Self-Curing Epoxy Compounds

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Synopsis

A new series including eight structurally different self-curing epoxy compounds bearing azomethine linkages were synthesized, characterized and polymerized. 4-(2,3-Epoxypropoxy)benzaldehyde (EPB) or 2,3-epoxypropyl glyoxylate monohydrate (EPG), prepared by reacting 4hydroxybenzaldehyde or glyoxylic acid monohydrate, respectively, with excess of epichlorohydrin in the presence of benzyltrimethylammonium bromide as catalyst, were used as starting materials. EPB or EPG reacted with an equimolar amount of a substituted aromatic amine (4-aminobenzoic acid, 5-aminoisophthalic acid, 4-aminophenol, or 1,4-phenylene-diamine) to afford the epoxy compounds. They were characterized by IR and ¹H-NMR spectroscopy. Their thermal polymerization was investigated by DTA. The thermal stabilities of cured resins were evaluated by dynamic TGA and isothermal gravimetric analysis (IGA). The polymers of the epoxy compounds derived from EPB were stable up to 225–298°C in N₂ and afforded anaerobic char yield of 57–62% at 800°C.

INTRODUCTION

Epoxy resins are a very important class of thermosetting polymers that often exhibit high tensile strength and modulus, excellent chemical and corrosion resistance, and good dimensional stability.¹⁻³ However, these highly crosslinked systems are usually brittle, and consequently, they have limited utility in applications requiring high impact and fracture strengths. Such applications include reinforced plastics, matrix resins for composites, and coatings.

The ordinary epoxy compounds cannot be crosslinked at a reasonable rate by heat alone; even heating at 200°C has little effect. In order to convert the resins into crosslinked structures, it is necessary to add a curing agent. Most of the curing agents in common use can be classified into three groups; tertiary amines, polyfunctional amines, and acid anhydrides.

The present investigation deals with the synthesis, characterization, and polymerization of a new series of various self-curing and storage-stable epoxides bearing azomethine linkages. These glycidyl ethers and esters contain free carboxy, amino, or phenolic hydroxy groups in their molecules, and they can be thermally crosslinked without adding a curing agent. Preparation of these epoxides was accomplished in relatively high yields by simple methods utilizing inexpensive and readily available starting materials. In addition, the synthesized epoxy resins are expected to be sufficiently thermostable due to the relatively high thermal stability of azomethine segments.⁴⁻⁶

Recently, certain new epoxy compounds containing azomethine linkages have been synthesized, characterized, and polymerized.⁷

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EXPERIMENTAL

Characterization Methods

Melting temperatures were determined on an electrothermal melting point apparatus IA6304 and are uncorrected. IR spectra were recorded on a Perkin-Elmer 710B spectrometer with KBr pellets or NaCl cells. ¹H-NMR spectra were obtained using a Varian T-60A spectrometer at 60 MHz. Chemical shifts (δ values) are given in parts per million with tetramethylsilane as an internal standard. DTA and TGA were performed on a Du Pont 990 thermal analyzer system. DTA measurements were made using a high temperature (1200°C) cell in N₂ atmosphere at a flow rate of 60 cm³/min. Dynamic TGA measurements were made at a heating rate of 20°C/min in atmospheres of N₂ or air at a flow rate of 60 cm³/min. The epoxy equivalent weights (EEW) were expressed in g/mole of epoxy groups and determined by the pyridinium chloridepyridine method.⁸

Reagents and Solvents

4-Hydroxybenzaldehyde and 4-aminobenzoic acid (Aldrich) were recrystallized from distilled water. 4-Aminophenol (Merck) was recrystallized from ethanol 95%. 5-Aminoisophthalic acid (Aldrich) was recrystallized from a mixture of DMF/water (vol. ratio 3:1). 1,4-Phenylenediamine (Aldrich) was sublimed at about 110°C under vacuum (2-3 mm). Epichlorohydrin and acetonitrile (Aldrich) were purified by distillation. *N*,*N*-Dimethylformamide (DMF) (Aldrich) was dried by refluxing and fractionally distilled from calcium hydride. Benzyltrimethylammonium bromide (BTMA), glyoxylic acid monohydrate, benzene, and ethanol (Aldrich) were used as supplied.

