

Studies in the Molecular Weight Distribution of Epoxide Resins. II. Chain Branching in Epoxide Resins

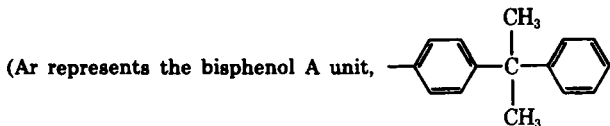
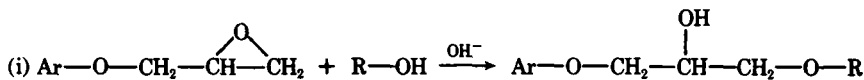
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Synopsis

The extent of side chain branching in epoxide resins based on bisphenol A has been determined by nuclear magnetic resonance spectrometry. The results indicate that for the resins studied in this paper, the extent of branching is very small. The number of branch points varies between 0.09 to 0.6 per molecule for epoxide resins whose number-average molecular weight lies between 1500 and 4000.

INTRODUCTION

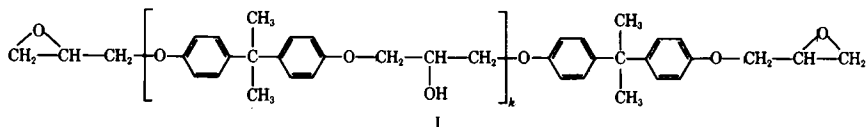
We have recently reported the results of a detailed study of the molecular weight distribution of epoxide resins based on bisphenol A.¹ The molecular weight distributions as determined by gel permeation chromatography of solid resins made by the base-catalyzed addition of variable amounts of epichlorohydrin to bisphenol A (the "taffy" process) and by the polyaddition reaction of the diglycidyl ether of bisphenol A to bisphenol A (the "advancement" process) were compared with the theoretical distribution calculated from probability statistics. A parameter of great interest in this connection is the extent of chain branching in these resins. The reaction which leads to chain branching during the synthesis of solid epoxide resins either by the "taffy" process, or by the "advancement" process is caused by the base-catalyzed addition of epoxide to the aliphatic hydroxyl groups (mainly secondary OH) present in the mixture:



and R, an aliphatic group, e.g., $\text{—CH}_2\text{—}\underset{\text{|}}{\text{CH}}\text{—CH}_2\text{—}$

A nuclear magnetic resonance method (NMR) for the determination of branching in epoxide resins has recently been published.^{2,3,6} The

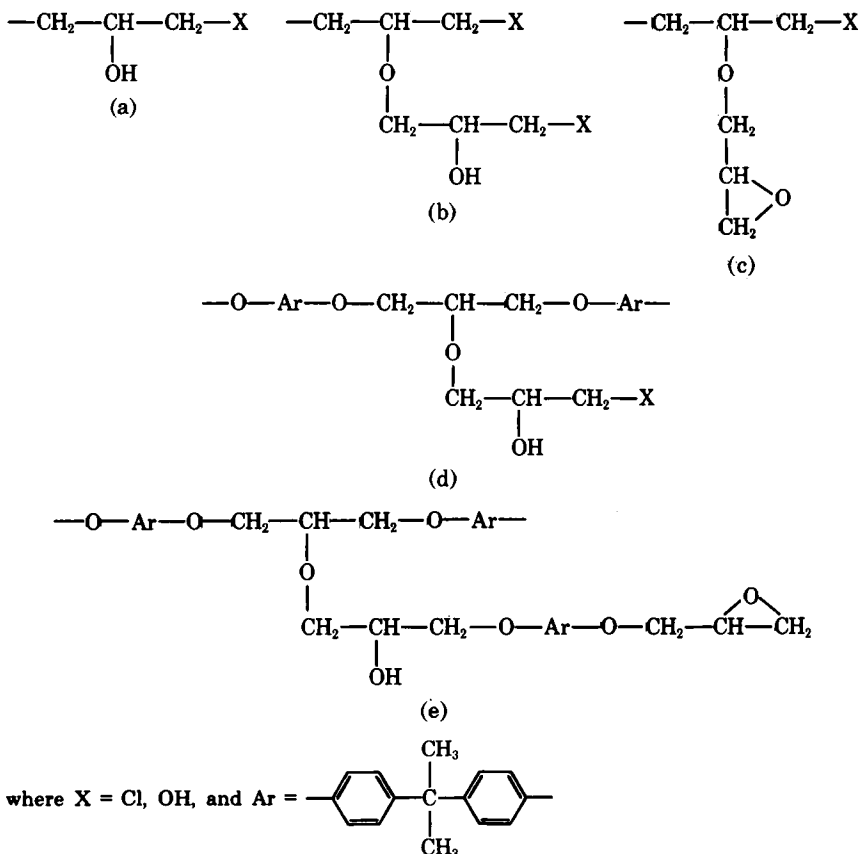
method was based on an idealized model for the structure of the molecules in an epoxide resin. It was assumed that each polymer molecule (I),



contains two epoxide endgroups and has a molecular weight M_k given by

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

Such a model ignores the fact that in practice most resins contain small amounts of functional groups other than epoxide groups either as endgroups or as side chains pendent to the main polymeric backbone, for example:



