Epoxy Resins Based on Aromatic Glycidylamines. I. Analysis of *N,N*-Diglycidylaniline by GPC and HPLC

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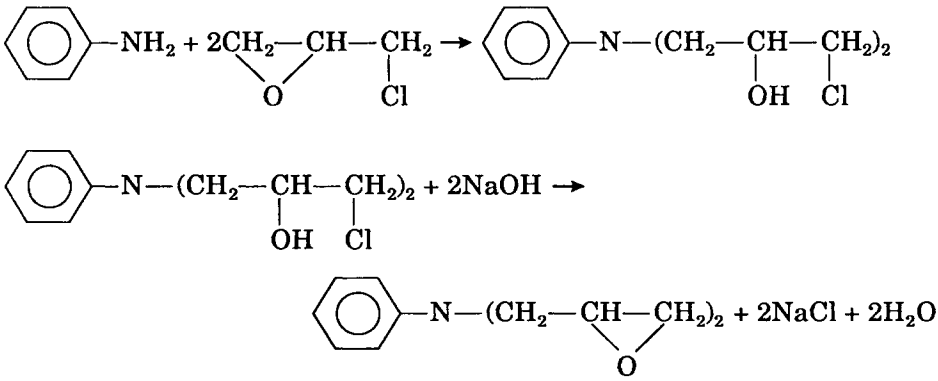
Synopsis

N,N-bis(2,3-epoxypropyl)aniline (*N,N*-diglycidylaniline, DGA) and an intermediate of its synthesis, *N,N*-bis(2-hydroxy-3-chloropropyl)aniline (*N,N*-dichlorohydrin of aniline, DCHA), were analyzed by GPC and HPLC. The main impurities were isolated by semipreparative HPLC and their structure was identified by mass, IR, and NMR spectroscopy. Attention was also paid to the mechanism underlying the formation of these impurities.

INTRODUCTION

DGA is used both as a low viscosity reactive diluent of epoxy resins and as a two-functional epoxy resin. From the analytical point of view, it is also a suitable model compound in studying the synthesis and curing of the most common *N*-glycidyl derivative, *N,N,N',N'*-tetrakis(2,3-epoxypropyl)-4,4'-diaminodiphenylmethane (*N,N,N',N'*-tetraglycidyl-4,4'-diaminodiphenylmethane, TGDDM).

Synthesis of DGA proceeds in two steps according to the following scheme:



Aniline is first added on epichlorohydrin to yield DCHA which is then dehydrochlorinated by sodium hydroxide.

This scheme does not show all reactions that proceed during the synthesis of DGA. The product contains only about 80% of DGA; the residual byproducts

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influence unfavorably such properties as storage stability, viscosity, reactivity, etc.

The aim of this work is to identify the major impurities in DGA and to elucidate their formation.

EXPERIMENTAL

Synthesis of DGA

Aniline (186.2 g), epichlorhydrin (395 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 (13.6 g) was added in one portion and 50% aqueous NaOH solution (416 g) was added with stirring over 1 h. The mixture was stirred for 3 h at 50°C and for 1 additional hour at 70 to 80°C. Water (435 g) was then added; the separated organic layer was saturated with carbon dioxide and then washed with 150 g of 5% aqueous NaCl solution. The solvent was stripped at 120°C and a pressure of 1.3 kPa. The epoxide equivalent of the crude product (97% yield) was about 114 g/mol (theory 102.5 g/mol) and a typical chlorine content was 0.3 to 0.4%.

Synthesis of Pure DCHA

A mixture of aniline (279.3 g), epichlorhydrin (592 g), and water (54 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 DCHA with mp 76 to 78°C and chlorine content 25.31% (theory 25.49%) was 50%. The purity was 98.5% according to HPLC.

Determination of Epoxide Equivalent and Chlorine Content

To determine the epoxide equivalent, excess HCl in pyridine was added and titrated by NaOH. The chlorine content was determined by saponification with potassium hydroxide in a mixture of dioxane and ethylene glycol.

Gel Permeation Chromatography and High Performance Liquid Chromatography

The Spectra-Physics SP 8100 liquid chromatograph was used for HPLC and GPC analyses. The effluents were monitored with SP 8440 UV/VIS variable-wavelength detector at 280 nm. The SP 4200 computing integrator served for handling the data. This system provides for automatic reporting and plotting of background-corrected UV spectra and absorbance ratios during the course of a chromatographic run.

