

# Epoxy Resins Based on Aromatic Glycidylamines.

## IV. Preparation of *N,N,N',N'*-Tetraglycidyl-4,4'-Diaminodiphenylmethane from Aniline and Analysis of the Product by GPC and HPLC

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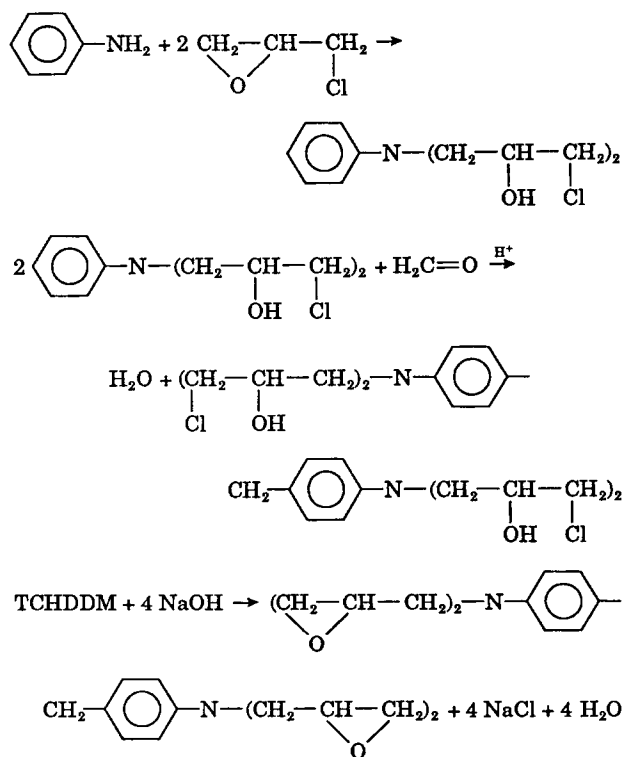
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### SYNOPSIS

Epoxy resins containing *N,N,N',N'*-tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) were prepared from aniline and epichlorohydrin and analyzed by GPC and HPLC. The product composition was compared with that of resins prepared from 4,4'-diaminodiphenylmethane (DDM) and epichlorohydrin, which had been analyzed in our previous work. A new byproduct designated Y4 was isolated by semipreparative HPLC and identified by NMR and mass spectroscopy. The course of formaldehyde condensation with *N,N*-dichlorohydrin of aniline (DCHA) was followed by GPC and HPLC and the mechanism of formation of Y4 was proposed on the basis of obtained results. Attention was also paid to the differences in reactivity of DCHA diastereoisomers.

### INTRODUCTION

Technical-grade TGDDM is commonly employed as a matrix for high-performance composites, especially in the aerospace industry, and its synthesis has therefore received considerable attention. TGDDM is usually prepared by dehydrochlorination of *N,N,N',N'*-tetrachlorohydrin of 4,4'-diaminodiphenylmethane (TCHDDM) with sodium hydroxide. Classically, DDM is used as the starting material<sup>1</sup> and the preparation then proceeds in two steps, where DDM is first added on epichlorohydrin to yield TCHDDM which is then dehydrochlorinated in the second step. In another approach aniline is used as the starting material.<sup>2,3</sup> In this case the synthesis proceeds in three steps according to the following scheme:



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Aniline is first added on epichlorohydrin to yield DCHA. DCHA is then allowed to condensate with formaldehyde to TCHDDM. The latter is finally dehydrochlorinated by sodium hydroxide.

The goal of this study is a comparison of resins prepared by the above two synthetic routes.

