

REVIEWS

Novel High Performance Materials. Calixarene Derivatives Containing Protective Groups and Polymerizable Groups for Photolithography, and Calixarene Derivatives Containing Active Ester Groups for Thermal Curing of Epoxy Resins

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ABSTRACT: This paper reviews our recent studies on the syntheses and functions of novel calixarene derivatives with excellent thermal stability as high performance materials. Calixarene derivatives containing protective groups such as *tert*-butoxycarbonyl (*t*-Boc), trimethylsilyl (TMS), and cyclohexenyl (CHE) groups were successfully prepared by the reaction of certain calixarenes, *p*-methylcalix[6]arene (**1a**), *p*-*tert*-butylcalix[8]arene (**1c**), and *C*-methylcalix[4]resorcinarene (**1d**) with the corresponding protecting reagents. Calixarene containing radically polymerizable groups such as methacryloyl groups and cationic polymerizable groups such as propargyl, vinyl ether groups were prepared in good yields. Calixarene derivatives containing cyclic ethers such as oxirane, oxetane, and spiro orthoesters were also prepared. Calixarene derivatives thus obtained had good film forming property and thermal stability. It was proved that the photoinduced deprotection of the calixarene derivatives containing protective groups in the presence of a photo-acid generator proceeded easily to give the corresponding calixarenes with phenol groups. Photoinitiated polymerization of the calixarenes with various polymerizable groups using suitable photoinitiators in the film state proceeded efficiently to produce crosslinked films. Furthermore, thermal curing of epoxy resins with calixarenes (**1a**, **1c**, **1d**), and calixarenes containing active ester groups using certain catalysts were studied to found that the calixarenes were useful curing agents for epoxy resins.

KEY WORDS Calixarene / Thermal Stability / Protective Group / Polymerizable Group / Photoinduced Deprotection / Radical Polymerization / Cationic Polymerization / Thermal Curing / Epoxy Resin /

Calixarenes are cyclic oligomers prepared¹ ordinarily from the reaction of phenols with aldehydes, and have attracted much interest in the field of host-guest chemistry.² Therefore, over the last 20 years, synthesis³ of various calixarene derivatives and chemical modification^{4,5} of calixarenes have been studied in attempting to induce the targeted character. We can consider that calixarene derivatives have further advantage in synthetic organic chemistry as starting materials due to polyfunctional hydroxyl groups, which are readily modified to various functional groups. That is, in polymer synthesis, calixarene derivatives can also be used as multifunctional initiators for the synthesis of star-shaped polymers. Kennedy and his co-workers⁶ reported the synthesis of a star-shaped polymer with eight arms of poly(*iso*-butylene) using calix[8]arene derivative as an initiator. Sawamoto and his co-workers⁷ succeeded in producing certain star-shaped polymer with 4–8 arms of poly(methyl methacrylate) using cal-

ixarene derivative as initiator.

Recently, it was also suggested that calixarenes have unique characteristics such as small molecular size, good film-forming properties,^{8,9} high glass transition temperature¹⁰ (T_g), excellent thermal stability,^{10,11} many reactive groups such as hydroxyl groups in small molecule, and so on. For example, Fujita *et al.* found⁸ that hexa-acetate of *p*-methylcalix[6]arene could be used as a negative type resist with ultrahigh resolution in electron beam lithography.

Photoinduced deprotection of certain protective groups at polymer side chains using photo-acid generators (PAG)s is applied for lithography based on the concept as chemical amplification.¹² In chemical amplification systems, photo generation of acids from PAG followed by acids catalyzed deprotection by heating can introduce polarity exchange of the matrix with high efficiency, that is, from hydrophobic property to hydrophilic one of the matrix. Ueda and his co-workers recently reported^{13,14}

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on three-component negative-working alkaline-developable photoresist based on calix[4]resorcinarene, a cross-linker, and a photo-acid generator. They also reported¹⁵⁻¹⁷ the synthesis of octa-*O-tert*-butyl carbonated *C*-hexylcalix[4]resorcinarene and its derivatives for positive-working alkaline-developable photoresist.

Meanwhile, UV and EB curing systems have been of great interest,^{18,19} and have been introduced in the fields of coatings, printing inks, photofabrications, adhesives, and solder masks. These systems are among the important methods of reducing use of harmful organic solvents, carbon dioxide due to the combustion of fossil fuels, and energy. Recently, these UV and EB curing systems have been further extended in some new technology fields such as microelectronics, micro-machines, three-dimensional fabrications, liquid crystal displays, optical media, and optoelectronic materials. In these curing systems, radically polymerizable polyfunctional (meth)acrylate monomers and oligomers have been widely used with appropriate photoinitiators, because these monomers and oligomers have high photochemical reactivity to produce the crosslinked insoluble lumps or films having excellent mechanical and physical properties. However, it was pointed out that some methacrylate monomers with low viscosity cause skin irritability,²⁰ an undesirable property for handling them during these processes.

Photo-initiating cationic polymerizations of polyfunctional epoxy compounds and polyfunctional vinyl ether compounds have been of interest²¹ as second generation's UV curing materials, since these monomers and oligomers have also high photochemical reactivity in the presence of appropriate photo-generating cationic catalysts and seem to cause little skin irritability. Polyfunctional vinyl ether monomers and oligomers were normally synthesized by the addition reaction of acetylene with polyfunctional alcohols or by the substitution reaction^{22,23} of polyfunctional phenols and carboxylic acids with 2-chloroethyl vinyl ether (CEVE) with the use of a phase-transfer catalysis.

The authors have reported²⁴⁻²⁶ new methods for the synthesis of polyfunctional vinyl ether monomers and oligomers by the regioselective addition reaction of glycidyl vinyl ether with acyl chlorides and silyl chlorides followed by the condensation reaction of the resulting monomers containing reactive chloromethyl groups with dicarboxylic acids using quaternary onium salts or crown ethers as the multifunctional catalysts. Crivello *et al.* reported^{27,28} that polyfunctional 1-propenyl ether monomers, which have mostly the same photochemical reactivity with polyfunctional vinyl ether monomers, were prepared by the isomerization of the corresponding allyl ether monomers.

Furthermore, thermal curing resins such as epoxy resins have also been used as encapsulant for semiconductor devices and intercalation insulating materials in the field of electronics, because they have good properties such as high T_g and good thermal stability as well as those for UV cured resins. To develop new cured materials with excellent chemical and physical properties for the great demand in those fields, new molecular design of curing agents are needed. Nishikubo has reported new curing reactions²⁹⁻³⁴ of epoxy resins with active carboxylic esters, which provide cured resins without hydroxyl groups. The authors considered that calixarenes could be used as curing agents for thermal curing epoxy resins with excellent properties, because oxirane groups of epoxy resins react easily with phenols and their active ester groups in the presence of suitable catalysts.

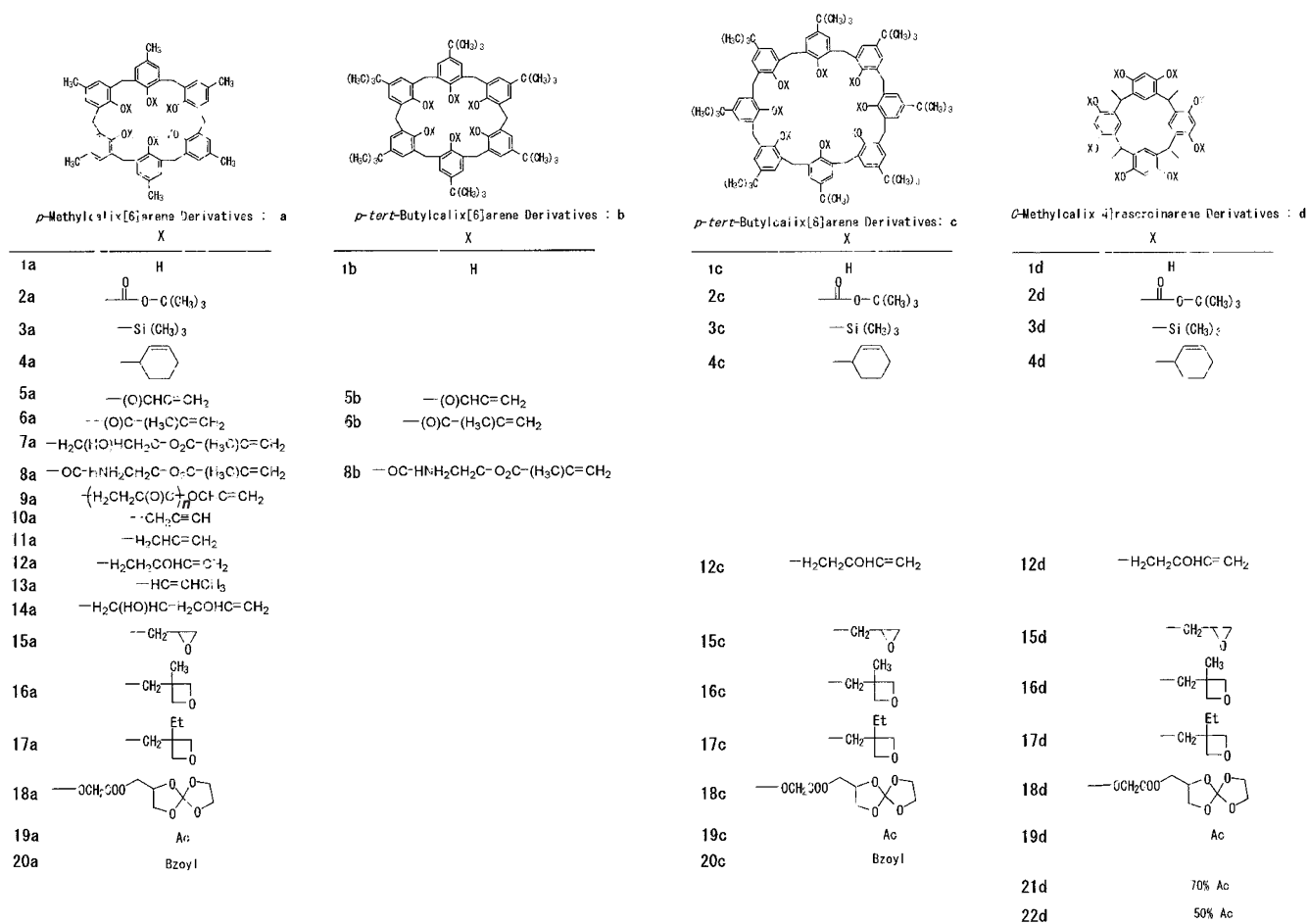
From all these background, we consider new advantage of calixarenes and their derivatives, and following molecular designs (Scheme 1). The first design of calixarene derivatives is the synthesis of photoreactive calixarene derivatives containing protective groups for the application to nano-lithography. The second design is the synthesis of calixarene derivatives containing photo-polymerizable groups for the application of high performance photo-curable materials. The third one of calixarenes is the application for the high performance epoxy resins by the reaction with calixarene derivatives.

