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# Studies in the Molecular Weight Distribution of Epoxide Resins. III. Gel Permeation Chromatography of Epoxide Resins Subject to Postglycidylation*

H. BATZER and S. A. ZAHIR, *Plastics Division, Ciba-Geigy AG, CH-4002 Basel, Switzerland*

## Synopsis

Unambiguous evidence has been provided for the existence of a branched structure in liquid epoxide resins which have been subjected to postepoxidation with excess epichlorohydrin in the presence of a powerful nucleophilic catalyst, tetramethylammonium chloride. Gel chromatography of the resin on Sephadex LH-20 followed by isolation and identification of the relevant fraction by spectroscopic techniques revealed the presence of a novel trifunctional epoxide having a molecular weight of 680.

## INTRODUCTION

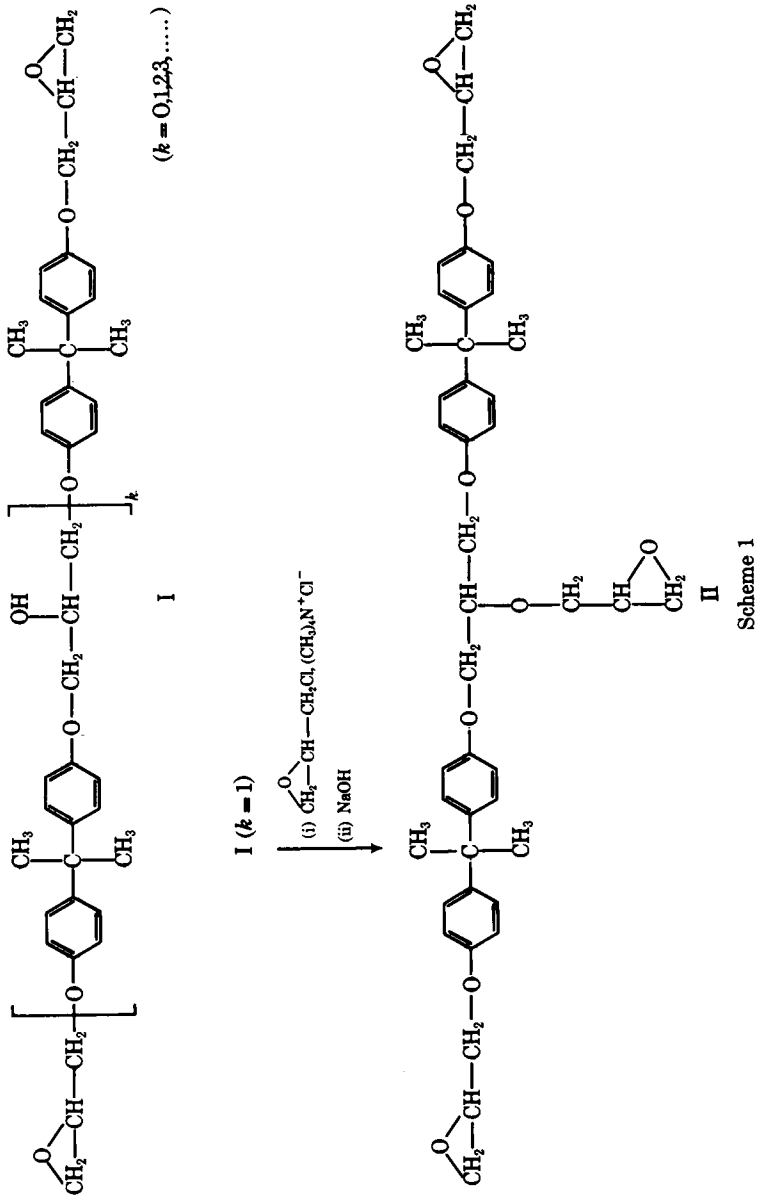
It has been shown[1,2] that the extent of branching in solid epoxide resins based on bisphenol A can be quantitatively determined by nuclear magnetic resonance (NMR). Chain branching in epoxide resins is caused by the base-catalyzed addition of epoxide to the aliphatic hydroxyl groups of the $-CH_2—CHOH—CH_2-$ functional group which forms part of the repeat unit of the polymer chain. The catalyst plays an important role in determining the extent of branching. Certain catalysts such as lithium salts and 1,1,3,3-tetramethylguanidine[3] are known to promote extensive etherification during the synthesis of epoxide resins. In order to get unambiguous evidence of the existence of the resin molecules with branched structures, a liquid epoxide resin (I) containing 14% dimer ($k = 1$) was further reacted with epichlorohydrin in the presence of a powerful nucleophilic catalyst, tetramethylammonium chloride. After ring closure with caustic soda (scheme 1; p. 610), the resins were examined by gel permeation chromatography.

