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Flexural Deformation Temperature of Amine-Cured Polyglycidyl and Poly-2,3-epoxybutyl Derivatives of Phenol

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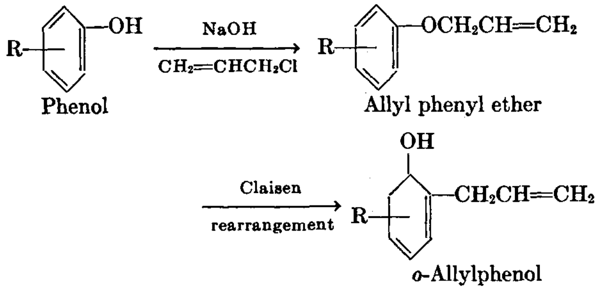
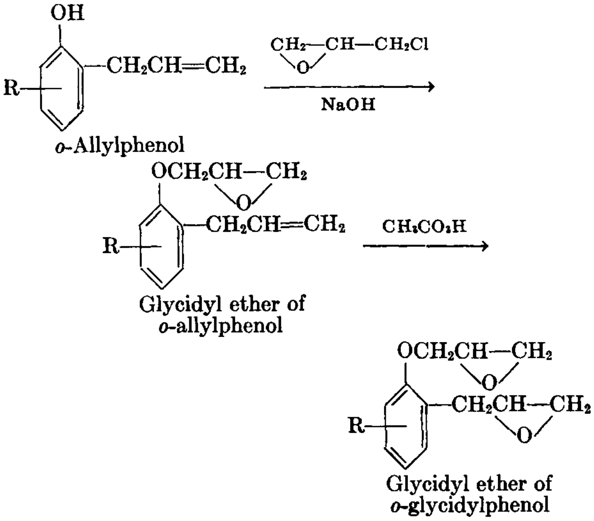
In this study an attempt is made to develop some qualitative indications of the effect of structure of epoxy compounds on the flexural deformation temperature (from now on referred to as FDT) of the same epoxy compounds after they have been cross-linked with amines. Other properties of the cross-linked compounds, such as Barcol hardness and flexural ultimate strength, are given in the tables but no attempt is made to correlate these properties with the structure beyond the following general observations: (*1*) aromatic rings tend to increase hardness, and (*2*) aromatic rings tend to decrease flexural ultimate strength.

The compounds under study are polyglycidyl and poly-2,3-epoxybutyl derivatives of phenols. These compounds were designed to have at least two epoxy groups per molecule. Preparation of polyglycidylphenols generally was carried out in the following manner:

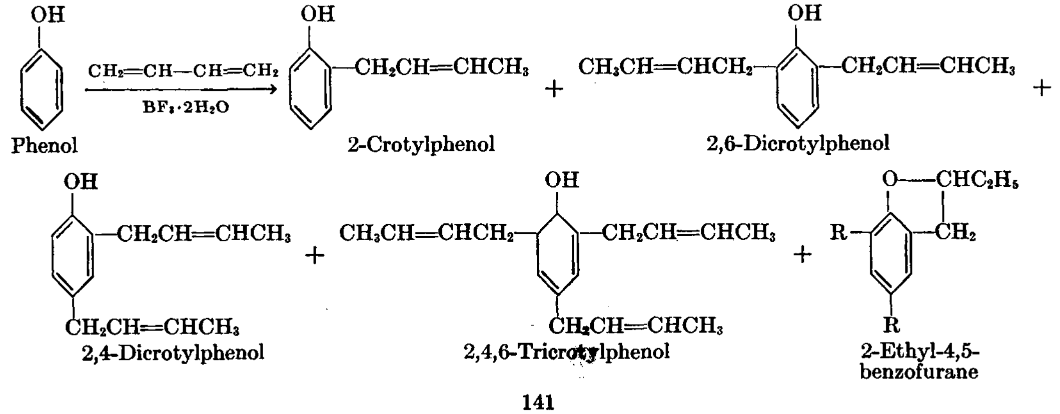


R may be hydrogen, alkyl, aryl or any other substituent. It may be ortho, meta, or para to the hydroxyl. If the above reactions are repeated diallyl- and eventually triallylphenols (if R is not hydrogen and is either ortho or para to the hydroxyl, diallylphenol is the limit of allylation) are formed. The allylphenols are then converted to glycidyl ethers with epichlorohydrin and finally to glycidyl ethers of glycidylphenols by epoxidation with peracetic acid:

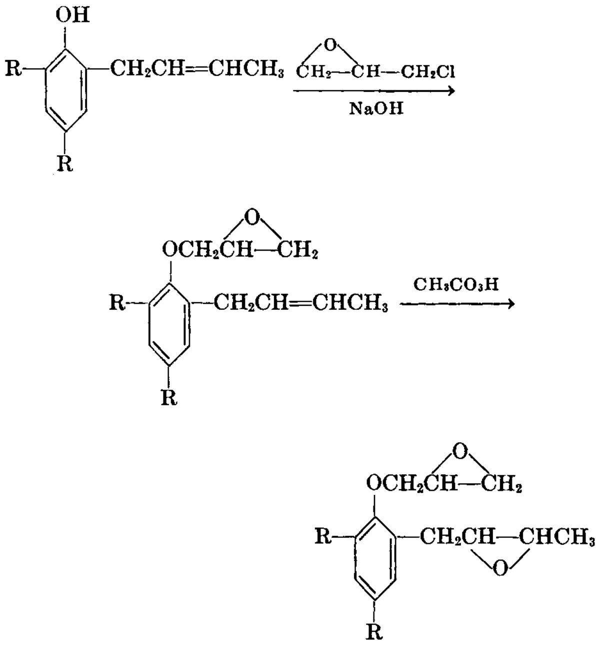


The same operations with di- and triallylphenols will yield glycidyl ethers of di- and triglycidylphenols, respectively.

Poly-2,3-epoxybutylphenols were prepared by polyalkylating phenol with butadiene in the presence of boron trifluoride dihydrate:



Phenolic products were separated from nonphenolic products by extraction with Claisen alkali. The alkaline layer was acidified and the phenols were converted into glycidyl ethers which were fractionated into glycidyl ethers of mono-, di-, and tricrotylphenols. The glycidyl ethers of crotylated phenols were then epoxidized with peracetic acid.



