

Studies in the Molecular Weight Distribution of Epoxide Resins. I. Gel Permeation Chromatography of Epoxide Resins

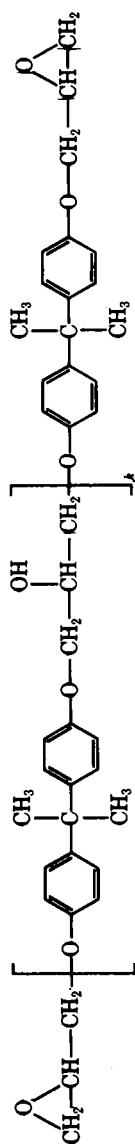
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Synopsis

The molecular weight distributions as measured by gel permeation chromatography of solid epoxide resins made by the direct addition of epichlorohydrin to bisphenol A (the "taffy" process) and by the reaction of low molecular weight liquid epoxide resins whose main constituent is the diglycidyl ether of bisphenol A with bisphenol A (the "advancement" process) have been compared with the theoretical distribution calculated by the application of Flory statistics. The model used for predicting the molecular weight distribution has been shown to be too simple to describe the real size distribution of these resins. For resins prepared by the "taffy" process, incompleteness of reaction, the presence of monofunctional epoxides, and the possibility of branching reactions through the epoxide-hydroxyl reaction lead to a distribution that more nearly resembles one calculated for a resin having a higher epoxide value than that actually measured. In the case of resins prepared by the "advancement" process, the presence of small amounts of the higher oligomeric diepoxides and monofunctional epoxides in the starting material used for the synthesis lead to complex molecular weight distributions that are not easy to deduce theoretically. The experimentally determined molecular weight distributions for the higher molecular weight epoxide resins (epoxide value < 2 eq/kg) made by the "advancement" process resemble more nearly those calculated for resins having lower epoxide values than those actually measured.

INTRODUCTION

It is well known that the molecular weight distribution of linear condensation polymers is a function of the mechanism of the polymer-forming reaction. Considerable theoretical work has already been done on the molecular size distribution in linear polycondensations.¹⁻⁴ Flory's statistical method¹ is based on the assumption that the reactivity of a functional group is independent of the size of the molecule to which it is attached and that ring formation does not occur. The application of Flory's statistics for calculation of the molecular weight distribution of epoxide resins based on bisphenol A is of particular interest because such resins can be synthesized by two different methods, both methods leading to products having the structural formula I:

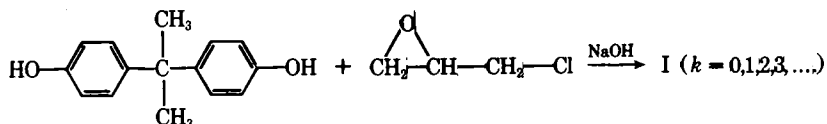


I

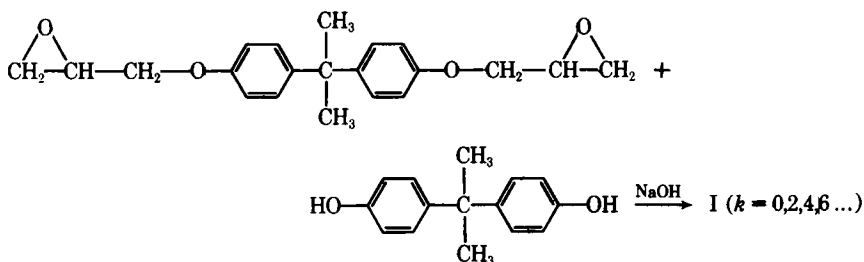
 $k = 0, 1, 2, 3, \dots$ "taffy" process

 $k = 0, 2, 4, 6, \dots$ "advancement" process

In the so-called "taffy" process, bisphenol A is reacted with varying proportions of epichlorohydrin under alkaline conditions:



This procedure leads to products containing both odd- and even-numbered diepoxide oligomers of the type shown in formula I, where $k = 0, 1, 2, 3$, etc. In the "fusion" or the "advancement" process, the main constituents of the final resin are oligomeric diepoxides of formula I, where the nonzero values of k are even integers, since the process involves the base-catalyzed condensation of varying amounts of bisphenol A with a low molecular weight epoxy resins whose main constituent is the diglycidyl ether of bisphenol A:



Although it is relatively easy to calculate the number-average molecular weight of such polymers, exact equations for the weight-average and Z-average molecular weights are cumbersome to derive from the weight fraction distribution functions. The availability of high-speed digital computers enables the ready computation of the moments of the molecular weight distribution for any given epoxide content.

