# Preparation and Cured Properties of Novel Cycloaliphatic Epoxy Resins

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## SYNOPSIS

Preparation and characterization of novel cycloaliphatic epoxy resins, which are derived from octadienyl compounds, were studied. From a model peracetic acid epoxidation reaction using 2,7-octadienyl acetate-1, the structure of the liquid resins is estimated to be mainly terminal epoxides and some amount of inner epoxide depending on the epoxide content. The epoxy resins offer lower toxicity and lower vapor pressure. The reactivity of the resin with acid anhydrides is moderate but faster than that of traditional cyclohexane epoxide-type resins and slower than that of the glycidyl ester-type resins. This reactivity was also examined using model compounds. The heat deflection temperature of the hexahydrophthalic anhydride-cured resins is shown to be directly proportional to the number of epoxy groups in the molecules. The flexural strength of the cured resins is nearly equivalent to that of the commercial resins, although the flexural elongation of the resins is larger than that of the rigid cyclohexane epoxide-type resins. The thermal stability of the cured resins is comparable to typical rigid cycloaliphatic resins; furthermore, high water resistance of the cured resins is suggested to be attributed to the hydrophobic character of the $C_8$ chain by cross-linking. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

The cycloaliphatic epoxy resins display inherently lower levels of ionic impurities, resin viscosities, and good high-temperature electrical characteristics and are acknowledged to be superior in arc and tracking resistance.[1] This is an advantage of the commercialized bisphenol A-type epoxy resins (DGEBA), which have variation in molecular weight and suitable reactivity with various kinds of hardeners. On the other hand, the cycloaliphatic epoxy resins are specific in their unusual reactivity and small variations in molecular weight.

The cured properties of the unmodified state are hardness, brittleness, and lack of toughness.[2] These limitations, when using the cycloaliphatic epoxy resins for casting, have shown the need to improve the performance of the cycloaliphatic epoxy resins.[3]

This article deals with these new types of cycloaliphatic epoxy resins that are derived from 2,7-octadienol-1. When we first reported these new types of cycloaliphatic epoxy resins,[4] they were prepared through multiple steps from butadiene. However, now it is industrially noteworthy, since 2,7-octadienol-1, the starting material of our epoxy resin, has recently been reported to be produced commercially by the direct preparation from butadiene and water.[5,6] We report here the preparation and some characterization of this new type of epoxy resin and its cured properties.

## EXPERIMENTAL

### Materials

Peracetic acid was obtained from the Mitsubishi Gas Chemical Co.; hexahydrophthalic anhydride (HHPA) and tetrahydrophthalic anhydride (THPA), from the New Japan Chemical Co.; bisphenol A-type epoxy resin, Epikote 828, from the Shell Chemical Co.; hydrogenated bisphenol A epoxy

resin E-4080, from the Asahi Denka Kogyo Co.; cycloaliphatic epoxy resin, Araldite CY-175 and 185, from Ciba Geigy; and ERL-4221 and 090, from U.C.C.

## Characterization

Molecular weight distribution was estimated using a Toyo Soda high-speed liquid chromatograph. ^{1}H-NMR spectra were measured using a Varian Associate 60 MHz spectrometer, differential scanning calorimetry was performed on a Perkin-Elmer DSC-1B calorimeter, and flexural properties (ASTM-D790-63T) were determined on a Shimazu autograph (Model DDS-5000). The epoxy value was measured by trimethylbenzyl–ammonium bromide perchloric acid titration,[7] and the $I_2$ value, by iodine titration using the Hanus method.[8]

## Preparation of 2,7-Octadienyl Acetate-1 (1-AOD)

1-AOD was prepared from butadiene and acetic acid according to the procedure in the patent literature.[9] 1-AOD was purified by rectification at 80°C/5 mmHg.

## Preparation of 2,7-Octadienol-1 (1-HOD)

1-HOD was prepared from 1-AOD according to the procedure described in the patent literature.[10]

## Preparation of Di(2,7-octadienyl)-hexahydrophthalate

The mixture of 10.88 kg HHPA, 23.0 kg 1-HOD, 2.58 kg xylene, and 9.2 g zinc diacetate was heated to 120°C for 30 min and then up to 195°C under a $N_2$ stream with stirring in an esterification apparatus having a condensation column for removing the water formed. The reaction was continued for 24 h until no further water was evolved. The remaining xylene and excess 1-HOD were then completely removed under reduced pressure at 200°C/1 mmHg. The condensate product was found to be the diester of HHPA.