R may be hydrogen or crotyl groups. Where R groups are crotyls they are epoxidized. Crotylated phenols are converted to glycidyl ethers before fractionation to prevent the formation of benzodihydrofurans during fractionation of crotylated phenols.

The formation of allyl phenyl ether, Claisen rearrangement of allyl phenyl ether, and the formation of glycidyl ether of *o*-allylphenol are all high yield reactions. Thus, the overall yield of pure glycidyl ether of *o*-allylphenol, which encompasses three different steps is 70% based on phenol. The product analyzed 8.4% oxirane O (theoretical 8.4).

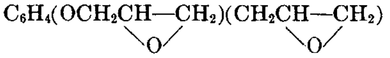
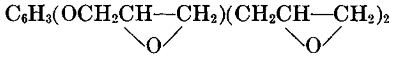
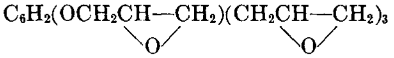
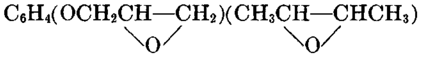
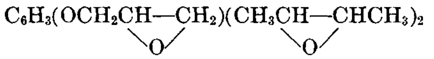
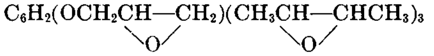
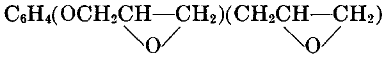
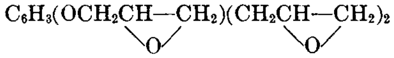
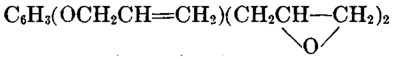
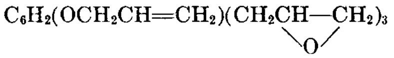
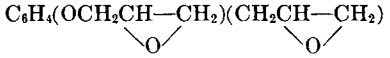
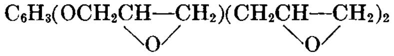
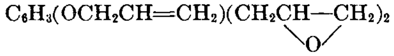
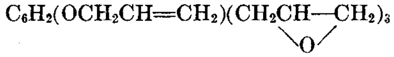
The Claisen rearrangements of higher boiling allyl ethers of allylated phenols generally gives poorer yields (larger residues) than allyl phenyl ether. These yields may be greatly improved by carefully controlling time and temperature of Claisen rearrangement. Most of the intermediates before epoxidation should be obtained in a reasonable degree of purity by fractional distillation.

It was noticed that the allyl group on the benzene ring epoxidizes much more readily than the allyl group attached to the oxygen of the allyl ether of *o*-allylphenol. Therefore, unless allyl ethers of glycidylphenols were specifically wanted, gycidyl ethers of allylated phenols were prepared and epoxidized. Epoxidation is seldom a quantitative reaction. Epoxidation of terminal double bonds presents special difficulties because terminal double bonds are not as readily epoxidized as nonterminal double bonds and the terminal epoxies are much more reactive than the nonterminal epoxies. Among secondary reactions in epoxidations are hydrolysis, acidolysis, and reaction products of epoxies with secondary alcohols which were formed in hydrolysis of acidolysis. The latter are generally materials of high viscosity. To minimize the undesirable secondary reactions, anhydrous solutions of peracetic acid in organic solvents were developed by Phillips and co-workers.[1,2] In our experience higher oxirane oxygen values were obtained when such solutions of peracetic acid in organic solvents were used as epoxidizing agent.

Lower molecular weight diepoxy compounds such as glycidyl ether of *o*-glycidylphenol or 2,6-diglycidylanisole may be purified by fractional distillation, but the majority of the compounds prepared in this study could not be so purified because of thermal instability in the distillation range. Thus, the purity of the compounds prepared ranged from 76.2 to 96.5% based on the per cent oxirane oxygen. Most of the preparations, however, fall within 85–90% purity range. The degree of purity is indicated in the tables by comparing actual per cent oxirane O with the theoretical. It is difficult to be sure how much of the overall effect on the FDT of a cured epoxy is due to unexpoxidized allyl or crotyl groups, and how much to the partial hydrolysis and or acidolysis of the oxirane group. Attempts to answer some of these questions in a qualitative way were made by deliberately introducing unepoxidized allyl groups and measuring their effect on the FDT of the cured resins.

This work indicates, as might be expected, that the choice of the curing agent for the epoxies is very important. Some curing agents, such as *m*-phenylenediamine and certain imidazolines, show great differences in FDT when cured with epoxies of different structures. Other curing agents, notably Versamid No. 125, show relatively little difference when cured with epoxies of different types (see Tables I and II). Moreover, one does not necessarily get parallel results on the same set of epoxies with the different curing agents. Thus, when epoxies A and B are cured with curing agents X and Y, AX (epoxy cured with X) may have a

