Epoxy Resins Based on Aromatic Glycidylamines. II. Preparation of *N,N,N′,N′*-Tetraglycidyl-4,4′-Diaminodiphenylmethane from 4,4′-Diaminodiphenylmethane: Analysis of Product by GPC and HPLC

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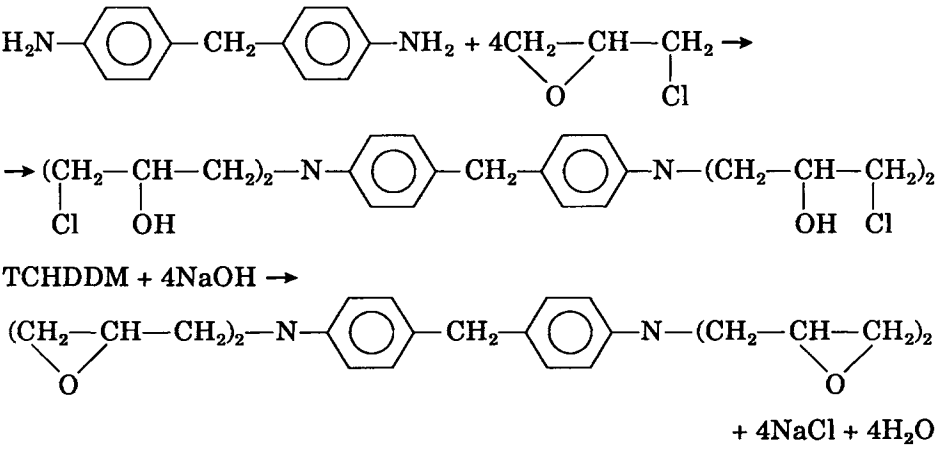
Synopsis

N,N,N′,N′-tetrakis(2,3-epoxypropyl)-4,4′-diaminodiphenylmethane (*N,N,N′,N′*-tetraglycidyl-4,4′-diaminodiphenylmethane, TGDDM) and an intermediate of its synthesis, *N,N,N′,N′*-tetrakis(2-hydroxy-3-chloropropyl)-4,4′-diaminodiphenylmethane (*N,N,N′,N′*-tetrachlorohydrin of 4,4′-diaminodiphenylmethane, TCHDDM), were analyzed by GPC and HPLC. The main impurities were identified by analogy with *N,N*-diglycidylaniline (DGA) and *N,N*-dichlorohydrin of aniline (DCHA) that had been analyzed in our previous work,[1] and by IR, NMR, and mass spectroscopy after their isolation by semipreparative HPLC. Attention was also paid to quantitative determination of the TGDDM content and to GPC elution behavior of TGDDM and TCHDDM-based oligomers.

INTRODUCTION

TGDDM is the most commonly used glycidylamine. Epoxy resins containing TGDDM are widely used in the manufacturing of graphite fiber-reinforced composites for aerospace, machine, and electrotechnical industry applications. The cured materials have excellent mechanical and insulating properties even at high temperatures, good resistance to both water and chemical agents.

Synthesis of TGDDM proceeds, similarly as in the case of DGA, in two steps according to the following scheme:



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4,4'-Diaminodiphenylmethane (DDM) is first added on epichlorohydrin to yield TCHDDM which is then dehydrochlorinated by sodium hydroxide. This scheme does not show all reactions that proceed during the synthesis of TGDDM. The technical product (epoxy resin) contains about 75% of TGDDM; the residual byproducts influence unfavorably storage stability, viscosity, reactivity, with respect to curing agents, the T_g-values of cured materials, and the properties of cured materials above 200°C.[2-4]

Identification of major impurities in technical TGDDM is the aim of this work.