ANAL: Titration of free COOH by alkali shows $0.92 \times 10^{-2}$ eq mol/100 g, and the iodide value was 239 I g/100 g. ^{1}H-NMR in $CCl_4$: 1.1–1.7 (M, 6H) $CH_2$ and $CH_2$ of cyclohaxane, 1.8–2.25 (M, 4H) $CH_2$ adjacent to double bond, 2.5–2.82 (M, 1H) of 1,2-cyclohaxane dicarboxylate, 4.25–4.5 (D, 2H) $CH_2$ of ester in $C_8$ chain, and 4.63–6.0 (M, 5H) H of double bond in $C_8$ chain (ppm).

## Preparation of the Epoxy Resin

Di(2,7-octadienyl)hexahydrophthalate, 972 g, was dissolved in 2530 g of $CHCl_3$ in a three-necked flask. The mixture was cooled and kept below 20°C. Added dropwise with stirring to the above solution while maintaining the temperature at 35°C for 2 h was 1750 g of 31.8% peracetic acid aqueous solution neutralized with 27.5 g of sodium acetate. After the reaction was continued for 4 h at a temperature of 40°C, $H_2O_2$, acetic acid, and any remaining peracetic acid were removed by washing with excess water several times until no more peroxide or peracetic acid was detected and the $CHCl_3$ solution was evaporated. The condensate was completely dried under vacuum at 90°C/0.2 mmHg. Yield of the epoxy resin was 1055 g.

ANAL: Epoxy value 0.557 eq mol/100 g, $I_2$ value 52 I g/100 g, and hydroxy value about 0.043 eq mol/100 g. ^{1}H-NMR in $CCl_4$ (ppm): 1.55 (S) $CH_2$ of $C_8$ chain and cyclohexane ring, 2.3–2.8 (M) CH of oxirane, 2.8–3.0 (M) CH of 1,2-cyclohexane dicarboxylate, 3.35–4.3 (M) $CH_2$ of ester and $CH_3$ of acetate, 4.3–4.6 (D) $CH_2$ of ester, and 4.8–6.0 (M) CH and $CH_2$ of remaining double bond.

## Curing of Di(2,7-epoxy-octyl)hexahydrophthalate with HHPA

Di(2,7-epoxy-octyl)hexahydrophthalate, 100 g, was well mixed in various ratios with HHPA and heated to 50°C under reduced pressure. To this mixture, 1 phr of $N,N$- dimethyl benzylamine (BDMA) was added and mixed well. The mixture was then poured into a preheated Teflon-coated steel mold and cured at 100°C for 2 h and then at 150°C for 3 h. Other epoxy resins were also cured using the same procedure. Mechanical properties were determined using ASTM procedures.

## Curing Behavior (Model Reaction of Curing)

The reaction of 7,8-epoxy-2-octenyl acetate-1, the terminal epoxide of 1-AOD, (A), with HHPA in the presence of several catalysts was carried out. (A), 18.4 g (0.1 mol), was mixed well with 15.4 g (0.1 mol) of HHPA and heated to 100°C. To this mixture, the 1 phr of BDMA was added and mixed well.

During the course of the reaction, sampling was done and the remaining epoxide content and the amount of unreacted (A) was determined by titration and by GC. Free carboxylic acid was also detected by titration with alkali.

## DSC Scan

The mixture of ( **A** ), HHPA, and BDMA was placed in an aluminum pan and examined by DSC (Perkin-Elmer DSC-IB) with a heating rate of 16°C/min from room temperature to 250°C in a nitrogen atmosphere. The reaction of 2,3-epoxy-7-octenyl acetate-1 (**B**) with HHPA and the reaction of dibutyl(4,5-epoxy)cyclohexyl-1,2-dicarboxylate (**C**) with HHPA were also examined using the same methods.

## RESULTS AND DISCUSSION

### Epoxidation of 2,7-Octadienyl Acetate

The epoxidation reaction of 2,7-octadienyl acetate-1 as a model reaction was carried out under the same conditions to understand the structure of the liquid epoxide resins. 2,7-Octadienyl ester has two types of double bonds: One is terminal and the other is internal. Therefore, the epoxidation proceeds as follows:
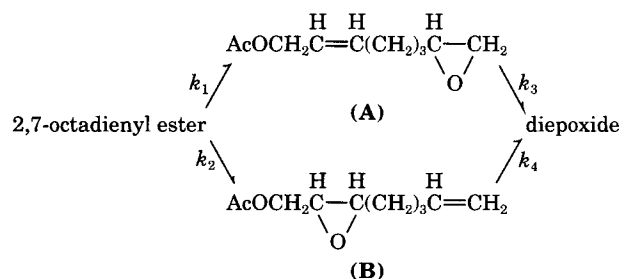


The rate constants and activation energies of the individual reactions are shown in Table I, which shows that $k_1$ was 1.66 times that of $k_2$ and that $k_4$ was also 1.76 times that of $k_3$. The activation energy values are almost of the same order. It was, therefore, expected that the structure of the liquid epoxy resin, ( **I** ), ( **II** ), and ( **III** ), would be mainly terminal epoxides and that the remaining olefinic bonds may be internal.

