Synthesis and Properties of a Novel, Liquid, Trifunctional, Cycloaliphatic Epoxide

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ABSTRACT: A novel cycloaliphatic triepoxide, 1,1-bis(2',3'-epoxycyclohexyloxymethyl)-3,4-epoxycyclohexane (II), and its precursor, 1,1-bis(2'-cyclohexenyloxymethyl)-3-cyclohexene, were synthesized. Their chemical structures were confirmed with IR spectroscopy, elemental analysis, and 1H NMR spectroscopy. II was easily cured with hexahydro-4-methylphthalic anhydride with 1,3,5-triethylhexahydro-1,3,5-triazine as a curing accelerator. The physical properties of the cured product were examined with thermo-mechanical analysis, thermogravimetric analysis, and dynamic mechanical analysis. Compared with the commercial diepoxide ERL-4221 under the same curing conditions, the cured product based on II showed a much higher glass-transition temperature (198 °C), a higher crosslinking density (2.08 × 10^{-3} mol/cm^3), and a lower coefficient of thermal expansion [6.2 × 10^{-5} /°C]. II may become a promising candidate material for modern microelectronic packaging. © 2001 John Wiley & Sons, Inc. J Polym Sci Part A: Polym Chem 39: 2799–2804, 2001

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INTRODUCTION

Cycloaliphatic epoxy resins have good heat and chemical resistance, superior mechanical and electrical properties, and excellent processability, and they have been found to be useful in a variety of industrial applications, such as paints, coatings, inks, reactive diluents, acid scavengers, molded articles, filament-wound or glass-reinforced articles, vacuum-pressure impregnation of coils, encapsulation of electronic circuit elements, printed circuit-board coatings, and chemical intermediates. Unlike aromatic epoxides, cycloaliphatic epoxies do not have a strong UV chromophore and are highly resistant to UV light; they are, therefore, more durable for outdoor applications, such as electrical insulators. Moreover, cycloaliphatic epoxides usually have low viscosity before curing and good adhesion properties after curing. Because their synthesis involves the peracid epoxidation of olefins rather than the condensation of epichlorohydrin with phenols, the cycloaliphatic epoxides are essentially free of chloride. For these reasons, they have been widely used in microelectronic packaging applications, in which even very low levels of chloride can cause corrosion of microcircuits.

Despite the many aforementioned advantages of cycloaliphatic epoxides, a review of epoxide studies revealed that most current cycloaliphatic epoxides are difunctional compounds and that the epoxycyclohexyl moiety is linked via ester bonds (e.g., ERL-4221). The low crosslinking density (\( \rho \)) of the cured difunctional epoxides results in a relatively low glass-transition temperature...
Moreover, under a high-temperature, moist environment, the ester bonds can be hydrolyzed and yield large amounts of carboxylic acid groups, which may cause severe erosion to metal wire in integrated circuits and decrease the working life of electronic devices. With the rapidly increasing operating power, frequency, and interconnection density of integrated circuits (e.g., for flip-chip and multichip module packaging), to meet the requirement of the integrated circuit (IC) packaging industry, it is important to find new ester-free liquid epoxides with higher $T_g$’s after curing.

This work was undertaken to synthesize a new, trifunctional, ester-free, cycloaliphatic epoxide. The cycloaliphatic structure increases the likelihood that the synthesized epoxide will be liquid at ambient temperature; trifunctionality may result in a high $\rho$ value after curing and, therefore, a high $T_g$, whereas the epoxycyclohexyl linkage via ether bonds instead of ester bonds is expected to greatly improve its moisture resistance. This article describes its synthesis and characterization as well as its thermal and mechanical properties after curing.

**EXPERIMENTAL**

**Materials**

Cyclohexene was refluxed with sodium and distilled before use. Carbon tetrachloride was dried with phosphorus pentoxide. 3-Cyclohexene-1,1-dimethanol, $m$-chloroperoxybenzoic acid ($m$-CPBA), and 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate (ERL-4221™) were used as received from Aldrich Chemical Co. 3-Bromocyclohexene was prepared with cyclohexene with $N$-bromosuccinimide according to the literature.10 Hexahydro-4-methylphthalic anhydride (HMPA) was used as a curing agent. 1,3,5-Triethylhexahydro-s-triazine was used as a curing accelerator.

