Epoxy Resins from Dinaphthols

V. C. E. BURNOP, *Esso Research Centre, Abingdon, England*

Synopsis

Epoxy resins were prepared from di-α-naphthol(4,4′-dihydroxy-1,1′-dinaphthyl) and di-β-naphthol(2,2′-dihydroxy-1,1′-dinaphthyl). The resins consisted mainly of the reaction product of 1 mole of dinaphthol with 2 moles of epichlorhydrin. They contained chlorine, however, and were correspondingly deficient in diepoxide functionality. The resins from di-α-naphthol were crystalline, had m.p. 200°C., and were not miscible with conventional curing agents. Di-β-naphthol gave resins with softening points in the range 50–70°C., which cured with diethylenetriamine or the anhydrides of dibasic acids, giving hard but brittle products. The brittleness was not removed by curing with plasticizing curing agents, such as tetrapropenyl succinic anhydride. The cured di-β-naphthol-based resins had thermal stabilities similar to analogous epoxy resins based on bisphenol A.

Introduction

Epoxy resins are conventionally prepared in the reaction of bisphenol A and epichlorhydrin in the presence of sodium hydroxide. In the general formula for these resins (I) the value n is controlled by varying the proportions of reactants. Thus n increases as the proportions of epichlorhydrin and sodium hydroxide decrease relative to bisphenol A.

$$CH_2—CH \cdot CH_2 \, [OROCH_2 \cdot CHCH_2]_n \, OROCH_2 \cdot CH—CH_2$$
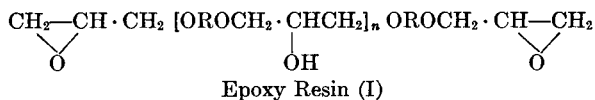
Epoxy Resin (I)

The value of epoxy resins lies in the reactivity of the epoxy and hydroxyl groups. Treatment with curing agents, such as amines or anhydrides, gives insoluble, crosslinked products with notable mechanical and electrical properties. This paper describes the preparation and properties of epoxy resins prepared from dinaphthols. These resins were expected to have structure (I) where R is dinaphthyl. The preparation and cure of epoxy resins from a dinaphthol, presumably di-β-naphthol (IV) have been previously reported[1] but only one curing agent (hexamethylenediamine) was used under unspecified conditions. A more detailed investigation was therefore desirable.

Experimental

The required dinaphthols were prepared by ferric chloride oxidation of α- and β-naphthols.[2,3] α-Naphthol gives a mixture of 4,4′-dihydroxy-

1,1'-dinaphthyl (II) and 1,1'-dihydroxy-2,2'-dinaphthyl (III), while β-naphthol gives 2,2'-dihydroxy-1,1'-dinaphthyl (IV). Substances (II) and (III) proved difficult to separate. Substance (III) was removed from the crude mixture by extraction with boiling benzene, and the residual (II) was recrystallized repeatedly from isopropanol. Substance (III) was not obtained sufficiently pure to justify conversion to resins.

OH

(II)
Di-α-naphthol

(III)

(IV)
Di-β-naphthol
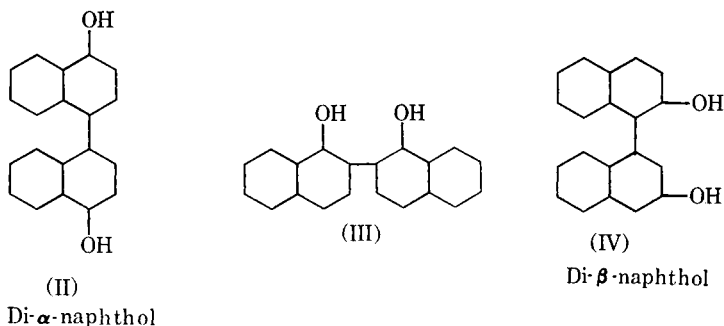
Preparation of Resins

The reaction between the dinaphthols and epichlorhydrin was carried out by two methods: the direct method, in which solid sodium hydroxide was added to a solution of dinaphthol in excess epichlorhydrin at 95°C., and the reverse method, in which a limited amount of epichlorhydrin was added to a solution of the dinaphthol in 10% aqueous sodium hydroxide between 45 and 95°C. These are conventional methods.[4] With bisphenol A the direct method gives a resin of structure (I) with $n = 0$, and the reverse method gives $n = 2$–4.