EXPERIMENTAL

Synthesis of Technical TGDDM

DDM (198 g), epichlorohydrin (393 g), methyl isobutyl ketone (170 g), and water (36 g) were stirred for 8 h at 80°C. The temperature was then lowered to 50°C, 56% aqueous trimethyl-2-chloroethylammonium chloride solution (13.8 g) was added in one portion and 42% aqueous NaOH solution (476 g) was added with stirring over 30 to 40 min. The mixture was stirred for 3 h at 50°C and 1 additional hour at 70–80°C. Water (454 g) was then added to dissolve salt. The separated organic layer was saturated with carbon dioxide, diluted with methyl isobutyl ketone (230 g), and then washed with 150 g 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 typical products (obtained in 94 to 95% yield) was about 120 g/mol (theory 105.6 g/mol) and the chlorine content was 0.35 to 0.45%.

Synthesis of Pure TCHDDM

A mixture of DDM (198 g), epichlorohydrin (416 g), methyl isobutyl ketone (400 g), and water (36 g) was kept at room temperature for 3 weeks. At first the mixture had to be cooled because the reaction was exothermic. The obtained crystals were recrystallized twice from ethanol. The yield of the white crystals of TCHDDM with mp 138 to 139°C and chlorine content 24.79% (theory 24.95%) was 52%. The purity was 97.7% according to HPLC.

Synthesis of Pure TGDDM

Pure TCHDDM (285 g), methyl isobutyl ketone (210 g), and 56% aqueous trimethyl-2-chloroethylammonium chloride (6.9 g) were heated to 50°C and 42% aqueous NaOH solution (238 g) was added with stirring over 30 to 40 min. The mixture was stirred for 3 hours at 50°C and then for 1 h at 70 to 80°C. Water (227 g) was then added; the separated organic layer was saturated with carbon dioxide and washed with 75 g of 5% aqueous NaCl solution. The solvent was stripped at 120°C and a pressure of 1.3 kPa. The product was filtered. The epoxide equivalent of the obtained product (95% yield) was 112 g/mol, the chlorine content was 0.26%, viscosity at 25°C was 70 Pa s, and purity was 92.7% according to HPLC.

Gel Permeation Chromatography and High Performance Liquid Chromatography

The reversed-phase HPLC with gradient elution was carried out using Separon SGX C 18 columns (250 × 4 mm for analytical and 250 × 8 mm for semipreparative HPLC). A tetrahydrofuran (THF)–methanol–water gradient (10% THF, 40% methanol at 0 min; 25% THF, 47% methanol at 42 min; 25% THF, 75% methanol from 46 to 50 min) was used for the analyses of TGDDM. Samples of TGDDM were prepared as 0.35% solutions in THF. A methanol–water gradient (60% methanol from 0 to 15 min; 84% methanol at 57 min; 100% methanol from 60 to 62 min) was used in analyses of TCHDDM. The TCHDDM samples were injected as 0.65% solutions in methanol. In GPC, the concentration of the injected THF solutions was 0.20% (TGDDM) and 0.15% (TCHDDM). UV detection at 280 nm was mostly used. For some analyses of TGDDM, detection at 254 nm was used as well. The concentration of the samples in this case was sevenfold lower.

To identify the HPLC peaks of *N,N,N'*-triglycidyl-N'-(2-hydroxy-3-chloropropyl)-4,4'-diaminodiphenylmethane (TGCHDDM), TGDDM was derivatized with HCl and NaOH. To identify compounds containing hydroxyl groups or amine hydrogens, TGDDM was treated with acetic anhydride in the presence of *N*-methylimidazole.[1]

The determination of epoxide equivalent, chlorine content, and the instrumental equipment for HPLC, IR, NMR, and mass spectroscopy were described in our previous work.[1]

RESULTS AND DISCUSSION

Representative GPC and HPLC chromatograms of TGDDM-based epoxy resin are in Figure 1, chromatograms of technical TCHDDM are in Figure 2. Only peaks of TGDDM and TCHDDM can be unambiguously identified in the chromatograms.