## Epoxidation of Di(2,7-octadienyl)-hexahydrophthalate

Commercially available peracetic acid (produced from $H_2O_2$) contains a small amount of sulfonic acid as a catalyst. Therefore, peracetic acid was neutralized with sodium acetate before using.

The opening reaction of the formed epoxide was found at a high reaction temperature when an excess of sodium acetate was used. As mentioned in the Experimental section, the yield and the selectivity of the epoxide were very good when the reaction conditions were properly chosen.

Dichloromethane and chloroform were the best solvents. In other solvents, the reaction rate was slow and in the order benzene < toluene < ethyl acetate. The structure of the liquid epoxy resin was determined from $^1$H-NMR. A small amount of internal olefin was confirmed in the liquid resins.

The amount of epoxide in the liquid resins was measured by titration with trimethylbenzyl–ammonium bromide–perchloric acid. From the IR spectrum and iodide titration, a small amount of the hydroxyl group was found to have been formed. Therefore, selectivity of the epoxide formation was over 93%. The structures of the liquid resins CE-(I), -(II), and -(III) are shown in Figure 1.

### Properties of Liquid Resin CE-(I), -(II), and -(III)

These resins are derivatives from $C_8$ chains having two types of epoxy groups—one in a terminal position and the other in an internal position. The molecular weights of these resins are about 450–550, as shown in Figure 2. A high-speed liquid chromatogram of CE-(III) shows the presence of a small amount of oligomers. The viscosity is moderately low at room temperature even though diluents and flexibilizers are not present. This accounts for the high boiling points of over 200°C/1 mmHg and low vapor pressure.

**Table I  Rate Constants and Activation Energies of the Peracetic Acid Epoxidation of 1-Acetoxy-2,7-Octadiene**

| $k$ (L/mol min) | Temperature (°C) | | | | Activation Energy (kcal/mol) |
| --- | --- | --- | --- | --- | --- |
| | 17 | 25 | 30 | 35 | |
| $k_1$ | $2.74 \times 10^{-3}$ | $6.09 \times 10^{-3}$ | $9.81 \times 10^{-3}$ | $1.55 \times 10^{-2}$ | 16.85 |
| $k_2$ | $1.65 \times 10^{-3}$ | $3.70 \times 10^{-3}$ | $6.07 \times 10^{-3}$ | $9.70 \times 10^{-3}$ | 17.25 |
| $k_3$ | $1.43 \times 10^{-3}$ | $3.22 \times 10^{-3}$ | $5.28 \times 10^{-3}$ | $8.52 \times 10^{-3}$ | 17.78 |
| $k_4$ | $2.52 \times 10^{-3}$ | $5.70 \times 10^{-3}$ | $9.30 \times 10^{-3}$ | $1.47 \times 10^{-2}$ | 17.80 |
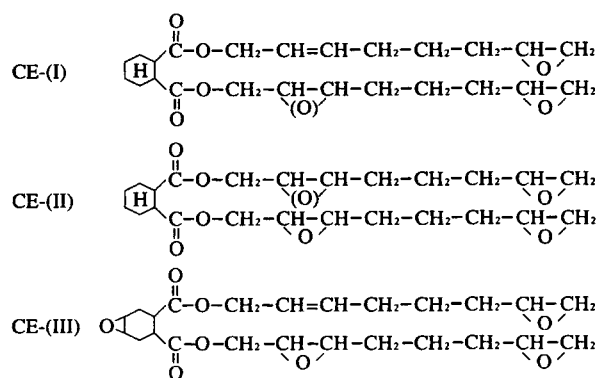
**Figure 1** Idealized chemical structure of the epoxy resin.



**Elution Volume**

**Figure 2** High-speed liquid chromatogram of CE-(III).

The toxicity of resins with high epoxy values has often been the source of serious irritation and health hazards due to handling of these resins and hardeners. The results of toxicity and irritation testing with CE-(I), -(II), and -(III) are shown in Table II. It should be noted that these new resins have relatively low toxicity as compared to other epoxy resins of this type.

