

Thermally Initiated Cationic Polymerization and Properties of Epoxy Siloxane

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ABSTRACT: Difunctional epoxy siloxane monomers containing disiloxane, trisiloxane, and tetrasiloxane were prepared by hydrosilylation of an α,ω -difunctional Si—H-terminated siloxane with a vinyl-functional epoxide. Cationic polymerization of these monomers using 3-methyl-2-butenyltetramethylenesulfonium hexafluoroantimonate and their reactivities were examined. The reactivity order was disiloxane > trisiloxane > tetrasiloxane. Thermal discoloration of these polymers increased with catalyst concentration and also with the length of dimethyl siloxane. UV discoloration was also accelerated by catalyst. From the thermo gravimetric analysis, it was found that the thermal stabilities

of polymers increased with increasing the length of dimethyl siloxane chain. Mechanical properties of polymers were also tested by thermal mechanical analysis and dynamic mechanical analysis, and it was found that the flexibility of polymers was increased with increasing siloxane chain length. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2010–2019, 2006

Key words: epoxy siloxane; cationic polymerization; differential scanning calorimetry (DSC); thermo gravimetric analysis (TGA); discoloration

INTRODUCTION

Epoxy functional siloxanes are well known for many years, and have been used as a silane coupling agent and for silicone exfoliation.^{1–3} Many researches on synthesis and cationic polymerization of epoxy siloxanes have been reported, and these siloxanes are expected to be a hybrid material, having the characters of both an organic polymer and a ceramic.^{4–6}

Light emitting diode (LED) encapsulation is one of the important applications of transparent epoxy resin, and anhydride curing of bisphenol A glycidyl ether has been used for this purpose. Recently, the emission spectrum wavelength of LED are becoming shorter and light output intensity are rapidly increasing. As a result, discoloration of epoxy encapsulant and following light output intensity decrease has become an issue.⁷

We are estimating the factor of discoloration to be oxidation, following the optical absorption by unsaturated bond. The discoloration behavior of hydrogenated bisphenol A glycidyl ether has been investigated both by anhydride curing⁸ and by cationic po-

lymerization.⁹ In the next step, we have paid attention to chemical bond dissociation energy in epoxy resin. Epoxy siloxane is one of the candidates, and anhydride curing of epoxy siloxane and discoloration has already been reported.¹⁰

From a series of studies, we found that catalyst structure and catalyst concentration are most important factors for discoloration. Needless to say, satisfaction of thermal properties and mechanical properties are necessary for LED encapsulant.

One of the desirable characteristics for monomer is high reactivity. The ideal monomer can be cured with minimum catalyst concentration, and as a result, they will have good discoloration stability. It is reported that epoxy siloxane has good reactivity in cationic polymerization,¹¹ and it can be easily polymerized both by photo-induced or thermally-induced polymerization. On the other hand, the polymer is brittle, lack flexibility, and has poor mechanical properties.

In this paper, we presented the preparation and cationic polymerization of epoxy siloxanes with different dimethyl siloxane length, to improve its mechanical properties. In the cationic polymerization of these monomers, the effect of catalyst concentration on discoloration behavior during both thermal and UV treatment are discussed. In addition, the mechanical properties of these polymers have been studied.

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EXPERIMENTAL

Materials

1,1,3,3-Tetramethyldisiloxane was purchased from Shin-Estu Chemical. 1,1,3,3,5,5-Hexamethyldisiloxane and 1,1,3,3,5,5,7,7-octamethyldisiloxane were obtained from Gelest. 3-Vinyl-7-oxabicyclo[4,1,0] heptane was a gift from Daicel Chemical Industry Co., Ltd. Tri(triphenylphosphine)-rhodium(I) chloride (Wilkinson's catalyst) and polymer-bound Wilkinson's catalyst (PBWC) were purchased from Gelest. Propylene carbonate solution of 3-methyl-2-butenyltetramethylene-sulfonium hexafluoroantimonate (66 wt %, CP-77) was obtained from Asahi Denka Co., Ltd. All chemicals were used without further purifications.

Synthesis of 1,3-bis[2-(3{7-oxabicyclo[4.1.0]heptyl})ethyl]-tetramethyldisiloxane⁸ (I)

To a 100-mL round-bottom flask fitted with reflux condenser and magnetic stirrer, 4.03 g (0.03 mol) of 1,1,3,3-hexamethyldisiloxane, 8.70 g (0.075 mol) of 3-vinyl-7-oxabicyclo[4,1,0] heptane, and 10 mL of *n*-hexane were added. To the solution, 0.2 mL chloroform solution containing 5 mg of Wilkinson's catalyst was added. The reaction mixture was heated at 65°C for 6 h in an oil bath. The course of the reaction was monitored with infrared spectroscopy by the disappearance of Si—H band at 2125 cm⁻¹. After the infrared band completely disappeared, the reaction was terminated. The unreacted starting materials and solvent were removed under reduced pressure and high vacuum. The fraction that distilled out of the flask while heating at 220–230°C at 1 mmHg was collected as the product. 9.18 g (80% of theoretical value) of the desired product was obtained as colorless oil.

¹H-NMR (CDCl₃, 270 MHz, δ, ppm): 3.12 (m, 4H, O—CH—epoxy ring), 2.18–0.80 (m, 18H, —CH₂—cyclohexane ring), 0.40–0.46 (m, 4H, —CH₂—Si), 0.00 (s, 12H, CH₃—Si).

Synthesis of 1,5-bis[2-(3{7-oxabicyclo[4.1.0]heptyl})ethyl]-hexamethyltrisiloxane⁹ (II)

To a 100-mL round-bottom flask fitted with reflux condenser and magnetic stirrer, 6.25 g (0.03 mol) of 1,1,3,3,5,5-hexamethyltrisiloxane, 8.70 g (0.075 mol) of 3-vinyl-7-oxabicyclo[4,1,0] heptane, 40 mL of toluene, and 11 mg of PBWC were added. The reaction mixture was heated at 100–115°C for 48 h in an oil bath. The course of the reaction was monitored with infrared spectroscopy by the disappearance of Si—H band at 2125 cm⁻¹. After the infrared band completely disappeared, the reaction was terminated, and the reaction mixture was filtered for the removal of catalyst. The

unreacted starting materials and solvent were removed under reduced pressure and high vacuum. After purification by flash chromatography over silica gel with chloroform as an eluent, 11.38 g (83% of theoretical value) of the desired product was obtained as colorless oil.

