Analysis of the epoxidation of bisphenol A and phenolic Novolacs with epichlorohydrin

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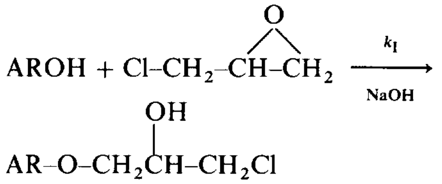
Theoretical equations based on a kinetic scheme were developed to predict the number average molecular weight, $\bar{M}_n$, the weight per epoxy equivalent, *WPE*, and the number average functionality, $\bar{f}$, of resins arising from the epoxidation of bisphenol A or phenol-formaldehyde Novolacs with epichlorohydrin. Good agreement with experimental results was obtained by assuming a reactivity ratio of chain extension over epoxidation close to 0.5. Significant departures were shown, however, for the epoxidation of high molecular weight Novolacs. This was ascribed to the formation of intramolecular rings by reaction of terminal epoxides and phenolic hydroxyls, thus reducing the epoxidation efficiency, i.e. transformation of phenolic hydroxyls into aryl glycidyl ethers. The characterization of a commercial epoxidized Novolac showed that the epoxidation efficiency was 84.3%, most of the remaining fraction being composed of intra- and intermolecular $-CH_2CHOH-CH_2-$ bridges.

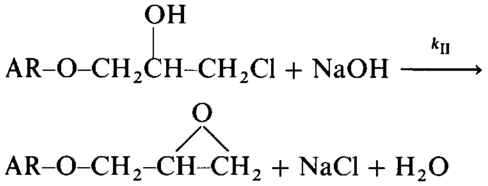
(Keywords: Novolac; epoxidation; kinetic study)

INTRODUCTION

Epoxy resins are usually obtained by addition of epichlorohydrin (ECH) to compounds containing active hydrogen groups, followed by dehydrochlorination. The epoxidation of phenolic hydroxyl groups (AR–OH) takes place through the following reactions:



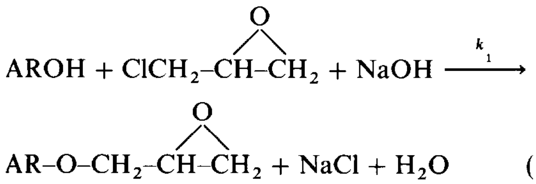
$$\mathrm{AROH} + \mathrm{Cl{-}CH_2{-}\overset{O}{\widehat{CH{-}CH_2}}} \xrightarrow[\mathrm{NaOH}]{k_\mathrm{I}} \mathrm{AR{-}O{-}CH_2\overset{OH}{\overset{|}{C}}H{-}CH_2Cl} \tag{1}$$



$$\mathrm{AR{-}O{-}CH_2\overset{OH}{\overset{|}{C}}H{-}CH_2Cl} + \mathrm{NaOH} \xrightarrow{k_\mathrm{II}} \mathrm{AR{-}O{-}CH_2{-}\overset{O}{\widehat{CH{-}CH_2}}} + \mathrm{NaCl} + \mathrm{H_2O} \tag{2}$$

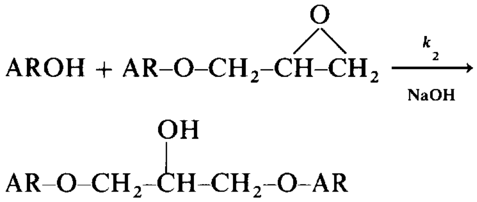
NaOH is used as a catalyst for the nucleophilic ring-opening of the epoxide group on the primary carbon atom of epichlorohydrin and as a dehydrochlorinating agent for conversion of the chlorohydrin to the epoxide group.

As step (2) is very much faster than step (1)[1], the epoxidation may be represented by the overall reaction:



$$\mathrm{AROH} + \mathrm{ClCH_2{-}\overset{O}{\widehat{CH{-}CH_2}}} + \mathrm{NaOH} \xrightarrow{k_1} \mathrm{AR{-}O{-}CH_2{-}\overset{O}{\widehat{CH{-}CH_2}}} + \mathrm{NaCl} + \mathrm{H_2O} \tag{3}$$