TCHDDM separates into three components in HPLC. The elution times of TCHDDM1, TCHDDM2, and TCHDDM3 almost coincide in GPC and, owing to the presence of four asymmetric carbon atoms in the molecule TCHDDM, the peaks can be assigned to the various diastereoisomers. The areas of peaks TCHDDM1 : TCHDDM2 : TCHDDM3 are approximately in the ratio 1 : 2 : 1. TCHDDM1 has been identified as a diastereoisomer with different configuration of asymmetric carbons on *N* and *N'* (RS–RS), TCHDDM2 has the same configuration on *N* and different configuration on *N'* (RR–RS, SS–RS), and TCHDDM3 has the same configuration of asymmetric carbons on both *N* and *N'* (RR–RR, SS–SS, RR–SS). The identification of TCHDDM2 is based on the fact that the theoretical number of arrangements of asymmetric carbons in TCHDDM2 is twice that in TCHDDM1 or TCHDDM3. TCHDDM1 and TCHDDM3 have been isolated by semipreparative HPLC and their configuration has been determined by ^{1}H-NMR spectroscopy. The determination is based on the shift and splitting of ^{1}H NMR signals of the chlorohydrin groups after addition of $Eu(TFC)_3$.[1]

To determine the relationship between the GPC and HPLC curves and to aid the chromatograms interpretation, the GPC peaks TGDDM, Z1, D, and T

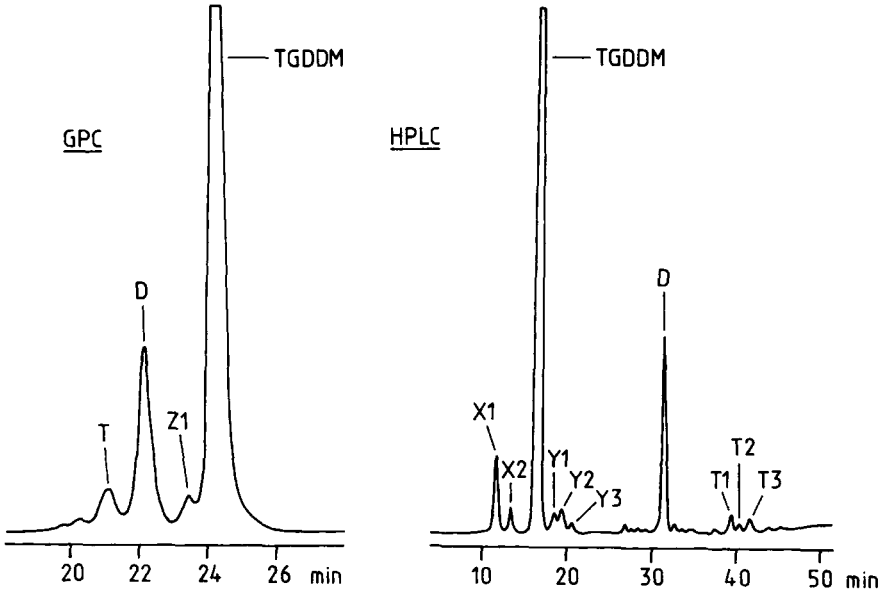


Fig. 1. GPC and HPLC chromatograms of TGDDM-based epoxy resin.

were collected and analyzed by HPLC. The TGDDM peak in GPC consists of HPLC peaks TGDDM, X1 and X2. The peak Z1 in GPC consists of peaks Y1, Y2, and Y3. The peak D in GPC corresponds to the single HPLC peak D. The peak T in GPC includes HPLC peaks T1, T2, and T3.

