Anal. calcd for C₁₃H₁₂ONF₆Sb. C: 35.98, H: 2.79, N: 3.23. Found. C: 35.89, H: 2.81, N: 3.27.

UV: λ_{max} = 423 nm (ε_{max} = 4600), λ_{max} = 247 nm (ε_{max} = 19,800).

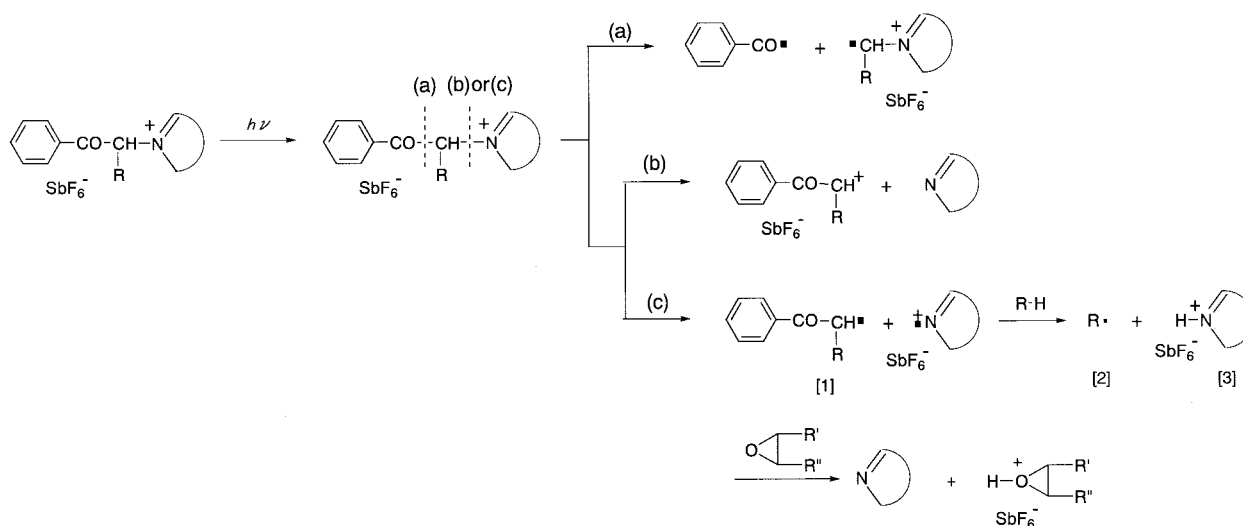
RESULTS AND DISCUSSION

Synthesis of initiators

We have previously reported that pyridine derivatives and benzyl halides reacted easily to afford the corresponding *N*-benzylpyridinium halides.^{14,17} In this work, ammonium salts having benzoyl groups were newly synthesized, as shown in Scheme 3. Bromides were used as the halides to improve the yields of the ammonium salts. Nitrogen-containing heterocyclic compounds and bromides reacted easily to afford the corresponding ammonium bromides. Anion exchange of the ammonium bromides successfully proceeded with K₂SbF₆. The structures of these ammonium salts were confirmed by ¹H-NMR and IR spectroscopy besides elemental analysis.