Four Microgel (Chrompack) columns 250 × 7.7 mm (50, 100, 500, 10^3 Å) were used for GPC analysis with tetrahydrofuran (THF) (1 mL/min) as the mobile phase. The samples were prepared as 0.35% solutions in THF.

The reversed-phase HPLC with gradient elution was carried out using a Separon SGX C 18 column 250 × 4 mm (Tessek, Prague). A THF–methanol–water gradient (5% THF, 30% methanol from 0 to 5 min; 9% THF, 56% meth-

anol at 40 min; 9% THF, 91% methanol at 45 min) was used for the analyses of DGA. Samples of DGA were prepared as 0.75% solutions in THF. A methanol–water gradient (35% methanol from 0 to 10 min; 80% methanol at 40 min; 100% methanol at 50 min) was used in analyses of DCHA. The DCHA samples were injected as 1.1% solutions in methanol.

The flow rate of mobile phase in HPLC was 1 mL/min. The injected amount was 10 μL in HPLC and GPC. All experiments were carried out at 40°C.

A Separon SGX C 18 column 250 × 8 mm (Tessek, Prague) was used for semipreparative HPLC.

To identify the HPLC peak of *N*-glycidyl-*N*-(2-hydroxy-3-chloropropyl)aniline (GCHA), DGA was derivatized with HCl and NaOH. HCl (10 molar % of epoxy groups) was added to the DGA solution prepared for HPLC analysis. The mixture was left for 4 h at room temperature and then injected. A tenfold excess of powdered NaOH was added to the DGA solution prepared for HPLC analysis; the mixture was stored with occasional shaking for 4 h at room temperature, filtered, and injected.

To identify compounds containing hydroxyl groups or amine hydrogens, DGA was treated with acetic anhydride in the presence of *N*-methylimidazole as a catalyst.[1,2] 20 μL of *N*-methylimidazole and 20 μL of acetic anhydride were added to 1 mL of DGA solution prepared for HPLC analysis. The sample was injected after 1 h at room temperature.

Spectroscopy

IR spectra were measured on the spectrometer Pye Unicam SP3-300A (KBr disc method). DGA was scanned as a film cast on a KBr plate.

NMR spectra were registered on the spectrometer Bruker AM 400 in 5 mm probes with $CDCl_3$ as a solvent and tetramethylsilane as internal standard. Tris/3-(2,2,2-trifluoro-1-hydroxyethylidene)-*d*-camphorato/europium [Eu(TFC)$_3$] (Merck) served as a chiral shift agent to discriminate between the DCHA diastereoisomers.

All mass spectra were determined using an AEI double focusing mass spectrometer operated through MSS electronic console. Samples were emitted into the ion source by direct inlet. The source temperature was 180°C, ionization energy 70 eV, Emission 100 μA and accelerating voltage 6 kV.

RESULTS AND DISCUSSION

Typical GPC and HPLC curves of DCHA obtained after the first step of DGA synthesis are shown in Figure 1, the chromatograms of the corresponding DGA are in Figure 2. Only peaks of DGA, DCHA, and *N*-(2-hydroxy-3-chloropropyl)aniline (CHA) can be unambiguously identified in the chromatograms. The retention time of CHA was determined from samples taken during the first step of DGA synthesis.

A comparison of chromatograms of several DCHA and corresponding DGA samples demonstrates that the relative areas of DCHA1 and DCHA2 peaks correspond approximately to the relative area of the DGA peak, and the same holds true for the respective groups of peaks CHA − X2a, X1b + X2b − X1a and D1b + D2b + D3b − Da.