The advent of gel permeation chromatography (GPC) made possible the rapid determination of the molecular weight distribution and the various moments of the molecular weight distribution of polymers. Although previous studies on the GPC of epoxy resins based on bisphenol A have been described in the literature,⁵⁻¹² no detailed analysis of the molecular weight distribution of epoxide resins made by the "taffy" or the "advancement" processes has as yet been reported. In this paper, the molecular weight distribution determined by GPC of several epoxide resins made by these two types of process are compared with the distributions calculated by the Flory statistical method.

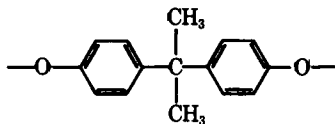
THEORETICAL COMPUTATION OF THE MOLECULAR WEIGHT DISTRIBUTION

Case I: Epoxide Resins Made by the Taffy Process

The products of the "taffy" reaction may be formally represented by the general formula II:



For $k > 0$, BB represents the glycidyl group ($-\text{CH}_2-\text{CH}(\text{O})-\text{CH}_2$) when present as an endgroup, or a glyceryl group ($-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-$) when present in the chain. When $k = 0$, BB represents the epichlorohydrin molecule. AA represents the nucleus of the bisphenol A molecule,



For $k > 0$, the molecular weight of the k th oligomer is given by eq. (1):

$$M_k = 340 + 284(k - 1) \quad k = 1, 2, 3, \dots \quad (1)$$

For $k = 0$, M_0 is 92.5, the molecular weight of epichlorohydrin.

For the case in which an excess of epichlorohydrin is used in the condensation reaction with bisphenol A, the weight fraction distribution at completion of the reaction, as calculated from the Flory statistics, is given by eq. (2):

$$w_k = (1 + 2k)r^k(1 - r)^2/(1 + r) \quad k = 0, 1, 2, \dots \quad (2)$$

where w_k = weight fraction of the k th oligomer, k = all integral values including zero, r = initial ratio of all phenolic groups to epoxide groups. (Since the epoxide groups were considered to be in excess, $r < 1$.)

The weight fraction of the unreacted epichlorohydrin in the condensed mixture ($k = 0$) is given by

$$w_0 = (1 - r)^2/(1 + r). \quad (3)$$

Since a resin made by the "taffy" process is freed from unreacted epichlorohydrin by washing or distillation, the final product will have a weight fraction distribution given by

$$w_k' = w_k/(1 - w_0) \quad (4)$$

for all integral values of k other than $k = 0$, w_k' is the weight fraction of the k th oligomer in the solid resin.

The moments of the molecular weight distribution, the number-average (\bar{M}_n), the weight-average (\bar{M}_w), and the Z-average (\bar{M}_z) may be calculated from the equations

$$\bar{M}_n = \frac{\sum w_k'}{\sum (w_k'/M_k)} \quad (5)$$

$$\bar{M}_w = \frac{\sum w_k' M_k}{\sum w_k'} \quad (6)$$

$$\bar{M}_z = \frac{\sum w_k' M_k^2}{\sum w_k' M_k} \quad (7)$$

The summations are carried out over all integral values of k other than zero.

A most widely used statistical measure of the breadth of a distribution is the standard deviation. The standard deviations of the number- and weight-average distributions, s_n and s_w , respectively, are given by

$$s_n = \left\{ \left(\frac{\bar{M}_w}{\bar{M}_n} - 1 \right) \bar{M}_n^2 \right\}^{1/2} \quad (8)$$

$$s_w = \left\{ \left(\frac{\bar{M}_z}{\bar{M}_w} - 1 \right) \bar{M}_w^2 \right\}^{1/2} \quad (9)$$

Since these polymers are terminated by epoxide groups, an important and easily accessible parameter is the epoxide equivalent per kilogram of polymer, p ; p is related to the number-average molecular weight by eq. (10):

$$p = 2000/\bar{M}_n \quad (10)$$

By means of an iterative numerical procedure in the computer program which was written to solve these equations, it was necessary to specify the desired epoxide value p and the molecular weights of the starting materials, in order to obtain the values of r , \bar{M}_n , \bar{M}_w , \bar{M}_z , s_n , s_w , and the integral weight distribution. To limit the number of iterative steps in the calculation, the following criteria were used to end the calculation: (a) the value of r ($r < 1$) is calculated to an accuracy of $r \pm 0.0001$, for an epoxide value $p \pm 0.0001$; (b) the summation in eqs. (5), (6), and (7) were carried out from $k = 1$ to 250.

