Cationic Polymerization of Hydrogenated Bisphenol-A Glycidyl Ether with Cycloaliphatic Epoxy Resin and Its Thermal Discoloration

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ABSTRACT: One of the key issues associated with epoxy resin–based LED encapsulant is discoloration under operating conditions that caused a decrease in light output. In this article, thermal cationic polymerization of hydrogenated bisphenol-A glycidyl ether using 3-methyl-2-butenyltetramethylenesulfonium hexafluoroantimonate and its discoloration are reported. Polymerization was followed by thermal analysis, FT-IR spectrum, and hardness measurements. Thermal discoloration was measured by yellowness index based on transmittance spectrum. Increased catalyst concentration causes acceleration in polymerization rates, but this also increased discoloration after thermal aging. In low catalyst concentration under 0.3 wt %, the hardness of plaque was low and required a high temperature to complete polymerization and this resulted in a highly colored plaque. Formulation with cycloaliphatic epoxy (3′-4′-epoxycyclohexane)-methyl 3′-4′-epoxycyclohexyl-carboxylate (CEL2021P) enhanced the polymerization even at low catalyst concentration and reduced thermal discoloration. With addition of di-*t*-butylphenol (BHT) as the oxidation inhibitor, the thermal discoloration was extremely improved but this also caused inhibition of polymerization as seen by thermal analysis. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1395–1400, 2005

Key words: cationic polymerization; hydrogenated bisphenol-A glycidyl ether; FT-IR; oxidation inhibitor; transparency; discoloration

INTRODUCTION

Transparent epoxy resins obtained by anhydride curing of bisphenol-A glycidyl ether are commonly used in light emitting diodes (LED) encapsulation applications.[1] More recently, the light output efficiency of LEDs has increased and new designs such as white LEDs that combined shorter wavelength semiconductors with phosphor are reported.[2,3] As the emission wavelength becomes shorter, the light output decrease due to epoxy discoloration becomes a major issue.[4]

The reason for epoxy discoloration is potentially due to the oxidation of aromatic groups in bisphenol-A glycidyl ether after UV absorption.[5] This UV discoloration issue is also commonly referred to as the weatherability issue common in outdoor paint applications. To improve the weatherability, a hydrogenated bisphenol-A glycidyl ether version was made by hydrogenation of aromatic group. Originally, this class of epoxy resin was prepared from hydrogenated bisphenol-A and epichrolohydrin[6] but it had a very high chlorine content, which makes it very difficult to use in semiconductor applications. After development of selective hydrogenation catalyst and improved purity of bisphenol-A glycidyl ether, hydrogenated bisphenol-A glycidyl ether could be prepared with low chlorine content.[7,8]

In previous literature, we investigated anhydride curing of hydrogenated bisphenol-A glycidyl ether and its discoloration. We found that UV discoloration was smaller but thermal discoloration was larger compared with the conventional bisphenol-A glycidyl ether of anhydride curing. The catalyst structures, such as amount of double bond and aromatic group, were more important factors for discoloration.[9]

Recent package requirements for LED are smaller and thinner, although evaporation of anhydride is one of the issues that causes errors because the anhydride content is reduced. There are some methods to reduce anhydride evaporation, for example, using a high concentration of reactive catalyst. Despite this, the amount of evaporation will still be difficult to control and discoloration of the resin will be increased. Due to these issues, cationic polymerization of epoxy resins is expected to be the best candidate for the next generation LED package because of its long history of use in coatings and paint applications.

Cationic polymerization of epoxy resin was reported by Crivello et al.[10] using triarylsulfonium salt

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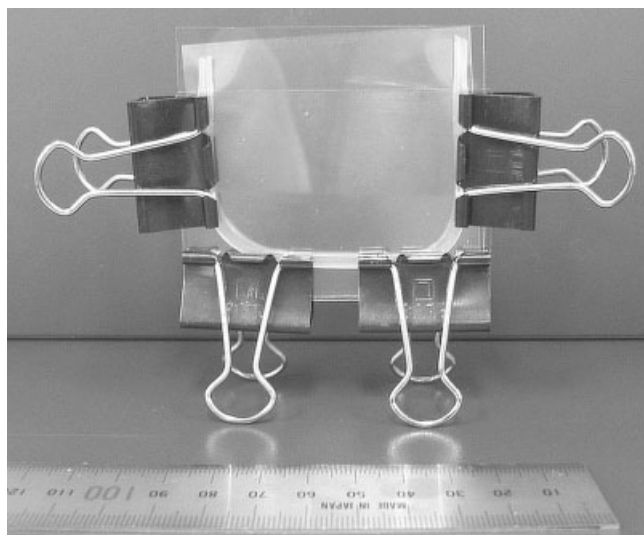
Figure 1 Plaque equipment.

