Studies in the Molecular Weight Distribution of Epoxide Resins. IV. Molecular Weight Distributions of Epoxide Resins Made from Bisphenol A and Epichlorohydrin

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Synopsis

The molecular weight distribution of epoxide resins made from bisphenol A and epichlorohydrin at high ratios of epichlorohydrin to bisphenol A are compared with the theoretically predicted distributions for two theoretical models: the "taffy" process A, the direct reaction of epichlorohydrin with bisphenol A; and the "taffy" process B, the self-polymerization of a monoglycidyl ether of bisphenol A followed by postglycidylation. At high ratios of epichlorohydrin to bisphenol A, process B is shown to give more low molecular weight products than process A. Deviations of the experimentally measured distributions from the theoretically predicted distributions for high epichlorohydrin/bisphenol ratios are attributed to the higher reactivity of epichlorohydrin to the phenolic compared with the aryl glycidyl ether functional group. Preliminary kinetic data are presented using a modified gel chromatographic method which enables the separation of most of the intermediates formed in this reaction.

INTRODUCTION

In our publication on the molecular weight distribution of epoxide resins,[1] we applied the statistical method of Flory[2] for the calculation of the molecular weight distribution. These epoxide resins may be made by two methods: namely, the "advancement" process, where the diglycidyl ether of bisphenol A is condensed with bisphenol A; and the so-called "taffy" process, where bisphenol A is reacted with a controlled excess of epichlorohydrin under alkaline conditions. The molecular weight distribution may be calculated assuming that the products of the reaction may be formally represented by $BB(AABB)_k$ produced by the polyaddition of a bifunctional monomer AA with an excess of a bifunctional monomer BB. AA represents the bisphenol moiety; and in the case of resins made by the "taffy" process, BB in the structural formula $BB(AABB)_k$ represents either the glycidyl group when present as a terminal group in the chain or a glyceryl group ($—CH_2CHOHCH_2—$) when present in the chain. The weight fraction of the kth oligomer in such a resin, w'_k, is given by eq. (1):

$$w'_k = \frac{w_k}{\sum\limits_{1}^{\infty} w_k} \tag{1}$$

where

$$w_k = \frac{(1 + 2k)r^k(1 - r)^2}{(1 + r)} \tag{2}$$

$k = 1,2,3,\ldots,$ r = initial ratio of all A groups to B groups.

In our previous publication,[1] we made the statement that when $k = 0$, BB represents the epichlorohydrin molecule and that the weight fraction of unreacted epichlorohydrin may be calculated from eq. (2).   In actual fact, the monomer BB ($k = 0$) has for our purposes, namely the calculation of the molecular weight distribution of the finished resin, only a conceptual significance. In order to conform to the formal mechanistic picture of the polyaddition
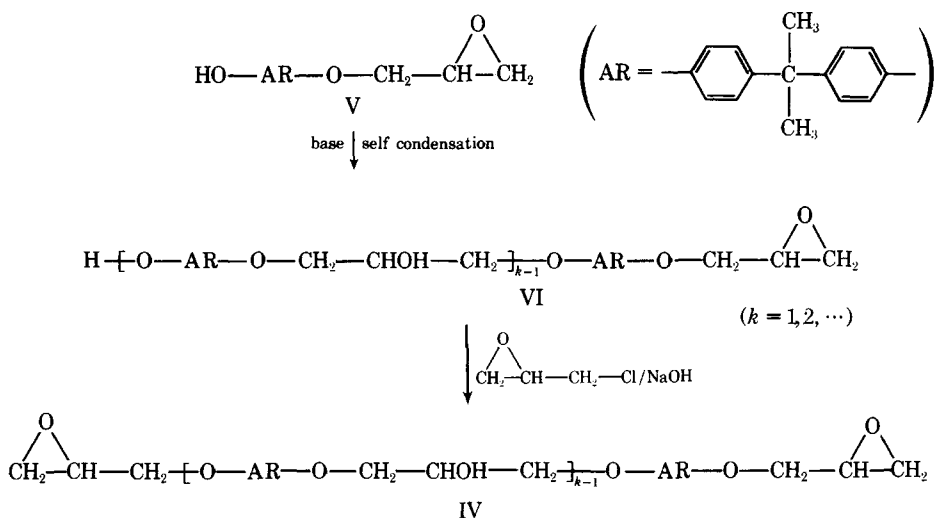
$$(k + 1)BB + kAA \rightarrow BB(AABB)_k$$

"taffy" type epoxide resins may be considered to be made by the condensation of 1,2-dichlorohydrin with bisphenol A (scheme 1), a process not normally carried out in practice:
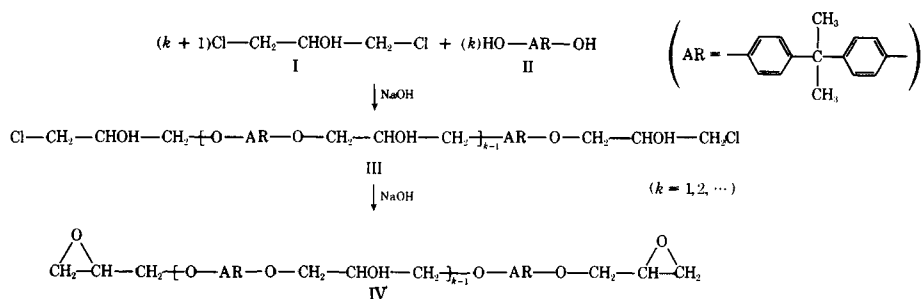
Scheme 1

Another conceivable way of synthesizing a 'taffy' type epoxide resin is illustrated in scheme 2:


Scheme 2

The monoglycidyl ether of bisphenol A (V) is self-polymerized to any desired degree of polymerization to yield a polymer (VI) terminated at one end by a glycidyl group and at the other, by a phenolic hydroxyl group. On further reaction of VI with epichlorohydrin in the presence of alkali, a "taffy" type epoxide resin is obtained having the same structural formula IV (scheme 1) as the conventional epoxide resin made by reacting epichlorohydrin with bisphenol A. Although the preparation of high molecular weight resins by the self-polymerization of the monoglycidyl ether of bisphenol A has been claimed in a patent,[8] no details of the synthesis of the monomer were revealed.