Case II: Epoxide Resins Made by the Fusion or the Advancement Process

The structural formula for resins made by the "advancement" process may be formally represented by BBAABB(AABBAABB) $_j$, $j = 0, 1, 2, \dots$. The molecular weight of the j th oligomer is given by

$$M_j = 340 + 568j \quad (11)$$

Since the polymer is made by the direct polyaddition of diglycidyl ether of bisphenol A with bisphenol A either in melt or in solution, the weight fraction of the j th oligomer is given by eq. (2). In the calculations of the moments of the molecular weight distribution eqs. (5), (6), and (7) must be modified by replacing all w_k ' by w_j .

The results from this theoretical computation are summarized in Table I. From this table it may be concluded that if no side reactions are present, there should be no significant difference in molecular weight distribution between "taffy" resins and resins made by the "advancement" process having the same epoxide value. Any difference in the moments of the molecular weight distribution between the "taffy" resins and the corresponding "advancement" resins is due to the numerical nature of the computation procedure.

TABLE I
Theoretically Computed Moments of the Molecular Weight Distribution
of Solid Epoxide Resins

Epoxide value, eq/kg	Pro- cess ^a	\bar{M}_n	\bar{M}_w	\bar{M}_z	\bar{M}_w/\bar{M}_n	s_n	s_w
0.400	t	4996	9838	14822	1.97	4918	7002
	a	4998	9667	14453	1.93	4830	6802
0.450	t	4442	8716	13136	1.96	4357	6207
	a	4444	8570	12809	1.93	4282	6027
0.500	t	3998	7817	11785	1.96	3907	5569
	a	3998	7686	11483	1.92	3840	5403
1.000	t	1999	3761	5678	1.88	1877	2685
	a	1999	3738	5572	1.87	1864	2618
1.500	t	1333	2418	3640	1.81	1203	1719
	a	1333	2423	3609	1.82	1205	1696
2.000	t	1000	1759	2631	1.76	871	1239
	a	1000	1760	2624	1.76	872	1233
2.500	t	800	1375	2037	1.72	679	954
	a	800	1357	2026	1.70	668	953
2.750	t	727	1241	1827	1.71	611	826
	a	727	1209	1805	1.66	592	849

^a t = taffy; a = "advancement".

EXPERIMENTAL

Resins

Commercially manufactured epoxide resins made both by the "taffy" and by the "advancement" process were used in this study. Their epoxide content varied from ca. 0.5 to 2.6 eq/kg. In the case of resins made by the advancement process, a liquid resin containing over 80% of the diglycidyl ether of bisphenol A was used instead of the pure monomeric diepoxide in the condensation process with bisphenol A.

Epoxide Content¹⁶

Epoxide resin, 0.2 to 1.0 g, was dissolved in 10 ml chloroform and diluted with 20 ml glacial acetic acid. Tetraethyl ammonium bromide, 2.5 g, was added and the mixture titrated potentiometrically at room temperature against 0.1*N* perchloric acid in glacial acetic acid. The indicator electrode was a glass electrode conditioned to glacial acetic acid. The reference electrode was a calomel electrode filled with 0.1*N* LiCl in glacial acetic acid.

Vapor Pressure Osmometry

A Hitachi Perkin-Elmer vapor pressure osmometer operating at 40°C was used for measurement of the number-average molecular weights.

Methyl ethyl ketone purified by fractional distillation on a high-efficiency column was used as the solvent, and recrystallized benzil was used as the molecular weight reference standard.

Gel Permeation Chromatography

The solid resins that were used in this study have number-average molecular weights that range from ca. 700 to 5000. For resins with molecular weights less than 1000, it is possible by the use of high-resolution gel permeation chromatography on Biorad SX-2 to determine quantitatively the percentage of lower oligomers present in the resin. For resins with number-average molecular weights greater than 1000, the molecular weight distributions were determined by analysis on a multiple column packed with Styragel of varying pore sizes and Biorad SX-2.

