

Photo and Thermal Polymerization of Epoxides and Vinyl Ethers by Novel Sulfonium Salts

Jun Young Kim, Prashant S. Patil, Byoung Jun Seo, Tae Soo Kim, Jinhwan Kim, Tae Ho Kim

Department of Polymer Science and Engineering, SungKyunKwan University, Suwon, Kyunggi-Do 440-746, Korea

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ABSTRACT: Novel Sulfonium salts with non-nucleophilic anions were synthesized and applicability of these salts as initiators was demonstrated by carried out polymerization (photo and thermal) of epoxides as well as vinyl ether monomers. Newly synthesized initiators showed good activity for the photo and thermal polymer-

ization. Synthesis, characterization, and activity of initiators have been described. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 858–862, 2008

Key words: photoinitiators; sulfonium salts; photo polymerization; thermal polymerization; UV-irradiation

INTRODUCTION

Photoinitiated polymerization have attracted increasing attention in recent years, because of the growth of applications in the manufacture of printed circuits, encapsulation of electronic components, decorative coatings, surface coatings, printing inks, adhesives, stereolithographic resins, and many others.^{1–7} Curing systems are widely used to improve the characteristics of polymeric materials in various fields. The curing systems are classified broadly into thermal-curing and UV-curing systems. UV-curing systems have a large advantage over thermal curing systems in the conservation of natural resources, energy conservation, space saving environmental preservation, and productivity. UV-curing systems are used in many coating applications.⁸ Ongoing efforts in many laboratories are being directed toward the improvement of the performance of cationically photopolymerizable systems. 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. Meanwhile hybrid curing systems consisting of epoxides and acrylates are useful for coatings, printings, and adhesives because they can compensate for the disadvantages of radical and cationic polymerizations, i.e., inhibition by oxygen and water and a slow polymerization rate. However, hybrid curing systems based on cationic photopoly-

merization and thermal polymerization are gaining importance for coatings and adhesions. Therefore, an investigation into initiators applicable to both photo and thermal cationic polymerizations may be an important subject in the near future. Onium salts having non-nucleophilic anions like BF_4^- , PF_6^- , AsF_6^- , or SbF_6^- are extremely efficient. A very important application is in microelectronics industry, especially in the field of photoresists. The photoacid generating compounds have been used for the catalyst that carries out the deprotection of functional polymers, which made it possible to develop various positive photoresists with environment-friendly lithographic processing.⁹

Vinyl ethers and epoxides are among the most reactive monomers polymerized by cationic polymerization. The photoinitiated cationic polymerization of epoxide compounds and vinyl ether compounds has led to new materials for new UV-curing systems because the polymerization of these monomers is not inhibited by atmospheric oxygen.¹⁰ The cured products of the epoxide compounds exhibit excellent chemical and thermal properties, adhesiveness, and mechanical properties. Thus, a wide range of applications is being considered for epoxide compounds. However, the epoxide compounds have low reactivity, and their cured products are often hard and brittle; this causes problems in impact resistance and workability. The photoinitiated cationic polymerization of vinyl ether compounds has received attention as a new UV-curing system because it is more highly reactive than the epoxide compounds.^{11–13} Lapin and coworkers^{14,15} reported the radiation-induced cationic polymerization of vinyl ether monomers and oligomers with photoinitiators such as sulfonium salts. Crivello and coworkers^{16–29} have developed aromatic sulfonium and iodonium

Correspondence to: P. S. Patil or T. H. Kim (pspat2k@hotmail.com or kimth@skku.edu).

