

# Synthesis of Novel Sulfonium Salts and Cationic Polymerization of Epoxides and Vinyl Ether

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**ABSTRACT:** Novel 1-methoxycarbonylethylmethylphenyl-sulfonium salts with nonnucleophilic anions, namely, hexafluorophosphate, hexafluoroantimonate, and tetrafluoroborate, were synthesized by the reaction of 1-methoxycarbonylethylphenylsulfide and dimethyl sulfate followed by anion exchange with potassium hexafluorophosphate, sodium hexafluoroantimonate, and sodium tetrafluoroborate, respectively. The cationic polymerization (photopoly-

merization and thermal polymerization) of epoxy and vinyl ether monomers was carried out to demonstrate the applicability of the newly synthesized sulfonium salts. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3157–3163, 2007

**Key words:** cationic polymerization; irradiation; photopolymerization

## INTRODUCTION

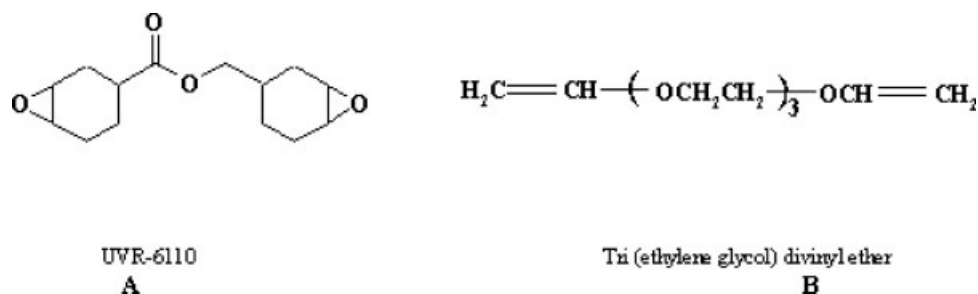
During the last 2 decades, significant progress has been made in the area of photocationic polymerization. Nowadays, photoinitiated cationic polymerizations are not being employed only for coatings, printings, adhesives, and release papers but also in applications such as holography and resists.<sup>1</sup> Considerable future potential for the growth of such systems exists because of the excellent properties of such coating systems, their low energy consumption, and their lack of environmental pollution.

The discovery of highly photosensitive (i.e., high-quantum-yield) and efficient cationic photoinitiators is the key to the development of this technology. Among the best photoinitiators that have been developed in recent years are diaryliodonium, triarylsulfonium, and ferrocenium salts<sup>2</sup> with nonnucleophilic anions such as  $\text{CF}_3\text{SO}_3^-$ ,  $\text{BF}_4^-$ ,  $\text{ClO}_4^-$ ,  $\text{FSO}_3^-$ ,  $\text{PF}_6^-$ ,  $\text{AsF}_6^-$ ,  $\text{SbF}_6^-$ , and  $(\text{C}_6\text{F}_5)_4\text{B}^-$ . Upon irradiation with UV light, these photoinitiators undergo irreversible fragmentation with the formation of Brønsted and Lewis acids, which initiate cationic polymerization. Several of these photoinitiators are now available as commercial products. In practical applications, photoinduced cationic polymerization systems have been limited in comparison with radical polymerization because it is difficult to develop initiators with both high sensitivity and a wide wavelength range. Photoinitiated cationic curing systems are much less inhibited by oxygen and water than free-radical systems. Although the rates of cationic

photopolymerization are slower than those of radical photopolymerization, the former is more predominant than the latter in thin-film curing because there is no effect from oxygen. Crivello and coworkers<sup>3</sup> extensively studied the photopolymerization of epoxides with triphenyl sulfonium salts and iodonium salts as cationic photoinitiators. Endo and coworkers<sup>4</sup> and Yagci and coworkers<sup>5</sup> also developed several benzylsulfonium<sup>4</sup> and benzylpyridinium salts<sup>5</sup> as thermally latent and photolabile initiators for the polymerization of styrene, vinyl ethers, and epoxides.

