

# Novel Latent Initiator for Cationic Polymerization of Epoxides

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**ABSTRACT:** A novel latent initiator for cationic polymerization of epoxides, a composite catalyst containing aluminum complexes and phenol derivatives protected with *tert*-butoxycarbonyl groups (*t*BOC), is reported. At a certain temperature, protected phenols generate the parent phenols which are coinicators with aluminum complexes. The deprotection temperature of the *t*BOC group depends on the structure of the phenol moieties. Bis(*p*-*t*-butoxycarbonyloxyphenyl)sulfone (Ph1) generates (*p*-dihydroxyphenyl)sulfone (PhH1) at around 150°C, the temperature at which the curing of epoxides is conventionally carried out. The thermally generated PhH1 and aluminum complexes initiate the curing of epoxides. Epoxy resin compositions containing these composite catalysts have a long shelf life at room temperature and are cured at around 150°C, showing that the composite catalyst has excellent latent properties. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 181–187, 2001

**Key words:** latent catalyst; epoxy resin; initiator; shelf life; electrical property

## INTRODUCTION

Epoxy resins have been utilized as insulation materials, coating materials, adhesives, and lamination materials.<sup>1</sup> Epoxy resins are supplied as mixtures containing polymerization initiators. Since initiators start epoxide polymerization even at room temperature, the viscosity of the mixtures increases during storage at room temperature. This has resulted in much industrial waste.

An increase in curing rates has been also required in terms of energy savings, which contradicts the long shelf life of the epoxy resin mixtures. Considering only fast curing, cationic polymerization is one of the best candidates, but the shelf life of epoxy resin mixtures containing cat-

ionic initiators, such as  $\text{BF}_3 \cdot \text{amine}$  adducts, are short. It has been reported that triarylsulfonium salts initiate photoinduced polymerization by employing light instead of heat:<sup>2</sup> the mixture has a long shelf life in the absence of light, but the mixture is not cured thermally at 150°C.<sup>2</sup> Some sulfonium salts and other onium salts thermally initiating epoxy compounds have been reported, but the shelf life is not satisfactory.<sup>3</sup>

These sulfonium salts have excellent curing properties. However, these initiators have an issue to be overcome when these are put into practical use in electrical fields. The electrical insulation of epoxy compounds, cured with these initiators, decreases at high temperatures over 100°C because of the residual acid components becoming ionic impurities in the cured resin matrices.<sup>4</sup> The authors have reported that novel cationic initiators, composite catalysts containing organic silanols and aluminum complexes (AS catalysts),

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resolved these problems and gave cured epoxy resins having excellent electrical-insulating properties.<sup>5</sup> Although the shelf life of the AS catalyst is improved, by employing alkoxy silanes instead of unprotected silanols, the latent properties are not fully satisfactory.<sup>6</sup> Our objective was to provide cationic initiators which have high activities around 150°C and provide a long shelf life at room temperature, based on AS catalysts.

Polyhydroxystyrenes protected with *t*-butyl carbonyl and pyranyl ether moieties have been reported to decompose to form polyhydroxystyrenes.<sup>7</sup> It has also been reported that some kinds of phenols, such as catechol, initiate epoxide polymerizations.<sup>8,9</sup> These precedents encouraged us to choose this type of protecting group for our application. However, the reported deprotection temperature for *t*-butyl carbonyloxy moieties was around 190°C, which was too high to be employed for the epoxide curing.<sup>8,9</sup> Protected silanols with *t*-butyl carbonyl or pyranyl ether moieties were one of the candidates, but these syntheses were not easy.

We focused our research on finding phenol derivatives which generate the parent phenol moieties at around 150°C. Of course, the generated phenols must have sufficient catalytic activities for epoxide polymerization. In this article, the relation between the catalyst activities and structures of parent phenols, and the relation between the deprotection temperatures and structures of *t*-butyl carbonyloxy derivatives, were examined in detail, and a catalyst structure exhibiting satisfactory latent properties is present.