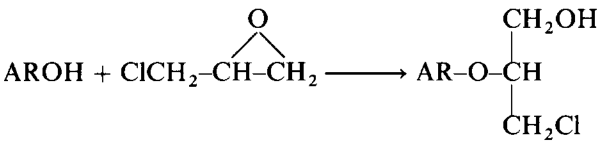
In turn, the generated epoxide may react with a phenolic hydroxyl group:



$$\mathrm{AROH} + \mathrm{AR{-}O{-}CH_2{-}\overset{O}{\widehat{CH{-}CH_2}}} \xrightarrow[\mathrm{NaOH}]{k_2} \mathrm{AR{-}O{-}CH_2{-}\overset{OH}{\overset{|}{C}}H{-}CH_2{-}O{-}AR} \tag{4}$$

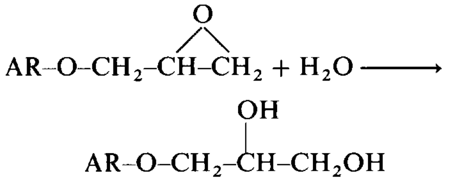
For the case of polyphenols like bisphenol A or phenol-formaldehyde Novolacs (*Figure 1*), reaction (4) constitutes a chain extension step. An excess of ECH is normally used to control the polymerization of the reactants to higher molecular weight species.

Several secondary reactions may also take place, e.g. a small amount of chlorine remaining in the products is ascribed either to incomplete dehydrochlorination or to an abnormal addition of ECH:



$$\mathrm{AROH} + \mathrm{ClCH_2{-}\overset{O}{\widehat{CH{-}CH_2}}} \longrightarrow \mathrm{AR{-}O{-}}\begin{matrix}\mathrm{CH_2OH}\\ |\\ \mathrm{CH}\\ |\\ \mathrm{CH_2Cl}\end{matrix} \tag{5}$$

Besides, the presence of α-glycols results from:



$$\mathrm{AR{-}O{-}CH_2{-}\overset{O}{\widehat{CH{-}CH_2}}} + \mathrm{H_2O} \longrightarrow \mathrm{AR{-}O{-}CH_2{-}\overset{OH}{\overset{|}{C}}H{-}CH_2OH} \tag{6}$$

Secondary reactions are kept to a minimum by an adequate control of pH, water concentration and temperature. Therefore, steps (3) and (4) are the most

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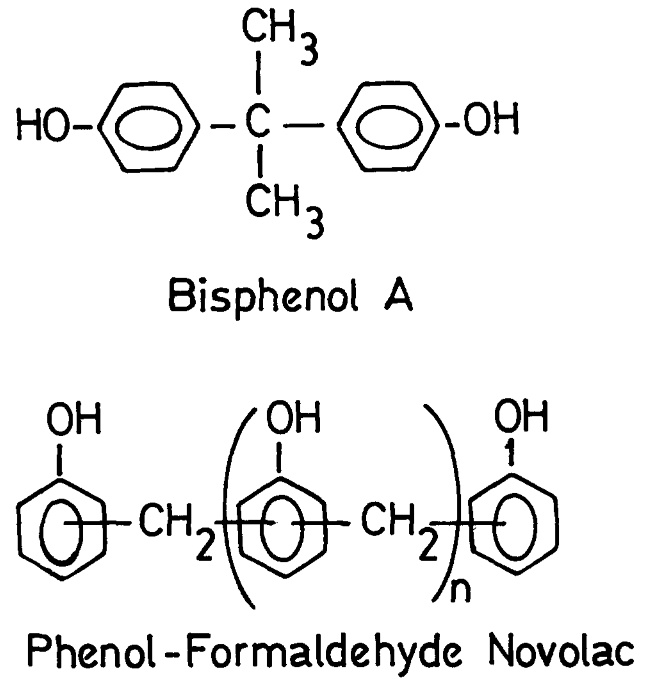

Figure 1 Structures of different polyphenols. The methylene links in the phenol-formaldehyde Novolac issue from the *o*, *o'* and *p* positions of the phenolic ring

important in determining the structure of the epoxidized products.

Batzer and Zahir[2,3] analysed the molecular weight distribution of epoxy resins derived from bisphenol A and epichlorohydrin, by assuming equal reactivity of steps (3) and (4). This led to deviations between the experimental measured distributions and theoretical estimations for high ECH/bisphenol A ratios. Deviations were attributed to the higher reactivity of ECH to the phenoxide compared with the aryl glycidyl ether, i.e. epoxidation takes place more rapidly than chain extension.

Fisch[1] estimated a value of $K = k_2/k_1 = 0.6$. On the other hand, the reactivity ratio of phenyl glycidyl ether and ECH in 57% aqueous methanol, at 40°C, was reported as[3,4]: $K = 0.48$, in rough agreement with Fisch's estimation.