## EXPERIMENTAL

### Synthesis of TGDDM

A mixture of aniline (558.6 g), epichlorohydrin (1182 g), and water (32 g) was stirred for 3 h at 60°C and then for 4.5 h at 80°C. Hydrochloric acid (121.2 g, 35.2%) was added in one portion, aqueous formaldehyde (270.6 g, 36.6%) was added over 30 min, and the mixture was kept at 80°C for 4.5–5 h. Methyl isobutyl ketone (800 g) and 1000 mL of 5% aqueous NaOH solution (to neutralize HCl) were added. The aqueous layer was then separated and 56% aqueous trimethyl-2-chloroethyl ammonium chloride solution (41.6 g) was added to the organic layer, the mixture was heated to 50°C, and 42% aqueous NaOH solution (1564 g) was added over 30–40 min. The mixture was stirred for 3 h at 50°C and for 1 additional hour at 70–80°C. Water (1620 g) was then added to dissolve NaCl. The separated organic layer was diluted with methyl isobutyl ketone (500 g), saturated with carbon dioxide, and washed with 540 g of 5% NaCl solution. The solvent was stripped at 120°C and a pressure of 1.3 kPa.

The product was filtered. The epoxide equivalent of a typical product was about 130 g/mol, chlorine content 0.4%.

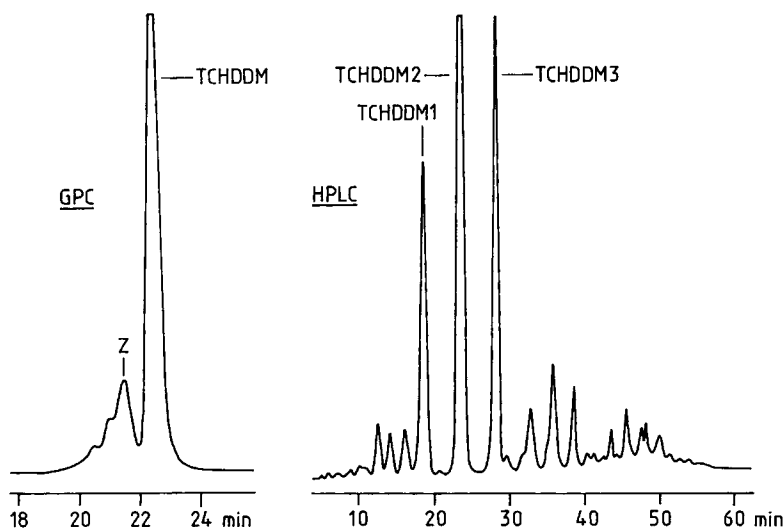
The determination of epoxide equivalent and chlorine content as well as the experimental equipment for HPLC, NMR, and mass spectrometry were described in our previous paper.<sup>4</sup>

GPC and HPLC analyses of TGDDM-based epoxy resins and of the intermediate (TCHDDM) were carried out using the same instrumental conditions as in the case of products prepared from DDM.<sup>5</sup>

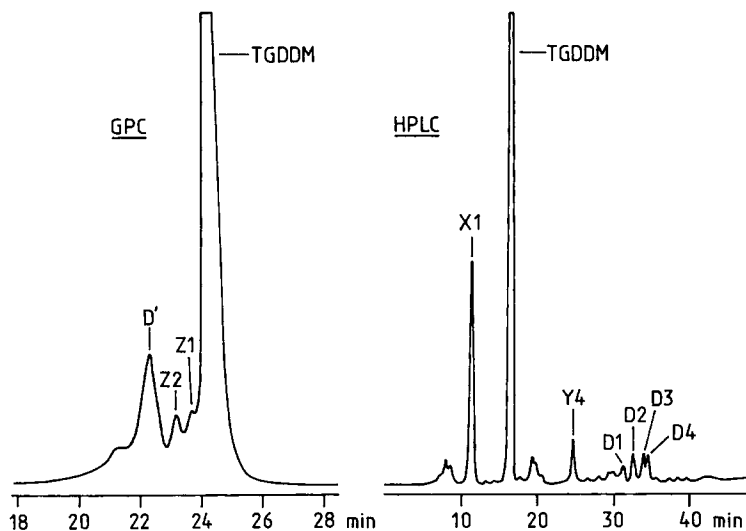
A Separon SGX C18 column (250 × 4 mm) (Tessek Prague) with gradient elution methanol–water (45% methanol at 0 min; 53% methanol at 10 min; 60% methanol at 30 min; 85% methanol at 60 min; 100% methanol from 63 to 65 min) was used for the analyses of samples withdrawn from the reaction mixture during condensation of DCHA with formaldehyde. Samples were injected as 1% solutions in methanol.

