PHOTOPOLYMERIZATION OF EPOXIDES WITH BENZYL SULFONIUM SALTS AS LATENT PHOTOINITIATORS

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Photoinitiator activity of benzyl *p*-hydroxyphenyl methyl sulfonium salts (**3**) was evaluated in the photopolymerization of phenyl glycidyl ether (PGE) under UV irradiation. These sulfonium salts served as good photoinitiators. The order of the activity of **3** as photoinitiators was **3b**(X=PF₆) > **3a**(X=SbF₆) >> **3c**(X=BF₄). Initiation species was estimated to be benzyl cation by the analyses of polymers obtained in the photopolymerization of PGE and *n*-butyl glycidyl ether (BGE) with *p*-chlorobenzyl *p*-hydroxyphenyl methyl sulfonium salt(**4**).

1.Introduction

Crivello and Lam previously reported that dialkyl *p*-hydroxyphenyl sulfonium salts (**1**) behave as latent photoinitiators for cationically polymerizable monomers such as cyclic ethers and vinyl ethers. Initiation species was proposed as proton (H⁺) generated from HO group on *para* position of benzene ring of **1**.¹

Meanwhile, we have recently found that benzyl *p*-hydroxyphenyl methyl sulfonium salt (**3a**) serves as a thermally latent initiator and the initiation species is benzyl cation.^{2,3,4} **3a** could initiate the cationic polymerization at lower temperature than that of **2**.

Since **3a** has its UV absorption band beyond 300nm like **1a** ($R^1=CH_3$), **3a** is expected to serve as a photoinitiator. In this paper, ability of **3** as latent photoinitiator, effect of counter anion, and effect of initiator concentration are examined. Further, structure of the initiation species is discussed from results of the photopolymerizations of PGE and BGE with **4** and **5**.

2. Method

Materials PGE and BGE were purified by vacuum distillation and stored over molecular sieves in the dark. Benzyl sulfonium salts(**2**, **3**, and **4**), dimethyl *p*-hydroxyphenyl sulfonium salt (**1a**), and benzyl *p*-methoxyphenyl methyl sulfonium hexafluoroantimonate(**5**) were prepared according to the previously reported method.^{2,3,4}

UV Spectra of Sulfonium Salts UV spectra of these sulfonium salts were measured using a Shimadzu UV-200S spectrophotometer in ethanol (concentration : 10ppm).

Photopolymerization of PGE : A General Method A solution of sulfonium salt (1mol%) in PGE (1.0g) was placed in a Pyrex tube. The tube was cooled, evacuated, and sealed off. It was irradiated in a "merry-go-round" photoirradiation apparatus using a 400W high pressure mercury lamp at 20°C . After the irradiation, the reaction mixture was cooled at -78°C . A small amount of the reaction mixture was immediately dissolved in CDCl₃ and subjected to ¹H NMR analysis. Conversion of PGE was estimated by integral ratio of two protons at 2.60~3.00ppm (—CH₂) of monomer to five protons at 2.60~4.41 ppm

($-\text{CH}_2-\text{CH}-\text{CH}_2-$, $-\text{O}-\text{CH}_2-\text{CH}-$) of monomer and polymer. CH_2Cl_2 (1 ml) was added to the mixture and the solution was poured into a large amount of methanol to precipitate polymer. After the methanol layer was removed by decantation, the residual viscous material was collected as methanol-insoluble polymer and dried under vacuum. The methanol layer was evaporated to give methanol-soluble polymer.

Photopolymerization of BGE A mixture of BGE (1.0g) and sulfonium salt (19.5mol% for BGE) was photopolymerized by the same method mentioned above. Conversion of BGE was determined by integral ratio of two protons at 2.50~2.95ppm ( ) of monomer to seven protons at 0.70~1.95ppm ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$) of monomer and polymer

in ^1H NMR spectrum of the reaction mixture. Dichloromethylene solution of the reaction mixture was poured into a large amount of hexane. From hexane layer, monomer and solvent were removed by evaporation under vacuum at 40°C to afford a transparent uncolored polymer.

Measurements FT-IR spectra were obtained with a PERKIN ELMER FT-IR-1640.