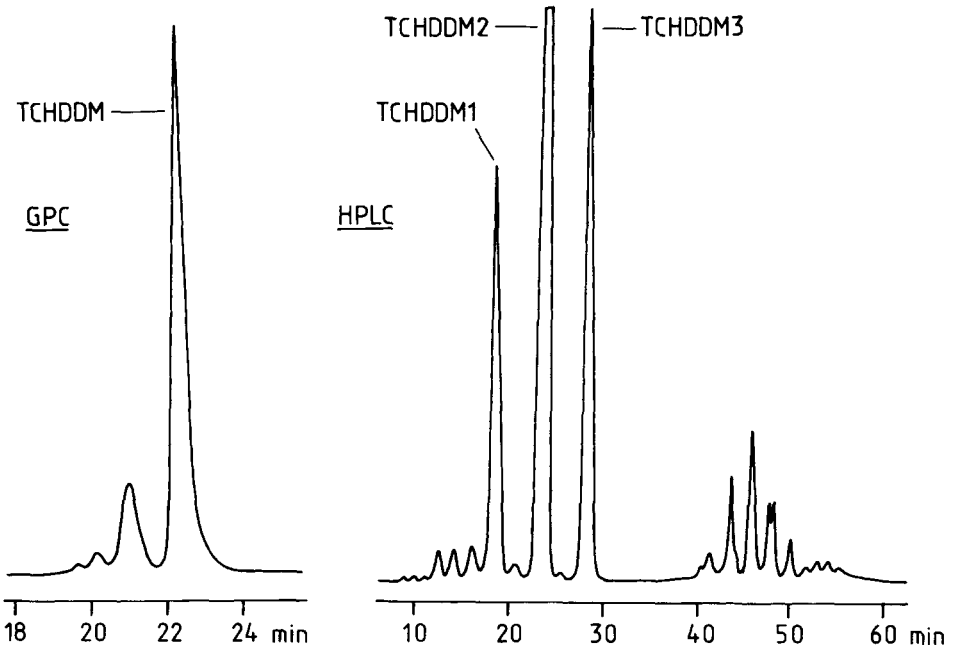
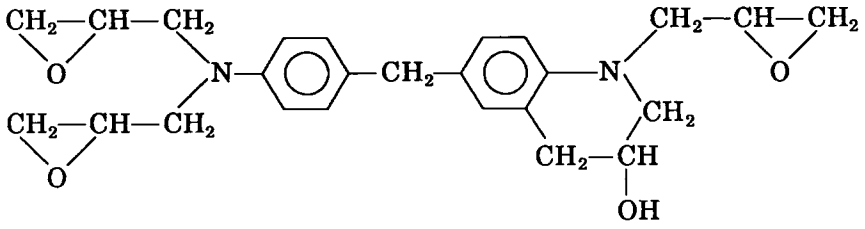


Fig. 2. GPC and HPLC chromatograms of TCHDDM.

Compound X1

Compound X1 has the same molecular weight (determined by MS) as TGDDM. An analogy with DGA and analysis of IR and NMR spectra suggest following structure



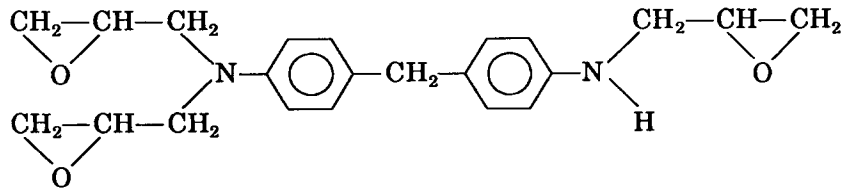
I

The signals of the carbon atom with the chemical shift 121.4 ppm in the ^{13}C-NMR spectrum corresponds to the ortho-substitution on the aromatic ring. The signal at 64.3 ppm indicates the presence of a secondary hydroxyl group on six-membered saturated ring. The presence of a hydroxyl group is confirmed by a broad diffuse band at 3400 cm^{-1} in the IR spectrum, corresponding to the stretching vibration $\nu(O-H)$. The absorption bands $\nu(C-O) + \delta(O-H)$ at 1050 and 1070 cm^{-1} confirm the presence of a secondary hydroxyl group, where the α-carbon atom forms a part of a saturated six-membered ring. The presence of a hydroxyl group in the molecule of X1 is also in agreement with the significant increase of retention time after derivatization with acetic anhydride.