## Curing Behavior of the Resins

### Model Studies on the Reactivity of the Epoxide

DSC scans of the terminal epoxide, inner epoxide, and cyclohexane epoxide as a model reaction of CE-(I), -(II), and -(III), respectively, with HHPA are shown in Figures 3 and 4. The peak temperature shifted to high temperature in the order of terminal, inner, and cyclohexane epoxide. Further, the same model reaction was detected by gas chromatography, and the titration of the epoxide and carboxylic acid was as is shown in Figure 5. Apparently, it was concluded that the terminal epoxide (A) of the octenyl showed behavior similar to the glycidyl ether of the phenol, contrary to the reactivity of the inner epoxides (B) and (C).

Several catalysts were used for testing the reactivities of the epoxides, as shown in Figures 6 and 7. The reactivities of the epoxides with HHPA in the presence of amines were estimated by the nucleophilicity of the epoxide,[11] which was estimated by the electrophilicity of the epoxide in the presence of stannous octoate.[12] Therefore, the reactivity of the cyclohexane epoxide (C) is understood to be higher than the alkyl-substituted glycidyl ester and the terminal epoxide in the reaction of the HHPA–stannous octoate system.

### Curing of the CE-(I), -(II), and -(III) Resins with HHPA Hardener

The gel time of the CE resins using HHPA hardener in the presence of BDMA is shown in Table III and Figure 8 at a temperature above 100°C, in comparison with traditional cycloaliphatic epoxy resins. These results are consistent with the reactivity results of the model reaction as expected.

Gel time of the CE resins is faster than that of the cyclohexane epoxide-type resin (CY-185) and slower than that of the glycidyl ester type resin (E-190, 191). Accordingly, curing during the casting

**Table II   Properties of Liquid Resins**

|  | CE-(I) | CE-(II) | CE-(III) |
|---|---|---|---|
| Appearance | Transparent | Transparent | Transparent |
| Epoxy equivalent weight | 200–208 | 175–182 | 135–140 |
| Viscosity (cps) |  |  |  |
| 30°C | 600–800 | 1200–2000 | 1200–2000 |
| 50°C | 150–200 | 250–340 | 200–214 |
| 80°C | 30–50 | 60–80 | 45–50 |
| $LD_{50}$ mouse, oral g/kg | 27 | 20 | 5.6 |
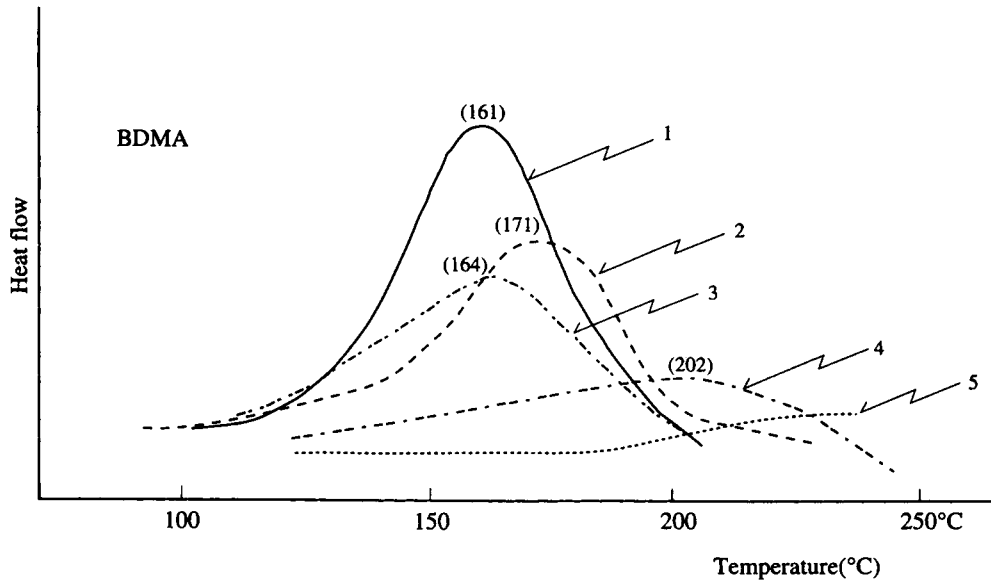
1. Phenyl glycidyl ether , 2. Terminal epoxide of 1-AOD
3.Cyclohexanol glycidyl ether , 4. Inner epoxide of 1-AOD
5. 4,5 epoxy 1,2- cyclohexane dicarboxylic acid methyl ester