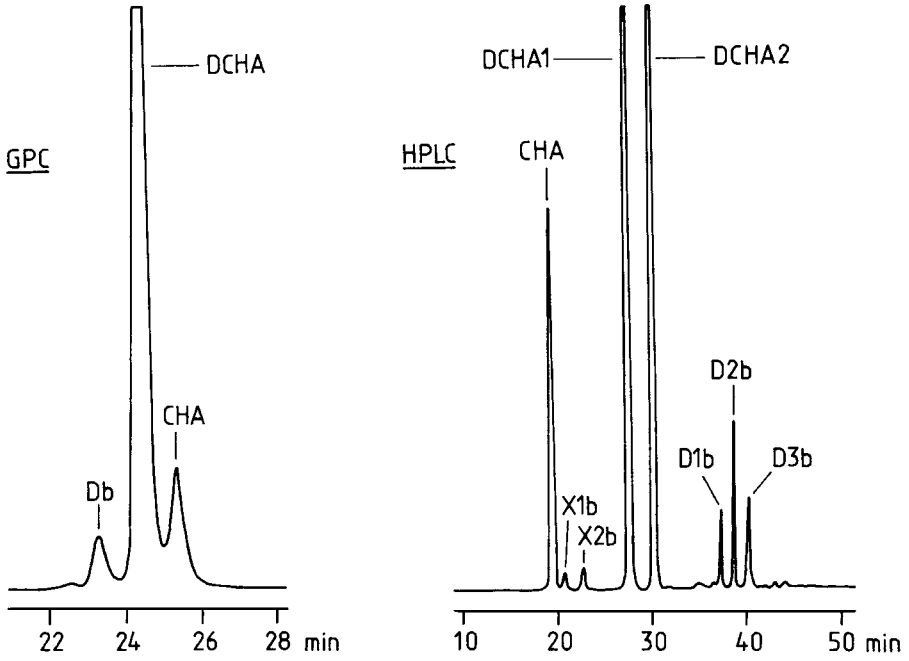


Fig. 1. GPC and HPLC chromatograms of DCHA.

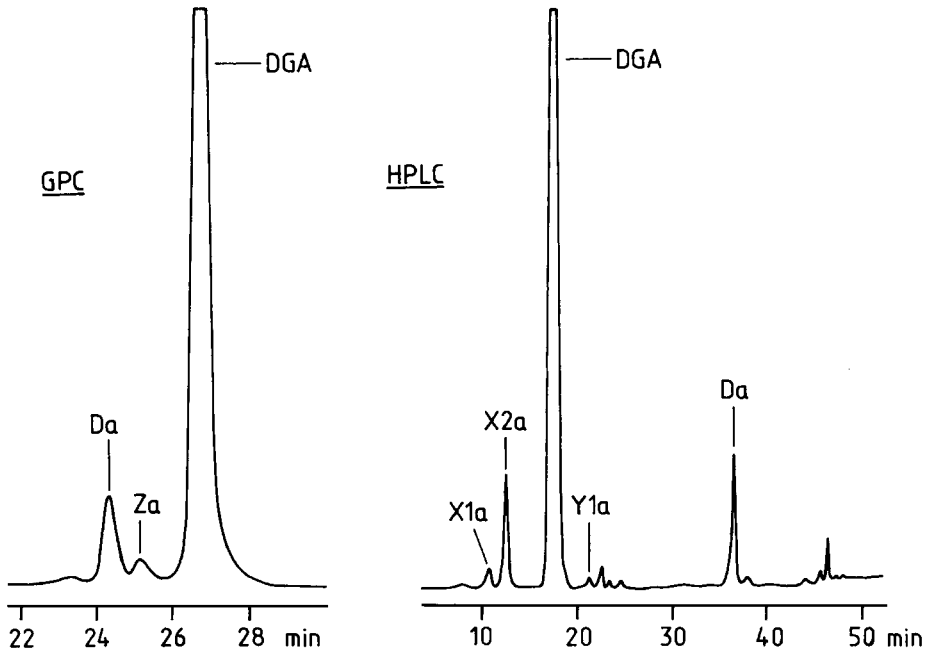


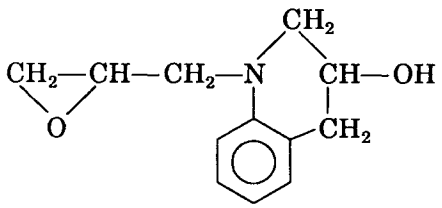
Fig. 2. GPC and HPLC chromatograms of DGA.

DCHA separates into two components in HPLC. The elution times of DCHA1 and DCHA2 almost coincide in GPC as do the elution times of compounds D1b, D2b, and D3b. The compounds DCHA1 and DCHA2 were isolated by means of semipreparative HPLC. It has been confirmed by NMR that DCHA1 and DCHA2 are diastereoisomers. Discrimination of diastereoisomers was achieved by adding the chiral shift agent $Eu(TFC)_3$. DCHA1 has been identified as a diastereoisomer with RS configuration of asymmetric carbons, while DCHA2 is a mixture of enantiomers with RR and SS configuration of asymmetric carbons. This interpretation is based on the splitting of ^1H-NMR signals of the chlorohydrin groups in DCHA2 spectrum after the addition of $Eu(TFC)_3$. It may be assumed by analogy that the triplet of chromatographic peaks D1b, D2b, D3b also corresponds to diastereoisomers.