Compound I can be formed by intramolecular cyclization of one chlorohydrin group of TCHDDM at elevated temperatures and dehydrochlorination of the product, or by thermal treatment of TGDDM. Both mechanisms were verified experimentally (Figs. 3 and 4).

Compound X2

The content of compound X2 was markedly higher in those TGDDM samples where the addition of DDM on epichlorohydrin was not purposefully completed. The maximum of UV absorption of X2 is shifted to lower wavelengths in comparison with TGDDM, similarly as in the case of the pair *N*-glycidylaniline (GA)–DGA (GA 241 nm, DGA 250 nm; X2 259 nm, TGDDM 262 nm). After the treatment with acetic anhydride, the retention of the acetylated product slightly decreases as in the case of GA. We suppose that this peak belongs to *N,N,N'*-triglycidyl-4,4'-diaminodiphenylmethane (TrGDDM).



II

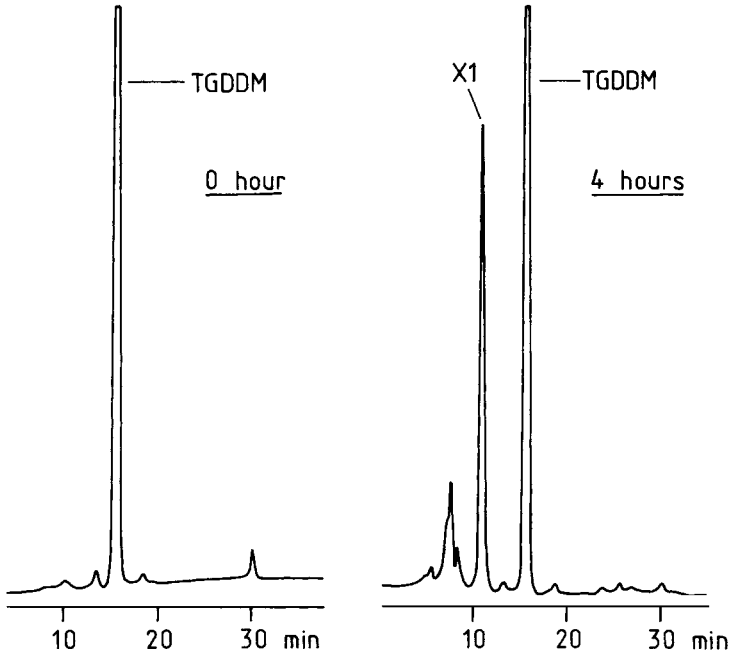


Fig. 3. HPLC chromatograms of TGDDM prepared from TCHDDM thermally treated at 110°C.

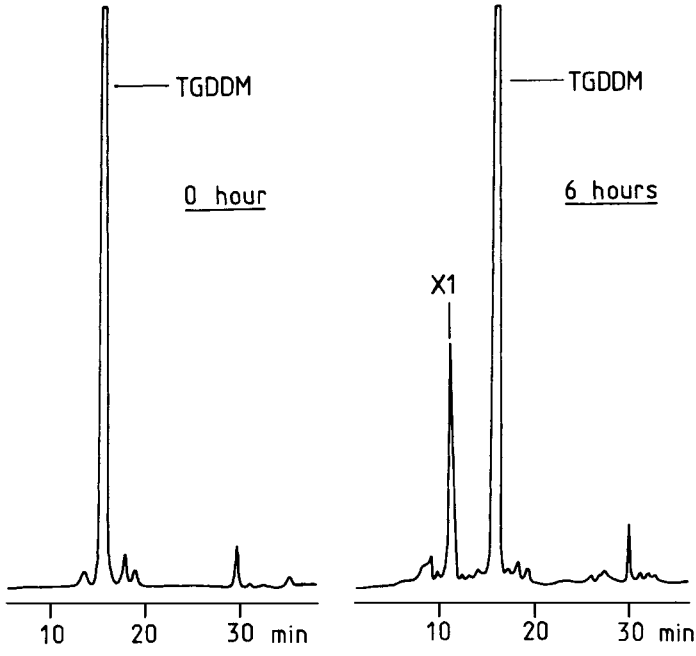
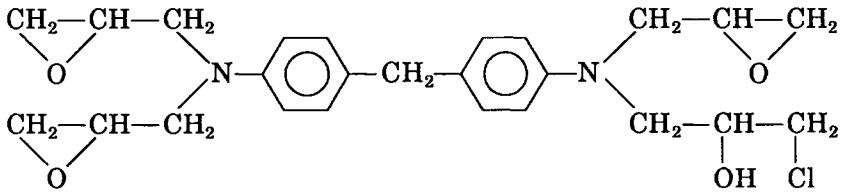