## EXPERIMENTAL

### Postglycidylation of a Liquid Epoxide Resin

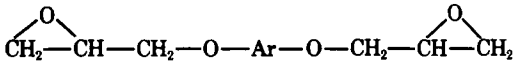
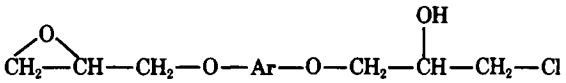
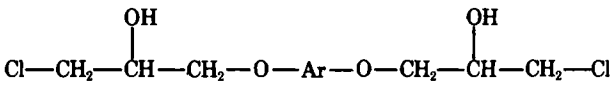
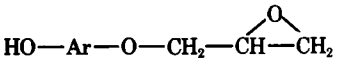
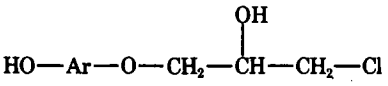
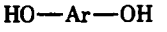
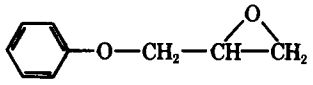
One kilogram of a commercial liquid epoxide resin, Araldite 6010, with an epoxide equivalent of 5.3 eq/kg was reacted with 10 moles epichloro-

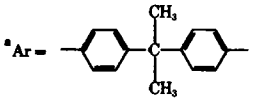
* The authors wish to dedicate this paper to Professor Dr. Eugen Müller, Emeritus Professor of Chemistry at the University of Tübingen, W. Germany, in honor of his 70th birthday.




Scheme 1

TABLE I
Distribution Coefficients, $K_d$, for Various Compounds when Chromatographed on Two Types of Gel Matrix

| Structure[a] | Molecular weight | $K_d$ Biorad SX2 | $K_d$ Sephadex LH20 |
|---|---|---|---|
| I, $k = 5$ | 1760 | 0.09 | 0.14 |
| I, $k = 4$ | 1476 | 0.15 | 0.20 |
| I, $k = 3$ | 1192 | 0.24 | 0.29 |
| I, $k = 2$ | 908 | 0.38 | 0.42 |
| I, $k = 1$ | 624 | 0.61 | 0.65 |
| II | 680 | 0.61 | 0.51 |
|  | 340 | 1.00 | 1.00 |
|  | 376.5 | 0.83 | 1.25 |
|  | 413 | 0.72 | 1.56 |
|  | 284 | 0.96 | 1.77 |
|  | 320 | 0.81 | 2.10 |
|  | 228 | 0.92 | 3.02 |
|  | 150 | 1.34 | 1.56 |

[a] Ar = 

hydrin and 0.03 mole tetramethylammonium chloride at reflux temperatures for 1 hr. A 50% solution of caustic soda, 0.8 mole, was then added over 1 hr. The solution was maintained at reflux for a further 30 min, neutralized with an aqueous solution of $Na_2HPO_4$. After separation of the aqueous layer, the organic layer was concentrated in a rotary evaporator. The epoxide equivalent of the final product was 5.55 eq/kg.

## Gel Permeation Chromatography (GPC)

The GPC analysis of the liquid resin which had been subjected to further glycidylation was carried out on two different gels, namely, a polystyrene gel, Biorad SX2, and a dextran gel, Sephadex LH-20. The GPC analysis

