Selective preparation of oligomeric naphthylene ether and its applications to epoxy resin for silicon carbide power semiconductor device materials

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ABSTRACT: In this study, a novel method for selective synthesis of naphthylene ether trimers by self-condensation of 2,7-dihydroxynaphthalene in the presence of catalytic amount of potassium hydroxide was reported. An epoxy resin from the trimers was prepared and properties of the cured epoxy resin were examined. The cured resin showed not only good physical thermal stability, such as high glass transition temperature and low thermal expansion coefficient, but also good chemical thermal stability like high thermal decomposition temperature. Additionally, low moisture absorption of the cured resin was confirmed. From these results, the newly prepared epoxy resin with naphthylene ether skeletons was considered to be suitable for advanced applications such as silicon carbide power semiconductor device. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43339.

KEYWORDS: glass transition; synthesis and processing; thermosets; thermal properties; thermogravimetric analysis (TGA)

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INTRODUCTION

Epoxy resins are accepted as excellent thermosetting materials and have been widely used in a broad range of industrial fields such as electronics, paints, adhesives, and composite materials. Specifically, they are better suited for high-tech applications such as high-density printed circuit boards and highly integrated semiconductor packaging. In such applications, dimensional change at high temperatures has been a serious problem because such deformation causes warpage of the articles.[1] Therefore, improvement of physical thermal stability such as raise of glass transition temperature (T_g) and reduction of coefficient of thermal expansion has been required. On the other hand, recent efforts of research and development have been focused on creation of novel materials for power semiconductor devices. Especially, materials for silicon carbide (SiC) power semiconductor devices are required because the SiC power devices are expected as those for driving and controlling on-vehicle motors due to their higher operation temperature, exceeding 200°C, than that of the silicon devices.[2,3] However, as a result of this high operation temperature, the materials for the SiC devices are required to have not only good physical thermal stability but also good chemical thermal stability such as thermal decomposition temperature. To guarantee the operation of the modules for ten years, which is the expected lifetime for car applications, the epoxy resins used for these applications should have T_g of more than 200°C and thermal decomposition temperature of more than 380°C.

Bisphenol-A-type epoxy resin (E-BPA, Table I) is a popular bifunctional epoxy resin, but it cannot provide sufficiently high thermal properties because the T_g of the cured resin is as high as 136°C when the resin is cured by phenol novolac resin (see Table II) as a typical hardener in electronic applications. Even the cresol-novolac type epoxy resin (E-OCN, Table I), which is a typical multifunctional epoxy resin and the most widely used in composite applications, cannot achieve the target thermal performance, because the T_g of the E-OCN resin cured by phenol novolac does not exceed 200°C.[4–6]

On the other hand, naphthalene unit has received much attention as a key thermal-resistant chain structure because of its higher rigidity than benzene. Tri- and tetrafunctional epoxy molecules (E-3FN and E-4FN, Table I) have been prepared by reactions of 2-naphthol and/or 2,7-dihydroxynaphthalene with formaldehyde (Scheme 1) and the following epoxidation of the resultant dimeric hydroxynaphthalenes.[7,8] It is notable that only

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Table I. Structures of Epoxy Resins Used for Comparison

Name	Structure
E-BPA	
E-OCN	
E-F3N	
E-F4N	

single isomer is obtained in each reaction shown in Scheme 1.[8] Although E-3FN and E-4FN had attractive and unique structures, their cured resins did not satisfy the required thermal properties shown above. E-4FN could provide the cured resins with T_gs of more than 230°C, but it had poor chemical thermal stability due to its methylene linkage between naphthalene rings. Therefore, it is difficult to use the cured resins composed of E-4FN to applications which require high thermal durability for a long time.

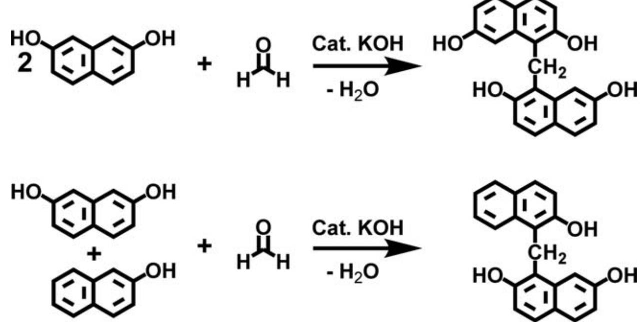
The aim of the present study is to develop a novel high performance epoxy resin possessing excellent physical and chemical thermal stabilities at the same time. In order to achieve this target, we have adopted the following three strategies.

1. Introduction of polyaromatic groups in the main chain to increase main-chain rigidity and chemical thermal stability.
2. Introduction of aromatic ether bonds instead of easily degradable methylene linkages.[9]
3. Decrease in molecular weight and molecular weight distribution to decrease viscosity of the resin.

We conceived "oligomeric naphthylene ether (ONE)" as a molecular design satisfying the above three strategies. In principle, naphthylene ether oligomers can be prepared by dehydra-

Table II. Structures of Hardeners Used in this Study

Name	Structure
Hardener A: Phenol novolac resin	
Hardener B: 2-Ethyl-4-methylimidazole	



Scheme 1. Synthetic schemes of dimeric naphthols.

tion condensation of dihydroxynaphthalenes or oxidative coupling of hydroxynaphthalenes. However, the products prepared by these reactions are known to have a serious problem of increasing viscosity due to formation of higher molecular weight compounds, and therefore, these products cannot be applied to transfer molding, which is utilized for sealing of IC chips.[10]

For the condensation between 2,7-dihydroxynaphthalene (2,7-DHN) and formaldehyde, it is reported that the use of alkaline catalyst leads to selective formation the 2:1 product (Scheme 1).[8] Therefore, inspired by this reaction, we prepared ONE by alkaline-catalyzed self-condensation of dihydroxynaphthalenes. Herein, we report successful synthesis of the ONE from 2,7-DHN, preparation of the epoxidized ONE (E-ONE) and properties of the cured resin prepared from E-ONE.

EXPERIMENTS

Materials

Materials Used for Synthesis. 2,7-Dihydroxynaphthalene (2,7-DHN, Sugai Chemical Co.), 1,6-dihydroxynaphthalene (1,6-DHN, Sugai Chemical Co.), benzyl alcohol (INEOS ChlorVinyls), *N*-methylpyrrolidone (99%) (NMP, Kanto Chemical Co.), 48% potassium hydroxide aqueous solution (Asahi Glass Co.), sodium dihydrogenphosphate (anhydrous) (Yoneyama Chemical Industry Co.), epichlorohydrin (ECH, Daiso Co.), 48% sodium hydroxide aqueous solution (Asahi Kasei Co.), isopropyl alcohol (IPA, Tokuyama Co.), and 4-methyl-2-pentanone (MIBK, Shell Chemicals Co.) were used without purification.