In this article, we would like to report on the synthesis, characterization, and photochemical reaction of *p*-alkylcalixarene and *C*-methylcalix[4]resorcinarene derivatives containing protective groups. Synthesis, characterization, and photochemical reaction of *p*-alkylcalixarene, and *C*-methylcalix[4]resorcinarene derivatives containing radically polymerizable groups, cationically polymerizable groups, and pendant cyclic ether groups such as oxirane, oxetane, and spiro ortho ester groups are also described. Furthermore, thermal curing reaction of epoxy resins with calixarenes and calixarene derivatives containing ester groups using quaternary onium salts as catalysts, and properties of the cured materials are also reported.

CALIXARENES CONTAINING PROTECTIVE GROUPS³⁵

Synthesis

Photoinduced deprotection of the calixarenes containing protective groups induces polarity exchange of the calixarene derivatives, which will be applied for photolithography. Therefore, we designed calixarene derivatives with protective groups such as *tert*-



Scheme 1.

butoxycarbonyl (*t*-BOC), trimethylsilyl ether (TMSE), and cyclohexenyl ether (CHE) groups.

Calixarene derivatives containing *t*-BOC groups **2a**, **2c**, and **2d** were prepared in high yields, respectively, by the reaction of calixarenes *p*-methylcalix[6]arene **1a**, *p*-*tert*-butylcalix[8]arene **1c**, and *C*-methylcalix[4]resorcinarene **1d** with di-*tert*-butyl dicarbonate using triethylamine as a base in pyridine at room temperature for 24 h (Scheme 2). Ueda *et al.*^{16,17} recently reported the synthesis of similar *C*-calix[4]resorcinarene derivatives containing *t*-BOC groups.

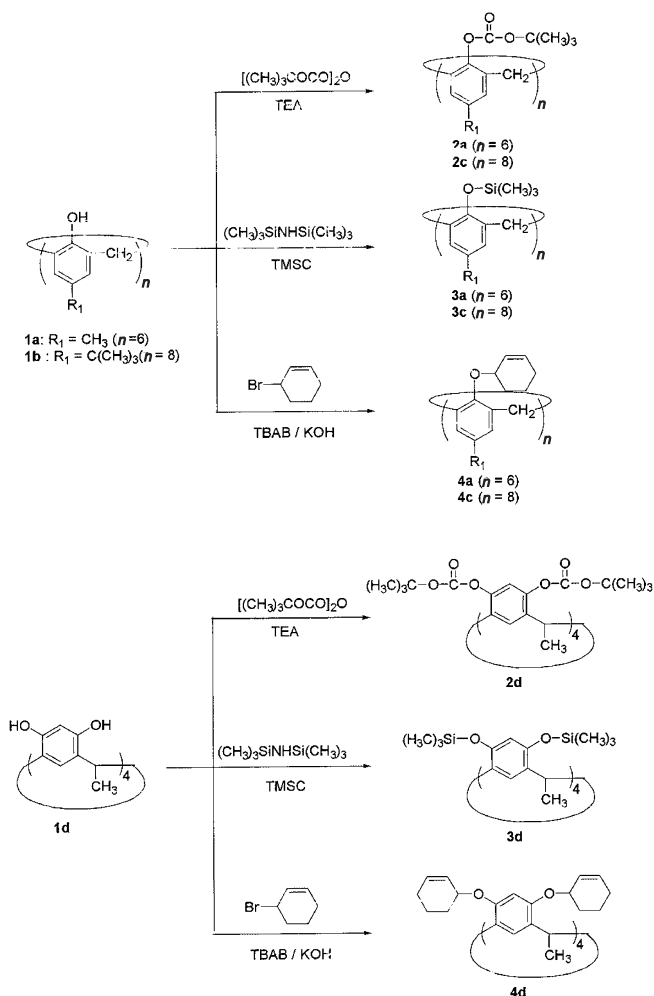
Calixarene derivatives containing TMSE groups as protective groups **3a**, **3c**, and **3d** were successfully prepared, respectively, in high yields by the reaction of **1a**, **1c**, and **1d** with excess amount of 1,1,1,3,3,3-hexamethyldisilazane (HMDS) using catalytic amount of trimethylsilyl chloride (TMSC) as an accelerator in THF at reflux temperature for 48 h.

Calixarene derivatives containing CHE groups **4a**, **4c**, and **4d** were successfully prepared, respectively, by the reaction of **1a**, **1c**, and **1d** with slightly excess amount of 3-bromocyclohexene (BCH) using KOH and TBAB as a phase transfer catalyst in NMP at 60 °C for

48 h. The structures of the obtained calixarene derivatives prepared were well identified by IR and ¹H NMR spectral data, and elemental analysis.

Calixarene derivatives **2a**, **2c**, and **2d** containing *t*-BOC groups and **4a**, **4b**, and **4c** containing CHE groups were soluble in common organic solvents excepting methanol and 2-propanol. On the other hand, the calixarene derivative **3a** containing TMSE group was soluble in acetone, ethyl acetate, 1,4-dioxane, chloroform, and NMP, and was insoluble in DMF and DMAc. Calixarene **3c** was only soluble in 1,4-dioxane, chloroform, toluene, and THF, and calixarene **3d** was soluble in ethyl acetate, 1,4-dioxane, chloroform, and THF. This shows that the solubility of calixarene derivatives **3a**, **3c**, and **3d** containing TMSE groups in organic solvents, especially in aprotic polar solvents, was low due to hydrophobicity of the pendant TMSE groups in calixarenes.

The deprotection temperature of calixarene derivatives containing certain protective groups was examined using TGA analysis. As shown in Figure 1, *t*-BOC groups in **2a**, **2c** and **2d** released reasonable amounts of carbon dioxide and isobutylene to form corresponding calixarenes such as **1a**, **1c** and **1d** over 200 °C, respec-



Scheme 2.

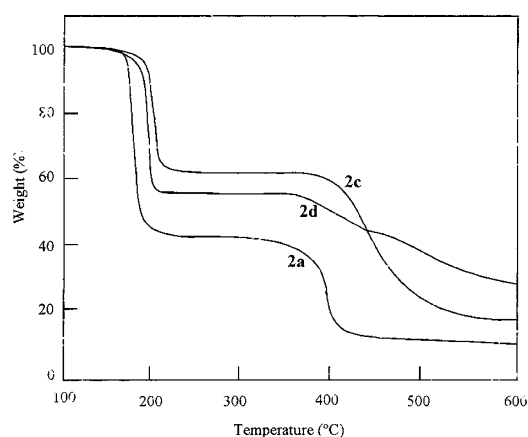


Figure 1. TGA curve of calixarene **2a**, **2c**, and **2d** containing pendant *t*-BOC groups at a heating rate of $10^\circ\text{C min}^{-1}$ under nitrogen atmosphere.

tively.

The temperatures at 5% or 10% weight loss of mass are summarized in Table I. The temperatures at $T_d^{5\%}$ and $T_d^{10\%}$ of calixarene derivative **2a** were 178 and 184°C , respectively. The $T_d^{5\%}$ and $T_d^{10\%}$ of calixarene derivative **2c** were 173 and 174°C , respectively. Fur-

Table I. TGA data of CRA and *p*-alkylcalix[*n*]arene derivatives containing various protecting groups^a

Calixarene	$T_d^{5\%b}$	$T_d^{10\%c}$
2a	178	184
2c	189	194
2d	173	174
3a	328	348
3c	400	424
3d	293	310
4a	184	194
4c	180	197
4d	185	192

^aTGA was performed at a heating rate of $10^\circ\text{C min}^{-1}$ under nitrogen atmosphere. ^b $T_d^{5\%}$: The temperature at 5% weight loss. ^c $T_d^{10\%}$: The temperature at 10% weight loss.

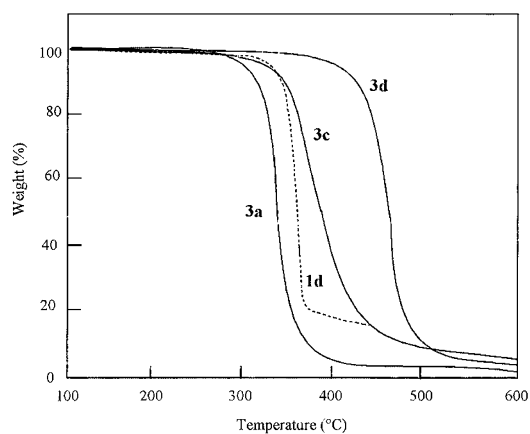
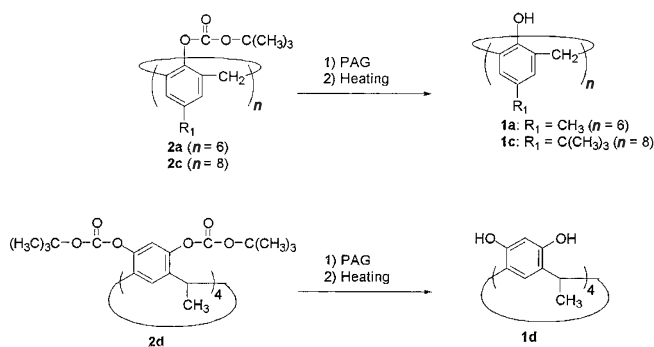


Figure 2. TGA curve of calixarenes **3a**, **3c**, and **3d** containing pendant *t*-BOC groups and **1d** at a heating rate of $10^\circ\text{C min}^{-1}$ under nitrogen atmosphere.

thermore, the $T_d^{5\%}$ and $T_d^{10\%}$ of calixarene derivative **2d** were 189 and 194°C , respectively. It is suggested that calixarene derivatives with backbone of **1a** had relatively lower deprotection temperature, which seemed to indicate a more suitable character for a chemically amplified resist, than those of calixarene derivatives with backbones of **1c** and **1d**.