**Figure 3**   DSC thermograms of the model compounds with HHPA.

process may be easy to control, since the reactivity of the CE resins is moderate, thus producing a slow heat generation. Also, it shows that processing is easy when the systems or the blending formulations with bisphenol A epoxy resins are chosen, since the reactivity of the CE resin is closer to that of the bisphenol A epoxy resin than to that of the cyclohexane epoxy-type resins.
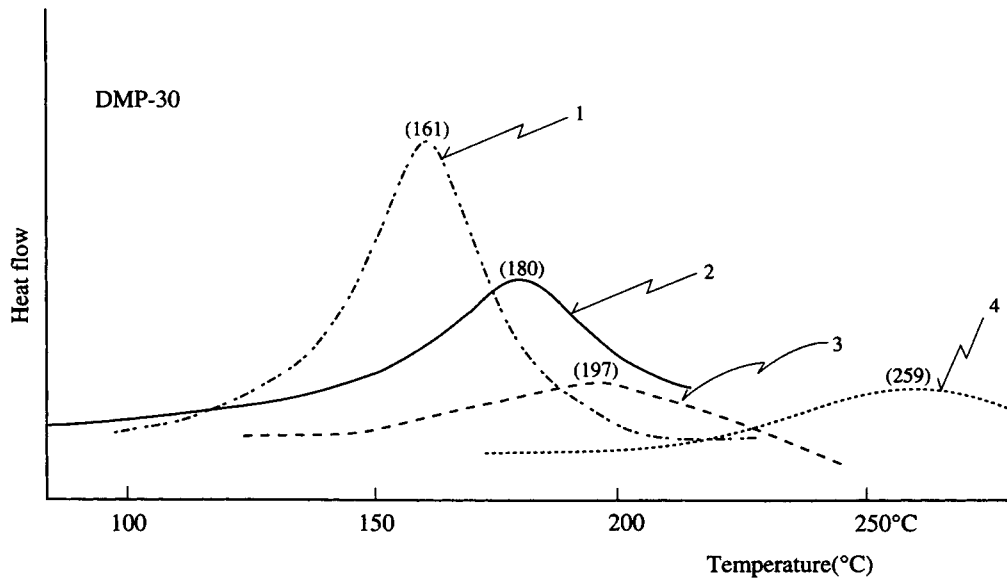


1. Phenyl glycidyl ether , 2. Terminal epoxide of 1-AOD
3.Inner epoxide of 1-AOD , 4. 4,5 epoxy cyclohexane
1,2- dicarboxylic acid dimethyl ester

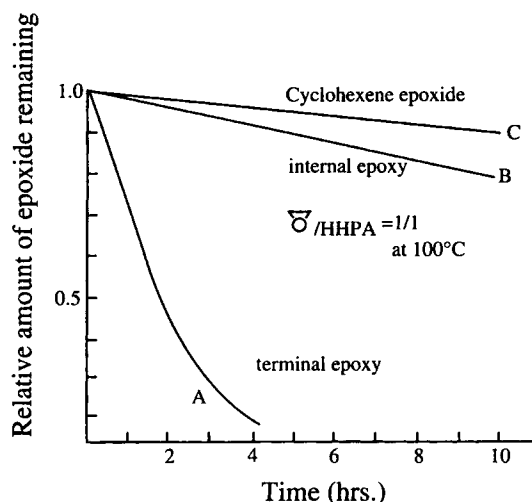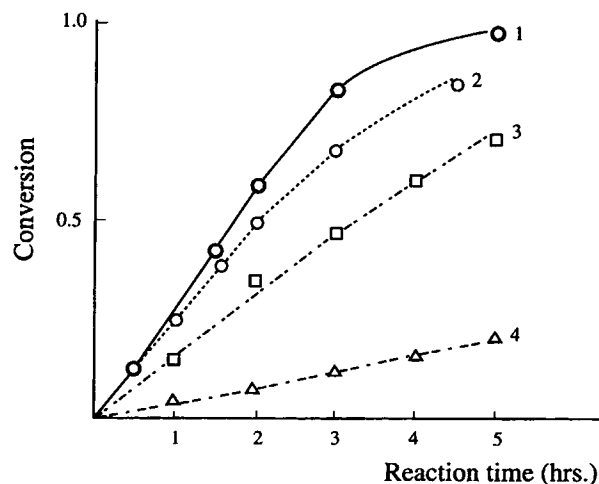**Figure 4**   DSC thermograms of the model compounds with HHPA.