TABLE I[a]
Effect of Functionality of Epoxies on the Properties of Cured Resins

	Epoxy compound (A)	Curing agent (B)	(A) in mixture, %	Oxirane O in (A), %	Theoretical oxirane O in (A), %	FDT, °C.	Barcol hardness	Flexural ultimate strength
(*1*)	 $\mathrm{C_6H_4(OCH_2\underbrace{CH{-}CH_2}_{O})(CH_2\underbrace{CH{-}CH_2}_{O})}$	*m*-Phenylenediamine	80	14.8	95.5	155	86	16,400
(*2*)[b]	 $\mathrm{C_6H_3(OCH_2\underbrace{CH{-}CH_2}_{O})(CH_2\underbrace{CH{-}CH_2}_{O})_2}$	"	80	16.63	90.8	214	66	
(*2'*)[c]	"	"	80	14.22	77.7	184	78	11,830
(*3*)[b, c]	 $\mathrm{C_6H_2(OCH_2\underbrace{CH{-}CH_2}_{O})(CH_2\underbrace{CH{-}CH_2}_{O})_3}$	"	80	16.71	79.2	246	70	8,950
(*4*)[d]	 $\mathrm{C_6H_4(OCH_2\underbrace{CH{-}CH_2}_{O})(CH_3\underbrace{CH{-}CHCH_3}_{O})}$	"		13.81	95.2			
(*5*)[b]	 $\mathrm{C_6H_3(OCH_2\underbrace{CH{-}CH_2}_{O})(CH_3\underbrace{CH{-}CHCH_3}_{O})_2}$	"	84	14.97	90.7	286	62	
(*5'*)[c]	"	"	78.5	12.58	76.2	157	73	
(*6*)[c]	 $\mathrm{C_6H_2(OCH_2\underbrace{CH{-}CH_2}_{O})(CH_3\underbrace{CH{-}CHCH_3}_{O})_3}$	"	80	14.18	79.7	209	68	
(*7*)	 $\mathrm{C_6H_4(OCH_2\underbrace{CH{-}CH_2}_{O})(CH_2\underbrace{CH{-}CH_2}_{O})}$	Versamid 125	50	14.8	95.5	65	57	10,700
(*8*)[b]	 $\mathrm{C_6H_3(OCH_2\underbrace{CH{-}CH_2}_{O})(CH_2\underbrace{CH{-}CH_2}_{O})_2}$	"	46	16.63	90.8	93	55	
(*9*)	 $\mathrm{C_6H_3(OCH_2CH{=}CH_2)(CH_2\underbrace{CH{-}CH_2}_{O})_2}$	"	55	12.04	92.6	75	61	15,200
(*10*)	 $\mathrm{C_6H_2(OCH_2CH{=}CH_2)(CH_2\underbrace{CH{-}CH_2}_{O})_3}$	"	45	13.85	87.1	69	61	8,650
(*11*)[b]	 $\mathrm{C_6H_4(OCH_2\underbrace{CH{-}CH_2}_{O})(CH_2\underbrace{CH{-}CH_2}_{O})}$	Versamid 140	65	14.8	95.5	79	68	15,800
(*12*)	 $\mathrm{C_6H_3(OCH_2\underbrace{CH{-}CH_2}_{O})(CH_2\underbrace{CH{-}CH_2}_{O})_2}$	"	55	16.63	90.8	131	48	
(*13*)[b]	 $\mathrm{C_6H_3(OCH_2CH{=}CH_2)(CH_2\underbrace{CH{-}CH_2}_{O})_2}$	Diimidazoline of isophthalic acid and TET	80	12.04	92.6	152	85	6,200
(*14*)[b]	 $\mathrm{C_6H_2(OCH_2CH{=}CH_2)(CH_2\underbrace{CH{-}CH_2}_{O})_3}$	"	75	13.3	83.6	174	88	7,000

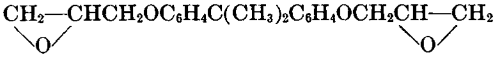
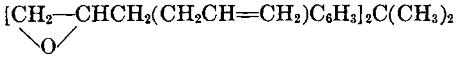
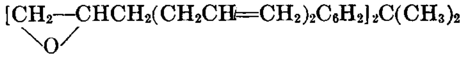
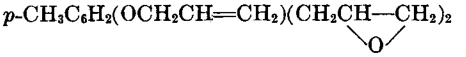
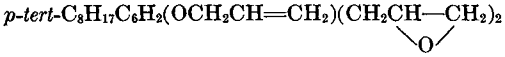
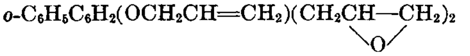
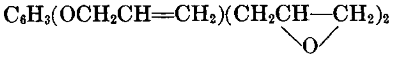
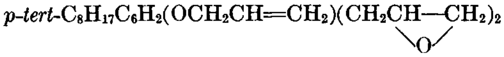
[a] Optimum percentage given unless otherwise indicated.
[b] Not necessarily optimum proportions were used.
[c] Considerably less than theoretical per cent oxirane oxygen.
[d] None of the samples could be forced out of the molds.

higher FDT than BX while AY may have a lower FDT value than BY. The optimum percentages of epoxy and curing agent had to be determined experimentally because purely stoichiometric relations seldom produce maximum FDT. It was also established that proportions of epoxies and curing agents which will produce a maximum FDT will not necessarily produce maximum hardness or maximum flexural ultimate strength.

In most cases initial curing was done at relatively low temperatures, and higher temperatures (150 to 200°C.) were used to post cure the resin to the maximum FDT for the mixture used. A single mold of each mixture was made. The following curing agents were used in this study: *m*-phenylenediamine, Versamids No. 125 and 140, diimidazoline from isosebacic acid and triethylenetetramine,[3] and diimidazoline from isophthalic acid and triethylenetetramine.

In general we tried to establish the effects of functionality, per cent oxirane oxygen, presence of alkyl, allyl, or aryl groups in the epoxy compound,

TABLE II[a]
Effect of Ring Substitution on Properties of Cured Polyglycidylphenols

Epoxy compound (A)	Curing agent (B)	(A) in mixture, %	Oxirane O in (A), %	Theoretical oxirane O in (A), %	FDT, °C.	Barcol hardness	Flexural ultimate strength
(1)  $\underbrace{CH_2—CH}_{O}CH_2OC_6H_4C(CH_3)_2C_6H_4OCH_2\underbrace{CH—CH_2}_{O}$	*m*-Phenylenediamine	80	8.2	87.2	140	85	7,500
(2)  $[\underbrace{CH_2—CH}_{O}CH_2(CH_2CH{=}CH_2)C_6H_3]_2C(CH_3)_2$	"	88	6.44	84.7	85	60	
(3)  $[\underbrace{CH_2—CH}_{O}CH_2(CH_2CH{=}CH_2)_2C_6H_2]_2C(CH_3)_2$	"	89.5	6.00	93.7	64	50	
(4)[a]  $p\text{-}CH_3C_6H_2(OCH_2CH{=}CH_2)(CH_2\underbrace{CH—CH_2}_{O})_2$	Diimidazoline of acid and TET	65	11.54	93.8	117	80	12,350
(5)  $p\text{-}tert\text{-}C_8H_{17}C_6H_2(OCH_2CH{=}CH_2)(CH_2\underbrace{CH—CH_2}_{O})_2$	"	70	8.29	92.7	103	69	7,950
(6)  $o\text{-}C_6H_5C_6H_2(OCH_2CH{=}CH_2)(CH_2\underbrace{CH—CH_2}_{O})_2$	"	80	9.52	95.2	127.5	78	6,450
(7)  $C_6H_3(OCH_2CH{=}CH_2)(CH_2\underbrace{CH—CH_2}_{O})_2$	Versamid 125	55	12.05	92.6	75	61	15,200
(8)  $p\text{-}tert\text{-}C_8H_{17}C_6H_2(OCH_2CH{=}CH_2)(CH_2\underbrace{CH—CH_2}_{O})_2$	"	60	8.29	92.7	65	5	10,500

[a] Not necessarily optimum proportions were used.

and the differences between glycidyl and 2,3-epoxybutyl groups on the FDT of the cured resins (Table I).