The interesting question now arises as to whether the resin IV made according to scheme 2 has the same molecular weight distribution as that made by the conventional process (scheme 1).

THEORETICAL CALCULATION OF THE MOLECULAR WEIGHT DISTRIBUTION OF EPOXIDE RESINS MADE ACCORDING TO SCHEME 2

The reactions represented in scheme 2 may be formulated as

$$k(A—B) \longrightarrow A—B+A—B\underset{k-2}{)}A—B$$
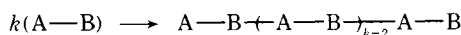
where A represents the phenolic hydroxyl group and B, the glycidyl functional group. The weight fraction, m'_k of the oligomer k after a given degree of polyaddition is, according to Flory,[2]

$$m'_k = kp^{k-1}(1 - p)^2 \tag{3}$$

where p = extent of reaction. The molecular weight of the kth oligomer M'_k is

$$M'_k = 284k \tag{4}$$

and the mole per kilogram of the kth oligomer n'_k is

$$n'_k = 1000m'_k/M'_k \tag{5}$$

If we define

$$\beta = p^{k-1}(1 - p)^2 \tag{6}$$

we obtain

$$n'_k = 1000\beta/284 \tag{7}$$

On converting polymer VI into the diepoxide IV (scheme 2), the mole fraction is not altered, but because the molecular weight of the diepoxide oligomers IV is given by

$$M_k = 340 + 284(k - 1) \tag{8}$$

the weight fraction m_k of the diepoxide oligomer is now

$$m_k = \frac{n'_k M_k}{\sum n'_k M_k} = \frac{\beta M_k}{\sum \beta M_k} \tag{9}$$

The weight-average molecular weight $\overline{M}_w$ is

$$\overline{M}_w = \frac{\sum m_k M_k}{\sum m_k} = \frac{\sum \beta M_k{}^2}{\sum \beta M_k} \tag{10}$$

and the number-average molecular weight $\overline{M}_n$ is

$$\overline{M}_n = \frac{\sum m_k}{\sum m_k/M_k} = \frac{\sum \beta M_k}{\sum \beta} \tag{11}$$

Since there are two epoxide endgroups per molecule, the epoxide equivalent E is given by

$$E = 2000/\overline{M}_n \tag{12}$$

Noting the fact that

$$\sum \beta = \sum p^{k-1}(1-p)^2 = (1-p) \tag{13}$$

$$\sum k\beta = \sum kp^{k-1}(1-p)^2 = 1 \tag{14}$$

and

$$\sum k^2\beta = \sum k^2 p^{k-1}(1-p)^2 = (1+p)/(1-p) \tag{15}$$

Equations (9), (10), (11), and (12) reduce to

$$m_k = \frac{M_k\beta}{56(1-p) + 284} \tag{16}$$

$$\overline{M}_w = \frac{[56(1-p) + 284]^2 + 284^2 p}{(1-p)[56(1-p) + 284]} \tag{17}$$

$$\overline{M}_n = \frac{56(1-p) + 284}{(1-p)} \tag{18}$$

$$E = \frac{2000(1-p)}{56(1-p) + 284} \tag{19}$$

Through the application of eqs. (16)–(19), it is thus possible to calculate, for a resin of a given epoxide content prepared according to scheme 2, the weight distribution and the moments of the molecular weight distribution.

COMPARISON OF THE THEORETICALLY COMPUTED DISTRIBUTION FOR EPOXIDE RESINS MADE BY THE DIFFERENT PROCESSES

In Table I, a comparison is made of the moments of the molecular weight distribution $(\overline{M}_n, \overline{M}_w)$ and the standard deviation of the distribution* s_n for epoxide resins based on bisphenol A made by the following processes: (a) bisphenol A and epichlorohydrin—process A; (b) self-polymerization of monoglycidyl bisphenol A followed by postglycidylation—process B; (c) polyaddition of the diglycidyl ether of bisphenol A and bisphenol A, the "advancement" reaction—process C.

The actual weight distribution function for resins having epoxide values of 2.0, 1.0, and 0.5 eq/kg and made by processes A, B, and C are illustrated in Figures 1, 2, and 3, respectively. Although the actual distribution functions are really step functions, for the sake of convenience the distributions are plotted in Figures 1, 2, and 3 as continuous functions. These theoretically computed results in-

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* The standard deviation of the number-average distribution is defined by the equation $s_n = (\overline{M}_w/\overline{M}_n - 1)^{1/2}\overline{M}_n$.

TABLE I
Theoretically Computed Moments of Molecular Weight Distribution[a]

Epoxide value, eq/kg	Process	$\overline{M}_n$	$\overline{M}_w$	s_n
	A	1000	1759	871
2.0	B	1000	1623	623
	C	1000	1760	872
	A	2000	3761	1877
1.0	B	2000	3613	1796
	C	2000	3738	1864
	A	4000	7817	3907
0.5	B	4000	7609	3799
	C	4000	7686	3840

