

Preparation and Properties of Calix[4]arene-Based Epoxy Resins

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Introduction

Calix[4]arene macrocycles are the subject for increasing interest in the field of supramolecular chemistry and host-guest chemistry as basic skeletons for the synthesis of host compounds for ions or neutral molecules.¹⁻³ Although quite a large number of reports exists on the molecular calix[4]arenes, those on polymeric precursors are limited.⁴⁻¹² Recently, calix[4]arene-based polymers have just begun to receive attention, as these new polymers may then be processed into materials suitable for the chemical sensor devices such as ion selective electrodes and filtration/extraction membranes.^{13,14}

There is some structural analogy between polymeric linear phenolic novolak molecules and calixarenes which could also be called 'cyclic phenol resin'. Thus it seems promising to further enhance the sensitivity of calixarene derivatives by applying various techniques, which are generally used to reduce the required dose of commonly used novolak resin.¹⁵⁻¹⁹ Up to now, this method has not been applied to the non polymeric class of calixarenes. In the microelectronic process, the smallest obtainable structure size as well as the line edge roughness is strongly influenced by the size of the typical novolak based polymeric resist molecules. Therefore, the search for prospective nonpolymeric resist materials has become a high interest.

In this paper, various glycidyl calix[4]arene derivatives were prepared using ECH under different conditions, and their curing behavior and thermal properties were examined using epoxy systems with 4,4'-diaminodiphenylmethane and boron trifluoride-isopropylamine as a crosslinker and a cationic catalyst, respectively.

Experimental

Materials and Measurements. *p*-*tert*-Butylcalix[4]arene (**1**) was prepared by the method previously reported.² Cesium carbonate, potassium carbonate, sodium hydroxide, epichlorohydrin (ECH, Aldrich Chem. Co.) were used as received.

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Dimethylformamide (DMF) and acetonitrile were dried from molecular sieves (4 Å) and distilled over phosphorus pentoxide. DDM (Aldrich Chem. Co.) and BEFIA (Labochemie Apolda, GMBH) were used without further purification.

FTIR spectra were obtained with a Biorad Excaliber FTS-3000MX spectrophotometer and ¹H NMR spectra were recorded on a Varian Unity Inova (200 MHz) spectrometer. Elemental analyses were performed using a Yanaco MT-3 CHN instrument. DSC measurements were performed on a Perkin-Elmer DSC 7 under nitrogen at a heating rate of 10 °C/min. TGA measurements were carried out on a Shimadzu TGA 50 thermal analyzer at a heating rate of 10 °C/min under nitrogen. Epoxy equivalent weight value (EEW) was determined according to the conventional method.²⁰

Preparation of Calix[4]arene-Containing Epoxy Resin.

A three neck round-bottomed flask (250 mL), equipped with mechanical stirrer and thermometer, was charged with **1** (13.05 g, 33 mmol), ethanol (100 mL) and ECH (40.00 g, 432 mmol). Then a solution of NaOH (2.76 g, 69 mmol) dissolved in distilled water (20 mL) was added dropwise for 1 h at 60 °C, and the reaction mixture was heated to 80 °C for 6 h.¹⁴ Then the mixture was poured into methanol and filtered. The final product was washed with methanol and water three times, and dried at 60 °C under vacuum to give a white powdery product.

2: Yield 96%. IR (KBr, cm⁻¹): 3500-3400 (br, O-H), 3010-2920 (aromatic C-H), 2875 (aliphatic C-H), 1680 (aromatic C=C), 1584 (C-C), 1298, 1249, 1210, 1151, 1084, 1047 (C-O), 842, 771. ¹H NMR (CDCl₃): δ 7.8 (s, phenolic OH), 7.12-6.86 (m, 4 ArH_m), 4.05-4.23 (m, -O-CH₂-CH(O-)-), 3.68-3.72 (m, 8 H, 4 ArCH₂Ar), 3.51-3.59 (m, -O-CH₂-CH(O-)-), 2.78-2.92 (m, CH₂(O-)CH-), 0.99-1.25 (2 s, -C(CH₃)₃).