To determine the relationship between the GPC and HPLC curves and to aid the data interpretation, the GPC peaks DGA, Za, Da, and the fraction eluting before Da were collected and analyzed by HPLC. The DGA peak in GPC consists of HPLC peaks DGA, X1a and X2a. The peak Za in GPC consists of four HPLC peaks with retention times between 21 and 24.5 min. The peak Da in GPC corresponds to a simple HPLC peak Da. The GPC peak eluting before peak Da includes HPLC peaks eluting beyond 43 min.

Compound X1a

Compound X1a has the same molecular weight as DGA (determined by MS). An analysis of IR and NMR spectra leads to the following structure



I

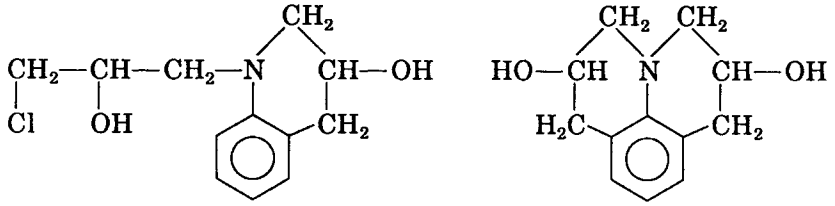
IR and NMR spectra indicate structural changes between DGA and X1a. Opening of the oxirane ring leading to the formation of a secondary alcohol is reflected in the IR spectrum as a broad diffuse band at 3400 cm^{-1}, corresponding to the stretching vibration $\nu(O-H)$. A specific band confirming the structure of X1a is the band corresponding to the in-plane deformation vibration $\delta(O-H)$ and the stretching vibration $\nu(C-O)$, which in secondary alcohols usually lies at 1100 cm^{-1}. Cyclization of the chain carrying this hydroxyl group results in a shift of this band to lower wave numbers. Indeed, intensive absorption bands appear at 1070 and 1050 cm^{-1} in the IR spectrum of compound X1a. A similar shift of this band (including a splitting) can be observed in IR spectra of compounds containing a secondary hydroxyl, where the α-carbon atom forms a part of a saturated six-membered ring.[3] The character of substitution of the benzene ring is also changed: in comparison with the monosubstituted aromatic ring in DGA, the absorption band at 690 cm^{-1} is absent in the spectrum of X1a and the intensity of the band at 750 cm^{-1} is doubled, thus confirming the ortho-substitution of the benzene ring. Further confirmation is provided by the signal

of a carbon atom with a chemical shift 119.5 ppm in the ^{13}C-NMR spectrum. The signal at 63.6 ppm indicates the presence of a secondary hydroxyl group on a six-membered saturated ring.

The presence of a hydroxyl group in the molecule of X1a is in agreement with the significant increase of retention time after derivatization with acetic anhydride.

The formation of a similar compound during thermal treatment of *N*-ethyl-*N*-glycidylaniline has been described by Attias et al.[4] A similar 1,2,3,4-tetrahydro-3-hydroxyquinoline structure has been previously identified by Davies and Savige[5] in products of the reaction between *N*-methylaniline and epichlorohydrin at high temperatures.

The mechanism of formation of compound I was investigated by following by means of HPLC the changes brought about by a thermal treatment of pure DCHA at 85°C. The chromatograms of pure DCHA after 8 and 40 h at 85°C are shown in Figure 3. The areas of peaks X1b and X2b increase after prolonged thermal treatment. It has been verified by HPLC analysis of thermally treated samples that dehydrochlorination of compounds X1b and X2b yields compound X1a. The peaks X1b and X2b then belong to diastereoisomers of compound II; by analogy, the peaks X3b and X4b may be assigned to diastereoisomers of compound III.