Ideally, a photoinitiator should be stable in the desired monomer in the absence of light for as long as possible, yet upon irradiation it should efficiently initiate cationic polymerization. For this reason, the initiator should be as pure as possible because even slight trace of impurities may induce polymerization over a long period of time. The most effective method of purification is recrystallization. Normally, photoinitiators that can be readily crystallized have a melting point substantially above room temperature. Although onium salts possess high quantum yields, they are soluble only in polar, cationically polymerizable monomers. This severely limits their utility. Furthermore, the phenyl-substituted onium salts show appreciable acute oral toxicity. Hence, the manipulation of the structure of the photoinitiator is generally required to simultaneously optimize these two properties. The introduction of methoxy groups is effective for lowering the initiation temperature because of their greater electron-donating ability. Considering all these things, we decided to synthesize sulfonium salts with carbonyl and methoxy groups. In this article, we report the synthesis of novel sulfonium salts having different counteranions and their application to the cationic

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**Figure 1** (A) Structure of UVR-6110 and (B) structure of tri(ethylene glycol)divinyl ether.

polymerizations of 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexylcarboxylate (UVR-6110) and tri(ethylene glycol)divinyl ether monomers.

## EXPERIMENTAL

### Materials

Analytical-reagent-grade chemicals such as benzene thiol, methyl  $\alpha$ -bromopropionate, dimethyl sulfate, tetrabutylammonium bromide (TBAB), UVR-6110 [Fig. 1(A)], and tri(ethylene glycol)divinyl ether [Fig. 1(B)] were purchased from Aldrich Chemical, Ltd. (Kyunggi Do, Yongin City, Korea) and were used as received. Potassium hexafluorophosphate ( $\text{KPF}_6$ ), sodium hexafluoroantimonate ( $\text{NaSbF}_6$ ), and sodium tetrafluoroborate ( $\text{NaBF}_4$ ) were purchased from TCI (Tokyo, Japan).

### Measurements

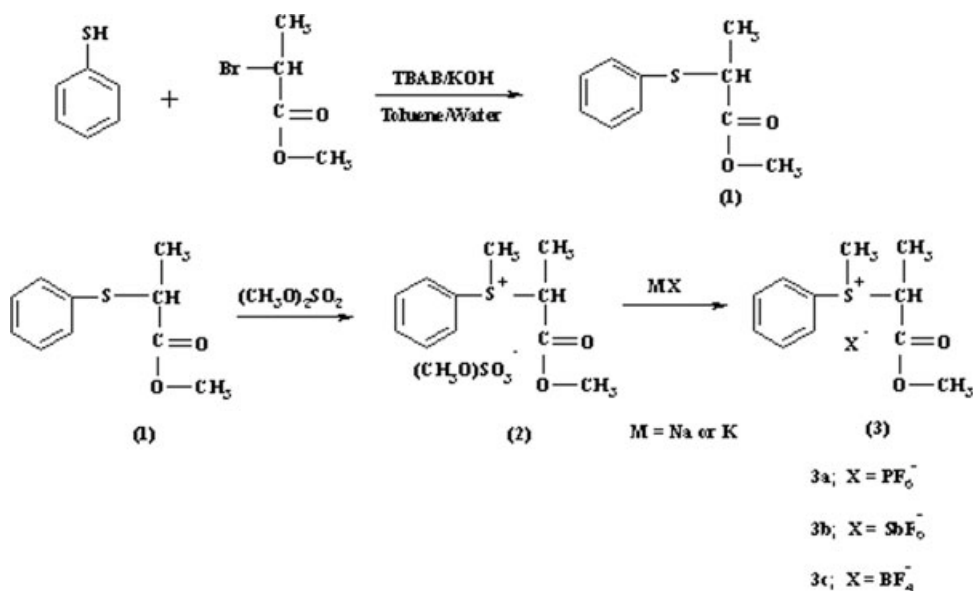
Ultraviolet-visible spectra were recorded on a Unicam UV2-100 spectrometer. Fourier infrared transform spectra were recorded on a Unicam 5000 spectrometer with the KBr pellet technique.  $^1\text{H-NMR}$ ,  $^1\text{H-}^1\text{H}$  correlation

spectroscopy (COSY) NMR, and heteronuclear chemical-shift correlation (heteronuclear multiple quantum correlation) spectra were recorded on a Varian Unity Inova 500 spectrometer at room temperature in  $\text{CDCl}_3$  and acetone- $d_6$  with tetramethylsilane as an internal standard. Differential scanning calorimetry (DSC) was performed on a TA 2910 DSC instrument at a heating rate of  $10^\circ\text{C}/\text{min}$  under a flow of  $\text{N}_2$  gas.