Representative Synthesis of Glycidyl *tert*-butylcalix[4]arene. 1 (13.06 g, 20 mmol), ECH (18.71 g, 200 mmol), cesium carbonate (4.69 g, 15.3 mmol) and DMF (60 mL) were allowed to heat at 80 °C for 2 days under nitrogen. The solvent was evaporated under reduced pressure. The crude residue was dissolved in methylene chloride and acidified with aqueous hydrochloric acid (0.1 N). The organic layer was washed with deionized water several times and dried with anhydrous magnesium sulfate. Recrystallization was performed using diethyl ether. Other derivatives **4-6** with different contents of glycidyl group were prepared by similar methods described above.

4: Yield 75%. IR (KBr, cm⁻¹): 3500-3380 (br, O-H), 3010-2920 (aromatic C-H), 2875 (aliphatic C-H), 1678 (aromatic C=C), 1580 (C-C), 1295, 1250, 1210, 1150, 1082, 1045 (C-O), 840, 772. ¹H NMR (CDCl₃): δ 7.8 (s, phenolic 2 OH), 7.14 (d, 4 H, 2 ArH_m(1,3-alt)), 6.88 (d, 4H, 2 ArH_m(2,4-alt)), 4.04-4.20 (m, 4H, -O-CH₂-CH(O-)-), 3.69-3.76 (m, 8 H, 4 ArCH₂Ar), 3.49-3.62 (m, 2H, -O-CH₂-CH(O-)-), 2.78-

2.94 (m, 4H, CH₂(O-)CH-), 1.25 (s, 18H, -C(CH₃)₃), 0.99 (s, 18H, 2 -C(CH₃)₃).

6: Yield 77%. IR (KBr, cm⁻¹): 3020-2980 (aromatic C-H), 2880 (aliphatic C-H), 1678 (aromatic C=C), 1580 (C-C), 1290, 1250, 1220, 1150, 1080 (C-O), 840, 770. ¹H NMR (CDCl₃): δ 7.14 (d, 8 H, 2 ArH_m), 4.02-4.16 (m, 8H, -O-CH₂-CH(O-)), 3.69-3.74 (d, 8 H, 4 ArCH₂Ar), 3.48-3.66 (m, 4H, -O-CH₂-CH(O-)), 2.76-2.92 (m, 8H, CH₂(O-)CH-), 1.34, 1.25, 0.99 (s, 36H, 4-C(CH₃)₃), Anal. Calcd for C₅₆H₇₂O₈ (Mw, 873.13); C, 77.03; H, 8.31. Found: C, 77.22; H, 8.24.

Curing Procedure for Glycidylated 1 with Diamines and Cationic Catalyst. **2** and DDM (1/0.75) as a curing agent were dissolved in 2-methoxyethanol/ethanol (1/4, v/v) to obtain a well-mixed resin. After the solvent was evaporated, the resin powder was placed in a Teflon mold or aluminum pan and cured at 180 °C for 1 h, followed by post-curing at 220 °C for 4 h.

2 and BTFIA (1 mol%) as a cationic catalyst were dissolved in 2-methoxyethanol/ethanol (1/4, v/v) to obtain a well-mixed resin. After the solvent was evaporated, the resin powder was placed in a Teflon mold or aluminum pan and cured at 120 °C for 5 min, followed by post-curing at 100 °C for 4 h to obtain a cured specimen for thermal stability.

Results and Discussion

Neri *et al.*²¹ reported the generation of various calix[4]arene conformers during glycidylation reaction using glycidyl *p*-toluenesulfonate in the presence of a base. The various conformers of tetraglycidylated **1** were reported to be partial cones, 1,2-alternate and 1,3-alternate. But in this experiment, the ratio of these conformations was not determined, due to the insignificance in application as epoxy resins. Beside this, the more economical ECH was preferred to glycidyl *p*-toluenesulfonate as a glycidylating agent in the literature.