Our aim is to solve the simple kinetic scheme derived from equations (3) and (4), in order to provide a set of equations for the number average molecular weight, $\bar{M}_n$, the number average functionality, $\bar{f}$, and the weight per epoxy equivalent, *WPE* (only two of the three parameters are independent), of epoxy resins derived from the reaction of bisphenol A or phenolic Novolacs with epichlorohydrin. The comparison of theoretical predictions with experimental results will enable us to obtain information related to the epoxidation efficiency and the actual structure of epoxidized phenolic Novolacs.

KINETIC SCHEME

By calling A = phenolic OH, B = epichlorohydrin and E = epoxy group, the following kinetic scheme arises from equations (3) and (4):

$$-\mathrm{d}A/\mathrm{d}t = A(k_1B + k_2E) \qquad (7)$$

$$-\mathrm{d}B/\mathrm{d}t = k_1AB \qquad (8)$$

$$\mathrm{d}E/\mathrm{d}t = A(k_1B - k_2E) \qquad (9)$$

Dividing equations (7) and (9) by equation (8), making $K = k_2/k_1$ and solving for $K \neq 1$, we get:

$$(A/B_0) = (A_0/B_0) - 2 + [(1 - 2K)(B/B_0) + (B/B_0)^K]/(1 - K) \qquad (10)$$

$$(E/B_0) = (B/B_0)[(B_0/B)^{1-K} - 1]/(1 - K) \qquad (11)$$

Equation (10) may be rewritten in terms of the stoichiometric ratio, $r = A_0/B_0$, the overall conversion of phenolic hydroxyls, P_A, and the partial conversion in the first step (equation (3)), $P_{A_1} = P_B/r$, as:

$$rP_A = 2 - [(1 - 2K)(1 - rP_{A_1}) + (1 - rP_{A_1})^K]/(1 - K) \qquad (12)$$

Equation (12) enables one to calculate P_{A_1} and $P_{A_2} = P_A - P_{A_1}$, from selected values of the stoichiometric ratio, r, and the overall conversion, P_A.

EPOXIDATION OF BISPHENOL A WITH EPICHLOROHYDRIN

This reaction leads to the family of diglycidylether of bisphenol A resins (DGEBA).

Number average molecular weight, $\bar{M}_n$

$\bar{M}_n$ may be calculated by dividing the total mass, on a basis free from ECH, by the total number of moles. By calling A_2 the number of moles of bisphenol A ($M_{A2} = 228\ \mathrm{g\ mol^{-1}}$), we get:

$$\bar{M}_n = [A_2M_{A2} + 56P_{A_1}(2A_2)]/[A_2 - P_{A_2}(2A_2)] = (228 + 112P_{A_1})/(1 - 2P_{A_2}) \qquad (13)$$

Equation (13) assumes that every time that the chain extension step occurs, the total number of moles is decreased by one unit, i.e. no intramolecular rings are formed. This is an acceptable assumption due to the chain stiffness of the DGEBA molecule.

From equations (12) and (13), $\bar{M}_n$ of a generic DGEBA resin may be determined as a function of the molar excess of ECH used in the synthesis, $M = 2/r$, and the final overall conversion of phenolic hydroxyls. In order to define the value of K, we may compare $\bar{M}_n$ predictions with experimental results. For example, DGEBA resins obtained with $M = 10$ and $P_A = 1$ have $\bar{M}_n$ values close to 370[5]. This corresponds to $K = 0.48$, in excellent agreement with the experimental K values previously reported. Then, we will take a constant value of $K = 0.5$ as representing the reactivity ratio of chain extension over epoxidation.

Using equation (12) with $K = 0.5$ and $M = 2/r$, equation (13) may be written as:

$$\bar{M}_n = [228 + 112P_A(1 - P_A/2M)]/[1 - P_A^2/M] \qquad (14)$$

Equation (14) predicts the correct limit, $\bar{M}_n = 340\ \mathrm{g\ mol^{-1}}$ corresponding to pure DGEBA when the synthesis is carried out under the following conditions: $M \rightarrow \infty$ and $P_A = 1$. For $M < 2$, small variations in the ECH excess and/or in the final conversion level lead to large variations in the resulting $\bar{M}_n$.