High-Resolution Chromatography on Biorad SX-2

The column was 120 cm long and had an inside diameter of 2.54 cm. The solvent was distilled tetrahydrofuran, and the chromatogram was run at 22°C. A 1-mm flow-through cell in a Beckmann UV spectrophotometer set at 277 nm was used as the detector. The flow rate was 0.3 ml/min. In the quantitative analyses of these GPC curves, correction was made for the change in the extinction coefficient with oligomer number by means of a calibration curve based on the measured extinction coefficients of the monomeric diepoxide and two epoxide polymers having molecular weights of 1500 and 6000, respectively.

The calibration curve, based on the assumption that the main peaks in the high-resolution GPC curves (Figs. 4 and 5) are oligomeric diepoxides is illustrated in Figure 1. In this figure, a distribution coefficient, K_d , is used instead of elution volume as abscissa. K_d is defined by the equation

$$K_d = (V_e - V_0)/(V_m - V_0) \quad (12)$$

where V_e is the peak elution volume, V_0 is the void volume, and V_m is the elution volume of diglycidyl ether of bisphenol A. In order to cause the points corresponding to all oligomeric species to fall on a smooth curve, it was necessary to correct for the hydrogen bonding which occurs between the solute molecules containing hydroxyl groups and the solvent (tetrahydrofuran, molecular weight = 72). Thus, instead of using the molecular weights given by eq. (13),

$$M_k = 340 + 284k \quad (k = 0,1,2,\dots) \quad (13)$$

the apparent molecular weights, M'_k , defined by the equation

$$M'_k = 340 + 284k + 72k \quad (k = 0,1,2,\dots) \quad (14)$$

were used as the molecular weights of the eluting oligomers.

Gel Permeation Chromatography on Styragel and Biorad SX-2

A bank of five columns in series, each 100 cm in length and having an inside diameter of 0.9 mm was used to determine the molecular weight dis-