When **1** was reacted with ECH using sodium hydroxide in a conventional glycidylation process, partially glycidylated *p*-*tert*-butylcalix[4]arene **2** was obtained with a 96% yield. The aromatic protons of calix[4]arene were shown at 7.14 and 6.88 ppm and new signals appeared at 4.23, 3.59, and 2.80 ppm corresponding to glycidyl groups in the ¹H NMR spectrum. The broad band between 3300 and 3500 cm⁻¹ was attributable to hydroxyl groups, which was derived from ring opening of epoxy ring, in IR spectrum. EEW value of product **2** was 258-263 g/eq corresponding to the degree of glycidylation of 3.38.

The reaction of glycidylation with ECH in acetonitrile in the presence of K₂CO₃ is described in Scheme I. Refluxing of **1** in acetonitrile afforded 1,3-diglycidyl calix[4]arene **3** and **4** according to the amount of ECH. The white powdery solid was soluble in common organic solvents such as DMF, NMP, acetone, THF, and chloroform.

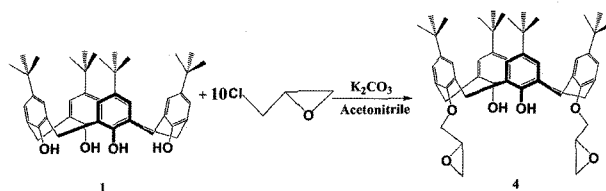
Treatment of **1** with ECH in the presence of cesium car-

bonate as a base in DMF yields **5** and the fully derivatized **6** as shown in Scheme II. It was reported that the use of cesium carbonate as a base gave the best yield for the synthesis of calix[4]arene ether due to the cesium effect.^{22,23} In the preparation of calix[4]arene having two glycidyl groups, however, we found that the use of K₂CO₃ as a base provided the better yield. On the other hand, the use of K₂CO₃ as a base gave a poor yield in preparing calix[4]arene with tetraglycidyl content. The best reaction conditions were found to be in the case of using Cs₂CO₃ as a base in DMF, providing the desired product with a 87% yield. The reaction condition and corresponding isolated yields are listed in Table I.

Compound **6** was purified by recrystallization and characterized in a usual way using IR, NMR spectroscopy and elemental analysis. Due to the excess of ECH used in the synthesis, oligomeric epoxy resin was found after the purification. This was proven by thin layer chromatography and the presence of a band in the IR spectrum between 3300 and 3500 cm⁻¹, which would show the presence of hydroxyl groups. The integral values of aromatic protons at 7.14 ppm based on the aromatic proton intensity of **1** did not change, and new signals appeared at 4.16, 3.66, and 2.92 ppm indicating that glycidyl groups were fully introduced to **1**. **6** was white powdery solid having a melting point of 127 °C and soluble in common organic solvents such as DMF, NMP, *m*-cresol, ethanol, THF, and 1,2-dimethoxyethane.

DDM was used as a curing agent. The epoxy resins **2** and **6** were cured by using epoxy/diamine with mole ratios of 1/0.75 and 1/1, respectively. The curing behavior was examined at 10 °C/min under nitrogen by DSC to obtain the optimum curing conditions for preparing diamine-cured epoxy networks. Table II summarized the results of the curing behavior of **2** and **6**. Figure 1 shows the dynamic scan of the **2**- and **6**-DDM mixture. DDM and **6** melted around 100 and 128 °C, respectively. The curing reaction started at about 170 °C, with a maximum of the exothermic peak at 225 °C. At about 250 °C the cure was complete, as it can be inferred

Scheme I



Scheme II

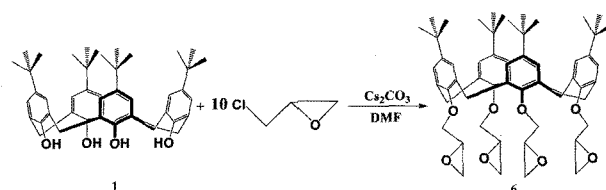


Table I. Conditions and Results for the Preparation of Glycidyl Calix[4]arenes

Compounds	Base	Solvent	Epichlorohydrin	EEW ^a (DG) ^b	Yield (%)
2	NaOH	EtOH	excess	258-263 (3.38)	96
3	K ₂ CO ₃	CH ₃ CN	5 eq	460-465 (1.79)	68
4	K ₂ CO ₃	CH ₃ CN	10 eq	440-445 (1.98)	75
5	Cs ₂ CO ₃	DMF	5 eq	310-315 (2.80)	55
6	Cs ₂ CO ₃	DMF	10 eq	220-225 (3.96)	87

^aEpoxy equivalent weight. ^bDegree of glycidylation.