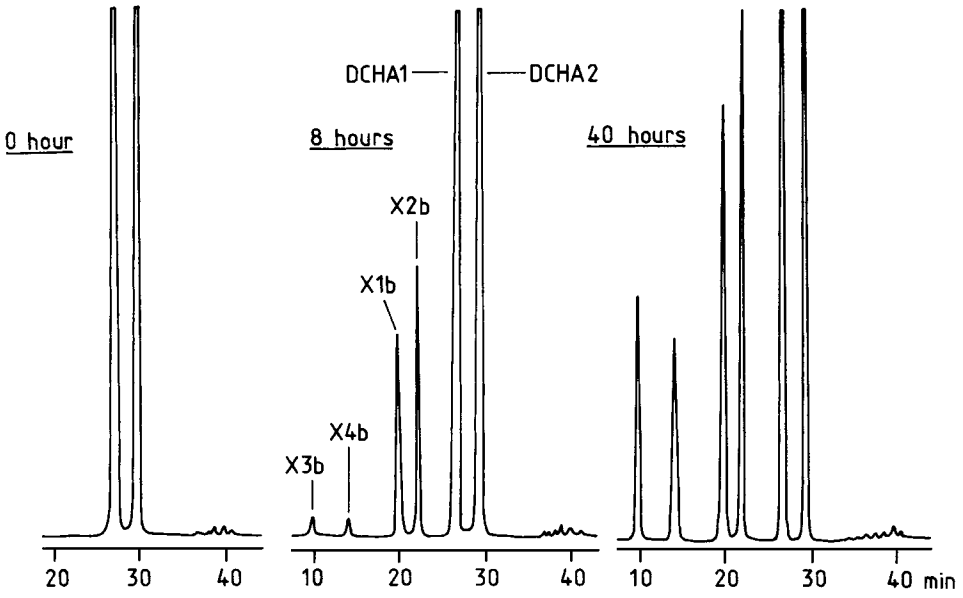
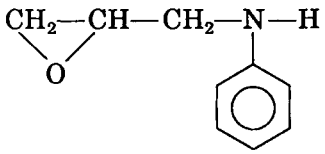


Fig. 3. HPLC chromatograms of DCHA after thermal treatment at 85°C.

The possibility that compound I is formed by intramolecular cyclization of DGA at elevated temperatures was confirmed by thermal treatment of DGA at 180°C (Fig. 4). As DGA is never exposed to such high temperatures (at lower temperatures, compound I is not formed) during synthesis, we suppose compound I to be formed largely by intramolecular cyclization of DCHA and by dehydrochlorination of compound II.

Compound X2a

The content of component X2a corresponds to the content of CHA in DCHA before dehydrochlorination. Its molecular weight (149) determined by MS corresponds to *N*-(2,3-epoxypropyl)-aniline IV (*N*-glycidylaniline, GA). The maximum of UV absorption is shifted to lower wavelengths in comparison with DGA, similarly as in the case of the pair CHA-DCHA (DCHA 253 nm, CHA 242 nm; DGA 250 nm, X2a 241 nm). After the treatment with acetic anhydride, the retention time of the acetylated product slightly decreases, apparently owing to the formation of an amide.



IV

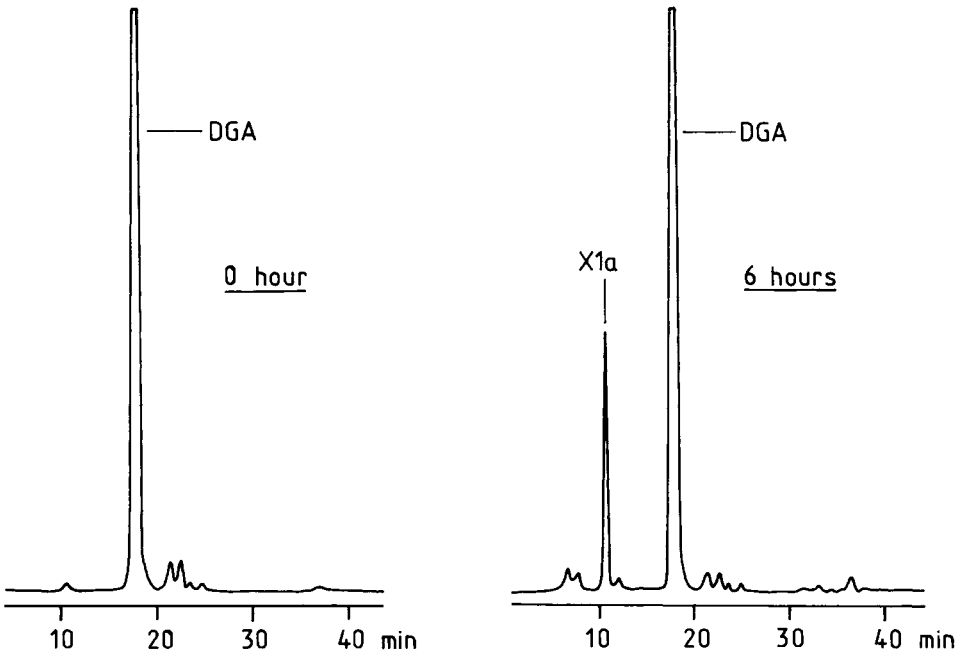
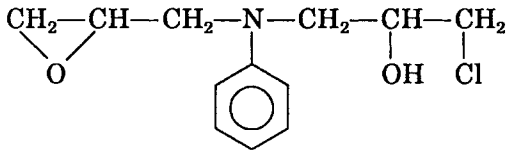


