

Thermoinitiated Cationic Polymerization of Epoxy Resins by Sulfonium Salts

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Synopsis

Catalytic activities of benzyl sulfonium salts with nonnucleophilic anions (BF_4^- , PF_6^- , AsF_6^- , SbF_6^-) for epoxy polymerization were examined. The order of reactivities correlated well with nonnucleophilicity of anions. Epoxy resins catalyzed by these salts are characterized by longer shelf-life and shorter gel time at high temperature. Some physical properties of cured product were compared with those cured by a commonly used BF_3 amine complex.

INTRODUCTION

Various cationic polymerization catalysts based on Lewis acids, their adducts, or their onium salts have been studied.¹ Among them, it should be noted that aromatic sulfonium salts and iodonium salts, extensively investigated by Crivello and his co-workers,² represented a new methodology of photoinduced cationic polymerization for epoxy resins. The aromatic onium salts have apparent thermal stability allowing for long term storage in epoxy formulations in the absence of light, and have remarkable light-sensitivity allowing for rapid cure upon irradiation for UV light. Crivello's interest is also directed towards thermal polymerization utilizing thermally stable aromatic onium salts in the presence of coinitiators.³ Coinitiators give rise to decomposition of aromatic onium salts and the polymerization is initiated.

Aliphatic sulfonium salts, on the other hand, have received little attention as cationic polymerization initiators for epoxy resins. Recently it has been shown by Pappas et al. and us that aliphatic sulfonium salts can be excellent latent initiators for epoxy resins without the aid of coinitiators.⁴ Reports have already been made that benzyl sulfonium salts work as a latent thermal catalysts for the polymerization of spiro ortho carbonates or bicyclo ortho esters.^{5,6}

In this paper, catalytic activity of benzyl sulfonium salts, having different counteranions for the cationic polymerization of epoxy resins, was investigated.

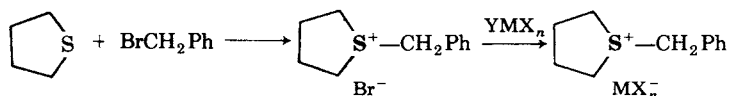
EXPERIMENTAL

Benzyl sulfonium salts were all derived from the corresponding bromides,⁷ which could be easily obtained from benzyl bromide and tetrahydrothiophene in acetone as a solvent. Aqueous solution of the bromide was treated with

TABLE I
 Benzyl Sulfonium Salts 1

Anion	mp (°C)	Yield (%)	Alkaline salt
BF ₄ ⁻	75-77	40	NaBF ₄
PF ₆ ⁻	167-69	89	KPF ₆
AsF ₆ ⁻	158-60	95	KAsF ₆
SbF ₆ ⁻	119-21	82	NaSbF ₆

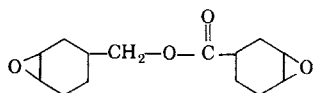
alkaline salt (Y = Na or K) having the desired anion structure



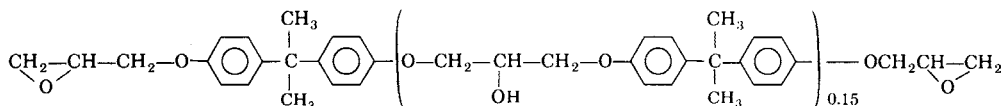
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(MX_n = BF₄⁻, PF₆⁻, AsF₆⁻, SbF₆⁻). Their melting points and yields are listed on Table I. Care has to be taken in the case of hexafluoroantimonate salts in that the addition of sodium hexafluoroantimonate be made in powder form; otherwise, some of the fluorine atoms tend to be partially hydrolyzed to give less reactive catalyst.

Epoxy resins used in this studies were obtained from the following manufactures and were used without purification: 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexylcarboxylate (epoxy A) (Union Carbide Co., ERL-4221) and bisphenol A diglycidyl ether (epoxy B) (Asahi Denka K.K., Ep-4100).