Figure 2 DSC thermograph of YX8000 epoxy resin with CP-77 catalyst. (A) CP-77 1.0 wt %; (B) CP-77 0.15 wt %.

photopolymerizaion. Since then, this system has been used in a wide range of industries, such as coatings, paints, and adhesives.[11] Besides photopolymerization, thermal cationic polymerization has been developed using similar catalysts.[12,13] The benefits of thermal polymerization are storage stability of uncured resin formulation and high reactivity compared with the anhydride curing system. Due to this high reactivity, one can expect to achieve a low discoloration encapsulant with a very low catalyst concentration.

As one of the approaches to reduce discoloration, we report the thermal cationic polymerization of hydrogenated bisphenol-A glycidyl ether. First, the effect of catalyst concentration on polymer properties and discoloration was studied. We also discuss the effect of the addition of cycloaliphatic epoxy compounds and the addition of oxidation inhibitors on polymerization and discoloration.

EXPERIMENTAL

Materials

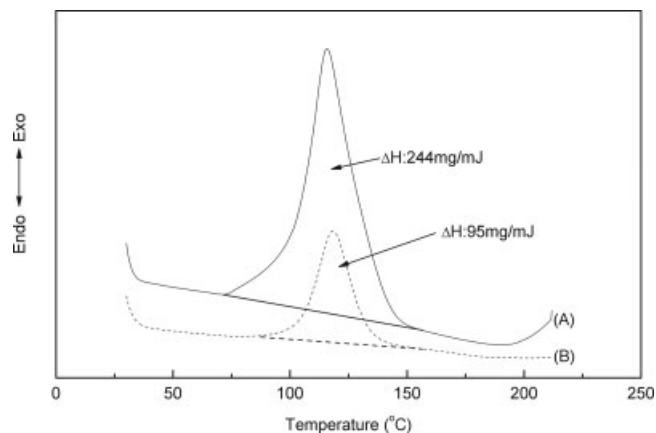Hydrogenated bisphenol-A glycidyl ether (YX8000) was generously donated by Japan Epoxy Resin Co.

Ltd. Semiconductor grade cycloaliphatic epoxy resin (3'-4'-epoxycyclohexane)methyl 3'-4'-epoxycyclohexyl-carboxylate (CEL2021P) was obtained from Daicel Chemical Industry Ltd. The cationic polymerization catalyst, a propylene carbonate solution of 3-methyl-2-butenyltetramethylenesulfonium hexafluoroantimonate (66 wt %, CP-77) was obtained from Asahi Denka Co. Ltd. 2,4-Di-*tert*-butyl-hydroxyltoluene (BHT) were purchased from Aldrich. All chemicals were used as received.

Curing of hydrogenated bisphenol-A glycidyl ether

A typical procedure was used as follows: YX8000 and CP-77 were mixed in a flask and evacuated to remove oxygen. The mixture was then fed into a 2-mm-thick casting unit (Figure 1) and cured in an oven at 120°C for 12 h. Thermal aging of epoxy plaques was done by placing them in an oven maintained at 150°C.

Measurement

Differential scanning calorimetry (DSC) was done using a Shimadzu DSC60 at heating rate of 5°C/min under a flow of N_2 gas. TGA was done with a Shimadzu TG/DTA 60 at a heating rate of 10°C/min

TABLE I
Effect of Catalyst Concentration on Polymerization and Discoloration

YX8000 (wt %)	CP-77 (wt %)	Hardness		DSC ΔH (mg/mJ)	Yellowness index	
		Initial	After thermal aging at 150°C for 24 h		Initial	After thermal aging at 150°C for 24 h
99.0	1.0	80	85	244	1.13	77.0
99.5	0.5	80	80	202	1.09	10.3
99.7	0.3	60	75	165	0.99	12.1
99.85	0.15	15	78	149.9	0.88	8.2