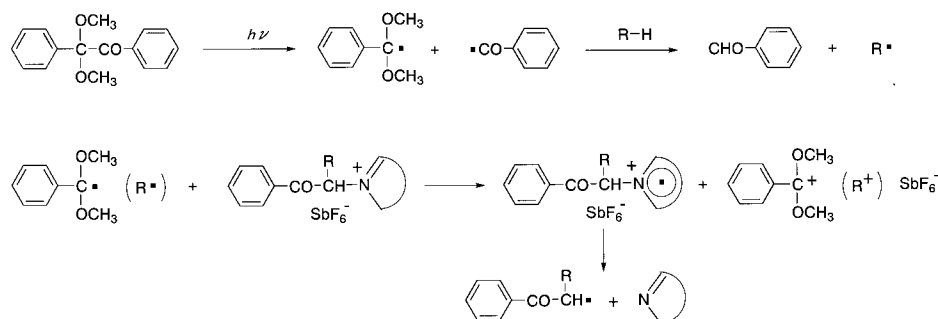
Photopolymerization

N-Phenacylpyridinium salt¹¹ (**3c**) serve as a photocationic initiator. However, this pyridinium salt shows a low photoactivity (Fig. 1) because this salt may generate pyridine. Therefore, we introduced electron-withdrawing groups such as a cyano group into the pyridine ring to decrease the basicity. Further, we examined other heterocyclic compound, and introduced a carbonyl group into the ammonium salts to increase the photoactivity. The photoactivity of the ammonium salts was evaluated by real-time FTIR spectroscopy (Figs. 1–4) under fixed conditions (24–25°C, 28–29%RH). It was confirmed that the newly synthesized ammonium salts worked effectively as

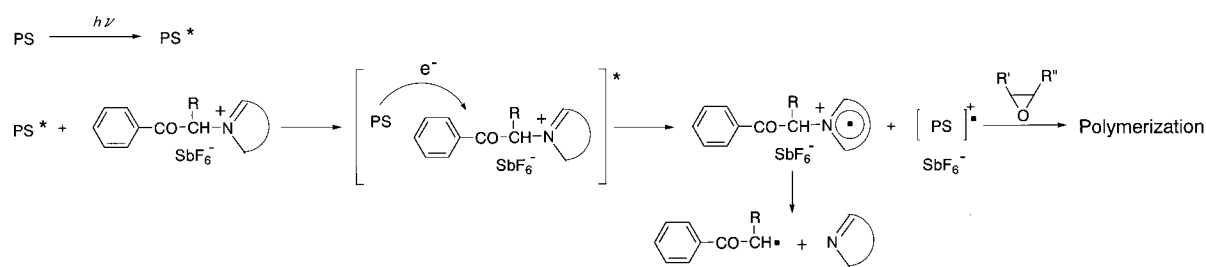


Scheme 4

Path 1



Path 2



Scheme 5

photocationic initiators to polymerize an epoxy monomer (UVR-6110) smoothly as shown in Figure 1. The photopolymerization rate was in the order of **1b** > **1a** > **3b** > **3a** > **1d** > **2a** > **1c** > **3c**. Especially, ammonium salts **1b** exhibited the same photoactivity as TPS, which is a typical photocationic initiator. The effect of *N*-substituent on the photoactivity of the was in the order of α -benzoylbenzyl > phenacyl > 1-benzoyl-ethyl, and that of heterocyclic systems was *p*-cyanopyridine > benzothiazole > 3-bromoquinoline > pyrazine.

Figure 2 depicts the time-conversion curves in the photopolymerization of an acrylate (M-210) in the presence of ammonium salts **1a**–**3c** as the initiators. In this experiment, the coated compounds were covered with a polyethylene film of 32 μm in thickness to avoid the inhibition by oxygen. The ammonium salts also served as photoradical initiators. The photoactivity of these ammonium salts was in the order of **2a** > **1a** > **3c** > **3a** > **1d** > **1c** > **1b** > **3b**. Especially, **2a** exhibited considerably higher photoactivity compared with other salts and benzophenone (typical free radical photoinitiator), which may be attributed to the formation of acryloyl radical species as shown in Scheme 4(c). The photoactivity of these ammonium salts was in the order of benzothiazole > 3-bromoquinoline > pyrazine > *p*-cyanopyridine, which was almost the same result as the photocationic polymerization.

These results lead to the assumption that the photoreaction occur via paths (b) and (c) simultaneously

as shown in Scheme 4. It is thought that cationic polymerization of epoxide, although it is possible to radically polymerize, cannot take place in the case of photoinitiation reaction of path (a). In path (b), a carbonium cation may be generated by photoirradiation. In path (c), it is supposed the carbon–nitrogen bond homolytically cleaves by photoirradiation to generate a carbon radical and an ammonium cation radical. Subsequently, the cation radical may transform into a protonated ammonium cation by hydrogen abstraction probably from a surrounding monomer. The active species of radical polymerization seems to be [1] and/or [2], and that of cationic polymerization seems to be [3]. From the results of the photocationic and

TABLE I
Thermal Polymerization of UVR-6110
with Ammonium Salts^a

<i>N</i> -onium salt ^b	DSC	
	Peak temp. (°C)	ΔH (J/g)
1a	141	-522
1b	171	-526
1c	136	-443
1d	142	-578
2a	132	-499
3a	115	-360
3b	158	-580
3c	232	-226

^a 0.5 mol % per epoxy group.