As shown in Figure 2, TGA curve of **3a** was similar to that of **1d**, although initial decomposition temperature of **3a** was lower than that of **1a**. This means that calixarenes containing TMSE groups **3a**, **3c** and **3d** did not produce corresponding calixarenes such as **1a**, **1c** and **1d** just by thermal treatment at the elevated temperature. As summarized in Table I, calixarenes containing TMSE groups **3a**, **3c** and **3d** had higher decomposition temperatures than calixarene containing pendant *t*-BOC groups **2a**, **2c** and **2d**. Furthermore, it is found that calixarene derivatives containing CHE groups had similar deprotection temperatures to calixarene derivatives containing *t*-BOC groups.



Scheme 3.

Photoinduced Deprotection of Calixarenes Containing Protective Groups

The photoinduced deprotection of calixarene **2d** containing *t*-BOC groups was examined using bis-[4-(diphenylsulfonio)phenyl]sulfide bis(hexafluorophosphate) (DPSP) as a PAG upon photoirradiation with a 250-W high-pressure mercury lamp followed by heating at appropriate temperatures in the film state (Scheme 3).

The conversion of the *t*-BOC groups in the calixarene **2d** was estimated from the decrease of the absorption peaks due to C=O stretching at 1759 cm^{-1} in the IR spectra. The deprotection of the pendant *t*-BOC groups in **2d** with 5 mol% of DPSP was not found upon only photoirradiation in the film state. However, each reaction occurred smoothly, when the reaction of **2d** was carried out with 5 mol% of DPSP upon photoirradiation followed by heating for 30 min at certain temperatures such as 100, 120, and 150°C . The deprotection rate increased with increasing the heating temperature, and the degree of deprotection of the *t*-BOC groups reached about 95% upon only 10 s of irradiation and heating at 150°C for 30 min.

The deprotection rate of the *t*-BOC groups in **2d** was also affected by the DPSP concentration and the irradiation time, when the thermal treatment of **2d** was carried out at 150°C . As shown in Figure 3, the deprotection rate of the *t*-BOC groups increased with irradiation time. Then, the deprotection of *t*-BOC groups occurred almost quantitatively by heating them at 150°C for 30 min, when the photoirradiation using 5 mol% of DPSP was carried out for 60 s.

The photoinduced deprotection of calixarenes **3a**, **3c**, and **3d** containing TMSE groups with DPSP was also examined. The deprotection of **3d** was not confirmed in the film state, because a film of **3d** with good transparency could not be prepared by casting from a solution. The deprotection of TMSE groups in **3a** and **3c** with 5 mol% of DPSP was carried out in the film state upon photoirradiation with UV-light followed by

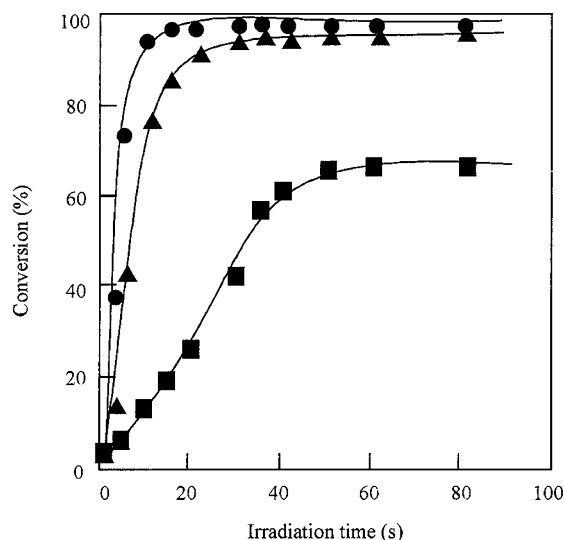


Figure 3. Effect of DPSP concentration and irradiation time on the photoinduced deprotection of the *t*-BOC groups of calixarene **2d**. The heating was performed at 150°C for 30 min: (●) with 5 mol% of DPSP, (▲) with 1 mol% of DPSP, and (■) with 0.2 mol% of DPSP.

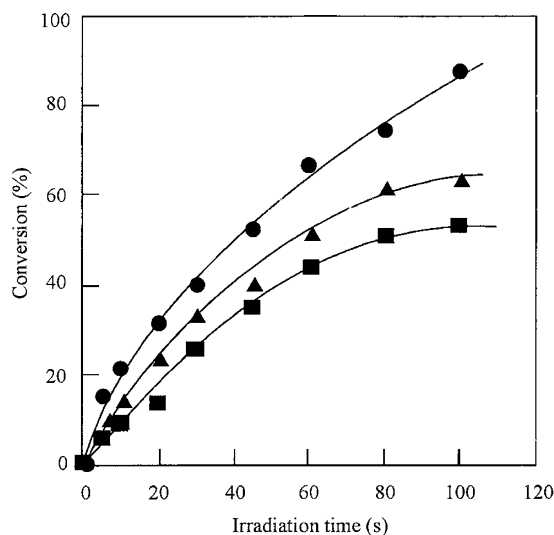


Figure 4. Effect of the heating temperature on the photoinduced deprotection of the CHE groups of calixarene **4d** by using photoirradiation for 100 s with 5 mol% of DPSP. The heating was performed for 30 min: (●) heated at 150°C , (▲) heated at 120°C , and (■) heated at 100°C .

heating at 150°C for 30 min. The conversions of both TMSE groups of **3a** and **3c** were about only 20% upon irradiation for 300 s. This result means that the deprotection rate of TMSE groups of calixarenes **3a** and **3c** was slower than those of *t*-BOC groups in calixarenes **2a** and **2c** under the same treatment conditions. It seems that some moisture was needed for effective photoinduced deprotection of the TMSE groups of the calixarene films as in the case of the deprotection of poly[4-(trimethylsilyloxy)styrene].³⁶

The photoinduced deprotection of calixarenes **4a**, **4c**,

Table II. Various calixarenes and calixarene (meth)acrylates

Calixarene	R	X	Appearance	Yield (%)	IDT(°C) ^a
1a	Me	H	Solid	84	345
1b	<i>t</i> -Bu	H	Solid	90	348
5a	Me	-CO-CH=CH ₂	Solid	93	434
5b	<i>t</i> -Bu	-CO-CH=CH ₂	Solid	85	406
6a	Me	-CO-C(CH ₃)=CH ₂	Solid	85	392
6b	<i>t</i> -Bu	-CO-C(CH ₃)=CH ₂	Solid	74	381
7a	Me	-CH ₂ CH(OH)CH ₂ -O-CO-C(CH ₃)=CH ₂	Solid	86	372
8a	Me	-CO-NH-CH ₂ CH ₂ -O-CO-C(CH ₃)=CH ₂	Solid	77	247
8b	Me	-CO-NH-CH ₂ CH ₂ -O-CO-C(CH ₃)=CH ₂	Solid	80	232
9a	Me	-(CH ₂ CH ₂ O) _{<i>n</i>} -CO-CH=CH ₂ (<i>n</i> = 2.5)	Liquid	84	382

^aInitial decomposition temperature.

and **4d** containing CHE groups with 5 mol% of DPSP were also enhanced by heating after the UV irradiation. As shown in Figure 4, the deprotection rate increased with irradiation time and heating temperature, and the conversions of the CHE groups of **4d** were about 87, 64, and 53% upon photoirradiation for 100 s followed by heating for 30 min at 150, 120, and 100°C, respectively.

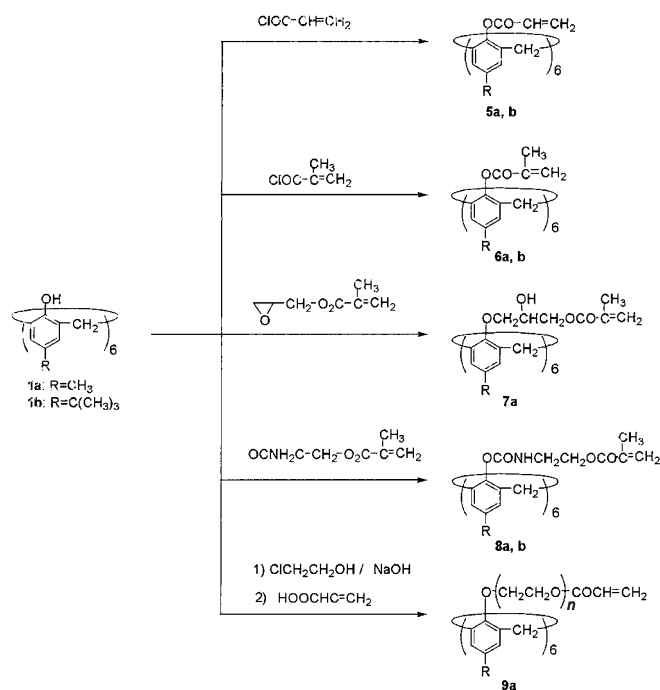
From these results on the photo-induced deprotection of the certain protective groups, such as *t*-BOC, TMSE and CHE in the calixarene derivatives, it was found that the pendant *t*-BOC groups in calixarenes had the highest deprotection rate. As the substrate of the protecting groups, *C*-methylcalix[4]resorcinarene was found to be better matrix than *p*-methylcalix[6]arene and *p*-*tert*-butylcalix[8]arene from the viewpoint of the deprotection rate of the aforementioned protective groups.