In the NMR method for determining the extent of branching, the parameter measured is the ratio of the glyceryl groups which act as branch points to the total number of glyceryl groups. The contribution of structures (a) to (e) cannot, therefore, be ignored. In this paper, a modified

method of calculation of the extent of branching from NMR data is presented using a more realistic model for the structure of bisphenol A-based epoxide resins. The extent of branching of some solid resins previously studied by gel permeation chromatography¹ has also been measured.

EXPERIMENTAL

Resins

Three technical resins whose molecular weights had previously been characterized by gel permeation chromatography and by vapor pressure osmometry¹ were selected for this study (see Table II). Two of these resins were made by the "taffy" process. The third resin was made by the "advancement" process.

NMR Method of Determining Side Chain Branching

The method involves reacting trichloroacetyl isocyanate with the hydroxyl groups present in the epoxide resin to form a urethane. This produces a downfield shift of the associated carbinol methine proton absorption in the NMR spectra. From the integrated peak areas it is possible to calculate the relative number of protons associated with unbranched ($-\text{CH}_2-\text{CH}-\text{CH}_2-$) and branched ($-\text{CH}_2-\text{CH}-\text{CH}_2-$) functional groups.



Approximately 0.1 g resin was dissolved in 0.5 ml deuteriochloroform; 0.1 g trichloroacetyl isocyanate was added, and after 5 min a few drops of deuterium oxide. The solution was scanned on a Varian 100-MHz NMR spectrometer and the peaks integrated. The means of five such integrations were taken to calculate the relative number of protons associated with the different functional groups.

Method of Calculation

The peak positions, type, and number of protons belonging to the different functional groups present in epoxide resins before and after reaction with trichloroacetyl isocyanate are set out in Table I. The total number of functional groups per kilogram of resin having the structure $-\text{CH}_2-\text{CH}-\text{CH}_2-$ ($\text{R}' = \text{H}$ or alkyl) is $n + m$, where n is the number of



such units which form part of the chain backbone, and m is the number of such units which belong to pendent or endgroups. $N + M$ represent the total number of branched points per kilogram resin, N being the number of branch points on the backbone of the polymer chain, and M the branch points on side chains or end groups.

TABLE I
 NMR Analysis of Epoxy Resins*

Structure	Peak position, ppm	Number of groups, eq/kg	No. of protons before CCl ₃ NCO		No. of protons after CCl ₃ NCO	
			eq/kg	Area = A°	eq/kg	Area = A
	2.8	<i>p</i>	2 <i>p</i>	A° _{2.8}	2 <i>p</i>	A _{2.8}
	3.3	<i>p</i>	<i>p</i>	A° _{3.3}	<i>p</i>	A _{3.3}
	1.6	<i>q</i>	6 <i>q</i>	A° _{1.6}	6 <i>q</i>	A _{1.6}
	7.0	<i>q</i>	8 <i>q</i>	A° _{7.0}	8 <i>q</i>	A _{7.0}
	4.0	<i>p</i>	2 <i>p</i>		2 <i>p</i>	
	4.0	<i>n - N</i>	5(<i>n - N</i>)	A° _{4.0}	4(<i>n - N</i>)	A _{4.0}
	4.0	<i>N</i>	5 <i>N</i>		5 <i>N</i>	
	4.0	<i>m - M</i>	5(<i>m - M</i>)		4(<i>m - M</i>)	
	4.0	<i>M</i>	5 <i>M</i>		5 <i>M</i>	
	5.5	<i>n - N</i>	0.0	0.0	<i>n - N</i>	A _{5.5}
	5.5	<i>n - N</i>	0.0		<i>m - M</i>	

* A°_{2.8}, A°_{3.3}, A°_{1.6}, A°_{7.0} and A°_{4.0} are the integrated peak areas for the untreated resin at 2.8, 3.3, 1.6 and 7.0 ppm. The corresponding values for the resin treated with trichloroacetyl isocyanate are A_{2.8}, A_{3.3}, A_{1.6}, A_{7.0}, and A_{4.0}.

