

Molecular Weight Distributions in Epoxy Resins

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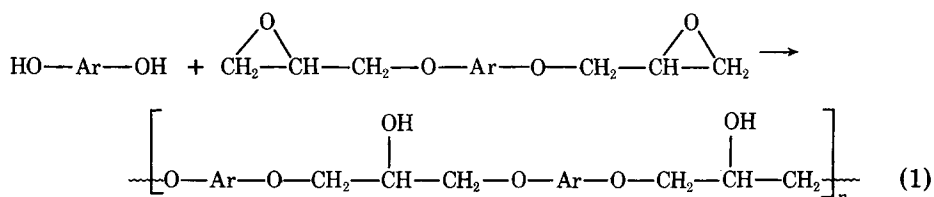
Synopsis

An exact procedure for calculating the weight-average and number-average molecular weights of epoxy resins made by the advancement process is presented. The calculation can take into account the presence of high molecular weight diepoxides and monofunctional epoxides in diglycidyl ether of bisphenol A and indicates that the presence of the latter has a very significant effect. A model for the taffy process based on the overall reactions of the process was developed. Analytical solutions could be obtained if the dehydrohalogenation reactions were assumed to be fast. The predictions of the model are in good agreement with the observed values reported earlier.

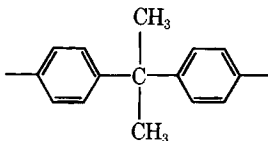
INTRODUCTION

Epoxy resins are generally manufactured either by the taffy process or by the advancement process. In the taffy process a diol, such as bisphenol A, is reacted with a controlled excess of epichlorohydrin under the catalytic influence of alkali. The taffy process consists of (1) formation of chlorohydrins, (2) dehydrochlorination, and (3) reaction between the phenolic group and the glycidyl ether group. Let the reaction rate constants of these reactions be k_1 , k_2 , and k_d , respectively. It is generally observed¹⁻³ that the dehydrochlorination reaction is very fast and that the taffy process is controlled by the rate of the other steps. Thus, in accordance with these observations as well as to simplify the task, it is assumed in this paper that $k_d \gg k_2$ and k_1 . If k_d is very large, the concentrations of all chlorohydrin species will be extremely small.

In the advancement process, bisphenol A is reacted with the diglycidyl ether of bisphenol A (DGEBA):

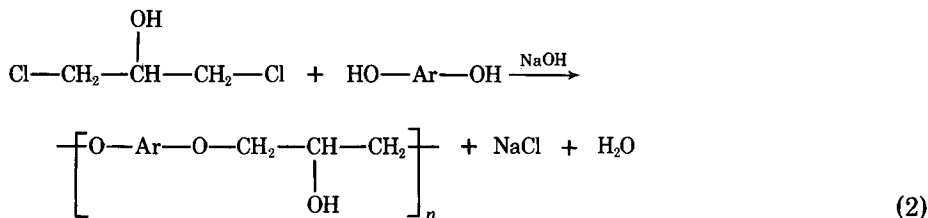


where Ar is



This reaction is clearly the same as the textbook example of step polymerization of AA and EE where A can react with only E, and vice versa.

Flory⁴ developed statistical methods for calculating the molecular weight distribution (MWD) in linear step polymerization (polycondensation) reactions assuming that all the functional groups are equally reactive. Batzer and Zahir⁵ applied these methods to calculate the weight-average (\bar{M}_w) and number-average (\bar{M}_n) molecular weights of epoxy resins generated by the advancement process. The taffy resin was visualized by these authors^{2,5} as a product of 1,2-dichlorohydrin with bisphenol A:



Batzer and Zahir⁵ assumed that both chlorines (or, in essence, epichlorohydrin and the glycidyl ether functional group) are equally reactive, which enabled them to apply Flory's⁴ methods to calculate the \bar{M}_w and \bar{M}_n of taffy resin also. They compared their theoretical results with the results obtained from GPC of commercial taffy and advancement resins. Their results for the taffy process showed small discrepancies between the theoretically computed and observed MWD. A lower reactivity of the glycidyl ether group than that of the epoxide group in epichlorohydrin was proposed as an explanation for the discrepancy between the results. Batzer and Zahir later proposed² an alternative, purely hypothetical model where the taffy resin was considered as a product obtained by the self-polymerization of monoglycidyl ether of bisphenol A followed by postglycidylation. The results of this model were in better agreement with the observed values than those predicted by their earlier model.