SYNTHESIS AND CHARACTERIZATION OF CALIXARENES CONTAINING POLYMERIZABLE GROUPS

Calixarenes Containing (Meth)acryloyl Groups¹¹

Polyfunctional (meth)acrylates with calixarene backbones [calixarene (meth)acrylates], *p*-methylcalix[6]arene containing acryloyl group **5a**, *p*-*tert*-butylcalix[6]arene containing acryloyl group **5b**, *p*-methylcalix[6]arene **6a**, and *p*-*tert*-butylcalix[6]arene **6b** were synthesized with good yields by the condensation reaction of *p*-methylcalix[6]arene **1a** and *p*-*tert*-butylcalix[6]arene **1b** with acryloyl chloride (AC) or methacryloyl chloride (MAC) using triethylamine as HCl acceptor, respectively (Scheme 4 and Table II).

p-Methylcalix[6]arene containing methacrylate groups **7a** was obtained with 86% yield by the addition reaction of **1a** with glycidyl methacrylate (GMA) in the presence of TBAB as a catalyst. Calix[6]arenes containing methacryloyl group **8a** and **8b** were prepared by the addition reaction of **1a** and **1b** with 2-(methacryloyloxy)ethylisocyanate (MOI) in the

**Scheme 4.**

presence of dibutyltin dilaurate as a catalyst. The precursor of calixarene (**6a**) was synthesized by the condensation reaction of **1a** with 2-chloroethanol using sodium hydroxide and TBAB. The hydroxyl value of the ethoxylated product (244 mg; KOH/g) indicates that average ethoxylation for each phenolic hydroxyl group of **1a** is 2.5. *p*-Methylcalix[6]arene with acryloyloxy(oligo(oxyethylene)) **9a** was also synthesized by the condensation reaction of this precursor with acrylic acid using *p*-toluenesulfonic acid.

All of the calixarene (meth)acrylates excepting **9a** were solid at room temperature. The obtained *p*-alkylcalixarene derivatives containing polyfunctional (meth)acrylate groups were well confirmed by IR and ¹H NMR spectra.

All calixarene acrylates were soluble in such solvents as acetone, ethyl acetate, chloroform, dichloromethane, 1,4-dioxane, DMF, and NMP. Calixarene acrylate **9a**

was also soluble in methanol and toluene at room temperature.

Thermogravimetric analysis (TGA) of the starting *p*-alkylcalixarenes and the resulting calixarene (meth)acrylates was examined under nitrogen to confirm their thermal stability. The initial decomposition temperatures (IDTs) of **1a** and **1b** were 345 and 348 °C, respectively. On the other hand, IDTs of calixarene acrylates **5a** and **5b** were 434 and 406 °C, respectively, as shown in Figure 5.

This means that calixarene acrylates **5a** and **5b** had very high thermal stability as polyfunctional (meth)acrylate oligomers, although the IDT of **5b** was lower than that of **5a** due to the decomposition of *p*-*tert*-butyl groups on the calixarene residue. IDT data of the other calixarene (meth)acrylate are also summarized in Table II.

The IDTs of calixarene methacrylates **6a** and **6b** were 392 and 381 °C, respectively. This result suggests that *p*-alkylcalixarene acrylates **5a** and **5b** have higher thermal stability than *p*-alkylcalixarene methacrylates **6a** and **6b** possibly due to effective radical polymerization of acrylate groups of **5a** and **5b**. That is, a thermal crosslinking reaction of calixarene derivatives enhanced effectively their thermal stability, because calixarene (meth)acrylates **5a**, **5b**, **6a** and **3b** showed

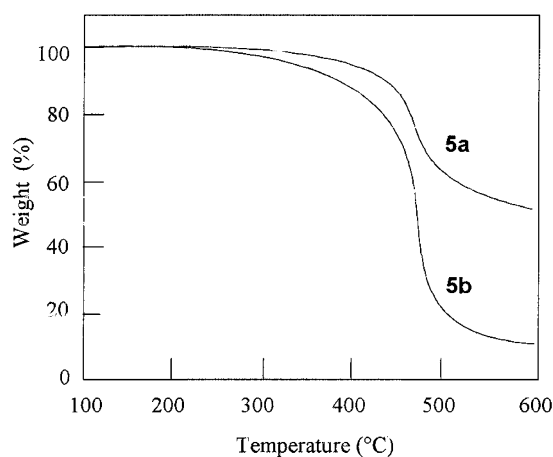
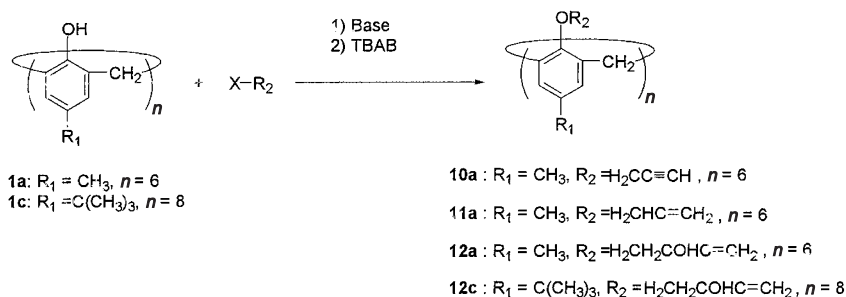


Figure 5. TGA curve of **5a** and **5b** at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere.



Scheme 5.

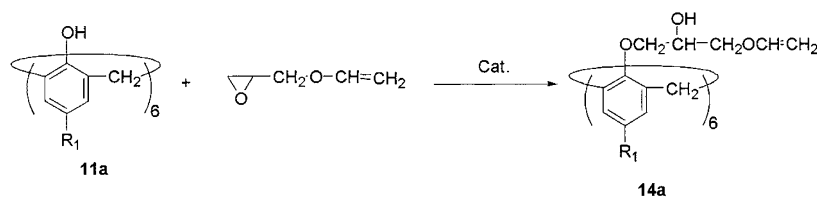
much higher thermal stability than calixarenes **1a** and **1b** did. The IDTs of **9a** and **7a** were lower than those of **5a** and **6a**. It seems that the thermal stability of calixarene (meth)acrylates decreased with the introduction of spacer chain between calixarene backbones and (meth)acrylate groups. The IDTs of **8a** and **8b** were much lower than those of **5a** and **5b**. It seems that urethane linkages between calixarene backbones and methacrylate groups were ascribable to lower IDTs of **8a** and **8b** than other calixarene derivatives such as **5a** and **5b**.

Calixarenes Containing Cationically Polymerizable Groups¹⁰

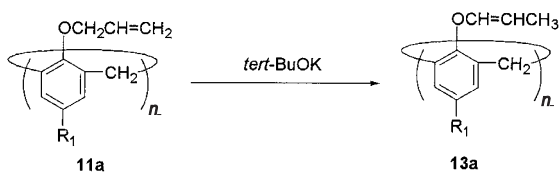
Calixarene containing cationically polymerizable groups such as propargyl, allyl, and vinyl ether groups were prepared by the substitution reactions of **1a** or **1c** with certain unsaturated alkyl halides, propargyl bromide (PB), allyl bromide (AB), and 2-chloroethyl vinyl bromide (CEVE) using KOH or NaH and TBAB (Scheme 5). The substitution reactions proceeded smoothly with 100% degree of substitution to give the targeted calixarene derivatives with good isolated yields. These results mean that *p*-alkylcalixarenes such as **1a** and **1c** can be modified easily to form new functional calixarene derivatives by the substitution reaction of potassium or sodium salts of **1a** or **1c** with appropriate alkyl halides using phase-transfer catalysis under mild reaction conditions.

The isomerization of calixarene **11a** containing allyl ether groups was carried out using *tert*-BuOK in NMP at 80 °C according to the reported method by Crivello *et al.*^{27,28} The reaction proceeded quantitatively under this reaction condition, and the corresponding calixarene **13a** containing 100 mol% of *Z*-1-propenyl ether groups, which was confirmed by ¹H NMR spectrum, was obtained in 80% yield (Scheme 6).

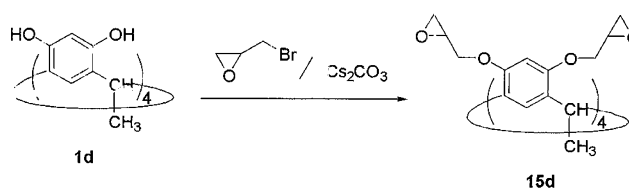
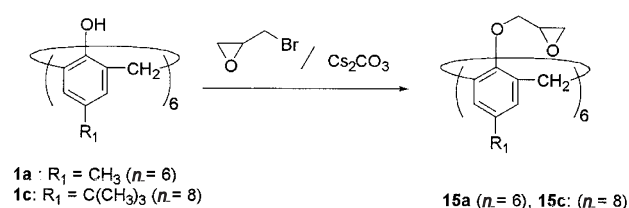
p-Methylcalix[6]arene containing hydroxyalkyl vinyl ether groups **14a** was also prepared by the addition reaction of **1a** with glycidyl vinyl ether (GVE) in NMP at 110 °C for 48 h (Scheme 7).



Scheme 7.



Scheme 6.



Scheme 8.

Table III. UV spectra and thermal properties of calixarene derivatives

Calixarene	$\lambda_{\text{max}}^{\text{a}}$ (nm)	T_{g}^{b} (°C)	$T_{\text{d}}^{10\% \text{c}}$ (°C)
10a	280	314	412
11a	272	203	363
12a	280	245	371
12c	279	177	378
13a	280	226	349
14a	280	148	374

^aMeasured at film state. ^b T_{g} : Glass transition temperature.^c $T_{\text{d}}^{10\%}$: The temperature at 10% loss of mass.

T_{g} s of calixarene derivatives **10a–14a** are summarized in Table III. This result shows that the calixarene derivatives **10a–14a** containing cationically reactive groups have high T_{g} values, which is an important characteristic of photo-curable oligomers. The temperature at 10% loss of mass ($T_{\text{d}}^{10\%}$) of calixarene derivatives **10a–14a** excepting calixarene **10a** showed higher temperature than 350 °C. This means that these calixarene derivatives have excellent thermal stability as photo-curable oligomers.