[a] The values of $\overline{M}_n, \overline{M}_w$, and s_n for the processes A and C were taken from our previous publication.[1]

dicate that although no practically significant differences exist in the moments of the molecular weight distribution of epoxide resins made by the "taffy" process A and the "advancement" process, there is a small but significant difference between the "taffy" process B and the other two. This difference is greater for the lower molecular weight resins than for the higher molecular weight resins. For lower molecular weight resins, the products obtained through the "taffy" process B exhibit a narrower molecular weight distribution than those synthesized by processes A or C.
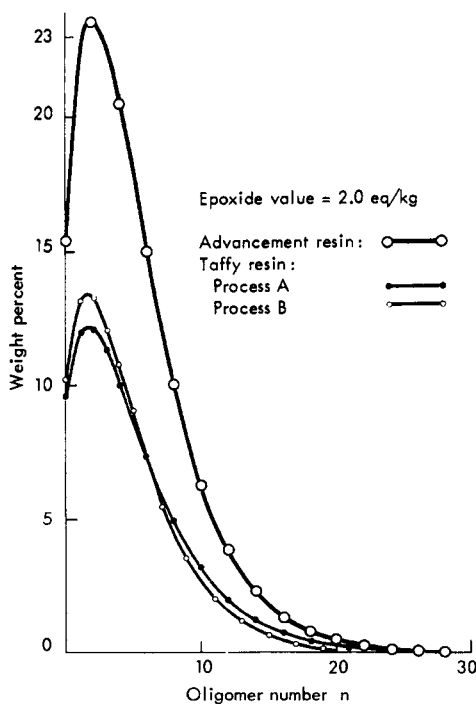

Fig. 1. Theoretical weight distribution functions computed for bisphenol A epoxide resins (epoxide value 2.00 eq/kg) made by advancement process C and the two "taffy" processes A and B.
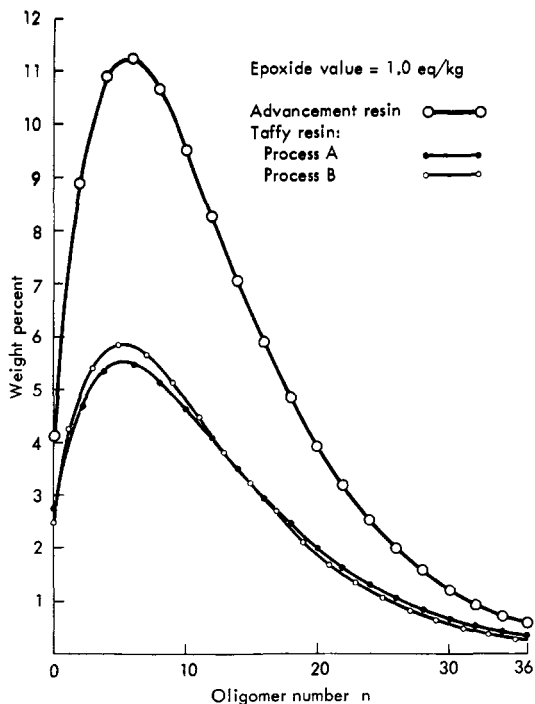
Fig. 2. Theoretical weight distribution functions computed for bisphenol A epoxide resins (epoxide value = 1.00 eq/kg) made by "advancement" process C and by the two "taffy" processes A and B.

COMPARISON OF EXPERIMENTALLY MEASURED DISTRIBUTIONS WITH THE THEORETICALLY COMPUTED DISTRIBUTIONS FOR A LOW MOLECULAR WEIGHT "TAFFY" RESIN

In Table II, a comparison is made between the moments of the molecular weight distribution $(\overline{M}_n, \overline{M}_w)$ computed theoretically from their epoxide values for "taffy" type solid epoxide resins made by processes A and B, respectively,
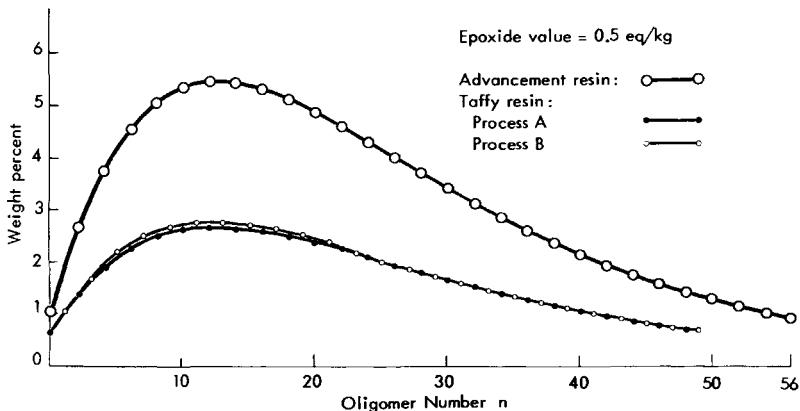

Fig. 3. Theoretical weight distribution functions computed for bisphenol A epoxide resins (epoxide value = 0.50 eq/kg) made by "advancement" process C and by the two "taffy" processes A and B.

TABLE II
Comparison of Experimentally Determined Moments of Molecular Weight
Distribution for Solid Epoxide Resins Made by the "Taffy" Process with
Theoretically Computed Values[a]

| Epoxide value, eq/kg | $\bar{M}_n$ | | | $\bar{M}_w$ | | |
| | Theory | Experiment | | Theory | | Experiment |
	Process A and Process B	GPC	VPO	Process A	Process B	GPC[b]
2.14	934	939	908	1632	1493	1512
1.08	1852	1740	1592	3461	3318	3149
0.52	3846	3011	3730	7500	7301	6834

[a] The experimentally measured values for $\bar{M}_n$ and $\bar{M}_w$ are taken from our previous publication.[1] GPC = Gel permeation chromatography; VPO = vapor pressure osmometry.

and the experimentally measured values.[1]   The lower weight-average molecular weights predicted for process B-type resins are in better agreement with the measured values than those predicted for resins prepared by process A. Although process B represents only a theoretical model, the depression in the $\bar{M}_w$ values suggests that epichlorohydrin acts not only as a bifunctional monomer, but also assumes to some extent the role of a monofunctional terminator.

As indicated in the preceding theoretical section, the differences between the two processes should be more apparent for the lower molecular weight epoxide resins made from high ratios of epichlorohydrin to bisphenol A.