¹H-NMR (CDCl₃, 270 MHz, δ, ppm): 3.12 (m, 4H, O—CH—epoxy ring), 2.18–0.77 (m, 18H, —CH₂—cyclohexane ring), 0.48 (m, 4H, —CH₂—Si), 0.04 (s, 18H, CH₃—Si).

Synthesis of 1,7-bis[2-(3{7-oxabicyclo[4.1.0]heptyl})ethyl]-octamethyltetrasiloxane⁹ (III)

To a 100-mL round-bottom flask fitted with reflux condenser and magnetic stirrer, 8.48 g (0.03 mol) of 1,1,3,3,5,5,7,7-octamethyltetrasiloxane, 8.70 g (0.075 mol) of 3-vinyl-7-oxabicyclo[4,1,0] heptane, 40 mL of toluene, and 11 mg of PBWC were added. The reaction mixture was heated at 100–115°C for 48 h in an oil bath. The course of the reaction was monitored with infrared spectroscopy by the disappearance of Si—H band at 2125 cm⁻¹. After the infrared band completely disappeared, the reaction was terminated, and the reaction mixture was filtered for the removal of catalyst. The unreacted starting materials and solvent were removed under reduced pressure and high vacuum. After purification by flash chromatography over silica gel with chloroform as an eluent, 14.02 g (88% of theoretical value) of the desired product was obtained as colorless oil.

¹H-NMR (CDCl₃, 270 MHz, δ, ppm): 3.12 (m, 4H, O—CH—epoxy ring), 2.18–0.77 (m, 18H, —CH₂—cyclohexane ring), 0.48 (m, 4H, —CH₂—Si), 0.04 (s, 24H, CH₃—Si).

Curing of epoxy siloxane

Typical procedure is as follows: epoxy siloxane and CP-77 catalyst were mixed in flask and dried *in vacuo* to remove oxygen. Then, the mixture was fed into 2-mm thick casting unit and this unit was kept in dry oven at 120°C for 1 h and then at 150°C for 1 h.

Thermal aging and UV irradiation

Thermal aging of plaques was done at 150°C in dry oven. UV irradiation was performed with high-pressure mercury lamp (Ushio electric SP-V) equipped with deep cut filter to block wavelengths shorter than 350 nm. The light output distribution spectrum is shown in Figure 1. The radiation intensity of resin surface was 5000 mW/cm² and spot diameter was 5 mm.

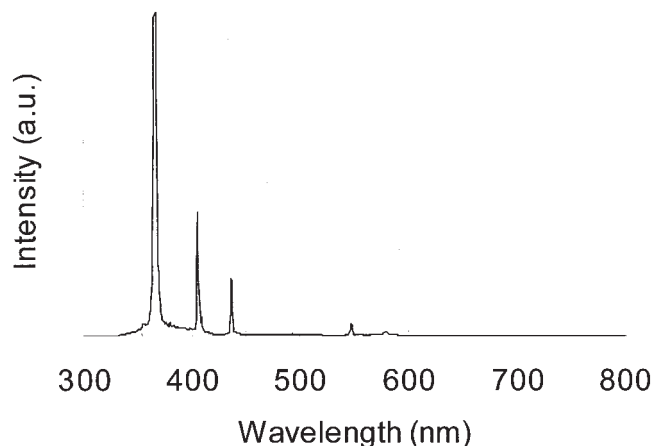


Figure 1 Light output distribution spectrum of UV light source.

Analysis

$^1\text{H-NMR}$ was recorded on JEOL JNM-EX270 (270 MHz). Differential scanning calorimetry (DSC) was performed with Shimadzu DSC60 at a heating rate of $5^\circ\text{C}/\text{min}$ under a flow of N_2 gas. Thermo gravimetric analysis (TGA) was done with Shimadzu TG/DTA60 at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere. Thermal mechanical analysis (TMA) was recorded on Shimadzu TMA60 at a heating rate of $5^\circ\text{C}/\text{min}$ under a flow of N_2 gas. Dynamic mechanical analysis (DMA) was performed by Seiko Instruments DMS 6100 at a heating rate of $4^\circ\text{C}/\text{min}$ under nitrogen atmosphere. Fourier transform infrared (FTIR) spectrum was recorded on Shimadzu FTIR-8300. Transmittance spectrum of polymerized plaque was measured on Shimadzu UV-3100 from 300 to 800 nm, and the yellowness index was calculated from the spectrum. Shore D hardness of cured plaque was measured with Durometer.

RESULTS AND DISCUSSION

Synthesis of epoxy siloxanes

Epoxy siloxanes are prepared by the hydrosilylation of α,ω -difunctional Si—H-terminated siloxane with a

vinyl functional epoxide (Scheme 1). Platinum complex is commonly used as the catalyst in this reaction,¹² although it may cause ring-opening polymerization of epoxy group occasionally.¹³ In this study, we used Wilkinson's catalyst (Tetrakis(Triphenylphosphine)Palladium(0)) to avoid ring-opening polymerization during hydrosilylation.⁶ In case of synthesis of higher molecular weight epoxy siloxanes such as **II** and **III**, PBWC was used because of the difficulty of distillation. After completion of hydrosilylation, PBWC was easily collected by filtration. In each monomer synthesis, the yield was over 80% and their purity as determined by GPC was almost 100%. The obtained epoxy siloxane monomers were confirmed their characterization by $^1\text{H-NMR}$. Figure 2 shows the $^1\text{H-NMR}$ spectrum of **I**.