Table II. Thermal Properties of Cured Glycidyl Calix[4]arenes Resins

Epoxy Resin (A)	Curing Agents (B)	A/B (mole/mole)	Endo ^a	Exo ^b	10%wt Loss (°C)	Residual Weight (%)	
			(°C)			400°C	500°C
2	DDM ^c	1/0.75	95, 108	220	336	52	28
	BTFIA ^d	1/0.01	82-90	220	332	49	31
6	DDM	1/1	100, 128	225	372	80	38
	BTFIA	1/0.01	100	127, 195	374	71	34

^aEndotherm. ^bExotherm. ^c4,4'-diaminodiphenylmethane. ^dBorontrifluoride isopropylamine.

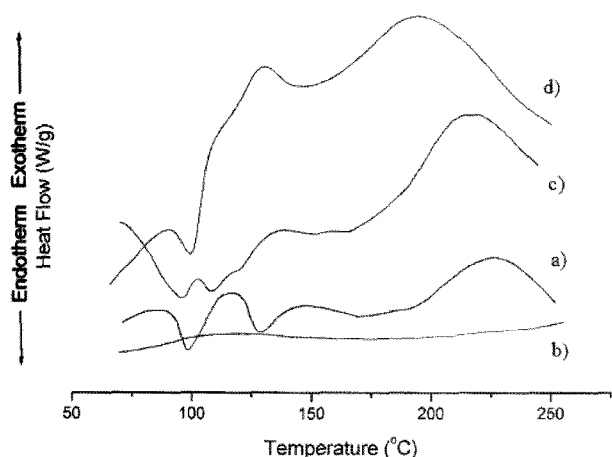


Figure 1. DSC thermograms of a) 6/DDM, b) 6/DDM (2nd scanning), c) 2/DDM, and d) 6/BTFIA and at a heating rate of 10 °C/min in nitrogen.

from the analysis of the second heating scan where the absence of exotherms indicates no post-cure in the resin as shown in Figure 1(b). In fact, tetraglycidyl epoxy resin with a higher cross-link density is expected to give a higher glass transition temperature.

IR spectroscopy was used to follow thermal curing of a sample on KBr salt plate. In addition, the epoxy resin 6 displayed a rapid change within 30 min at the temperature of exotherm in the IR spectra in Figure 2. The intensity of absorbance at 3330-3400 cm⁻¹ based on N-H characteristic band decreased and the broad O-H band around 3500 cm⁻¹ appeared as shown in Figure 3. Changes in IR spectra are consistent with the reaction of aromatic diamine with an

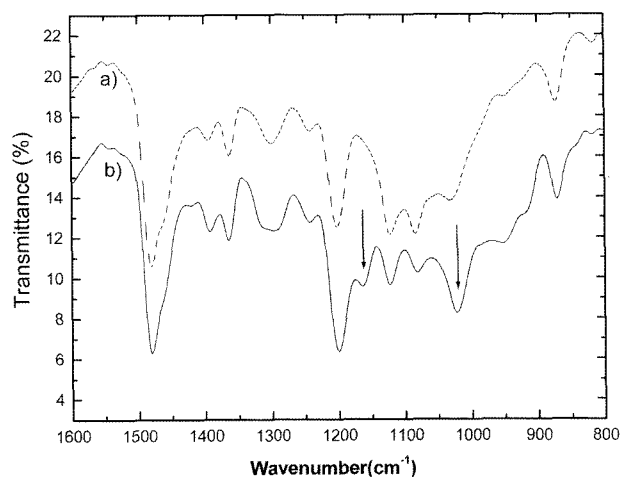


Figure 2. Superimposed IR spectra of 6 cured at 120 °C with BTFIA, after a) 0 h and b) 1 h.

epoxide ring to generate secondary and tertiary amine and hydroxyl group. The variation of IR spectrum result also indicates that cross-linking of the 6 proceeded almost quantitatively by thermal curing process.