Number average functionality, $\bar{f}$

The number average functionality arises from the ratio of the total number of epoxides to the total number of moles. The former is obtained as the difference between the epoxides generated by equation (3) and those consumed by equation (4). Then:

$$\bar{f} = 2(P_{A_1} - P_{A_2})/(1 - 2P_{A_2}) \qquad (15)$$

Using equation (12) with $K = 0.5$, we get:

$$\bar{f} = 2P_A(1 - P_A/M)/(1 - P_A^2/M) \qquad (16)$$

Equation (16) predicts that $\bar{f} = 2$ for $P_A = 1$. For low M values it is difficult, however, to carry out the reaction to complete conversion. This leads to $\bar{f} < 2$ for DGEBA resins of moderate and high molecular weights.

Weight per epoxy equivalent, WPE

The weight per epoxy equivalent is given by:

$$\begin{aligned} WPE &= \bar{M}_n/\bar{f} \\ &= [114 + 56P_A(1 - P_A/2M)]/P_A(1 - P_A/M) \end{aligned} \qquad (17)$$

EPOXIDATION OF A PHENOL-FORMALDEHYDE NOVOLAC WITH EPICHLOROHYDRIN

The epoxidation of the phenolic Novolac (*Figure 1*) with ECH may also be considered as a competition between epoxidation and chain extension steps. As for the case of bisphenol A, the reactivity ratio will be taken as $K = 0.5$.

Number average molecular weight, $\bar{M}_n$

The starting Novolac (*Figure 1*) is characterized by a number average molecular weight:

$$\bar{M}_{n(\mathrm{Nov})} = 200 + 106n \qquad (18)$$

If we take N moles of the Novolac, with $(2 + n)N$ phenolic hydroxyls, after conversion P_{A_1} in the epoxidation step and P_{A_2} in the chain extension step, we get:

$$\bar{M}_n = [200 + 106n + 56P_{A_1}(2 + n)]/[1 - P_{A_2}(2 + n)] \qquad (19)$$

Equation (19) is written for a basis free of ECH and assuming that no intramolecular cycles are present.

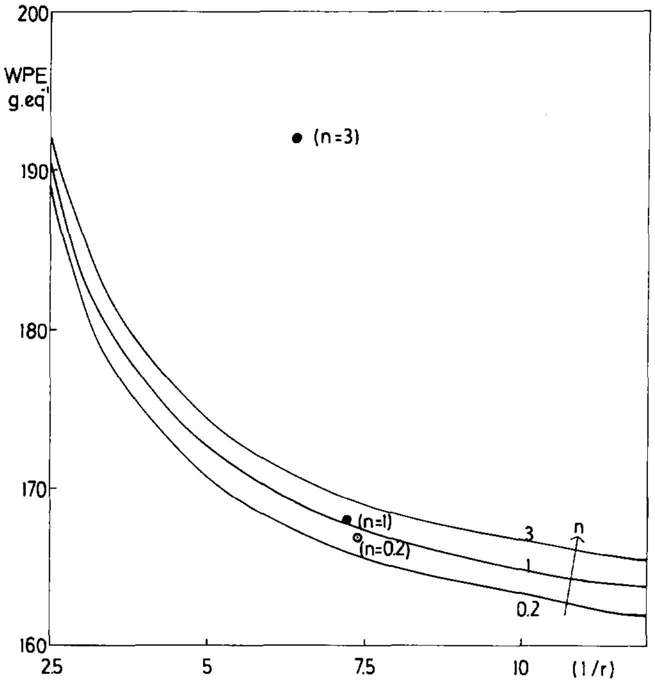

Figure 2 Weight per epoxy equivalent of an epoxidized Novolac, *WPE*, as a function of the ratio of ECH moles over phenolic hydroxyls, $1/r$, for complete conversion ($P_A = 1$) and different starting Novolacs. Points represent experimental values[6]

Number average functionality, $\bar{f}$

With a similar procedure to that used in deriving equation (15), we get:

$$\bar{f} = (2 + n)(P_{A_1} - P_{A_2})/[1 - (2 + n)P_{A_2}] \qquad (20)$$

Using equation (12) with $K = 0.5$, defining the stoichiometric ratio as $r = (2 + n)N/B_0$, and taking the particular case of $P_A = 1$, leads to:

$$\bar{f}(P_A = 1) = (2 + n)(1 - r/2)/[1 - (2 + n)r/4] \qquad (21)$$

When the ECH excess is such that $r \rightarrow 0, \bar{f}(P_A = 1) \rightarrow (2 + n)$, implying that the efficiency in the epoxidation of phenolic hydroxyls is 100%. For a bifunctional starting Novolac, i.e. $n = 0, \bar{f}(P_A = 1) = 2$, independently of the ECH excess.