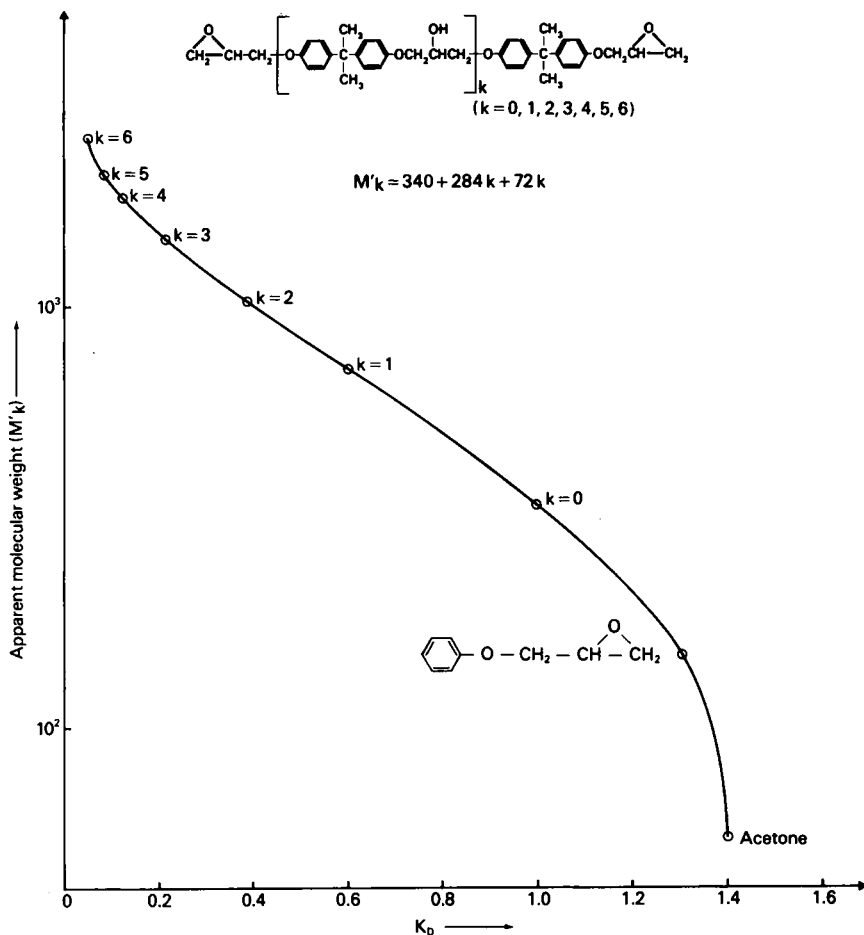


Fig. 1. Calibration curve for GPC columns packed with polystyrene gel Biorad SX2, with tetrahydrofuran as eluant. Peak positions for diepoxide oligomers are expressed as distribution coefficients K_d . The molecular weights are corrected for hydrogen bonding of hydroxyl groups with the solvent.

tribution of the epoxide resins. The first two columns were packed with Styragel of 10^4 Å pore size. The third column was packed with Styragel of 10^3 Å pore size, followed by two columns packed with Biorad SX-2 to improve the resolution on the low molecular weight side. Distilled tetrahydrofuran was used as the eluant, and the chromatograms were run at 22°C . The detector was a Waters-R4 differential refractometer thermostated at 40°C .

The output of the detector was "digitalized" through an analog-digital interfacing system and the results punched on paper tape for later analysis on the IBM computer 360/65. Calibration was carried out with narrow distribution polystyrene standards on the high molecular weight side. In the low molecular weight ranges, the separately identifiable peaks of the

oligomers in epoxide resins were incorporated into the calibration curve. The molecular weights (M) were converted into their unperturbed end-to-end chain lengths r_0 by means of the eq. (15):

$$r_0^2 = A(M) \quad (15)$$

where $A = 0.735$ for polystyrene and 1.10 for polymers based on bisphenol A and epichlorohydrin. A calibration curve was plotted of $\log_{10}(r_0^2)$ versus K_d . The digitalized data were subjected to a moving-point averaging procedure before being corrected for the baseline. By means of a numerical integration procedure, the corrected data were normalized, and the cumulative and differential distributions were calculated. The program also computes the moments of the molecular weight distribution and, as a measure of polydispersity, the standard deviations of the number-average and the weight-average distributions. No correction was made for the change in refractive index with oligomer number in the analysis of the GPC curves.

RESULTS AND DISCUSSION

In Table II, the theoretically predicted moments of the molecular weight distribution are compared with the experimental values. With the exception of resins having epoxide values of approximately 2 eq/kg, the GPC and VPO values for \bar{M}_n are lower than those predicted from the epoxide value. The reproducibility of the GPC measurements on two control samples was, in terms of the coefficient of variation (6 degrees of freedom), 4% for \bar{M}_n and 6% for \bar{M}_w .

In Figures 2 and 3, the theoretically predicted cumulative distribution curves for the resins tabulated in Table II are compared with the experimentally determined values (GPC). The overall agreement between the theory and experiment is within the experimental error of the GPC method of measurement and confirms the validity of the assumptions used in the derivation of the theoretical size distribution equations. A closer examina-

TABLE II
Comparison of Experimentally Determined Moments of Molecular Weight Distribution (GPC, VPO) for Solid Resins with Theoretically Computed Values*

Resin	Process	Epoxide value, eq/kg	Theory	\bar{M}_n		\bar{M}_w	
				GPC	VPO	Theory	GPC
A	a	1.90	1050	1030	1150	1862	1838
B	t	2.14	934	939	908	1632	1512
C	a	1.10	1818	1763	1706	3380	3648
D	t	1.08	1852	1740	1592	3461	3149
E	a	0.65	3077	2499	2688	5863	5609
F	t	0.52	3846	3011	3730	7500	6834

* t = "taffy" process; a = "advancement" process.