Preparation of Starting Materials

4-(2,3-Epoxypropoxy)benzaldehyde (EPB)

A flask was charged with 4-hydroxybenzaldehyde (7.00 g, 57.3 mmol), epichlorohydrin (25 mL), and a catalytic amount of BTMA. The mixture was refluxed for 2 h. Excess of epichlorohydrin and volatile components were subsequently removed by distillation under reduced pressure. The viscous liquid obtained was treated with dilute sodium hydroxide at 65°C for 2 h. Then, it was washed with water and dried into a vacuum oven at about 70°C overnight. The product was obtained as a viscous liquid which cannot be distilled (9.70 g, 95%).

IR cm⁻¹: 1700 (C=O); 1258, 1163, 827 (ether); 2935, 2850, 1427 (CH₂); 1312 (CH); 3030, 1604, 1513, 1583, 1455 (aromatic).

¹H-NMR (CDCl₃) δ : 9.73 (s, 1H, CHO); 7.90–7.75 (d, 2H, aromatic ortho to -CHO); 7.12–6.98 (d, 2H, other aromatic); 3.75 (m, 2H, <u>CH</u>₂OPh); 3.37 (m, 1H, <u>CH</u>CH₂O); 2.80 (m, 2H, epoxy CH₂).

2,3-Epoxypropyl Glyoxylate Monohydrate (EPG)

A flask was charged with glyoxylic acid monohydrate (5.44 g, 59.1 mmol), epichlorohydrin (20 mL), and a catalytic amount of BTMA. The flask was

immersed into a oil-bath, whose the temperature was gradually raised to the boiling point of epichlorohydrin (117° C). The mixture was refluxed for 1.5 h. Excess of epichlorohydrin and volatile components were subsequently removed by distillation under reduced pressure. 2,3-Epoxypropyl glyoxylate monohydrate was obtained as a viscous liquid which cannot be distilled (8.40 g, 96%). The product was miscible with dilute sodium hydroxyde or water.

IR cm⁻¹: 1767 (ester C=O); 1753 (aldehyde C=O); 1287-1220 (ester and ether C-O stretching); 1114, 840 (ether); 2930, 1440 (CH₂); 1342 (CH).

¹H-NMR (CDCl₃) δ : 5.40 (s, 1H, (OH)₂C<u>H</u>); 3.73 (m, 2H, COOCH₂); 3.12 (m, 1H, <u>CH</u>CH₂O); 2.58 (m, 2H, epoxy CH₂).

Preparation of Epoxides 1a-1d and 2a-2d

Epoxides 1a and 2a

A flask equipped with N_2 inlet was charged with a solution of EPB (1.6392 g, 9.2 mmol) and 4-aminobenzoic acid (1.2617 g, 9.2 mmol) in acetonitrile (15 mL). The solution was stirred and heated at 70°C under N_2 for 10 h. The solvent was stripped off by distillation under reduced pressure and the residue was dried into a vacuum oven at about 60°C to yield epoxide 1a as a pale yellow solid (2.32 g, yield 85%, melting temperature 186–225°C).

Epoxide 2a was similarly prepared as a brown viscous liquid by reacting EPG (3.4655 g, 23.4 mmol) with 4-aminobenzoic acid (3.2091 g, 23.4 mmol) utilizing acetonitrile (20 mL) as solvent (4.55 g, yield 78%).

Epoxides 1b and 2b

The same procedure was used to prepare epoxide 1b from the reaction of EPB (2.7261 g, 15.3 mmol) with 5-aminoisophthalic acid (2.7716 g, 15.3 mmol) utilizing DMF (20 mL) as solvent (4.28 g, yield 82%, brown viscous liquid).

Similarly, the reaction of EPG (2.3252 g, 15.7 mmol) with 5-aminoisophthalic acid (2.8441 g, 15.7 mmol) in DMF (20 mL) afforded epoxide 2b as a pale yellow viscous liquid (3.68 g, 80%).

Epoxides 1c and 2c

Epoxide 1c was similarly prepared as a brown semisolid by reacting EPB (2.4945 g, 14.0 mmol) with 4-aminophenol (1.5278 g, 14.0 mmol), utilizing ethanol (20 mL) as solvent (3.24 g, yield 86%, melting temperature 46-53°C).

The reaction of EPG (2.6658 g, 18.0 mmol) with 4-aminophenol (1.9643 g, 18.0 mmol) in ethanol (20 mL) afforded epoxide 2c as a brown viscous liquid (3.15 g, yield 79%).

