Synthesis and Polymerization of Novel Epoxy Compounds Having an Adamantane Ring and Evaluation of their Heat Resistance and Transparency

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ABSTRACT: Three adamantane derivatives substituted by epoxy groups, 1,3-bis(glycidyloxy)adamantane (**2a**), 5,7-dimethyl-1,3-bis(glycidyloxy)adamantane (**2b**), 1,3,5-tris(glycidyloxy)adamantane (**2c**), were synthesized from the corresponding adamantanediol or triol in good yields. These three epoxy compounds were polymerized with an acid anhydride, and the heat resistance of the resulting resins was evaluated. The resin prepared from **2c** exhibited high heat resistance with the glass transition temperature (T_g) of 208°C and low degree of coloring by heating. The epoxy compounds were also found to be potentially useful as the precursors of high heat-resistant resins by thermal homopolymerization. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 496–504, 2009

Key words: synthesis; high-performance polymers; light-emitting diodes; crosslinking; transparency

INTRODUCTION

Adamantane-based compounds and polymers have attracted much attention as functional materials. For example, it has been reported that acrylate derivatives having an adamantane ring are usable as the precursors of resists toward ArF and KrF excimer-laser with excellent transparency and dry-etching resistance.[1–3] Adamantane derivatives are anticipated also as high heat resistance and colorless transparent materials. The thermal stability arises from the cage diamond-like skeleton. The adamantane ring system consists of fused strain-free chair-form cyclohexane rings and essentially has no configuration strain. In addition, at least three C—C bonds should be cleaved for the fragmentation of the adamantane cage structure, which is also responsible for the high thermal stability of the adamantane-based materials. Recently, poly-adamantane derivatives were synthesized and proven to show good heat resistance by their thermogravimetric analysis (TGA).[4] It is also noted that adamantane unit is reactive at the bridgehead positions that can be readily substituted with electrophiles by Friedel–Crafts type reactions,[5] making the smooth access to reactive monomers possible.

Epoxy compounds are widely used as adhesive materials in various fields including the area of electronic device. **BisA** (Chart 1) is well established as a useful precursor of an encapsulant for light-emitting diodes (LEDs). However, **BisA** cannot be applied to blue or white LED because of the low light resistance against UV–VIS light (<600 nm). The encapsulant derived from **BisA** colors to yellow by photooxidation of benzene rings as shown in Chart 1.[6] To avoid the coloring, aliphatic epoxy compounds, such as **HGBisA** and AE (Chart 2), have been extensively studied. [6]

We pay our attention to adamantane ring and expected that the adamantane derivatives bearing two or more epoxy groups may be useful as precursors of encapsulants for LED, as mentioned earlier. As such compounds, adamantane derivatives bearing two cyclohexene oxide groups linked by ester spacers have been reported.[7] However, the existence of flexible and less thermally stable spacers in the molecules would suppress the thermal stability of the resins prepared by polymerization of the adamantane derivatives, and those directly substituted by glycidyloxy groups seem to be of higher potential as excellent resin precursors. Although papers concerning the synthesis of a monoglycidyloxy-substituted adamantane derivative have appeared,[8,9] no adamantane derivatives directly substituted by two or more glycidyloxy groups have been reported so far.

In this article, we report the synthesis of novel epoxy-containing adamantane derivatives, 1,3-bis

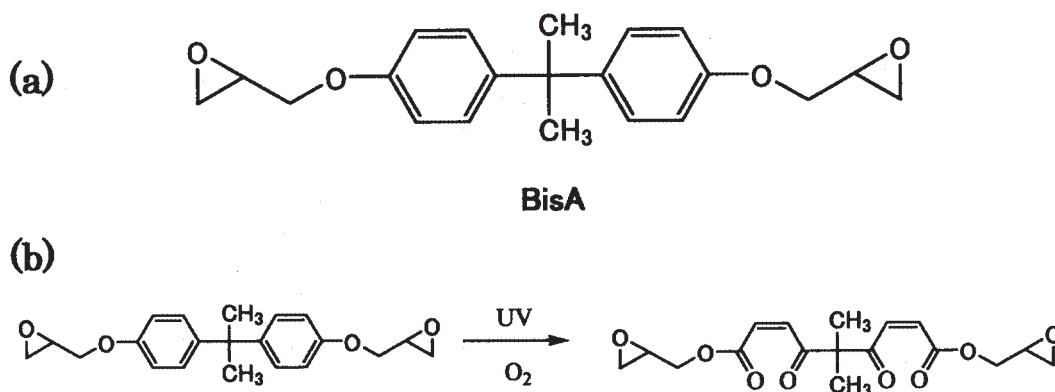*Correspondence to:* T. Maehara (t-maehara@tokuyama.co.jp).

Chart 1 (a) Structure and (b) decomposition of **BisA**.