A quantitative analysis by means of high-resolution gel permeation chromatography (GPC) of the weight fraction of the lower oligomers present in a low molecular weight solid epoxide resin (epoxide value = 2.63 eq/kg) made by the "taffy" process A was presented in our previous publication.[1]   These results are now compared in Table III with the theoretically computed values for resins having the same or slightly higher epoxide values and made by the "taffy" processes A and B, respectively.   It is evident that although the epoxide resin was

TABLE III
Comparison of Weight Fraction of Oligomers Present in a "Taffy" Resin
(Epoxide Value = 2.63 eq/kg) with Theoretically Computed Values for "Taffy" Resins
for Processes A and B, Respectively

Molecular weight	Weight %				
	Experiment (GPC)	Theory			
		Process A		Process B	
	$E = 2.63$[a]	$E = 2.63$	$E = 3.0$	$E = 2.63$	$E = 2.75$
340	21.4	15.9	19.7	18.0	19.8
624	20.2	17.2	19.8	19.7	20.9
908	15.2	15.5	16.7	17.2	17.6
1192	11.4	12.9	13.0	13.4	13.3
⩾1476	31.7	38.5	30.8	31.7	28.4

[a] E = Epoxide value (eq/kg).

TABLE IV
Comparison of Oligomer Content of Liquid Resin Made from Epichlorohydrin and
Bisphenol A (Molar Ratio 6.64:1) Determined by GPC with
Theoretically Computed Values

	Oligomer concentration, mole/kg			
	Experiment	Theory		
Molecular weight	(GPC)	Process A mole ratio[a] = 6.64	Process A mole ratio = 9:1	Process B p = 0.1
340	2.43	2.23	2.41	2.42
624	0.23	0.31	0.24	0.24
908	0.02	0.04	0.026	0.024
1192	—	0.006	0.003	0.002
Epoxide value, eq/kg calculated	5.37	5.18	5.42	5.38
Epoxide value, eq/kg measured	5.28			

[a] The mole ratio refers to mole ratio of epichlorohydrin to bisphenol A and is equal to $1/r$.

made by the "taffy" process A, the experimentally measured distribution matches more closely the molecular weight distribution of the resin made by the "taffy" process A or B for resins calculated to have epoxide values higher than the measured epoxide value.* An epoxide value of 2.63 eq/kg would imply for process A-type resins an initial theoretical epichlorohydrin/bisphenol A ratio of 1.55. The results presented in Table III suggest that the actual molecular weight distribution corresponds to a resin synthesized using an initial epichlorohydrin/bisphenol A ratio of 1.66. The latter value is in close agreement with the experimental value of 1.73 for this ratio obtained by extrapolation of published values.[3]

An even sharper test between the experimental and theoretical molecular weight distributions is provided by the GPC analysis of a liquid epoxide resin made using an epichlorohydrin/bisphenol A ratio of 6.64:1. In such a case, all the oligomeric species can be quantitatively separated by GPC on Biorad SX2.[6] The results are presented in Table IV. The concentrations of the identifiable satellite peaks which accompany the parent oligomer diepoxide peak (mainly monoepoxy monochlorohydrins or dichlorohydrins of the diepoxide oligomer) have been added to the concentration of the parent oligomer diepoxide in order to compare the experimentally measured distribution with the theoretically predicted distributions.

It is apparent from Table IV that the experimental value for the monomer content of the liquid resin is larger than that calculated for a "taffy" resin made by process A with an epichlorohydrin/bisphenol A ratio of 6.64:1. In fact, the molecular weight distribution more nearly resembles that made by the "taffy"

* The gel used for the chromatographic separation of the oligomers (Biorad SX2) had a molecular weight cut-off around 2000. It was, therefore, not possible to separate quantitatively oligomers having molecular weight greater than 1476 ($k = 4$).
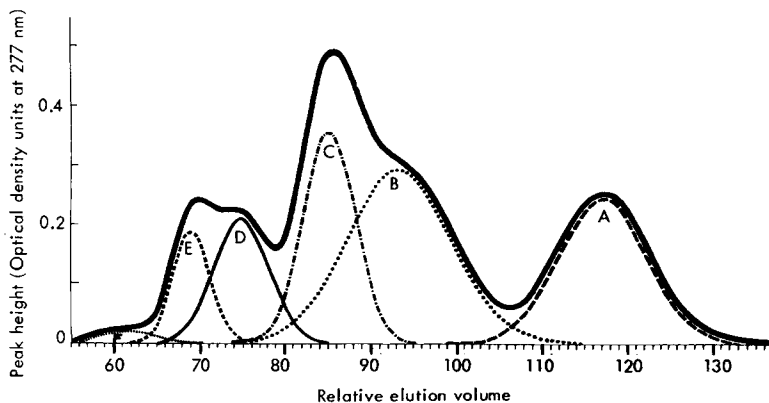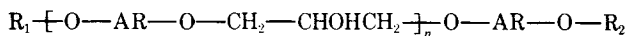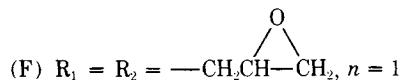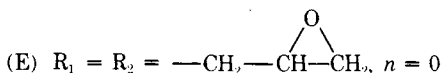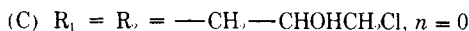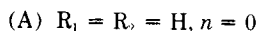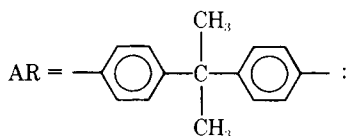
Fig. 4. Typical chromatographic curve of a sample taken from a kinetic run of the reaction of bisphenol A (0.2 m/l.) with epichlorohydrin (1.28 m/l.) and NaOH (0.4 m/l.) in methanol at 25°C. Gel = Sephadex LH 20; solvent = $CHCl_3/C_2H_5OH$, 2:1 (v/v). The various peaks shown in the curve are of reaction products having the general structural formula

$$R_1 \text{---} [O\text{---}AR\text{---}O\text{---}CH_2\text{---}CHOHCH_2]_n \text{---} O\text{---}AR\text{---}O\text{---}R_2$$

where

$$AR = \text{---} \bigcirc \text{---} \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} \text{---} \bigcirc \text{---} \; :$$