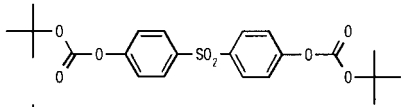
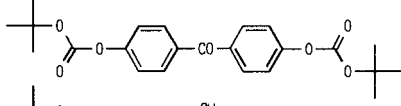
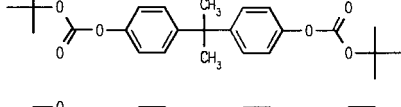
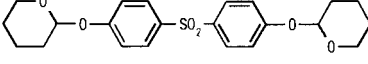
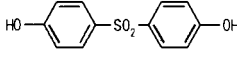
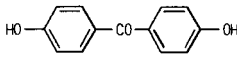
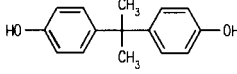
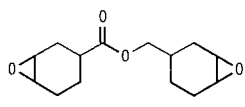
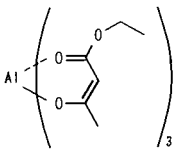
## EXPERIMENTAL

### General Procedures

Table I summarizes the abbreviations and compound structures employed in this research. PhH1, PhH2, and PhH3 were commercially available and used after recrystallization. Ep1 (Celloxide 2021) was purchased from the Daiseru Chemical Co. (Tokyo, Japan) and used without further purification. All solvents were dried on CaH<sub>2</sub> and distilled before use. The initiators were dissolved in Ep1 below 50°C. The compositions are summarized in Table II.

<sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded on a JEOL Model GSX-270 spectrometer, and all NMR data are reported in ppm (δ) downfield from tet-

**Table I** Chemical Structures and Their Abbreviations

	Ph1
	Ph2
	Ph3
	Ph4
	PhH1
	PhH2
	PhH3
	Ep1
	A1

ramethylsilane. IR spectra were obtained as KBr disks using a Hitachi FT/IR-7000 spectrometer. Thermal analyses were performed on a SEIKO EXSTAR6000 thermal analyzer at a heating rate of 5°C/min for thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The viscosity of epoxy resins was measured with a Tokyo Keiki ELD viscometer. The shelf life of the epoxy compounds was evaluated by monitoring the increase in the viscosity of Ep1 stored at 30°C. The viscosity was measured at 25°C. Gel time was determined by measuring the time when 0.5 g of the epoxy compounds on a hot plate gelled at various temperatures.

The relative acidity of various phenols was assumed from subtraction of the <sup>1</sup>H-NMR chemical shift of OH groups for phenols in a polar solvent

**Table II Epoxy Resin Compositions**

No.	Compound	Coinitiator		All	
		Wt %	Mol %	Wt %	Mol %
C1	PhH1	3	3	0.5	0.3
C2	PhH2	2.57	3	0.5	0.3
C3	PhH3	2.74	3	0.5	0.3
C4	Ph1	5.4	3	0.5	0.3
C5	SI-60	5	—	—	—

Epoxy compound: Ep1; SI-60: sulfonium compound commercially available from Sanshin Chemical Co., Yamaguchi, Japan.

( $d_6$ -dimethyl sulfoxide (DMSO) from that in a less polar solvent ( $d_6$ -acetone). Blocked phenols were prepared as follows:

#### Bis(*p*-*t*-butoxycarbonyloxyphenyl)sulfone (Ph1)<sup>10</sup>

To a solution of bis(*p*-hydroxyphenyl)sulfone (62.5 g, 0.250 mol) in dry THF (120 mL) was added anhydrous potassium carbonate (92.5 g, 0.689 mol) under nitrogen. After being cooled to 0°C, a solution of di-*tert*-butyl dicarbonate (110.3 g, 0.505 mol) containing a catalytic amount of 18-crown-6 (2.7 g, 0.01 mol) in THF (25 mL) was added and then the mixture was stirred for 4 days at ambient temperature. The mixture was poured into water and extracted with ethyl acetate. The organic layer was washed with brine and evaporated *in vacuo* to dryness. The crude product was purified by crystallization from acetone to afford a solid material (83.25 g, 74.0%).

IR (KBr)  $\nu_{\max}$  3080, 2975, 2925, 1760, 1585, 1485, 1275, 1260, 1215, 1145, 1105, 895, 825, 765  $\text{cm}^{-1}$ ; <sup>1</sup>H-NMR (270 MHz, DMF- $d_7$ )  $\delta$  1.48 (8H, s), 7.52 (4H, *d*,  $J$  = 8.97 Hz), 8.10 (4H, *d*,  $J$  = 8.97 Hz); <sup>13</sup>C-NMR (67.5 MHz, DMF- $d_7$ )  $\delta$  27.52, 84.80, 123.61, 130.24, 139.61, 151.50, 155.58.