Fig. 4. HPLC chromatograms of DGA before and after thermal treatment at 180°C.

Compound Y1a

Peak Y1a is more pronounced in chromatograms of samples with a higher chlorine content. The area of peak Y1a markedly increases after addition of HCl on DGA. On the contrary, the peak Y1a fully disappears after the treatment of DGA with NaOH. Thus, it may be assumed that this peak corresponds to *N*-(2-hydroxy-3-chloropropyl)aniline V present owing to incomplete dehydrochlorination.



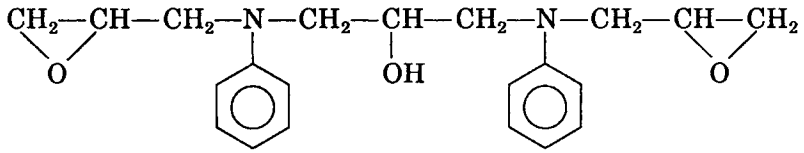
V

The higher retention time of this peak in comparison with that of DGA 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 Za) in GPC is in agreement with the higher molecular weight of GCHA and with the possibility of association of its hydroxyl group with THF.

As the chlorine content determined by saponification in the analyzed samples was higher than that calculated from the content of GCHA, it is probable that some other peaks correspond to chlorine-containing compounds [e.g., *N*-glycidyl-N-(1-hydroxy-3-chloro-2-propyl)aniline].

Compound Da

The molecular weight of compound Da determined by MS is 354. This molecular weight can correspond to dimer VI, and the structure was indeed verified by IR and NMR.



VI

The signals of carbons in monosubstituted aromatic rings are at least qualitatively preserved in the ^{13}C-NMR spectrum in comparison with the spectrum of DGA. The signal at 68.7 ppm then corresponds to a secondary —OH group of an aliphatic chain. The absorption band δ(O—H) + ν(C—O) at 1100 cm^{-1} in the IR spectrum of compound Da lends support to the assumption that the α-carbon atom does not belong to a saturated ring. The IR spectrum of Da in the region of out-of-plane deformation vibration γ(H—C=) proves that only monosubstituted aromatic nuclei are present.

The considerable increase of retention time of Da after derivatization with acetic anhydride confirms the presence of a hydroxyl group in the molecule of Da.

Dimer VI or higher oligomers can arise by the reaction of amine hydrogens in aniline or CHA with chlorine of chlorohydrin groups under splitting off of HCl, or by the reaction of hydrogen atoms of GA with the epoxide groups of DGA.

Participation of the first mechanism has been confirmed by experiment where a mixture of CHA and DCHA (prepared by addition of aniline on epichlorohydrin in the molar ratio 2 : 3) was treated at elevated temperature: pronounced peaks of oligomers appeared in the GPC chromatogram (Fig. 5) of the mixture CHA–DCHA kept at 85°C for 8 h. The peak lying between peaks Db and DCHA probably belongs to the product of reaction between two CHA molecules.

The second mechanism of formation of dimer VI has been confirmed by heating of DGA containing GA. A larger peak of dimer Da and peaks of higher oligomers appeared in HPLC chromatogram (Fig. 6) after 48 h at 100°C.

As the sum of relative areas of peaks D1b + D2b + D3b approximately corresponds to the relative area of peak Da, we assume these peaks to be various diastereoisomers of chlorohydrin of dimer VI. From this fact it is also obvious that dimer and eventually the higher oligomers arise mostly during the addition of aniline on epichlorohydrin.

CONCLUSIONS

N-glycidylaniline, *N*-glycidyl-*N*-(2-hydroxy-3-chloropropyl)aniline, the tetrahydroquinoline compound of structure I, and dimer VI were identified as major impurities in DGA samples. Compounds I and VI arise mainly during the addition of aniline on epichlorohydrin, but can be also formed during thermal treatment of DGA.