## RESULTS AND DISCUSSION

Typical GPC and HPLC curves of TCHDDM obtained by condensation of DCHA with formaldehyde (125 mol % of formaldehyde) are shown in Figure 1, chromatograms of TGDDM prepared by the described procedure in Figure 2. Only peaks of TCHDDM, TGDDM, and X1 can be positively identified in the chromatograms.



**Figure 1** GPC and HPLC chromatograms of TCHDDM prepared by condensation of DCHA with 125 mol % of formaldehyde.



**Figure 2** GPC and HPLC chromatograms of TGDDM-based epoxy resin prepared from aniline by the procedure described in the subsection Synthesis of TGDDM.

TCHDDM separates into three components—diastereoisomers with the respective RS–RS, RS–RR (RS–SS), and RR–RR (RR–SS, SS–SS) configurations of asymmetric carbons.<sup>5</sup> Peak X1 belongs to a 1,2,3,4-tetrahydro-3-hydroxyquinoline derivative.<sup>5</sup>

HPLC analysis of collected GPC fractions has shown that GPC peak D'—in contrast to peak D in resins from DDM—consists of HPLC peaks D1, D2, D3, and D4; peak Z2 in GPC corresponds to HPLC peak Y4.

Comparison of chromatograms of resins prepared from aniline and from DDM shows three major differences. The products from aniline are characterized by (i) the presence of compound Y4, (ii) a high content of compound X1 (typically about 18%, whereas the products prepared from DDM contain some 5% of X1), and (iii) the presence of a higher number of components eluting approximately at the position of dimer D.<sup>5</sup> For comparison, the GPC and HPLC chromatograms of the resin prepared from DDM are shown in the second part of this series.<sup>5</sup>

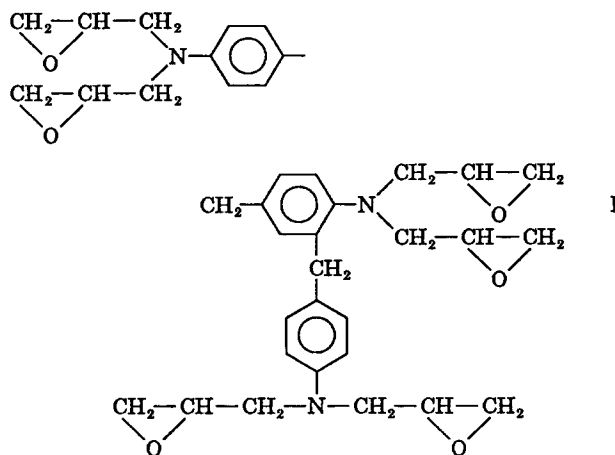
Compounds containing secondary amine hydrogen or chlorine<sup>5</sup> (X2, Y1, Y2, Y3) could be, of course, present in the resins, and the corresponding peaks were indeed found in chromatograms of some samples.

The high content of compound X1 is a specific feature of TGDDM-based epoxies prepared from aniline. It can be associated with the technology of their preparation, where the reaction mixture is thermally exposed for a relatively long time before dehydrochlorination and a higher number of 2-hy-

droxy-3-chloropropyl groups can therefore undergo cyclization.