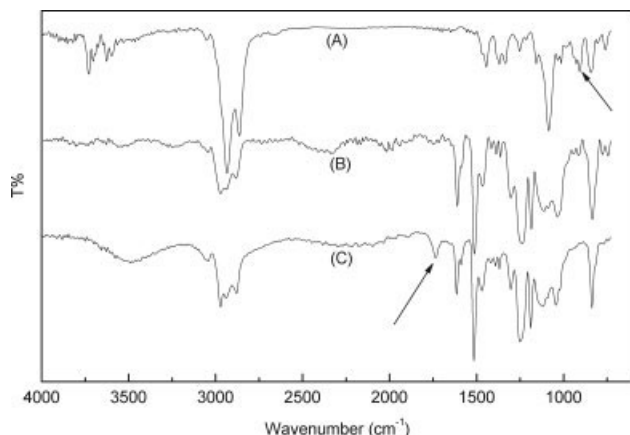Curing condition: 120°C for 12 h.

Figure 3 FT-IR spectrum of (A) YX8000 monomer; (B) YX8000 after polymerization with 0.15 wt % of CP-77; and (C) after thermal aging at 150°C for 24 h of b.

Figure 4 Transmittance spectrum of YX8000 epoxy cured with CP-77 catalyst before thermal aging and after thermal aging at 150°C 24 h: (A and A′) CP77 1.0 wt %; (B and B′) CP77 0.5 wt %; and (C and C′) CP77 0.15 wt %.

under nitrogen atmosphere. FT-IR spectra were recorded with a Shimadzu FTIR-8300. Transmittance spectra of polymerized plaque were measured with a Shimadzu UV-3100 from 300 to 800 nm and the yellowness index were calculated from these spectrum intensities.[14] Shore D hardness of cured plaques were measured using a Durometer.

RESULTS AND DISCUSSION

In previous studies of hydrogenated bisphenol-A glycidyl ether with anhydride cure, the catalyst structure was the most important for UV discoloration even at concentrations of 0.5 wt % or less. At the time of this publication, there were several commercially available cationic catalysts for curing epoxy resins. We chose to
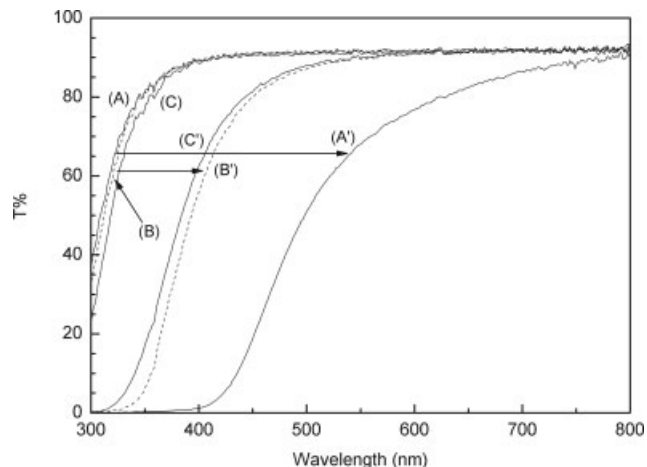
work with 3-methyl-2-butenyltetramethylenesulfonium hexafluoroantimonate because of its nonaromatic structure.

Polymerization of hydrogenated bisphenol-A glycidyl ether

First, the effect of catalyst concentration on polymerization was examined. Polymerization was exothermic; enthalpy (ΔH) and onset temperature were analyzed by DSC as shown in Figure 2 and Table I. The onset temperature and maximum temperature of polymerization were almost stable but ΔH changed with catalyst concentration.
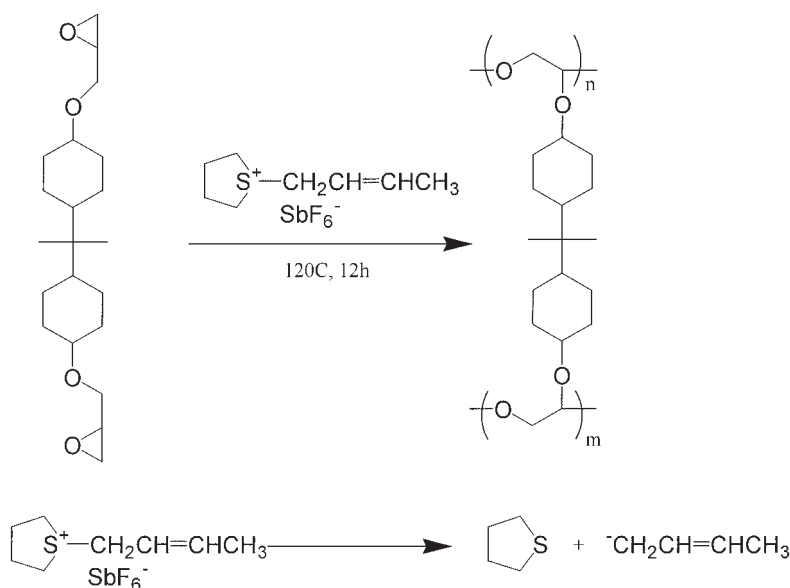
Scheme 1