#### 4,4'-Bis(*t*-butoxycarbonyloxy)benzophenone (Ph2)

To a solution of 4,4'-dihydroxybenzophenone (53.5 g, 0.25 mol) in dry THF (120 mL) was added anhydrous potassium carbonate (92.5 g, 0.689 mol) under nitrogen. After being cooled to 0°C, a solution of di-*tert*-butyl dicarbonate (110.3 g, 0.505 mol) containing a catalytic amount of 18-crown-6 in dry THF (25 mL) was added and then the mixture was stirred for 3 h. The mixture was poured into water and extracted with ethyl acetate. The organic layer was washed with brine

and evaporated *in vacuo* to dryness. The crude product was purified by crystallization from acetone to afford solid material (80.7 g, 78%).

<sup>1</sup>H-NMR (270 MHz, CDCl<sub>3</sub>)  $\delta$  1.58 (18H, s), 7.30 (4H, *d*,  $J$  = 8.98 Hz), 7.84 (4H, *d*,  $J$  = 8.98 Hz); <sup>13</sup>C-NMR (67.5 MHz, CDCl<sub>3</sub>)  $\delta$  27.65, 84.21, 121.16, 131.53, 134.77, 151.15, 154.21, 194.29.

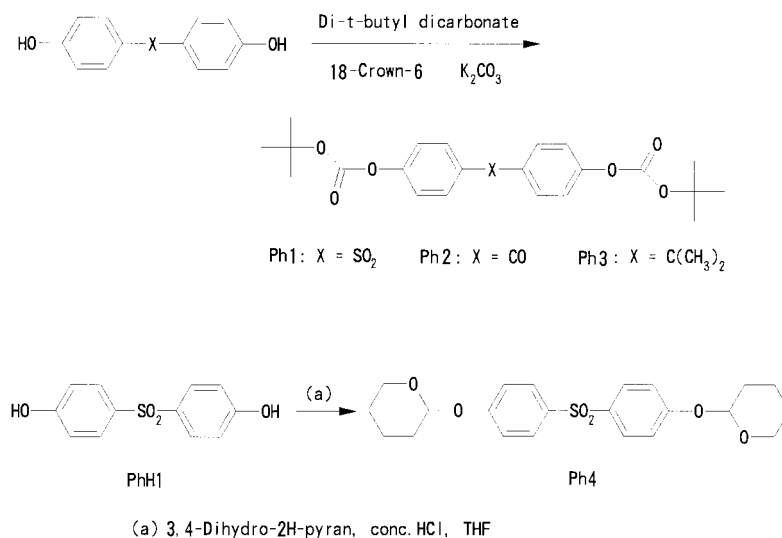
#### 2,2-Bis(*p*-*t*-butoxycarbonyloxyphenyl)propane (Ph3)

To a solution of 2,2'-bis-(4-hydroxyphenyl)propane (22.84 g, 0.100 mol) in dry THF (80 mL) was added anhydrous potassium carbonate (37.72 g, 0.273 mol) under nitrogen. After being cooled to 0°C, a solution of di-*tert*-butyl dicarbonate (43.68 g, 0.200 mol) containing a catalytic amount of 18-crown-6 (2.64 g, 0.10 mol) in dry THF (25 mL) was added and then the mixture was stirred for 1 day at ambient temperature. The mixture was poured into water and extracted with ethyl acetate. The organic layer was washed with brine and evaporated *in vacuo* to dryness. The crude product was purified by crystallization from acetone to afford a solid material (28.13 g, 65.6%).

IR (KBr)  $\nu_{\max}$  3030, 2960, 2925, 2870, 1750, 1740, 1500, 1365, 1270, 1255, 1215, 1140, 1010, 885, 835, 815, 735  $\text{cm}^{-1}$ ; <sup>1</sup>H-NMR (270 MHz, acetone- $d_6$ )  $\delta$  1.54 (18H, s), 1.64 (s, 6H), 7.04 (4H, *d*,  $J$  = 8.54 Hz), 7.21 (4H, *d*,  $J$  = 8.54 Hz); <sup>13</sup>C-NMR (67.5 MHz, acetone- $d_6$ )  $\delta$  27.58, 30.83, 42.33, 83.23, 120.59, 127.65, 130.54, 147.69, 148.87, 151.98.