### Syntheses

#### Synthesis of 1-methoxycarbonylethylphenylsulfide (1)

To a 500-mL, three-necked, round-bottom flask equipped with a magnetic stirrer and thermowell were added benzene thiol (11.0 g, 0.1 mol), methyl  $\alpha$ -bromopropionate (16.7 g, 0.1 mol), and 100 mL of toluene. Then, a solution of 100 mL of aqueous KOH (5.6 g, 0.1 mol) and TBAB (1.5 g, 5 mmol) was poured into the flask. The resulting mixture was stirred at  $80^\circ\text{C}$  for 12 h. The reaction was monitored with thin-layer chromatography. After that, the mixture was added to 150 mL of distilled water and separated. The toluene layer was washed three times with 30 mL of distilled water and concen-



**Scheme 1** Synthesis of the sulfonium salts.

TABLE I  
Characteristics of the Synthesized Sulfonium Salts

Salt	mp (°C)	$\alpha_{\max}$ (nm)	IR (cm <sup>-1</sup> )	Yield (%)
3a	111	266	3048, 2971, 1733, 1455, 1331, 1086, 842	80
3b	99.2	266	3042, 2966, 1735, 1452, 1330, 1082, 659	62
3c	Oil	268	3036, 2957, 1742, 1447, 1325, 1062	35

trated. The crude product was purified by column chromatography with hexane/chloroform (90 : 10 v/v) as the eluent.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>,  $\delta$ ): 1.49–1.52 (d, 3H), 3.68 (s, 3H), 3.79–3.83 (m, 1H), 7.27–7.35 (m, 3H), 7.43–7.48 (m, 2H).

#### Synthesis of 1-methoxycarbonylethylmethylphenylsulfonium hexafluorophosphate (3a)

A mixture of **1** (9.8 g, 0.05 mol) and dimethyl sulfate (6.3 g, 0.05 mol) was stirred at 50°C for 10 h. Then, it was poured into 100 mL of distilled water, washed

with 20 mL of ethyl acetate, and separated. KPF<sub>6</sub> (9.2 g, 0.05 mol) was added to the aqueous layer and stirred for 30 min. The desired product was precipitated out and was collected by filtration. The product was recrystallized from methanol to remove impurities.

Yield: 80%. mp: 111°C. IR (KBr, cm<sup>-1</sup>): 3048, 2971, 1733, 1605, 1455, 1331, 1086, 842. <sup>1</sup>H-NMR (acetone-*d*<sub>6</sub>,  $\delta$ ): 1.63 and 1.87 (d, *J* = 7.308 Hz, 3H), 3.69 (s, 3H), 3.78 and 3.91 (s, 3H), 5.10–5.18 (m, 1H), 7.81–7.88 (m, 2H), 7.91–7.98 (m, 1H), 8.13–8.19 (m, 2H). UV: ( $\lambda_{\max}$ ) = 266 nm.