**Characterization**

Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer model 7 FTIR spectrometer. $^1$H NMR spectra were obtained on a DMX-300 NMR spectrometer (Bruker). The spectra were determined in chloroform-$d_1$ with tetramethylsilane as an internal standard. Elemental analyses were carried out on a Heraeus CHN-O Rapid analyzer. Dynamic mechanical analysis (DMA) was performed with a PerkinElmer 7 series thermal analysis system at a frequency of 3 Hz and a heating rate of 10 °C/min under a nitrogen atmosphere. A differential scanning calorimetry (DSC) thermogram was obtained with a PerkinElmer 7 series thermal analysis system at a heating rate of 10 °C/min under a nitrogen atmosphere. Thermal expansion plots were recorded on a DuPont TMA 2940 thermomechanical analyzer at a heating rate of 5 °C/min under a nitrogen atmosphere, and the coefficient of thermal expansion (CTE) was calculated from the curves. The epoxy equivalent weight (EEW) of the triepoxide was measured according to a titration procedure described in the literature.11

**Synthesis of 1,1-Bis(2’-cyclohexenoyloxy)methyl)-3-cyclohexene (I)**

Into a 1000-mL, four-neck, round-bottomed flask equipped with a thermometer, a nitrogen inlet, an addition funnel, and a mechanical stirrer, there were placed 20.3 g (0.844 mol) of sodium hydride, 1.0 g of 18-crown-6-ether (phase-transfer catalyst), and 370 mL of dimethyl sulfoxide. The mixture was stirred at room temperature for 0.5 h, and then 30 g (0.211 mol) of 3-cyclohexene-1,1-dimethanol was added in small portions over a 1-h period under a nitrogen atmosphere and maintained at this temperature for 2 h. The reaction mixture was then heated to 60 °C, a solution of 122 g (0.76 mol) of 3-bromocyclohexene in 80 mL of dimethyl sulfoxide was added dropwise to the aforementioned mixture with vigorous stirring over a period of 5 h, and the stirring was continued for 24 h at 60 °C. After cooling, the reaction mixture was filtered and washed with dichloromethane ($3 \times 100$ mL). The light yellowish filtrate was concentrated with a rotary evaporator. The residue was partitioned between ether ($2 \times 200$ mL) and brine (100 mL). The organic layers were combined, dried with anhydrous sodium sulfate, filtered, and evaporated. The crude product was purified by fractional distillation under reduced pressure. There was obtained 26.1 g (yield 41%) of I as a colorless liquid with a boiling point of 180–182 °C at 2 mmHg.

**Elem. Anal.** Caled. for C$_{20}$H$_{30}$O$_2$: C, 79.47%; H, 9.93%. Found: C, 80.05%; H, 10.22%. IR ( neat): 3024, 2935, 2860, 1653, 1437, 1395, 1317, 1162, 1087, 950, 899, 725, 656, 580 cm$^{-1}$. $^1$H NMR (CDCl$_3$, $\delta$, ppm): 5.61–5.79 (s, s, 6H, =CH), 3.78 (t, 2H, CHO), 3.29–3.40 (s, 4H, CH$_2$O), 1.26–1.99 (m, 18H, CH$_2$).
Synthesis of 1,1-Bis(2',3'-epoxycyclohexyloxymethyl)-3,4-epoxycyclohexane (II)

A 2000-mL, three-neck, round-bottomed flask equipped with a thermometer, an addition funnel, and a mechanical stirrer was first cooled in an ice bath for 10 min. It was then charged with 146 g (0.845 mol) of m-CPBA and 1000 mL of dichloromethane, and this mixture was cooled to 0 °C with stirring. To this mixture was added dropwise a solution of 74 g (0.245 mol) of I in 60 mL of dichloromethane over 2 h, and the reaction mixture was maintained at 0 °C. After further stirring for a period of 10 h at 0 °C, the reaction mixture was filtered. The filtrate was washed with a solution of sodium sulfite, then with a solution of sodium bicarbonate, and finally with deionized water to neutralization. The organic phase was dried over anhydrous sodium sulfate, and the solvent was removed on a rotary evaporator and distilled under reduced pressure to give the final product. There was obtained 69.4 g (81% yield) of the pure product, II, as a colorless liquid with a boiling point of 193–195 °C at 1 mmHg.