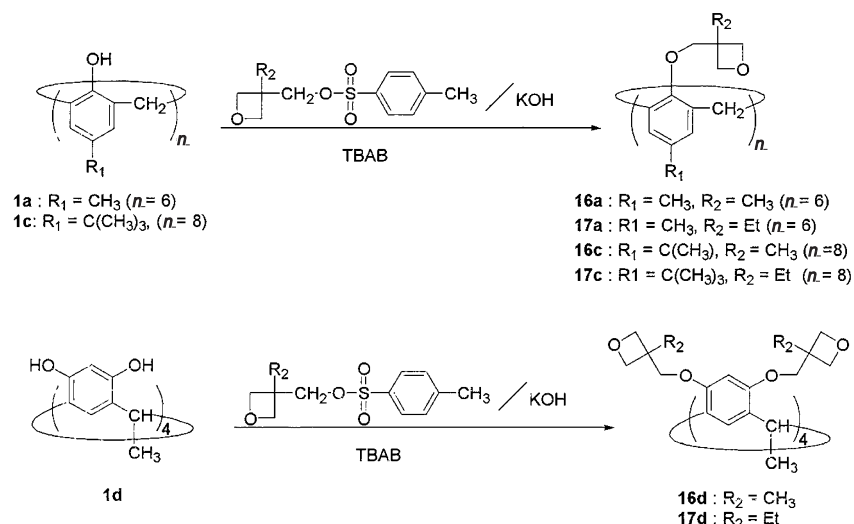
All calixarenes **10a–14a** were insoluble in water, cyclohexane, and acetonitrile, however, they were soluble in ethyl acetate, chloroform, dichloromethane, toluene, and 1,4-dioxane, as well as THF, DMF, DMAc, NMP, and DMSO

Calixarenes Containing Cyclic Ether Groups^{37,38}

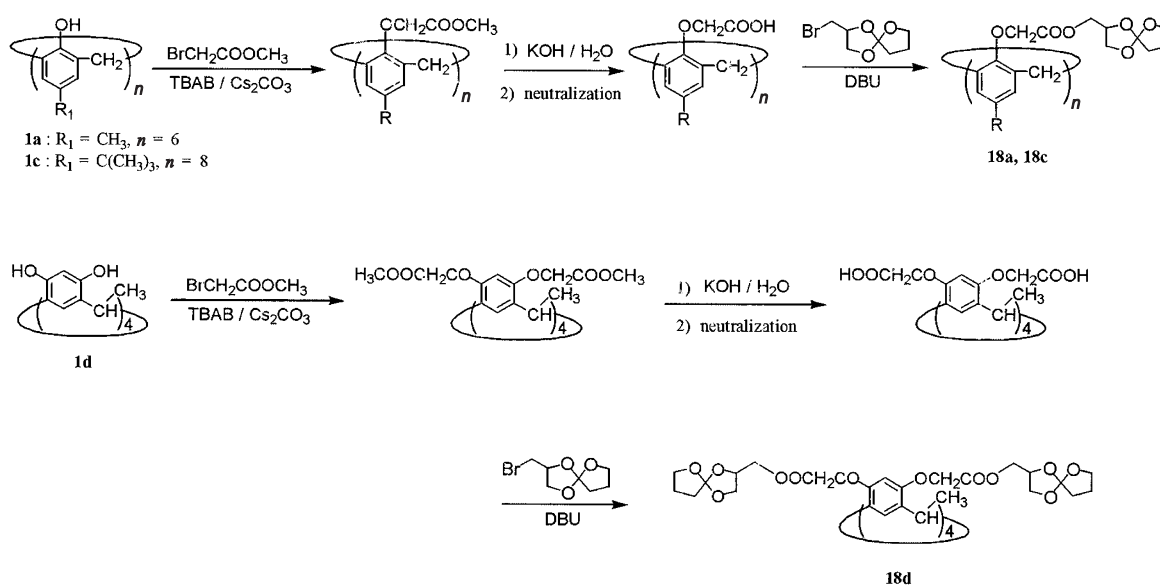
Synthesis of *p*-methylcalix[6]arene containing oxirane groups **15a** by the substitution reaction of **1a** with equivalent amount of epibromohydrin (EBH) was examined using bases such as pyridine, triethylamine, DBU, KOH, or NaOH in MNP at 50 °C for 12 h, however, no soluble products were obtained. It seems that the anionic ring-opening polymerization of EBH or oxirane groups introduced in **1a** might have occurred as a side reaction during the reaction. On the other

hand, when the reactions using weak inorganic bases such as Na_2CO_3 , K_2CO_3 , or Cs_2CO_3 under the same conditions, soluble products were produced. The targeted *p*-methylcalix[6]arene derivative **15a** was successfully prepared with 88% yield from the reaction of **1a** with 1.2 times amount of EBH and 1.2 times amount of Cs_2CO_3 at 50 °C for 48 h. Based on the above reaction conditions, *p*-*tert*-butylcalix[8]arene containing oxirane groups **15c** and *C*-methylcalix[4]resorcinarene containing oxirane groups **15d** were also prepared with good yields (Scheme 8). These results show that cesium carbonate is a suitable base for the substitution reaction of calixarenes with EBH to synthesize calixarene derivatives containing oxirane groups. The synthesized calixarenes containing oxirane groups were well confirmed by IR and ^1H NMR spectra, and elemental analysis.

It is well known that oxetane groups have high reactivity on cationic polymerization with certain cationic initiators. We designed new polyfunctional oxetane oligomers with calixarene backbones as new materials for photoinitiated cationic curing system. (3-Methyl-oxetan-3-yl)methyl-4-toluenesulfonate (MOMT) and (3-ethyloxetanyl-3-yl)methyl-4-toluenesulfonate (EOMT), as starting materials for the synthesis of calixarenes containing oxetane groups, were synthesized by the reaction of *p*-toluenesulfonyl chloride with 3-hydroxymethyl-3-methyloxetane and 3-hydroxymethyl-3-ethyloxetane, respectively (Scheme 9). Substitution reactions of calixarenes **1a**, **1c**, and **1d** with MOMT or EOMT were performed using KOH and TBAB, be-



Scheme 9.



Scheme 10.

cause it is well known³⁹ that substitution reactions of alcohol and phenol with tosylate or sulfonate proceed smoothly to give the corresponding ethers in the presence of inorganic strong bases and phase transfer catalysts under mild reaction conditions. Calixarenes containing 3-methyloxetane groups **16a**, **16c**, and **16d** with 100% degree of substitution were obtained in good yields by the reaction of **1a**, **1c**, and **1d** with slightly excess amount of MOMT at 70 °C for 24 h in NMP. Calixarenes containing 3-ethyloxetane groups **17a**, **17b**, and **17c** were also prepared by the reaction with EOMT under the same conditions as applied for the synthesis of calixarenes **16a**.

All of the synthesized calixarenes containing pendant oxetane groups were confirmed by IR and ¹H NMR spectra, and elemental analysis. These results mean that calixarenes such as **1a**, **1c**, and **1d** can be modified easily to form new photo-functional calixarene derivatives

by the substitution reaction of potassium salts of **1a**, **1c**, and **1d** with MOMT or EOMT using phase-transfer catalysis under relatively mild reaction conditions.

Synthesis of calixarene containing spiro ortho ester groups was attempted using the substitution reaction of **1a** with 2-bromomethyl-1,4,6-trioxaspiro[4.4]nonane (BMTSN) using KOH and TBAB, based on the substitution reaction of calixarenes with EBH, however, no corresponding calixarene derivatives was obtained at all.

It is considered that direct introduction of spiro *ortho* ester groups into calixarene molecules by the reaction of BMTSN seemed to be very difficult to achieve due to both the steric hindrance of calixarene molecules and spiro ortho ester groups, and that the elimination reaction of BMTSN proceeded⁴⁰ as a side reaction to give the corresponding 2-methylene-1,4,6-trioxaspiro[4.4]nonane. Therefore, we examined the

introduction of an appropriate spacer chain between calixarene molecules and spiro *ortho* ester groups as shown in Scheme 10.

The substitution reaction of **1a**, **1c**, and **1d** with methyl α -bromoacetate (MBA) was conducted using Cs_2CO_3 and TBAB in NMP at 70 °C for 48 h, and corresponding calixarenes with spacer moieties were obtained in good yields. Then, the hydrolysis of the obtained calixarenes was performed using excess amount of KOH and TBAB in the mixed solvent of 1,4-dioxane and water to give calixarene derivatives with carboxymethoxy groups in good yields. Calixarenes containing spiro *ortho* ester groups **18a**, **18c**, and **18d** were prepared in good yields by the substitution reaction of calixarene derivatives with carboxymethoxy groups with excess amount of BMTSN using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base in NMP. All of the synthesized calixarenes containing pendant spiro *ortho* ester groups were confirmed by IR and ^1H NMR spectra, and elemental analysis.

It is found that calixarene derivatives containing cyclic ether groups and spiro *ortho* ester groups have excellent thermal stability as new photo-functional materials. The temperatures $T_d^{5\%}$ and $T_d^{10\%}$ of all calixarene derivatives containing oxirane and oxetane groups recorded higher than 350 °C. The temperatures $T_d^{5\%}$ and $T_d^{10\%}$ of calixarenes derivatives containing spiro *ortho* ester groups were higher than 315 °C. Interestingly, calixarene derivatives with *C*-methylcalix[4]resorcinarene structures had higher thermal stability than the corresponding calixarene derivatives with *p*-methylcalix[6]arene or *p*-*tert*-butylcalixarene structures.

PHOTOINITIATED POLYMERIZATION OF CALIXARENE DERIVATIVES

Photoinitiated Radical Polymerization of Calixarenes Containing (Meth)acryloyl Groups¹¹

The photoinitiated radical polymerizations of calixarene (meth)acrylates **5a**, **6a**, **7a**, and **8a** were carried out with 50 wt% of 2-phenoxyethyl acrylate (PEA) as a diluent, because these calixarene derivatives were solid at room temperature. Photoirradiation of the calixarene (meth)acrylates composites including 1 wt% of benzyl dimethyl ketal as a photoinitiator was performed using a high-pressure mercury lamp (20 mW cm^{-2}) under nitrogen atmosphere or in air. As shown in Figure 6, the conversion of C=C double bond of acrylate groups in **5a**, which was estimated by IR spectrum, was higher than that of methacrylate groups in **6a** under the same conditions.