TABLE II
Effect of CEL2021P Concentration on Polymerization

CEL2021 (wt %)	BHT (wt %)	Hardness		DSC	
		Initial	After thermal aging at 150°C for 24 h	Onset temperature (°C)	ΔH (mJ/mg)
0	0	15	79	76	150
1	0	35	75	76	163
5	0	50	78	72	181
10	0	82	80	69	188
20	0	85	82	66	219
100	0	87	88	63	368
10	0	82	84	69	205
10	0.1	79	81	71	196
10	0.3	77	82	74	198
10	0.5	73	82	78	194
10	1.0	67	85	85	184
10	2.0	62	83	88	167

CP-77 0.15 wt %, curing condition: 120°C for 12 h.

We prepared 2-mm-thick plaques to measure the Shore D hardness before and after thermal aging. The hardness was increased with increasing catalyst concentration and maximum hardness was about 80. In lower catalyst concentrations less than 0.4 wt %, the hardness was increased after extended thermal aging and reached 85. These results indicate that polymerization at lower catalyst concentrations was not complete at 12 h at 120°C. For example, at 0.15 wt % concentration of catalyst, hardness of plaque reached 80 after 16 h at 150°C.

Polymerization of YX8000 with CP-77 was also confirmed by IR spectrum. As shown in Figure 3, the absorption signal assigned to C–O stretching of he epoxy group at 916 cm^{-1} is completely depleted upon curing.

We also recorded transmittance spectra before and after thermal aging as shown in Figure 4. The optical absorption shifted to a longer wavelength after thermal aging, and shifted to a longer wavelength with increasing catalyst concentration.

Considering the proposed polymerization mechanism as shown in Scheme 1,[15] tetrahydrothiophene generated during polymerization remains in cured polymer and will be easily dehydrated to generate discolored species. In addition, hydrogenated bisphenol-A glycidyl ether itself can be oxidized. After thermal aging, new absorption was observed at 1755 cm^{-1} for the carbonyl group in the IR spectrum and this peak intensity was increased with increasing yellowness index. Under 0.3 wt % of catalyst concentration, polymerization seems to be incomplete because the hardness was much lower than 80. A Shore D hardness value of 80 was achieved after continued curing at 150°C for 12 h, but thermal discoloration and the presence of a carbonyl group by FTIR was observed. From these results, the discoloration is due to polymer
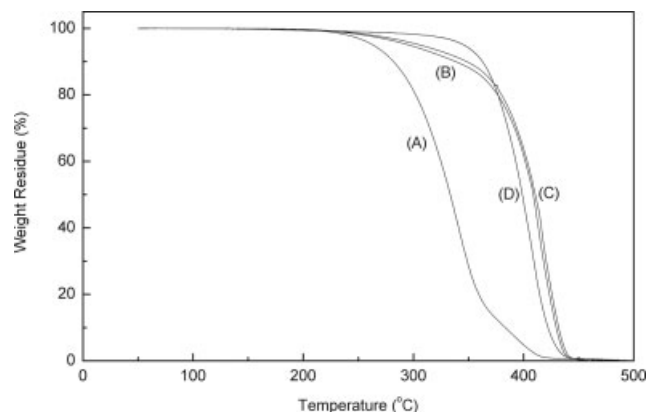