Attempts to prepare epoxy resins from di-α-naphthol (II) gave crystalline solids of high melting point (Table I). Normal curing procedures could not be applied to these products, since homogeneous melts with curing agents could not be made. The high chlorine and low epoxide contents suggested that these solids were not pure epoxy resins of structure (I). The use of excess alkali did not reduce the chlorine content significantly (Table I, run 3).

The di-β-naphthol (IV) gave epoxy resins of softening points 50–70°C. by the direct method (Table II, runs 4–7). The softening point and molecular weight decreased as the proportion of epichlorhydrin in the reaction mixture increased. The epoxide group contents of 0.27–0.38 per 100 g. were again considerably lower than the expected value of 0.50 for (I), where $n = 0$ and R = dinaphthyl. This was shown not to be due to faulty technique, since run 8, in which bisphenol A replaced dinaphthol, gave a product with an epoxide group content (0.50 per 100 g.) closer to the theoretical value of 0.59 for (I), where $n = 0$ and $R = -C_6H_4-CMe_2-C_6H_4-$. Run 6 was carried out under quantitative conditions and it was found that 1 mole of di-β-naphthol reacted with 2.07 moles of epichlorhydrin. Anal-

TABLE I
Epoxy Resins from Di-α-naphthol

		Reaction conditions				Reaction products							
Run no.	Proced.	Molar ratio[a] ECH/ dinaphthol	Molar ratio NaOH/ dinaph- thol	React. temp., °C.	Reaction time, hr.	Yield, wt.-% based on dinaph- thol	Analysis, % C	H	Cl	M.p., °C.	Epoxide groups per 100 g.	Hydroxyl groups per 100 g.	Mol. wt.[b]
1	Direct	15	2.2	95	1.5	146	74.8	5.5	3.6	196–200	0.32	0.11	412
2	Direct	15	2.2	95	2.0	146	—	—	—	198–202	0.32	—	—
2	Recrystallized from dioxane	—				—	71.9	5.2	3.2	206	0.37	—	410
3	Reverse	1.5	3.5	45–95	1	127	73.8	5.2	2.8	>360	0.16	—	—

a ECH, epichlorhydrin.
b By microosmometer in benzene solution.

TABLE II

Epoxy Resins from Di-β-naphthol

| Run no.	Proceed.	Molar ratio ECH/ dinaph- thol	Molar ratio NaOH/ dinaph- thol	React. temp., °C	React. time, hr.	Yield, wt.-% based on dinaphthol	Analysis, %			Soft. pt.,[a] °C	Epoxide groups per 100 g.	Hydroxyl groups per 100 g.	Mol. wt.[b]
							C	H	Cl				
4	Direct	4	1.7	95	4	140	68.1	5.1	2.5	69	0.28	0.06	457
5	"	8	2.2	"	4	146	71.9	5.1	2.0	59	0.27	0.09	443
6	"	10	2.1	"	1.5	140	76.7	5.3	1.8	55	0.38	0.10	413
7	"	20	2.0	"	4	134	74.6	5.6	5.6	52	0.27	0.12	424
8	" (bisphenol A)	8	2.2	"	4	149	71.2	6.9	2.0	viscous	0.50	0.00	393
9	Reverse	8	2.1	"	1.5	108, resin; 20, crystals	76.2	5.4	1.6	122	0.03	—	540
							71.3	5.6	3.2	180–190	0.07	—	—
10	"	2	1.9	45–95	1.5	108, resin; 9, crystals.	77.1	5.5	2.7	123	0.11	—	560
							69.8	5.6	2.8	180–190	0.06	—	—

[a] Ring-and-ball method; crystalline material by capillary method.

[b] By microosmometer in benzene solution.

TABLE III
Comparative Analysis of Resin Run 6

Analysis	Resin 6 (found)	Structure (V) (calcd.)	Structure (VI) (calcd.)
C, %	76.7	78.4	71.8
H, %	5.3	5.5	5.3
Cl, %	1.8	0.0	8.2
Mol. wt.	413	398	435
Epoxy equiv. (groups per 100 g.)	0.38	0.50	0.23
Hydroxyl value (groups per 100 g.)	0.10	0.0	0.23
Yield, wt.-% on dinaphthol	140	139	152

ysis of this resin (Table III) indicated that it was probably a mixture of the expected diepoxide (V) with about 30% of the hydroxy ether (VI).