#### 4,4'-Sulfonyldiphenol bis(2-tetrahydropyranyl)ether (Ph4)<sup>11</sup>

To a solution of 4,4'-sulfonyldiphenol (904.3 mg, 3.613 mmol) in dry THF (11 mL) was added 3,4-



Scheme 1

dihydro-2H-pyran (3.107 g, 36.94 mmol) and 4 drops of concentrated hydrochloric acid. The mixture was stirred for 2 h at ambient temperature. The mixture was neutralized by adding a diluted sodium hydroxide solution and extracted with ethyl acetate. The organic layer was washed with brine and evaporated *in vacuo* to dryness. The crude product was purified by chromatography on silica gel (toluene/EtOAc 3:1) to afford a solid material (692.0 mg, 45.7%).

<sup>1</sup>H-NMR (270 MHz, CDCl<sub>3</sub>) δ 1.45–2.10 (12H, m), 3.52–3.65 (2H, m), 3.70–3.86 (2H, m), 5.746 (2H, *t*, *J* = 2.78 Hz), 7.099 (4H, *d*, *J* = 8.76 Hz), 7.834 (4H, *d*, *J* = 8.76 Hz); <sup>13</sup>C-NMR (67.5 MHz, CDCl<sub>3</sub>) δ 18.31, 24.94, 29.95, 61.70, 96.09, 116.54, 129.38, 134.44, 160.58.

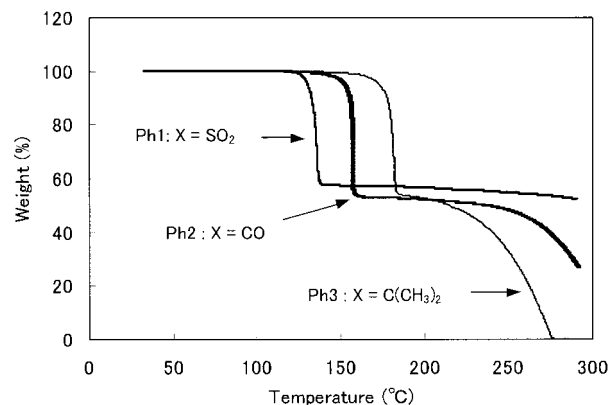
## RESULTS AND DISCUSSION

### Thermal Properties of *t*-butoxycarboxy Derivatives

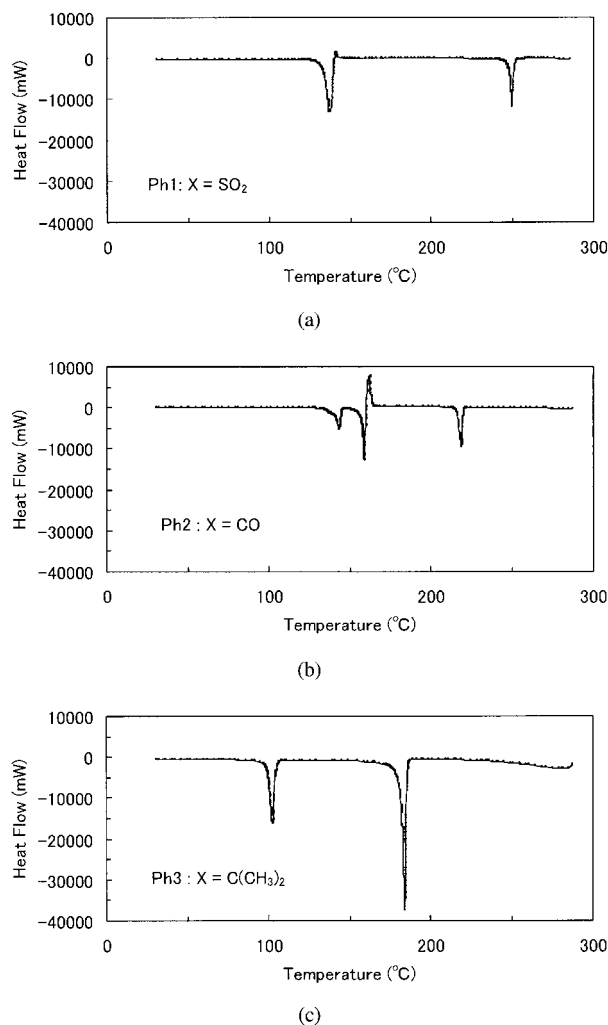
The phenol derivatives, Ph1, Ph2, Ph3, and Ph4, were synthesized by the reaction of the corresponding phenols and di-*t*-butyl dicarbonate or 3,4-dihydro-2H-pyran according to the procedures shown in Scheme 1. TGA (5°C/min) and DSC (5°C/min) curves of these phenol derivatives are shown in Figures 1 and 2, respectively. Melting points and decomposition temperatures for