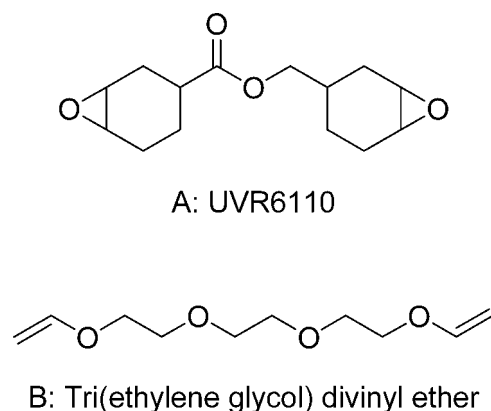


Figure 1 Structures of UVR-6110 and tri(ethylene glycol) divinyl ether.

salts as photocationic initiators as well as new cationically polymerizable vinyl ether and epoxide monomers. For instance, the necessity of increasing the reactivity of these systems to provide competitive polymerization rates with those of free radical systems has resulted in the design and synthesis of novel monomers, photoinitiators, and photosensitizers. Many other researchers^{30–39} also developed several onium salts as thermally latent and photolabile initiators for the polymerization of styrene, vinyl ethers, and epoxides.

In continuation of our previous work,⁴⁰ we report herein the synthesis of novel sulfonium salts with different counter anions and their application for the photo and thermal polymerization of UVR-6110 and tri(ethylene glycol) divinyl ether monomers.

EXPERIMENTAL

Materials

AR grade chemicals such as benzenethiol, 1-bromoethyl benzene, dimethyl sulfate, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexylcarboxylate (UVR-6110) [Fig. 1(A)] and tri(ethylene glycol) divinyl ether [Fig. 1(B)], 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), employed in this study were purchased from Aldrich Chemical (St. Louis, MI) and were used as received. Potassium hexafluorophosphate (KPF₆) and sodium hexafluoroantimonate (NaSbF₆) were purchased from TCI (Tokyo, Japan).

Measurements

UV-visible spectra were recorded on Unicam UV2-100 spectrometer. FT-IR spectra were recorded on Unicam 5000 spectrometer using KBr pellet technique. ¹H NMR, spectra were recorded on Varian Unity Inova 500 spectrometer at room temperature

in CDCl₃ and Acetone-d₆ by using tetramethylsilane as an internal standard. Differential scanning calorimeter (DSC) was done on TA 2910 DSC instrument at a heating rate of 10°C/min under a flow of N₂ gas.

Photoreactive measurement

The mercury lamp of intensity 6.5 mW/s at 365 nm wavelength was used for irradiating the thin film (1.25 ± 0.1 μm thickness) of monomer containing 3 wt % photoinitiators on KBr plate. They were kept at a distance of 1 cm from Hg lamp for irradiation. To measure the photoactivities of the photoinitiators, samples (monomer containing 3 wt % photoinitiators) were irradiated with different time intervals. The changes have monitored continuously by the IR spectra of the polymer films. The disappearance of the characteristic absorption bands at ~ 795 cm⁻¹ for epoxy ring, and ~ 1622 cm⁻¹ for vinyl ether double bonds was observed by IR spectroscopy. The degree of conversion was calculated from the decrease in IR absorbance after a given exposure⁴¹:

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

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

Syntheses

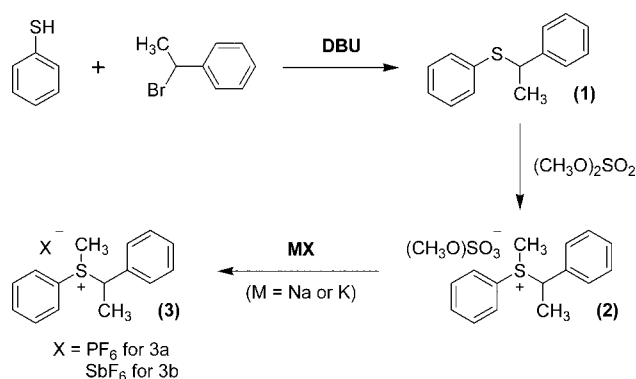
Synthesis of 1-phenylethylphenyl sulfide (1)

To a stirred mixture of DBU (7.6 g, 0.05 mmole) and benzenethiol (5.5 g, 0.05 mmole) in benzene (60 mL) was added (1-bromoethyl) benzene (9.25 g, 0.05 mmole), and the reaction mixture was stirred at room temperature for 2 h. The precipitated DBU-HBr salt was removed by filtration. The filtrate was washed with water, dried with anhydrous sodium sulfate and concentrated. The crude product was purified by column chromatography using hexane/benzene (95 : 5, v/v) as an eluent.