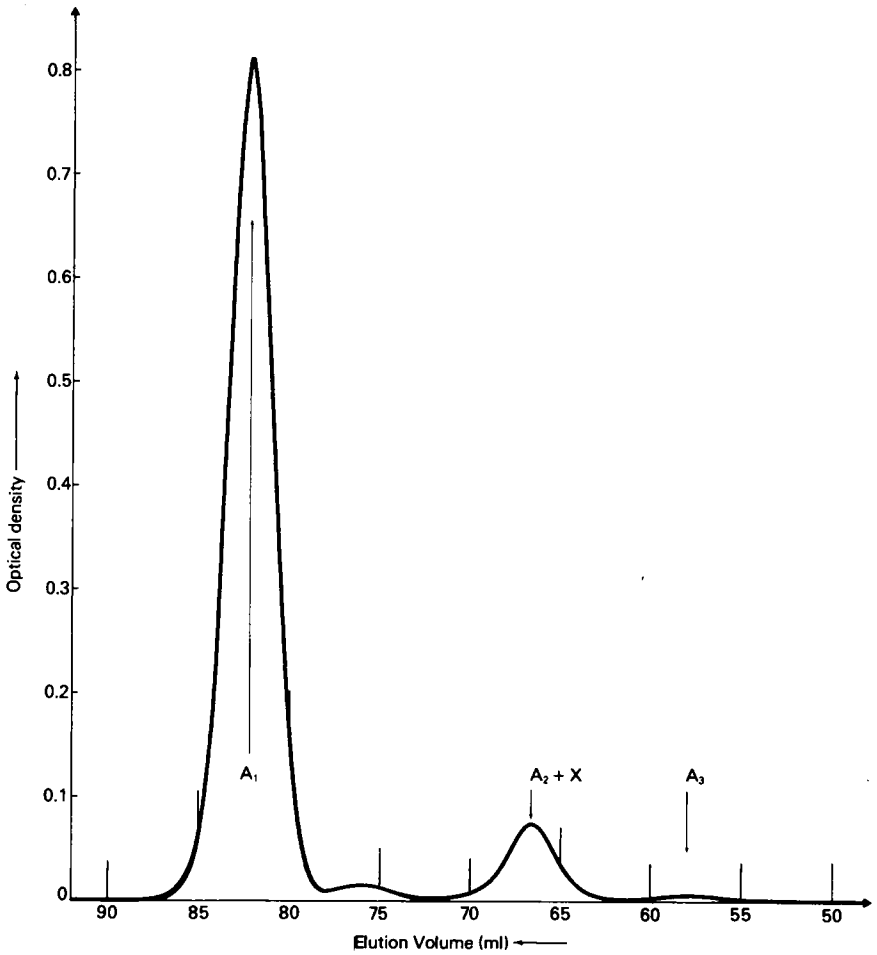



Fig. 1. GPC of a postglycidylated liquid epoxide resin on polystyrene gel Biorad SX2. Solvent is tetrahydrofuran.

of epoxide resins on Biorad SX2 has already been described.[4] Sephadex LH-20 is an epichlorohydrin-crosslinked dextran gel which has been made hydrophobic by reacting some of the hydroxyl groups on the polymer matrix with propylene oxide. When this gel is swollen in a chloroform/ethanol (2:1 v/v) mixture, it exhibits not only molecular sieving properties, but also adsorption properties. Molecules containing chlorohydrin and phenolic groups are, through adsorption on the gel matrix, well separated from their corresponding diepoxides. The positions of GPC peaks were characterized by the distribution coefficients, $K_d$, defined as

$$K_d = (V_e - V_0)/(V_m - V_0)$$

where $V_e$ = elution volume of the peak, $V_0$ = void volume (i.e., the volume where the very high molecular weight molecules are completely excluded