(glycidyloxy)adamantane (**2a**), 5,7-dimethyl-1,3-bis (glycidyloxy)adamantane (**2b**), and 1,3,5-tris(glycidyoxy)adamantane (**2c**). Their heat resistance was examined by TGA, indicating high yields of the resins by thermal polymerization. We prepared colorless transparent epoxy resins by the copolymerization of the epoxy compounds with an acid anhydride and evaluated their glass transition temperatures (T_g) by differential scanning calorimeter (DSC) and their coloring upon heating in air.[10]

EXPERIMENTAL

Materials

Dry N,N-dimethylformamide (DMF) and N,N-dimethylacetoamide (DMAC) were purchased from Wako Pure Chemical Industries Ltd. (Japan). Sodium hydride (in oil), allyl bromide, and m-chloroperbenzoic acid (m-CPBA) were obtained (special grade) from the same company. 1,3,5-Adamantanetriol was purchased from Tokyo Chemical Industry Co., Ltd. (Japan). 1,3-Adamantanediol was obtained as reported in our patent.[11] Tetra-n-butylphosphonium-O,O-diethylphosphorodithioate was obtained from Nihon Chemical Industrial Co., Ltd. (Japan). 4-Methylhexahydrophthalic anhydride (70% pure with hexahydrophthalic anhydride as an impurity) was obtained from New Japan Chemical Co., Ltd. (Japan). **HGBisA** was purchased from Japan Epoxy Resins Co., Ltd. (Japan). **AE** was obtained from Daicel Chemical Industries Co., Ltd. (Japan).

Measurements

^{1}H and ^{13}C NMR spectra were recorded on a JEOL Model JNM-LA 500 spectrometer (500 MHz for 1H and 125 MHz for ^{13}C). Mass spectra were obtained using a JEOL Model JMS-9 Ultra Quad GC/MS. TGA was recorded on a Seiko Instruments Exstar 6000 TG/DTA6000. DSC was recorded on a Seiko Instruments Exstar 6000 DSC6200. Transmittances of the resin plates were monitored at room temperature on a Hitachi U-3210 Spectrophotometer with irradiation by UV–VIS light from vertical direction. IR spectra were measured at room temperature on a Perkin Elmer FTIR Spectrometer Spectrum One (B).

Synthesis of monomers

Synthesis of 5,7-dimethyl-1,3-dichloroadamantane

A mixture of 11.4 g (0.08 mol) of sodium sulfate, 530 g of concentrated sulfuric acid, and 131 g (0.80 mol) of 1,3-dimethyladamantane was placed in a 2000-mL four-necked flask with nitrogen flow. To this, 373 g (3.20 mol) of chlorosulfonic acid was added, keeping the temperature below 30°C for 2 h. After stirring for 1 h at 28°C, 187 g (1.60 mol) of chlorosulfonic acid was added, and stirring was conducted at 25°C for additional 20 h. The reaction mixture was cooled to about 10°C, and 400 g of water was gradually added to the mixture so that the temperature of the reaction mixture did not exceed 30°C by water cooling. To this, 660 g of dichloromethane was added,
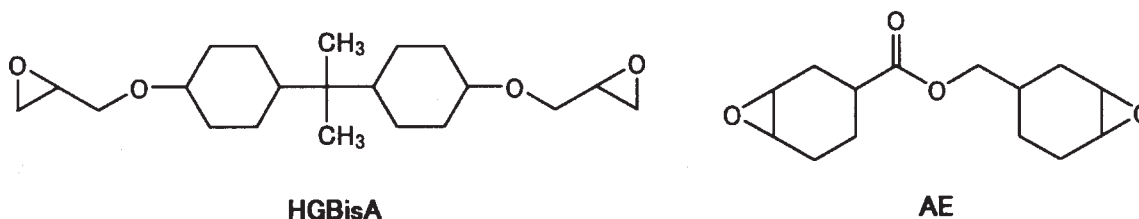

Chart 2 Structures of aliphatic epoxy compounds.

and then the aqueous layer was separated. The organic layer was washed with aqueous sodium hydroxide and then aqueous sodium sulfate, whereby the organic layer became neutral. The organic layer was concentrated under reduced pressure to give 145 g of 5,7-dimethyl-1,3-dichloroadamantane as a pale yellow solid in 78% yield: GC-MS m/z 232 (M^+); ^1H NMR (δ in CDCl$_3$) 0.95 (s, 6H), 1.16 (s, 2H, CH$_2$ of Ad), 1.70–1.79 (m, 8H, CH$_2$ of Ad), 2.32 (s, 2H, CH$_2$ of Ad).

Synthesis of 5,7-dimethyl-1,3-adamantanediol

A mixture of 145 g (0.63 mol) of 5,7-dimethyl-1,3-dichloroadamantane and 103 g (1.25 mol) of sodium acetate, 91.5 g (1.25 mol) of DMF, and 730 g of ion-exchanged water was placed in a glass-made autoclave. The reaction mixture was stirred at 150°C at 0.3 MPa for 30 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure to give 285 g of a pale yellow solid. The solid was washed with ion-exchanged water to remove sodium chloride from the solid. After drying the solid under reduced pressure, the solid was heated in boiling ethyl acetate for 1 h and cooled to 5°C. After stirring at 5°C, the mixture was filtered to give 110 g of 5,7-dimethyl-1,3-adamantanediol as a white solid in 89% yield: GC-MS m/z 196 (M^+); ^1H NMR (δ in CD$_3$OD) 0.93 (s, 6H), 1.06 (s, 2H, CH$_2$ of Ad), 1.27–1.35 (m, 8H, CH$_2$ of Ad), 1.56 (s, 2H, CH$_2$ of Ad), 4.82 (s, 2H, OH).