¹H NMR (CDCl₃) δ: 1.68–1.69 (d, 3H, CH₃), 4.38–4.42 (q, 1H, CH), 7.24–7.37 (m, 10H, Ar-H). Mass (m/z): 214 (M⁺)

Synthesis of 1-phenylethylmethylphenyl sulfonium hexafluorophosphate (3a)

The mixture of 1-phenylethylphenyl sulfide (1) (2.14 g, 0.01 mol) and dimethylsulfate (1.26 g, 0.01 mol) was stirred at 50°C for 8 h. Then it was poured into 100 mL of distilled water, washed with 20 mL



Scheme 1 Synthesis of sulfonium salts.

of ethyl acetate, and separated. Potassium hexafluorophosphate (1.84 g, 0.01 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: 68%. mp: 155°C. IR (KBr, cm⁻¹): 3048, 2971, 1733, 1605, 1455, 1331, 1086, 842. ¹H NMR (acetone-d₆), δ: 1.70–1.71 (d, 3H, CH₃), 3.49 (s, 3H, S—CH₃), 4.39–4.40 (m, 1H), 7.24–7.35 (m, 5H, Ar—H), 7.71–8.0 (m, 5H, Ar—H). UV : λ_{max} = 265 nm.

Synthesis of 1-phenylethylmethylphenyl sulfonium hexafluoroantimonate (3b)

The title compound (3b) was synthesized in a similar manner to the method of synthesizing 1-phenylethylmethylphenyl sulfonium hexafluorophosphate (3a) by using NaSbF₆ instead of KPF₆.

Yield: 65%. mp: 157°C. IR (KBr, cm⁻¹): 3042, 2966, 1735, 1600, 1452, 1330, 1082, 659. ¹H NMR (acetone-d₆), δ: 1.70–1.71 (d, 3H, CH₃), 3.51 (s, 3H, S—CH₃), 4.39–4.40 (m, 1H), 7.24–7.35 (m, 5H, Ar—H), 7.71–8.0 (m, 5H, Ar—H). UV : λ_{max} = 265 nm.

RESULTS AND DISCUSSION

Synthesis of photoinitiators

The synthetic route for the photoinitiators is outlined in Scheme 1. Benzenethiol treated with (1-bromoethyl) benzene in the presence of DBU by known procedure⁴² to give sulfide which was easily reacted with dimethyl sulfate to afford the corresponding

sulfonium methyl sulfates in good yield. The anion exchange of the sulfonium methyl sulfate proceeded smoothly with KPF₆ and NaSbF₆.

Synthesized sulfonium salts namely, 1-phenylethylmethylphenyl sulfonium hexafluorophosphate (3a) and 1-phenylethylmethylphenyl sulfonium hexafluoroantimonate (3b) were obtained in the form of white crystals and were characterized by UV, IR, and NMR spectroscopy. The characterization data is depicted in Table I.

Photolysis

Photolysis was conducted at 25°C with high pressure mercury (Hg) lamp. Solutions of photoinitiator in acetone-d₆ were placed in Pyrex NMR sample tubes and irradiated. The samples were withdrawn at different time intervals (0, 20, 40, 60 min) and their NMR spectra were recorded. The disappearance of starting material was followed by the integration of the appropriate peaks. The photolysis of a Sulfonium salt leads to the formation of cations, radical, and radical-cationic species. The cationic species interact with the monomer or impurities in the reaction mixture to generate a protonic acid corresponding to the anion of the sulfonium salt. The protonic acid is the primary species that initiates polymerization. The photodecomposition rate of 3a in the photolysis is shown in Figure 2.