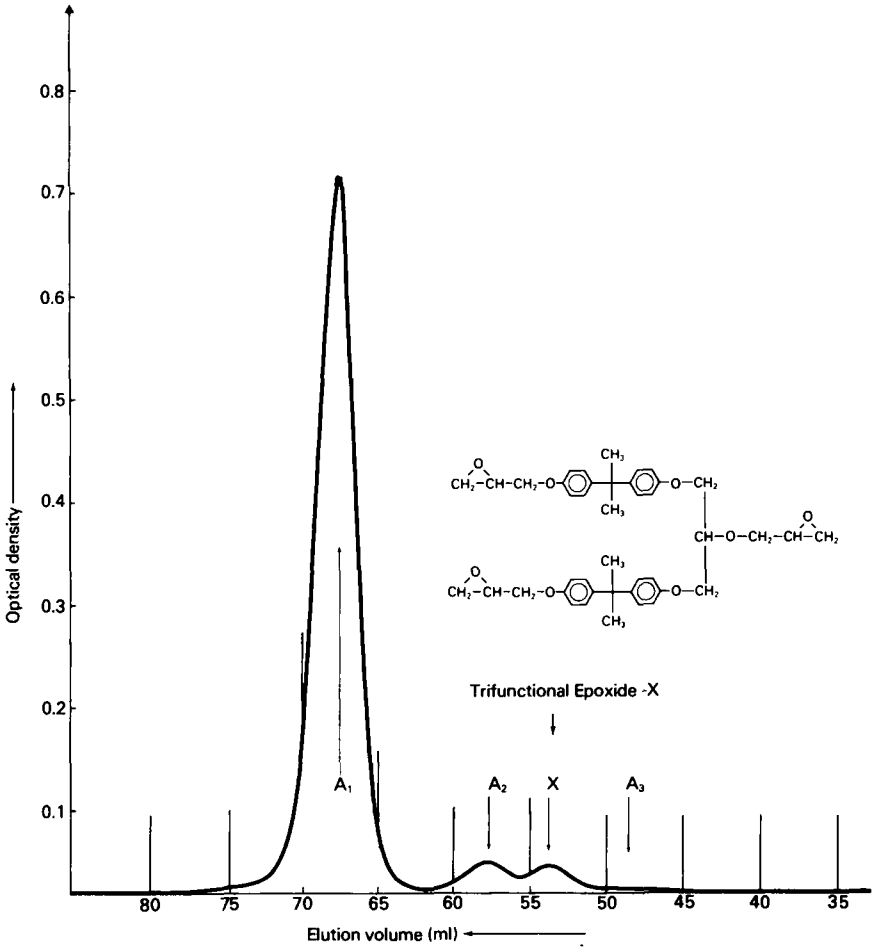


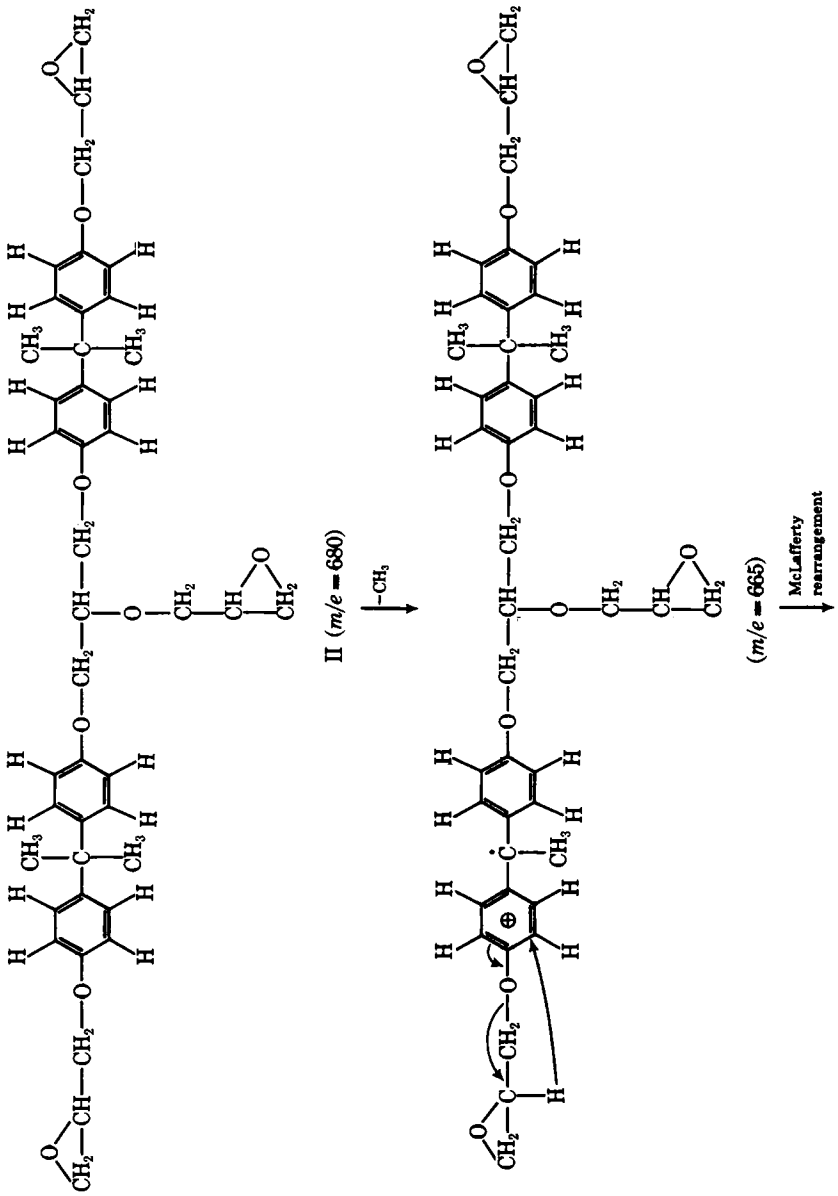

Fig. 2. GPC of a postglycidylated liquid resin on dextran gel, Sephadex LH 20. Solvent is a chloroform/ethanol mixture (2:1, v/v).

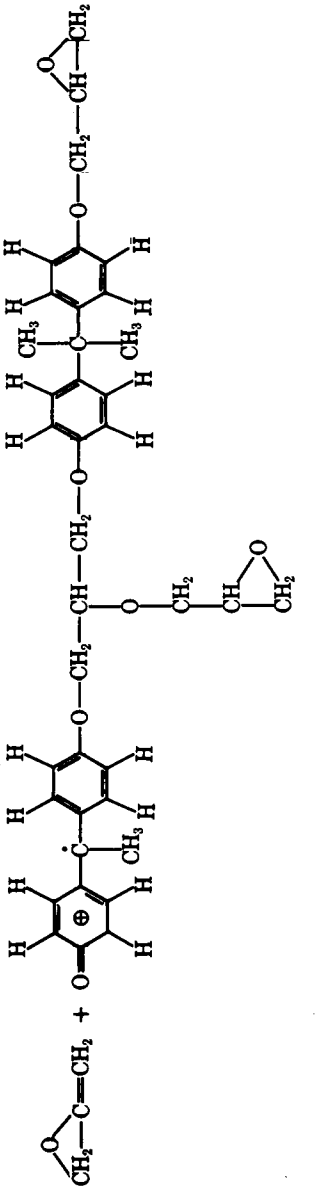
from the gel), and $V_m$ = elution volume of diglycidyl ether of bisphenol A ($k = 0$ in formula I).

Table I lists the $K_d$ values for various compounds when examined by GPC using the two types of gel matrix. The Sephadex gel was packed in glass columns 1 m in length by 2.54 cm internal diameter. The GPC's were carried out at 22°C. A 1% solution of the resin in chloroform was injected, and the detector was a Beckman UV spectrophotometer set at 277 nm.