(A) $R_1 = R_2 = H$, $n = 0$

(B) $R_1 = H$, $R_2 = \text{---}CH_2\text{---}CHOHCH_2Cl$ or $CH_2\text{---}\overset{O}{\overset{\diagup\diagdown}{CH}}\text{---}CH_2$, $n = 0$

(C) $R_1 = R_2 = \text{---}CH_2\text{---}CHOHCH_2Cl$, $n = 0$

(D) $R_1 = \text{---}CH_2CHOHCH_2Cl$, $R_2 = CH_2\text{---}\overset{O}{\overset{\diagup\diagdown}{CH}}\text{---}CH_2$, $n = 0$

(E) $R_1 = R_2 = \text{---}CH_2\text{---}\overset{O}{\overset{\diagup\diagdown}{CH}}\text{---}CH_2$, $n = 0$

(F) $R_1 = R_2 = \text{---}CH_2\overset{O}{\overset{\diagup\diagdown}{CH}}\text{---}CH_2$, $n = 1$

The full-line curve is the actual GPC profile. The dotted and dashed line curves are the corrected computer-separated individual peaks.

process A with an epichlorohydrin/bisphenol A ratio of 9:1, or one made according to process B stopped at a conversion of 10%.

KINETICS OF THE REACTION

In order to understand the reason for this discrepancy between the predicted and experimentally measured values for the molecular weight distribution of low molecular weight epoxide resins made by the "taffy" process A, it is necessary to delve into the kinetics of the reaction. Some preliminary work we have un-
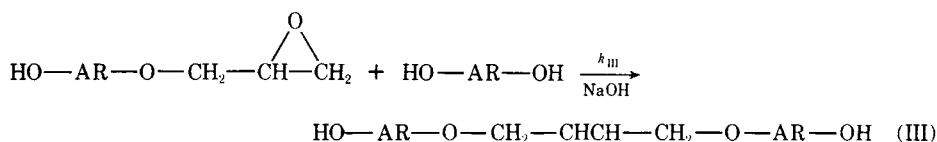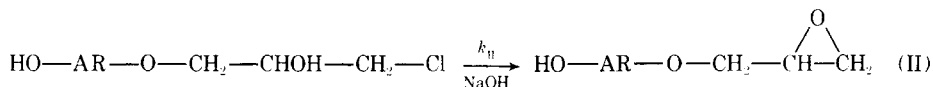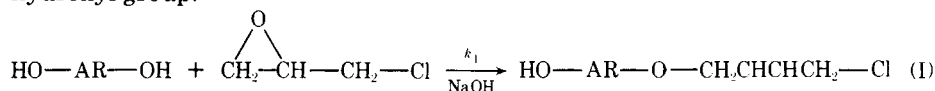
dertaken on the kinetics serves to illustrate the complexity of the reactions involved in the synthesis of such resins.

Samples obtained from the reaction of bisphenol A (0.2 m/l.) with epichlorohydrin (1.28 m/l.) and NaOH (0.4 m/l.) in methanol at 25°C were analyzed by gel permeation chromatography. Immediately after sampling, the samples were neutralized with acetic acid. The chromatography was carried out using the organophilic gel Sephadex LH 20, eluted with solvent mixture chloroform/ethanol 2:1 (vol/vol). A Beckman UV spectrophotometer fitted with a 1-mm flow-through cell was used as detector, and the peaks were monitored at 277 nm. A typical chromatographic curve taken from a kinetic run 140 min from the start of the reaction is illustrated in Figure 4. All the intermediate products other than the monoepoxy and monochlorohydrin of bisphenol A could be separated by means of this technique. In the particular column used for this study, the latter two products eluted as one peak. The peaks were identified by the use of model compounds and by their elution behavior.[6] Figure 5 depicts the kinetics of the reaction. In this figure, the uncorrected experimentally determined peak heights are plotted. In order to obtain the true concentrations, these peak heights (or better, the areas of the component peaks obtained by curve resolution by means of a computer[5]) should be multiplied by a calibration factor.
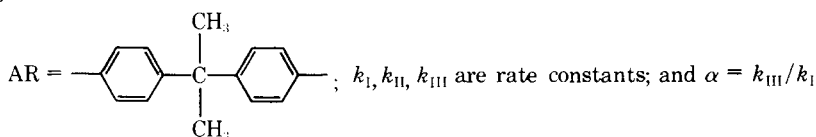
Although the information presented in Figure 5 is only of a semiquantitative nature, it nevertheless yields valuable information on the rate of formation of the various intermediates. The monochlorohydrin and monoglycidyl ether of bisphenol A (B, Fig. 5) are formed rapidly at first and soon reach a pseudostationary state where the rate of consumption of the monoadduct is equal to the rate of production. The same can be said of the dichlorohydrin of bisphenol A (C, Fig. 5). Dehydrochlorination to give glycidyl derivatives (in Fig. 5, D = monoglycidyl monochlorohydrin of bisphenol A, and E = diglycidyl ether of bisphenol A) begins almost with the formation of the chlorohydrins; but even after 6 hr of reaction at 25°C, a considerable amount of chlorohydrin groups is present. Even with the 6.4:1 excess of epichlorohydrin over bisphenol A and the low temperature of the reaction, it is seen that oligomer formation (F and G, Fig. 5) begins relatively early, approximately when the di- and the monochlorohydrin of bisphenol A have reached their stationary-state levels.