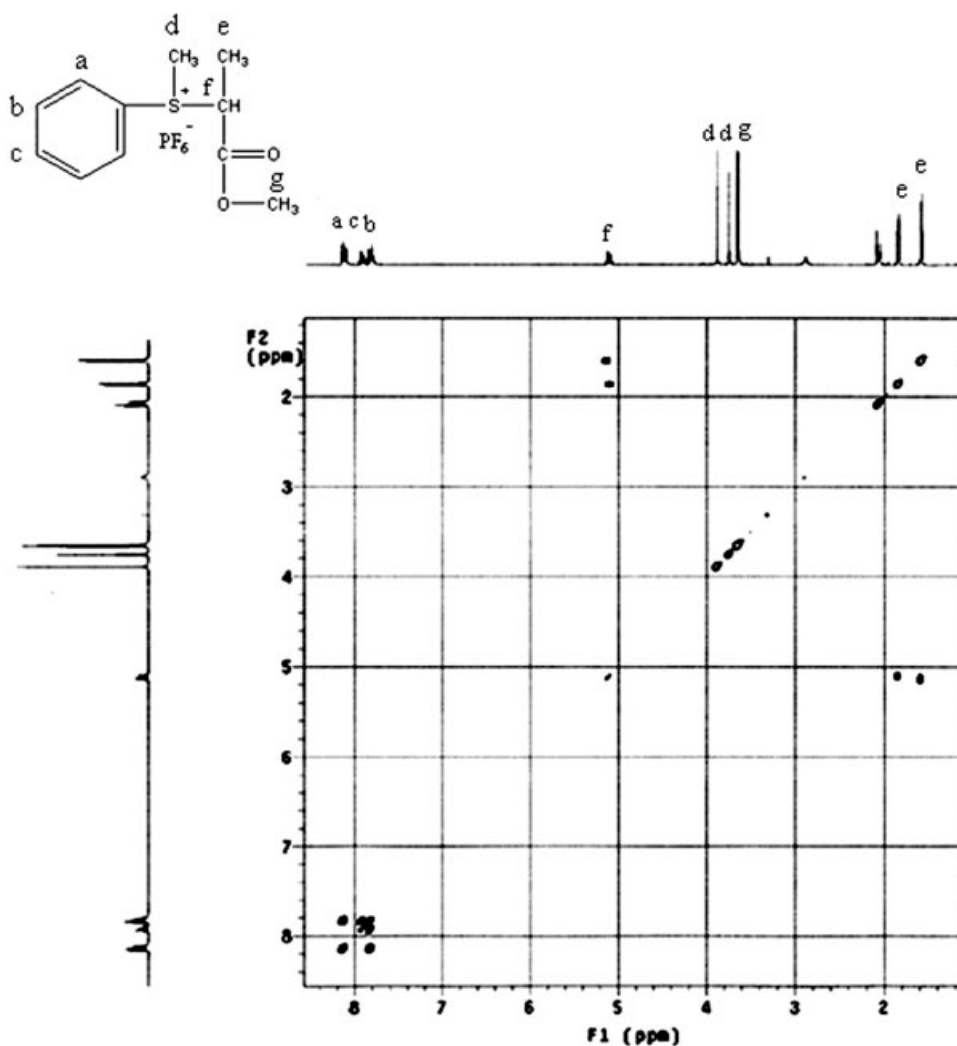


Figure 2 <sup>1</sup>H-<sup>1</sup>H COSY NMR spectrum of compound **3a** in acetone-*d*<sub>6</sub>.

### Synthesis of 1-methoxycarbonylethylmethylphenylsulfonium hexafluoroantimonate (**3b**)

The title compound (**3b**) was synthesized in a manner similar to the method of synthesizing **3a**, with NaSbF<sub>6</sub> used instead of KPF<sub>6</sub>.

Yield: 65%. mp: 99.2°C. IR (KBr, cm<sup>-1</sup>): 3042, 2966, 1735, 1600, 1452, 1330, 1082, 659. <sup>1</sup>H-NMR (acetone-*d*<sub>6</sub>, δ): 1.62 and 1.87 (d, *J* = 6.836 Hz, 3H), 3.70 (s, 3H), 3.78 and 3.91 (s, 3H), 5.12–5.19 (m, 1H), 7.82–7.88 (m, 2H), 7.91–7.98 (m, 1H), 8.13–8.19 (m, 2H). UV: λ<sub>max</sub> = 266 nm.

### Synthesis of 1-methoxycarbonylethylmethylphenylsulfonium tetrafluoroborate (**3c**)

A mixture of dimethyl sulfate (6.3 g, 0.05 mol) and 1 (9.8 g, 0.05 mol) was stirred at 50°C for 10 h. Then, the mixture was poured into 100 mL of distilled water, washed with 20 mL of ethyl acetate, and separated. NaBF<sub>4</sub> (5.45 g, 0.05 mol) was added to the water layer and stirred for an hour, and then methylene chloride was added to the mixture. The organic layer was

separated and concentrated. The desired product was obtained as a viscous oil.

Yield: 35% (viscous liquid). IR (KBr, cm<sup>-1</sup>): 3036, 2957, 1742, 1600, 1447, 1325, 1062. <sup>1</sup>H-NMR (acetone-*d*<sub>6</sub>, δ): 1.50 and 1.76 (d, *J* = 6.836 Hz, 3H), 3.50 (s, 3H), 3.73 and 3.90 (s, 3H), 4.90–4.99 (m, 1H), 7.75–7.81 (m, 2H), 7.85–7.90 (m, 1H), 7.98–8.03 (m, 2H). UV: λ<sub>max</sub> = 268 nm.

## RESULTS AND DISCUSSION

### Synthesis of the photoinitiators

The synthetic route for the photoinitiators is outlined in Scheme 1. Benzene thiol was treated with methyl α-bromopropionate in the presence of TBAB to yield the sulfide, which was easily reacted with dimethyl sulfate to afford the corresponding sulfonium methyl sulfates in good yields. The anion exchange of the sulfonium methyl sulfate proceeded smoothly with KPF<sub>6</sub>, NaSbF<sub>6</sub>, and NaBF<sub>4</sub>.