## RESULTS AND DISCUSSION

The GPC profiles of the postglycidylated resin analyzed on the polystyrene gel Biorad SX2 and Sephadex LH 20 are illustrated in Figures 1 and 2, respectively. The peaks labeled $A_1$, $A_2$, and $A_3$ in Figure 1 and 2 corre-


II (m/e = 680)
−CH3
(m/e = 665)
McLafferty rearrangement



($m/e$ = 609)

Scheme 2

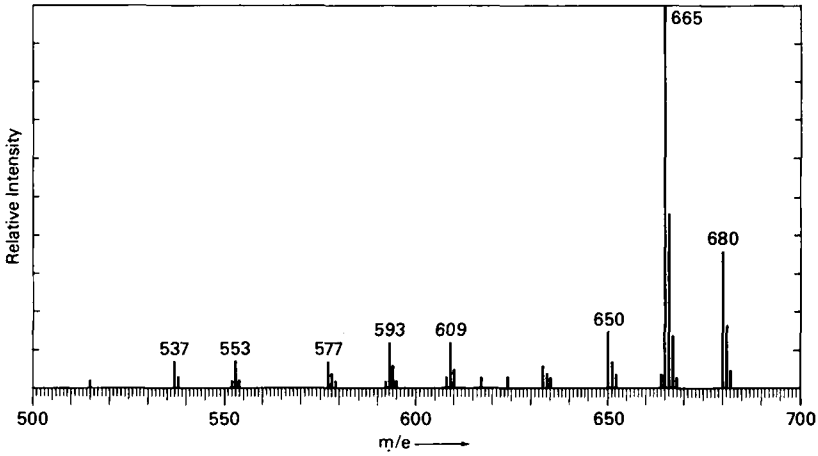



Fig. 3. Mass spectrum of product X present in a postglycidylated liquid epoxide resin. This product was isolated by fractionation on a GPC column packed with Sephadex LH20 (see Fig. 2).

