Determination of Chain Branching in Epoxy Resins by Nuclear Magnetic Resonance Spectrometry

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THE MOST COMMON commercial epoxy resins are the diglycidyl ethers of bisphenol A. In analyzing the reactivity of the resins it is desirable to know the type of reactive groups present and also their location. At the present time it is not possible to completely determine the structure of the resins, but it has now been found that an estimation of the number of branches in the molecule can be obtained from nuclear magnetic resonance spectrometry. In this paper we present results for some commercially available epoxy resins and for some model resins that were prepared in the laboratory.

MODELS

Epoxy resins are reaction products of epichlorohydrin and bisphenol A. An idealized reaction sequence is shown in Figure 1. In the first step epichlorohydrin is reacted with bisphenol A to give the diglycidyl ether of bisphenol A (structure I). Subsequent reaction with bisphenol A and epichlorohydrin gives either linear polymers with the generalized structure II or branched chain polymers depicted in Figure 2. From such structures it is relatively easy to calculate the number of protons in each atomic environment, providing the value of n, the number of repeat units is known. n may be calculated as

$$n = \frac{2(\text{EEW} - 170)}{284} \qquad (1)$$

where EEW is defined as the epoxy equivalent weight (*1*) of the resin. 170 is the EEW of the resin when $n = 0$.

Each molecule contains as many aliphatic hydroxyls as there are repeat units in the linear structure. In the present models, it is assumed that branching occurs only through these hydroxyls so that for every branch point in the nonlinear molecule, there is one hydroxyl–carbinol methine pair less than in the linear molecule of equal molecular weight.

The acetylation of hydroxyl groups is an established NMR technique for the structural determination of alcohols, but the chemical reaction is frequently slow. Goodlett (*2*) has reported that trichloroacetyl isocyanate reacts rapidly with alcohols and produces a downfield shift of the associated methylene and methine proton magnetic resonance.

This technique has now been applied to epoxy resins. In the resulting urethane structure, the NMR absorption of the methine proton appears downfield in an interference-free region. The relative concentration of this proton can be determined from peak areas. Comparison with the models gives a measure of chain branching.

EXPERIMENTAL

Approximately 0.1 gram of resin was dissolved in 0.5 ml of chloroform. To this solution was added three drops of trifluoroacetic acid and the mixture was scanned on a Varian A-60 NMR Spectrometer. If no extraneous peaks were present, 0.1 gram of trichloroacetyl isocyanate was added and after mixing for three to four minutes, the solution was again scanned and the peaks were integrated. The relative number of protons in each position was calculated. Peak positions were calculated in parts per million relative to tetramethylsilane (TMS) as an internal standard (Table I). Interferences, if any, were limited to overlapping resonances present

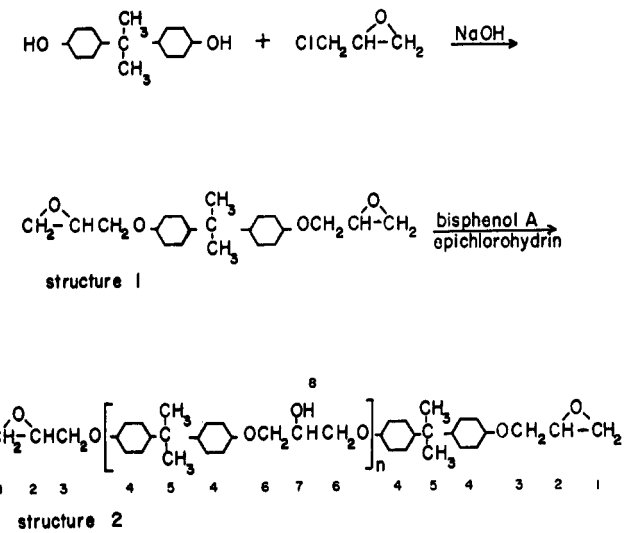

Figure 1. Idealized reaction mechanism. Numbers 1 to 8 refer to proton position, Table I

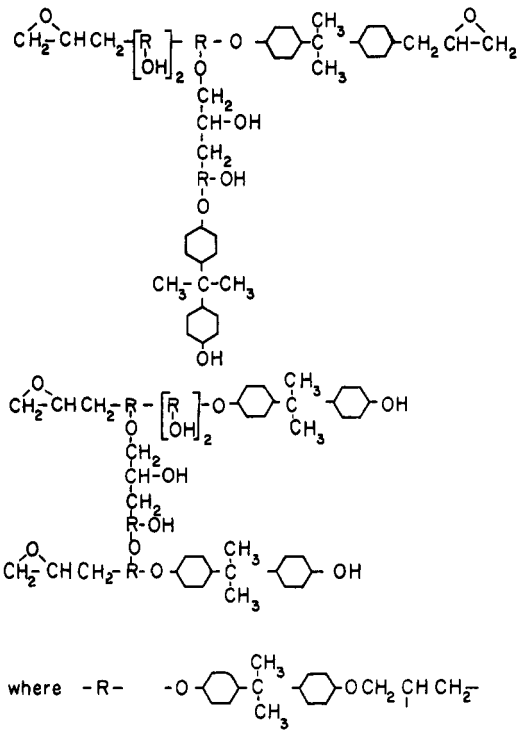

Figure 2. Possible chain branched configurations

(1) H. Lee and K. Neville, "Handbook of Epoxy Resins," McGraw-Hill, New York, 1967, pp 4–14.
(2) V. W. Goodlett, ANAL. CHEM., **37**, 431 (1965).