#### Compound Y4

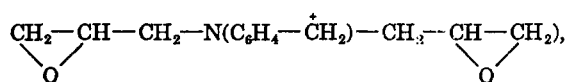
Compound Y4 was isolated by semipreparative HPLC and analyzed by NMR and mass spectrometry. The results lead to the following three-ring structure:



The molecular weight determined by MS is 639. The following major fragmentary ions were found in the mass spectrum:  $m/z = 596$  (the ion which arises after splitting-off of epoxyethyl group from the molecular ion), 582 (splitting-off of 2,3-epoxypropyl group), 218 (the ion

**Table I** Relative Area of Peak Y4 in HPLC Chromatograms of TGDDM-Based Epoxy Resins Prepared with Various Concentrations of Formaldehyde During Condensation of DCHA with Formaldehyde

CH <sub>2</sub> O (mol %) Based on DCHA	Relative Area (%)
100	1.2
110	3.1
125	11.3
150	20.2



118 (the ion  $\cdot\text{CH}_2-\text{C}_6\text{H}_4-\text{N}-\overset{+}{\text{C}}\text{H}_2$ ).

Signals of *p,p'*-methylene bridges (41.1 ppm) and *o,p'*-methylene bridges (36.6 ppm) in the ratio 1:1 were found in <sup>13</sup>C-NMR spectrum of compound Y4. Signals at 58.9 and 59.3 ppm indicate the presence of methylene carbons bonded to nitrogen atoms adjacent to an ortho substitution. The retention times in GPC and HPLC also correspond to a three-nucleus molecule.

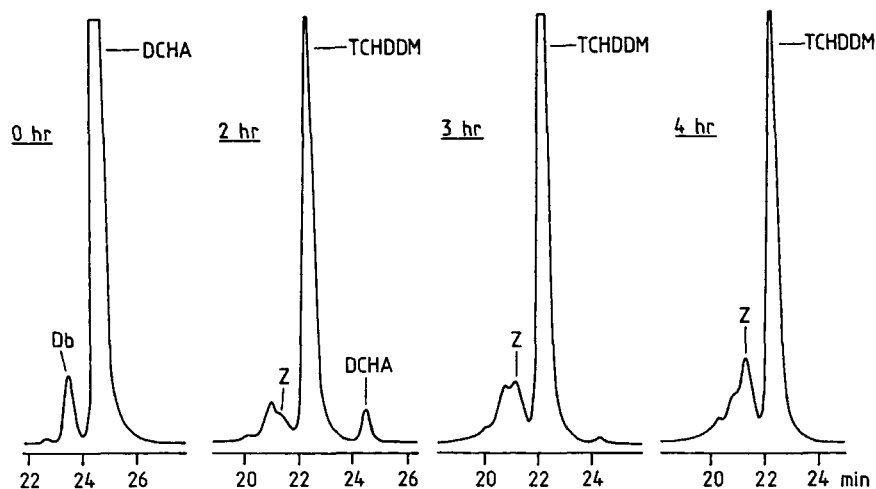
Unlike TCHDDM prepared from DDM, TCHDDM from aniline contains oligomeric compounds eluting approximately between 30 and 40 min. The oligomer peaks in HPLC chromatograms can be divided into two groups: group no. 1 with retention times between 30 and 40 min, group no. 2 with retention times above 40 min. Peak Z in GPC

corresponds to the oligomer group no. 1. The content of compound Y4 increases strongly with increasing concentration of formaldehyde present during condensation of DCHA (Table I).

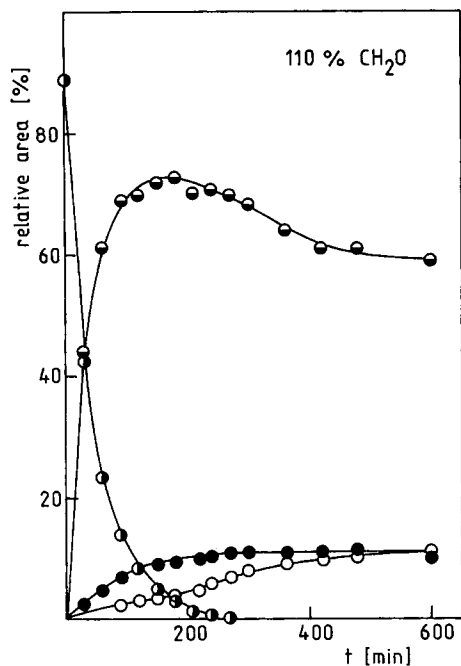
A GPC study of the course of DCHA condensation with formaldehyde showed that at higher formaldehyde concentrations the area of peak Z was markedly higher at the end of the reaction (Fig. 3). A detailed study of condensation by means of HPLC demonstrated that at higher formaldehyde concentrations the content of no. 1 oligomers increases, especially at the end of synthesis, whereas the content of the oligomeric group no. 2—after an initial fast grow—approached an approximately constant value (Figs. 4 and 5).