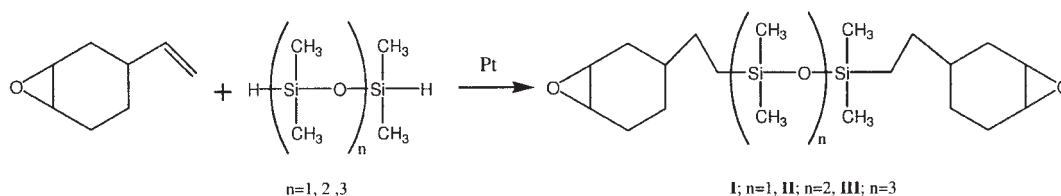
Cationic polymerization of epoxy siloxane

Thermal cationic polymerization of epoxy siloxane was performed with 3-methyl-2-butenyltetramethylenesulfonium hexafluoroantimonate (CP-77) catalyst. The completion of polymerization was confirmed by FTIR spectrum, and the characteristic absorption band at 920 cm^{-1} of epoxy groups completely disappeared after polymerization.

Polymerization reactivity of three epoxy siloxanes was compared by DSC with different catalyst concentration. Figure 3 shows DSC thermograms of polymerizations with 0.5 wt % of catalyst.

Cationic polymerization of epoxy siloxane is an exothermal reaction. With decreasing catalyst concentration, both exothermal peak temperature and ΔH decreased. Table I summarizes the polymerization and properties of epoxy siloxane, with changing catalyst concentration. Polymerization condition was fixed at 120°C for 1 h and then at 150°C for 2 h. As shown in Table I, exothermal peak temperature and ΔH decreased with increasing dimethyl siloxane unit. This indicated that reactivity order of epoxy siloxanes were **I** > **II** > **III**. In case of bisphenol A glycidyl ether and cycloaliphatic epoxy resin, polymerization reactivity decreased with increasing epoxy equivalent weight.

Hardness of polymer also increased with increasing catalyst concentration and decreased with increasing



Scheme 1

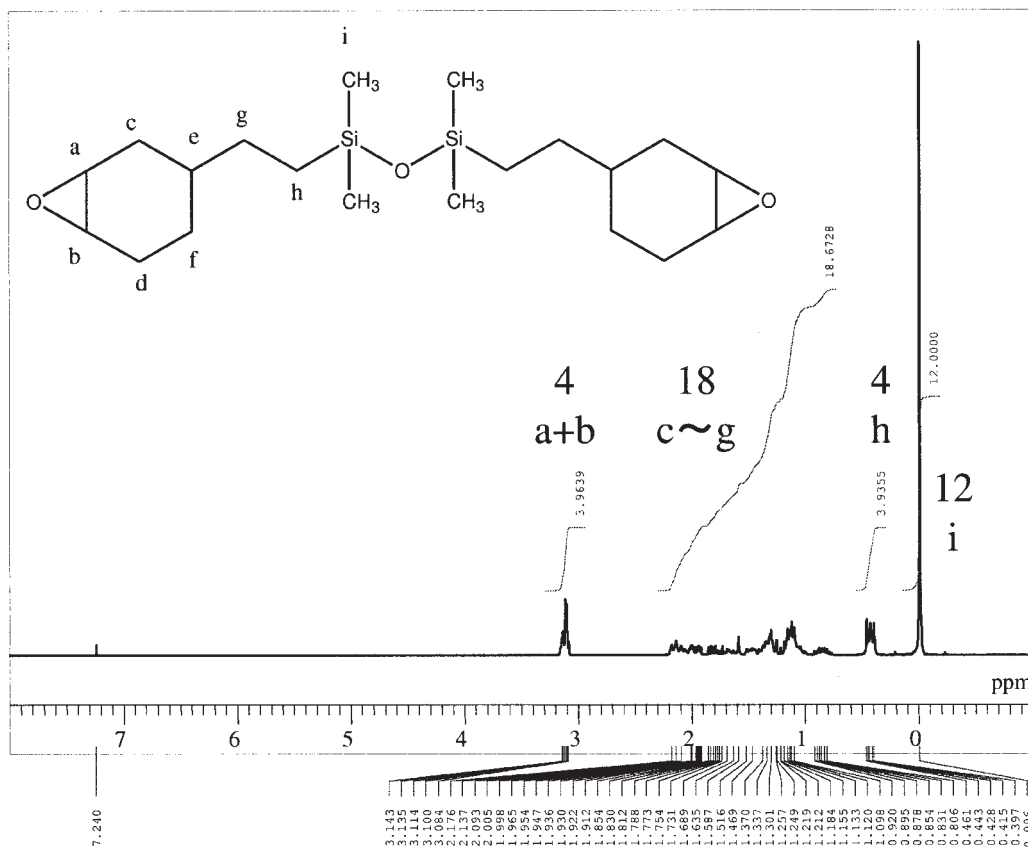


Figure 2 $^1\text{H-NMR}$ spectrum of epoxy siloxane monomer I.