Weight per epoxy equivalent, WPE

Using equations (19), (20) and (12), with $K = 0.5$, we obtain

$$WPE = \frac{[200 + 106n + (2 + n)56P_A(1 - rP_A/4)]}{[(2 + n)P_A(1 - rP_A/2)]} \qquad (22)$$

Figure 2 represents *WPE* as a function of the ratio of epichlorohydrin moles over phenolic hydroxyls, $1/r$, for a complete conversion ($P_A = 1$), and different starting Novolacs. In order to compare theoretical predictions with experimental results, a patent[6] describing a procedure to obtain epoxidized Novolacs with a very low amount of undesirable side reactions was selected. The experimental points shown in *Figure 2* correspond to three products given as examples in the patent[6]. It is observed that the theoretical prediction gives a remarkably good fitting to low molecular weight Novolacs, i.e. $n \leqslant 1$. However, a large departure is apparent for $n = 3$, implying that the epoxidation is not as efficient as it is claimed, for the case of high molecular weight Novolacs. Curiously, this fact is not discussed in the patent, due to the lack of a theoretical frame to interpret their experimental results.

Commercial epoxidized Novolacs show the same trends as those indicated in *Figure 2*. For example, reported *WPE* values for DEN 431 (Dow) and EPN 1139 (Ciba-Geigy), arising from the epoxidation of a Novolac with $n = 0.2$, are in the range $WPE = 172$–$179\,\mathrm{g\,eq.}^{-1}$, i.e. slightly in excess of the ideal value, possibly due to a small fraction of side reactions. The weight per equivalent increases to $WPE = 185\,\mathrm{g\,eq.}^{-1}$, for an epoxidized Novolac with $n = 3.5$ (XD7 855, Dow).

A key to understand the particular behaviour of high molecular weight Novolacs is given by Drumm and Le Blanc[7]. They discussed the fact that terminal rings of Novolacs with $n \geqslant 4$ can come within proximity regardless of the ratio of o/p links in the structure. Besides, the H bonding between terminal phenolic hydroxyls explains the change in the physical and chemical behaviour of Novolacs when the molecular weight increases to over 400. Thus, when one of the terminal phenolic hydroxyls

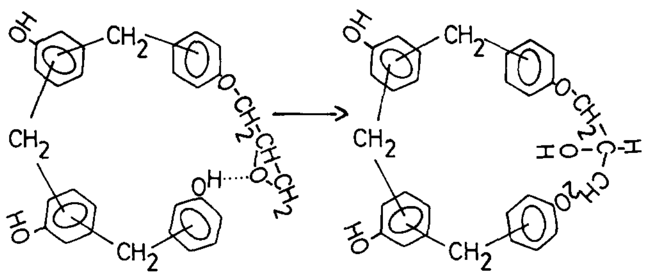

Figure 3 Intramolecular epoxy–AROH reaction in high molecular weight Novolacs

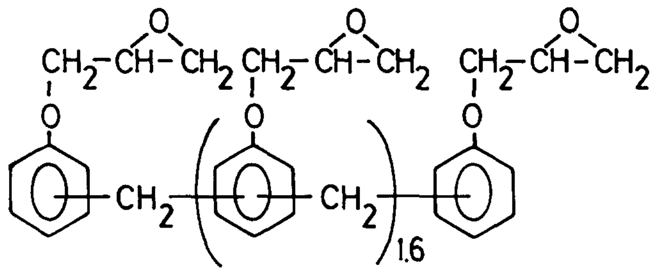

Figure 4 Structure proposed by the supplier of commercial epoxidized Novolacs (EPN 1138, Ciba–Geigy)

is epoxidized, there is a significant probability to approach the epoxy group to the unreacted terminal phenolic hydroxyl, such that an intramolecular epoxy–AROH reaction can take place. This situation, which is illustrated in *Figure 3*, leads to an average K value higher than 0.5 and qualitatively explains the increase in *WPE* observed for high molecular weight Novolacs.

It must be taken into account that a Novolac characterized by an average n value has in fact a broad distribution of molecular weights. The fraction involved in intramolecular bonding increases with n.