**3a** and **3b** were obtained in powder form. However, **3c** was obtained as a viscous oil, perhaps because the

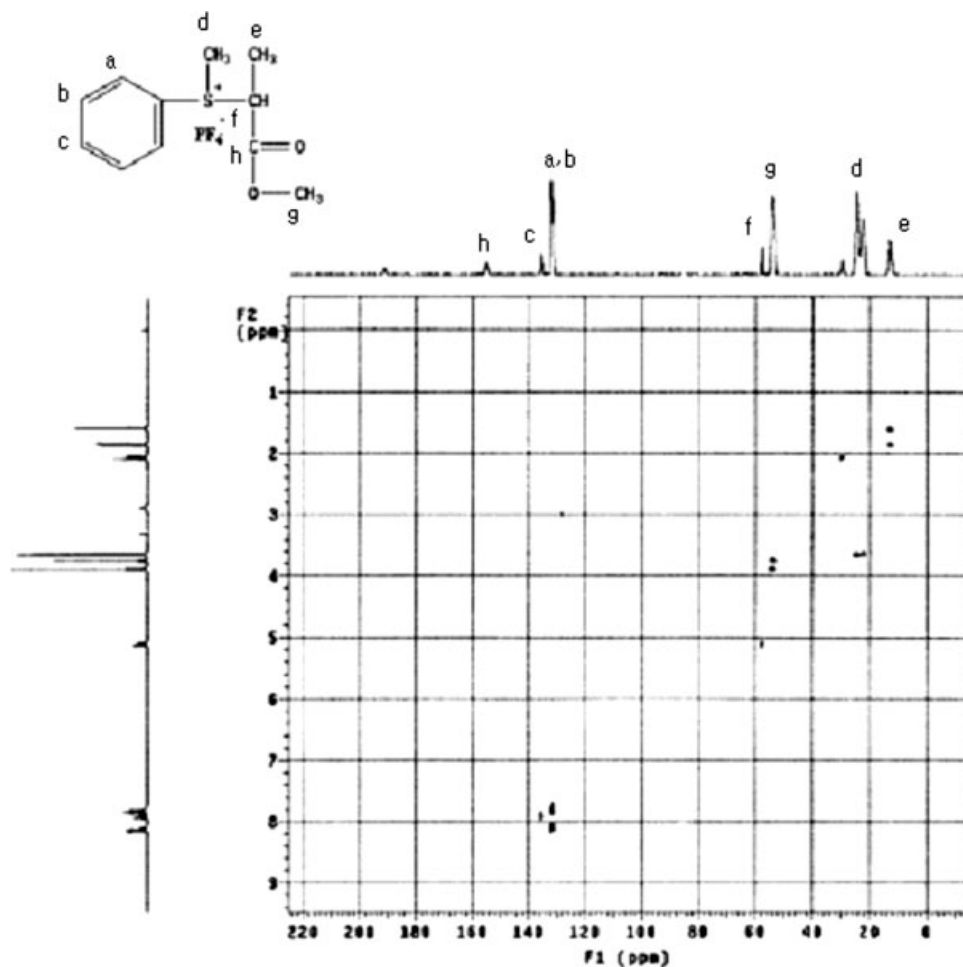


Figure 3 <sup>1</sup>H-<sup>13</sup>C COSY NMR spectrum of compound **3a** in acetone-*d*<sub>6</sub>.

molecular weight of the initiators was smaller than that of the initiators with counterions such as hexafluorophosphate and hexafluoroantimonate. Synthesized sulfonium salts were characterized by UV, IR, and NMR spectroscopy. The characterization data are given in Table I.

$^1\text{H}$ - $^1\text{H}$  coupling and  $^1\text{H}$ - $^{13}\text{C}$  coupling were verified by  $^1\text{H}$ - $^1\text{H}$  COSY and  $^1\text{H}$ - $^{13}\text{C}$  COSY NMR spectroscopy. The  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum (Fig. 2) shows the proton at 5.1 ppm corresponding to methine protons (*f*). However, signals at 1.62 and 1.88 could be assigned to the *e* protons, whereas signals at 3.77 and 3.91 correspond to *d* protons from two different diastereomers (because of the environmental difference influenced by  $\text{S}^+$ , i.e., because of chirality). The cross peaks in the  $^1\text{H}$ - $^{13}\text{C}$  COSY (heteronuclear multiple quantum correlation) NMR spectrum (Fig. 3) for carbon atoms *e* and *d* indicate the presence of two diastereoisomers differing with the magnetic environments of the corresponding protons: peaks at 1.62 and 1.88 for *e* protons and peaks at 3.77 and 3.91 for *d* protons.