Materials Used for Preparation of the Cured Resins. The structures of the hardener and catalyst used in this study were shown in Table II. Phenol novolac resin (DIC Co., PHENOLITE TD-2131) was adopted as a curing agent for the epoxy resins. Triphenylphosphine (TPP, Hokko Chemical Industry Co.) was used as a curing accelerator for the novolac-type hardener. As an initiator for homopolymerization of the epoxy resins, 2-ethyl-4-methylimidazole (2E4MZ, Shikoku Chemicals Co.) was used. As control epoxy resins, E-OCN [DIC Co., EPICLON N-695, epoxy equivalent weight (EEW): 214 g/equiv.], E-3FN (DIC Co., EPICLON EXA-4750, EEW: 188 g/equiv.), E-4FN (DIC Co., EPICLON HP-4700, EEW: 166 g/equiv.), and E-BPA (DIC Co., EPICLON 850-S, EEW: 188 g/equiv.) were used. The structures of these resins were shown in Table I.

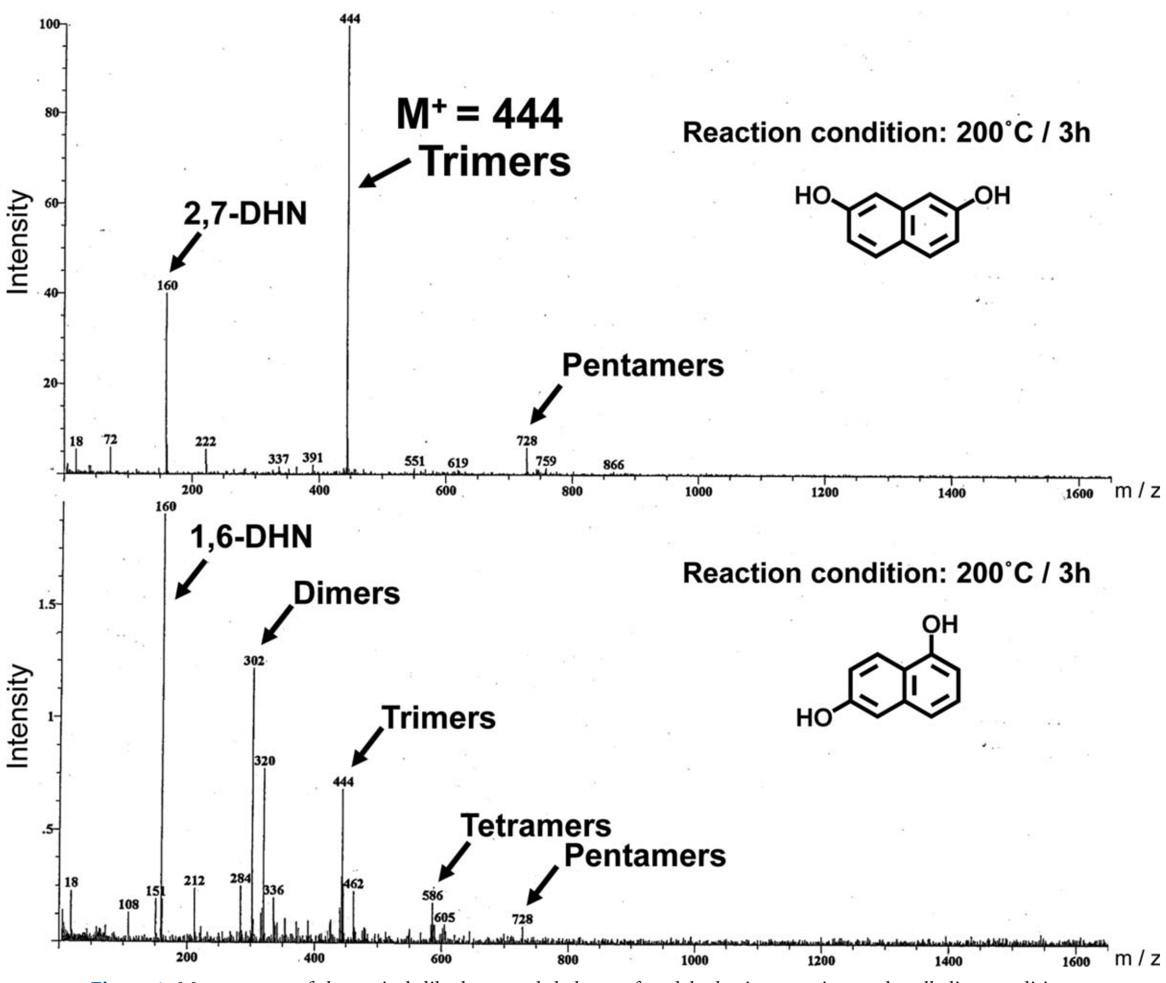


Figure 1. Mass spectra of the typical dihydroxynaphthalenes after dehydration reaction under alkaline condition.

Characterization. The molecular structures of the synthesized ONEs were characterized by field desorption mass spectroscopy (FD-MS) (JEOL Ltd., AX505H or JMS-T100GC "AccuTOF-GC," ion source; FD mode, emitter current; 20 mA), Fourier transform infrared (FT-IR) spectroscopy (JASCO Co., FT/IR-660Plus, KBr method), ^{13}C-NMR spectroscopy (JEOL Ltd., JNM FX-200, solvent; DMSO-d_6), and gel permeation chromatography (GPC) (TOSOH, HPLC-8020, column; TSK_{gel} $G2000H_{XL} + G2000H_{XL} + G3000H_{XL} + G4000H_{XL}$, solvent; THF, detector; RI). Hydroxyl group contents of the synthesized ONEs were measured as hydroxyl equivalent weight by acetylating the hydroxyl groups. The acetylation was carried out by using excess amount of acetic anhydride, and the amount acetic anhydride remaining after acetylation was measured by neutralization titration. Epoxy group contents of the synthesized epoxy resins were measured as EEW according to JIS K7236. Softening point of the resins was measured by the ring and ball method (JIS K7234).

Synthesis

Evaluation of the Effect of the Dihydroxynaphthalene Structures on Degree of Polymerization. In a flask equipped with a thermometer, a dropping funnel, a Dean–Stark trap with condenser, a nitrogen inlet and an agitator, 16 g (0.1 mol) of 2,7-DHN or 1,6-DHN was placed and heated at 200°C with stirring in a nitrogen gas flow. After DHN was melted, 2.3 g (0.02 mol) of 48% potassium hydroxide aqueous solution was added at 200°C. Then, the reaction was continued for 3 hours with removing the water through the Dean–Stark trap and then cooled to room temperature to give a dark-brown solid. The products obtained from 2,7-DHN and 1,6-DHN were characterized by FD-MS (Figure 1).