^1H NMR spectra were recorded on a Hitachi R-246 (60MHz) spectrometer and a JEOL FX-100 (90MHz) spectrometer, using tetramethylsilane(TMS) as internal standard. Weight and number - average molecular weights ($\overline{M}_w$ and $\overline{M}_n$) and molecular weight distribution ($\text{MWD}; \overline{M}_w/\overline{M}_n$) were determined by gel permeation chromatography (GPC) with a Toyo Soda HLC-8020 system with a data processor, equipped with three polystyrene gel columns (TSK gel, G2500H, G3000H, and G5000H), using tetrahydrofuran as an eluent, flow rate 1.0ml/min, and refractive index (RI) and ultraviolet (UV) detectors. Photopolymerizations were carried out with a rotary photochemical reactor(RH400-10W) manufactured by Riko Kagaku Sangyo.

3.Results and Discussion

UV Spectra of Sulfonium Salts

UV spectra of **1a**, **3a**, and **5** bearing aryl group on sulfur atom showed absorption bands around $300 \sim 350\text{nm}$, whereas **2** had no absorption band beyond 285nm . UV spectra of the benzyl sulfonium salts (**3b**, **3c**, and **4**) were nearly similar to that of **3a**.

Fig.1 Ultraviolet Spectra of Sulfonium Salts in Ethanol(10ppm) at 20°C .
(---); **1a** (---); **2** (—); **3a** (---); **5**

Since in this study the polymerization was carried out in Pyrex tubes under UV irradiation using a 400W high pressure mercury lamp, the initiators would be excited mainly by irradiation around 300~350nm.

Photoinitiated Cationic Polymerization with Benzyl *p*-Hydroxyphenyl Methyl Sulfonium Salts.

Photoinitiated cationic polymerization of PGE with **1a**, **2**, and **3** was carried out at 20°C.

Table I Effect of Counter Anion in Photopolymerization of PGE

Initiator	Time (min)	Conversion ^a (%)	Yield ^b (%)	$\overline{M}_n^c$	$\overline{M}_w/\overline{M}_n^c$
3a	60	42	28	4800	1.47
	90	48	38	4700	1.49
3b	60	47	38	4900	1.47
	90	53	47	4600	1.58
3c	60	9	0	—	—
	90	11	0	—	—

a Determined by ¹H NMR before precipitation.

b Yields of the insoluble polymer in methanol.

c Estimated by GPC (THF) based on polystyrene standard.

As shown in Fig.2, no polymerization occurred in the dark but prompt consumption of PGE took place as soon as the irradiation started. That is, **3a** and **3b** behaved as latent photoinitiators and were ca. 4 times more effective than **1a**. Further, the order of the activity of **3a**~**3c** was **3b** > **3a** >> **3c**. Namely, **3b** bearing PF₆⁻ as the counter anion showed the highest activity of all. Table I lists conversion of PGE and yield, $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ of the methanol-insoluble polymer in the photopolymerization with 1mol% of **3**. The conversion of PGE reached 53% with **3b** by 90min irradiation, in which yield of the methanol-insoluble polymer was 47%, whereas the conversion of PGE and the methanol-insoluble polymer was slightly low in the case of **3a**. $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ of the methanol-insoluble polymer with **3a** and **3b** were nearly similar. However, no methanol-insoluble polymer was formed in the photopolymerization of PGE with **3c** probably because of fast transfer reaction or termination.

Subsequently, the activity of **3a** as latent photoinitiators was examined in detail. Fig.3 shows time-conversion curves in the photopolymerization of PGE with various amounts of **3a** at 20°C under UV irradiation. The photopolymerizations with 1 and 0.5mol% of **3a** afforded the similar curves. However with 0.2mol%, slightly lowered conversions were observed.

Table II lists the detailed results of these photopolymerizations. When the photopolymerization of PGE was carried out with 0.2mol% of **3a**, $\overline{M}_n$ was higher than those with 0.5 and 1mol% of **3a** and $\overline{M}_w/\overline{M}_n$ was rather small value although the conversion of PGE and the yield of the methanol-insoluble polymer were low. From these results, it is obvious that the transfer reaction is sufficiently slower than the propagation reaction.