Photopolymerization

The reactivities of the epoxide and vinyl ether monomers with synthesized sulfonium salts were determined by means of FT-IR. This technique involves monitoring the change in the intensity of characteristic bands undergoing photopolymerization, as a function of time. FT-IR has been proved to be an extremely useful method for monitoring the kinetics of very rapid photopolymerization reactions. The progress of the polymerizations was monitored by following the decrease in the absorbance of characteristic IR bands of the epoxide (~ 795 cm⁻¹) or vinyl ether (~ 1622 cm⁻¹) groups in the respective monomers. The resulting data were averaged and the conversion vs. times curves are presented. Rates of photopolymerization were determined from linear portions of the slopes of the irradiation time/conversion curves. The time-conversion relationship in the

TABLE I
Characteristics of Synthesized Sulfonium Salts

Salts	mp (°C)	λ _{max} (nm)	FT-IR absorbance (cm ⁻¹)	Yield (%)
(3a)	155	265	3037, 2940, 1592, 1494, 1045, 1002, 842	68
(3b)	157	265	3029, 2933, 1589, 1494, 1045, 1004, 842	65

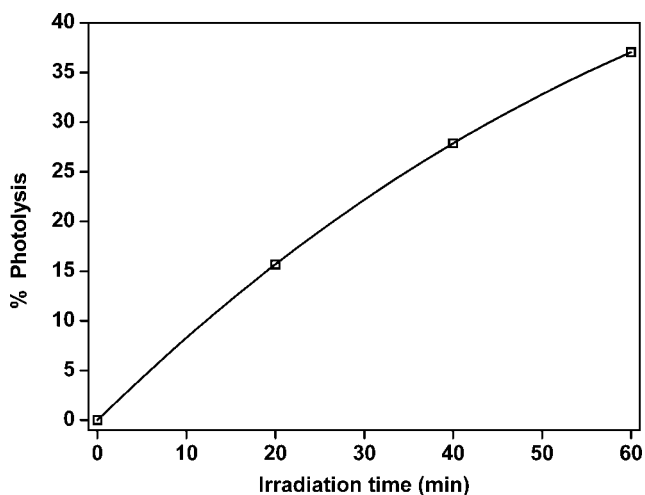


Figure 2 Time-conversion relationship in the photolysis of 3a.

photopolymerization of epoxy and vinyl ether monomer was shown in Figures 3 and 4, respectively. These newly synthesized photoinitiator showed better activity than our previous reported initiators.⁴⁰ Photopolymerization of tri(ethylene glycol) divinyl ether monomer was faster as compared with the UVR-6110 monomer by the synthesized initiators.

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 have been carried out with 3 wt % of sulfonium salts. Thermal polymerization of UVR-6110

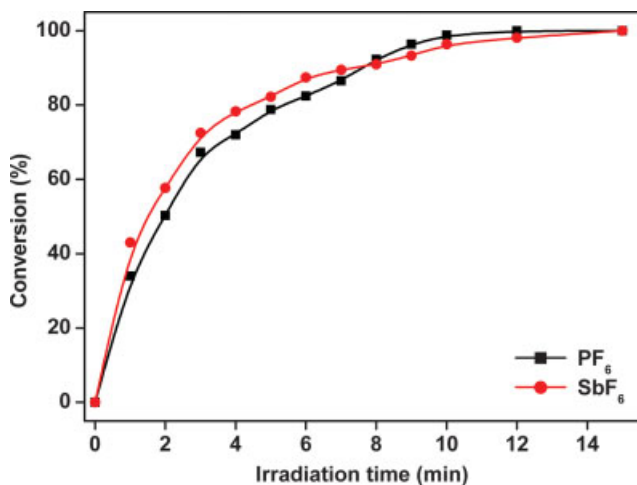


Figure 3 Time-conversion relationship in the photopolymerization of UVR-6110 monomer with 3 wt % sulfonium salts at 25°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