Effect of Functionality on FDT

The FDT of *m*-phenylenediamine-cured glycidyl ethers of mono-, di-, and triglycidylphenol increases progressively from 155°C. to 214°C. to 246°C. The last value could be much higher because the per cent oxirane oxygen is considerably lower than the theoretical value and because the two ingredients are not necessarily in optimum proportions. Functionality is apparently a very important factor in FDT. Even a small percentage of an epoxy of a higher functionality may raise FDT considerably. The small increase of per cent oxirane oxygen in part (*3*) of Table I over part (*2*) (16.7 to 16.6) increased FDT by at least 32°C. This is probably due principally to an increase in functionality. However, when per cent oxirane oxygen falls considerably below theory [see parts (*5*) and (*6*)], then FDT takes a drop which is probably due to the effect of unepoxidized allyl or crotyl group. Part (*6*) is still some 50°C. higher than (*5'*) and since they have similar per cent theoretical oxirane oxygen, this difference is due mainly to functionality.

No clear indication of the importance of functionality is available from the study of the glycidyl ethers of mono-, di-, and tri-2,3-epoxybutylphenol [see parts (*4*), (*5*), and (*6*)]. The glycidyl ether of monoepoxybutyl phenol when cured with *m*-phenylenediamine produced resins which could not be released from the molds. The glycidyl ether of diepoxybutyl phenol when cured with *m*-phenylenediamine produced on FDT above the capacity of the instrument (286°C.) while glycidyl ether of triepoxybutylphenol (which analyzed closer to glycidyl ether of crotyl diepoxybutylphenol) when cured the same reagent gave an FDT of only 209°. The functionality effects are also noticeable in cases of glycidyl ether of mono- and diglycidyl phenols cured with Versamids 125 and particularly with Versamid 140, respectively. With the increase in functionality the FDT of the cured epoxies increase from 65 to 93°C. and from 79 to 131°C., respectively [see parts (*7*), (*8*), and (*11*) and (*12*)]. No such indication is given by allyl ethers of di- and triglycidylphenols when cured with Versamid 125 [see parts (*9*) and (*10*)]. A reversal is seen there. This reversal is slight and it may be due to the fact that the diglycidyl compound had 92.6% theoretical oxirane oxygen while triglycidyl compound had only 87% theoretical oxirane oxygen.

The increase in FDT of the allyl ether of triglycidylphenol over that of the allyl ether of diglycidylphenol when cured with diimidazoline of isophthalic acid and triethylenetetramine is qualitatively in accord with the expected effect [see parts (*13*) and (*14*)]. However, this evidence is not unequivocal since the proportions for maximum FDT were not necessarily reached in these examples. The fact that diglycidyl compound had 92.6% of theoretical oxirane oxygen while the triglycidyl compound had only 83.6% suggest that the increase would be even greater for a purer triglycidyl compound.

Effect of Oxirane Per Cent on FDT

Examples (*2*), (*2'*), (*5*), (*5'*), and (*6*) in Table I show clearly what great effect on FDT is exercised by the difference in per cent oxirane oxygen in epoxides cured with *m*-phenylenediamine. A glycidyl ether of diglycidylphenol with 78% theoretical oxirane oxygen cured with *m*-phenylenediamine had an FDT of 184°C. whereas one with 91% theoretical oxirane oxygen had an FDT of 214°C.

The latter, moreover, is not necessarily a maximum value. An even greater sensitivity is noticed in the case of glycidyl ethers of di- and triepoxybutylphenols. The glycidyl ether of diepoxybutylphenol (76.2% theoretical oxirane oxygen) attained an FDT of 157°, but when per cent theoretical oxirane oxygen was boosted to 90.7% the FDT of the cured product was above the capacity of the instrument (286°C.). Again glycidyl ether of triepoxybutylphenol with 79.6% theoretical oxirane oxygen reached an FDT of only 209°.

A study of (*2*) and (*2'*) suggests that if theoretical per cent oxirane oxygen is boosted to about 90% from 79.2% in glycidyl ether of triglycidylphenol, it may attain an FDT in the neighborhood of 300°C. when cured with the same reagent. And the glycidyl ether of triepoxybutylphenol, if epoxidized to more than 90% theory, will probably give an FDT considerably in excess of 300°C.

Effect of Substituting Epoxybutyl for Glycidyl Groups in Glycidyl Ethers of Polyglycidyl Phenols

Unfortunately, we cannot compare glycidyl ether of *o*-glycidylphenol with the glycidyl ether of 2,3-epoxybutylphenol because cured samples of the latter could not be released from the mold. Glycidyl ether of diepoxybutylphenol when cured with *m*-phenylenediamine gives an FDT of over 286°C. while the glycidyl ether of diglycidylphenol similarly cured (but not necessarily in optimum proportions) gave an FDT of only 214°. The glycidyl ether of triepoxybutylphenol had an oxirane oxygen value of only 80% of theory (*6*) (it was much closer to a triepoxy than to a tetraepoxy compound). This material when cured gave a lower FDT (209°C.) than the cured glycidyl ether of triglycidylphenol (*3*) (FDT 246°C.) with 79% theoretical. The crotyl group has probably a more depressing effect on FDT than the allyl group.