Synthesis of 1,3-bis(allyloxy)adamantane (1a)

A mixture of 70 g (0.42 mol) of 1,3-adamantanediol, 350 mL of DMF, and 151 g (1.25 mol) of allyl bromide was placed in a 2000-mL four-necked flask in a nitrogen flow. To this, 41.7 g (1.04 mol) of 60% sodium hydride in oil was gradually added, keeping the temperature below 30°C. After stirring at room temperature for 2 h, the reaction mixture was cooled to 5°C, and 200 mL of water was added to the mixture slowly so that the temperature of the reaction mixture did not exceed 30°C. To this, 400 mL of dichloromethane was added, and then the aqueous layer was separated. The organic layer was washed with water, whereby the organic layer became neutral. The organic layer was concentrated under reduced pressure to give 151 g of a brown-colored liquid. The residue was distilled to give 96.2 g of 1a as a light yellow liquid in 91% yield: bp 119–120°C /1.0 mmHg; GC-MS m/z 248 (M^+), 191 (M^+-OCH$_2$CH=CH$_2$); ^1H NMR (δ in CDCl$_3$) 1.51 (s, 2H, CH$_2$ of Ad), 1.65–1.82 (m, 8H, CH$_2$ of Ad), 1.82 (s, 2H, CH$_2$ of Ad), 2.32 (s, 2H, CH of Ad), 3.97–3.98 (m, 4H, Ad—O—CH$_2$—), 5.10–5.29 (m, 4H, Ad—O—CH$_2$CH=CH$_2$), 5.88–5.95 (m, 2H, Ad—O—CH$_2$CH=CH$_2$).

Synthesis of 5,7-dimethyl-1,3-bis(allyloxy)adamantane (1b)

A mixture of 39.3 g (0.20 mol) of 5,7-dimethyl-1,3-adamantanediol, 200 g of DMAC, and 60.5 g (0.50 mol) of allyl bromide was placed in a 1000-mL four-necked flask with nitrogen flow. To this, 20.0 g (0.50 mol) of 60% sodium hydride in oil was gradually added, keeping the temperature below 30°C. After stirring at room temperature for 2 h, 24.2 g (0.20 mol) of allyl bromide and 8.0 g (0.20 mol) of 60% sodium hydride in oil were added to the mixture, and the stirring was conducted at room temperature for 1 h. The reaction mixture was cooled to 5°C and 120 mL of water was added to the mixture slowly so that the temperature of the reaction mixture did not exceed 30°C. To this, 280 g of dichloromethane was added, and the aqueous layer was separated, and then the organic layer was washed with water, whereby the organic layer became neutral. The organic layer was concentrated under reduced pressure to give 73.7 g of a brown-colored liquid, which was then distilled to give 44.0 g of 1b as a colorless liquid in 80% yield: bp 164–165°C/0.8 mmHg; GC-MS m/z 276 (M^+), 235 (M^+-CH$_2$CH=CH$_2$); ^1H NMR (δ in CDCl$_3$) 0.93 (s, 6H, Ad—CH$_3$), 1.08 (s, 2H, CH$_2$ of Ad), 1.36–1.45 (m, 8H, CH$_2$ of Ad), 1.71 (s, 2H, CH$_2$ of Ad), 3.96–3.97 (m, 4H, Ad—O—CH$_2$—), 5.10–5.28 (m, 4H, Ad—O—CH$_2$CH=CH$_2$), 5.87–5.94 (m, 2H, Ad—O—CH$_2$CH=CH$_2$).

Synthesis of 1,3,5-tris(allyloxy)adamantane (1c)

A mixture of 55.2 g (0.30 mol) of 1,3,5-adamantanetriol, 420 g of DMF, and 127 g (1.05 mol) of allyl bromide was placed in a 2000-mL four-necked flask with nitrogen flow. To this, 42.0 g (0.50 mol) of 60% sodium hydride in oil was gradually added, keeping the temperature below 30°C. After stirring at room temperature for 2 h, 36.2 g (0.30 mol) of allyl bromide and 12.0 g (0.30 mol) of 60% sodium hydride in oil were added to the mixture, and stirring was conducted at the temperature for 2 h. The reaction mixture was cooled to 5°C and 200 mL of water was added to the mixture slowly so that the temperature of the reaction mixture did not exceed 30°C. To this, 400 g of dichloromethane was added, and then the aqueous layer was separated. Then, the organic layer was washed with water, whereby the organic layer became neutral. The organic layer was concentrated under reduced pressure to give 96.6 g of a brown-colored liquid, which was distilled to give 74.2 g of 1c as a light yellow liquid in 81% yield: bp 136–138°C/0.3 mmHg; GC-MS m/z 304 (M^+), 247 (M^+-

OCH$_2$CH=CH$_2$); ^{1}H NMR (δ in CDCl$_3$) 1.64–1.65 (d, 6H, J = 3.05 Hz, CH$_2$ of Ad), 1.77–1.85 (m, 6H, CH$_2$ of Ad), 2.41 (m, 1H, CH of Ad), 3.97–3.98 (d, 6H, J = 5.50 Hz, Ad—O—CH$_2$—), 5.12–5.29 (m, 6H, Ad—O—CH$_2$CH=CH$_2$), 5.88–5.93 (m, 3H, Ad—O—CH$_2$CH= CH$_2$).