**Figure 5** Reactivity of the model epoxy compounds with HHPA.

## Cured Resin Properties

The physical, thermal, and mechanical properties of the CE resins cured with HHPA in the presence of BDMA are shown in Table IV. The properties of representative commercial resins are listed for comparison.
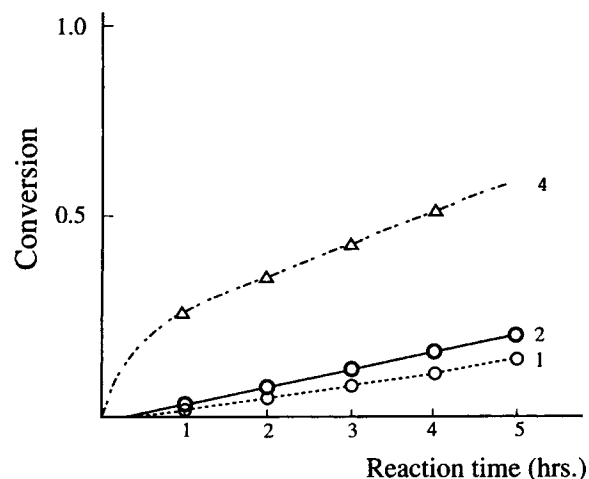
## Thermal Properties

The heat deflection temperature (HDT) of the CE resins is shown to be directly proportional to the



1. o — 2-Ethyl 4-methyl imidazole
2. o -- N,N-dimethyl benzyl amine
3. □ -- Diaza bicyclododecane
4. ▵ -- Stannous octoate

**Figure 6** Reactivity of the terminal epoxide of 1-AOD. The effect of the accelerators.



1. 2-Ethyl 4- methyl imidazole
2. N.N dimethyl benzyl amine
4. Stannous octoate

**Figure 7** Reactivity of the inner epoxide of 1-AOD. The effect of the accelerators.

number of epoxy groups in the molecules. The cured CE-(I) resin is soft and flexible, whereas the cured CE-(III) resin is rigid and hard. It is significant to note that even though the cured CE-(I) resin is soft and flexible it still has only a small weight loss when heated at high temperature (200°C).

## Mechanical Properties

The flexural properties of the cured CE resins are nearly equivalent when compared to the commercial resins, although, as expected from the structure of the CE resins, the flexural elongation of the CE resins is admittedly larger than that of the rigid cyclohexane epoxide type of resin. The CE-(II) resin has the greatest yield strength, whereas the CE-(I) has the greatest elongation among the CE resins. It is

**Table III Gel Time of the CE Resins; Reactivity at 100°C**

| | HHPA | MNA | HN-2200 (min) | HT-903 |
|---|---|---|---|---|
| CE-(I) | 50 | 72 | 52 | 29 |
| CE-(II) | 42 | 58 | 41 | 25 |
| CE-(III) | 40 | 59 | 42 | 21 |

Curing conditions; in the presence of BDMA 1%. HHPA: hexahydrophthalic anhydride; MNA: methyl nadic anhydride; HN-2200: methyl tetrahydrophthalic anhydride; HT-903: modified phthalic anhydride (Ciba Geigy).
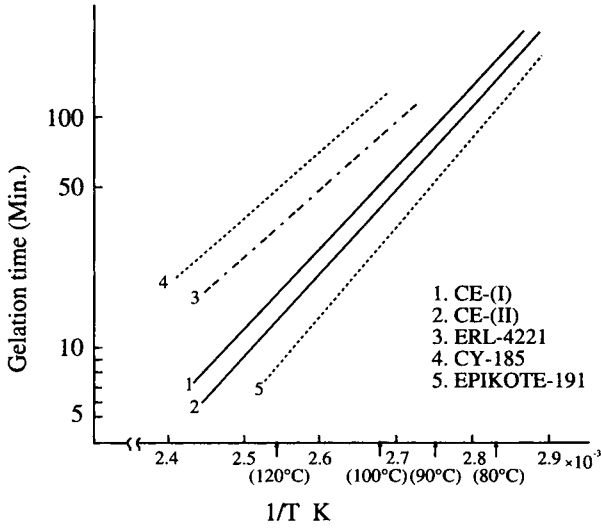
**Figure 8**    Gelation time of the CE resins.