Effect of Ring Substitution in the Polyglycidylphenols

The effect of allyl group substitution into the ring on the FDT of *m*-phenylenediamine-cured epoxies is quite obvious [see (*2*) and (*3*) in Table II]. When two allyls are ring-substituted into diglycidyl ether of bisphenol A (*2*), the FDT dropped from 140 to 85°C. Introduction of four allyl groups into diglycidyl bisphenol A (*3*) further depressed FDT of the *m*-phenylenediamine-cured product to 64°C. Longer paraffinic chains depressed FDT of diimidazoline of isosebacic acid and triethylenetetramine-cured epoxies more than the short chains in the same position. Thus, cured allyl ether of diglycidyl-*p*-cresol (*4*) had an FDT of 117°C. (not necessarily maximum) while the cured corresponding *p*-*tert*-octyl compound had a maximum FDT of 103°. Phenyl substituted epoxies, such as the cured *o*-phenyl derivative of the same compound (*6*), had a maximum FDT of 127.5°. Introduction of *p*-*tert*-octyl group into the allyl ether of diglycidyl phenol lowered FDT of the Versamid 125 cured compound from 75 to 65° [see (*7*) and (*8*)].

Conclusions: (*1*) Glycidyl ethers of polyglycidyl- or epoxybutylphenol are liquids of low viscosity (0.4–4.5 poises) which when cured with *m*-phenylenediamine yield products of very high FDT and good hardness. (*2*) Versamids, which are preferred by many as curing agents for epoxies for reasons other than high FDT, can cure some of the epoxies mentioned to very respectable FDT values. (*3*) To obtain highest FDT the following conditions should be met: (*a*) Substituents in the ring lacking oxirane groupings should be avoided; (*b*) three to four oxirane groups per molecule are desirable; (*c*) allyl or crotyl groups should be epoxidized to the fullest extent possible, and (*d*) hydrolysis and acidolysis of the epoxies should be minimized by the use of peracetic acid in anhydrous media.

EXPERIMENTAL

Glycidyl Ether of *o*-Allylphenol Prepared from Crude *o*-Allylphenol

A 500-ml. portion of allyl chloride was added during 1 hr. to a solution of 470 g. phenol in 226 g.

sodium hydroxide, 226 ml. water, and 2 l. methanol. The mixture was refluxed for 21 hr. Methanol was distilled out, water was added, and the product was taken up with Skellysolve B, washed with water, dried over sodium sulfate, filtered, evaporated to 190°, and rearranged. Rearrangement was complete in 6 hr.; it was refluxed for 7 hr. The crude rearranged product weighed 630 g. or 94% theory. The product was mixed with 2700 g. epichlorohydrin and 197 g. sodium hydroxide scales and distilled. 82 g. of water was recovered (theory 84.6 g.); 2100 g. epichlorohydrin was distilled out. The residue was diluted with water and extracted with MIBK. The MIBK extract was washed with water, dried over sodium sulfate, filtered, evaporated, and fractionated (Table III).

TABLE III

Fraction	Temp., °C.	μ	g.	n_D^{30}	Oxirane O, % (theory 8.42)
1	80	30	10	1.4392	
2	80–100	100	34	1.5227	
3	<100	35	34	1.5259	
4	100–5		51	1.5271	8.38, 8.45
5	105	20	71	1.5272	8.44, 8.35
6	105–6	25	481	1.5272	8.34, 8.32
7	106	20	60	1.5277	7.83, 7.82
8	106–35	30	38	1.5303	
Residue			101.5		
Total			879.5	(theory 893 g.)	

On the basis of fractions 4–7 an overall 70% yield was realized.

Allyl Ether of *o*-Allylphenol

o-Allylphenol (258 g.) was dissolved in 2 l. methanol, 45 g. sodium was added gradually in small pieces and, when all the sodium dissolved, the product was cooled to 14°; 192 g. allyl chloride was added during 5 minutes. The mixture was agitated and refluxed for 8 hours and was then allowed to stand overnight. It was still mildly alkaline. Refluxing was continued for 10 hours. The product was neutral. It was filtered and evaporated. The residue was taken up in 700 ml. Skellysolve B and washed with water, Claisen, alkali and water. The Skellysolve layer was dried over Na_2SO_4, and then it was filtered, evaporated and distilled. The distillate (b.p. 65° 250 μ) weighed 240 g., n_D^{30} 1.5200 (71.6% theory). The residue weighed 26.5 g. The Claisen alkali layer was acidified, extracted with Skellysolve B, washed, dried, and evaporated. It yielded but 1 g. residue which shows, that using this procedure, it is unnecessary to wash with Claisen alkali.

Glycidyl Ether of 2-Allyl-6-Phenylphenol

2-Allyl-6-phenylphenol (368 g.), 73 g. 97% sodium hydroxide scales, and 945 g. epichlorhydrin were agitated and subjected to distillation through a 2-ft. column; 29.5 ml. water was collected (theory 31.5). Recovered epichlorhydrin weighed 748 g. (35 g. epichlorhydrin unaccounted for). The product was taken up in MIBK, washed with water, dried over sodium sulfate, filtered, evaporated, and distilled through a Claisen head. The distillate boiled at 122–9° at 40 μ. It weighed 425 g., n_D^{30} 1.5803. The residue weighed 26.5 g. (it was not too viscous). The yield based on the distillate above 91.2%, and a viscosity of distillate 0.85–1.00 poise: 5.35% oxirane O, theory 6.00. The distillate was fractionated through a short Claisen head with the results shown in Table IV.

TABLE IV

Fraction	Temp., °C.	μ	g.	n_D^{30}	Oxirane O, %
1	<121	30	54	1.5825	5.25
2	<113	20	256	1.5800	5.59 (theory 6.0)
Residue			108.5	1.5788	5.01

Diglycidyl Ether of Diallyl Bisphenol A

Diallyl bisphenol A (200 g.), 1800 g. epichlorohydrin and 54 g. sodium hydroxide flakes were agitated and heated until 500 ml. distilled through a 2-ft. column. A total of 24.6 ml. water was collected (theory 25.2). The product was filtered and evaporated. The residue weighed 258 g. (theory 278 g.) n_D^{30} 1.5608, viscosity Y–Z (17.6–22.7 poises), 6.4% oxirane O (theory 7.6).