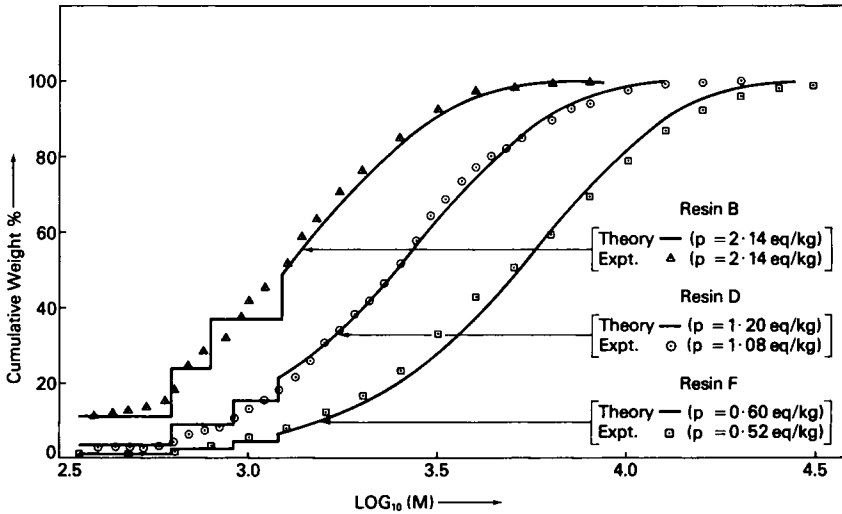


Fig. 2. Cumulative weight distribution curves for three epoxide resins made by the "taffy" process. The points are experimentally measured values (GPC). Full-line curves are theoretically deduced from Flory statistics for the epoxide value indicated in the figure.

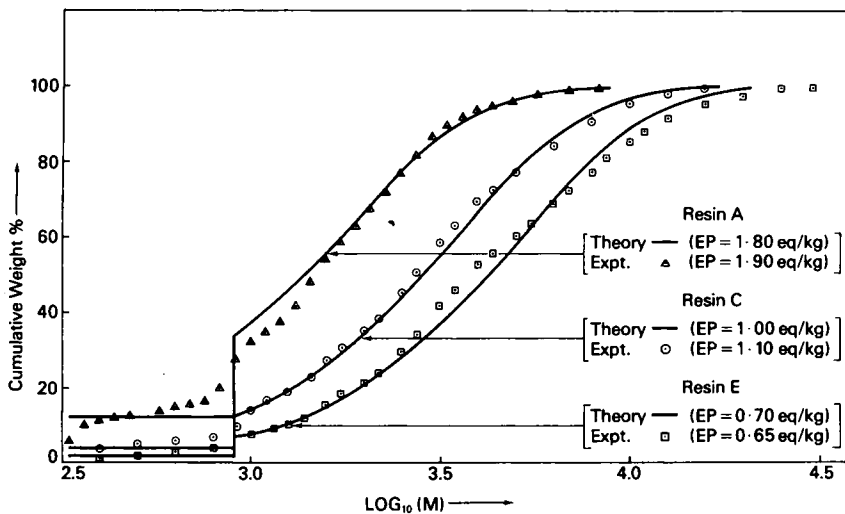


Fig. 3. Cumulative weight distribution curves for three epoxide resins made by the "advancement" process. The points are experimentally measured values (GPC). Full-line curves are theoretically deduced from Flory statistics for the epoxide value indicated in the figure.

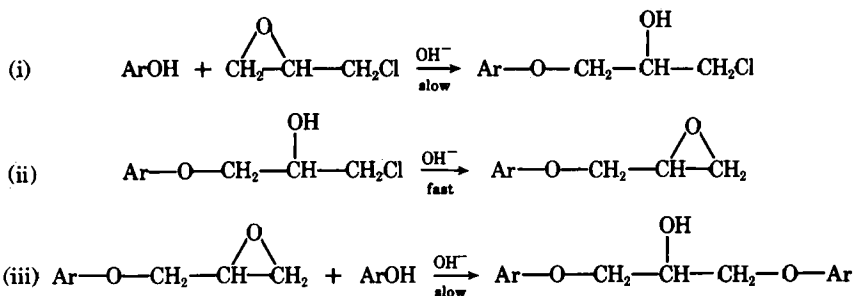
tion of the experimentally determined and theoretically predicted cumulative weight distribution curves revealed that small differences do exist.

Thus, for "taffy" resins, Figure 2, except for the lower molecular weight resins with an epoxide value of 2.14 eq/kg, the experimental points appear to show a close fit with the theoretical curves calculated for resins with

epoxide values approximately 0.1 eq/kg above the measured epoxide value. The stepwise nature of the molecular weight distribution for the theoretically predicted curves is indicated in the figures only for the lower oligomers.