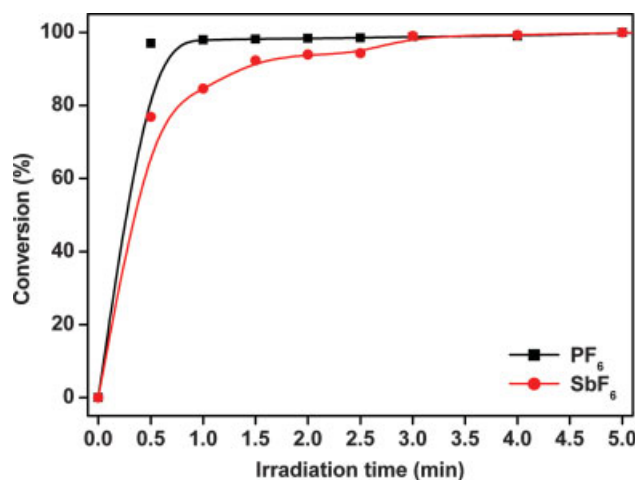


Figure 4 Time-conversion relationship in the photo polymerization of tri(ethylene glycol) divinyl ether monomer with 3 wt % sulfonium salts at 25°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

was initiated above 115°C and it proceeded rapidly above the initiating temperature whereas in case of tri(ethylene glycol) divinyl ether, polymerization was initiated above 83°C. Initiating temperatures of thermal polymerization for both the monomer system with these new sulfonium salts are lower than our previous reported sulfonium salts.⁴⁰ As shown in Figures 5 and 6, initiators showed better activity for thermal polymerization of divinylether than epoxide monomer. It is likely that the initiating species in the photoreaction is carbenium cation, which is same as that in the thermal reaction because almost the same effects have been observed in photo and thermal reactions.

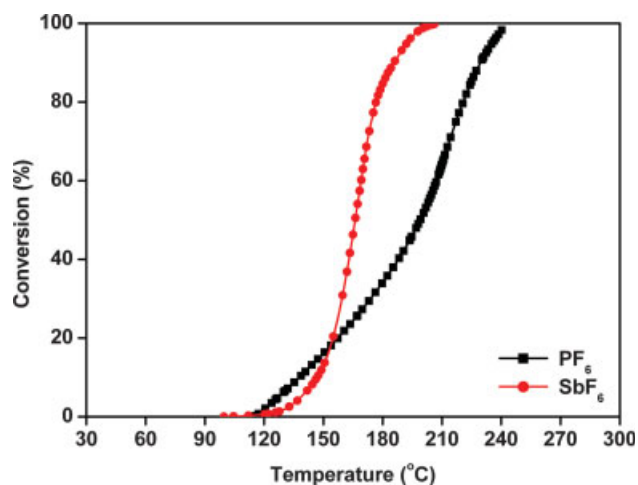


Figure 5 Temperature-conversion relationship in the thermal polymerization of UVR-6110 monomer with 3 wt % sulfonium salts. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

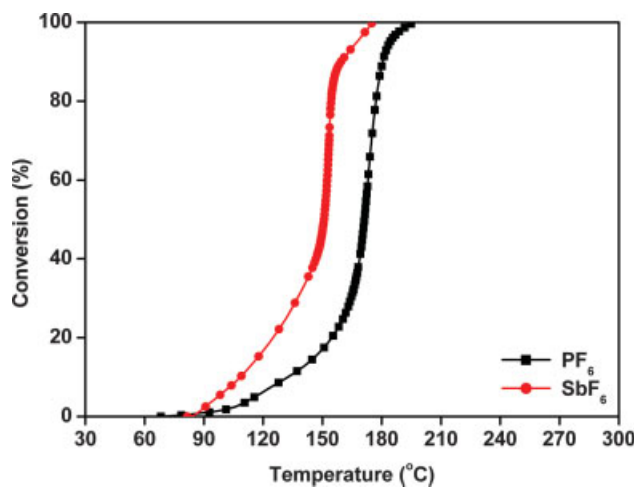


Figure 6 Temperature-conversion relationship in the thermal polymerization of tri(ethylene glycol) divinyl ether monomer with 3 wt % sulfonium salts. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSION

Novel sulfonium salts were synthesized and characterized by UV, IR, ¹H NMR spectroscopic techniques. The applicability of novel sulfonium salts as photoinitiators was investigated by carried out cationic polymerizations of epoxides and divinyl ether monomer with synthesized salts. It has been found that photopolymerization of vinyl ether monomer was faster as compared with the epoxide monomer by the synthesized initiators.

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