DISCUSSION

Fisch,[3] using the simple mechanistic model outlined in scheme 3 for the "taffy" process A, was able to make a numerical estimate of the ratio of the rate constants α for the addition of an aromatic glycidyl ether and epichlorohydrin to a phenolic hydroxyl group:

$$HO-AR-OH + CH_2-CH-CH_2-Cl \xrightarrow[NaOH]{k_I} HO-AR-O-CH_2CHCHCH_2-Cl \quad (I)$$

$$HO-AR-O-CH_2-CHOH-CH_2-Cl \xrightarrow[NaOH]{k_{II}} HO-AR-O-CH_2-CH-CH_2 \quad (II)$$

$$HO-AR-O-CH_2-CH-CH_2 + HO-AR-OH \xrightarrow[NaOH]{k_{III}}$$

$$HO-AR-O-CH_2-CHCH-CH_2-O-AR-OH \quad (III)$$

where

$$AR = \text{—}\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\text{—} \quad ; \quad k_I, k_{II}, k_{III} \text{ are rate constants; and } \alpha = k_{III}/k_I$$
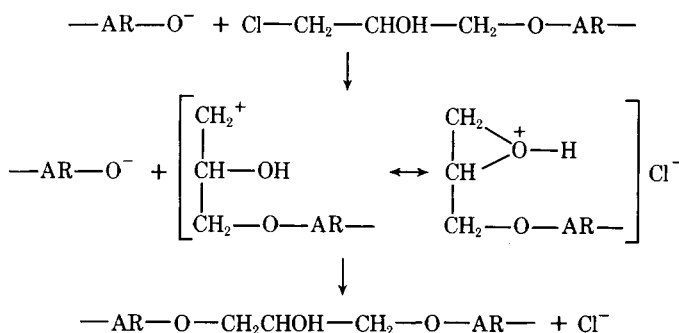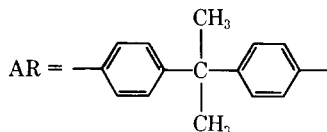
<div align="center">Scheme 3</div>

Assuming that the dehydrochlorination reaction (II) is very much faster than either reactions (I) or (III), i.e., $k_{II} \gg k_I$, Fisch[3] estimated a value of $\alpha = k_{III}/k_I$ = 0.6. That epichlorohydrin is more reactive to the phenoxide ion than an aromatic glycidyl ether is confirmed by studies made in our laboratories of the reactivities of several epoxides with a number of nucleophiles.[4] These studies reveal that in 57% aqueous methanol at 40°C, the reactivities relative to epichlorohydrin of glycidol, phenyl glycidyl ether, and epichlorohydrin are in the ratio of 0.24:0.48:1.

This higher reactivity shown by epichlorohydrin to a phenolic hydroxyl group would imply, all other factors being considered equal, that the experimentally measured molecular weight distributions would be weighted more to the low molecular side than the theoretically predicted distributions. The results described in this paper show that this is indeed the case for low molecular weight liquid epoxide resins made with a high mole ratio (6.64) of epichlorohydrin to bisphenol A. In the case of solid epoxide resins made using an epichlorohydrin-to-bisphenol mole ratio of less than 2, there is reasonably good, overall agreement between the experimentally measured molecular weight distributions and the values predicted for resins made according to process B (scheme 2).

Although the formation of monoglycidyl ether of bisphenol A and its corresponding chlorohydrin in reacting mixtures of epichlorohydrin and bisphenol A has been demonstrated (Figs. 4 and 5), it is unlikely that the reactions represented in scheme 2 are alone responsible for the formation of solid resins. A more realistic picture of the mechanism leading to the formation of solid resins would involve the reactions represented in schemes 2 and 3. A reaction, not discussed in either of the above schemes, but which might contribute to the chain lengthening process, is one that involves the direct alkylation of the chlorohydrin by the phenoxide anion:

$$\text{—AR—O}^- + \text{Cl—CH}_2\text{—CHOH—CH}_2\text{—O—AR—}$$

$$\downarrow$$

$$\text{—AR—O}^- + \left[\underset{\text{CH}_2\text{—O—AR—}}{\overset{\text{CH}_2^+}{\underset{|}{\overset{|}{\text{CH—OH}}}}} \quad \longleftrightarrow \quad \underset{\text{CH}_2\text{—O—AR—}}{\overset{\text{CH}_2}{\underset{|}{\overset{|}{\text{CH}}}}}\overset{+}{\text{O}}\text{—H} \right] \text{Cl}^-$$

$$\downarrow$$

$$\text{—AR—O—CH}_2\text{CHOH—CH}_2\text{—O—AR—} + \text{Cl}^-$$

where

$$AR = \text{—}\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\text{—}$$

The rate of this reaction is probably enhanced by the participation of the neighboring β-hydroxyl group in the formation and stabilization of the transition state. The competition for the phenoxide anion by the chlorohydrin and the aromatic glycidyl group would increase the chances of oligomer formation and partially compensate for the higher reactivity of epichlorohydrin.
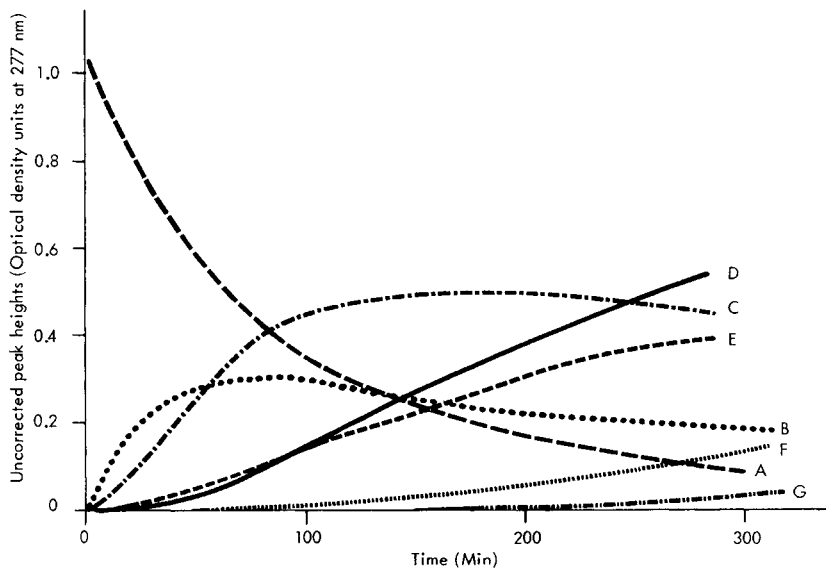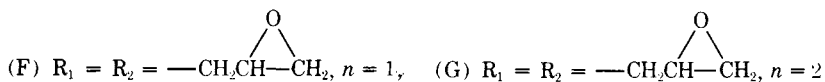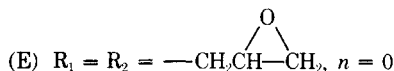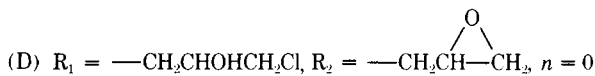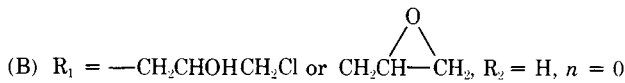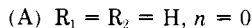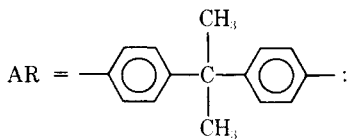