On the basis of obtained results we suppose that peaks in group no. 1 belong to various diastereoisomers of chlorohydrin of compound Y4. Peaks in group no. 2 probably belong to products formed by condensation of DCHA, dimer Db (present in technical grade DCHA<sup>4</sup>), and formaldehyde. After dehydrochlorination these compounds give rise to compounds D1, D2, D3, and D4. This assumption is supported by the fact that resins prepared from pure, recrystallized DCHA<sup>4</sup> do not contain compounds D1, D2, D3, D4.

It can be seen from Figure 5 that chlorohydrin of compound Y4 arises from TCHDDM. Thermal treatment of TCHDDM (80°C, 8 h) in the absence of formaldehyde (but in the presence of the respective amounts of HCl and water, the latter corresponding to the amount normally introduced with 150 mol % aqueous formaldehyde) proved that oligomers no. 1 do not arise without formaldehyde.



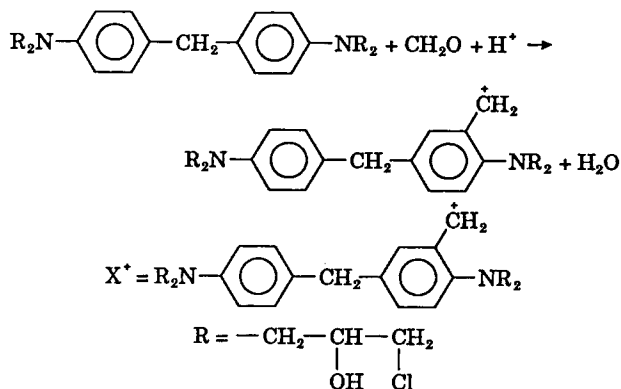
**Figure 3** GPC chromatograms of samples withdrawn during condensation of DCHA with 125 mol % of formaldehyde.



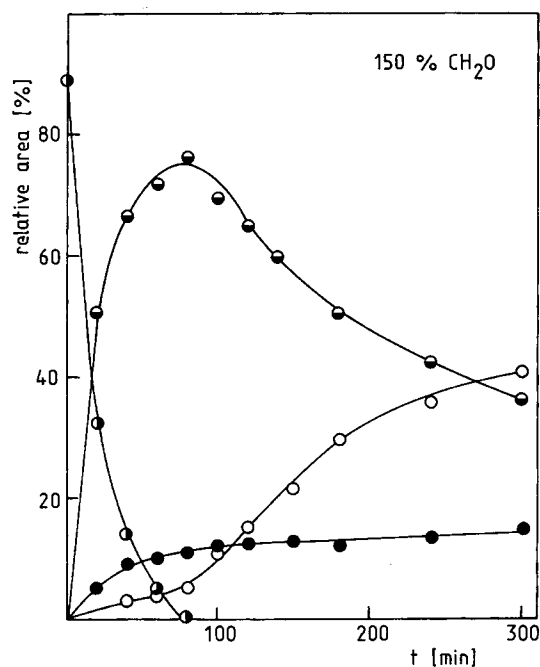
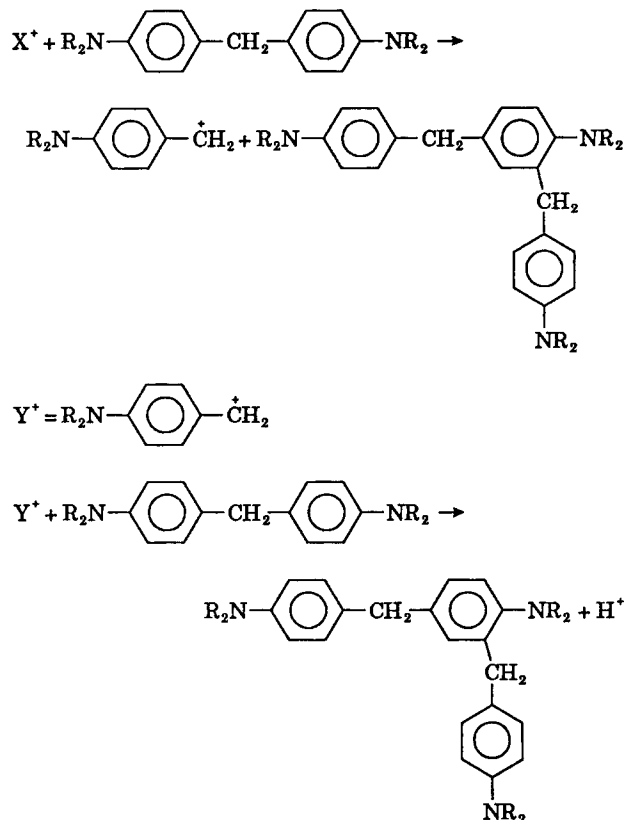
**Figure 4** Time dependences of relative areas of HPLC peaks: (●) DCHA; (○) TCHDDM; (◐) oligomer no. 1; (◑) oligomer no. 2. Condensation of DCHA with 110 mol % of formaldehyde.