Figure 5 TGA curves of (A) YX8000 monomer; (B) YX8000 after curing; (C) YX8000 with 10 wt % CEL2021P after curing; and (D) CEL2021P after curing. Each with CP-77 0.15 wt %.
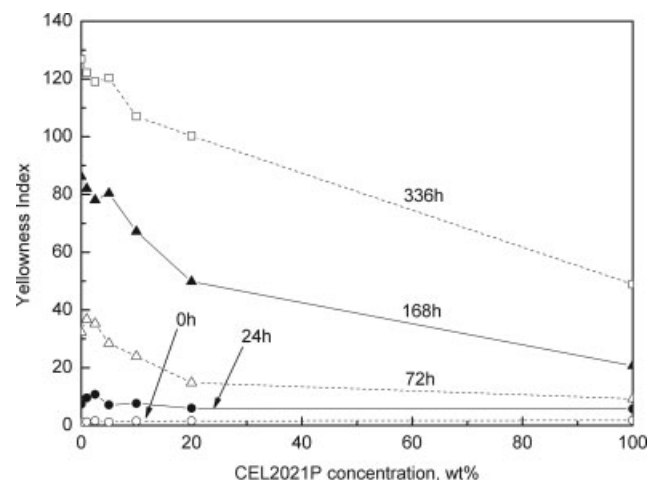

Figure 6 Effect of CEL2021P concentration on thermal discoloration. CP-77 0.15 wt %, thermal aging at 150°C.
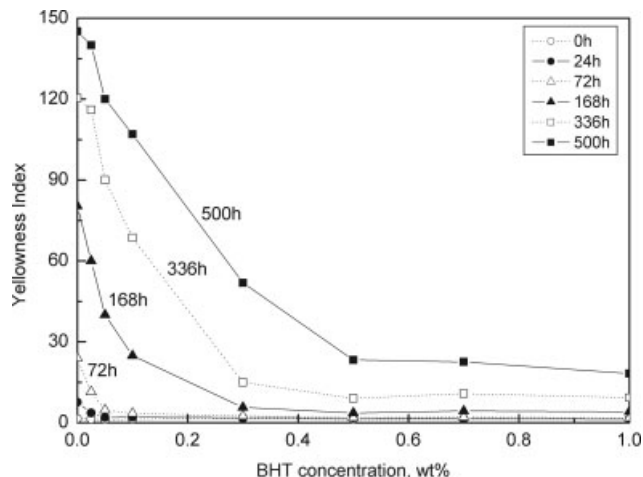
Figure 7 Effect of BHT concentration on thermal discoloration. YX8000 : CEL2021P = 90 : 10, CP-77 0.15 wt %, thermal aging at 150°C.

oxidation and is accelerated by catalyst concentration. To improve the thermal discoloration, it is necessary to improve the activity of the catalyst so that it can be used at low concentrations.

Formulation with cycloaliphatic epoxy resin (3′-4′-epoxycyclohexane)methyl 3′-4′-epoxycyclohexyl-carboxylate (CEL2021P)

It is reported that the cycloaliphatic epoxy CEL 2021P, has much higher cationic polymerization reactivity than that of bisphenol-A glycidyl ether.[16] To accelerate the polymerization with a low catalyst concentration, the effect of cycloaliphatic epoxy concentration on polymerization was studied.

Catalyst concentration was fixed at 0.15 wt % in formulation. As shown in Table II, onset temperature

and ΔH of CEL2021P were 65°C and 368 mJ/mg. But these values of YX8000 were 76°C and 150 mJ/mg, respectively. So the cationic polymerization reactivity of CEL2021P was higher than YX8000. Increasing CEL2021P concentration in YX8000, onset temperature was decreased and ΔH was increased. The initial hardness of plaques was also increased with increasing CEL2021P concentration.

Figure 5 shows TGA thermograms before and after curing with YX8000 and CEL2021P. Thermal stability of cured 10 wt % CEL2021P was slightly higher than YX8000 alone.

Figure 6 shows the relationship between CEL2021P concentration and yellowness index in thermal aging. The increase of yellowness index during thermal aging was decreased with increasing CEL2021P concentration. On the other hand, increasing CEL2021P concentration over 20 wt %, cracks were generated just after curing. The reason for crack generation seems to be both poor fracture toughness and a large polymerization exotherm. Therefore, a further oxidation inhibitor study was done with 10 wt % concentration.