The above new model for the taffy process, however, is purely hypothetical and has no relation to the chemical reactions taking place in the process. Thus, neither the initial molar ratio of epichlorohydrin to bisphenol A nor the reaction rate constants of the chemical reactions play any role in the theory. The fractional conversion of the epoxide groups in this model, which has to be fixed to match the observed \bar{M}_n , bears no relation to the fraction of epichlorohydrin consumed or the reaction time. Thus, even if more knowledge were available, the hypothetical model cannot be improved further. In this paper we intend to present a more realistic model for the taffy process based on a simplified kinetic scheme. Further, the theoretical results presented by Batzer and Zahir⁵ for the advancement process are only approximate because of certain simplifications made in the Flory theory used for the calculation of molecular weights. The error

TABLE I
Comparison of Theoretical \bar{M}_w for Taffy Process

\bar{M}_n	Equal reactivity method ⁵	\bar{M}_w		This work $k_2/k_1 = 0.6$	GPC
		Postglycidylation method ²			
934	1632	1493		1493.5	1512
1852	3461	3318		3318.1	3149
3846	7500	7301		7300.5	6834

$$[\text{EE}_n] = R^2(\beta - \gamma)^2(R\gamma)^n/4\phi \quad (11)$$

$$[\text{AA}_n] = (1 - \alpha)^2(R\gamma)^n/\phi \quad (12)$$

where R = initial ratio of epichlorohydrin to bisphenol A molecules, α = fraction of phenolic groups reacted, β = fraction of epichlorohydrin molecules reacted, γ = number of glycidyl ether groups reacted per number of epichlorohydrin molecules, $\phi = 1 - 2\alpha + R$.

From eqs. (3) to (8), assuming that order and molecularity of the reactions are the same, it can be shown that

$$\frac{d\alpha}{dt} = k_1RC_{A_0}[(1 - \alpha)(1 - \beta) + (k_2/k_1)(1 - \alpha)(\beta - \gamma)] \quad (13)$$

$$\frac{d\beta}{dt} = 2k_1C_{A_0}(1 - \alpha)(1 - \beta) \quad (14)$$

$$\frac{d(\beta - \gamma)}{dt} = 2k_1C_{A_0}[(1 - \alpha)(1 - \beta) - (k_2/k_1)(1 - \alpha)(\beta - \gamma)] \quad (15)$$

where C_{A_0} is the initial number of bisphenol A molecules. The above equations are obvious once it is realized that RC_{A_0} times $(\beta - \gamma)$ is the number of glycidyl ether groups present at any given time. The above equations can also be obtained from the kinetic equations for each species by realizing that the total number of hydroxyl and glycidyl ether groups per mole of reaction mixture are given respectively by

$$\sum_{n=0}^{\infty} (2[\text{AA}_n] + [\text{AE}_n]) \quad \text{and} \quad \sum_{n=0}^{\infty} (2[\text{EE}_n] + [\text{AE}_n])$$

By subtracting (15) from (14) and dividing the resulting equation by eq. (14), it can be shown that

$$\frac{d\gamma}{d\beta} = \frac{k_2(\beta - \gamma)}{k_1(1 - \beta)} \quad (16)$$

Solving this, one obtains

$$\gamma = \beta - [k_1(1 - \beta)/(k_2 - k_1)][1 - (1 - \beta)^{(k_2 - k_1)/k_1}]$$

or

$$\gamma = \beta + (1 - \beta) \ln(1 - \beta) \quad \text{if } k_1 = k_2 \quad (17)$$

further from the stoichiometry

$$2\alpha = R(\beta + \gamma) \quad (18)$$

Thus, with the help of (17), (18), and (9) to (12) the MWD at any given value of α can be computed. Moreover, after substituting (17) and (18) in (13), eq. (13) can be numerically integrated to obtain α as a function of time. Thus, the MWD can be obtained as a function of time.