Epoxides 1d and 2d

EPB (2.8509 g, 16.0 mmol) reacted similarly with 1,4-phenylenediamine (1.7304 g, 16.0 mmol) in benzene (20 mL) to afford epoxide 1d as a brown solid (3.56 g, yield 83%, melting temperature 73-85°C).

Epoxide 2d was prepared as a dark brown viscous liquid by reacting EPG (2.7547 g, 18.6 mmol) with 1,4-phenylenediamine (2.0116 g, 18.6 mmol) utilizing benzene (20 mL) as solvent (3.11 g, yield 76%).

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General Method for Curing of Epoxides

The epoxide isolated was heated in a shallow dish placed into a circulated air oven at 230°C for 15 h to afford a crosslinked polymer.

RESULTS AND DISCUSSION

Synthesis and Characterization of Epoxides

EPB and EPG were used as starting materials for preparing the epoxides. These starting materials were prepared by reacting 4-hydroxybenzaldehyde and glyoxylic acid monohydrate, respectively, with excess of epichlorohydrin in the presence of a catalytic amount of BTMA. The reactions were monitored by thin layer chromatography (TLC) and occurred at the boiling point of epichlorohydrin. EPB has been prepared by this method.⁹

The self-curing epoxides were prepared according to the reaction sequences outlined in Scheme 1:

$$HO - \bigcirc -CHO \xrightarrow{A}_{CH_2CL} \xrightarrow{A}_{CH_2O} \xrightarrow{O}_{CHO} \xrightarrow{H_2N-X}_{mol} \xrightarrow{A}_{l+1} \xrightarrow{A}_{CH_2O} \xrightarrow{O}_{CH=N-X}$$

$$HOOC - CHO \xrightarrow{A}_{CH_2CL} \xrightarrow{A}_{CH_2OOC} \xrightarrow{CHO}_{ROOC} \xrightarrow{H_2N-X}_{mol} \xrightarrow{A}_{-CH_2OOC} \xrightarrow{CH=N-X}_{2}$$

$$Ia, 2a : X = -\bigcirc -COOH$$

$$Ib, 2b : X = -\bigcirc -COOH$$

$$Ic, 2c : X = -\bigcirc -OH$$

$$Id, 2d : X = -\bigcirc -NH_2$$

$$Scheme 1$$

More particularly, EPB or EPG reacted with an equimolar amount of a substituted aromatic amine (4-aminobenzoic acid, 5-aminoisophthalic acid, 4-aminophenol or 1,4-phenylenediamine) to yield the azomethine glycidyl ethers 1 or glycidyl esters 2. The reactions occurred under mild conditions and a solvent of the substituted amine was used as reaction medium. The epoxy group might react with the substituted amine or in some cases with the reaction medium to yield undesirable byproducts. It is reasonable to accept that at this stage the amino group of the substituted amine preferred to react with the formyl group and not with the epoxy group of EPB or EPG. The first reaction was spontaneous and more favored than the second one. A literature survey revealed that the synthesis of epoxide 1a from EPB and 4-aminobenzoic acid has been included in a Japanese patent.⁹

The majority of the epoxy compounds synthesized were obtained as viscous liquids which cannot be distilled or semisolids. Their epoxy equivalent weights (EEW) are listed in Table I.

The structures of epoxides were confirmed by IR and ¹H-NMR spectroscopy. The most important IR absorptions, as well as the ¹H-NMR spectral data, are listed in Table I. Figure 1 presents typical IR spectra of epoxy compounds 1a and 2a. All compounds showed absorption bands around 1260, 1170, and 870 cm⁻¹, associated with the epoxy group. The ester groups in compounds 2a-2d were identified by the absorptions at about 1730 cm⁻¹. Compounds 1a, 2a, 1b, and 2b bearing carboxy groups showed a broad absorption around 3600–2800 (carboxylic OH) and a strong absorption at about 1700 cm⁻¹ (carboxylic C=O). The absorption at 3600–3200 cm⁻¹ of compounds 1c and 2c were assigned to the phenolic OH stretching vibrations. Compounds 1d and 2d exhibited absorptions near 3500–3200 and 1630 cm⁻¹, which assigned to NH stretching and NH deformation, respectively. Finally, the azomethine bond absorbed at about 1610 cm⁻¹.