**Figure 10**    Thermal stability of the CE resins.

reasonable to note that the yield strength of the CE-(II) resin when all the double bonds are substituted with an epoxide group resembles that of the diglycidyl ester of hexahydrophthalate, as expected from the structure (Fig. 9).

## Thermal Shock Resistance

When the cured resins with HHPA hardener were tested in the Olyphant Washer Test, the CE-(I) resin gave excellent results. The CE-(II) resin gave the same crack number value as that of the com-
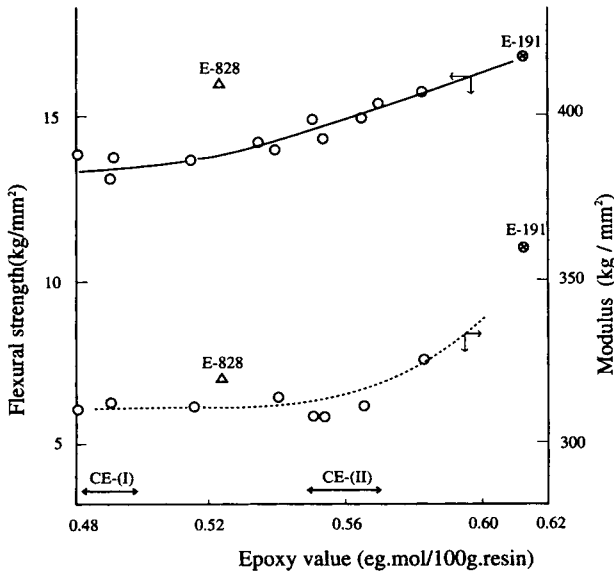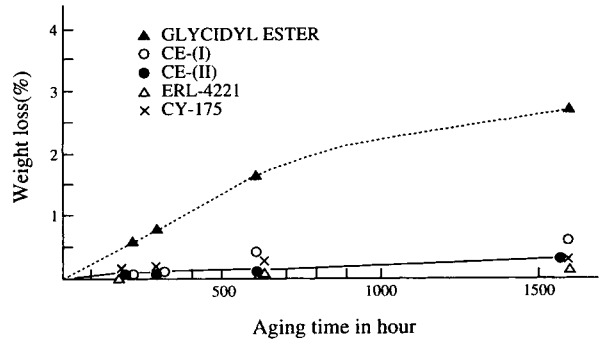


**Figure 11**    Thermal stability of the CE resins at 200°C.



**Figure 9**    The effect of the epoxide contents.
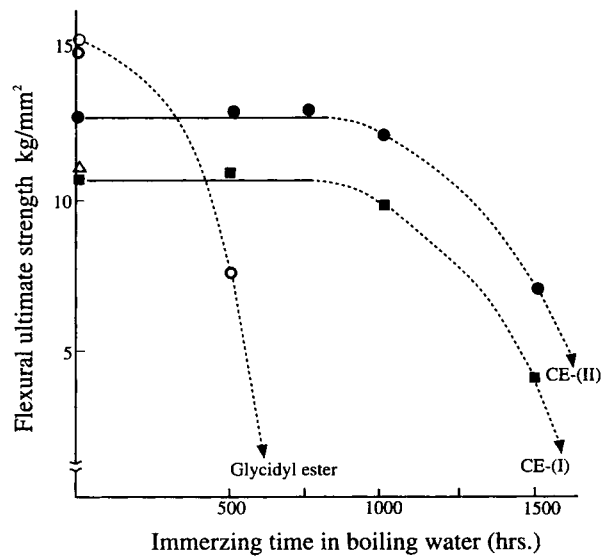


**Figure 12**    Water resistance of the cured resins.

**Table IV   Physical Properties of the CE Resins Cured with HHPA**

| | CE-(I) | CE-(II) | CE-(III) | Commercialized Resin | | | |
| | | | | Gy Ester | Modified Cyclo | Cyclo | DGEBA EW = 190 |
|---|---|---|---|---|---|---|---|
| Specific gravity | 1.19 | 1.21 | 1.23 | 1.26 | — | 1.22 | 1.21 |
| Shrinkage (%) | 4.10 | 3.90 | 4.00 | 4.20 | — | 2.70 | 2.40 |
| HDT (°C) | 65.00 | 95.00 | 150.00 | 100.00 | 90.0 | 180.00 | 118.00 |
| Weight loss (200°C) (%) | 2.00 | 1.80 | 1.20 | 5.10 | 4.5 | 1.00 | — |
| Water absorption (%) | 4.50 | 4.50 | 4.70 | −6.40 | — | — | 2.50 |
| Flexural strength (kg/mm$^2$) | 10.50 | 12.50 | 11.00 | 14.50 | 12.0 | — | 15.00 |
| Modulus, (kg/mm$^2$) | 300.00 | 310.00 | 310.00 | 350.00 | 260.0 | 350.00 | 350.00 |
| Elongation (%) | 9.00 | 8.00 | 5.00 | 8.80 | 6.6 | 3.70 | 8.50 |
| | −10.00 | −9.00 | −6.00 | | | | |