these phenol derivatives are summarized in Table III.

Ph1 lost 2-methylpropene and carbon dioxide at about 135°C, as evidenced by the one-stage weight loss (Fig. 1) and the endotherm centered at 135°C (Fig. 2). In DSC curves, Ph1 has two endothermic peaks at 135 and 245°C. The former corresponds to the deprotection reaction, and the latter, to the melting point of the PhH1 generated. Ph1 decomposed before the melting. Ph4 was much more stable than was Ph1. It was difficult to decrease the deprotection temperature for phenol moieties protected by the pyranyl ether. The deprotection temperatures for Ph2 and Ph3 were 156 and 183°C, respectively, which are much higher than the 135°C



**Figure 1** TGA curves for various *t*-butoxycarboxy derivatives. Abbreviations: See Table I.



**Figure 2** DSC curves for various *t*-butyloxycarboxy derivatives. Abbreviations: See Table I.

for Ph1. Ph2 has three endothermic peaks which correspond to the melting point of Ph2, the deprotection, and the melting point of Ph2 generated (213–215°C). Ph3 has only two peaks which correspond to the melting point of Ph3 and the decomposition. In the latter peak, the melting of PhH3 and the decomposition of Ph3 are overlapped. The deprotection temperatures are likely to depend on the acidity of phenols. Table IV summarizes the relative acidity for these phenols. The relative acidity increased in the order of PhH3 < PhH2 < PhH1, which was consistent with that for the stability of the blocked phenols. The same trends were reported for various compounds having hydroxy moieties blocked with isocyanates.<sup>12</sup> The O—(CO)— bond would be weakened by the electron-withdrawing substituents at the *para*-position.

**Table III Thermal Properties for Protected Phenols**

Measurement	Items			
	Ph1	Ph2	Ph3	Ph4
	X			
	SO <sub>2</sub>	CO	C(Me) <sub>3</sub>	SO <sub>2</sub>
Mp (°C)	134	141	100	146
T <sub>decomp.</sub>	134	156	183	174

T<sub>decomp.</sub>: decomposition temperature.

### Relation Between Catalyst Activities and Phenol Structures

Ep1 was employed in order to evaluate initiator activities for each phenol. The gel time decreased in the order of PhH2 > PhH3 > PhH1, as shown in Table IV. The initiator activity of PhH1 having the highest acidity was the largest. This implies that the reaction mechanism for the composite initiator should be the same as that for the AS catalysts.<sup>5</sup> The longer gel time for PhH2 than expected from the order of the acidity could be explained by side reactions turning the gel color deep yellow. The other gels cured by PhH3 and PhH1 were transparent. Ph1 shows the best behavior for latent catalysts, namely, the highest catalyst activity and the lowest deprotection temperature. The deprotection temperature is in the range of below 150°C, the temperature at which the curing of epoxy resins is commonly carried out.

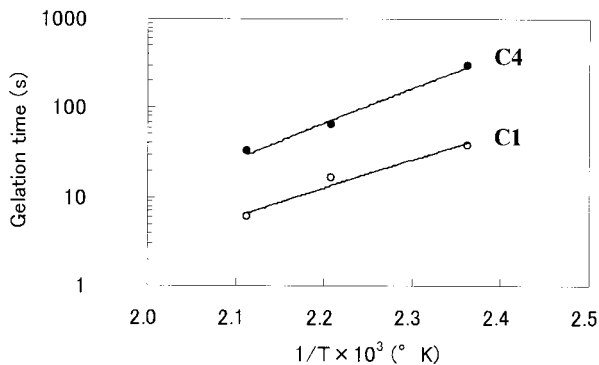
### Catalyst Activity of Latent Catalysts and Electrical Resistivity