Synthesis of ONE. In a flask equipped with a thermometer, a dropping funnel, a Dean–Stark trap with condenser, a nitrogen inlet and an agitator, 160 g (1.0 mol) of 2,7-DHN and 100 g of benzyl alcohol as a solvent were placed and heated at 200°C with stirring in a nitrogen gas flow. After 2,7-DHN was dissolved, 23.3 g (0.2 mol) of 48% potassium hydroxide aqueous solution was added dropwise for 1 hour at 200°C. Then, the reaction was continued for 20 hours with removing the water through the Dean–Stark trap. After the reaction was terminated, 10% sodium hydroxide aqueous solution was added to the solution and then filtered. The filtrate was neutralized by anhydrous sodium dihydrogenphosphate and poured into water to give a dark brown solid. The solid was finally dried to obtain 140.1 g of the product (ONE). Hydroxyl equivalent weight: 161 g/equiv., melting point: 311°C. ^{13}C-NMR (in DMSO-d_6, ppm): δ

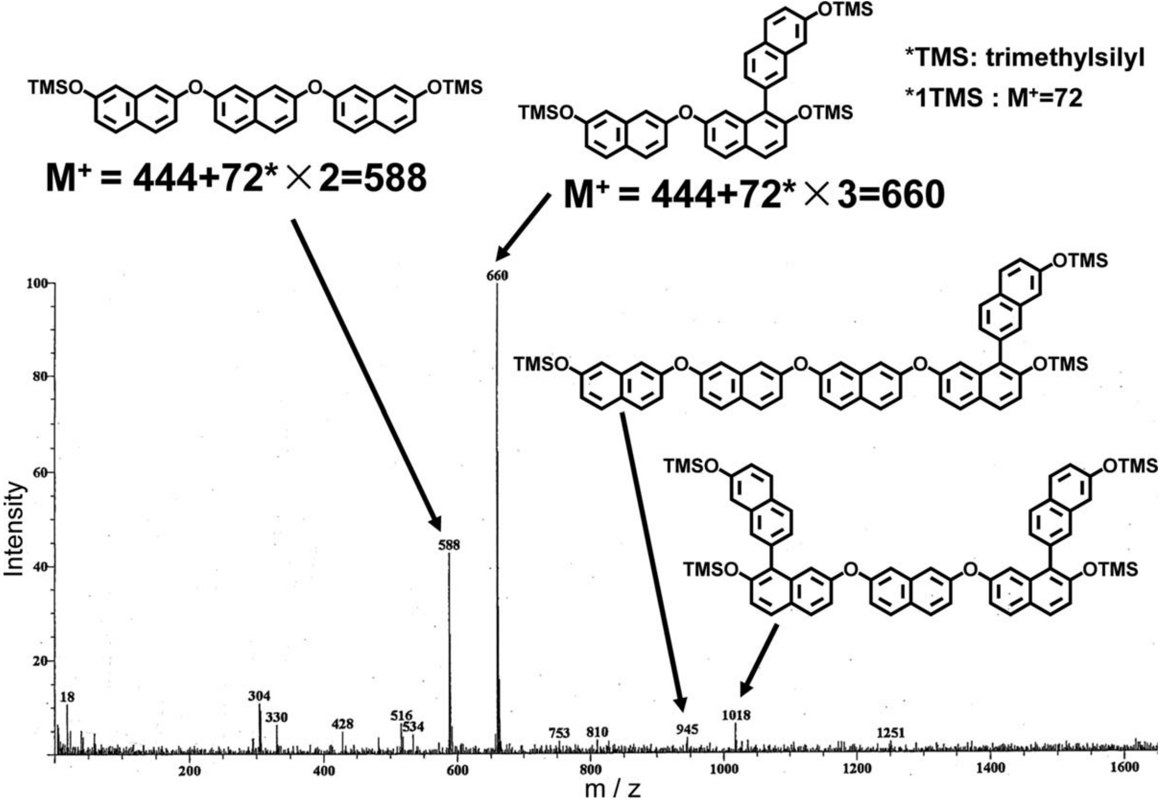
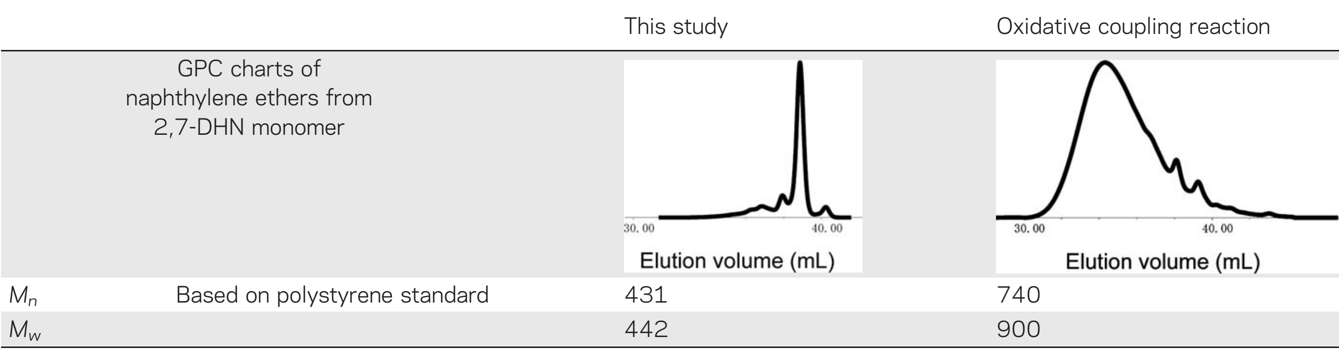


Figure 2. Mass spectrum of trimethylsilylated ONE.

154.9, 151.4, 150.3, 136.5, 135.8, 132.1, 130.9, 129.1, 128.7, 128.4, 127.2, 125.8, 124.9, 122.3, 119.3, 118.3, 115.5, 114.8, 114.1, 112.8, 117.4, 106.9. FT-IR (KBr, cm^{-1}): 3494, 3270-3425, 1618, 1515, 1445, 1369, 1246, 865, 834.

Synthesis of Epoxy Resin (E-ONE) from ONE. In a four-necked flask equipped with an agitator, a nitrogen inlet, a thermometer and a dropping funnel, 80.5 g of ONE (OH: 0.5 mol) was dissolved in 185.0 g (2.0 mol) of ECH, and 50.0 g (0.6 mol) of 48% sodium hydroxide aqueous solution was added dropwise over 5 hours at 60°C with stirring. After keeping the mixture at 60°C for 1 hour, 70.0 g of water was added and the system was vigorously stirred. Then, the aqueous phase was separated and the residual organic phase was distilled to remove the excess ECH. The residue was dissolved in 220 g of MIBK and the solution was washed with 70 g of water. The water phase was then separated and the residual water in the organic phase was removed though azeotropic distillation. After removal of the insoluble residue by filtration, MIBK was removed by distillation to give 103.0 g of the target epoxy resin (E-ONE). EEW: 247 g/equiv., softening point 104°C. FT-IR (KBr, cm^{-1}): 3413, 3057, 2997, 2923, 2874, 1619, 1515, 1442, 1388, 1245, 1031, 912, 859, 831.