in the original sample—for example, aromatic solvent—and could readily be corrected.

Having determined the relative number of protons in the molecule by NMR, we need to relate the number of carbinol methines to the number of chain branches. If N is the number of branch points, then the number of carbinol methines in a branched molecule is equal to $(n-N)$, where n is calculated from Equation 1. The number of benzylic methyl protons in the molecule is $(6n + 6)$. Thus:

$$N = n - 6A\,(n + 1) \qquad (2)$$

where A is the area ratio of the carbinol methine protons and the benzylic methyl protons. The latter area was selected because it showed least interference in the NMR spectrum. As a check on the accuracy of the results, the distribution of the protons in all positions within the model molecule may be calculated and compared with the results from the NMR spectrum.

Table I. Peak Positions, after Addition of Trichloroacetyl Isocyanate

Proton position in molecule[a]	Proton terminology	Peak position, ppm
(1)	Epoxide methylene	2.6–3.0
(2)	Epoxide methine	3.1–3.5
(3)	Ether methylene	*ca.* 4.0
(4)	Benzylic ring	6.5–7.4
(5)	Benzylic methyl	1.3–1.9
(6)	Ether methylene	*ca.* 4.3
(7)	Carbinol methine	5.3–5.8
(8)[b]	Carbinol hydroxyl	*ca.* 8.7

[a] See Figure 1, Structure II.
[b] Converted to >NH on reaction with isocyanate.

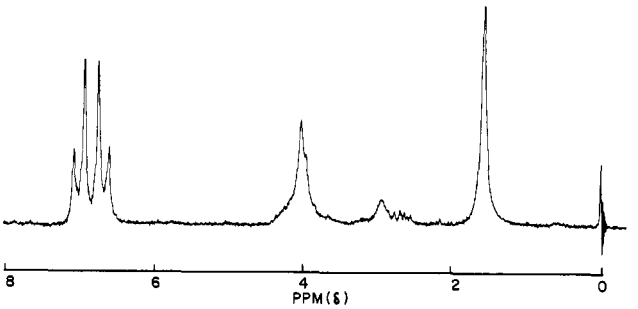

Figure 3. Typical NMR spectrum of unreacted epoxy resin

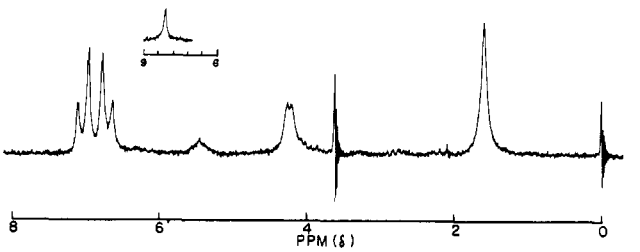

Figure 4. Spectrum of epoxy resin after reaction with trichloroacetyl isocyanate. Note appearance of NH peak at 8.7 ppm

RESULTS AND DISCUSSION

Examples of NMR spectra are shown in Figures 3 and 4. The first scan on the unreacted epoxy resin sample shows the carbinol hydroxyl absorption at about 2.8 ppm, superimposed in the epoxide methylene absorption. The area between 3.9 and 4.2 ppm is made up of contributions from both the ether methylene and the carbinol methine. On addition of the trichloroacetyl isocyanate, the carbinol hydroxyl peak grad-

Table II. Commercial Epoxy Resins

Sample EEW	n	N/n, %		Number of Protons (%) Epoxy CH_2	Epoxy CH	Ether CH_2	C_6H_5	CH_3	CH
1734	10.7	5.5	Calcd	1.8	0.8	20.6	41.3	30.9	4.4
			NMR	1.9	0.8	21.4	41.8	29.9	4.3
1829	11.4	0	Calcd	1.7	0.8	20.6	41.2	30.9	4.7
			NMR	2.0	1.0	21.1	41.1	29.8	4.6
979	5.6	0	Calcd	2.9	1.4	23.5	38.8	29.1	4.1
			NMR	3.1	1.4	20.9	39.9	30.0	4.4
911	5.1	10.7	Calcd	3.3	1.6	20.3	40.5	30.4	3.7
			NMR	3.4	1.5	20.6	41.6	29.3	3.6
3257	21.3	0	Calcd	0.46	0.93	20.8	41.6	31.2	4.96
			NMR	0.48	1.24	21.2	42.1	29.9	4.96
548	2.6	2	Calcd	2.7	5.5	19.6	39.2	29.4	3.5
			NMR	2.8	5.5	19.4	40.3	28.5	3.5