(V)   (VI)
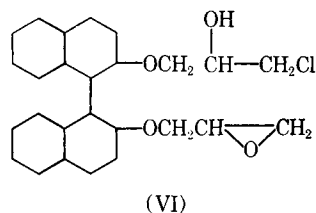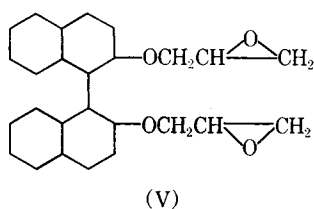
Structure (VI) contains chlorhydrin groups that should be convertible to epoxy groups by conventional techniques. When resin 6 was refluxed 2 hr. in dioxane with solid sodium hydroxide and the filtrate vacuum stripped at 100°C., the chlorine content was reduced from 1.83 to 0.09%. The resulting resin, however, was infusible and was no longer soluble in dioxane or other solvents. During the preparation of resin 6 a small amount of infusible and insoluble fibrous material was isolated; it had the empirical formula $C_{21}H_{31}ClO_8$. A similar product was formed when epichlorhydrin was refluxed with sodium hydroxide, and it was concluded that it was a polyglycerol.[4]

The reverse method of preparing the resins gave mixtures of resins of softening point 108°C. and crystalline materials of melting point 180–190°C., all of which contained appreciable amounts of chlorine (Table II, runs 9 and 10). Although the epoxide contents were low, the molecular weights were not proportionately higher. These materials were not investigated further.

Curing Di-β-naphthol-Based Resins

Several curing systems crosslinked the di-β-naphthol-based epoxy resins, but the products were, without exception, very brittle. Thus resins 4–7 (Table II) cured with 10 wt.-% of DETA (diethylenetriamine) within a few minutes at 100°C., giving brittle, infusible, and insoluble products. Under the same conditions resin 8, based on bisphenol A, gave a tough (i.e., not brittle) thermoset resin. Attempts were made to build in plasticity by

TABLE IV
Curing Experiments: Resin 6

Run no.	Curing agent[a]	Parts curing agent to 100 parts resin (w/w)	Moles curing agent epoxy equiv. of Resin II	Cure cond. hr. and °C.	M.p. of product, °C.	Remarks
a	DETA	5 (in 50 parts MEK)	0.13	(a) 18, 105	100	No cure
				(b) 80, 160	Infusible; chars 280	Dark and brittle
b	TPSA	10	0.10	(a) 18 160	Still soft at 160 135–140	Brittle
				(b) 80, 160	Infusible	
c	Maleic anh.	(+ trace Me₂NPh)	0.65	1, 160	Infusible	Brittle cold, rubbery at 610°C., dark
d	Maleic anh.	25	0.65	(a) 4, 160	Still soft at 160	
				(b) 80, 160	Infusible	Brittle
e	Succinic anh.	25	0.65	(a) 4, 160	Still soft at 160	
				(b) 10, 160	Infusible	
f	Maleic anh.	29	0.80	80, 160	Infusible	Hard, strong adhes. to glass, brittle
g	Phthalic anh.	58	1.00	80, 160	Infusible	Hard, strong adhes. to glass, brittle

[a] DETA, diethylenetriamine; TPSA, tetrapropenyl succinic anhydride.
[b] Based on epoxy equivalent of resin 6, Table II column heading expressed as a quotient.

TABLE V

Curing Resin 6 (Table II) and Epikote 828 with Anhydride[a]

Run no.	Epoxy resin	Curing agent	Parts curing agent to 100 parts resin (w/w)	Wt. loss on curing,[b] %	Color	Acetone-insol., %	Cured resin		
							Barcol hard., 20°C.	Barcol hard., 105°C.	M.p., °C.
h	Epikote 828	Maleic anh.	41	6.7	Yellow	0.8	38	29	360
i	"	TPSA;	111	0.5	Yellow	5.6	25	Rubbery	360
j	"	Phthalic anh.	61	1.4	Yellow	6.0	45	Rubbery	360
k	Resin 6	Maleic anh.	30	2.2	Brown	4.6	53	36	360
l	"	TPSA[c]	82	0.4	Dark brown	32.2	(shattered)	Rubbery	Decompd., 300
m	"	Phthalic anh.	45	0.3	Brown	17.1	47	35	Decompd., 300