Synthesis of 1,3-bis(glycydiloxy)adamantane (2a)

A mixture of 96.2 g (0.38 mol) of 1,3-bis(allyloxy)adamantane, 238 g (0.95 mol) of 69% m-CPBA, and 550 mL of dichloromethane was placed in a 2000-mL four-necked flask. After stirring the mixture for 24 h at room temperature, m-chlorobenzoic acid precipitated from the mixture was filtered and the filtrate was poured to 15% sodium sulfite aqueous solution. After stirring, the aqueous layer was separated. The organic layer was washed with 1N sodium hydroxide aqueous solution and then with ion-exchanged water, whereby the organic layer became neutral. The organic layer was concentrated under reduced pressure to give 106 g of a colorless liquid, which was then distilled to give 76.1 g of 2a as a colorless liquid in 71% yield: bp 164–165°C/1.0 mmHg; GC-MS m/z 280 (M$^+$), 223 (M$^+$-glycidyl), 207 (M$^+$-glycidyloxy); ^{1}H NMR (δ in CDCl$_3$) 1.49–1.50 (t, 2H, J = 2.75 Hz, CH$_2$ of Ad), 1.67–1.68 (d, 8H, J = 3.05 Hz, CH$_2$ of Ad), 1.76 (s, 2H, CH$_2$ of Ad), 2.32–2.33 (t, 2H, J = 2.75 Hz, CH of Ad), 2.59–2.80 (m, 4H, CH$_2$ of epoxy), 3.07–3.10 (m, 2H, CH of epoxy), 3.44–3.62 (m, 4H, Ad—O—CH$_2$—); ^{13}C NMR (d in CDCl$_3$) 30.7 (CH of Ad), 35.1 (CH$_2$ of Ad), 40.3 (CH$_2$ of Ad), 44.9 (CH$_2$ of epoxy), 45.2 (CH$_2$ of Ad), 51.3 (CH of epoxy), 61.7 (Ad—O—CH$_2$—), 74.7 (C—O of Ad); IR (neat) 2995 (C—H of epoxy), 2910, 2857 (C—H of AD), 1071, 908, 838 (C—O) cm^{-1}. Anal. Calc. for C$_{16}$H$_{24}$O$_4$: C, 68.54; H, 8.63. Found: C, 68.38; H, 8.85%.

Synthesis of 5,7-dimethyl-1,3-bis(glycydiloxy)adamantane (2b)

A mixture of 44.0 g (0.16 mol) of 5,7-dimethyl-1,3-bis(allyloxy)adamantane and 99.4 g (0.40 mol) of 69% m-CPBA, and 300 g of dichloromethane was placed in a 1000-mL four-necked flask. After stirring the mixture for 17 h at room temperature, m-chlorobenzoic acid precipitated from the mixture was filtered, and then the filtrate was poured to 15% sodium sulfite aqueous solution. After stirring, the aqueous layer was separated. The organic layer was washed with 1N sodium hydroxide aqueous solution and then with ion-exchanged water, whereby the organic layer became neutral. The organic layer was concentrated under reduced pressure to give 79 g of a colorless liquid, which was then distilled to give 38.2 g of 2b as a colorless liquid in 78% yield: bp 163–165°C/0.3 mmHg; GC-MS m/z 308 (M$^+$), 251

(M$^+$-glycidyl), 235 (M$^+$-glycidyloxy); ^{1}H NMR (δ in CDCl$_3$) 0.95 (s, 6H, Ad—CH$_3$), 1.08 (s, 2H, CH$_2$ of Ad), 1.34–1.41 (m, 8H, CH$_2$ of Ad), 1.66 (s, 2H, CH$_2$ of Ad), 2.59–2.80 (m, 4H, CH$_2$ of epoxy), 3.07–3.10 (m, 2H, CH of epoxy), 3.42–3.62 (m, 4H, Ad—O—CH$_2$—); ^{13}C NMR (δ in CDCl$_3$) 29.3 (CH$_3$ of Ad), 34.2 (CH$_2$ of Ad), 43.8 (C—CH$_3$ of Ad), 44.9 (CH$_2$ of epoxy), 46.7 (CH$_2$ of Ad), 49.8 (CH$_2$ of Ad), 51.3 (CH of epoxy), 62.0 (Ad—O—CH$_2$—), 75.6 (C—O of Ad); IR (neat) 2996 (C—H of epoxy), 2923, 2864 (C—H of AD), 1076, 906, 840 (C—O) cm^{-1}. Anal. Calc. for C$_{18}$H$_{28}$O$_4$: C, 70.10; H, 9.15. Found: C, 69.96; H, 9.20%.

Synthesis of 1,3,5-tris(glycydiloxy)adamantane (2c)