Epoxy A



Epoxy B

Bisphenol A bis(vinyloxyethylene) was synthesized using the procedure by Gallucci and Going.⁸ Gel time was recorded by measuring on a heated stainless steel plate (Nissin Kagaku Gel Tester).

DTA (differential thermal analysis) was recorded by Rigaku Denki TG-DTA. The weight of the sample was adjusted to lie within 15.0 ± 0.2 mg, and the sample was warmed in a standard aluminium pan at heating rate of 5°C/min with aluminium oxide as a reference.

RESULTS AND DISCUSSION

Curing Reactions

As is well known, the most widely used cationic polymerization catalysts in the field of epoxy technology are trifluoro-borane/amine complexes.⁹ Epoxy formulations catalyzed by these compounds are relatively stable at room temperature, and cure rapidly when exposed to high temperature. However, these amine complexes are not only generally hygroscopic, but also physical properties of cured epoxy resins such as electric properties tend to deteriorate at high temperature and high humidity. These defects are probably attributable to hydrophilic character of the amine. On the other hand, sulfonium compounds investigated in this study are not hygroscopic (although 1-Br is hygroscopic) and dissolve more easily into epoxy resins.

First of all, gel time was recorded for two typical epoxy resins catalyzed by 1(BF₄, PF₆, AsF₆, SbF₆) and the results are listed on Table II. The polymerization reaction proceeds by a cationic process. Inclusion of basic compounds such as triethyl amine severely retards the extent of polymerization, even at 0.1% level. Epoxy A, a cycloaliphatic epoxy resin, is more reactive than epoxy B. This is generally the case for cationic polymerization and epoxy group having more electronic density on oxygen atom is more labile to polymerization. The simplest sulfonium salts, trimethyl sulfonium salts, are very stable, and are not sufficiently reactive to polymerize the epoxy resins investigated below 200°C. Benzyl sulfonium salts having nucleophilic anions (such as Br, Cl) do not polymerize the epoxy resins. The order of reactivity, as can be seen from Table II, is consistent with other results of cationic polymerization (BF₄ < PF₆ < AsF₆ < SbF₆^(b)).

The sulfonium salts having anion structures BF₄ and PF₆ are less reactive and cannot cure conventional Bis-A type epoxy (epoxy B). This could be one of the reasons why sulfonium salts have not received much attention as polymerization catalysts for epoxy resins. On the other hand, hexafluoroantimonate can rapidly cure both epoxies A and B.

All of the catalyzed formulations showed longer storage stability in epoxy resins than the corresponding formulations catalyzed by BF₃/monoethylamine complex (Table II). The formulation with epoxy B and 1-SbF₆ did not

TABLE II
Gelation Time (at 150°C) and Shelf Life^a (at 25°C) of Epoxies A and B

Catalyst (wt %)	Epoxy A		Epoxy B	
	Gel time (s)	Shelf-life (weeks)	Gel Time (sec)	Shelf-life (weeks)
1-BF ₄ (3)	510	27	> 1500	> 50
1-PF ₆ (3)	240	28	> 1500	> 50
1-AsF ₆ (3)	100	26	450	> 50
1-SbF ₆ (1)	25	40	150	> 50
Ethyl amine/BF ₃ (3)	80	3	240	40
Trimethyl sulfonium-AsF ₆ (3)	> 1500	> 50	> 150	> 50

^a Time when the viscosity increase of epoxy formulation reached 5 times greater.

change at all even at 40°C over a period of 6 months. Apparent activation energies of polymerization of epoxy A and epoxy B by 1-SbF₆ estimated by DTA method or from gelation time are 25 and 30 kcal/mol, respectively.