STRUCTURE OF EPOXIDIZED NOVOLACS

In order to illustrate this point, the chemical structure of a commercial epoxidized Novolac (EPN 1138, Ciba–Geigy) will be analysed. *Figure 4* shows the structure indicated by the supplier assuming a 100% efficiency in the transformation of phenolic hydroxyls into phenyl glycidyl ethers. However, this would require an infinite ECH excess ($r \rightarrow 0$). Then, the structure shown in *Figure 4* only represents the major species present in the commercial product. This is evident by comparing the actual *WPE* value as reported by the supplier (176–181 g eq.$^{-1}$), with the *WPE* value arising from the proposed structure (158.7 g eq.$^{-1}$). The difference must be mainly ascribed to both intra- and intermolecular glyceryl groups ($-CH_2CHOHCH_2-$), arising from epoxy–AROH reactions.

A batch of EPN 1138 was characterized as follows:

(1) Weight per epoxy equivalent, determined by the standard method with pyridine chloride[8];

(2) Weight per (epoxy + OH) equivalent, determined by simultaneous reaction of epoxides with pyridine perchlorate and acetylation of hydroxyls with acetic anhydride[9];

(3) Residual chlorine, determined by calcination with K_2CO_3 at 550°C, and potentiometric titration with $AgNO_3$;

(4) Number average molecular weight, determined by both cryoscopy in dioxane and size exclusion chromatography (SEC, using a Waters 510 device provided with r.i. detector, set of ultrastyragel columns 100, 100, 500 and 10^4 Å, THF at 1 ml min^{-1}).

The following results were obtained:

(1) epoxides = WPE = 184.2 g eq.$^{-1}$; (2) epoxides + OH groups = WP(Ep + OH) = 172 g eq.$^{-1}$; (3) % Cl = 0.33; (4) $\bar{M}_n$ (cryoscopy) = 605 g mol^{-1}, $\bar{M}_n$ (SEC) = 592 g mol^{-1}.

Figure 5a shows the SEC chromatogram of EPN 1138, while *Figure 5b* represents the calibration curve relating the molar masses with the elution volume. There is no phenylglycidylether (PGE), i.e. epoxidized phenol, in the commercial product, as was proved by injecting pure