A mixture of 74.2 g (0.24 mol) of 1,3,5-tris(allyloxy) adamantane, 195 g (0.78 mol) of 69% m-CPBA, and 740 g of dichloromethane was placed in a 2000-mL four-necked flask. After stirring the mixture for 46 h at room temperature, m-chlorobenzoic acid precipitated as a solid was filtered, and then the filtrate was poured to 15% sodium sulfite aqueous solution. After stirring, the aqueous layer was separated. The organic layer was washed with 1N sodium hydroxide aqueous solution then with ion-exchanged water, whereby the organic layer became neutral. The organic layer was concentrated under reduced pressure to give 79 g of a colorless liquid, which was dissolved in methanol and washed with n-heptane to remove the oil from "sodium hydride in oil." After washing, the methanol layer was concentrated under reduced pressure to give 73 g of a colorless liquid, which was then crystallized from methanol/ diisopropyl ether to give 57.9 g of 2c as a white solid in 79% yield: mp 57–58°C; GC-MS m/z 352 (M$^+$), 351 (M$^+$-1), 295 (M$^+$-glycidyl), 279 (M$^+$-glycidyloxy); ^{1}H NMR (δ in CDCl$_3$) 1.61–1.62 (d, 6H, J = 2.95 Hz, CH$_2$ of Ad), 1.72–1.79 (m, 6H, CH$_2$ of Ad), 2.41–2.42 (m, 1H, CH of Ad), 2.59–2.80 (m, 6H, CH$_2$ of epoxy), 3.01–3.10 (m, 3H, CH of epoxy), 3.41–3.66 (m, 6H, Ad—O—CH$_2$—); ^{13}C NMR (δ in CDCl$_3$) 29.0 (CH of Ad), 39.4 (CH$_2$ of Ad), 44.6 (CH$_2$ of Ad), 44.8 (CH$_2$ of epoxy), 51.1 (CH of epoxy), 62.2 (Ad—O—CH$_2$—), 75.3 (C—O of Ad); IR (neat) 2999 (C—H of epoxy), 2943, 2863 (C—H of AD), 1070, 912, 837 (C—O) cm^{-1}. Anal. Calc. for C$_{19}$H$_{28}$O$_6$: C, 64.75; H, 8.01. Found: C, 64.85; H, 8.20%.

Polymerization

Polymerization of 2a

A mixture of 1.82 g (6.5 mmol) of 2a and 2.18 g (13 mmol) of 4-methylhexahydrophthalic anhydride was stirred for 30 min at room temperature. To this, 0.020 g of tetra-n-butylphosphonium-O,O-
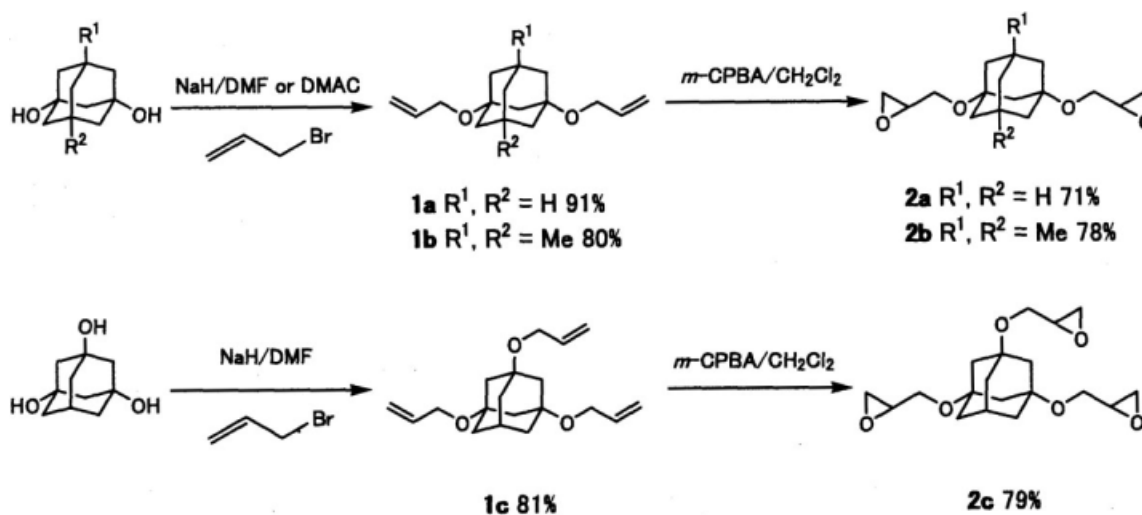
Scheme 1 Synthesis of epoxy compounds.

diethylphosphorodithioate was added, and the mixture was stirred for 30 min at room temperature. After stirring, the mixture was degassed under reduced pressure. The degassed mixture was heated at 100°C for 2 h, at 120°C for 0.5 h, at 150°C for 1 h, and at 170°C for 1h, giving the epoxy resin of **3a**. The resin plate with the thickness of 1 mm was prepared by polymerization of the mixture on a glass substrate under the same heating conditions as those described earlier: IR (resin plate) 2924, 2858 (C—H), 1801, 1729 (C=O) cm^{-1}.

Polymerization of 2b

A mixture of 1.91 g (6.2 mmol) of **2b** and 2.09 g (12 mmol) of 4-methylhexahydrophthalic anhydride was stirred for 30 min at room temperature. To this, 0.020 g of tetra-*n*-butylphosphonium-*O,O*-diethyl-phosphorodithioate was added, and then the mix-

ture was stirred for 30 min at room temperature. After stirring, the mixture was degassed under reduced pressure. The degassed mixture was heated at 100°C for 2 h, at 120°C for 0.5 h, at 150°C for 1 h, and at 170°C for 1 h. The resin plate with the thickness of 1 mm was prepared by polymerization of the mixture on a glass substrate under the same heating conditions as those described earlier: IR (resin plate) 2923, 2864 (C—H), 1802, 1730 (C=O) cm^{-1}.

Polymerization of 2c

A mixture of 1.64 g (4.7 mmol) of **2c** and 2.36 g (14 mmol) of 4-methylhexahydrophthalic anhydride was stirred for 30 min at room temperature. To this, 0.020 g of tetra-*n*-butylphosphonium-*O,O*-diethyl-phosphorodithioate was added, and then the mixture was stirred for 30 min at room temperature.