As a second measure of the cure behavior, DTA curves were recorded and are shown in Figure 1. Poorer catalytic activity for BF₄ and PF₆ salts is clearly shown. Even AsF₆ salt is not able to polymerize epoxy B effectively. On the other hand, SbF₆ salts afforded very sharp curves for epoxy A and rather normal curves for epoxy B even at initiator level as low as 1%. It should be noted that the BF₄ salt as well as the other three act as very effective

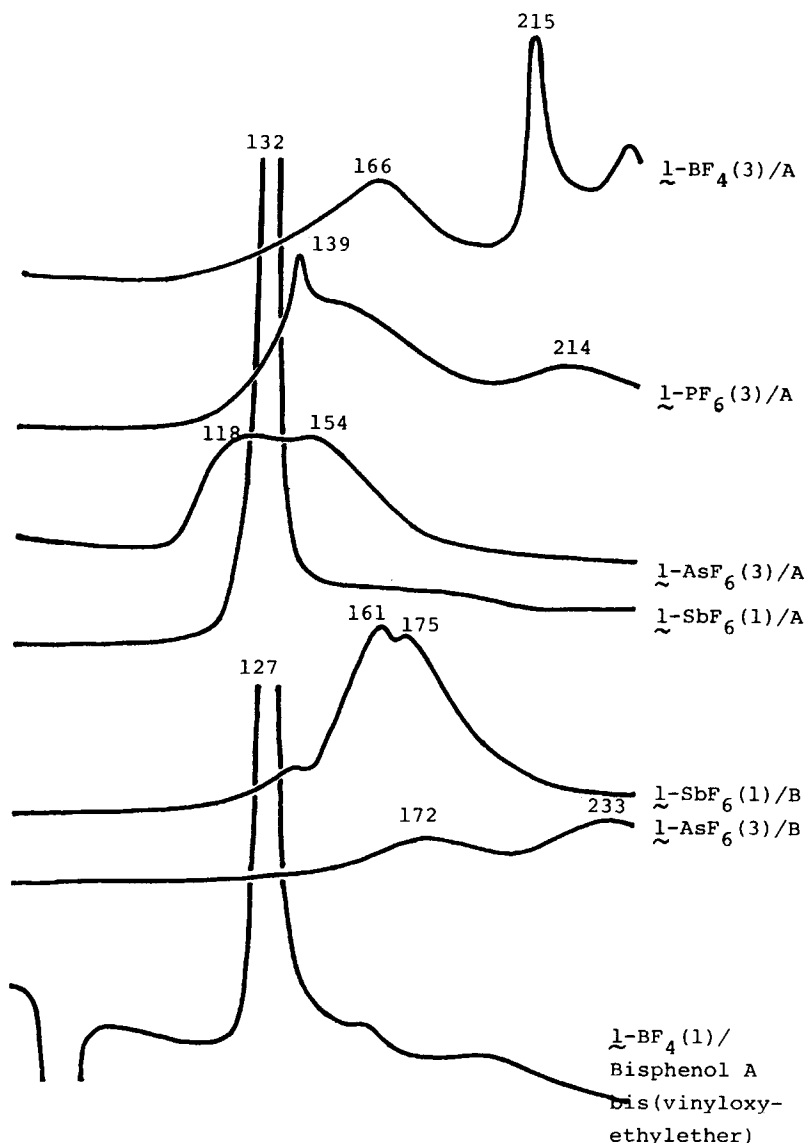


Fig. 1. DTA curves of epoxies A, B, and a vinyl monomer containing sulfonium salts 1. Sample weight: 15 mg, scan speed: 5 °C/min, (): wt% of 1 salts in monomers, numbers indicate temperatures (°C).

catalysts for the polymerization of vinyl ethers, which is generally recognized as a more reactive monomer for cationic polymerization.

PROPERTIES OF CURED EPOXY RESINS

Some properties of cured products were measured and are shown in Tables III and IV. Heat distortion temperatures correlate well with the gelation times and DTA curves discussed above. For 1-AsF₆ and 1-SbF₆ higher heat distortion temperatures are achieved with further post-curing above 180°C. As for chemical resistance, which is a general measure for extent of cure, weight changes after treatment with boiling water and methylethylketone (MEK) were investigated. Results for MEK are again consistent with other data. But the behavior with boiling water was rather anomalous, and further study has to be made.