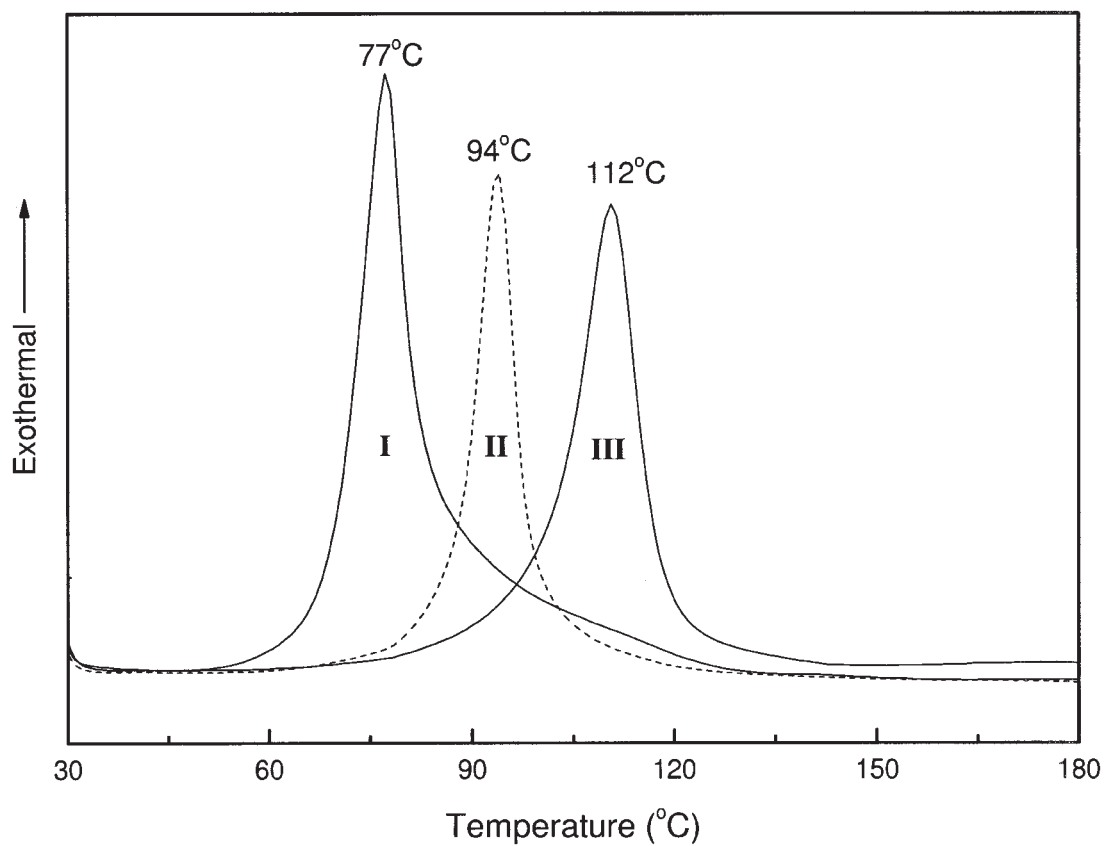


Figure 3 DSC thermograms of cationic polymerization of epoxy siloxane monomers with 0.5 wt % CP-77 catalyst.

TABLE I
Effect of CP-77 Catalyst Concentration on Cationic Polymerization of Epoxy Siloxane Monomers

Epoxy siloxane	CP-77 (wt %)	ΔH (J/g)	DSC peak	Hardness shore D	5% weight loss temperature ($^{\circ}\text{C}$)
III	None ^a	—	—	—	233
	0.05	204	115	23	281
	0.2	226	106	38	342
	0.5	268	94	48	347
	1.0	233	92	52	347
III + BHT^b	0.05	232	90	30	329
	1.0	245	83	55	374
II	None ^a	—	—	—	221
	0.05	251	110	53	314
	0.2	244	85	58	349
	0.5	220	79	66	359
	1.0	273	79	65	361
I	None ^a	—	—	—	224
	0.05	289	112	55	380
	0.2	311	101	75	382
	0.5	334	90	76	380
	1.0	340	86	72	374

Curing condition: 120 $^{\circ}\text{C}$ for 1 h and then 150 $^{\circ}\text{C}$ for 2 h.

^a Monomer.

^b 2,4-Di-*tert*-butyl hydroxyl toluene, 1.0 wt %.

epoxy equivalent weight. After thermal aging at 150 $^{\circ}\text{C}$ for 24 h, hardness increased again with low catalyst concentration. These results showed that polymeriza-

tion was not completed with low catalyst concentration and another crosslinking reaction occurred during thermal aging.

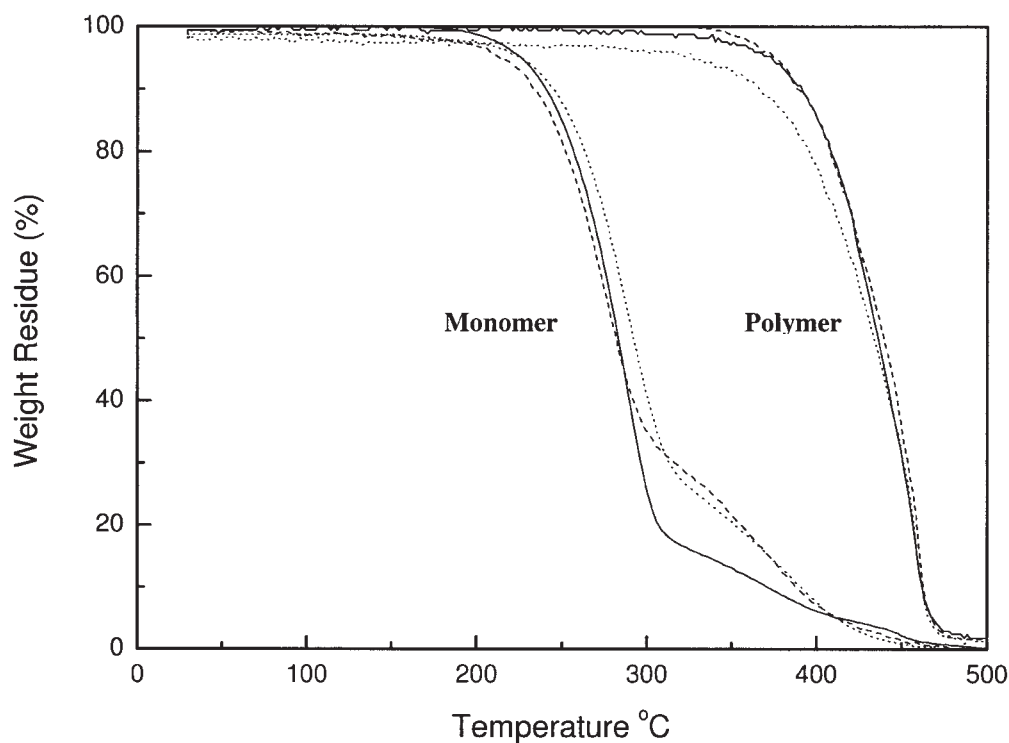


Figure 4 TGA spectrum of epoxy siloxane monomer and polymer: plain line, **I**; dash line, **II**; and dot line, **III**. CP-77 catalyst 0.5 wt %.