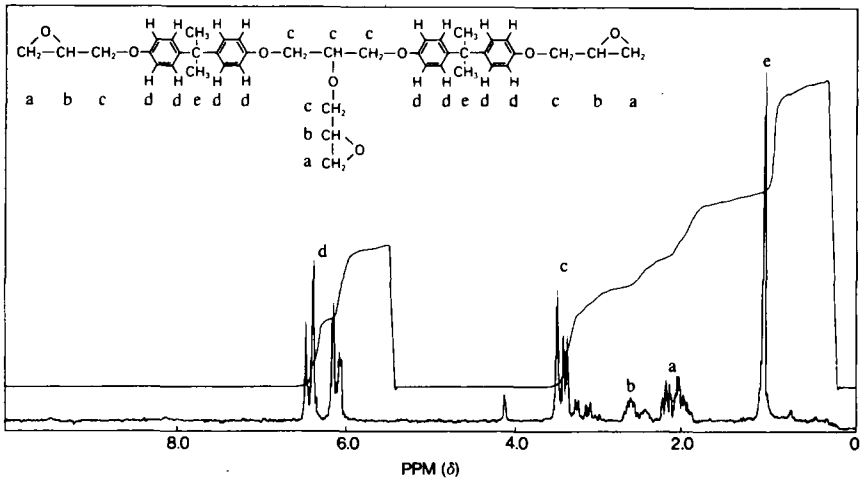



Fig. 4. Proton resonance spectrum (100 MHz) of product X present in a postglycidylated liquid epoxide resin. This product was isolated by fractionation on a GPC column packed with Sephadex LH 20.

spond to the oligomeric diepoxides (I) with oligomer numbers $k = 0$, 1, and 2, respectively. The peak labelled X in Figure 2 was isolated and its structure determined by spectroscopic analysis. The mass spectrum is illustrated in Figure 3. The presence of the parent molecular ion ($m/e$ = 680) and the appearance of fragment ions characteristic of the fragmentation of model diepoxides such as the diglycidyl ether of bisphenol A (scheme 2; pp. 614–615) suggests that the proposed structure II is correct.

The 100 MHz NMR spectrum of the isolated peak X is illustrated in Figure 4. The peak assignment and the relative number of protons confirm the proposed structure II.

When the same resin was analyzed on the polystyrene gel with tetrahydrofuran as eluant (Fig. 1), the peaks corresponding to the oligomeric diepoxide, $k = 1$ (molecular weight = 624), coincided with the peak for the product X (II, molecular weight = 680). In this case, the solute molecules containing hydroxyl groups were hydrogen bonded to the solvent tetrahydrofuran (molecular weight = 72). Thus, the solvated dimeric diepoxide (I, $k = 1$) now has an apparent molecular weight of 696 and elutes at practically the same elution volume as the novel trifunctional trisepoxide with the structure II.

It is necessary to remember that the production of this trifunctional epoxide (II) was carried out under conditions designed to promote the epoxide–aliphatic OH reaction (large excess epichlorohydrin, tetramethylammonium chloride as catalyst). In the synthesis of epoxide resins where NaOH is used as catalyst, the alcohol/epoxide reaction plays an important role only after the phenol is consumed, i.e., when the catalytic species changes from phenoxide ion to alkoxide ion.[5] The broad agreement between the theoretically predicted and experimentally measured molecular weight distribution of solid epoxide resins[4] and the small extent of branching actually measured for these resins[2] also tend to confirm this view.

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4. H. Batzer and S. A. Zahir, *J. Appl. Polym. Sci.*, **19**, 585 (1975).
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