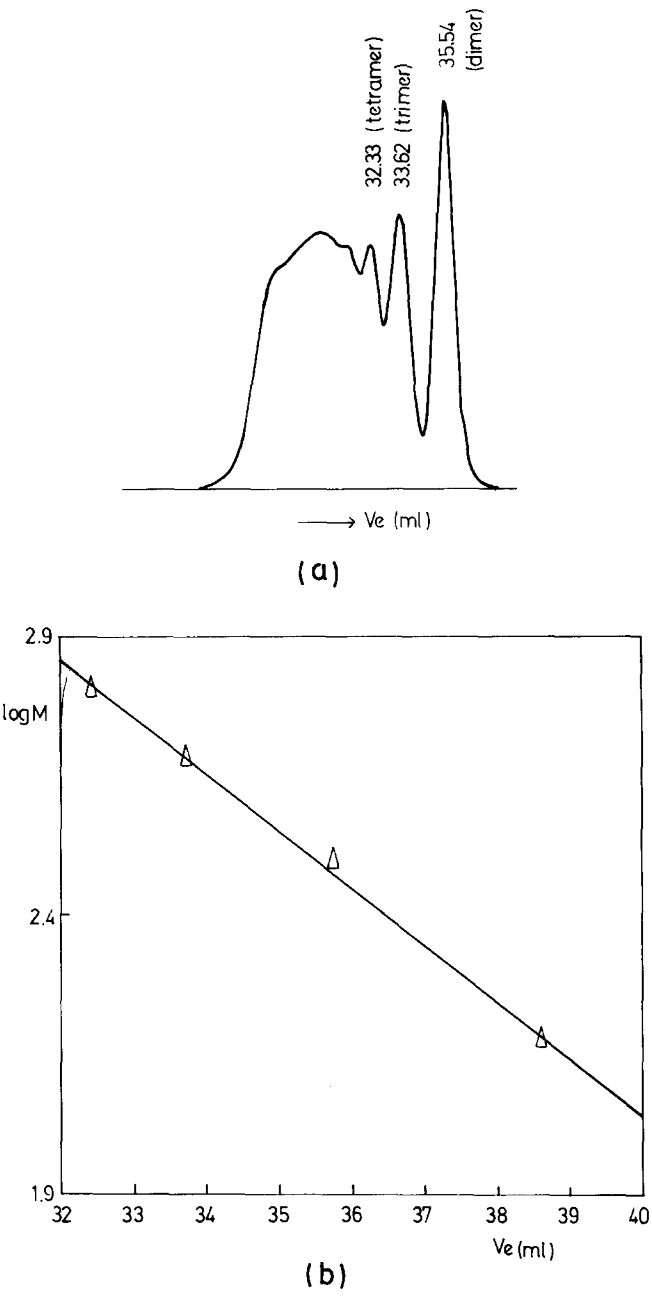

Figure 5 (a) SEC chromatogram of the commercial epoxidized Novolac (see text for experimental conditions); (b) calibration curve obtained by using peaks of dimer, trimer and tetramer (internal calibration), plus the peak of PGE, used as an external-calibration species belonging to the same family

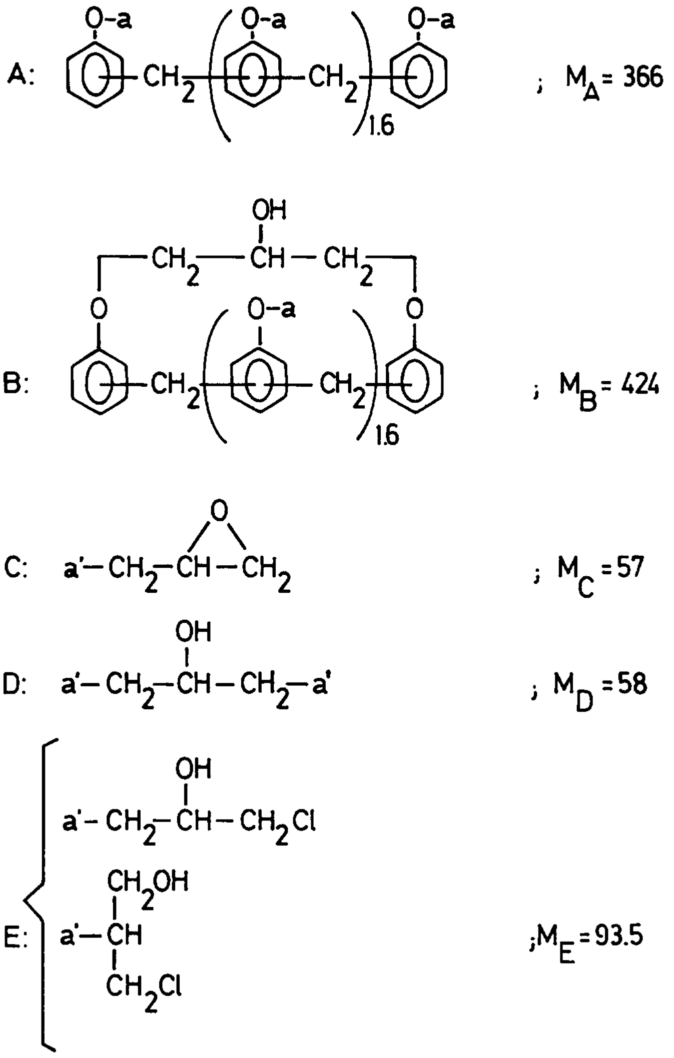

Figure 6 Actual structure suggested for the commercial epoxidized Novolac (EPN 1138, Ciba–Geigy). In order to build up the structure, bonds **a**, present in fragments A and B, must be joined with bonds **a**′, present in fragments C, D and E. The intramolecular epoxy–AROH reaction leads to fragment B while the intermolecular one leads to fragment D. Calculations (see text) show that A = 4.303, B = 1, C = 16.084, D = 0.365, E = 0.275

PGE (the elution volume was located at higher values). Thus, the phenol-formaldehyde Novolac was deprived of phenol before epoxidation. The peaks in *Figure 5a* are ascribed to the epoxidized dimer, trimer, tetramer and higher molecular weight species. This was corroborated by comparing SEC chromatograms of a phenol-formaldehyde Novolac synthesized in our laboratory, before and after epoxidation. The experimental points determining the calibration curve shown in *Figure 5b* are those representing PGE, dimer, trimer and tetramer. $\bar{M}_n$ was obtained by standard procedures after changing the elution volume scale into a molar mass one.