TABLE II
Results of Mak and Rogers² Recalculated by The Method
Presented in This Publication

Epoxide value, eq/kg	\bar{M}_n	Corrected results from data published by Mak and Rogers		Results of Mak and Rogers recalculated by the method described in this publication	
		% N/n	Branches per molecule f	% $\frac{N+M}{n+m}$	Branches per molecule f
1.82	1096	0.0	0.0	0.0	0.0
1.10	1822	12.2	0.6	13.5	0.7
1.02	1958	0.0	0.0	0.9	0.05
0.81	2472	22.5	1.7	19.7	1.6
0.77	2582	6.2	0.5	4.0	0.3
0.62	3244	12.2	1.2	11.4	1.5
0.58	3468	5.9	0.65	9.7	1.0
0.57	3480	0.0	0.0	2.9	0.3
0.55	3658	0.0	0.0	2.9	0.3
0.31	6514	0.0	0.0	0.5	0.08

It can easily be shown from Table I that

$$n + m = \left[\frac{A_{4.0} + A_{5.5} - A_{2.8}}{A_{2.8}} \right] \frac{2p}{5} \quad \text{eq/kg} \quad (2)$$

$$N + M = \left[\frac{A_{4.0} - 4A_{5.5} - A_{2.8}}{A_{2.8}} \right] \frac{2p}{5} \quad \text{eq/kg} \quad (3)$$

where p is the epoxide equivalent in eq/kg, and the A 's represent the areas of the integrated peaks at the peak positions in ppm, given by the subscripts. The number of branch points, f , per number-average molecule is given by

$$f = (N + M)\bar{M}_n/1000 \quad (4)$$

where \bar{M}_n is the number-average molecular weight. The total number of functional groups with the structure $-\text{CH}_2-\text{CH}-\text{CH}_2-$, per number-



average molecule g , is given by

$$g = (n + m)\bar{M}_n/1000. \quad (5)$$

The results of the previous publication² recalculated on the basis of the more realistic model presented in this paper are presented in Table II. It was assumed for the purpose of this calculation that the values for the percentage of the methine protons quoted in Tables II and III of the original publication² represent the carbinol methine protons which have been shifted downfield to 5.5 ppm on treatment with trichloroacetyl isocyanate. Calculations of the extent of branching on the assumption that the percentage methine protons in their² Tables II and III represent the total

number of methine protons from both the unbranched $-\text{CH}_2-\text{CH}-\text{CH}_2$ and the branched $-\text{CH}_2-\text{CH}-\text{CH}_2-$ functional groups led to results which



in some cases were widely divergent from those previously published.²

From eq. (3), it is evident that the parameter $N + M$, which measures the number of branch points per kilogram of resin, is obtained by the difference of two large numbers, namely, $A_{4.0}$ and $(4.A_{5.5} - A_{2.8})$. For small extents of branching, the area of the peak at 5.5 ppm, $A_{5.5}$, must be very carefully measured.

RESULTS AND DISCUSSION

The results presented in Table III indicate that the extent of branching in these resins is very small. This confirms the earlier work of Schechter and Wynstra,⁴ who showed that the dominant reaction in the mineral base-catalyzed addition of phenyl glycidyl ether to phenol was the addition of the epoxide to the phenolic OH group. The catalyst can, however, play an important role in determining the extent of branching. In a study of the selectivity of different catalysts in the reaction of diglycidyl ether of bisphenol A with bisphenol A⁵, it was shown that hydroxyethylamines were highly selective catalysts and lead to very little etherification reactions. The use of dimethylacetamide or 1,1,3,3-tetramethylguanidine as catalysts led to extensive branching.

In the early stages of the NaOH-catalyzed synthesis of solid epoxide resins, the concentration of free hydroxyl ions in the system buffered by bisphenol A is very low. The concentration of aliphatic hydroxyl groups is also small, and the rate of the epoxide-aliphatic OH reaction is very low. As soon as most of the phenolic groups are consumed, the buffer action is destroyed, and alkoxide ions replace the phenolate ions in the reaction mix-

TABLE III
Extent of Branching of Some Solid Epoxide Resins Made Both by the "Taffy" Process (Bisphenol A and Epichlorohydrin) and by the "Advancement" Process (Bisphenol A and Diglycidyl Ether of Bisphenol A)

	"Taffy"	"Advancement"	"Taffy"
Epoxide content, eq/kg	1.08	1.10	0.52
\bar{M}_n	1592	1706	3730
Number of epoxide groups per molecule	1.72	1.88	1.94
$\%(N + M)/(n + m)$	1.9	5.1	5.1
Total number of $-\text{CH}_2-\text{CH}-\text{CH}_2-$ units per molecule, g	4.70	5.34	11.75
Number of branch points per molecule, f	0.09	0.27	0.60

ture. The concentration of hydroxyl groups increases as the reaction progresses. Side chain branching would thus be expected to occur at appreciable rates late in the reaction of phenolic OH groups with epoxide. The concentration of phenolic OH groups in solid resins of the type studied in this paper varies between 10 and 30 meq/kg. The extent of branching can be reduced to very small levels if the catalyst is destroyed or the reaction frozen by cooling when all the phenolic OH groups have disappeared.

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