REACTION MECHANISM

Recently diphenyliodonium salts were investigated as thermal initiators for epoxy resins.¹⁰ It was found that the electron withdrawing nitro group on the benzene ring facilitated polymerization of epoxy resins. In the case of benzylsulfonium salts, our preliminary study showed that the electron withdrawing nitro group substituted at the para position on the benzene ring tends to

TABLE III
Heat Distortion Temperature of Cured Epoxy A^a

Catalyst	Amounts (wt %)	Cure conditions	HDT (°C)
1-BF ₄	3	140°C (2 h) + 160°C (2 h)	49
1-PF ₆	3	120°C (2 h) + 160°C (2 h)	85
1-AsF ₆	3	105°C (2 h) + 160°C (2 h)	171
1-SbF ₆	1	100°C (2 h) + 160°C (2 h)	172

^aASTM D-648 (264 psi; 6 mm thickness).

TABLE IV
Chemical Resistance of Epoxy A Cured by Benzyltetramethylene Sulfonium Salts^a

Anions	Cat. amt. (wt %)	Water ^b	MEK ^c
BF ₄	3	2.29%	Dec. ^d
PF ₆	3	1.97%	Dec. ^d
AsF ₆	3	2.22%	0.15%
SbF ₆	1	1.31%	-0.13%

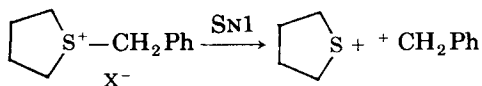
^aSize of specimens: 50 × 50 × 4 mm.

^bWeight increase (%) of the samples immersed in boiling water for 5 h.

^cWeight increase (%) in methyl ethyl ketone after 7 days at room temperature.

^dDecomposed to several pieces prior to measurement.

retard the polymerization; and the electron donating methoxy group gave higher polymerization rate. This results support an SN1 initiation mechanism in our case.



Thus it is suggested that one factor, which is important in the design of sulfonium type thermal initiator, will be electronic stability of the initiating carbenium ion, in addition to the other possible mechanistic factors controlling the reactivities of sulfonium salts such as steric effects and the possibility of SN2 and E2 mechanism. Studies on these hypotheses are now in progress.

References

1. (a) *Reactivity, Mechanism and Structure in Polymer Chemistry*, A. D. Jenkins and A. Ledwith, eds., Wiley, New York, 1974, Chap. 9; (b) J. A. Cella et al., *Am. Chem. Soc. Polym. Reprints* **22** (2), 113 (1981).
2. (a) J. V. Crivello, *Adv. Polym. Sci.*, **62**, 1 (1984); (b) J. V. Crivello et al., *J. Rad. Curing*, (Jul.), 2 (1977).
3. J. V. Crivello, U. S. Pat., 4,216,288 (1980).
4. (a) Asahi Denka Kogyo K. K., Jpn. Pat. Kokai 56-152,833 (1981); (b) S. P. Pappas and L. H. Hill, *J. Coatings Technol.*, **53**, 43 (1981); (c) S. P. Pappas and H. B. Feng, in *Cationic Polymerization and Related Process*, E. J. Goethals, Ed., Academic, New York, 1984, pp. 325-333.
5. T. Endo and H. Arita, *Makromol. Chem. Rapid Commun.*, **6**, 137 (1985).
6. T. Endo and H. Uno, *J. Polym. Sci., Polym. Lett. Ed.*, **23**, 359 (1985).
7. For general preparation method, see *The Chemistry of the Sulfonium Group*, edited by C. J. M. Stirling, Ed., Wiley, New York, 1981, Chap. II.
8. R. R. Gallucci and R. C. Going, *J. Org. Chem.*, **48**, 342 (1983).
9. H. Lee and K. Nevill, *Handbook of Epoxy Resins*, McGraw-Hill, New York, 1967.
10. J. Gu et al., *J. Appl. Polym. Sci.*, **30**, 2997 (1985).

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