#### Photoreactive measurements

A high-pressure mercury lamp was used for irradiating the thin films ( $1.25 \pm 0.1 \mu\text{m}$  thick) of the monomers containing 3 wt % photoinitiator on an IR plate. They were kept at a distance of 10 cm from the mercury lamp for irradiation. To measure the photoactivities of the photoinitiators, the samples (monomers containing 3 wt % photoinitiator) were irradiated for different times. The changes were monitored continuously with the IR spectra of the polymer films. The disappearance of the characteristic absorption bands at  $795 \text{ cm}^{-1}$  for epoxy rings and at  $1622 \text{ cm}^{-1}$  for vinyl ether double bonds was observed with IR spectroscopy. The degree of conversion was calculated from the decrease in the IR absorbance after a given exposure:<sup>6</sup>

$$\text{Extent of conversion (\%)} = \frac{A_T - A_0}{A_{\text{max}} - A_0} \times 100$$

where  $A_0$ ,  $A_T$ , and  $A_{\text{max}}$  are the absorption intensities after irradiation time 0, time  $T$ , and the time after which there is no further significant change in the absorbance, respectively.

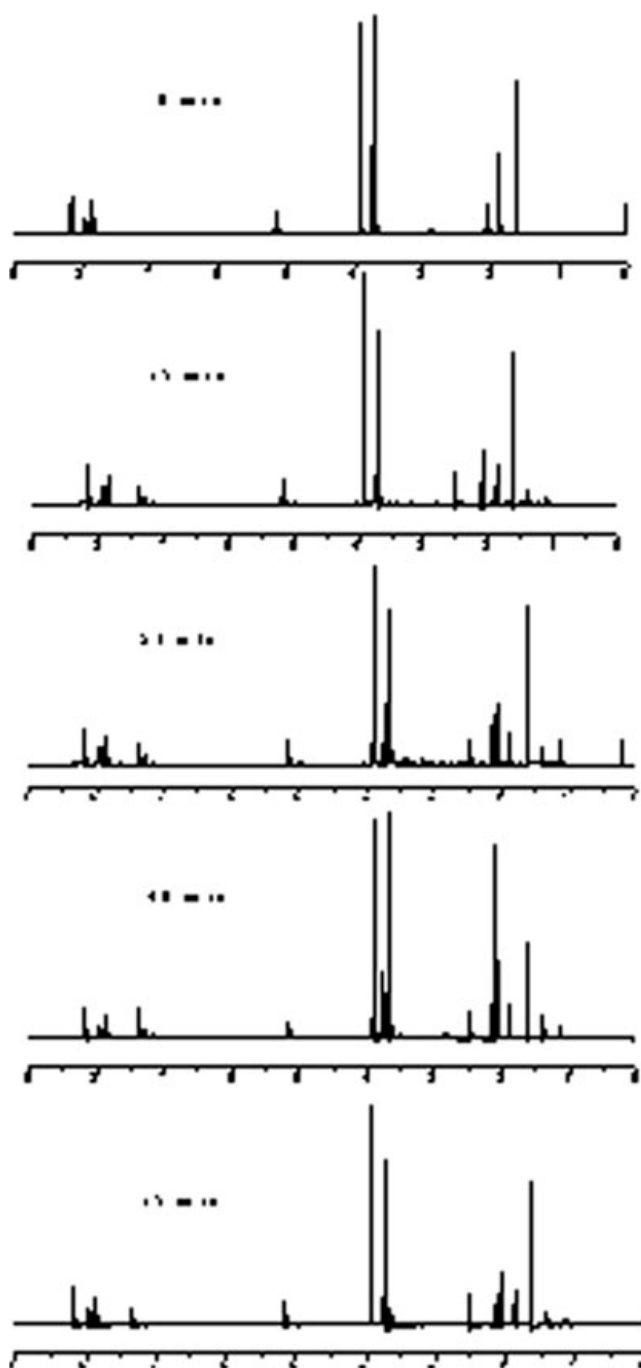
#### Photolysis

Photolysis was conducted at  $25^\circ\text{C}$  with a high-pressure mercury lamp. Solutions of the photoinitiator in acetone- $d_6$  were placed in Pyrex NMR sample tubes and irradiated. The samples were withdrawn at different times (0, 15, 25, 40, and 55 min), and their NMR spectra were recorded. The disappearance of the starting material was followed by the integration of the appropriate

absorption bands. As the photolysis (Fig. 4) proceeded, changes occurred in the aromatic region (7.20–7.40 ppm) and methyl band (2.50 ppm). The photodecomposition rate of **3a** in the photolysis is shown in Figure 5 and agrees with previously reported results.<sup>7</sup>