Effect of oxidation inhibitor on discoloration and polymerization

Formulation of cycloaliphatic epoxy accelerated the cationic polymerization with low catalyst concentration but discoloration issues still remained. In a previous article, we found some phenolic oxidation inhibitors such as BHT could reduce both thermal and UV discoloration, but phosphorus oxidation inhibitors increase the UV discoloration.[9]

The effect of BHT concentration in this system was first evaluated by the yellowness index and these results are shown in Figure 7. The yellowness index increase during thermal aging was high at low BHT
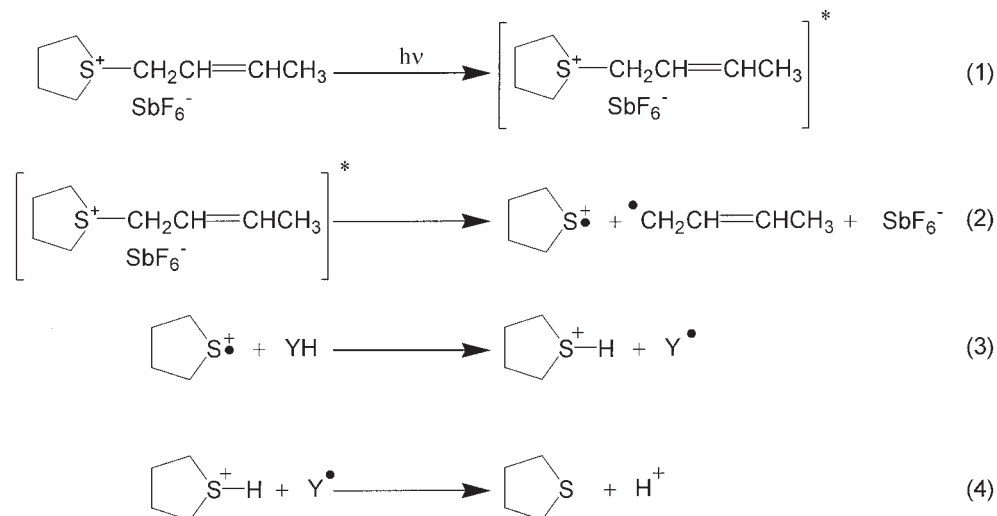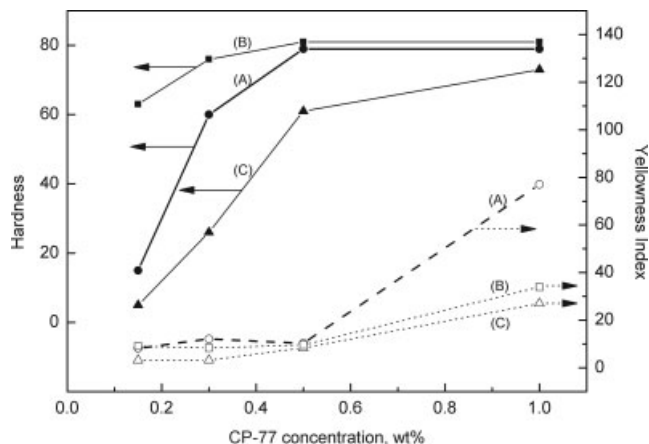

Scheme 2

Figure 8 Effect of catalyst concentration on hardness and thermal discoloration. (A) YX8000; (B)YX8000 : CEL2021P = 90 : 10; and (C) YX8000 : CEL2021P = 90 : 10 and BHT 1.0 wt %, thermal aging at 150°C for 24 h.

concentrations or without BHT and this discoloration increase was smaller with increasing BHT concentration.

The effect of BHT concentration on polymerization properties, such as hardness and thermal analysis data, are described in Table II. Increasing BHT concentration gave soft plaques after curing but their hardness was increased after extended thermal aging up to Shore D hardness of 85. The onset temperature was increased and ΔH was decreased with increasing BHT concentration.

From these results, it is clear that polymerization is inhibited by BHT. BHT is a radical scavenger, while the active polymerization species seems to be a cationic initiator. As shown in the polymerization mechanism in Scheme 2,[17] the radical species from catalyst are generated. These radical species will react with BHT instead of reacting with epoxide.

CONCLUSIONS

In the thermal cationic polymerization of hydrogenated bisphenol-A glycidyl ether using 3-methyl-2-butenyltetramethylenesulfonium hexafluoroantimonate, thermal discoloration and reactivity was a trade-off. As summarized in Figure 8, discoloration was decreased with decreasing catalyst concentration, but the hardness of the polymer was decreased. Formulating the cycloaliphatic epoxy of CEL2021P, the reactivity was increased even at low catalyst concentrations without increasing discoloration. Further addition of BHT reduced the reactivity because of polymerization inhibition, but discoloration was decreased, especially in a long-term aging test.

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