Fig. 4. HPLC chromatograms of TGDDM before and after thermal treatment at 180°C.

Compound Y1

Peak Y1 is more pronounced in chromatograms of samples with a higher chlorine content. The area of peak Y1 markedly increases after addition of HCl on TGDDM. On the contrary, peak Y1 fully disappears after the treatment of TGDDM with NaOH. Thus, peak Y1 may be assigned to *N,N,N'*-triglycidyl-*N'*-(2-hydroxy-3-chloropropyl)-4,4'-diaminodiphenylmethane (TGCHDDM)



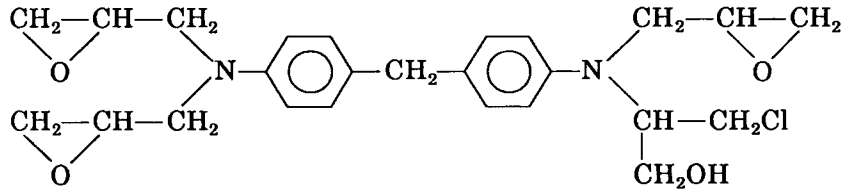
III

which may be present owing to incomplete dehydrochlorination. The presence of a chlorine atom is evident from MS spectrum and molecular weight also corresponds to this compound. The higher retention time of TGCHDDM in comparison with that of TGDDM is consistent with the separation mechanism of reversed-phase HPLC, where the presence of chlorine increases retention; the lower elution time of this compound (peak Z1) in GPC is in agreement with higher molecular weight of TGCHDDM and with the possibility of association of its hydroxyl group with THF.

Peak Y1 was not present in chromatograms of some samples, although all samples contained several tenths percent of chlorine determined by saponification. Consequently, other peaks must correspond to chlorine-containing compounds.

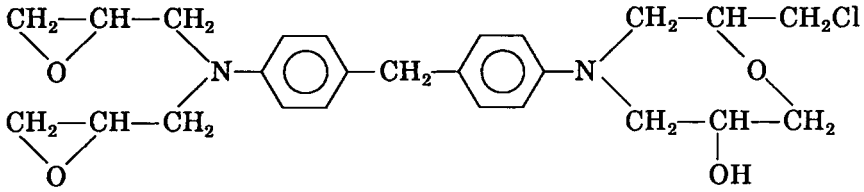
Compounds Y2 and Y3

Compounds Y2 and Y3 have the same molecular weight (determined by MS) as TGCHDDM, and the presence of one chlorine atom is evident from their MS spectra. As the relative area of peaks Y1 + Y2 is directly proportional to the chlorine content determined by saponification (the chlorine in chloromethyl groups of compound V is not determined by this method) (Fig. 5), we suppose compound Y2 to be *N,N,N'*-triglycidyl-*N'*-(1-hydroxy-3-chloro-2-propyl)-4,4'-diaminodiphenylmethane



IV

which can arise by an abnormal attack of amino group on epichlorohydrin.[5] The 1-hydroxy-3-chloro-2-propyl group undergoes dehydrochlorination with difficulty,[6] and thus the relative area of peak Y2 is not changed after treatment of TGDDM with NaOH. Since it has the same molecular weight as TGCHDDM and contains chlorine, compound Y3 can contain a seven-membered ring