Fig. 5. Kinetic plot of reaction between bisphenol A (0.2 m/l.) with epichlorohydrin (1.28 m/l.) and NaOH (0.4 m/l.) in methanol at 25°C. The ordinate represents the uncorrected peak heights taken directly from the chromatographic curve. Reaction products have the general structural formula

$$R_1 - [O - AR - O - CH_2 - CHOH - CH_2]_n - O - AR - O - R_2 \, ,$$

where

$$AR = -\langle \bigcirc \rangle - \underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}} - \langle \bigcirc \rangle - :$$

(A) $R_1 = R_2 = H$, $n = 0$

(B) $R_1 = -CH_2CHOHCH_2Cl$ or CH_2CH-CH_2, $R_2 = H$, $n = 0$

(C) $R_1 = R_2 = -CH_2CHOHCH_2Cl$, $n = 0$

(D) $R_1 = -CH_2CHOHCH_2Cl$, $R_2 = -CH_2CH-CH_2$, $n = 0$

(E) $R_1 = R_2 = -CH_2CH-CH_2$, $n = 0$

(F) $R_1 = R_2 = -CH_2CH-CH_2$, $n = 1$,   (G) $R_1 = R_2 = -CH_2CH-CH_2$, $n = 2$

Another factor that cannot be ignored is that under the heterogeneous conditions that is used for the preparation of "taffy" type solid resins, the active reaction site is the water/organic medium interface. One would expect that the more soluble chlorohydrin functional groups to be present in higher concentrations at this interface than either epichlorohydrin or the aromatic glycidyl functional group. The rates of reactions such as the dehydrochlorination reaction by the hydroxyl ion or the direct alkylation of the chlorohydrin leading to oligomer formation by the phenoxide anion would be enhanced at the interface.

Although quantitative data are lacking on the kinetics of the various reactions involved at reflux temperatures, a fairly clear picture of the chemistry of this very complex reaction emerges from the data presented in this paper. This is summarized in scheme 4:

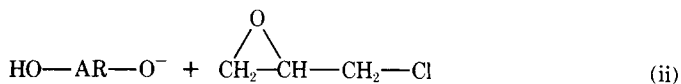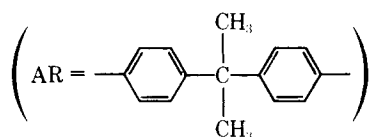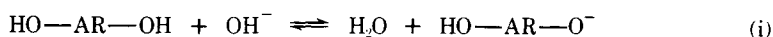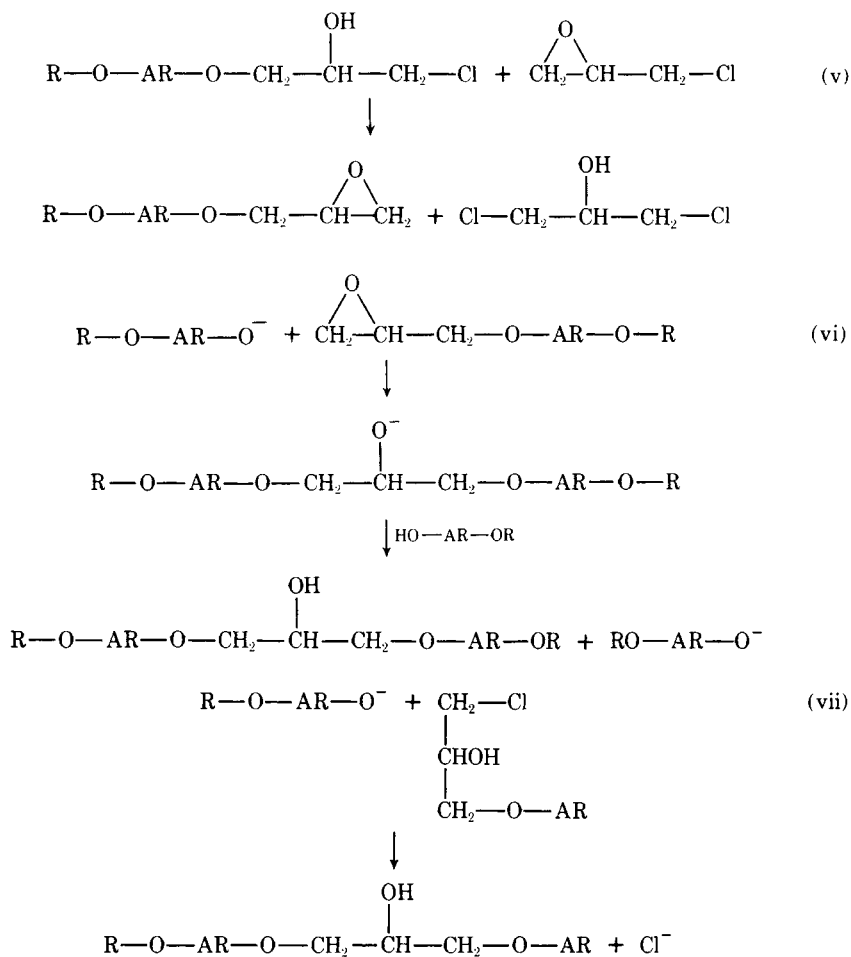$$HO\text{---}AR\text{---}OH + OH^- \rightleftharpoons H_2O + HO\text{---}AR\text{---}O^- \qquad (i)$$