Table III. GPC Charts of the Naphthylene Ethers Prepared by the Method in this Study and Oxidative Coupling Reaction



		This study	Oxidative coupling reaction
GPC charts of naphthylene ethers from 2,7-DHN monomer		30.00 40.00 Elution volume (mL)	30.00 40.00 Elution volume (mL)
M_n	Based on polystyrene standard	431	740
M_w		442	900

GPC: TOSOH HLC-8220, Columns: TSK_{gel} $G2000H_{XL}$ + $G2000H_{XL}$ + $G3000H_{XL}$ + $G4000H_{XL}$ Solvent: THF, Flow rate: 1 mL/min, Detector: RI.

Scheme 2. Synthetic scheme of the ONE.

Preparation of the Cured Resins. In the case using phenol novolac resin as a curing agent, an epoxy resin and the phenol novolac resin were mixed at 140°C with the equivalent ratio of 1:1. To the resulting homogeneous mixture, 1.0 wt % of TPP was added. The mixture was then cured at 150°C for 10 min, followed by postcuring at 175°C for 5 hours. In the case using 1.0 wt % of 2E4MZ as an initiator, an epoxy resin was melted at 130°C and 2E4MZ was added. The mixture was then cured at 150°C for 10 min followed by postcuring at 175°C for 5 hours.

Evaluation of the Cured Resins. Physical thermal stability of the cured resins were evaluated by measuring T_g and cross-linking density using dynamic mechanical analysis (DMA, Rheometric Ltd., RSA-2, tensile mode, frequency; 1 Hz, heating rate; 3°C/min under air). T_g was determined as the maximum point on the tanδ curve. Cross-linking density was determined from the storage modulus at $T_g + 40$°C according to the theory of rubber elasticity.[11] A coefficient of thermal expansion (α_1, from 60°C to 80°C) was evaluated by thermal mechanical analysis (TMA, Hitachi High-Tech Science, TMA/SS 6100, compression mode, heating rate; 3°C/min under N_2). Chemical thermal stability was evaluated by measuring 5% weight loss temperature (T_{d5}) using thermogravimetry analyzer (TGA, Mettler–Toledo International Inc., TGA/DSC1, heating rate; 5°C/min, under N_2) in accordance with IPC-TM-650 method. Moisture absorption was evaluated by a weight increase ratio of test pieces (size; 75 mm × 25 mm × 2.5 mm) at 85°C and 85% relative humidity for 300 hours.

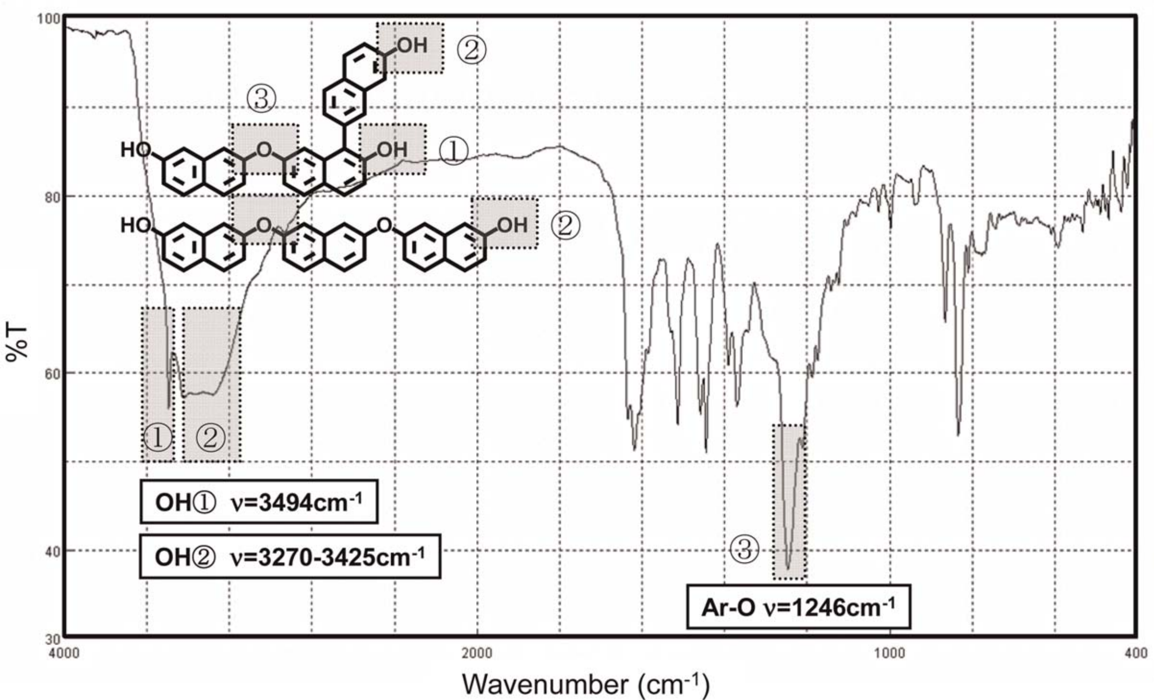


Figure 3. FT-IR spectrum of ONE.

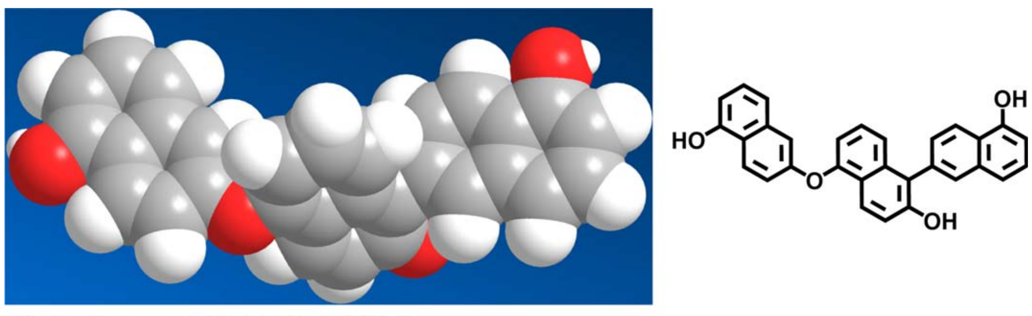
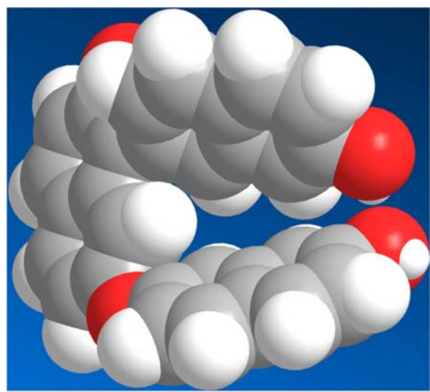