Diglycidyl Ether of Tetraallyl Bisphenol A

Tetraallyl bisphenol A (157 g.) (obtained by rearranging diallyl ether of diallyl bisphenol A), 1123 g. epichlorohydrin, and 33 g. sodium hydroxide flakes were agitated and heated in a flask provided with a 2-ft. column. 500 ml. were distilled, the flask was cooled, the contents filtered and evaporated. The residue weighed 185 g. (theory 202 g.), n_D^{30} 1.5568, 6.0% oxirane O (theory 6.4), viscosity V–Y (8.84–10.7 poises).

Claisen Rearrangement of Allyl Ethers of 2-Allyl-*p*-cresol

Allyl ether of 2-allyl-*p*-cresol (254 g.) was heated 2 hours at 220°. The reaction was very exothermic in the beginning and a temperature of 270° was momentarily reached. The product was distilled at 80–90° at 50 μ. The distillate weighed 104 g., n_D^{30} 1.5320. The residue weighed 142 g.

Claisen Rearrangement of Allyl Ether of *p-tert*-Octylphenol

p-tert-Octylphenol (618 g.) (Rohm & Haas), 216 g. sodium hydroxide scales, 2 l. *n*-propanol, and 300 ml. allyl chloride were agitated and refluxed for 3 hours. The product was neutral. It was filtered, evaporated, and rearranged at 220° for 2 hours. It distilled up to 112° at 100 μ. The distillate weighed 664 g., n_D^{30} 1.5090. The residue weighed 37 g. Total yield of distillate was 90%.

Claisen Rearrangement of Allyl Ethers of 2-Allyl-*p-tert*-Octylphenol

2-Allyl-*p-tert*-octylphenol (664 g.), 111 g. 97% sodium hydroxide, 2 l. *n*-propanol, and 300 ml. allyl chloride were agitated and refluxed for 7 hours. The product was acid. It was filtered, evaporated, and rearranged at 210° for 2 hours. The product distilled up to 120° at 60 μ. The distillate weighed 658 g., n_D^{30} 1.5120. The residue weighed 80 g. The total yield on the basis of distillate was 85.2%.

Claisen Rearrangement of Allyl Ethers of 6-Phenylphenol

Crude *o*-phenylphenol (510 g.), 126 g. 97% sodium hydroxide scales, and 2 l. of *n*-propanol were refluxed and mixed for 2 hours until all the sodium hydroxide went in solution or suspension. Then 300 ml. allyl chloride were added and the product was refluxed overnight. The product was still alkaline. 100 ml. allyl chloride was added and refluxing was continued for 5 hours. The mixture was neutral. It was filtered, evaporated, and rearranged at 220° for 2 hours (in the beginning it momentarily reached 250°). The product was distilled at 105° at 30 μ. The distillate weighed 564 g., n_D^{30} 1.5935. The residue weighed 36 g. Total yield was 95%. On the basis of the distillate alone, the total yield was 90%.

Claisen Rearrangement of Allyl Ethers of 2-Allyl-6-phenylphenol

2-Allyl-6-phenylphenol (562 g.) was refluxed and agitated with 100 g. 97% sodium hydroxide flakes and 2 l. *n*-propanol until all the caustic dissolved or went into suspension. Then 300 ml. allyl chloride was added and the mixture was agitated and refluxed overnight. The product was acid in the morning. It was filtered evaporated, and rearranged at 220° for 2 hours. Then it was distilled *in vacuo* at 125–142° at 75 μ. The distillate weighed 426 g., n_D^{30} 1.5893. The residue weighed 222 g. (it was viscous). The total yield was 96.8%, the total yield based on the distillate was 63.7%.

Diallyl Bisphenol A

Bisphenol A (228 g.), 82.5 g. sodium hydroxide scales, and 1 l. *n*-propanol were brought to a reflux. When everything went in solution or suspension, 200 ml. allyl chloride was slowly added. In 3 hours the product was virtually neutral. Agitation and reflux were continued for 3 hours and the product was allowed to stand overnight. The product was filtered and evaporated. The residue weighed 295 g. (theory 308 g.), n_D^{30} 1.5633, acid no. 25 (theory for monoallyl ether 209, for bisphenol A 492). The product was rearranged at 200–5° in xylene for 2 hours. It was filtered, evaporated, and distilled. The distillate weighed 242 g., n_D^{30} 1.5835, acid no. 364 (theory 364). The residue weighed 28 g., it was a glass, acid no. 254, mol. wt. 604 (theory for diallyl bisphenol A 308).

Crotylation of Phenol

Butadiene was passed through a rapidly agitated mixture of 188 g. phenol, 400 ml. hexane, and 30 g. boron trifluoride dihydrate. Addition took 5 hours; the temperature ranged from 20 to 28°. 16 g. of the catalyst was recovered. The product was washed with water, then with two moles of Claisen alkali. The upper layer was washed with 50% methanol, dried over sodium sulfate, filtered, evaporated, and distilled through a Claisen head (Table V).

The alkaline layer was acidified with hydrochloric acid, washed with sodium bicarbonate, dried over sodium sulfate, filtered, evaporated, and fractionated (Table VI).

Theoretical acid numbers are: monocrotylphenol 379, dicrotylphenol 277, and tricrotylphenol 219. The original ether fraction is 9.5%. However, there is more ether formation during distillation; this is

TABLE V

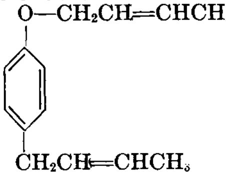
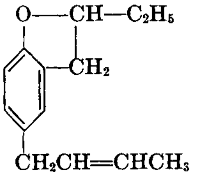
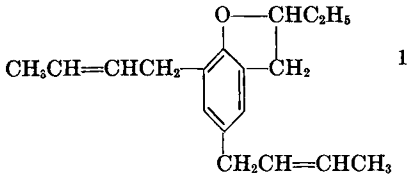
	g.	n_D^{30}	I_2 Value
Fraction 1 <180° at 16 mm.	18	1.5240	230.8, 230.6
Residue	14.5	1.5386	208.0, 208.7
Total	32.5		
Theoretical values for:			
			301
			150.5
			198.4

TABLE VI

Fraction	Temp., °C.		g.	n_D^{30}	Acid No.
1	<125	16 mm.	14	1.5340	344.8, 343.7
2	125–165	16 mm.	111.5	1.5353	349.6, 349.4
3	74–90	20 μ	25.5	1.5329	261.3, 260.7
4	90–100	20 μ	57	1.5327	260.4, 256.9
5	100–10	20 μ	14	1.5324	212.6, 211.2
6	110–20	45 μ	14	1.5340	211.1, 210.6
	(column replaced by tall Claisen head)				
	<195	50 μ	48	1.5493	190.2, 188.2
Residue			35	1.5607	4.6, 6.2
Total			319		

evidenced by the low acid number of the residue. The best procedure should be to make glycidyl ether of the crude, distill, and epoxidize it.