Preparation of Cured Products

Triepoxide II and HMPA as a hardener were mixed with a 1:0.85 equivalent ratio of epoxide to anhydride groups at room temperature. Into this homogeneous mixture was added and mixed 1.0 wt % 1,3,5-triethyl-hexahydro-s-triazine as a catalyst. The mixture was cured first at 140 °C for 2 h, then at 170 °C for 6 h, and finally at 200 °C for 4 h.

As a comparison, the commercial di epoxy ERL-4221 was also mixed with HMPA and 1,3,5-triethyl-hexahydro-s-triazine in the same ratio and cured under the same conditions mentioned previously.

RESULTS AND DISCUSSION

Synthesis

The new cycloaliphatic triepoxide (II) containing two secondary ether linkages was designed and prepared with the following two steps: the synthesis of I and its subsequent epoxidation, as shown in Scheme 1.

In dimethyl sulfoxide, I was easily prepared in a good yield (40–50%) from 3-cyclohexene-1,1-dimethanol, 3-bromocyclohexene, and sodium hydride under a nitrogen atmosphere at 60 °C, with 18-crown-6-ether as a phase-transfer catalyst to facilitate the reaction. The molar ratio of 3-cyclohexene-1,1-dimethanol, 3-bromocyclohexene, and sodium hydride was controlled to 1:2:2. The yield of product I was rather low when the reaction proceeded at room temperature, which might be attributed to both the steric hindrance of the 3-bromocyclohexene moiety and the poor solubility of the sodium hydride and cyclohexenyl-based sodium alcohalate in the solvent. Increased temperature was advantageous for the yield of I, but its yield decreased again when the temperature was raised over 80 °C. This might be due to the decomposition of 3-bromocyclohexene at high temperatures. Therefore, the preferred temperature range for this reaction was between 60 and 80 °C.

The tricyclohexenyl-containing diether compound (I) was subsequently epoxidized with m-CPBA in dichloromethane at 0 °C to give the desired triepoxide (II) in a yield of 80–90%.

The compounds I and II were characterized by elemental analyses and IR and 1H NMR spectra. The data from the elemental analyses of the tricycloolefin and cycloaliphatic triepoxide were in good agreement with the calculated values. In the IR spectrum of compound I [see Fig. 1(a)], the peaks at 3024, 1653, and 656 cm⁻¹ correspond to the absorption of cycloaliphatic double bonds. A strong characteristic band for the aliphatic ether linkage was observed at 1087 cm⁻¹. In the IR spectrum of compound II [Fig. 1(b)], the aforementioned absorptions of double bonds were ab-
sent, but the characteristic bands of the oxirane ring fused to cyclohexane were observed at 858, 826, and 799 cm$^{-1}$. This result indicates that the double bonds in the tricycolefin were completely converted into epoxy groups.

In the $^1$H NMR spectrum of compound I [Fig. 2(a)], all signals corresponding to the proposed structure were observed in chloroform-$d_1$. Protons on the double bonds of the cyclohexenyl rings appeared at 5.61–5.79 ppm. Both the aliphatic methylene protons and the protons in the cyclohexenyl rings nearest the ether bonds were observed at 3.29–3.78 ppm. The other cyclohexenyl ring protons were assigned at 1.26–1.99 ppm. In the $^1$H NMR spectrum of triepoxide II [Fig. 2(b)], the protons on the oxirane ring and those on ether carbon atoms were observed at 3.07–3.58 ppm; other cyclohexenyl ring protons were observed at 1.18–2.03 ppm, whereas the signals at 5.61–5.79 ppm for the double-bond protons in the cyclohexenyl rings of compound I disappeared. The EEW of triepoxide II was 128 g/equiv (calcd. 117 g/equiv).