Figure 4. Space-filling model of the most stable trimer of 1,6-DHN. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Calculation : B3LYP/6-31G(d)

Figure 5. Space-filling model of the most stable trimer of 2.7-DHN. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

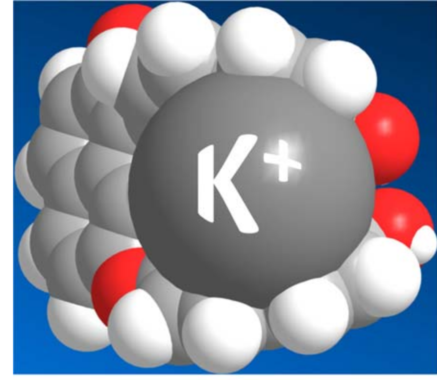
Effect of the Dihydroxynaphthalene Structures on Degree of Polymerization of the Oligomers

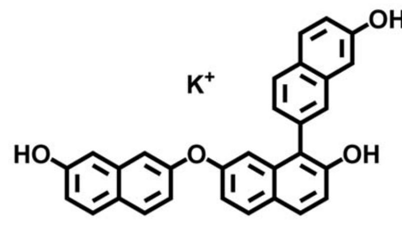
Difference of degree of polymerization between the oligomers prepared from 2,7-DHN and 1,6-DHN under alkaline condition was examined by FD-MS (Figure 1). As a result, when 2,7-DHN was used as the starting material, a large peak corresponding to the trimers having a molecular weight of 444 was detected with very small peak of the pentamers. On the other hand, when 1,6-DHN was used as the starting material, peaks corresponding to dimers, trimers, tetramers, and pentamers were sequentially detected. These results confirmed that the trimers were selectively formed only when the dehydration reactions were started from 2,7-DHN under the alkaline condition.

Synthesis and Characterization of ONE

On the basis of the results obtained in the previous section, ONE was prepared from 2,7-DHN under alkaline condition. Here, benzyl alcohol was used as a solvent to keep liquidity of the system even after the condensation proceeded. The FD-MS spectrum of the obtained ONE showed a remarkably large peak with the molecular weight of 444, which corresponded to the trimers (Figure S1, Supporting Information). Although the prepared ONE contained few compounds larger than pentamers, we call it "oligomeric" naphthylene ether because it was a mixture composed of different kinds of trimers and pentamers (see Figure 2). GPC chart of ONE also revealed that the molecular weight was around 440 with narrow molecular weight distribution (Table III). According to the previously reported oxidative coupling reactions, the weight-average molecular weights of the obtained naphthylene ethers were approximately 3000–10,000.[12,13] Even when 2,7-DHN was used as the starting material, enzymatic oxidative coupling in an aqueous medium resulted in formation of the oligomer with the molecular weight of 500–1000 (see Table III),[14] and the epoxy resin synthesized from this compound did not show sufficient fluidity for molding even at temperatures as high as 150°C–200°C. Therefore, the epoxy resin prepared from ONE is expected to show good processability due to its low viscosity derived from low molecular weight and molecular weight distribution.

The FD-MS spectrum of the trimethylsilylated ONE confirmed the presence of the trimer having three hydroxyl groups in addition to that with two hydroxyl groups (Figure 2). Additionally, an absorption corresponding to a hydroxyl group under large steric hindrance was detected at 3494 cm^{-1} in the FT-IR spectrum (Figure 3). These results suggest that ONE is a mixture of the compounds having naphthylene ether structures and/or





Calculation : B3LYP/6-31G(d)

Figure 6. Space-filling model of the most stable structure of 2,7-DHN trimer/K^+. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

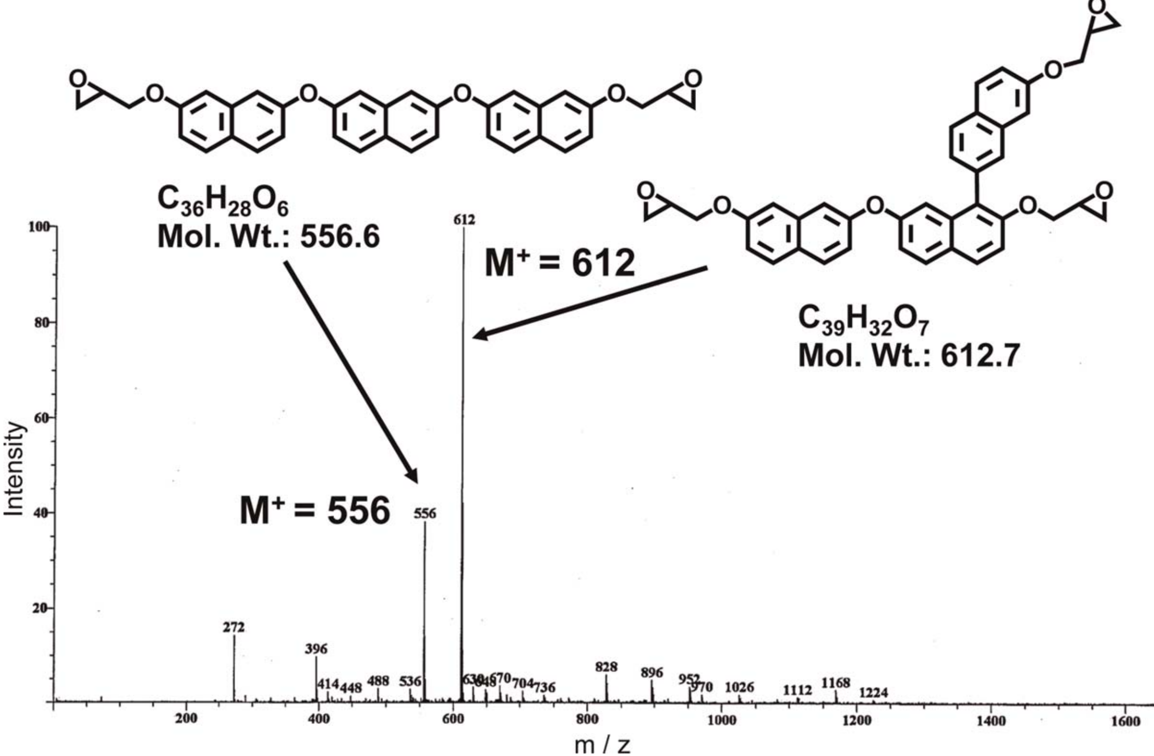


Figure 7. Mass spectrum of the E-ONE.

directly connected naphthalene nuclei (Scheme 2). Although the ratio between the naphthylene ether structure and naphthalene–naphthalene nuclei in ONE is unclear, comparison of the hydroxyl equivalent weight of ONE with the intensity ratio of the peaks in the FD-MS spectrum (Figure 2) indicated that the ratio is approximately 1:2, and from this ratio, the average number of functional groups in ONE is calculated to be 2.7. The dehydration reaction of 2,7-DHN was also carried out in the absence of the catalyst and in the presence of the increased amount (60 mol %) of KOH, but no reactions proceeded in both systems. In addition, no progress of the reaction was observed in the reaction using *N*-methylpyrrolidone as an aprotic polar solvent.