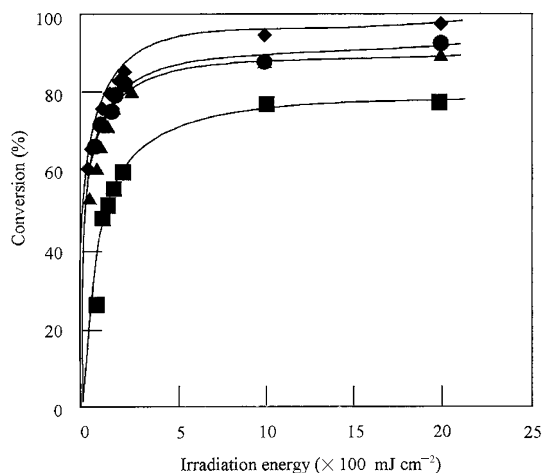


Figure 6. Rate of photopolymerization of calixarene methacrylates diluted with PEA (50/50, w/w) in the presence of benzyl dimethyl ketal (1 wt%) under nitrogen atmosphere by using a high-pressure mercury lamp (20 mW cm^{-2} at 360 nm). (◆) **5a**, (■) **6a**, (▲) **7a**, (●) **8a**.

Table IV. Conversion of calixarene (meth)acrylates by photoirradiation

Calixarene	Conv.% in N_2 ^a	Conv.% in air ^b	Acryloyl eq. (g mol^{-1}) ^c
5a	97	68	174
6a	77	60	188
7a	90	61	262
8a	91	74	275
9a	80 ^d	—	284

^aConversion (%) of calixarene (meth)acrylates diluted with PEA (50% w/w) in the presence of benzyl dimethyl ketal (1 wt%) as photoinitiator upon irradiation for 2000 mJ by high-pressure mercury lamp under nitrogen atmosphere. ^bConversion (%) of calixarene (meth)acrylates under the same irradiation conditions in the air. ^c(Meth)acryloyl equivalent of each calixarene (meth)acrylates. ^dConversion (%) of **9a** without PEA under the same irradiation.

This result shows that acrylate groups bonded in the calixarenes had higher photochemical reactivity than methacrylate groups did. It is also showed that both conversion of acrylate groups in **5a** and methacrylate groups in **6a** under nitrogen atmosphere were much higher than those in the air (Table IV). The sequence of the degree of the conversion of methacrylate groups was **8a** = **7a** > **6a** in nitrogen atmosphere, and **8a** > **7a** = **6a** in the air. This result indicates that the introduction of flexible alkyl spacer chain between calixarene backbone and methacryloyl groups enhanced the photochemical reactivity of methacrylate groups, although the introduction of alkyl spacer chain decreased the concentration of methacrylate groups. Moreover, **9a** was easily polymerized without PEA and indicated relatively high conversion of acrylic double bond.

Photoinitiated Cationic Polymerization of Calixarenes

Containing Cationically Polymerizable Groups¹⁰

The photoinitiated cationic polymerizations of calixarenes **10a**, **12a**, **12c**, **13a**, and **14a** were examined using 5 mol% of 4-morpholino-2,5-dibutoxybenzenediazonium hexafluorophosphate (MDBZ) or DPSP as a PAG in the film state using a 250 W high-pressure mercury lamp. As shown in Figure 7, when MDBZ was used, the rate of the photochemical reaction increased as following order, **10a** > **12a** > **12c** > **13a** > **14a**. This result means that calixarenes **10a** having 1-propenyl ether groups and calixarene **14a** having hydroxyl alkyl vinyl ether groups did not proceed effectively using MDBZ. On the other hand, when DPSP

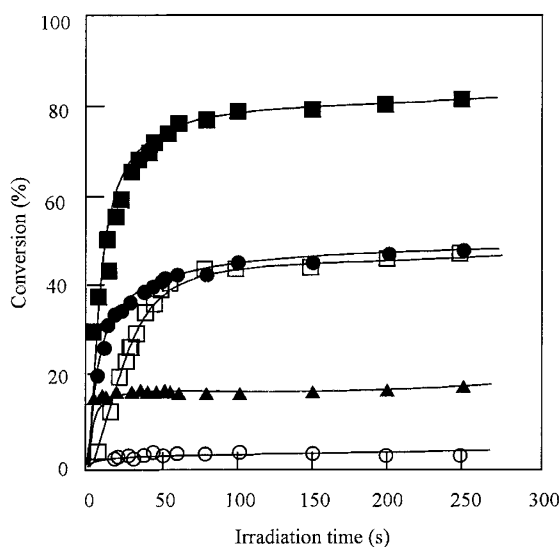


Figure 7. Rates of photopolymerization of calixarenes **10a**, **12a**, **12c**, **13a**, and **14a** with MDBZ (5 mol%): (■) calixarene **10a**, (□) calixarene **12c**, (▲) calixarene **13a**, (●) calixarene **12a**, (○) calixarene **14a**.

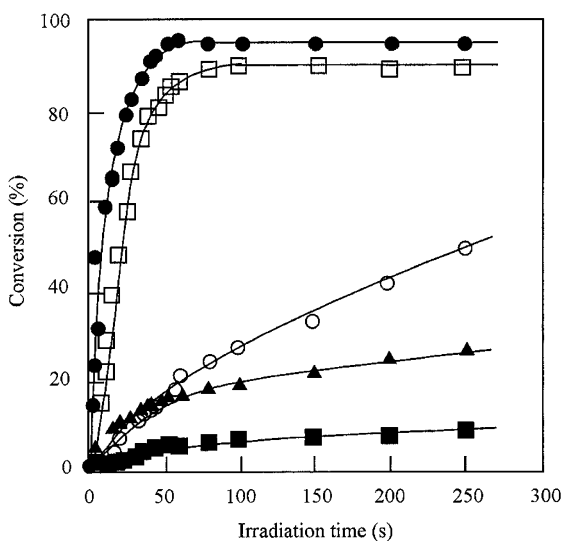


Figure 8. Rates of photochemical reaction of calixarenes **10a**, **12a**, **12c**, **13a**, and **14a** with DPSP (5 mol%): (■) calixarene **10a**, (●) calixarene **12a**, (□) calixarene **12c**, (▲) calixarene **13a**, (○) calixarene **14a**.

was used, the rate of the photochemical reaction increased as following order, **12a** > **12c** > **14a** > **13a** > **10a** (Figure 8). This result means that although DPSP has good activity as a PAG to the vinyl ether groups in the calixarenes, the photoinitiated cationic polymerization of calixarene **13a** is strongly hindered by the hydroxyl groups in the molecule. It has been reported⁶ that the photoinitiated cationic polymerization of 1-propenyl ether groups in liquid monomers proceeded very smoothly as did as the photoinitiated polymerization of vinyl ether groups. However, the photoinitiated cationic polymerization of 1-propenyl ether groups in calixarene **13a** did not proceed smoothly. This may be due to the steric hindrance of calixarene structures or due to the inhibition of molecular motion of 1-propenyl ether groups bonded directly to the rigid calixarene backbone. From these results, it was found that combination with photo-acid generators is a very important factor for the photo-crosslinking reaction of calixarene derivatives containing certain cationically polymerizable groups, even though these calixarene derivatives have high photochemical reactivity.

Photoinitiated Cationic Polymerization of Calixarenes Containing Pendant Cyclic Ether Groups^{37,38}

The photoinitiated cationic polymerizations of calixarenes **15a**, **15c**, and **15d** containing oxirane groups were examined using 5 mol% of DPSP in the film state using a 250 W high-pressure mercury lamp. As shown in Figure 9, the rate of the reaction increased as following order, **15d** > **15a** > **15c**, and the conversions of **15d**, **15a**, and **15c** were reached 61,

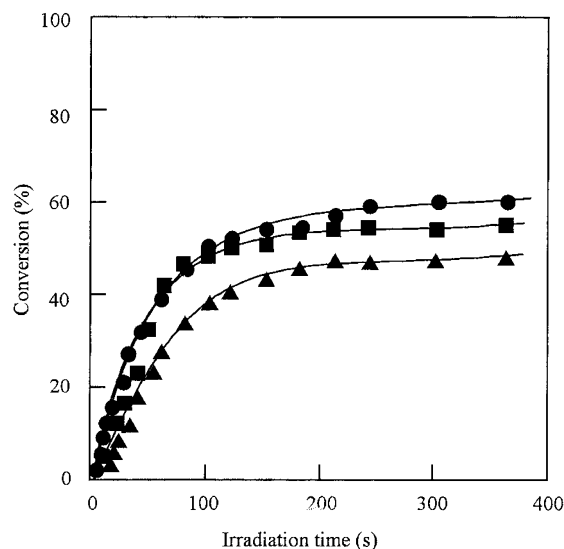


Figure 9. Rates of the photochemical reaction of calixarenes **15a**, **15c**, and **15d** containing pendant oxirane groups with DPSP (5 mol%): (●) calixarene **15d**, (■) calixarene **15a**, and (▲) calixarene **15c**.

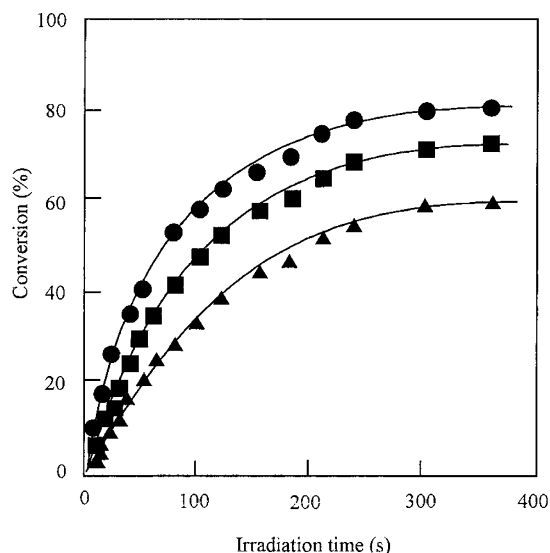


Figure 10. Rates of the photochemical reaction of calixarenes **16a**, **16c**, and **16d** containing pendant (3-methyloxetane-3-yl)methyl groups with DPSP (5 mol%): (●) calixarene **16d**, (■) calixarene **16a**, and (▲) calixarene **16c**.