Thus, chlorohydrin of compound Y4 must be formed by the reaction of TCHDDM with formaldehyde.

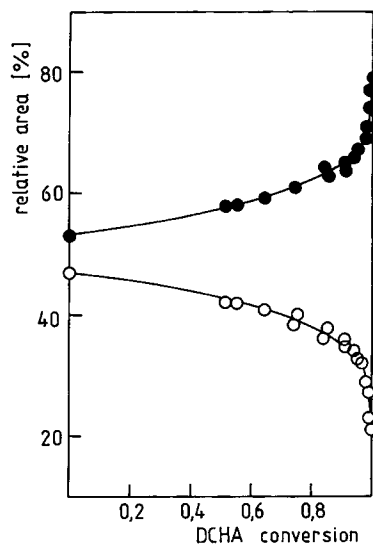
The formation of chlorohydrin of compound Y4 was not studied in more detail, but we propose the following feasible mechanism. Cation  $X^+$  arises by the reaction of TCHDDM with formaldehyde in an acidic medium,



$X^+$  then attacks TCHDDM in p-position to the  $-\text{NR}_2$  group, yielding chlorohydrin of compound Y4 and cation  $Y^+$ , which can react with an additional molecule of TCHDDM:



**Figure 5** Time dependences of relative areas of HPLC peaks: (●) DCHA; (○) TCHDDM; (◐) oligomer no. 1; (◑) oligomer no. 2. Condensation of DCHA with 150 mol % of formaldehyde.



**Figure 6** Relative content of DCHA diastereoisomers during condensation of DCHA with formaldehyde: (○) DCHA1; (●) DCHA2.

Figure 6 demonstrates that the reactivity of individual DCHA diastereoisomers with respect to formaldehyde differs significantly: Diastereoisomer DCHA1 (with RS configuration of asymmetric carbons<sup>4</sup>) reacts more readily than diastereoisomer DCHA2 [with RR (SS) configuration<sup>4</sup>].

## CONCLUSIONS

TGDDM-based epoxy resins prepared from aniline differ from resins from DDM by (i) a higher content of 1,2,3,4-tetrahydro-3-hydroxyquinoline derivative X1, (ii) a different type of oligomer (D1, D2, D3, D4), and (iii) the presence of the three-nucleus by-product Y4, which arises from the reaction of TCHDDM with formaldehyde followed by dehydrochlorination of the product. The diastereoisomers of DCHA exhibit different reactivity with respect to formaldehyde, the diastereoisomer with RS configuration being the more reactive.

## REFERENCES

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