Figure 6 shows the actual structure suggested for the commercial epoxidized Novolac. In order to build up the structure bonds **a**, present in fragments A and B, must be joined with bonds **a**′, present in fragments C, D and E. This representation gives an average structure for the epoxidized Novolac. The value of $n = 1.6$, characterizing the molecular weight of the starting Novolac, is the one stated by the supplier. It may be seen that the intramolecular reaction between epoxy groups and phenolic hydroxyls gives place to fragment B, whereas the corresponding intermolecular reaction leads to fragment D.

The number of moles of every fragment was calculated, by taking $B = 1$ as a basis.

As $\sum \mathbf{a} = \sum \mathbf{a}'$, it can be verified that

$$1.6 + 3.6A = C + 2D + E \tag{23}$$

In order to determine the system, three parameters arising from the experimental characterization can be identified. We take $WPE = 184.2$ g eq.$^{-1}$, $\bar{M}_n = 600$ g mol^{-1}, % Cl = 0.33. Then:

$$\text{Total mass: } M_T = 366A + 424 + 57C + 58D + 93.5E$$

$$\text{Total number of moles: } N_T = A + 1 - D$$

From *WPE*

$$184.2 = M_T/C \tag{24}$$

From $\bar{M}_n$

$$600 = M_T/N_T \tag{25}$$

From %Cl

$$E = 0.0033 M_T/35.5 \tag{26}$$

By solving the system of four equations (23–26) in four unknowns, we obtain

$$A = 4.303, \quad C = 16.084, \quad D = 0.365, \quad E = 0.275$$

The experimental value of the weight per equivalent of epoxy plus OH groups was WP (Ep + OH) = 172 g eq.$^{-1}$. The value arising from the proposed structure is WP (Ep + OH) = $M_T/(1 + C + D + E) = 167.2$ g eq.$^{-1}$, in close agreement.

From the proposed structure, we get:

% epoxidation = 84.3

% intramolecular cycles = 10.5

% chain extension = 3.8

% chlorine-containing residues = 1.4.

Although some variations in the reported values may be admitted owing to experimental errors in the characterization and in the assumed *n* value for the starting Novolac, it is clear that the efficiency of the epoxidation is significantly less than 100%, and that most of the secondary structures are $-CH_2-CHOH-CH_2-$ bridges, involved in both intra- and intermolecular bonds.

CONCLUSIONS

Epoxidation of bisphenol A with epichlorohydrin

The reactivity ratio of chain extension over epoxidation steps must be close to $K = 0.5$ in order to match experimental and predicted values of the number average molecular weight of DGEBA resins. This agrees with the few values reported in the literature, i.e. Fisch[1] estimated a value of $K = 0.6$ and Batzer and Zahir[3] reported a value of $K = 0.48$.

Theoretical equations for predicting the number average molecular weight, $\bar{M}_n$, the number average functionality, $\bar{f}$, and the weight per epoxy equivalent, *WPE*, were developed as a function of the conversion of phenolic hydroxyls, P_A, and the molar ratio of ECH over bisphenol A, *M*. These equations may be used to fix the initial molar excess of ECH to obtain a desired *WPE* at complete conversion of phenolic hydroxyls, or to estimate the number average functionality of the resulting DGEBA resin when complete conversion is not attained.

Epoxidation of a phenol-formaldehyde Novolac with epichlorohydrin

Theoretical equations for predicting $\bar{M}_n$, $\bar{f}$ and *WPE* as a function of conversion, ECH excess and average molecular weight of the starting Novolac (n value), were developed by assuming $K = 0.5$, i.e. the same value as in the case of bisphenol A. An excellent fitting of predicted and experimental *WPE* values was shown for low molecular weight Novolacs ($n \leqslant 1$), epoxidized under controlled conditions to avoid side reactions. For high n values, however, experimental *WPE* values are significantly greater than predicted; i.e. the epoxidation is less efficient even when operating under controlled conditions. Then, the efficiency claimed by certain patents for the epoxidation of high molecular weight Novolacs cannot be taken on absolute terms. This loss of efficiency arises from the formation of intramolecular rings by reaction of terminal epoxides and phenolic hydroxyls.

Structure of epoxidized Novolacs

No commercial epoxidized Novolac has the structure usually represented, i.e. 100% of phenolic hydroxyls transformed into arylglycidylethers. The characterization of a particular commercial product showed that the epoxidation efficiency was 84.3%, the fraction of $-CH_2-CHOH-CH_2-$ bridges was 14.3% (10.5% of intramolecular cycles and 3.8% of chain extension), and the remaining 1.4% was ascribed to chlorine-containing residues.

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