From these results, it is revealed that the selective formation of the trimers is accomplished only when 2,7-DHN was reacted under a catalytic amount of potassium hydroxide in a polar protic solvent. The reaction mechanism has yet to be fully elucidated, but judging from the result that the reaction proceeded only in protic solvent, donation of proton from the solvent and/or stabilization of anions generated in the reaction intermediates by the solvent are likely to be involved in the reaction mechanism. Furthermore, as shown in Figure 1, the trimers of 2,7-DHN are considered to be thermodynamically most stable, while such specific stability of the trimers was not observed in the reaction products from 1,6-DHN.

In order to clarify the reason for the stability of the 2,7-DHN trimers, we have optimized the structures of all the trimers of 1,6-DHN and 2,7-DHN by density functional theory (DFT) calculation at the B3LYP/3-31G(d) level using Gaussian 09 package. Space-filling models of the optimized structures for 1,6-DHN trimer and 2.7-DHN trimer are shown in Figures 4 and 5, respectively. It was revealed that the 2,7-DHN trimer was stabilized by 4.1 kcal/mol when compared with the 1,6-DHN trimer due to the presence of the hydrogen bond between the terminal hydroxyl groups of which the distance was 2.0 Å. The effect of the addition of potassium ion on the selectivity of the

Table IV. Differences in Physical and Chemical Thermal Stabilities and Cross-Linking Density between E-ONE and Other Epoxy Resins

Test items	Remarks	Hardener	E-ONE	E-BPA	E-OCN	E-3FN	E-4FN
Glass transition temperature	DMA[a] (°C)	A	221	136	183	200	236
		B	315	183	191	292	326
5% weight loss temperature (N_2)	TGA[b] (°C)	A	394	389	372	373	379
5% weight loss temperature (Air)	TGA[b] (°C)	A	398	394	382	384	384
Cross-linking density	(mmol/mL)	A	2.1	1.9	8.2	5.1	8.9

[a] DMA: Heating rate: 3°C/min, frequency: 1 Hz, under air.
TGA: Heating rate: 5°C/min, under N_2 or air, 100 mL/min.

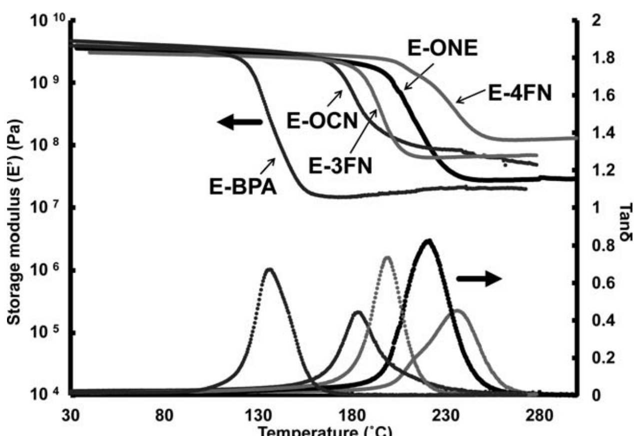


Figure 8. DMA charts of E-ONE and other epoxy resins cured by the hardener A.

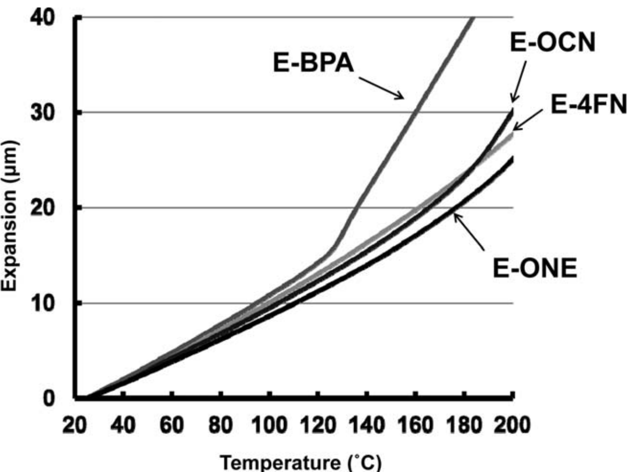


Figure 9. TMA charts of E-ONE and other epoxy resins cured by the hardener A.

reaction was also examined by DFT calculation. Space-filling model of the most stable structure of the system composed of the 2,7-DHN trimer and potassium ion was depicted in Figure 6. As a result of the calculation, it was revealed that the inclusion of the potassium ion by the 2,7-DHN trimer stabilized the system by 10.5 kcal/mol when compared with the 2,7-DHN trimer itself.

Synthesis of the Epoxy Resin (E-ONE) from ONE

The epoxy groups were introduced to ONE by the reaction with ECH in the presence of NaOH. The absorption corresponding to the epoxy group was detected at 912 cm^{-1} in the FT-IR spectrum of the product (Figure S2, Supporting Information). Typical chemical structures and FD-MS spectrum of the obtained epoxy resin were shown in Figure 7. The FD-MS spectrum indicated the main components of E-ONE was derived from trimeric naphthylene ethers. E-ONE was found to be soluble in conventional solvents like ethyl methyl ketone. E-ONE showed melt viscosity of 3 Pa s at 150°C, while the epoxy resin prepared from naphthylene ether oligomer with the molecular weight of 500–1000 (see Table III) did not melt even at temperatures of 150°C–200°C.

Thermal Properties of the Cured Epoxy Resin (E-ONE)

We used T_g as an indicator of physical thermal stability and the T_gs measured by DMA were shown in Table IV. The DMA charts were also shown in Figure 8. The T_g of E-ONE cured by the hardener A (phenol novolac) was 85°C and 38°C higher than those of the commonly-used E-BPA and E-OCN cured by the same hardener, respectively. Comparison of the T_g of E-ONE cured by the hardener A with those of the existing naphthalene-type epoxy resins revealed that E-ONE showed 21°C higher T_g than E-3FN, even though both epoxy resins contain the trifunctional epoxy compounds as the main component.