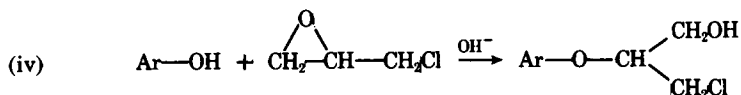
For resins made by the "advancement" process (Fig. 3), however, approximate agreement between the experimental points and the theoretical curves is only obtained when the theoretically deduced cumulative weight distributions are calculated for resins with epoxide value about 0.1 eq/kg below the measured epoxide value.

The explanation of these anomalies lies in the complexity of the reactions involved in the synthesis of technical epoxide resins. The reactions leading to the taffy resins are schematically illustrated below (scheme 1):



where ArOH represents a phenolic functional group.

The reactions shown above have been presented as normal additions of the phenolic group to the epoxide. Brode and Wynstra¹³ have shown by studies on model reactions between phenol and epichlorohydrin that the abnormal addition of the phenolate ion to the epoxide group,



occurs only to a very small extent (less than 1 mole-% of the normal addition product). The dehydrohalogenation reaction (ii) is normally very rapid, compared with reactions (i) and (iii). In practice, "taffy" resins are made under heterogeneous conditions. Under these conditions, it is likely that complete dehydrohalogenation does not occur. Further, the possibility of hydrolysis of a small percentage of the epoxide groups leading to α -glycol endgroups cannot altogether be excluded.

A side reaction that can lead to chain branching is the base-catalyzed addition of epoxide to the aliphatic hydroxyl groups (mainly secondary OH), present in the mixture:

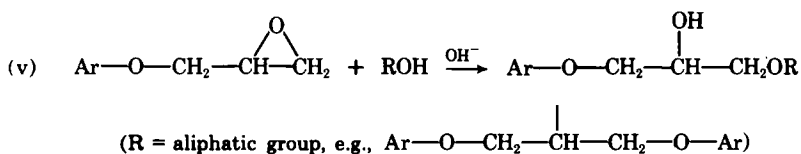


TABLE III
Weight Per Cent of Oligomers Present in a "Taffy" Resin Having an
Epoxide Value $p = 2.63$ eq/kg*

Oligomer number k	Molecular weight	Weight per cent		
		GPC	Theory	
		$p = 2.63$	$p = 2.63$	$p = 3.00$
0	340	21.4	15.9	19.7
1	624	20.2	17.2	19.8
2	908	15.2	15.5	16.7
3	1192	11.4	12.9	13.0
4	1476	31.7	38.5	30.8

* See Fig. 4.

of a methyl group, are always present. Molecules containing chlorine atoms were easily identified because the presence of the isotopes ^{35}Cl and ^{37}Cl gives rise to a characteristic pattern in the set of peaks representing the parent ion of mass M and the ion of mass $M-15$.

The fact that the stoichiometric balance cannot be maintained due to incomplete dehydrohalogenation and the presence of monofunctional epoxides in the reacting mixture can appreciably limit the molecular weight attainable. By means of a computer program,¹⁴ it was possible to resolve the GPC curve shown in Figure 4 into its component peaks. Since in the "taffy" process the reaction must first go through the chlorohydrin before the epoxide is formed, it is necessary, in order to compare the experimental distribution with the theoretically predicted Flory distribution for a resin with epoxide value of 2.63 eq/kg, to add to the area of the parent oligomer diepoxide peak the areas of the accompanying satellite peaks. The results are summarized in Table III. It is seen that the experimentally determined distribution differs considerably from the theoretically calculated one for a resin having an epoxide value of 2.63 eq/kg, but resembles that calculated for an epoxide value of 3.0 eq/kg.

In the case of resins made by the "advancement" process, however, the situation is quite different. As may be seen from Figure 5, not only oligomers with oligomer numbers $k = 0, 2, 4$, etc., are present as major components, but also smaller amounts of oligomers, $k = 1, 3, 5$, etc. This is because of the presence of small amounts of the oligomer $k = 1$ (up to 14%) and $k = 2$ (up to 2%) in the liquid epoxide resin used for reaction with bisphenol A (see scheme 2):

In Table IV, the weight per cent of the major oligomeric diepoxides present in the resin (as deduced from Fig. 5) are compared with the theoretical distribution which would have been obtained if pure diglycidyl ether of bisphenol A had been used instead of the commercially obtained liquid resin in the reaction with bisphenol A.