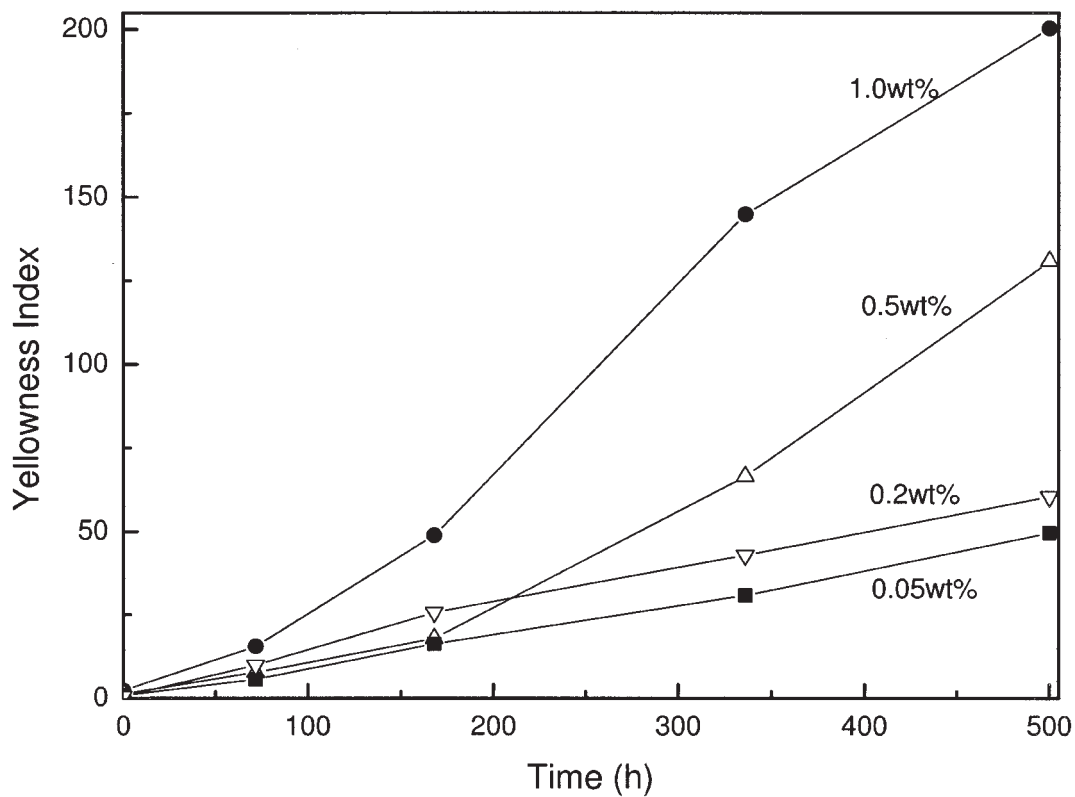


Figure 5 Effect of CP-77 catalyst concentration on yellowness index during thermal aging of epoxy siloxane I polymer. Temperature = 150°C.

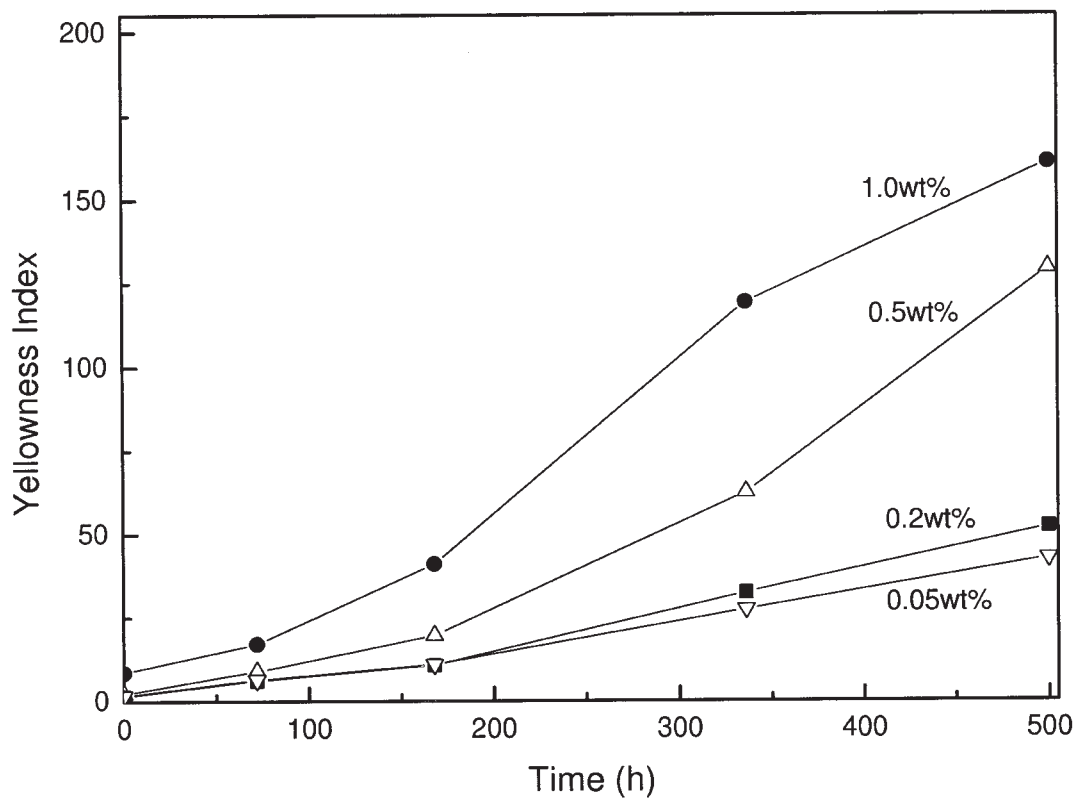


Figure 6 Effect of CP-77 catalyst concentration on yellowness index during thermal aging of epoxy siloxane II polymer. Temperature = 150°C.