55, and 48 mol% at 360 s, respectively. This result showed the rate of the photoinitiated cationic polymerization of oxirane groups in calixarenes was affected by the structures of calixarene backbones, that is, *C*-methylcalix[4]resorcinarene derivative containing the oxirane groups (**15d**) had higher rate than those of *p*-methylcalix[6]arene derivative (**15a**) and *p*-*tert*-butylcalix[8]arene derivative (**15c**). The photoinitiated cationic polymerizations of calixarenes **15a**, **15c**, and **15d** were also performed with 5 mol% of (η -cyclopentadiene)(η -1-isopropylbenzene)iron (CBI), and conversions of oxirane groups of, **15a**, **15c**, and **15d** were reached 25, 33, and 37 mol% at 360 s, respectively. These results mean that DPSP had higher activity than CBI on the photoinitiated cationic polymerization of calixarene derivatives containing oxirane groups in the film state.

The photoinitiated cationic polymerizations of calixarenes **16a**, **16c**, and **16d** containing 3'-methyl-3'-oxetanylmethoxy groups were also examined using 5 mol% of DPSP under the same irradiation conditions. As shown in Figure 10, the reaction rate increased as following order, **16d** > **16a** > **16c**, and the conversions of **16d**, **16a**, and **16c** reached 81, 73, and 60 mol% at 360 s, respectively. This may be due to good mutual solubility between calixarene **16d** and DPSP, or to higher concentration of the oxetane groups in the same cubic measures of the calixarene derivatives. From these examinations on the photoinitiated cationic polymerization, it was also proved that calixarene derivatives containing oxetane groups had higher photochemical reactivity than calixarene derivatives containing oxirane groups when DPSP or CBI was used.

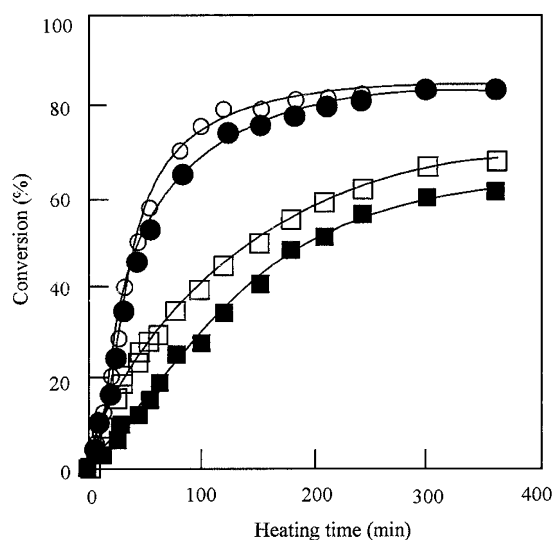


Figure 11. Rates of the cationic polymerization of calixarene **18d** (containing spiro *ortho* ester groups) with DPSP (5 mol%) upon UV irradiation for 5 min followed by heating at (○)170, (●) 150, (□) 120, and (■)100 °C.

The photoinitiated cationic polymerization of calixarenes containing spiro *ortho* ester groups was examined in the film state with 5 mol% of certain photo-acid generators such as MDBZ, DPSP, and CBI upon UV irradiation using a 250 W high-pressure mercury lamp. The conversions of the spiro *ortho* ester groups were estimated from the decrease of the absorption peaks at 1050 cm^{-1} assignable to spiro *ortho* ester groups in the IR spectra.

Calixarene **18d** films containing 5 mol% of PAG did not show any decrease of the absorption peaks, when the photoirradiation of the polymer films was performed for 30 min. Therefore, thermal treatment of the irradiated calixarene **18d** films upon 5 min was examined by a heating at 150 °C. When the photoinitiated cationic polymerization of calixarene **18d** film was carried out with 5 mol% of DPSP upon photoirradiation for 5 min followed by heating at certain temperatures such as 100, 120, 150, and 170 °C, each reaction occurred smoothly. As shown in Figure 11, the reaction rate increased as with the heating temperature increased, and the conversion of the spiro *ortho* ester groups in **18d** reached 83% by heating at 170 °C for 360 min.

The photoinitiated cationic polymerization of calixarenes **18a**, **18c**, and **18d** films containing spiro *ortho* ester groups was also performed with 5 mol% of DPSP upon 5 min irradiation using a 250 W high-pressure mercury lamp. As shown in Figure 12, the rate of the reaction increased as following order, **18d** > **18a** > **18c**, and the conversions of **18d**, **18a**, and **18c** reached 84, 72, and 57 mol% by heating at 360 min, respectively. This may be due to good mutual solubility between cal-

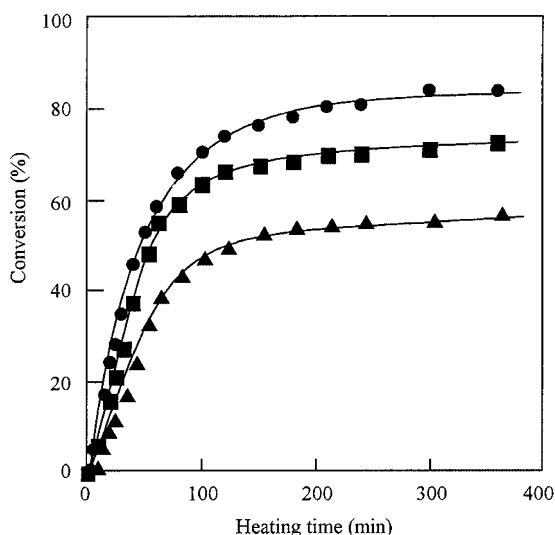


Figure 12. Rates of the cationic polymerization of calixarenes (●) **18d**, (■) **18a**, and (▲) **18a** (containing spiro *ortho* ester groups) with DPSP (5 mol%) upon UV irradiation for 5 min followed by heating at 150 °C.

ixarene **18d** and DPSP, or to higher concentration of the spiro *ortho* ester groups in the same cubic measures of the calixarene derivatives.

THERMAL CURING REACTION OF EPOXY RESINS WITH CALIXARENES

*Thermal Curing Reaction of Epoxy Resins with Calixarenes*⁴¹

The reaction behavior of thermal curing of epoxy resins with calixarenes using certain catalysts was examined in bulk. The conversions of the reaction could be monitored by decrease of the characteristic peak of oxirane groups at 910 cm^{-1} in FT-IR spectrum. The curing reaction of a commercially available epoxy resin, Epikote 828, with *p*-methylcalix[6]arene **1a** (molar ratio of oxirane groups: OH groups = 1:1) was conducted using 4 mol% of catalysts such as amines, potassium phenoxide/18-crown-6 complex (18-C-6/KOPh), and quaternary onium salts at 190 °C. Table V summarized conversions of oxirane groups of **1a** at 10 min and 4 h, and T_g s of the resulting cured resins. The reaction was accelerated efficiently in initial stage by *N,N'*-dimethylaminopyridine (DMAP) and DBU, and the conversions were 61 and 81% at 10 min and 93 and 93% at 4 h, respectively. A crown ether complex, 18-C-6/KOPh and tetrabutylphosphonium bromide (TBPB), tetraphenylphosphonium bromide (TPPB) or chloride (TPPC) were also effective catalysts for the curing reaction, and the conversion reached over 95% at 4 h. In all cases, T_g s of the resulting materials were 194–206 °C. It was found that tetrabutyl or tetraphosphonium salts were suitable catalysts for the curing reaction of

Table V. Curing reaction of Epikote828 with **1a** using 4 mol% of various catalysts at 190 °C

Catalysts	Conversion (%)		T_g^c (°C)
	at 10 min ^a	at 4 h ^b	
TBPB	25	95	206
TPPB	44	96	195
TPPC	32	96	202
18-C-6/KOPh	36	95	206
TPP	15	94	204
DMAP	61	93	194
DBU	81	93	197

^aThe conversion was given by thermal curing reaction of Epikote828 with **1a** using various catalysts at 190 °C for 10 min. ^bThe conversion was given by thermal curing reaction of Epikote828 with **1a** using various catalysts at 190 °C for 4 h. ^cMeasured by DSC at heating rate of 10 °C min^{-1} under N_2 .

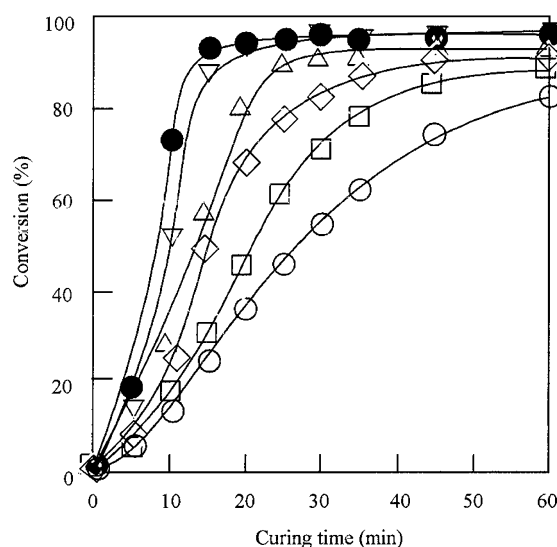


Figure 13. Curing reaction of Epikote828 with **1a** using 4 mol% of TBPB at various temperatures. (○) 170 °C, (□) 180 °C, (◇) 190 °C, (△) 200 °C, (▽) 210 °C, (●) 220 °C.

Epikote 828 with **1a**, considering catalytic activity, T_g , and miscibility of the used catalysts.