TABLE I
Thermal Properties of Epoxy Compounds Having an Adamantane Ring[a]

Epoxy compound	T_{d5} (°C)	wt loss/% at 200°C	wt loss/% at 260°C
2a	222	2.0	22
2b	215	2.5	28
2c	255	0.8	6.3
HGBisA	240	1.0	10
AE	209	3.5	31

[a] TGA was carried out at a rate of 10°C/min in air. T_{d5} is the temperature resulting in 5% weight loss from the initial weight. Weight loss at 200°C and at 260°C is given on the basis of the initial weight of the epoxy compound.
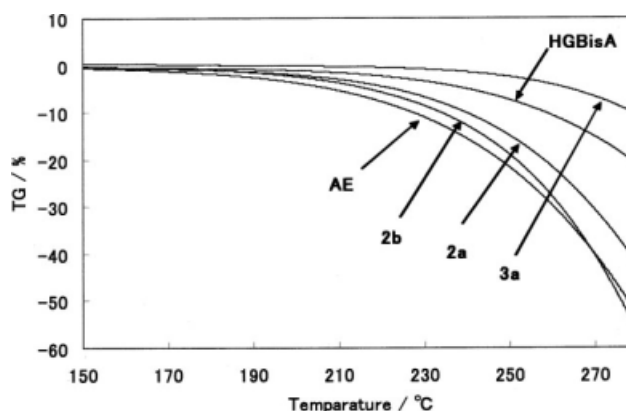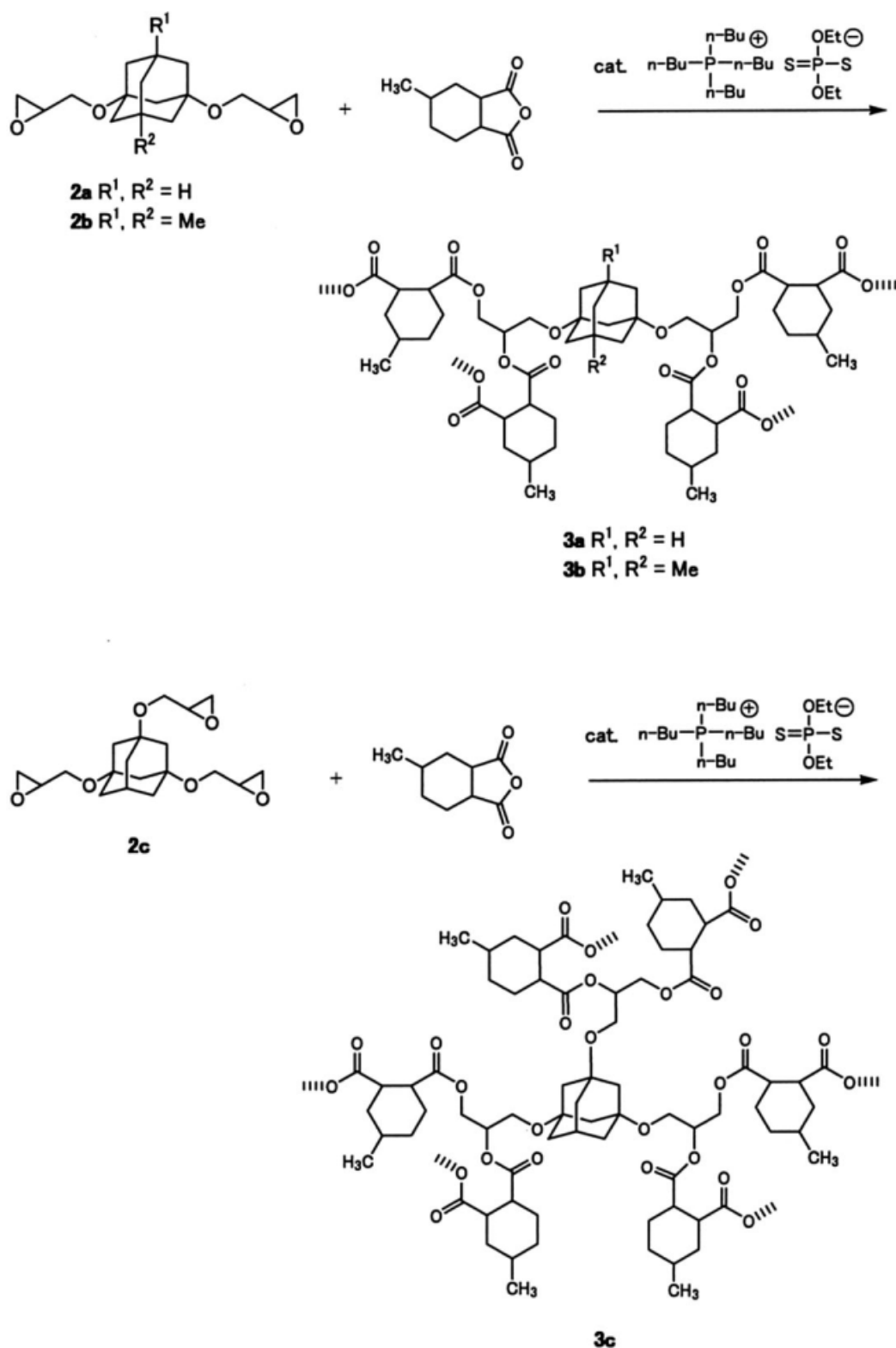
Figure 1   TGA curves of epoxy compounds in air.

Scheme 2 Preparation of the resins from **3a–c** and their ideal structures.