Cross-linking densities of the epoxy resins cured by the hardener A were calculated from the DMA charts[11] and shown in Table IV. As shown in the table, T_g of the cured epoxy resins is usually positively correlated with their cross-linking density. However, E-ONE showed very high T_g despite its low cross-linking density. For example, as mentioned above, T_g of E-ONE cured by the hardener A was 38°C higher than that of E-OCN, but cross-linking density of the cured E-ONE was about one fourth of that of E-OCN. In addition, the difference in T_g between E-ONE and E-4FN was only about 15°C while E-4FN had 4.2-fold higher cross-linking density than E-ONE. Such a high T_g of the cured E-ONE in spite of its low cross-linking density is attributed to the molecular structure of E-ONE, that is, the rigidity provided by the directly bonded naphthalene nuclei and naphthylene ether structures. High physical thermal stability of these structures was also evidenced by the high T_g exceeding 300°C of the self-polymerized E-ONE with 2E4MZ (= hardener B) as an initiator (Table IV and Figure S3, Supporting Information).

Thermal expansion coefficient ($\alpha 1$) at temperatures below T_g was measured by TMA as another indicator of physical thermal stability (Figure 9) and the results were shown in Table V. The thermal expansion coefficient of E-ONE was 17%–27% lower than those of other epoxy resins examined in this study. It has been reported that the cured epoxy resins having naphthalene skeletons had low thermal expansion coefficients due to the increased packing density of the polymer chains induced by π–π

Table V. Differences in Moisture Absorption and Thermal Expansion between E-ONE and Other Epoxy Resins

Test items	Remarks	Hardener	E-ONE	E-BPA	E-OCN	E-4FN
Moisture absorption	85°C/85%RH, 300 h (%)	A	1.3	1.4	1.6	2.3
Coefficient of thermal expansion	TMA[a], $\alpha 1$ (ppm)	A	49	67	59	60

[a] Range: 60°C–80°C, Load: 88.8 mN, Heating rate: 3°C/min, under N_2, 250 mL/min.

Scheme 3. Typical thermal decomposition mechanism of cured epoxy resin.

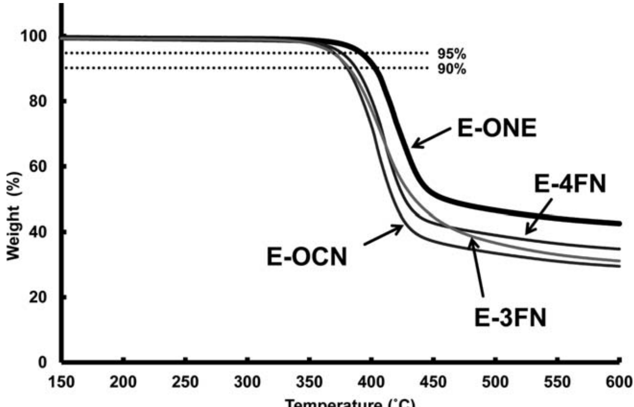


Figure 10. TGA charts of E-ONE and other epoxy resins cured by the hardener A.

stacking of the polycyclic aromatics.[15,16] Similarly, the low thermal expansion coefficient of E-ONE would be attributed to the stacking effect of its naphthalene skeletons in the main chain. On the other hand, E-4FN, which also has naphthalene rings, showed high thermal expansion coefficient. The long distance between epoxy groups of E-ONE resulted in low cross-linking density of 2.1 mmol/mL of the cured resin (Table IV). Therefore, the distances between the cross-linked points of the cured E-ONE were also long and this increased motility of the polymer chains to facilitate the π–π stacking of the naphthylene groups. On the other hand, the cured E-4FN showed high cross-linking density of 8.9 mmol/mL (Table IV) and this means that the distances between cross-linked points were short. Thus, the motion of the polymer chains in the cured E-4FN were restricted by the cross-linking points and this inhibited the π–π stacking of the naphthylene groups.

We used 5% weight loss temperature (T_{d5}) obtained by TGA measurement as an indicator of chemical thermal stability. The TGA charts and the values of T_{d5}s in N_2 and air were shown in Figure 10 and Table IV, respectively. T_{d5}s of E-ONE were the highest among the epoxy resins examined in this study, suggesting that E-ONE has high chemical thermal stability. When chemical thermal stability of cured epoxy resins is considered from their molecular structures, the structures that firstly decompose would be the aliphatic ether moieties derived from the glycidyl groups and the methylene moieties in the novolac structure (Scheme 3).[17] This degradation mechanism is also supported by the recent study based on DFT calculation.[18] Therefore, in the cases that physical thermal stability like T_g is increased by increasing cross-linking density, though it is a common technique to increase T_g, chemical thermal stability is usually decreased due to the increase in the concentration of aliphatic ethers generated from the glycidyl ether groups.[19] On the other hand, as mentioned above, E-ONE can achieve high T_g without increasing cross-linking density. This means that the cured E-ONE has smaller amount of aliphatic ether moieties, and therefore, chemical thermal stability of the cured E-ONE can be improved without sacrificing its physical thermal stability.

Various commercially available epoxy resins shown in Table I and Figure 11 were cured with the hardener A according to the same procedure as the curing of E-ONE, and the concentrations of aliphatic ethers generated during the cross-linking reactions were calculated from the equivalent compounding ratio between the epoxy resins and hardener A. The relationship between the calculated concentrations and T_{d5} is illustrated in Figure 12. This figure demonstrates that T_{d5} of the epoxy resins is generally decreased with increasing concentration of aliphatic ether moieties. However, in the cases of the cured resins from E-3FN, E-OCNs, and E-TMBP, the decreases in chemical thermal stability are larger than those expected from the amounts of the aliphatic ether moieties. These results would be due to the presence of an easily degradable methylene bond (E-3FN) or methyl groups attached to the phenol nuclei (E-OCNs and E-

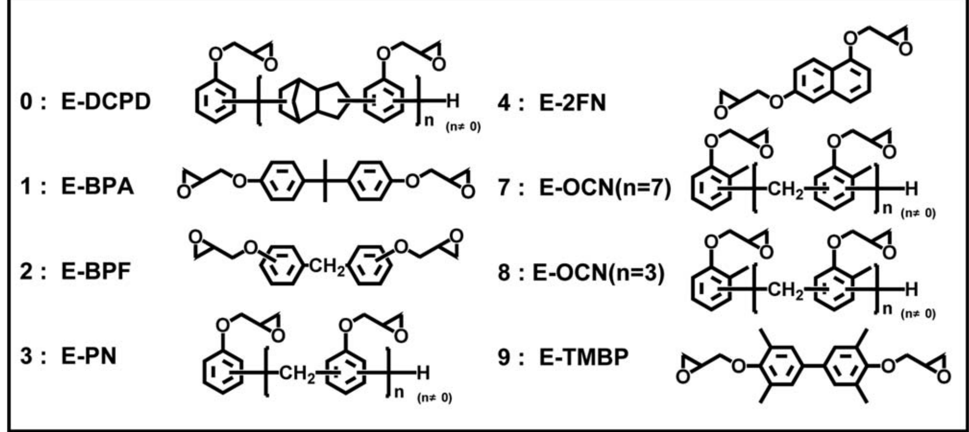


Figure 11. Chemical structures of epoxy resins used for evaluation of 5% weight loss temperature.