Figure 3 shows relations between temperature and gel time for C4 and C1. At 150°C, the actual

**Table IV Relative Acidities for Various Phenols and Gel Times at 150°C**

	$\Delta \delta = \delta(d_6\text{-DMSO}) - \delta(d_6\text{-Acetone})$ (ppm)	Gel Time at 150°C (sec)
Ph1	1.18	40
Ph2	1.12	221
Ph3	1.04	137

Relative acidity of various phenols: ( $\delta$  ppm for OH of phenols in *d*<sub>6</sub>-DMSO) – ( $\delta$  ppm for OH of phenols in *d*<sub>6</sub>-acetone). See Experimental section. Concentration of phenols: 0.2M.

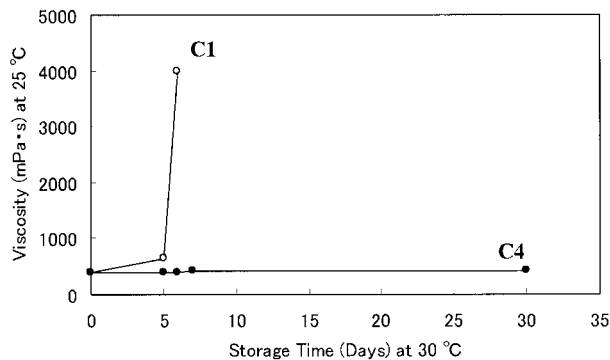


**Figure 3** Relation between gel times and temperatures for epoxy resins (C4 and C1) containing protected phenol (Ph1) and the parent phenol (PhH1).

gel time for Ep1 initiated with the PhH1 (mixture C1) was 40 s, which is much faster than that with Ph1 (mixture C4), namely, about 300 s. This would be explained by the delay of the decomposition of the *t*-butoxycarbonyloxy group. Activation energy for the gelation was 75.2 kcal/mol for C4, slightly higher than that for C1 (59.8 kcal/mol).

Figure 4 shows changes of viscosity for mixtures C4 and C1. The viscosity of C4 containing Ph1 did not change after 30 days, in contrast to that of C1 which gelled after only 5 days. C4 was proved to have outstanding stability in terms of storage at ambient temperature.

When C4 was cured at 150°C, CO<sub>2</sub> and 2-methylpropene evolved.<sup>7</sup> Therefore, the cured products should become porous. However, when the coating thickness was less than 2 mm, it was possible to obtain clear coating films without any voids, as shown in Photo 1.



**Figure 4** Increase in the viscosity for epoxy resins (C4 and C1) containing protected phenol (Ph1) and the parent phenol (PhH1).

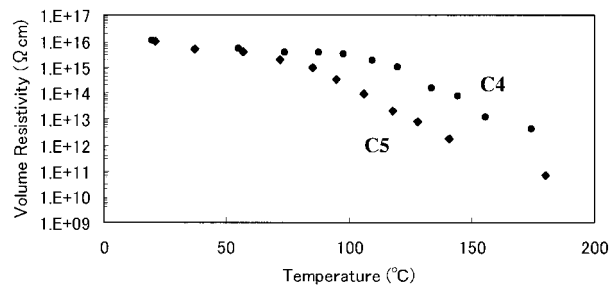


**Photo 1** Cured C4 film at 150°C for 30 min.

Electrical properties were obtained on a 5-cm-diameter disk (2-mm-thick) of the cured resin. Figure 5 shows the electrical resistivity for C4 and C5. It is clear that the electrical resistivity for cured C4 is two orders better than that for cured C5 at higher than 150°C, probably due to a lesser amount of ionic impurities remaining in the cured matrices.<sup>5</sup>

## CONCLUSIONS

The initiator containing Ph1 and Al1 was found to initiate epoxide curing at temperatures higher than 150°C. However, any increase in the viscosity was not observed at room temperature for the epoxy resin mixtures. This was achieved by finding that (1) Ph1 released PhH1 specifically at a low temperature around 150°C and (2) composite catalysts composed of PhH1 and Al1 had high catalyst activities.



**Figure 5** Electrical resistivities for epoxy resins (C4 and C5) containing protected phenol Ph1 and strong acid-type sulfonium salt SI-60.