The quantities of interest are \bar{M}_n and \bar{M}_w . Since one molecule of HCl is eliminated for each epichlorohydrin molecule reacted, the molecular weights of AE_n , EE_n , and AA_n , denoted respectively by M_{AE_n} , M_{EE_n} , and M_{AA_n} are given respectively by $[(n + 1)M_A + (n + 1)(M_{\text{EP}} - M_{\text{HCl}})]$, $[(n + 1)M_A + (n + 2)(M_{\text{EP}} - M_{\text{HCl}})]$, and $[(n + 1)M_{\text{AA}} + n(M_{\text{EP}} - M_{\text{HCl}})]$. In the above, the molecular

weights of bisphenol A, epichlorohydrin, and HCl are denoted by M_A , M_{EP} , and M_{HCl} , respectively. Hence, by definition,

$$\bar{M}_n = \frac{\sum_{n=0}^{\infty} \{[AE_n]M_{AE_n} + [EE_n]M_{EE_n} + [AA_n]M_{AA_n}\}}{\sum_{n=0}^{\infty} \{[AE_n] + [EE_n] + [AA_n]\}} \quad (19)$$

$$= \frac{M_A + R\beta(M_{EP} - M_{HCl})}{1 - \alpha + (R/2)(\beta - \gamma)} \quad (20)$$

and

$$\bar{M}_w = \frac{\sum_{n=0}^{\infty} \{[AE_n]M_{AE_n}^2 + [EE_n]M_{EE_n}^2 + [AA_n]M_{AA_n}^2\}}{\sum_{n=0}^{\infty} \{[AE_n]M_{AE_n} + [EE_n]M_{EE_n} + [AA_n]M_{AA_n}\}} \quad (21)$$

$$= \frac{\{M_A^2(1 + R\gamma) + 4\alpha M_A(M_{EP} - M_{HCl}) + (M_{EP} - M_{HCl})^2\}}{\{(1 - R\gamma)[M_A + R\beta(M_{EP} - M_{HCl})]\}} \times \frac{\{\alpha + \alpha^2 + (\alpha - R\gamma) + (\alpha - R\gamma)^2\}}{\quad} \quad (22)$$

It is to be noted that in calculating \bar{M}_n and \bar{M}_w , the unreacted epichlorohydrin has not been included. This is done because the unreacted epichlorohydrin is distilled off from the taffy resin.

Advancement Process

This process is similar to the polymerization of a diol and a diacid. The results given by Flory⁴ for the weight fraction distribution for such a linear polycondensation process are applicable only to the case when both monomers are equal in molecular weight. This has been pointed out by Case⁶ as well as Grethlein,⁷ who gave results for polycondensation of monomers of unequal molecular weight. However, Batzer and Zahir⁵ used the weight fraction distribution given by Flory⁴ for condensation of bisphenol A and its diglycidyl ether (DGEBA) together with the true molecular weights of the oligomers for the calculation of \bar{M}_n and \bar{M}_w . We present below an analytical method based on the treatment by Case⁶ to obtain the exact number- and weight-average molecular weights of such distributions:

TABLE II
Comparison of Theoretical \bar{M}_w for Advancement Process

Epoxide value ⁵	Theoretical ⁵ \bar{M}_n	\bar{M}_w ⁵	\bar{M}_w eq. (24)	\bar{M}_w , eq. (27) $\psi = 0$	With 3% monoepoxide		\bar{M}_w from GPC	\bar{M}_n from VPO
					\bar{M}_n	\bar{M}_w		
1.9	1050	1862	1919.7	1898.7	1020	1834	1838	1150
1.1	1818	3380	3481	3466.8	1731	3285	3648	1706
0.65	3077	5863	6015	6001	2847	5529	5609	2688

1. Number fraction distribution:

Molecules containing n glycidyl ether and $(n - 1)$ bisphenol units:

$$\delta(1 - \alpha)^2(\alpha\delta)^{n-1}/\phi \quad n \geq 1$$

Molecules containing n glycidyl ether and n bisphenol units:

$$2(1 - \alpha)(1 - \delta)(\alpha\delta)^n/\phi \quad n \geq 1$$

Molecules containing $(n - 1)$ glycidyl ether and n bisphenol units:

$$(1 - \delta)^2\alpha(\alpha\delta)^{n-1}/\phi \quad n \geq 1$$

In the above, α and δ are the fraction of phenolic and glycidyl ether groups reacted, respectively, and $\phi = \alpha + \delta - 2\alpha\delta$.