The ¹H-NMR spectra of epoxy compounds showed multiplets around 3.90, 3.60, and 2.50 δ , associated with the epoxy groups. They also exhibited a singlet approximately at 8.50 δ assigned to the azomethine protons. Figure 2 presents the ¹H-NMR spectra of epoxide 1a and its starting material EPB. It is seen that the aromatic protons of the latter showed two well-separated peaks every one of two protons centered at 7.83 and 7.05 δ . The peak at 7.83 δ was assigned to the aromatic protons ortho to formyl group due to the deshielding effect of the strong electron-withdrawing carbonyl group. Epoxide 1a showed two singlets every one of one proton at 9.70 and 8.40 δ assigned to the carboxyl and azomethine protons, respectively. The proton of the former singlet was exchangeable to D₂O.

Curing of Epoxides and Thermal Properties of Polymers

Thermal polymerization of self-curing epoxy compounds was investigated by DTA in N₂. Figures 3 and 4 present typical DTA traces of epoxy compounds 1a, 1c, 1d, and 2d, before and after curing, respectively. Curing of epoxy compounds was accomplished by heating at 230°C for 15 h. The uncured epoxy compounds started to release heat at 154–240°C. Since the completely cured epoxy resins did not show an exotherm in this temperature region, these exotherms were attributed to their thermal polymerization.

The onset temperatures (T_0) for polymerization were determined from the DTA traces and are as follows: (1a) 238°C; (2a) 240°C; (1b) 192°C; (2b) 198°C; (1c) 205°C; (2c) 211°C; (1d) 154°C; (2d) 164°C. The relative polymerization reactivity of epoxy compounds can be assessed by comparing the T_0 values. Thus, an epoxy compound which shows lower T_0 under the same set of curing conditions presents higher polymerization reactivity. It is seen that the glycidyl esters 2 showed a somewhat lower reactivity than did the respective glycidyl ethers 1. Upon comparing the T_0 of epoxy compounds **a**, **c**, and **d** bearing COOH, OH, and NH₂ polymerization groups, respectively, of

		Epoxy Equivalent Weights as well as IR and ¹ H-NMR Spectra	l Data of Epoxy Compounds
Compound	EEW ^{a,b} (g/mol)	IR wave number (cm ⁻¹)	¹ H-NMR chemical shifts (δ in ppm) ^e
la	328 (297.3)	1256, 1156, 882 (ether); 1684 (carboxylic C=0); 3600-2800 (carboxylic OH); 1592 (C=N); 1577, 1508,	9.70 (s, 1H, COOH); 8.40 (s, 1H, CH=N); 7.93-6.57 (m, 8H, aromatic); 3.98 (m, 2H, <u>CH</u> ₂ OPh); 3.58 (m, 1H,
1b	376 (341.3)	1427 (aromatic) 1260, 1174, 830 (ether); 1720 (carboxylic C=O); 3615- 2810 (carboxylic OH); 1606 (C=N); 1580, 1517, 1435 (aromatic)	$\overline{CH}CH_2O$); 2.85 (m, 2H, epoxy CH ₂) 9.37 (b, 2H, COOH); 8.37–7.87 (m, 3H, aromatic ortho to CO and 1H, CH=N); 7.43–6.47 (m, 4H, other aromatic); 3.92 (m, 2H, $\overline{CH_2}OPh$); 3.53 (m, 1H,
1c	297 (269.3)	1263, 1183, 850 (ether); 3607–3210 (OH); 1625 (C==N); 1597, 1535, 1473 (aromatic)	CHCH ₂ O); 2.53 (m, 1H, epoxy CH ₂) 8.78 (bs, 1H, OH); 8.48 (s, 1H, CH=N); 7.78-6.63 (m, 8H, aromatic); 3.97 (m, 2H, <u>CH₂OP</u> h); 3.63 (m, 1H, CHCH O); 9.67 (m, 9H arovy CH.)
ld	295 (268.3)	1240, 1157, 824 (ether); 3500–3200 (NH stretching); 1620 (NH deformation); 1603 (C—N); 1570, 1508, 1450 (aromatic)	8.47 (s, 1H, VH $_{\odot}$), 2.03 (m, 2.15, 300.5) (m, 8H, aromatic); 5.63 (bs, 2H, NH $_{\odot}$); 3.98 (m, 2H, \overline{CH}_{\odot} OPh); 3.62 (m, 1H, CHCH,O); 9.83 (m, 2H, enoxy CHA)
2a	276 (249.2)	1270, 1186, 853 (ether); 1734 (ester $C=0$); 1713 (earboxylic $C=0$); 3560-2900 (carboxylic OH); 1622 ($C=N$); 1590, 1543, 1428 (aromatic)	7.83-7.52 (m, 1H, CH = N and 2H, aromatic ortho to -COOH); 7.10 (bs, 1H, COOH); 6.63-6.48 (m, 2H, other aromatic); 3.53 (m, 2H, COOH ₂); 3.02 (m, 1H, CUCH ON: 9.43 (m, 9H 2000CH ₂); 3.02 (m, 1H,
2b	323 (293.2)	1273, 1185, 890 (ether); 1723 (ester C=O); 1707 (carboxylic C=O); 3520-2800 (carboxylic OH); 1600 (C=N): 1565. 1500. 1440 (aromatic)	2.0.0172/01, 2.45 (m, 2.11, epoxy C112) 8.45-8.35 (h, 2H, COOH and 1H, CH=N); 7.87-7.38 (m, 3H, aromatic); 3.80 (m, 2H, COOCH ₂); 3.10 (m, 1H, CHCH ₆ O): 2.63 (m, 2H, epoxy CH ₆)
2c	245 (221.2)	1248, 1167, 859 (ether); 1728 (ester C=O); 3600-3200 (OH); 1627 (C=N); 1600, 1580, 1440 (aromatic)	7.53 (s, 1H, CH = N); $7.20-6.63$ (m, 4H, aromatic); 6.52 (bs, 1H, OH); 3.57 (m, 2H, COOCH ₂); 3.14 (m, 1H, CHCH-O); 9.48 (m, 2H, arovy CH-)
2d	241 (220.2)	1257, 1173, 817 (ether); 1730 (ester C=O); 3540-3180 (NH stretching); 1633 (NH deformation); 1615 (C=N); 1513, 1450 (aromatic)	7.23-6.80 (m, 1H, CH = N and 4H, aromatic); 6.63 (bs, 2H, NH ₂); 3.65 (m, 2H, COOCH ₂); 3.18 (m, 1H, C <u>CH</u> CH ₂ O); 2.57 (m, 2H, epoxy CH ₂)