## REFERENCES

1. (a) Lee, H.; Neville, K. *Handbook of Epoxy Resins*; McGraw-Hill, New York, 1967; (b) Kakiuchi, H. *Epokishi Jushi*; Shoko-do: Tokyo, Japan, 1977.
2. (a) Crivello, J. V.; Lam, J. H. W. *J Polym Sci Polym Chem Ed* 1979, 17, 977–999; (b) Crivello, J. V. *Annu Rev Mater Sci* 1983, 13, 173, and references cited therein.
3. (a) Nakano, S.; Endo, T. *Prog Org Coat* 1996, 28, 143; (b) Hamazu, F.; Akashi, S.; Koizumi, T.; Takata, T.; Endo, T. *J Polym Sci Part A Polym Chem* 1991, 19, 1675; (c) Crivello, J. V.; Lockhart, T. P.; Lee, J. L. *J Polym Chem Polym Chem Ed* 1983, 21, 97; (d) Toneri, T.; Watanabe, K.; Sanda, F.; Endo, T. *Macromolecules* 1999, 32, 1293; (e) Pappas, S. P.; Hill, L. W. *J Coat Tech* 1981, 53, 43; (f) Barton, J. M.; Buist, G. J.; Hamerton, I.; Howlin, B. J.; Jones, J. R.; Liu, S. *J Mater Chem* 1994, 4, 379; (g) Ricciardi, F.; Romanchick, W. A.; Joullie, M. M. *J Polym Sci Polym Lett Ed* 1983, 21, 633.
4. Hayase, S.; Suzuki, S.; Wada, M.; Inoue, Y.; Mitsui, H. *J Appl Polym Sci* 1984, 29, 269.
5. (a) Hayase, S.; Onishi, Y.; Suzuki, S.; Wada, M.; Kurita, A. *J Polym Sci Part A Polym Chem Ed* 1987, 25, 753; (b) Hayase, S.; Onishi, Y.; Suzuki, S.; Wada, M. *Macromolecules* 1986, 19, 968; (c) Hayase, S.; Onishi, Y.; Suzuki, S.; Wada, M. *Nippon Kagakukai-shi* 1985, 328; (d) Hayase, S.; Onishi, Y.; Suzuki, S.; Wada, M. *Macromolecules* 1985, 18, 2778; (e) Hayase, S.; Onishi, Y.; Suzuki, S.; Wada, M. *J Polym Sci Polym Chem Ed* 1983, 21, 467; (f) Hayase, S.; Onishi, Y.; Yoshikiyo, K.; Suzuki, S.; Wada, M. *J Polym Sci Polym Chem Ed* 1982, 20, 3155; (g) Hayase, S.; Ito, T.; Suzuki, S.; Wada, M. *J Polym Sci Polym Chem Ed* 1981, 19, 2977; (h) Hayase, S.; Ito, T.; Suzuki, S.; Wada, M. *J Polym Sci Polym Chem Ed* 1981, 19, 2185.
6. Hayase, S.; Onishi, Y.; Suzuki, S.; Kurokawa, T. *Koubunshi Ronbunshu* 1984, 41, 581.
7. (a) Ito, H.; Willson, C. G. *Polym Eng Sci* 1983, 23, 1012; (b) Frechet, J. M. J.; Eichler, E.; Ito, H.; Willson, C. G. *Polymer* 1983, 24, 995; (c) Ito, H.; Willson, C. G.; Frecht, J. M. J.; Farrall, M. J.; Eichler, E. *Macromolecules* 1983, 16, 510.
8. Markovitz, M. U.S. Patent 3 812 214, 1974.
9. Ito, H.; Ueda, M.; England, W. P. *Macromolecules* 1990, 23, 2589.
10. Houlihan, F.; Bouchard, F.; Frechet, J. M. J. *Can J Chem* 1985, 63, 153.
11. Dauben, W. G.; Bradlow, H. L. *J Am Chem Soc* 1952, 74, 559.
12. (a) Mukaiyama, T.; Hoshion, Y. *J Am Chem Soc* 1956, 78, 1946; (b) Bayer, O. *Das Diisocyanat—Polyadditions Verfahren*; Carl Hansen Verlag; Munich, 1963; p 12.