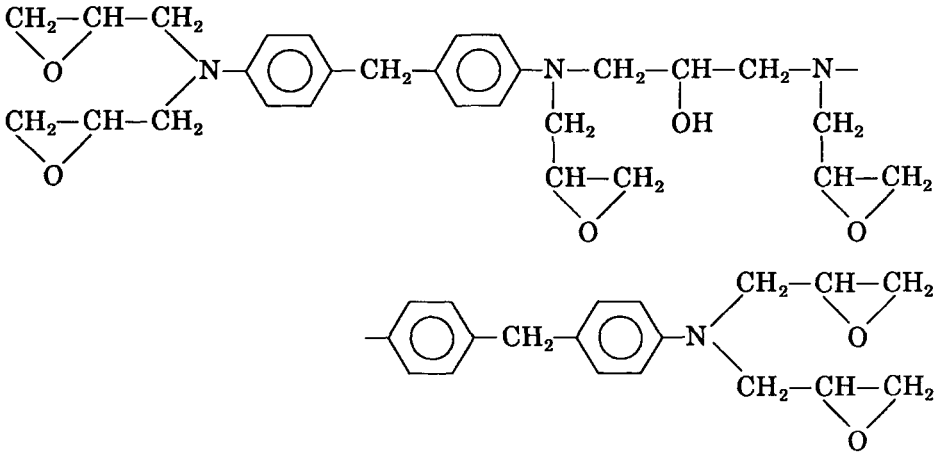


V

which arises from dehydrochlorination of two neighboring chlorohydrin groups.

Compound D

An analogy with DGA[1] allows us to suppose that compound D is dimer:



VI

This assumption is supported by the presence of a signal at 68.6 ppm in ^{13}C-NMR spectrum and of the absorption band $\nu(C-O) + \delta(O-H)$ at 1100 cm^{-1} in IR spectrum, which correspond to a secondary hydroxyl group in an aliphatic chain. The considerable increase of retention time after derivatization with acetic anhydride confirms the presence of a hydroxyl group in the molecule of compound D. The presence of dimer VI in TGDDM-based epoxy resins has been assumed by some authors.[7,8]

Oligomers

The presence of oligomers with higher molecular weight than that of dimer VI is evident from GPC chromatograms. We assume these compounds to be the trimer and tetramer and small amount of higher oligomers of similar struc-

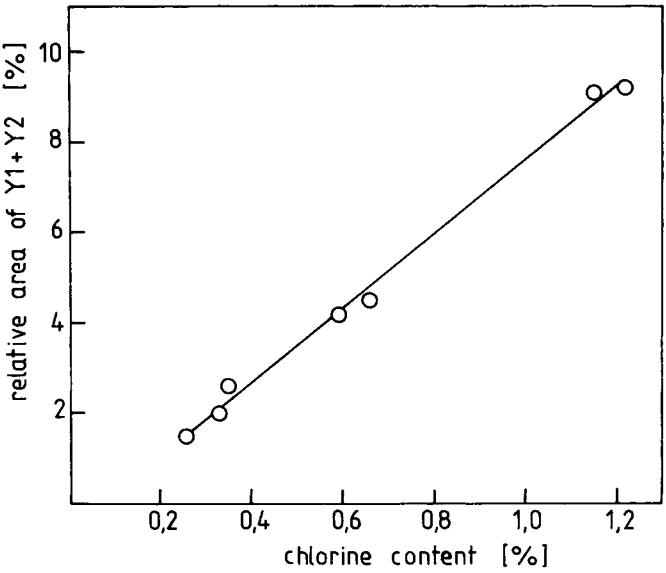


Fig. 5. The relative area of peaks Y1 + Y2 vs. the chlorine content determined by saponification.

ture as dimer VI. Elution times of compounds T1, T2, and T3 are identical in GPC; thus, it may be assumed that these compounds correspond to the isomeric trimers (branched and linear isomer, diastereoisomers). The molecular weight of individual oligomers is given by the equation $M = 422 + 366.n$, where $n = 0$ for TGDDM, $n = 1$ for dimer VI, $n = 2$ for trimer, etc.