Glycidyl Ether of Mixed Crotylated Phenols

Mixed crotylated phenols (425 g.), 128 g. sodium hydroxide flakes, and 1800 g. epichlorohydrin were heated in a 5-l. flask. After 43 ml. of water distilled, the remainder was distilled *in vacuo*. The residue was taken up in MIBK and washed with water. A bad emulsion resulted. Emulsion was broken with methanol and salt, but parts of the product re-emulsified. The clear upper layers were dried over sodium sulfate, filtered, evaporated, and fractionated *in vacuo* through a modified Claisen Column (Table VII).

TABLE VII

Fraction	Temp., °C.	μ	g.	n_D^{30}	Oxirane O, %
1	<100	50	7	1.5000	
2	100–20	30	35	1.5252	7.06, 7.16
3	130–3	30	125	1.5260	7.11, 7.16
4	133–40	40	73	1.5258	6.03, 6.01
5	140–50	30	45	1.5260	5.54, 5.52
	(column replaced by short Claisen head)				
	134–80	40	82	1.5275	4.98, 4.92
Residue (quite mobile)			25	1.5470	
Total			392		

Fractions 2 and 3 were combined and refractionated through a 1-ft. modified Claisen column (Table VIII).

TABLE VIII

Fraction	Temp., °C.	μ	g.	n_D^{30}	Oxirane O, %
1	<88	25	6	1.5225	6.04, 6.12
2	88–93	20	45	1.5257	7.25, 7.19
3	93–103	20	7	1.5260	7.57, 7.60
4	103		75	1.5263	7.42, 7.44
Residue			24		5.87, 5.86
Total			157		

Fractions 5 and 6 were combined and refractionated (Table IX).

TABLE IX

Fraction	Temp., °C.	μ	g.	n_D^{30}	Oxirane O, %
1	<145	20	23.5	1.5257	5.30
2	145–63	30	80	1.5262	5.15, 5.14
Residue			21.5	1.5359	
Total			125		

Theoretical oxirane values were: for monocrotylphenol 7.84, for dicrotylphenol 6.2, for tricrotylphenol 5.12.

Epoxidation of Glycidyl Ether of *o*-Allylphenol

Glycidyl ether of *o*-allylphenol (280 g.) was added at once to a solution of 12 g. anhydrous sodium acetate in 300 ml. 40% peracetic acid. Agitation at 20–5° was continued for 7 hours. The initially formed emulsion cleared in 15 minutes. The product was poured into 4 l. in ice-cold brine. The diepoxy compound sank to the bottom. The product was extracted four times with a total of 1.5 l. MIBK. The MIBK solution was washed with sodium bicarbonate, sodium sulfite, and brine. It was dried over sodium sulfate, filtered, evaporated, and fractionated (Table X).

TABLE X

Fraction	Temp., °C.	μ	g.	n_D^{30}	Oxirane O, %
1	<100	40	3	1.4495	(largely solvent, discarded)
2	100–15	40	8	1.5269	
3	115–30	40	18.5	1.5289	
4	130–7	30	234	1.5315	14.45, 14.50
Residue			29	1.5368	6.88, 6.91
Total			289.5		

On the basis of fraction 4 and considering fractions 2 and 3 as recovered original material, the yield was 85% of theory. Only 9.5% of the original material did not react. Residue amounted to 10.4% of the original material. Loss was 4.3%.

31 ml. 50% hydrogen peroxide was added during 65 minutes to a rapidly agitating mixture of 35 g. Dowex 50X8, 12.5 g. distilled acetic acid, 95 g. glycidyl ether of *o*-allylphenol, and 200 ml. of benzene. The product was mixed with a solution of 28 g. sodium bicarbonate in 500 ml. of water. Despite the presence of the solvent the resin absorbed some oil and floated on the surface. The resin was shaken with benzene twice, the benzene solution was washed with water, sodium sulfite solution, and water, dried over sodium sulfate, filtered, evaporated, and fractionated (Table XI).

Yield was about 64% if the recovery of fractions 1 and 2 is taken into consideration. At least 11 g. of the original material was unaccounted for. It is hoped that better resins will increase conversion and yields by the *in situ* peracetic acid method.

TABLE XI

Fraction	Temp., °C.	μ	g.	n_D^{30}	Oxirane O, %
1	<100	40	14	1.5268	
2	100–15	30	39	1.5278	
3	115–35	75 (decomp.)	29	1.5307	15.49, 15.53 (th. 15.53)
Residue			2		
Total			84		

Epoxidation of Allyl Ether of *o*-Allylphenol

Allyl ether of *o*-allylphenol (238 g.) was added slowly to a solution of 22 g. sodium acetate in 550 ml. 40% peracetic acid. The addition took 8 minutes. The mixture was agitated 7 hours at 13–15°, packed in ice, and allowed to stand overnight. The product separated into two yellow layers (temperature was still 15°) and was poured into 2.5 l. saturated sodium chloride and extracted three times with MIBK. The MIBK extract was shaken with saturated sodium carbonate until alkaline, washed with saturated sodium chloride solution until it contained no peroxides, washed finally with very little sodium sulfite, dried over sodium sulfate, filtered, and distilled *in vacuo*. The distillate weighed 233 g.; the residue weighed 9 g. The distillate was fractionated *in vacuo* (Table XII).