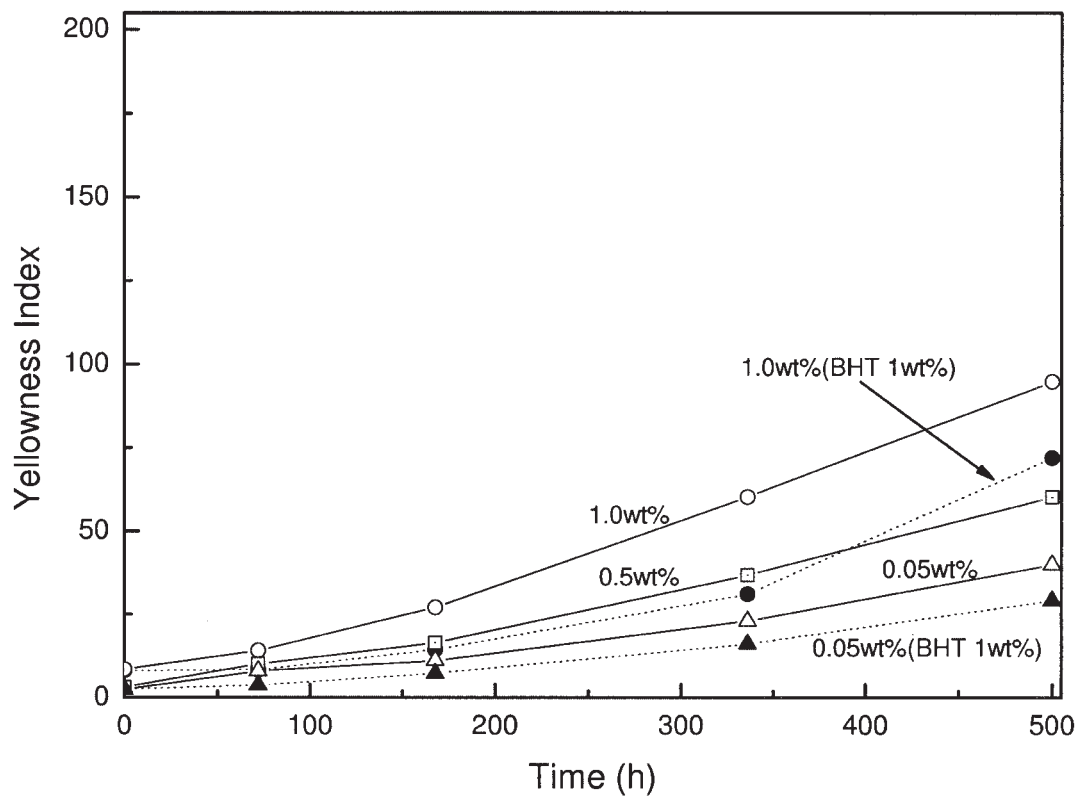


Figure 7 Effect of CP-77 catalyst concentration on yellowness index during thermal aging of epoxy siloxane III polymer. Temperature = 150°C.

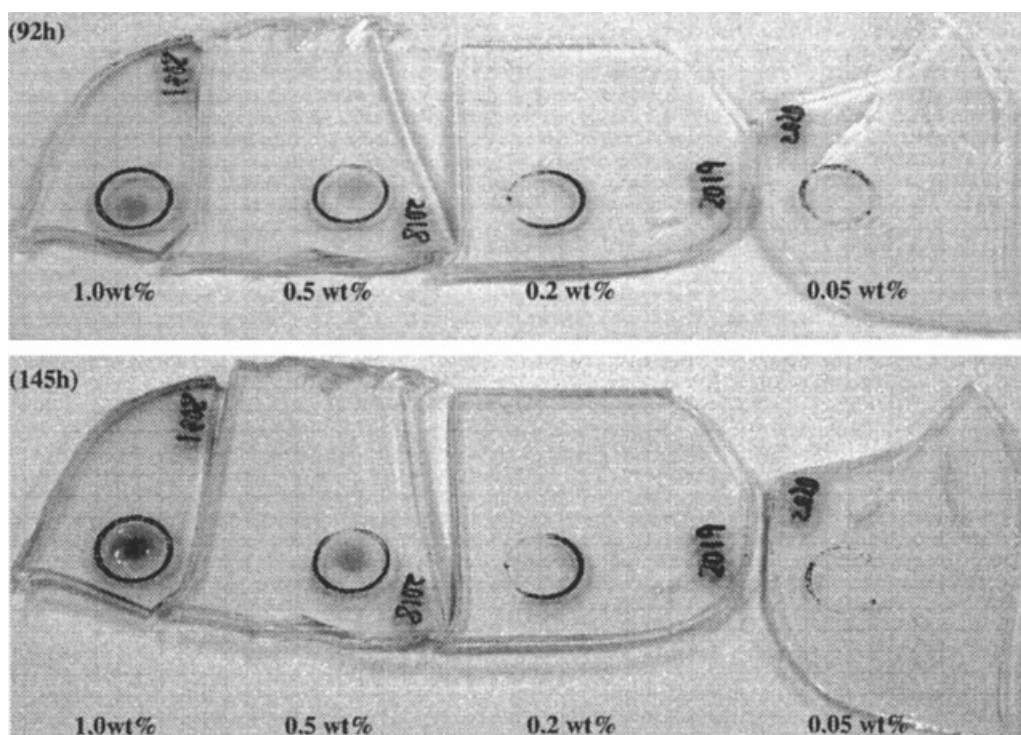


Figure 8 Discoloration behavior of epoxy siloxane polymer III with different catalyst concentration during UV irradiation.