BTFIA was used as a cationic catalyst. The curing behavior of 2 and 6 was examined at 10 °C/min under nitrogen by DSC to obtain the optimum curing conditions for preparing acid catalyzed epoxy networks. The polymerization process is initiated by a strong acid, which is generated by heat. During heating, the acid protonates the oxirane substructures resulting in ring opening and generation of a carbocation at the glycidyl calix[4]arene molecules. These carbocations react with other neutral epoxides in a series of crosslinking reactions.

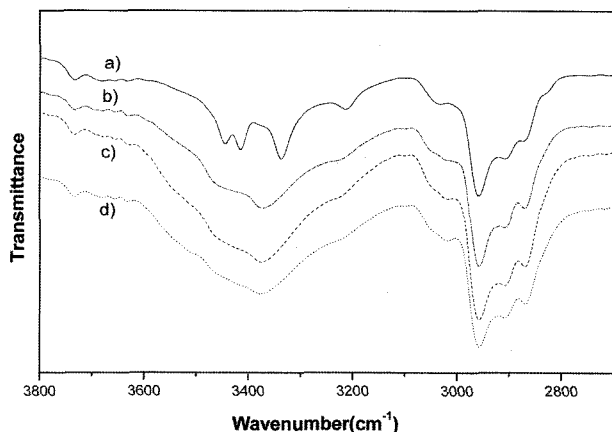


Figure 3. Superimposed IR spectra of **6** cured at 120°C with DDM, after a) 0 h, b) 0.5 h, c) 1 h, and d) 12 h.

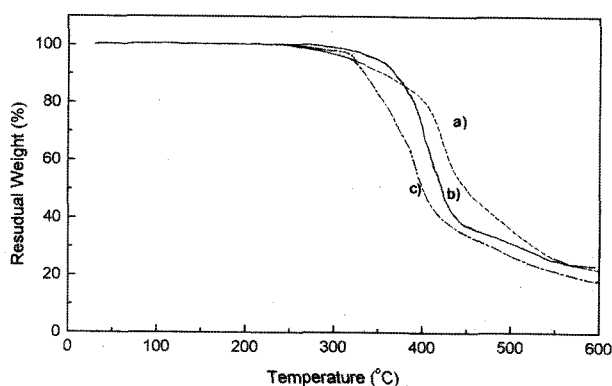


Figure 4. TGA thermograms of a) **6**/DDM, b) **6**/BTFIA, and c) **2**/DDM at a heating rate of 10°C/min under nitrogen.

The onset temperature of exotherms for **2** and **6** started just after the endothermic melting transition or decomposition temperature of a cationic catalyst. IR spectra showed a spectral change after the curing of epoxy resin. A strong absorption band between 1300 and 950 cm^{-1} indicates the presence of a -C-O linkage formed during opening of an epoxide ring as shown in Figure 3.

The thermal properties of the cured epoxy resins were evaluated by thermogravimetric analyses (TGA) under nitrogen. Figure 4 shows the TGA thermograms of **2** and **6**. From TGA curves, stabilities of the epoxy resins cross-linked with aromatic diamine and cationic catalyst were evaluated. Data are summarized in Table II. The temperature corresponding to 10% weight loss ($T_{10\%}$) and the char yield at 400 and 500°C were listed in Table II. Diamine cured epoxy system showed higher residual weight than that of the acid catalyzed epoxy resin due to the introduction of aromatic moiety.

The thermal stability of **6** containing more glycidyl groups is probably enhanced through more crosslinking. The first stage weight loss was caused from the pyrolysis of the ali-

phatic unit. For DDM cured resins, however, the decomposition of the epoxy resins was not so clearly distinguishable from the decomposition of the polymer backbone. **6**/DDM system has been found to be the most thermally stable compared to other system and showed that about 81% residual weight has been observed at 500°C.

In conclusion, various *p*-*tert*-butylcalix[4]arenes containing epoxy compounds were prepared from **1** and ECH in the presence of a base. They underwent curing reaction by using aromatic diamine as a curing agent and a cationic catalyst in ring opening reaction. The use of glycidylated **1** could be comparable to conventional phenolic epoxy resin.

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