TABLE XII

Fraction	Temp., °C.	μ	g.	n_D^{30}
1	<40	70	5	1.4810
2	40–55	70	22	1.5192
3	55–75	60	10	1.5207
4	75–90	60	9	1.5257
5	90–92	40	112	1.5278
6	92–108	35	10	1.5284
7	108–120	40	10	1.5303
8	120–127	45	48	1.5322
	% oxirane O 13.1, 13.0 (theory 15.5%)			
Residue			8	
Total			229	

Fraction (2) is unreacted allyl ether of *o*-allylphenol, fraction (5) is monoepoxy, and fraction (8) is largely diepoxy compound.

Triepoxidation of Allyl Ether of Triallyl phenol

Peracetic acid (553 g.) in propyl acetate (17.8% peracetic acid, 2% H_2O_2) was added to 100 g. allyl ether of triallylphenol at 55–60° during 40 minutes. The reaction was exothermic and had to be cooled from time to time. It was no longer exothermic 35 minutes after the addition was complete. The solution was agitated for 4 hours after the addition was complete. It was then mixed with 500 ml. benzene and washed with sodium chloride solution, sodium bicarbonate solution, and finally with a small amount of sodium sulfite. There was a small mechanical loss. The product was dried over sodium sulfate, filtered, and evaporated. The residue weighed 114 g. (theoretical maximum 118.9 g., n_D^{30} 1.5357, Gardner viscosity N-O (3.4–3.7 poises), % oxirane O 14.9 (theoretical 15.4).

Epoxidation of Glycidyl Ether of Dicrotylphenol

Peracetic acid (370 g.) in propyl acetate (19.4% peracetic acid and 2.02% H_2O_2) was added during 95 minutes at 55–60° to 104 g. fairly pure glycidyl ether of dicrotylphenol. The temperature was maintained at 60° for 3 hours after the addition was complete. It was treated as in the preceding example. The yield was 112 g. (theoretical maximum 117 g.), n_D^{30} 1.5211, viscosity Q (4.35 poises) % oxirane O 15.0 (theoretical maximum 16.5).

Epoxidation of Glycidyl Ether of Dicrotylphenol with 40% Peracetic Acid

A solution of 5 g. anhydrous sodium acetate in 125 ml. 40% peracetic acid was added with external cooling to 71 g. relatively pure glycidyl ether of dicrotylphenol. Suddenly the temperature went up to 60° and 20 ml. of water had to be added to bring the temperature down. At the time all the reagent was added the emulsion cleared. Agitation was continued 6 hours at 30–5°. The product was dissolved in 300 ml. of benzene, washed with sodium chloride solution, sodium bicarbonate solution, dried over sodium sulfate, filtered, and evaporated. The residue weighed 76 g., n_D^{30} 1.5249, viscosity W (10.7 poises), 12.6% oxirane O (theoretical maximum 16.5).

Epoxidation of Allyl Ether of Diallyl-*p*-cresol

Allyl ether of diallyl-*p*-cresol (113 g.) was mixed with 12 g. sodium acetate and 300 ml. 40% peracetic acid at 25° for 7 hours. The product was poured into 4 l. cold brine, extracted with MIBK, washed with brine, sodium bicarbonate, and sodium sulfite, dried over sodium sulfate, filtered, evaporated, and stripped to 127° at 120 μ (vapor). The distillate weighed 17 g., n_D^{30} 1.5244. The residue weighed 96 g., n_D^{30} 1.5299, % oxirane O 11.54 (theoretical 12.3).

Epoxidation of Allyl Ether of Diallyl-*p*-*tert*-octylphenol

Allyl ether of diallyl-*p*-*tert*-octylphenol (326 g.), 24 g. sodium acetate, and 600 ml. 40% peracetic acid were agitated 7 hours at 25°. The product was poured into 4 l. cold brine, extracted with MIBK, washed with brine, sodium bicarbonate, and sodium sulfite, dried over sodium sulfate, filtered, evaporated, and fractionated through a modified Claisen head. 64 g. distilled up to 150° at 100 μ, n_D^{30} 1.4999, 2.09% oxirane O. The residue weighed 268 g., n_D^{30} 1.5101, 5.23% oxirane O. The residue was re-epoxidized yielding 239 g., n_D^{30} 1.5140, 8.29% oxirane O (theory 8.94%), viscosity 22 poises.

Epoxidation of Allyl Ether of Diallyl-*o*-phenylphenol

Allyl ether of diallyl-*o*-phenylphenol (200 g.) was agitated 7 hours at 25°C. with a solution of 16 g. dry sodium acetate in 400 ml. 40% peracetic acid. The product was treated as described above. The yield was 206 g., n_D^{30} 1.5753, 7.76% oxirane O. The product was re-epoxidized using the same procedure. The yield was 187 g., n_D^{30} 1.5779, 9.52% oxirane O (theory 10.0%). The viscosity was 148 poises.

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Synopsis

A number of polyglycidyl and poly-2,3-epoxybutyl derivatives of phenols were prepared. An attempt was made to correlate the flexural deformation temperatures of the amine cured polyepoxies with the following structural characteristics of the epoxy compounds: per cent oxirane, functionality, ring substituents other than epoxy (such as alkyl, alkenyl, aryl), and substitution of 2,3-epoxybutyl for glycidyl group.

Résumé

Un certain nombre de dérivés polyglycidiques et poly 2,3-époxybutyliques du phénol, a été préparé. On a pu prouver la corrélation entre les températures de déformation par courbure des résines époxydes traitées aux amines, décrits précédemment et les caractéristiques structurelles suivantes des composés époxy: le % oxirane, la fonctionnalité, les substituants des noyaux autres que les époxy (tels que les alcoyles, alkényles et aryles), la substitution du 2,3 époxybutyle dans le cas du groupe glycidyle.

Zusammenfassung

Eine Anzahl von Polyglycidyl- und Poly-2,3-epoxybutylderivaten des Phenols wurde dargestellt. Es wurde versucht die Biege-Verformungstemperatur der oben angegebenen amin-behandelten Polyepoxyde zu folgenden Strukturcharakteristika der Epoxyverbindungen in Beziehung zu setzen: Prozent an Oxiran, Funktionalität, andere Ringsubstituenten als Epoxy (nämlich Alkyl, Alkenyl, Aryl), Substitution der 2,3-Epoxybutyl- für die Glycidylgruppe.

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