Table III. Laboratory Preparations

Sample EEW	n	N/n, %		Number of Protons (%) Epoxy CH_2	Epoxy CH	Ether CH_2	C_6H_5	CH_3	CH
1622	10.0	12.5	Calcd	1.8	0.94	20.7	41.3	31.0	4.1
			NMR	1.4	0.92	20.9	41.0	31.5	4.2
1291	7.7	4.5	Calcd	2.3	1.1	20.5	40.9	30.7	4.3
			NMR	2.3	1.1	20.4	40.7	31.0	4.3
1236	7.43	20	Calcd	2.4	1.2	20.6	41.2	30.9	3.6
			NMR	2.2	1.0	20.5	41.3	30.7	3.5
1740	10.8	0	Calcd	0.8	1.7	20.6	41.2	30.8	4.7
			NMR	0.8	1.9	21.0	42.0	29.8	4.6

ually disappears until excess reagent is added and a new peak occurs at 8.7 ppm due to the NH, Figure 4. Simultaneously the carbinol methine peak moves downfield to between 5.3 and 5.8 ppm.

In the case of branched chain molecules, some of the chains will be terminated by phenolic hydroxyls, which will react with the isocyanate and also contribute to the NH peak. The corresponding shift of the benzylic ring protons is of the order of 0.3 ppm. Detection of these groups in the resins reported here was not attempted. The peak occurring at 3.7 ppm is due to an impurity in the particular sample of trichloroacetyl isocyanate used in the present series of experiments.

Typical values for chain branching found in commercial epoxy resins are given in Table II, while Table III lists results for laboratory resins prepared under known and controlled conditions according to the model structures. In each case the distribution of protons, calculated by consideration of the model structures is in excellent agreement with that measured by NMR spectrometry. Where branching occurred, it was of the order of 10 to 20%, the range one might expect from statistical considerations. The percentage of chain branching is expressed as the ratio of the number of branch points in the molecule to the number of repeat units. Values less than 5% are within experimental error and the polymers are regarded as being linear.

In summary, trichloroacetyl isocyanate reacts rapidly with hydroxyls present in the reaction products of bisphenol A and epichlorohydrin and allows a measurement of the carbinol methine to be made from NMR spectra. Combined with considerations of model structures, this gives a rapid means of calculating the number of chain branch points in epoxy resin molecules.

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Multielement Neutron Activation Analysis of Biological Material Using Chemical Group Separations and High Resolution Gamma Spectrometry

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IT HAS LONG been recognized that many elements play vital roles in life processes. In recent years, studies have been conducted to determine which trace elements are essential for plant and animal life. Allaway (*1*) has stated that the trace elements, iron, copper, zinc, manganese, boron, sodium, cobalt, molybdenum, and vanadium appear essential for plant life. Those necessary for animal life include: iron, iodine, copper, zinc, manganese, cobalt, molybdenum, and selenium as essential trace elements, and fluorine, boron, barium, and strontium as probably essential. It has also been observed that many elements, especially if present in excess quantities, produce toxicologic effects upon life processes. Although nearly all elements are found in living matter, the roles of many elements have not yet been well characterized.

Many studies have been undertaken to examine the biologically significant elements, but most investigations have been concerned with at best the determination of a few elements. To gain an overall view of the elemental patterns of biological materials, a few survey approaches have been carried out. Tipton and Cook (*2*) have used emission spectrography as a survey tool. However, the method often suffers from lack of sensitivity for many elements of interest. X-ray fluorescence has been used in the analysis of kale (*3*), but the number of elements determined is limited. Of the methods available for survey analysis for trace elements, spark source mass spectrography (*4*) and neutron activation appear to be most applicable.

Many investigators have applied neutron activation analysis for single element determination by chemically separating pure radioisotopes, followed by gamma counting. Others have used neutron activation as a strictly instrumental technique for determination. As a survey tool Nadkarni and Ehmann (*5–7*) have determined 15 elements in various plant tissues by instrumental neutron activation analysis (INAA). High activities and complex gamma spectra, however, often prohibit the determination of many elements by strictly instrumental means. Samsahl *et al.* (*8*) have constructed an exotic scheme for automated separation of pure radioisotopes of about 40 elements, but many years were spent in development and the system is indeed quite complex.

Utilizing the experience gained in this laboratory in analyzing geological samples (*9*), it was decided to combine chemical group separations and high resolution gamma spectrometry with INAA for analysis of biological specimens to obtain maximum elemental information with a minimum of chemical separations. Information could be obtained on 31 elements with the neutron flux available.

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