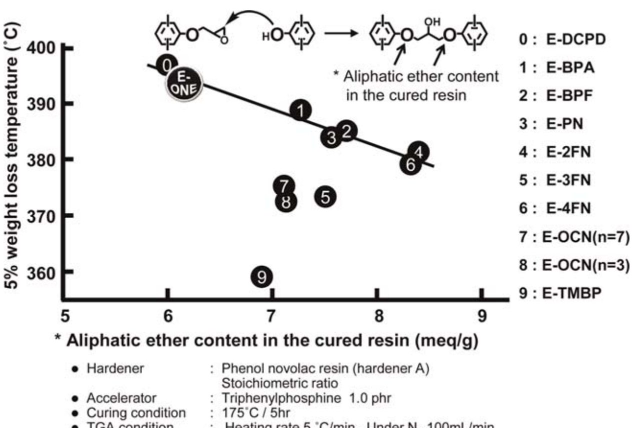


Figure 12. Relationship between the aliphatic ether contents and 5% weight loss temperatures for the cured epoxy resins.

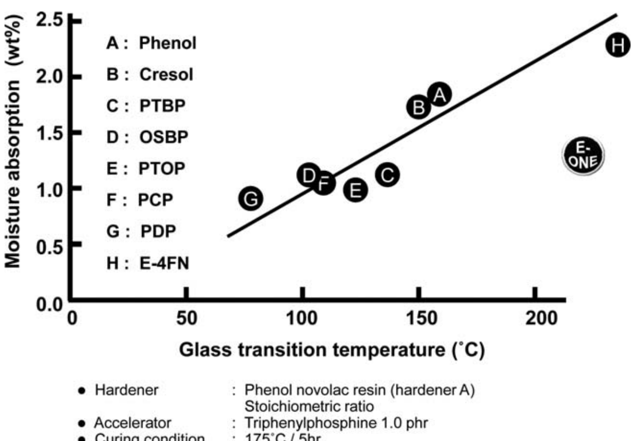


Figure 14. Relationship between moisture absorption and T_g of the cured epoxy resins including E-ONE, E-4FN, and phenol-novolac-type resins.

TMBP). In contrast, the cured E-ONE exhibits very high chemical thermal stability because the skeleton of E-ONE consists of only directly bonded naphthalene rings and aromatic ethers that are robust to thermal decomposition.

Moisture Absorption Property of the Cured E-ONE

Low moisture absorption is one of the important properties for the cured epoxy resin used for electric and electronic applications. The degrees of saturated moisture absorption of the cured epoxy resins after being left for 300 h at 85°C and 85% humidity were shown in Table V, and the moisture absorption of the cured E-ONE was found to be smaller than those of the corresponding cured E-BPA, EOCN, and E-4FN. For further elucidation of the relationship between moisture absorption and molecular structure of epoxy resins, the phenol-novolac-type epoxy resins with various alkyl groups (Figure 13) were cured with the hardener A in the same condition as the curing reaction of E-ONE, and the relationship between their T_gs and degrees of saturated moisture absorption is illustrated in Figure 14. In the cured resins other than E-ONE, the degree of moisture absorption is found to be proportional to T_g, probably because T_gs of these resins are increased by increasing cross-linking density which leads to increasing polar group concentration. This relationship may also be explained from the free volume theory reported in the previous studies.[20,21] However, moisture absorption of the cured E-ONE showed different tendency from other resins because high T_g of the cured E-ONE is derived not from its cross-linking density but from its rigid main-chain structure.

CONCLUSIONS

The dehydration condensations of dihydroxynaphthalenes under alkaline condition revealed that the reaction from 2,7-DHN selectively gave the trimeric products, though that from 1,6-DHN resulted in formation of various oligomers. On the basis of these results, ONE which consists largely of the trimers was successfully prepared. The epoxy resin, E-ONE, obtained by the epoxidation of ONE had good processability and its cured resins showed not only good physical thermal stability, such as high T_g and low thermal expansion coefficient, but also good chemical thermal stability like high thermal decomposition

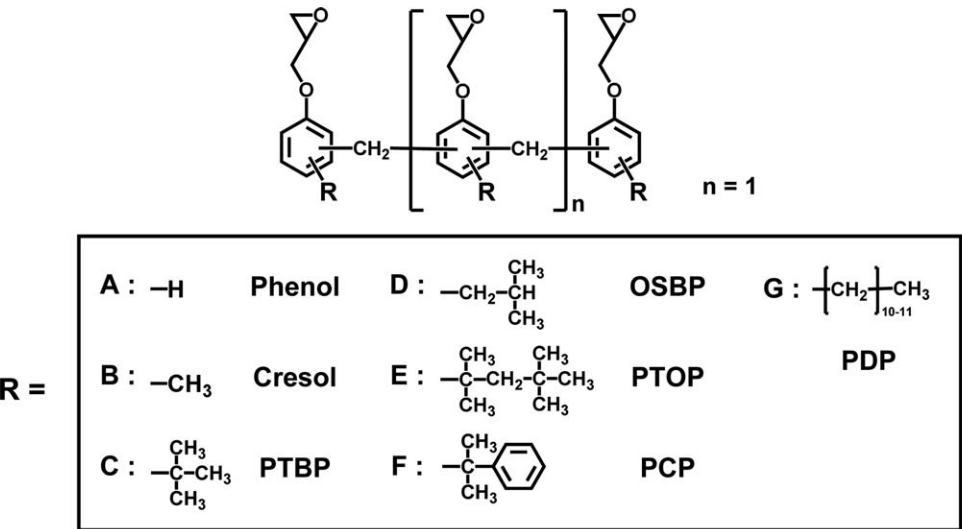


Figure 13. Chemical structures of phenol-novolac-type epoxy resins with various alkyl groups used for evaluation of moisture absorption Ref. 22.

temperature. The maximum T_g and T_{d5} achieved by the cured resins from the E-ONE were 315°C and 394°C, respectively. The excellent thermal stability could be attributed to the molecular structure of E-ONE, that is, the naphthylene ether structure and the structure in which naphthalene nuclei are directly bonded. Additionally, good solubility of E-ONE in conventional solvents and low moisture absorption of the cured E-ONE were also confirmed. From these results, E-ONE as the novel epoxy resin with naphthylene ether skeletons is considered to be suitable for advanced applications such as SiC power semiconductor device. The studies to prepare composite materials using E-ONE for the advanced semiconductor devices are in progress.

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