TABLE II
Heat of Formation with *N*-Phenacylbenzotiazolium Salts

<i>N</i> -phenacyl- benzotiazolium salts	Heat of formation (kcal/mol)						
	[1]	[2]	[2] - [1]	[3]	[3] - [1]	[4]	[4] - [1]
1a	-87.098	-47.864	+39.234	-68.167	+18.931	-66.904	+20.194
2a	-119.083	-82.835	+36.248	-142.089	-23.006	-195.843	-76.76
3a	-114.027	-32.067	+81.960	-89.347	+24.680	-202.572	-88.545

radical polymerization, we presume that the reactions of **1b**, **1c**, and **3b** occur mainly via path (b), **1a**, **2a**, **3a**, and that of **3c** does via path (c). The reaction of **1d** may occur approximately via paths (b) and (c).

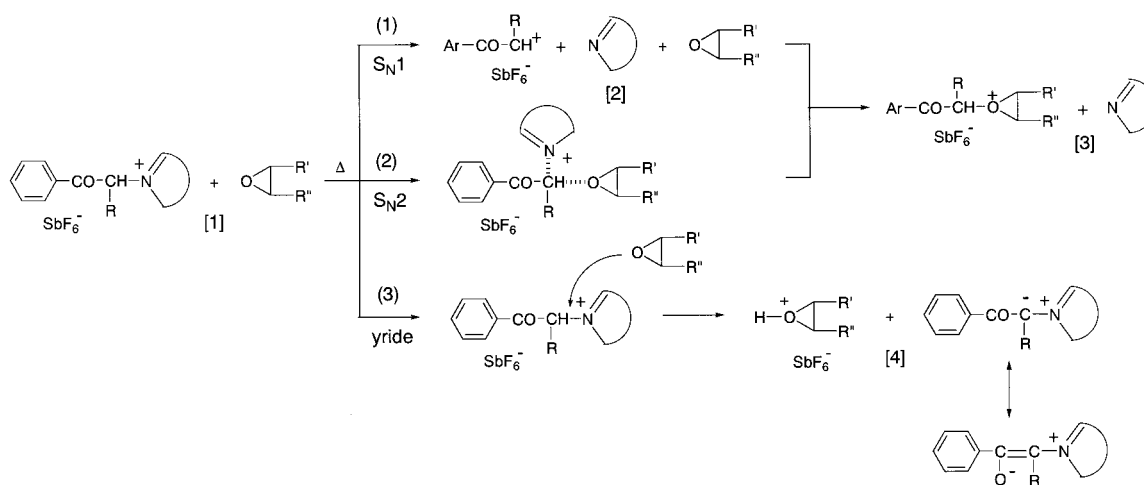
The photoactivation efficiency of **1c** and **3c** in the cationic polymerization was lower compared with other ammonium salts. Therefore, we examined the effect of sensitizers (Scheme 2) to enhance the photoinitiation activity of the salts. Figure 3 depicts the time-conversion curves of the epoxy monomer (UVR-6110) in the presence of EDMA and DMPA measured by real-time FTIR spectroscopy. Comparing the time-conversion relationship in Figure 1, it was confirmed that EDMA and DMPA accelerated the reaction rates in all cases. These results suggest that the photosensitization includes two mechanisms (Scheme 5). One is path 1, where a photoradical initiator accelerates the reaction,¹⁰ and the other is path 2, where an electron-donating compound accelerates the reaction.^{18,19} In path 1, the ammonium salts react with a radical species generated by decomposition of the sensitizer, resulting in the formation of a cation species, phenacyl radical, and heterocyclic derivatives. In path 2, one electron transfers from the sensitizer to the ammonium salt, resulting in the formation of a radical species and heterocyclic derivatives. The sensitizer transforms into a cation radical, which subsequently ab-

stracts hydrogen from a neighboring monomer and so on to generate HSbF₆.