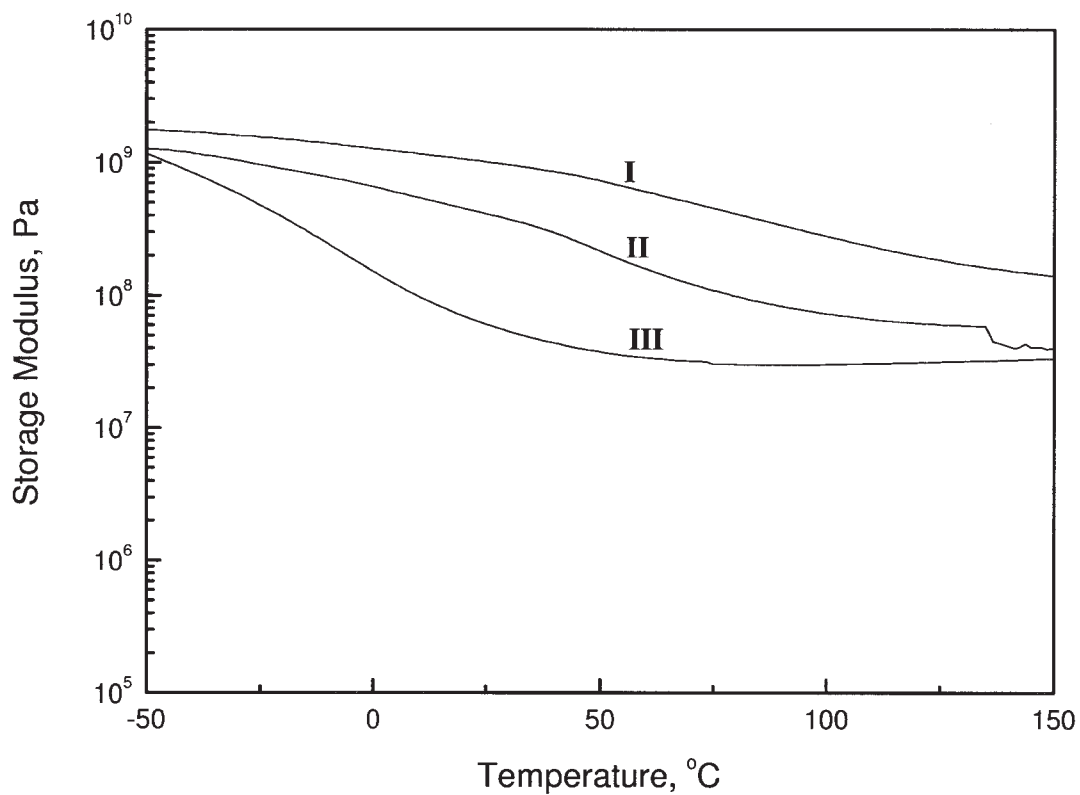


Figure 9 Storage modulus of epoxy sioxane polymers, as measured by DMA. Temperature scan rate = $4^{\circ}\text{C}/\text{min}$ in nitrogen.

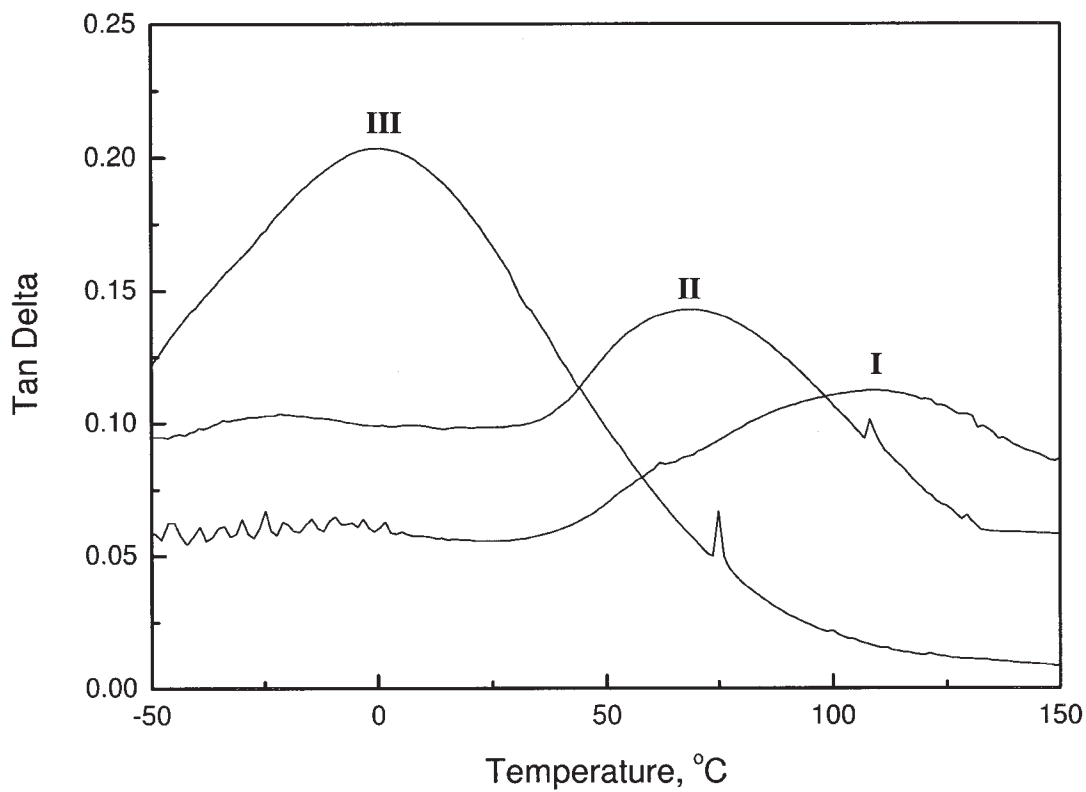


Figure 10 Tan delta plot of epoxy sioxane polymers as measured by DMA. Temperature scan rate = $4^{\circ}\text{C}/\text{min}$ in nitrogen.