Table II Photopolymerization of PGE with **3a** at 20°C :

Effect of Initiator Concentration

Conc. (mol%)	Time (min)	Conversion ^a (%)	Yield ^b (%)	$\overline{M}_n^c$	$\overline{M}_w/\overline{M}_n^c$
0.2	60	31	16	5400	1.28
	90	40	24	5400	1.33
0.5	60	39	28	5300	1.40
	90	48	38	5100	1.43
1.0	60	42	28	4800	1.47
	90	48	38	4700	1.49

a Determined by ¹H NMR before precipitation.

b Yields of the insoluble polymer in methanol.

c Estimated by GPC (THF) based on polystyrene standard.

Initiation Species

Crivello et al. reported that the initiation species is proton (H⁺) generated from HO group of **1a** in cationic photopolymerizations of cyclic ether and vinyl ether with **1a**.¹ We have shown that benzyl cation is a true initiation species in the thermal polymerization of PGE with **3**.^{2,3,4}

In the photopolymerization of PGE with **3a**, a few possible initiation species such as benzyl cation, proton, and methyl cation are conceivable as shown in the following scheme.

In order to clarify the initiation species of this photopolymerization, the activity of **5** as a photoinitiator was compared with **1a** and **3a**.

Fig.4 Time-Conversion Curves of Photopolymerization of PGE with 1mol% of **1a**, **3a**, and **5** at 20°C.
(○); **1a**, (●); **3a**, (□); **5**

As shown in Fig.4, time-conversion curve of the photopolymerization with **5** was similar to that with **3a**, whereas **1a** indicated the lowest activity, in spite of similar UV spectra of the three sulfonium salts. These results demonstrate that benzyl group of **3a** is indispensable but HO group on aryl group is not always necessary. Namely, it is suggested that the initiation species is a cationic species which is derived from benzyl group, i.e., benzyl cation or proton (path a or path c). Further, the resulting methanol-insoluble polymer ($\overline{M}_n=4000$, $\overline{M}_w/\overline{M}_n=1.47$) obtained in the photopolymerization of PGE with 8.5mol% of **4** for 4h at 20°C had 3.94% of chlorine atom by the elemental analysis. This result suggests that the initiation species is benzyl cation. However, under this condition the aromatic substitution reaction with benzyl cation on benzene ring of poly(PGE) can also take place to generate new cationic species (H^+) as follows. Therefore, the obtained polymer might have benzyl groups not only at the initiation terminal but also in the side chain.

Then, we selected BGE as an epoxide which cannot undergo Friedel-Crafts reaction as mentioned above. The photopolymerization of BGE with 19.5mol% of **1a** and **4** was carried out for 4h at 25 °C. As a result, the conversion of BGE reached 82% in the case

of **4** but was only 15% in the case of **1a**. The obtained polymer had 4.51% of chlorine and the corresponding aromatic signal was observed at 6.7~7.6ppm in its ^1H NMR spectrum. Furthermore, UV absorption was confirmed in the GPC measurement. These results clearly suggest the incorporation of benzyl group into poly (PGE), indicating initiation by benzyl cation.

4. Conclusion

It was clarified that benzyl *p*-hydroxyphenyl methyl sulfonium salts (**3a** and **3b**) serve as excellent latent photoinitiators in the photopolymerization of PGE. The initiation species was determined to be benzyl cation which could be generated by the heterolysis of C-S bond between benzyl group and sulfur atom.

Consequently, benzyl sulfonium salt **3** bearing phenol structure on sulfur atom can serve as not only thermally latent initiator but also photo latent initiator.

References

1. J.V. Crivello and J.H.W. Lam, *J. Polym. Sci. Polym. Chem. Ed.*, **18**(1980)1021.
2. F.Hamazu, S.Akashi, T.Koizumi, T.Takata, and T.Endo, *J. Polym. Sci. Polym. Chem. Ed.*, **29**(1991)1675.
3. F.Hamazu, S.Akashi, T.Koizumi, T.Takata, and T.Endo, *J. Polym. Sci. Polym. Chem. Ed.*, **29**(1991)1845.
4. F.Hamazu, S.Akashi, T.Koizumi, T.Takata, and T.Endo, *J. Polym. Sci. Polym. Chem. Ed.*, Submitted for publication.