Properties of Cured Products

To evaluate the performances of the HMPA-cured triepoxide, we used the commercial cycloaliphatic diepoxide ERL-4221 as a comparison. The results of thermomechanical analyses (TMAs) are summarized in Table I. The inflection point of the thermal expansion plot was defined as $T_{g,TMA}$. The cured triepoxide II showed a much higher $T_{g,TMA}$ than cured ERL-4221 did, reflecting a higher crosslinking network density. Furthermore, the TMA results showed that the triepoxide II polymer had smaller coefficients of thermal expansion (CTE) in the glassy and rubbery regions. The lower CTE might result from the high $\rho$ value and restricted molecular mobility because of the crowded structure of three cyclohexyl rings in the main chain. The DSC results in Table I indicate that the cured triepoxide II also gave a much higher $T_{g,DSC}$ than cured ERL-4221 did.

Figure 3 illustrates the spectra of dynamic mechanical analyses (DMA) of the cured samples as a function of temperature at a heating rate of 10

Table I. Thermal Analysis and TMA of the Cured Polymers

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_{g,DSC}$ (°C)</th>
<th>$T_{g,TMA}$ (°C)</th>
<th>Glassy Region</th>
<th>Rubbery Region</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>184</td>
<td>191</td>
<td>6.21</td>
<td>13.4</td>
</tr>
<tr>
<td>ERL-4221</td>
<td>149</td>
<td>137</td>
<td>6.76</td>
<td>15.7</td>
</tr>
</tbody>
</table>
°C/min from room temperature to 275 °C, and the results are summarized in Table II. The peak temperature of tan δ was taken as $T_g$. These two samples displayed a slightly different dynamic mechanical behavior [storage modulus ($E'$) and tan δ, loss tangent] by DMA. As seen in Table II, the cured triepoxide II retained higher $E'$ values at both low and high temperatures than the cured ERL-4221, which implied that the cured triepoxide II had a higher ρ value than the cured ERL-4221. ρ was determined as follows:

$$\rho = \frac{E'}{3RT} \quad (1)$$

where $E'$ is the storage modulus at $T_g + 50 \, ^\circ C$, $R$ is the gas constant, and $T$ is the absolute temperature at $T_g + 50 \, ^\circ C$.

ρ was $2.08 \times 10^{-3}$ and $1.49 \times 10^{-3} \, \text{mol/cm}^3$ for the cured triepoxide II and ERL-4221, respectively. The higher ρ value of II may be responsible for its lower CTE.

**CONCLUSION**

A novel, ester-free, cycloaliphatic triepoxide (II) and its precursor tricycloolefin were synthesized, and their structures were confirmed with IR, elemental analysis, EEW, and $^1$H NMR measurements. The thermal and mechanical properties of the triepoxide cured with HMPA were examined with TMA, thermogravimetric analysis, and DMA. The cured polymer based on the new triepoxide showed a higher $T_g$ (198 °C). To our knowledge, this is among the highest $T_g$'s for liquid epoxies (cured with HMPA) reported previously in the literature. Furthermore, the cured triepoxide exhibited a higher $E'$ value in the glassy region and a lower thermal expansion coefficient compared with those for cured ERL-4221. These excellent properties make it a promising candidate as a flip-chip, underfill-packaging material.

**Table II.** DMA of the Cured Polymers

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_g$ (°C)</th>
<th>Glassy Region$^a$</th>
<th>Rubbery Region$^b$</th>
<th>$\rho$ (10$^{-3}$ mol/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>198</td>
<td>2.82</td>
<td>0.027</td>
<td>2.08</td>
</tr>
<tr>
<td>ERL-4221</td>
<td>164</td>
<td>2.07</td>
<td>0.019</td>
<td>1.56</td>
</tr>
</tbody>
</table>

$^a$ Storage modulus at 30 °C.

$^b$ Storage modulus at $T_g + 50 \, ^\circ C$. 

![Figure 3. DMA spectra of (a) cured cycloaliphatic epoxide II and (b) cured ERL-4221.](image)
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REFERENCES AND NOTES