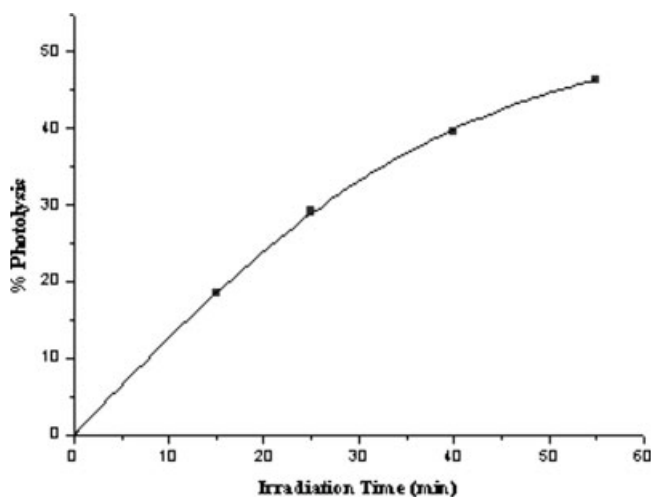
#### Photopolymerization

The photopolymerization of UVR-6110 and tri(ethylene glycol)divinyl ether was carried out by the irradiation



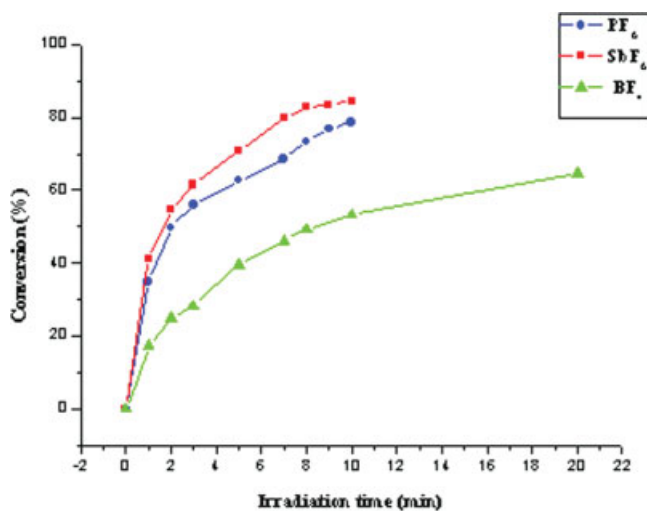
**Figure 4** NMR study of the photolysis of compound **3a** in acetone- $d_6$  versus the irradiation time.



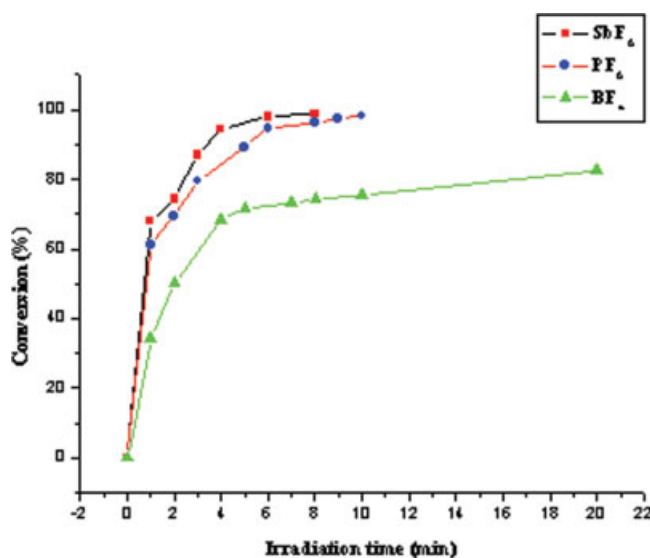


**Figure 5** Time-conversion relationship in the photolysis of 3a.

tion of the thin films on IR plates. The conversion was monitored with IR spectroscopy. Figures 6 and 7 show the time-conversion relationship in the photopolymerization of epoxy and vinyl ether monomer, respectively. Among the cationic photoinitiators listed in Table I, photoinitiator **3b** was more active than **3a** and **3c** with respect to the polymerization of UVR-6100 and tri(ethylene glycol)divinyl ether. The change in the activity might have been contributed by the variation between the cleavage energies and/or the different nucleophilicities of the counteranions. The order of reactivity of the sulfonium salts possessing the same cation, but different anions, was found to be  $\text{SbF}_6^- > \text{PF}_6^- > \text{BF}_4^-$ .