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TABLE I

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^a Epoxy equivalent weights in g/mol of epoxy groups.
^b Numbers in parentheses indicate the calculated values.
^c In DMSO-d₆ solution (b = broad; bs = broad singlet; m = multiplet; s = singlet).



Fig. 1. IR spectra of epoxy compounds 1a and 2a.



Fig. 2. 1 H-NMR spectra of epoxy compounds 1a and EPB.



Fig. 3. DTA traces of epoxy compounds 1a (– \triangleright –), 1c (– \Diamond –), 1d (– \bigcirc –) and 2d (– \bullet –) in $N_2.$

glycidyl ethers 1 and glycidyl esters 2, it is seen that the reactivity of these groups toward the epoxy group increased in the following order:

 $\rm COOH < OH < NH_2$



Fig. 4. DTA traces of cured resins $1a'(- \triangleright -)$, $1c'(- \Diamond -)$, $1d'(- \bigcirc -)$ and $2d'(- \bullet -)$ in N₂.

This order of reactivity is absolutely reasonable, because the acid- or basecatalyzed cleavage of an epoxide involves nucleophilic attack:



Finally, it can be seen that epoxy compound **b** showed considerably higher polymerization reactivity than did epoxy compound **a**, both of glycidyl ethers 1 and glycidyl esters 2, because the latter contain two carboxy groups per molecule of epoxide.

Throughout the text, the polymers obtained by curing (at 230° C for 15 h) the epoxy compounds 1a-1d and 2a-2d are referred to by the designations 1a'-1d' and 2a'-2d', respectively.

The self-curing epoxy compounds are thermally polymerized by reacting the epoxy group with the polymerization group (COOH, OH, NH_2) of other molecule. As an example, the structure of 1d' should initially be as follows:



Thus, a linear polymer results at the first stage of curing. Taking into consideration the possible side reactions, it seems likely that the structure of cured resins to be complex. More particularly, the pendent OH group of 1d' may react with another epoxy group to produce an ether linkage:



Consequently, heating a self-curing epoxy compound produces a 3-dimensionally crosslinked system rather than a linear polymer. The extent of the etherification reaction, which is catalyzed by acids, ¹⁰ will determine the cured properties and the optimum curing conditions of resins.