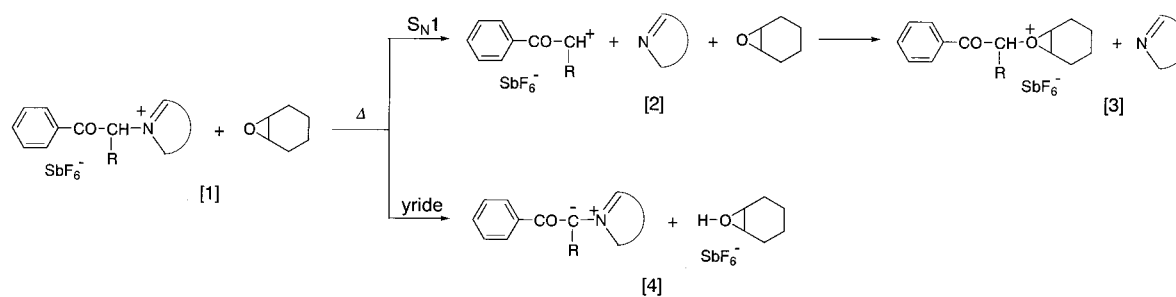
The photoactivation efficiency of the ammonium salts in a pigment system (particularly in the case of Titanium oxide) may be very low, because they have no absorption longer than 380 nm. Therefore, we examined the effect of sensitizers (Scheme 2) to enhance the photoinitiation activity of the ammonium salts. Figure 4 depicts the time-conversion curves of an epoxy monomer (UVR-6110) in the presence of EDMA using a filter-cutting UV light shorter than 387 nm, measured by real-time FTIR spectroscopy. It was confirmed that the benzothiazolium salts were sensitized by EDMA.

Thermal polymerization

We examined the thermal polymerization of epoxy monomer UVR-6110 with the ammonium salts **1a–3c** by DSC. Table I summarizes the maximum temperatures and enthalpy (ΔH) values of exothermic transitions, which correspond to the polymerization-initiating temperatures and polymerization rates, respectively. These salts could polymerize the epoxide at relatively low temperatures (115–171°C) except **3c**. We demonstrated that the thermal activity of *N*-benzylpyridinium salts increased by introducing electron-



Scheme 6



Scheme 7

donating groups such as methoxy group into the benzyl group, presumably due to an increase of stability of the generating benzyl cation. However, the initiating temperature of these ammonium salts was in the order of **3a** > **2a** > **1c** > **1a** > **1d** > **3b** > **1b** > **3c**, contrary to our previous knowledge. That is to say, it may follow the order of **3a** < **2a** < **1a** in the case of benzothiazolium salts. Consequently, it may be suggested that the thermal reaction of the ammonium salts proceeds via ylide formation (3), as shown in Scheme 6. Table II summarizes simulation results of the heat of formation for the reaction between benzothiazolium salts and epoxide, which are shown in Scheme 7, by MOPAC. The relationship between DSC results and activation energies ([2]-[1]), by which it has been assumed that the thermal reaction proceeded with $\text{S}_{\text{N}}1$, could not be observed. Further, the relationship between DSC results and the heat of formation [3] the reaction is subject to progress when the value of the heat of formation [3] is smaller than the value of [1], also could not be found. On the other hand, good correlation between the difference of the heat of formation: [4]-[1] and DSC results in Table I was observed. These results suggest that thermal reaction of ammonium salts and epoxide proceeds via ylide formation.

SUMMARY

In this article, we demonstrated that ammonium salts having phenacyl groups served as initiators in thermal cationic, photocationic, and radical polymerizations. *N*-Phenacylpyridinium salts **1b** and **3b** with a cyano group exhibited higher cationic thermal- and photoactivity. Benzothiazolium salts **1a** and **3a** were ther-

mally more active than the corresponding other salts. Pyrazinium salt **1c** exhibited higher thermal activity, while the photoactivity was lower. α -Phenyl-substituted and nonsubstituted *N*-phenacylpyridinium salts showed higher cationic photoactivity than the corresponding α -methyl-substituted one, while the radical photoactivity was the opposite order. The photoactivity of *N*-phenacylammonium salts was improved by the addition of aromatic compounds such as EDMA and DMPA as sensitizers.

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