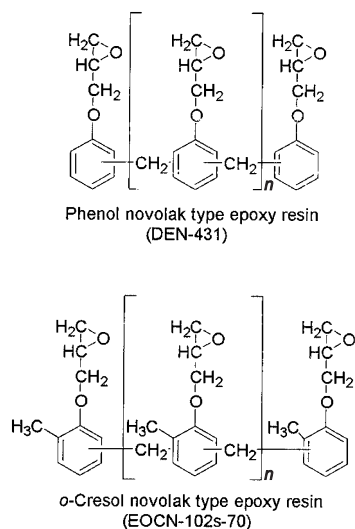
Figure 13 shows the time-conversion curves of the curing reaction of Epikote 828 with **1a** using 4 mol% of TBPB at various temperatures. The reaction proceeded smoothly at high temperature, and the conversion reached 95% for 15 min at 220 °C.

In epoxy resin curing system, the relationships between conversions, degrees of crosslinking and T_g s are very important factors to understand properties of the cured materials. The curing reaction of Epikote 828 with calixarene derivatives **1a**, **1c**, and **1d** using 4 mol% of TBPB was carried out at 190 °C for 4 h, and the conversions and T_g s of the obtained resins were summarized in Table VI. The conversions of the reaction increased as following order, **1a** > **1c** > **1d**. On the other hand, T_g s of the obtained resins increased as following

Table VI. Curing reaction of Epikote828 with calixarenes, **1a**, **1c**, and **1d**^a

Calixarene	Conversion (%) ^b	T_g (°C) ^c	$T_d^{10\%}$ (°C) ^d
1a	95	206	364
1c	87	188	365
1d	85	242	377

^aThe curing reaction of Epikote 828 with calixarenes was carried out using 4 mol% of TBPB at 190 °C for 4 h. ^bMeasured by FT-IR spectrum. ^cMeasured by DSC at heating rate of 10 °C min⁻¹ under N₂. ^dMeasured by TGA at heating rate of 10 °C min⁻¹ under N₂.

**Scheme 11.**

order, **1d** > **1a** > **1c**. This means that the degree of crosslinking of the obtained resin with **1d** is the highest degree, which would be due to the density of OH groups in the mixture of Epikote 828 and calixarenes used. It was also proved that the cured resins with the calixarenes had good thermal stability; the IDTs were over 360 °C in nitrogen atmosphere.

Curing reaction of certain commercially available epoxy resins with **1a** using 4 mol% of TBPB was also examined at 200 °C for 4 h (Scheme 11). The reaction of phenol novolak type epoxy resin DEN-431 or *o*-cresol novolak type resin EOCN-102s-70 with **1a** proceeded with 95% and 86% conversion, respectively, and T_g s of the cured resins were 203 and 214 °C (Table VII). Thus, it was proved that the curing reaction of epoxy resins with calixarene **1a**, **1c**, and **1d** using quaternary phosphonium salts proceeded efficiently high temperature 170–220 °C to obtain cured resin with high T_g s and good thermal stability.

Thermal Curing Reaction of Epoxy Resins with Calixarenes Containing Active Ester Groups⁴²

The epoxy resins without hydroxyl groups are seemed to have low water-absorbing property in addition to high thermal property. Based on the regioselective

Table VII. The cured resins of various epoxy resins with **1a**^a

Epoxy resin	Conversion (%) ^b	T_g (°C) ^c
DEN-431	95	203
EOCN-102s-70	86	214
Epikote828	95	209

^aThe curing reaction of various epoxy resins with **1a** was carried out using 4 mol% of TBPB at 200 °C for 4 h. ^bMeasured by FT-IR spectrum. ^cMeasured by DSC at heating rate of 10 °C min⁻¹ under N₂.

Table VIII. Thermal properties of the cured resin of Epikote828 with calixarenes containing ester groups^a

Calixarenes	Temp. (°C)	Conv. (%) ^b	T_g (°C) ^c	$T_d^{10\%}$ (°C) ^d
19a	190	67	105	344
	200	73	113	345
	210	75	127	347
	220	82	135	347
19c	190	46	98	362
	200	55	107	363
	210	68	117	362
	220	47	114	364
19d	190	64	117	348
	200	65	124	347
	210	66	127	348
	220	69	134	347
20a	190	82	99	339
	200	85	107	337
	210	87	115	340
	220	91	124	343
20c	190	64	94	350
	200	67	106	351
	210	76	111	350
	220	73	108	349

^aThis cured resin was given by thermal curing reaction of Epikote828 with calixarenes using 4 mol% for 6 h. ^bMeasured by FT-IR spectrum. ^cMeasured by DSC at heating rate of 10 °C min⁻¹ under N₂. ^dMeasured by TGA at heating rate of 10 °C min⁻¹ under N₂.

tive addition reaction of oxiranes⁴³ with active carboxylic esters using quaternary onium salts catalysts, we designed calixarenes containing ester groups as new curing agents for epoxy resins without hydroxyl groups. Calixarenes containing methyl or phenyl ester groups were prepared in high yields by the reaction of the corresponding starting calixarenes with acetic anhydride or benzoyl chloride in the presence of pyridine. The curing reaction of Epikote 828 with *p*-methylcalix[6]arene containing methyl ester groups (**19a**), *p*-*tert*-butylcalix[8]arene containing methyl ester groups (**19c**), *C*-methylcalix[4]resorcinarene containing methyl ester groups (**19d**), *p*-methylcalix[6]arene containing phenyl ester groups (**20a**), and *p*-*tert*-butylcalix[8]arene containing phenyl ester groups (**20c**) using 4 mol% of TPPB were examined at prescribed temperatures for 6 h, and results were

Table IX. Thermal properties of the cured resin of Epikote828 with mixed curing agents^a

Composition (19d/1d)	Conversion (%) ^b	T _g (°C) ^c	T _d ^{10%} (°C) ^d
100 / 0	78	137	366
70 / 30	85	170	362
50 / 50	92	197	363
30 / 70	94	217	364
0 / 100	96	233	368

^aThis cured resin was given by thermal curing reaction of Epikote828 with mixed curing agents using 4 mol% of TBPB at 210 °C for 6 h. ^bMeasured by FT-IR spectrum. ^cMeasured by DSC at heating rate of 10 °C min⁻¹ under N₂. ^dMeasured by TGA at heating rate of 10 °C min⁻¹ under N₂.

summarized in Table VIII. Based on the conversions, the order on the efficiency of the curing reaction with calixarene derivatives at 210 °C was as follows; **20a** > **20c**, **19a** > **19c**, **19d**. T_gs of the obtained resins increased gradually as following order; **19a**, **19d** > **19c**, **20a** > **20c**. It seemed that the curing reactions did not proceed effectively in the late stage, that is, bulky acetyl or benzoyl groups of the cross-linked matrixes would hinder the reaction. T_gs of the resulting resins were relatively lower than those of resins cured with calixarenes, due to the ester groups in the cross-linked resins. IDTs of the cured resins with the calixarenes containing ester groups were 340–365 °C. Thus, it was suggested that the cured resins have good thermal stability.

*Curing Reaction of Epoxy Resins with the Mixtures of Calixarenes and Calixarenes Containing Partial Ester Groups*⁴⁴

Curing reaction of Epikote 828 can be conducted with mixtures of calixarenes and calixarenes containing ester groups to obtain cured resins including hydroxyl groups and ester groups, which is expected to have good balances on the properties of T_g, thermal property, water-absorbing property, mechanical properties, etc. The curing reaction with various ratios of mixtures of *C*-methylcalix[4]resorcinarene **1d** and *C*-methylcalix[4]resorcinarene containing methyl ester groups **19d** was carried out using 4 mol% of TBPB at 210 °C for 6 h. As shown in Table IX, conversions of oxirane groups and T_gs of the obtained resins increased with the ratio of **1d**. The decomposition temperatures of the obtained resins were about 365 °C in all ratios of **1d** and **19d**.

Curing reaction of Epikote 828 with *C*-methyl[4]resorcinarenes containing partial methyl ester groups, **22d** (50% methyl ester) in the presence of 4 mol% of TBPB were also conducted at various temperatures for 6 h, and the results were summarized

Table X. Thermal properties of the cured resin of Epikote828 with **22d**^a

Curing temp. (°C)	Conversion (%) ^b	T _g (°C) ^c	T _d (°C) ^d
150	77	175	361
170	79	178	362
190	84	185	366
210	90	194	365

^aThis cured resin was given by thermal curing reaction of Epikote828 with **22d** using 4 mol% of TBPB at 210 °C for 6 h.

^bMeasured by FT-IR spectrum. ^cMeasured by DSC at heating rate of 10 °C min⁻¹ under N₂. ^dMeasured by TGA at heating rate of 10 °C min⁻¹ under N₂.

in Table X. The conversions increased gradually with reaction temperatures, and the conversion reached 90% at 210 °C. The T_gs of obtained resins also increased with the temperatures. This means that the conversions correspond to degrees of cross-linking in the curing system.

The characteristics of the curing system of epoxy resins with the calixarene derivatives as curing agents are summarized as follows. (1) The cured epoxy resins with calixarenes **1a**, **1c**, and **1d** showed high T_gs. (2) The cured epoxy resins with the calixarenes containing active ester groups have lower T_gs compared with those with **1a**, **1c**, and **1d**. (3) In the case of curing of epoxy resins with mixtures of calixarenes and calixarenes containing ester groups, or calixarenes containing partially ester groups, the balance of high T_gs can be controlled by the contents of ester groups of the calixarenes used.

CONCLUSION

The authors have developed successful synthetic methods of a variety of calixarene derivatives containing functional groups such as protective groups and various polymerizable groups. It was found that the novel calixarene derivatives had good thermal stability, which is an advantage as high performance materials. The photoinduced deprotection of the calixarenes containing protective groups such as *t*-Boc, TMS, and CHE groups readily proceeded to give the corresponding products. It was demonstrated that radical polymerization, cationic polymerization, and cationic ring-opening polymerization of calixarene derivatives containing certain polymerizable groups could be achieved to give crosslinked materials with excellent thermal stability. The obtained materials are very useful as high performance materials for UV and EB curing systems. It was also presented that the calixarenes **1a**, **1c**, and **1d**, and calixarenes containing active ester groups have high potentials as curing agents with good thermal stability for novel epoxy resin systems. The calixarene

derivatives presented in this paper are useful materials for applications in the field of electronics, etc.

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