The mixture was degassed under reduced pressure. The degassed mixture was heated at 100°C for 2 h, at 120°C for 0.5 h, at 150°C for 1 h, and 170°C for 1 h. The resin plate with the thickness of 1 mm was prepared by polymerization of the mixture on a glass substrate under the same heating conditions as those described earlier: IR (resin plate) 2928, 2864 (C—H), 1802, 1729 (C=O) cm^{-1}.

Polymerization of HGBisA and AE

HGBisA and **AE** were polymerized by the procedure, similar to that for **2a–c**.

RESULTS AND DISCUSSION

Synthesis of epoxy compounds

Di- and triallyloxyadamantanes (**1a–c**) were prepared by treatment of 1,3-adamantanediol, 5,7-dimethyl-1,3-adamantanediol, and 1,3,5-adamantanetriol, respectively, with allyl bromide and sodium hydride in DMF or DMAC, as shown in Scheme 1. These allyloxy compounds were purified by distillation in good yields.

Oxidation of the allyl compounds by *m*-CPBA in dichloromethane led to the expected epoxy compounds (**2a–c**). The epoxy compounds were purified by distillation or recrystallization in good yields, as shown in Scheme 1. The structures of the epoxy compounds were verified by using NMR spectra, IR spectra, GC-MS, and elemental analysis.

Heat resistance of epoxy compounds

Thermal properties of the present epoxy compounds were examined by TGA. Temperatures of 5% weight loss (T_{d5}) and total weight loss at 200 and 260°C in air were listed in Table I, and TGA curves are shown in Figure 1, together with those for typical epoxy compounds **HGBisA** and **AE** as the reference (Chart 2).

All of the epoxy compounds we had synthesized (**2a–c**) showed higher T_{d5} than that for **AE**, probably due to the existence of the thermally stable adamantane ring. In particular, **2c** exhibited excellent thermal stability, revealing higher T_{d5} and lower weight loss, even than **HGBisA**, which is known as a precursor of high heat-resistant material. Trifunctionality of **2c** would lead to the higher densities in the crosslinked polymeric materials, which were produced during TGA, being responsible for the better thermal stability, as compared with other epoxides examined.

Synthesis of epoxy resins

The epoxy compounds were polymerized with 4-methylhydorophtharic anhydride in the presence of tetra-*n*-butylphosphonium-*O,O*-diethylphosphorodithioate as a promoter, as shown in Scheme 2.

To complete the reactions, we used 2 molar equiv of the acid anhydride for **2a** and **2b**, and 3 molar equiv of the acid anhydride was used for **2c**. In this polymerization, 0.5 wt % of the promoter based on the mixture of the epoxy compounds and the acid
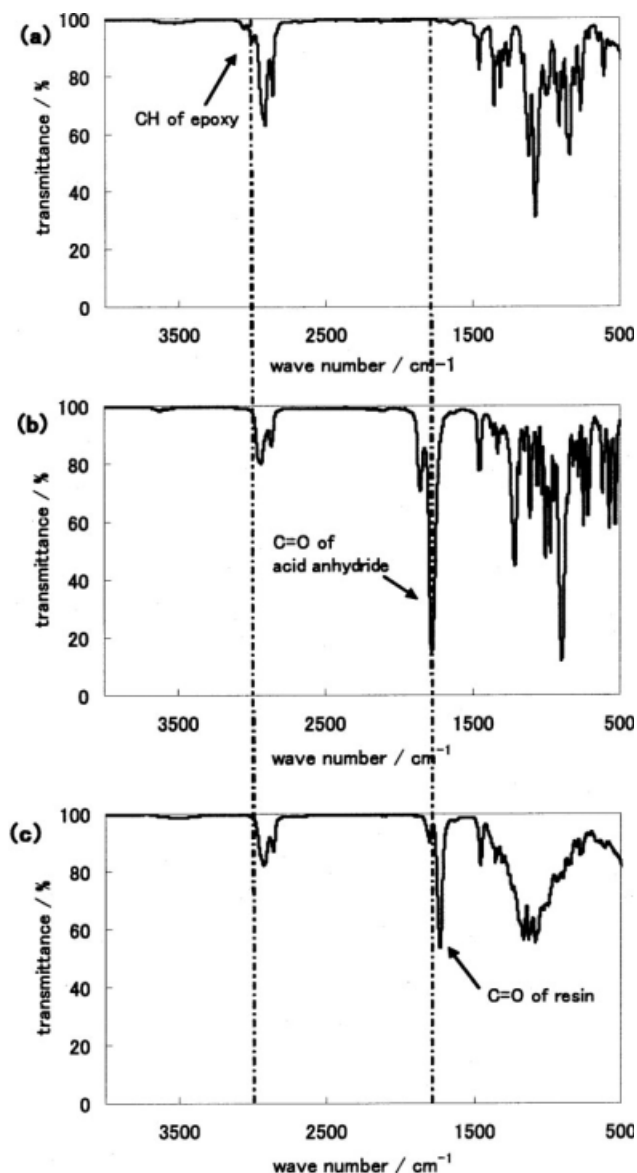

Figure 2 Changes of FTIR spectra before and after polymerization: (a) **2a**; (b) 4-methylhexahydrophthalic anhydride; (c) **2b**.

anhydride was taken, and the reaction mixtures were heated in four steps, i.e., at 100°C (2 h), 120°C (0.5 h), 150°C (1 h), and then 170°C (1 h) to prevent the appearance of voids and cracks in the resulting resin. The resins thus obtained were colorless, highly transparent, and very rigid.