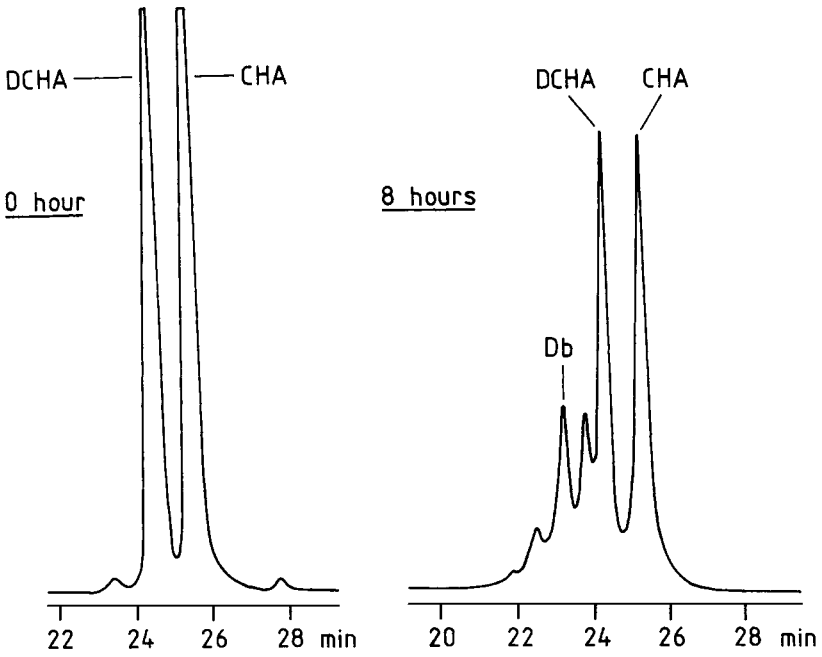


Fig. 5. GPC chromatograms of a mixture of CHA and DCHA before and after thermal treatment at 85°C.

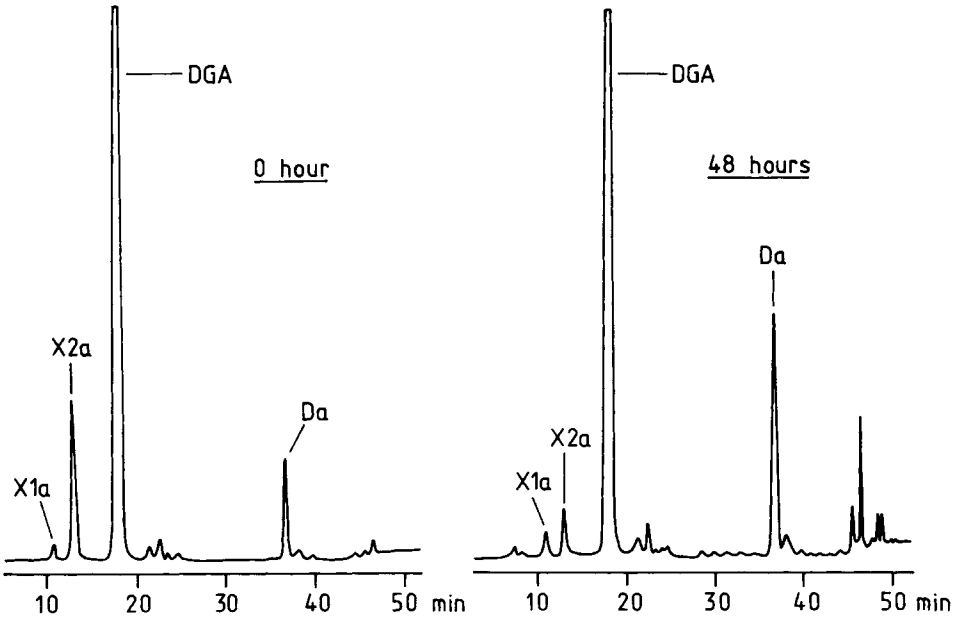


Fig. 6. HPLC chromatograms of DGA before and after thermal treatment at 100°C. The relative areas of individual peaks before and after thermal treatment are: DGA: 83.2–80.3%, X1a: 0.8–0.8%, X2a: 7.0–1.4%, Da: 5.0–8.6%.

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