[a] In all cases 0.8 mole of curing agent per 1.0 mole of epoxy group was employed.
[b] Curing time, 140 hr., at 160°C.
[c] TPSA, tetrapropenyl succinic anhydride.

reaction with long-chain compounds.   Thus, resin 4 prereacted for 1 hr. at 100°C. with 0.6–1.0 part by weight of the long-chain amine Primene JMT (Rohm and Haas; mol. wt. 340) and then heated 1 hr. at 160°C. with 0.1 part of maleic anhydride.   However, only brittle resins were formed, with softening points in the range 82–97°C.   Details of further curing experiments with resin 6 are given in Table IV.   In curing run "a" methyl ethyl ketone (MEK) was used as diluent; otherwise, the curing agent (DETA) reacted too vigorously at the lowest temperature at which the mixture could conveniently be stirred.   The MEK, which evaporated at the cure temperature, retarded cure.   The hardest resins were obtained by curing with maleic or phthalic anhydrides (runs "f" and "g"), but long curing times and high temperatures were required.

Finally, resin 6 was cured for 140 hr. at 160°C. with maleic, tetrapropenylsuccinic, and phthalic anhydrides, with 0.8 mole of curing agent to each resin epoxide group.   Epikote 828 (Shell Chemical, epoxy resin; epoxy value 0.52, hydroxyl value, 0.08) was cured under similar conditions. The properties of the cured resins are given in Table V.   With both resins the cure, as measured by acetone solubility, was most complete with maleic anhydride, and the resins based on Epikote 828 were more fully crosslinked
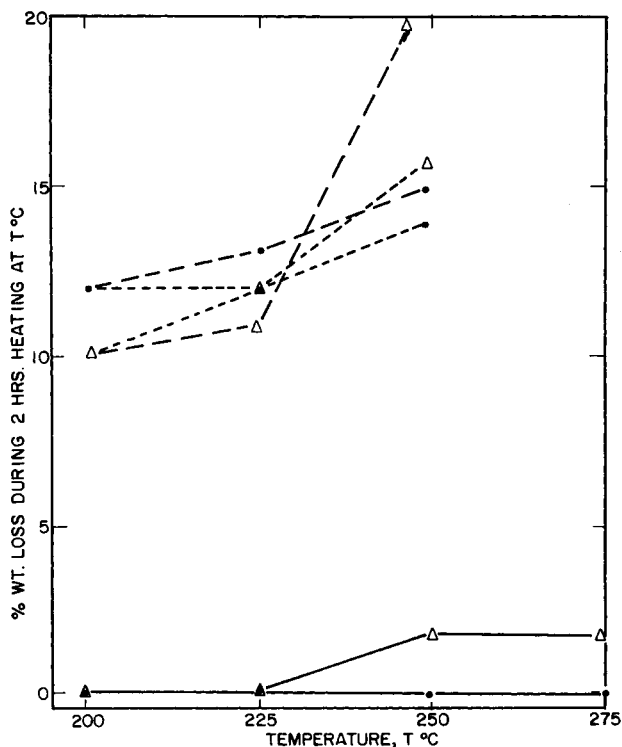

Fig. 1. Thermal stability in nitrogen of (△) cured resin 6 and (●) Epikote 828.   Curing agent: (———) maleic anhydride; (— —) phthalic anhydride; (- - -) TPSA.

than those based on resin 6. The cured dinaphthol-based resins were harder than those from Epikote 828 but were very brittle.