2. M_w and M_n can be calculated easily since there is no elimination product and they are given by

$$\bar{M}_n = (\delta M_A + \alpha M_E)/\phi \quad (23)$$

$$\bar{M}_w = \frac{(1 + \alpha\delta)(\delta M_A^2 + \alpha M_E^2) + 4\alpha\delta M_A M_E}{(1 - \alpha\delta)(\delta M_A + \alpha M_E)} \quad (24)$$

M_A and M_E are, respectively, the molecular weights of bisphenol A and DGEBA. Further, from stoichiometry, α/δ is equal to the initial molar ratio of DGEBA to bisphenol A.

The advancement resins are made from commercially available DGEBA. Such commercial samples are rarely pure and contain diepoxides of higher molecular weight as well as monofunctional epoxides. Polymerization of such a mixture can be treated as step polymerization of AA (bisphenol A) with EE (DGEBA), E'E' (high molecular weight diepoxide), and EX (monofunctional epoxide) where E and E' can react with only A, E and E' cannot react with each other, and X cannot react at all. Formulas for calculation of MWD or even \bar{M}_w for such systems are not available. However, \bar{M}_w for such systems can be derived easily from the expectation theory developed by Macosko and Miller.⁸ It can be shown that⁹ even though they derived expressions for nonlinear polymers, their expressions are applicable to linear polymers also. Macosko and Miller⁸ considered the step polymerization of polyfunctional molecules $A_{f_1}, A_{f_2}, \dots, A_{f_k}$ with $B_{g_1}, B_{g_2}, \dots, B_{g_l}$, where A can react with B only and f_1, f_2, \dots, f_k and g_1, g_2, \dots, g_l are the functionalities of the molecules. They derived an expression for \bar{M}_w after assuming that the reactivity of A and B groups belonging to all the molecules is the same. Our case is step polymerization of AA with EE, E'E', and EX. Hence, $f_1 = 2, f_2 = \dots = f_k = 0, g_1 = g_2 = 2, g_3 = 1, g_4 = \dots = g_l = 0$. We will assume that an epoxy group belonging to EE or E'E' or EX has the same reactivity. Let R = initial ratio of EE to AA molecules, ν = initial ratio of E'E' to EE molecules, and ψ = initial ratio of EX to EE molecules. By stoichiometry,

$$2\alpha = R(2 + 2\nu + \psi)\delta \quad (25)$$

where α and δ are the same as defined earlier. A reaction started with one mole of AA and R moles of EE would contain $2(1 - \alpha)$ phenolic ends, $R(2 + 2\nu + \psi)(1 - \delta)$ epoxy ends, and $R\psi$ X ends. Hence,

$$\bar{M}_n = \frac{R(M_E + \nu M_{E'} + \psi M_X) + M_A}{1 + R(1 + \nu + \psi) - 2\alpha} \quad (26)$$

where M_E , $M_{E'}$, and M_X are the molecular weights of EE, E'E', and EX, respectively. Now applying Macosko and Miller's results,⁸ we get

$$\begin{aligned} \bar{M}_w &= \frac{M_A^2 + R(M_E^2 + \nu M_{E'}^2 + \psi M_X^2)}{M_A + R(M_E + \nu M_{E'} + \psi M_X)} + 2R\delta \\ &\times \frac{R\delta(M_E + \nu M_{E'} + \frac{1}{2}\psi M_X)^2 + 2M_A(M_E + \nu M_{E'} + \frac{1}{2}\psi M_X) + (1 + \nu)\delta M_A^2}{[1 - (1 + \nu)R\delta^2][M_A + R(M_E + \nu M_{E'} + \psi M_X)]} \end{aligned} \quad (27)$$

Note that when $\psi = \nu = 0$, eq. (27) will reduce to eq. (24).

RESULTS AND DISCUSSION

In either the taffy or the advancement process, since the desired end product is a diepoxide, the initial amount of bisphenol A taken is less than the amount of epichlorohydrin or DGEBA. Thus, at the end of the reaction the fraction of phenolic groups reacted, α , is 1. Results will be computed only for this case.

Taffy Process

The calculations for this process can be done if the ratio k_2/k_1 is known. Working with bisphenol A and epichlorohydrin, Fisch³ reported a value of 0.6 for k_2/k_1 . Batzer and Zahir² reported that the epoxide group of phenyl glycidyl ether reacts only 0.48 times as fast as epichlorohydrin. Since the results available are for bisphenol A resins, a value of 0.6 was assumed for k_2/k_1 . \bar{M}_w values were calculated for the same \bar{M}_n given by Batzer and Zahir⁴ for a k_2/k_1 of 0.6 and are presented in Table I. For comparison, the theoretical values obtained by assuming equal reactivity of epichlorohydrin and glycidyl ether groups⁵ and the hypothetical model of self-polymerization of monoglycidyl ether of bisphenol A followed by postglycidylation² are also presented.