**Figure 6** Time-conversion relationship in the photopolymerization of the epoxide monomer with 3 wt % sulfonium salts at 25°C. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

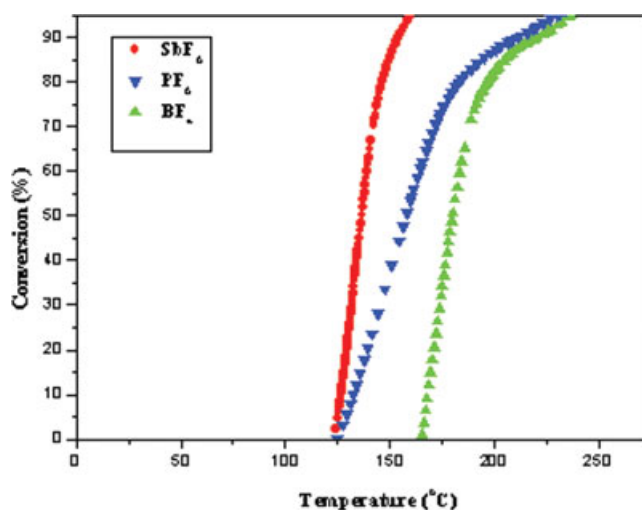


**Figure 7** Time-conversion relationship in the photopolymerization of tri(ethylene glycol)divinyl ether with 3 wt % sulfonium salts at 25°C. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

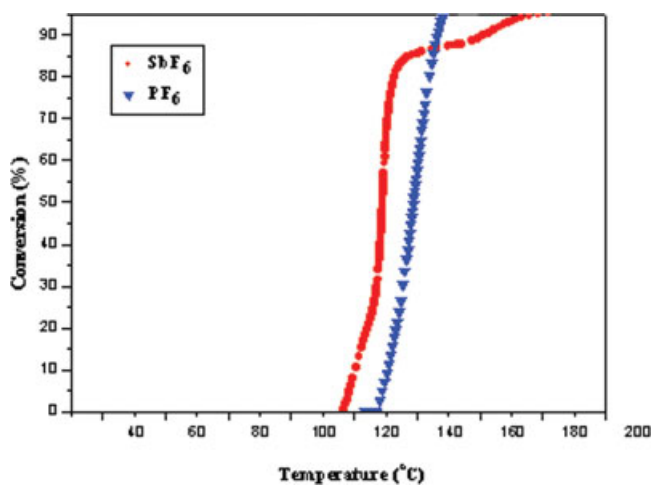
### Thermal polymerization

The thermal polymerization of UVR-6110 and tri(ethylene glycol)divinyl ether was examined with DSC. The polymerizations of epoxy and vinyl ether monomers were carried out with 3 wt % concentrations of sulfonium salts **3a–3c**.

The thermal polymerization of UVR-6110 did not occur below 125°C, but it proceeded rapidly above the initiating temperature; for tri(ethylene glycol)-



**Figure 8** Temperature-conversion relationship in the thermal polymerization of the epoxide monomer with 3 wt % sulfonium salts. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 9** Temperature–conversion relationship in the thermal polymerization of the tri(ethylene glycol)divinyl ether monomer with 3 wt % sulfonium salts. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

divinyl ether, polymerization occurred only above 105°C.

As shown in Figures 8 and 9, the initiator with counteranion  $\text{SbF}_6^-$  was more active than those with  $\text{PF}_6^-$  and  $\text{BF}_4^-$ . The order of activity of the initiators, depending on the nature of the counteranion, was in good agreement with previously reported results ( $\text{SbF}_6^+ > \text{PF}_6^- > \text{BF}_4^-$ ). It is likely that the initiating species in the photoreaction is the carbenium cation, which is the same as that in the thermal reaction because almost the same effects have been observed in photoreactions and thermal reactions.

## CONCLUSIONS

Novel sulfonium salts have been synthesized and characterized with UV, IR,  $^1\text{H-NMR}$ , and two-dimensional NMR spectroscopy techniques. In the photolysis test, the photodecomposition rate of the synthesized salts is in good agreement with those of previously reported

sulfonium salts. The use of these novel photoinitiators to carry out cationic polymerizations of epoxides and divinyl ether has been described. Sulfonium salts with counteranion  $\text{SbF}_6^-$  have better activity than those with counteranions  $\text{PF}_6^-$  and  $\text{BF}_4^-$ .

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