TABLE II
Mechanical Properties of Epoxy Siloxane Polymers

Epoxy siloxane	CTE (ppm)		T_g (°C)		Storage modulus (Pa)	
	α_1	α_2	TMA	DMA	-40°C	120°C
I	162	207	95.6	116.1	17.0×10^8	19.8×10^7
II	187	232	74.1	75.1	11.9×10^8	6.2×10^7
III	284	274	46.1	7.2	8.4×10^8	3.1×10^7

CP-77, 0.5 wt %. Curing condition: 120°C for 1 h and then 150°C for 2 h.

Thermal stability of epoxy siloxane polymers

The TGA of both epoxy siloxane monomers and their cured polymers are shown in Figure 4. Table I summarizes the 5% weight loss temperature, which was used as an index of thermal stability. The polymers displayed excellent thermal stability and their onset of thermal decomposition appeared at ~300–350°C. The 5% weight loss temperature of monomer was under 230°C but those of polymers were 280–380°C. Thermal stability increased with increasing catalyst concentration in monomer **II** and in monomer **III**, whereas thermal stability of polymer was not changed by catalyst concentration in monomer **I**.

As mentioned earlier, curing schedule was not enough for low catalyst concentration. Insufficient polymerization would have unreacted epoxy group in the polymer and the crosslinking structure may not have been optimized.

Thermal and UV discoloration

Thermal discoloration decreased with decreasing catalyst concentration but increased again with concentrations lower than 0.2 wt %. Figures 5–7 describe the effect of yellowness index on catalyst concentration.

Initial discoloration just after curing increased with increasing catalyst concentration, and also with increasing epoxy equivalent weight. On the other hand, thermal discoloration during thermal aging increased with decreasing epoxy equivalent weight of epoxy siloxane.

To distinguish initial discoloration and thermal discoloration, we have prepared polymer of **III** with and without oxidation inhibitor. Di-*t*-butyl-hydroxytoluene (BHT) was used as oxidation inhibitor and this is effective to inhibit thermal discoloration in hydrogenated bisphenol A glycidyl ether.^{5,6}

As shown in Figure 7, initial yellowness index was constant regardless of the presence of BHT but following thermal discoloration was restrained by BHT. In general, phenolic oxidation inhibitors, such as BHT, inhibit the generation of peroxide radicals. Initial discoloration seems to be generating the chromophore from catalyst residue and phenolic oxidation inhibitor

could not work for. Thus, thermal discoloration will occur mainly in trunk polymer and this will be accelerated by catalyst residue.

Then, UV discoloration of epoxy siloxane polymer was studied. Figure 8 shows photographs of UV irradiation test of **III**, with different catalyst concentration. Oxidization took place from the surface of polymer toward an inner side. As oxidation proceeded, the encapsulant color changed from water clear to brown, and then became char. Discoloration occurred early, since catalyst concentration was high. We could not find any discoloration until 500 h in 0.02 wt % catalyst.

Mechanical property of polymers

The mechanical properties of epoxy siloxane polymers were investigated by DMA and TMA. The results of DMA analysis are shown in Figures 9 and 10. The mechanical properties of the resin will be related directly to the length of dimethyl siloxane. As the dimethyl siloxane length of monomer increases, the storage modulus of polymer has decreased very progressively. Polymer **III** displays the lowest glass-transition temperature (7.2°C), whereas the T_g 's for **II** and **I** are, respectively, 75.1°C and 116.1°C.

From TMA analysis, we found similar T_g value, as shown in Table II. Coefficient of linear thermal expansion below T_g (α_1) and above T_g (α_2) also decreased with increasing epoxy equivalent weight. In case of **I**, the obvious differences between α_1 and α_2 were observed but **III** showed almost same CTEs.

CONCLUSIONS

The three epoxy siloxane monomers with different length of dimethyl siloxanes showed good reactivity in thermal cationic polymerization and gave hard materials. The discoloration of these polymers can be reduced with decreasing catalyst concentration, epoxy tetrasiloxane shown lowest thermal discoloration. Short siloxane groups led to highly rigid, glasslike matrices, whereas longer siloxane groups produced more flexible materials with considerable elongation. Many new applications for these resins are antici-

pated, including optoelectric encapsulation. Further development of these polymers in LED device application, is now under investigation and will be reported soon.

References

1. Kornilove, Y. I.; Bereesneva, N. K. *Rus. Pat.* 202,524 (1967); *Chem Abstr* 1968, 68, 87874.
2. Pleuddemann, E. P.; Fanger, G. *J Am Chem Soc* 1959, 1, 2632.
3. Kerr, S. R. *Adhesives Age* 1996, September, 26.
4. Crivello, J. V.; Song, K. Y.; Ghoshal, R. *Chem Mater* 2001, 13, 1932.
5. Lin, E. K.; Wu, W. L.; Zhang, C. X.; Laine, R. M. In *Proceedings of the International Symposium on Advanced Packaging Materials: Processes, Properties and Interfaces, 1999*; p 63.
6. Ramirez, C.; Abad, M. J.; Barral, L.; Cano, J.; Diez, F. *J Therm Anal Cal* 2003, 72, 421.
7. Narendran, N.; Gu, Y.; Freyssiner, J. P.; Yu, H.; Deng L. *J Cryst Growth* 2004, 268, 449.
8. Morita, Y. *J Adhes Soc Jpn* 2003, 39, 410.
9. Morita, Y. *J Appl Polym Sci* 2005, 97, 1395.
10. Morita, Y. *J Appl Polym Sci* 2005, 97, 946.
11. Crivello, J. V.; Lee, J. L. *J Polym Sci Polym Chem Ed* 1990, 28, 479.
12. Jang, M.; Crivello, J. V. *J Polym Sci Polym Chem Ed* 2003, 41, 3056.
13. Fan, M.; Crivello, J. V. *J Polym Sci Polym Chem Ed* 1991, 29, 1853.