Thermal Stability of Epoxy Resins from Di-β-naphthol

The thermal stability of the anhydride-cured resin 6 and Epikote 828 (runs "h" to "m," Table V) were determined in nitrogen and air between 200 and 275°C. by measuring the weight losses over 2 hr. In both air and nitrogen the resins cured with maleic anhydride were far more stable than those cured with TPSA (tetrapropenyl succinic anhydride) or phthalic anhydride, the most stable being Epikote 828. The TPSA-cured resins were the least stable, especially in air; see Table VI and Figures 1 and 2. The dinaphthol resins were, for a given curing agent, about as stable thermally as those based on Epikote 828 resin.
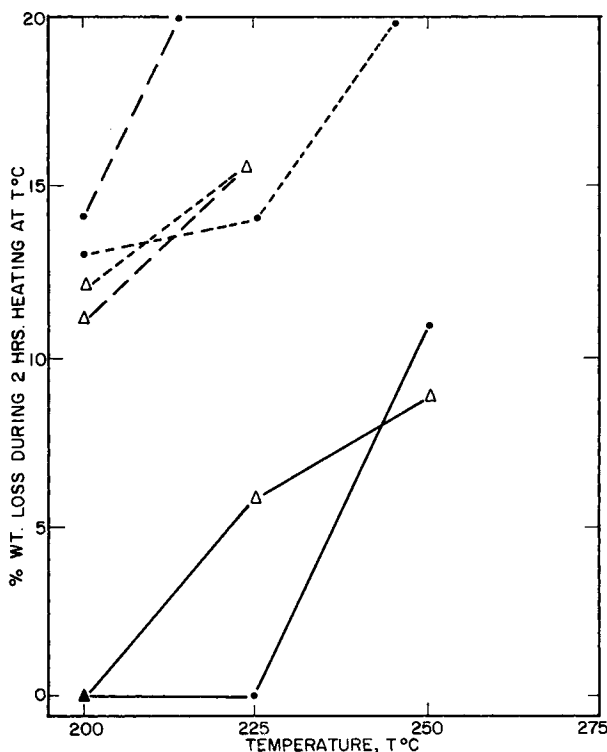

Fig. 2. Thermal stability in air of (△) cured resin 6 and (●) Epikote 828. Curing agent: (———) maleic anhydride; (- - -) phthalic anhydride; (— —) TPSA.

Conclusions

Di-α-naphthol, 4,4'-dihydroxy-1,1'-dinaphthyl, reacts with epichlorhydrin and alkali to give crystalline, insoluble products of melting point 200°C. These properties make curing impossible by methods normally

TABLE VI

Thermal Stability of Cured Resin 6 and Cured Epicote 828[a]

Cure run[b]	Epoxy resin	Curing agent	Wt. loss after 2 hr. at temp. (°C.), %						
			In nitrogen				In air		
			200	225	250	275	200	250	250
h	Epikote 828	Maleic anhydride	0	0	0	0	0	0	11
i	"	TPSA[c]	12	13	15	—	14	23	—
j	"	Phthalic anhydride	12	12	14	2	13	14	21
k	Resin 6	Maleic anhydride	0	0	2	—	0	6	9
l	"	TPSA[c]	10	11	21	—	11	16	—
m	"	Phthalic anhydride	10	12	16	—	12	16	—

[a] Curing conditions: see Table V. All resins pass 100-mesh seive.

[b] See Table V.

[c] TPSA, tetrapropenyl succinic anhydride.

used for epoxy resins. Di-β-naphthol, 2,2'-dihydroxy-1,1'-dinaphthyl, gives resins with softening points in the range 50–70°C. These resins contain chlorine and are correspondingly deficient in epoxide functionality. The epoxy resins from di-β-naphthol can be cured with diethylenetriamine or with the anhydrides of dibasic acids, but the products are brittle. The brittleness is not overcome by the use of plasticizing curing agents, such as tetrapropenyl succinic anhydride. The cured resins have thermal stabilities similar to those of resins based on bisphenol A.

It is concluded that the poor mechanical properties of the cured products may be due to lack of diepoxy functionality in the uncured resins.

References

1. T. Sulimson, *Rev. Chim. (Bucharest)*, **7**, 593 (1956).

2. J. D. Edwards, Jr. and J. L. Cashaw, *J. Am. Chem. Soc.*, **76**, 6141 (1954).

3. I. S. Ioffe and B. K. Krisherstsov, *J. Gen. Chem. (U.S.S.R.)*, **9**, 1136 (1939).

4. W. R. Sorensen and T. W. Campbell, *Preparative Methods of Polymer Chemistry*, Interscience, New York, 1961.

5. W. Fisch, *Chimia*, **16**, 66 (1962).