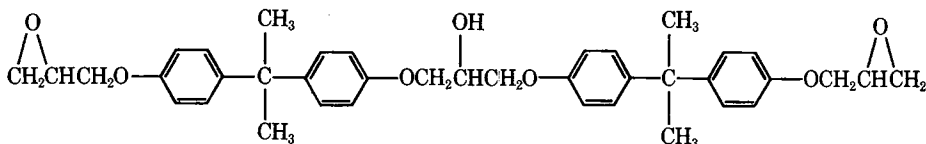
The \bar{M}_w values in Table I were calculated for a given value of \bar{M}_n by solving (17), (18), and (20) iteratively to obtain R , β , and γ and then using eq. (22). However, the results could have been computed directly if R , the initial ratio of epichlorohydrin to bisphenol A, for these resins was known, since then β and γ could have been calculated from eq. (22). In view of the agreement between the GPC and our theoretical values, we can conclude that the model based on the reactions taking place in the taffy process and the assumption that dehydrohalogenation occurs rapidly works well after using the experimentally observed value of k_2/k_1 .

Advancement Process

In the following calculations we used the epoxide values reported by Batzer and Zahir⁵ as the basis of our calculations. It may be pointed out that their theoretical $\bar{M}_n = 2000/(\text{epoxide value})$.

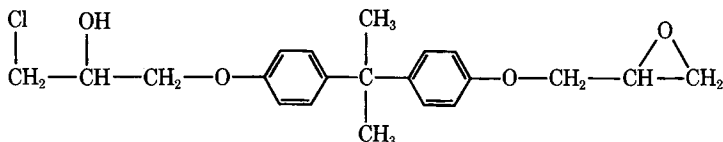
First assuming that the product was obtained from condensation of bisphenol A and pure DGEBA, \bar{M}_w values were calculated for the same \bar{M}_n given by Batzer and Zahir³ to facilitate comparison. Since \bar{M}_n is known, δ can be calculated from (23), and then \bar{M}_w can be calculated from (24). The results are presented in Table II.

Batzer and Zahir⁵ mentioned that the DGEBA used in the reaction was not pure and contained a large (14% by weight) amount of high molecular weight diepoxide (E'E') of the type



as well as a small (2% by weight) amount of condensation product of one molecule of bisphenol A with two molecules of DGEBA. For simplicity, the presence of the latter small quantity was ignored. Hence, ν is known, and from the \bar{M}_n given by Batzer and Zahir⁵ R can be calculated from eq. (26) and the \bar{M}_w from (27). These results are also presented in Table II under the heading $\psi = 0$. From these results it is clear that the high molecular weight diepoxide has only a marginal effect.

Batzer and Zahir⁵ also referred to the presence of monofunctional epoxides in DGEBA. For simplicity, let us assume only the following type (EX) is present:



From the results presented in Table IV of Reference 5, it appears that the monofunctional epoxides may be present anywhere from 3% to 5% by weight. A different procedure has to be adopted to account for the presence of monofunctional epoxide since it affects \bar{M}_n also. For this case \bar{M}_n was calculated from eq. (26) by first calculating R using the following equation for epoxide value:

$$\text{epoxide value} = 1000 \frac{R(2 + 2\nu + \psi) - 2}{M_A + R(M_E + \nu M_{E'} + \psi M_X)} \quad (28)$$

It was assumed that 3% by weight of monofunctional epoxide was present. \bar{M}_w was then calculated from (27). These results are presented in Table II. We see from the results that the effect of monofunctional epoxides is considerable and in the right direction. It may also be noted that the new \bar{M}_n values are closer to the more reliable \bar{M}_n values obtained from VPO. The reason for these changes is mainly the lower values of the new \bar{M}_n . As can be worked out from eq. (28), if $\psi = 0$, \bar{M}_n is still given by $2000/(\text{epoxide value})$. Thus, the presence of high molecular weight diepoxides alone will not alter the \bar{M}_n at a given epoxide value. The new \bar{M}_n values are low only due to the presence of monofunctional epoxides.

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