Gy ester: diglycidyl hexahydrophthalate; modified cyclo: ERL 4221 + ERL 4090 (50/50); cyclo: ERL 4221.

mercial types of glycidyl ester resins, whereas the CE-(III) resin gave results similar to conventional rigid resins with an internal epoxy substitution.

There are many types of flexibilizers available for commercial use; however, these systems usually decrease the HDT and cause some sacrifice in many of the other physical properties. In general the CE-(I) and -(II) resin system is well balanced with respect to high-temperature stability, water resistance, mechanical properties, HDT, and thermal shock resistance, particularly when compared with a con-

ventional cycloaliphatic resin modified with flexibilizers.

## Thermal Stability and Water Resistance

### Thermal Stability

The weight loss of the cured CE resins at high temperature is shown in Figures 10 and 11 and compared with conventional cycloaliphatic epoxy resins modified with flexibilizers. It is apparent how the thermal
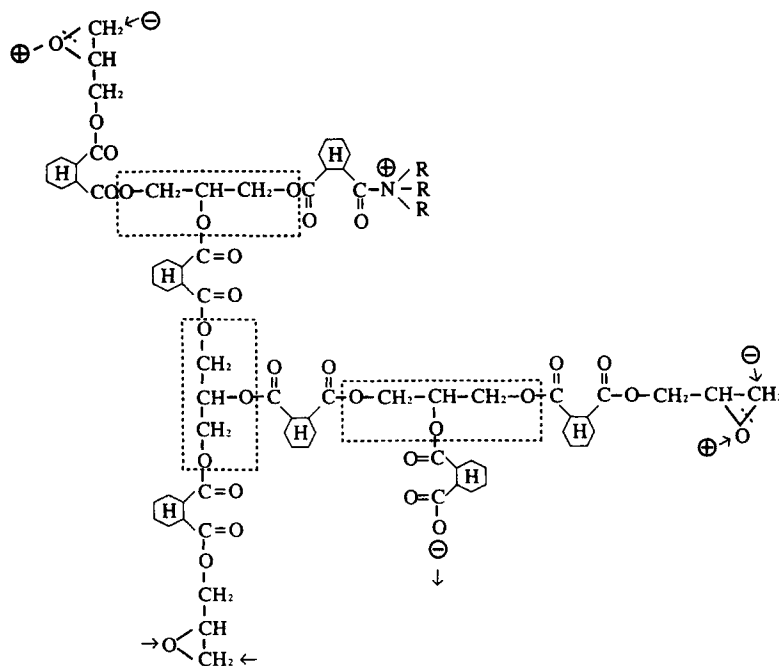


**Figure 13**  Model structure of the cured diglycidyl hexahydrophthalate with HHPA.

stability of the CE resins compares to a typical rigid cycloaliphatic resin. These results are explained by the fact that the epoxide group attached in the $C_8$ chain has a role in the thermal stability in comparison with the structure of glyceride or flexible polyether units.

### Water Resistance

One of the characteristic properties of the CE resins is a high water resistance level, as shown in Figure 12. Glycidyl esters and modified resins using flexibilizers generally have been known to produce surface cracking degradation due to high water absorption after exposure to boiling water conditions.[13] This ability of the CE resins to resist degradation is attributed to the hydrophobic character of the $C_8$ chain by cross-linking (Fig. 13).

## CONCLUSIONS

1. Novel cycloaliphatic epoxy resins were obtained in good yield by the peracetic acid epoxidation of di(2,7-octadienyl)hexahydrophthalate or tetrahydrophthalate, which was derived from the dimerization of butadiene.
2. The structure of the resin includes a terminal epoxide and some amount of inner epoxide depending on the epoxide content.
3. The reactivity of the resin with acid anhydrides is moderate but is faster than that of traditional cyclohexane epoxide-type resins and slower than that of the glycidyl ester-type resins.
4. The basic properties of the cured resins are well balanced in mechanical strength, ther-

mal stability, and water resistance, which are attributed to the hydrophobic nature of the $C_8$ units.

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