$$HO\text{---}AR\text{---}O^- + CH_2\text{--}CH\text{---}CH_2\text{---}Cl \qquad (ii)$$

$$HO\text{---}AR\text{---}O\text{---}CH_2\text{---}CH\text{---}CH_2\text{---}Cl \qquad (iii)$$

HO---AR---OH

$$HO\text{---}AR\text{---}O\text{---}CH_2\text{---}CH\text{---}CH_2\text{---}Cl + HO\text{---}AR\text{---}O^-$$

$$OH^- + R\text{---}O\text{---}AR\text{---}O\text{---}CH_2\text{---}CH\text{---}CH_2\text{---}Cl \qquad (iv)$$

$$R\text{---}O\text{---}AR\text{---}O\text{---}CH_2\text{---}CH\text{---}CH_2\text{---}Cl + H_2O$$

$$R\text{---}O\text{---}AR\text{---}O\text{---}CH_2\text{---}CH\text{---}CH_2 + Cl^-$$

$$R = H, \quad CH_2\text{---}CH\text{---}CH_2\text{---}Cl, \quad CH_2\text{---}CH\text{--}CH_2$$

$$R—O—AR—O—CH_2—\overset{\overset{\displaystyle OH}{|}}{CH}—CH_2—Cl \;+\; \overset{\overset{\displaystyle O}{\diagup\diagdown}}{CH_2—CH}—CH_2—Cl \qquad (v)$$

$$\downarrow$$

$$R—O—AR—O—CH_2—\overset{\overset{\displaystyle O}{\diagup\diagdown}}{CH—CH_2} \;+\; Cl—CH_2—\overset{\overset{\displaystyle OH}{|}}{CH}—CH_2—Cl$$

$$R—O—AR—O^- \;+\; \overset{\overset{\displaystyle O}{\diagup\diagdown}}{CH_2—CH}—CH_2—O—AR—O—R \qquad (vi)$$

$$\downarrow$$

$$R—O—AR—O—CH_2—\overset{\overset{\displaystyle O^-}{|}}{CH}—CH_2—O—AR—O—R$$

$$\downarrow {\scriptstyle HO—AR—OR}$$

$$R—O—AR—O—CH_2—\overset{\overset{\displaystyle OH}{|}}{CH}—CH_2—O—AR—OR \;+\; RO—AR—O^-$$

$$R—O—AR—O^- \;+\; \begin{array}{c} CH_2—Cl \\ | \\ CHOH \\ | \\ CH_2—O—AR \end{array} \qquad (vii)$$

$$\downarrow$$

$$R—O—AR—O—CH_2—\overset{\overset{\displaystyle OH}{|}}{CH}—CH_2—O—AR \;+\; Cl^-$$

Scheme 4

The initial step (i) involves the production of phenoxide anions by the reaction of base with bisphenol A. Since the systems is buffered by bisphenol A, the concentration of free hydroxyl ions is determined by the above equilibrium. The phenoxide anion adds to the epichlorohydrin to produce the chlorohydrin through a slow reaction (ii), followed by a fast proton transfer reaction (iii) which leads to the regeneration of the phenoxide anion.

Dehydrohalogenation of the chlorohydrin by hydroxyl ions (iv) is a fast reaction. Dehydrohalogenation also proceeds by a slower reaction (v) where the epoxide group of epichlorohydrin acts as a weak base. The formation of the dichlorohydrin $ClCH_2CHOHCH_2Cl$ does not necessarily mean a loss of epichlorohydrin since the reaction with alkali can regenerate it quantitatively. It can also participate in oligomer formation by reactions similar to (vii).[7]

Steps (vi) and (vii) of scheme 4 are the reactions involved in the formation of polymers. These reactions will proceed until all the phenolic hydroxyl groups are consumed. Since reaction (i), which leads to the production of phenoxide ions, is an equilibrium reaction, it would be possible, by controlling the rate of

alkali addition, to have some control over the concentration of free phenoxide anions, and so in effect be able to alter the molecular weight distribution. Thus, if initially the system is buffered with excess bisphenol, the concentration of free hydroxyl ions is low and the rate of formation of the glycidyl groups through reaction (iv) is small. Oligomer formation can only take place by reaction (vii) and by reaction of the glycidyl groups formed through reaction (v). If, however, as is usually the case in the preparation of solid resins, bisphenol A and epichlorohydrin are allowed to react in a strongly alkaline environment, the chlorohydrins produced by reactions (ii) and (iii) are converted into glycidyl groups by the fast reaction (iv) and into oligomers by reaction (vii). Since the glycidyl groups are produced when there is an abundance of phenoxide anions, oligomer formation by reaction (vi) can also take place. To what extent the various products are formed will depend also on the reaction conditions and the solvent/water ratio, the latter ratio affecting both the absolute and the relative rates of the various reactions. The hydrolysis and the base-catalyzed polymerization of epichlorohydrin to polyglycerols[3] is a minor side reaction which can also affect the molecular weight distribution of the final epoxide resin. The epichlorohydrin/bisphenol A is reduced to slightly lower values. This change in stoichiometry can, in effect, partially compensate for the higher reactivity of epichlorohydrin.

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