Due to the concurrent reaction of the oligomeric diepoxides $k = 0, 1, 2$ with bisphenol A, a very complex distribution is obtained. A further complication arises owing to the presence of monofunctional epoxides

TABLE IV
Weight Per Cent of Oligomers Present in a Resin Prepared by the
"Advancement" Process Having an Epoxide Value $p = 2.35$ eq/kg^a

Oligomer number	Molecular weight	Weight per cent	
		GPC $p = 2.35$	Theory $p = 2.35$
0	340	16.0	20.5
*	376.5-413.0	1.9	—
1	624	2.6	—
*	660.5-697	1.7	—
2	908	15.5	27.9
*	944.5	2.1	—
3	1192	6.8	—
4	1476	11.1	21.1
5	1760	42.2	30.4

^a See Fig. 5; * = satellite peaks accompanying main oligomeric diepoxide peaks.

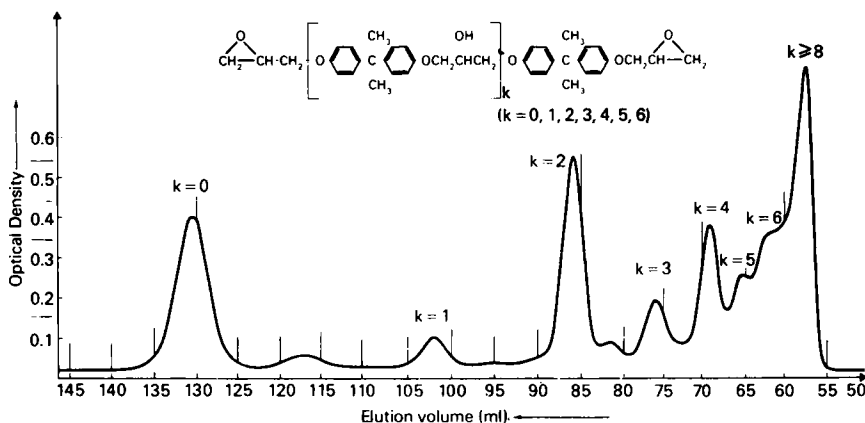


Fig. 5. High-resolution GPC curve (polystyrene gel Biorad SX2, with tetrahydrofuran as solvent) of a low molecular weight solid epoxide resin made by the "advancement" process.

(II, $R_1 = -\text{CH}_2-\text{CH}(\text{O})-\text{CH}_2$) in the liquid resin used for the reaction with bisphenol A. Such monofunctional epoxides contribute terminal units incapable of condensing with other molecules and therefore limit the ultimate molecular weight attainable.

Side reactions such as cyclization during chain growth can also lead to deviations from the theoretically predicted distributions. It is known that the reactions of bisphenol A and epichlorohydrin in ethanol or methanol lead to small amounts of cyclic dimer.¹⁵ We have confirmed this work and shown further that the cyclic dimer elutes at $K_d = 0.74$ (elution volume = 111 ml in Figs. 4 and 5) in columns packed with polystyrene gel, Biorad SX2, and tetrahydrofuran as eluant. It is apparent from these

figures that under the conditions used in the commercial process for the synthesis of solid epoxide resins, cyclic dimer formation is not favored.

CONCLUSIONS

A simple idealized model may be used for the calculation of the approximate molecular weight distribution of bisphenol A-based epoxide resins by means of Flory statistics. However, it has been shown to be inadequate to describe exactly the real size distribution of these resins. For resins prepared by the "taffy" process, incompleteness of reaction, the presence of monofunctional epoxides, and the possibility of branching reactions through the epoxide-hydroxyl reaction lead to a distribution that more nearly resembles one calculated for a resin having a higher epoxide value than that actually measured. In the case of resins prepared by the "advancement" process, the presence of small amounts of the higher oligomeric diepoxides and monofunctional epoxides in the starting material used for the synthesis lead to complex molecular weight distributions that are not easy to deduce theoretically. The experimentally determined molecular weight distributions for the higher molecular weight epoxide resins made by the "advancement" process studied in this paper (epoxide content <2 eq/kg) resemble more nearly those calculated for resins having lower epoxide values than those actually measured.

The authors would like to express their thanks to Drs. W. Hofmann, E. Forster, and B. P. Stark for valuable discussions and suggestions, and are grateful to the Management of Ciba-Geigy AG for permission to publish this paper.

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Received July 23, 1974