The thermal stabilities of cured resins were ascertained by dynamic TGA in N_2 and air atmospheres. Figure 5 presents primary TGA traces for polymers 1a', 2a', 1c', and 2c' in N_2 and air. Several TGA data are listed in Table II. More particularly, the initial decomposition temperature (IDT), the polymer decomposition temperature (PDT), the maximum polymer decomposition temperature (PDT_{max}), the temperature of complete pyrolysis (TCP), both in N_2 and air as well as the anaerobic char yield (Y_c) at 800°C, and the temperatures at which the polymers showed a weight loss of 30 and 60% in air are tabulated in Table II.

The polymers were stable up to 200-298 °C both in N₂ and air, and afforded an anaerobic char yield of 48–62% at 800 °C. The polymers of glycidyl ethers 1' were, in most cases, more heat-resistant than those of the respective glycidyl esters 2'. The more aromatic structure of the former should be responsible for this behavior. However, polymer 2a' showed better thermal characteristics than



Fig. 5. TGA thermograms of polymers 1a' (---), 2a' (- \cdot -), 1c' (--) and 2c' ($\cdot \cdot \cdot \cdot$) in N_2 and air.

polymer 1a'. Upon comparing the polymers a', c', and d' both of glycidyl ethers 1' and glycidyl esters 2', it is seen that d' was the less thermostable due to the thermally sensitive -NH- linkages. The structures of the synthesized epoxy compounds did not influence remarkably the anaerobic char yield of cured resins. The IDT in air was slightly lower than that in N₂, indicating that degradation of polymers was not affected greatly by the presence of oxygen.

Polymer						In air					
	In N ₂									Temp (°C) for weight loss	
	IDT* (°C)	PDT ^b (°C)	PDT _{max} ° (°C)	TCP ^d (°C)	Y _c (800°C)* (%)	IDT (°C)	PDT (°C)	PDT _{max} (°C)	TCP (°C)	30%	60%
1a'	267	307	370, 415	527	58	267	313	385, 549	633	512	560
1b'	283	317	351, 463	519	62	267	307	347, 530	664	482	580
1c′	298	325	389, 422	482	53	278	321	363, 578	619	444	533
1ď	225	275	336, 415	483	57	225	298	392, 523	623	467	541
2a'	286	325	370, 441	512	62	275	303	367, 519	664	484	551
2b'	244	286	344, 422	578	49	225	276	407, 512	660	420	547
2c'	221	272	344, 400	467	55	217	267	315, 512	649	437	540
2ď	202	278	332, 441	369	48	200	278	325, 597	657	484	572

TABLE II TGA Data of Polymers Obtained by Curing of Epoxy Compounds

* Initial decomposition temperature.

^b Polymer decomposition temperature.

^c Maximum polymer decomposition temperature.

^d Temperature of complete pyrolysis.

* Char yield at 800°C.



Fig. 6. IGA traces of polymer 1a' in static air at 260, 280, 300, 320, and 340°C.

The present investigation was expanded to include the evaluation of the thermooxidative stability of polymer 1a' by isothermal gravimetric analysis (IGA). Figure 6 presents the IGA traces for this polymer in static air at 260, 280, 300, 320, and 340°C. After 20 h isothermal aging at these temperatures, polymer 1a' showed a weight loss of 14.7, 22.7, 39.0, 56.0, and 82.7%, respectively. The results reveal that an increased degradation of the polymer occurred above 280°C under these conditions.

CONCLUSIONS

- 1. EPB and EPG prepared from the reaction of 4-hydroxybenzaldehyde or glyoxylic acid monohydrate with excess of epichlorohydrin in the presence of a quaternary ammonium bromide as catalyst, were used as starting materials for the synthesis of new epoxides.
- 2. The epoxides were synthesized by reacting EPB or EPG with an equimolar amount of a substituted aromatic amine.
- 3. The self-curing epoxides contained free carboxy, hydroxy, or amino groups, and they were thermally polymerized without adding a curing agent. Their polymerization started at 154–240°C.
- 4. The epoxide containing free amino group started its polymerization at the lowest temperature but afforded the less thermostable polymer.
- 5. Curing of epoxides yielded a complex crosslinked system rather than a linear polymer.

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