To know the structure of the resins, we characterized them by IR spectrometry. As a typical example, the IR spectra of **2a**, 4-methylhexahydrophthalic anhydride, and **3a** are presented in Figure 2. As shown in Figure 2, the C—H stretching vibration bands of the epoxy group of **2a** around 3000 cm^{-1} disappeared in the IR spectrum of **3a**, indicating that almost all of the epoxy units had been consumed in this polymerization. In addition, the C=O stretching

TABLE II
IR Spectra Before and After Polymerization[a]

Assignment	Band position (cm^{-1})						
	2a	**3a**	**2b**	**3b**	**2c**	**3c**	Acid anhydride
CH of epoxy	2,995	ND[b]	2,996	ND[b]	2,999	ND[b]	–
C=O	–	1,801 (w)	–	1,802 (w)	–	1,802 (w)	1,850 (m)
		1,729 (s)		1,730 (s)		1,729 (s)	1,777 (s)

[a] Compounds **2a**, **2b**, **2c**, and the acid anhydride were analyzed as neat liquid or solid, while resins, **3a**, **3b**, **3c** were analyzed as neat plate. The symbols in parentheses indicate the relative intensity of the signal, w: weak; m: middle; s: strong.
[b] Not detected.

vibration bands of the acid anhydride at 1730 cm^{-1} and 1777 cm^{-1} shifted to 1729 cm^{-1} on polymerization, which clearly indicated the ester formation. In the IR spectrum of **3a**, a weak band at 1801 cm^{-1} was also observed. This may be due to the intermolecular anhydride formation. Similar changes of the IR spectra were observed for the formation of **3b** and **3c** (Table II).

Heat resistance of resins

Thermal properties of the epoxy resins **3a–c** were examined by DSC and T_gs are listed in Table III. We also polymerized **HGBisA** and **AE** under the same conditions, as those for **3a**, **3b**, and **3c**, to give corresponding epoxy resins, **HGBisA-R** and **AE-R**, those T_gs are also listed in Table III.

As expected, all of the epoxy resins we had synthesized (**3a–c**) were found to be more thermally stable than **HGBisA-R**, with respect to T_gs. The rigidity of the adamantane ring would be responsible for the heat resistance. However, as compared with **AE-R**, **3a** and **3b** showed lower T_gs. On the other hand, **3c** exhibited highly heat-resistant properties with higher T_g than that of **AE-R**. It seems likely that high T_g of **3c** arises from the network structure because of the trifunctionalized adamantane unit.

We also evaluated the epoxy resins, concerning their coloring by heating in air. The resin plates of 1 mm in thickness were heated at 150°C, and their deterioration of transparency by coloring was examined, as shown in Figure 3. As can be seen in Figure 3, the transmittances of the resins monitored at

TABLE III
T_gs of Epoxy Resins[a]

Epoxy resin	**3a**	**3b**	**3c**	**HGBisA-R**	**AE-R**
T_g (°C)[b]	152	145	208	129	185

[a] DSC was carried out at a rate of 20°C/min in Ar. Heating and cooling were carried out in two cycles.
[b] T_g is a medial point of initial and end of grass transition in the second heating step.

400 nm decreased gradually, as increasing the heating period, and reached about 20, 30, and 60% of the original ones, respectively, after 144 h heating. For **3a** and **3b**, the coloring level was almost the same as that of **HGBisA-R**. However, they could not keep high transparency as compared with **AE-R**. In contrast, **3c** showed much lower coloring, similar or less inferior to that of **AE-R**. This seems to indicate that **3c** has high potential as a highly transparent resin even at high temperature. Again, this is probably ascribed to the rigidity of the adamantane ring. The rigid adamantane ring would suppress the reactivity of the resins toward air oxidation.

CONCLUSIONS

We successfully synthesized novel three epoxy compounds having an adamantane ring (**2a–c**) with high purity. It was indicated that these epoxy compounds have high heat resistance by TGA. In particular, **2c** showed the highest decomposition temperature among five epoxy compounds examined, including **HGBisA** and **AE**. Regarding the epoxy resins, obtained from the copolymerization of the epoxy compounds with an acid anhydride, **3c** showed the highest T_g. For coloring deterioration by heating, **3c** exhibited small extent of coloring, as small as that of **AE-R**. As mentioned earlier, it is found that
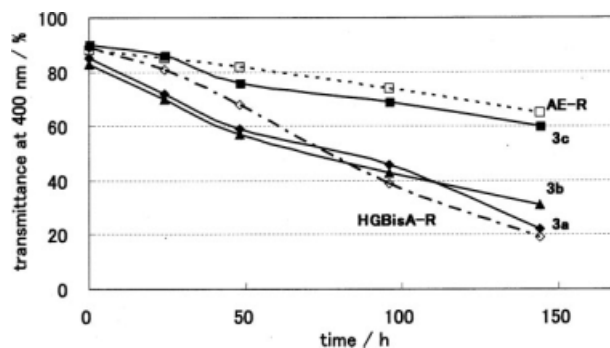

Figure 3 Coloring of the resin plates (1 mm in thickness) at 150°C.

introduction of an adamantane ring to epoxy compounds efficiently contribute on the improvement of heat resistance, which are potentially useful for precursors of high heat-resistant adhesive and encapsulant materials of LED.

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