GPC calibration curves of TGDDM and TCHDDM-based oligomers are shown in Figure 6. The curves were obtained by relating the logarithms of molecular weight to the elution times of DGA, TGDDM and its oligomers, and of DCHA, TCHDDM, and its oligomers. A very good correlation of both dependences supports the proposed oligomer structure. The calibration curves of TGDDM and TCHDDM-based oligomers differ markedly. Taking into account that THF can associate with hydroxyl groups,[9] one obtains a single molecular weight–elution time relationship by adding multiples of THF molecular weight corresponding to the number of hydroxyl groups to the molecular weight of individual compounds (Fig. 6B).

TGDDM Content

The content of TGDDM is an important measure of the quality of TGDDM-based epoxy resins, as it influences viscosity, storage stability, and some properties of cured resins. HPLC analyses of samples differing in the content of TGDDM have shown that the relative area of TGDDM peak (detection at 280 nm) corresponds approximately to the actual TGDDM content determined by means of calibration of detector response by pure TGDDM (obtained by semi-preparative HPLC). Detection at 254 nm worsens the estimation of TGDDM content. Owing to the coelution of TGDDM and compounds X1, X2, GPC is less suitable for the determination of TGDDM content, but it is very sensitive with regard to the detection of even small amount of oligomers.

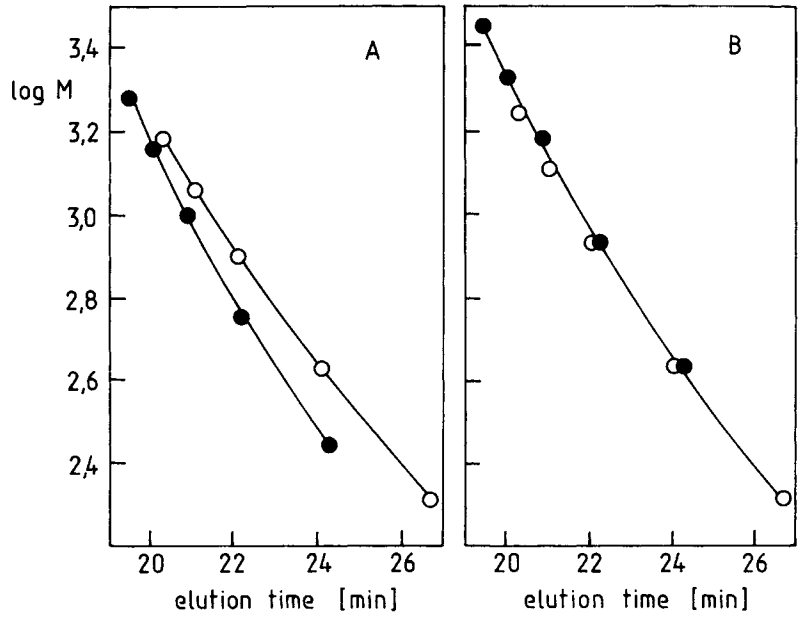


Fig. 6. GPC calibration curves for TGDDM (○) and TCHDDM (●) based oligomers: (A) without association with THF and (B) with association of hydroxyl groups with THF.

CONCLUSIONS

N,N,N'-triglycidyl-4,4'-diaminodiphenylmethane, *N,N,N'*-triglycidyl-*N'*-(2-hydroxy-3-chloropropyl)-4,4'-diaminodiphenylmethane and two chlorine-containing compounds of the same molecular weight, 1,2,3,4-tetrahydro-3-hydroxyquinoline compound of structure I, dimer VI, and higher oligomers of similar structure were identified as major byproducts in epoxy resins based on *N,N,N',N'*-tetraglycidyl-4,4'-diaminodiphenylmethane. The content of TGDDM can be estimated from the relative area of its peak in HPLC chromatogram registered with detection at 280 nm.

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