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Chemical structure of networks resulting from curing of diglycidylamine-type resins with aromatic amines

1. Detection and characterization of cyclisation reactions on model compounds

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Summary

A model compound (I), representative of the structure resulting from the first step of curing in diglycidylamine-aromatic amine systems, was prepared from diglycidylamine and N-ethylaniline. After thermal treatment, the fraction resulting from intramolecular processes, that is to say possessing the same molecular weight as the initial compound (I), was isolated by preparative GPC. This fraction was shown by GPC, HPLC and ^{13}C NMR spectroscopy, to contain morpholine, as well as corresponding 7-membered cyclic ethers which were identified by comparison with the products of a process said to actually give morpholine derivatives. Another non ether-forming cyclisation reaction was also detected, resulting in the formation of a 3-hydroxy-1,2,3,4 tetrahydroquinoline derivative, by attack on an aromatic nucleus by the epoxy directly bonded to it. Apparently, this reaction has not been previously described.

Introduction

Unlike most other epoxy-amine resins, the systems based on tetraglycidyl diaminodiphenylmethane (TGDDM) with diamino diphenylsulfone (DDS) as hardener are characterized by the complexity of their curing mechanism originating from :

- existence of N,N-diglycidylamine groups in the resin,
- the low basicity, and consequently the low reactivity of the hardener.

After the first stage of the curing process, which is the addition of a primary amine onto an epoxy group, and which does not present any difficulty, the low reactivity of the resulting secondary amine gives rise to several unusual reactions of epoxy groups, resulting in a complex network comprising various structural features.

The purpose of the present work was to investigate, by using model compounds, the reactional capacity of an epoxy function, when reactive amines are not present, but in the same structural and functional environment as that resulting from the first stage of curing. In such a case, various possibilities have already been put forward in the literature, for instance etherification by hydroxy-epoxy or epoxy-epoxy reaction and especially cyclic ether (morpholine) formation by an intramolecular reaction (1,2).

However, as no direct evidence was ever given for the latter process, the first object and the first step of this work was to isolate such a cyclic ether if it were actually formed, and thus to obtain analytical and spectroscopic data which would facilitate identification of it in all products containing it.

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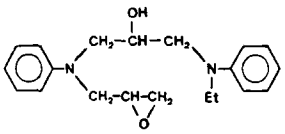
Results and discussion

1. Occurence of intramolecular reactions

In order to confirm the possibility of intramolecular reactions during curing processes and, more specifically, of the formation of morpholine ring, the reactivity of compound (I) was studied during a thermal treatment (prepared from N-ethylaniline and diglycidylaniline ; molar ratio 1:4).



(I)

Compound (I) can be considered as a model molecule for the product of the first step of amine-epoxy addition. In this way, it can also be regarded as a model of the structure leading, in a second step, to morpholine formation by intramolecular addition of the other epoxy with the hydroxy group resulting from the first step.

Comparison of GPC chromatograms of compound (I) (fig. 1a) and of products obtained by heating it for 6h at 180°C (fig. 1b) shows that reactions actually occur. Heat-treated (I) gives three peaks at retention times 13.29, 13.93 and 14.64 mn. The first two are assigned to inter-molecular reaction products, because their retention times are appreciably different from that of (I). The latter peak, on the contrary, is only slightly shifted (≈ -0.1 mn) in comparison to the compound (I) peak ; this can be attributed either to the product of a reaction with little or no molar weight modification, or to residual (I), or to a mixture of both.

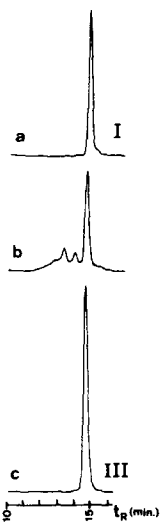


Fig. 1 - GPC chromatograms
a) (I)
b) Heat treated (I)
c) (III)

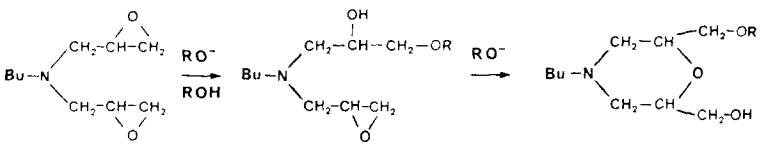
Analysis of the product related to the latter peak supported the hypothesis of an intramolecular process. The corresponding fraction (II) was isolated by preparative GPC. The HPLC chromatogram of (II) (fig. 2a) consists mainly of two peaks at retention times 6.06 and 7.09 mn on the one hand, and a group of 4 fused peaks at 11.85, 12.63, 13.11 and 13.98 mn on the other hand. The 75 MHz ^{13}C NMR spectrum (fig. 3b), although too complex to be interpreted at first sight, shows the presence of bands between 70 and 80 ppm, characteristic of ether group carbons.

As the slight difference in GPC retention times of this fraction and of its precursor (I) can be interpreted by a mere structural or functional modification, changing hydrodynamic volume only without changing molar weight, all these results are compatible with intervention of an intramolecular process resulting in cyclic structures including possibly morpholine. Yet, the multiplicity of HPLC peaks of the product remains to be explained. This is the reason why the next step of our study was to compare it with a true morpholine, identically substituted, but synthesized by another reactional path.

2. Comparison of the intramolecular reaction product with a "true" morpholine

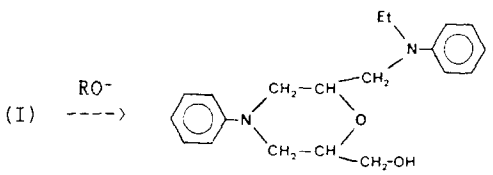
2.1. Synthesis of the morpholine

Sorokin et al. (3) have shown that the base catalysed reaction of N-butyl-diglycidylamine results in the formation of a morpholine derivative.



Identification of this compound was confirmed by comparison with a product resulting from dehydration by concentrated H_2SO_4 of the corresponding diol derivative (3).

This synthesis mode was adapted to our case, taking into account the structural analogy between our precursor compound (I) and the intermediate molecule of the reaction path given before. Thus, (I) was treated by BuONa with the same experimental conditions as that described in the above mentioned article. GPC chromatogram of the resulting product (III) consisted essentially of only one peak corresponding to the same molecular weight as (I) and as the fraction (II) previously isolated from heat-treated (I) (fig. 1c). The anticipated reaction was thus the following :



2.2. Comparison of (III) with (II)

Comparison of HPLC chromatograms of (II) (fig. 2a) and (III) (fig. 2b) made it clear that (III) is a part of (II). More accurately, the chromatogram of (III) includes the same pattern consisting of four fused peaks at 11.85, 12.63, 13.11 and 13.98 mn, but does not contain the other two peaks at 6.06 and 7.09 mn present in (II). The existence of four peaks is not incompatible with the hypothesis of a morpholine structure, due to its non planar configuration and the presence in it of two asymetric carbons, but we will see later (part 2.3) that another interpretation is more probable.

Similar conclusions can be drawn from ^{13}C NMR spectra (fig. 3a and 3b) since the spectrum of (III) is a sub-set of the spectrum of (II).

However, the spectrum of (III) itself remains very complex and requires further investigation to establish direct links between it and the structure of the product. As for the bands of (II) which are not included in the spectrum of (III), they are discussed and interpreted in part 3.

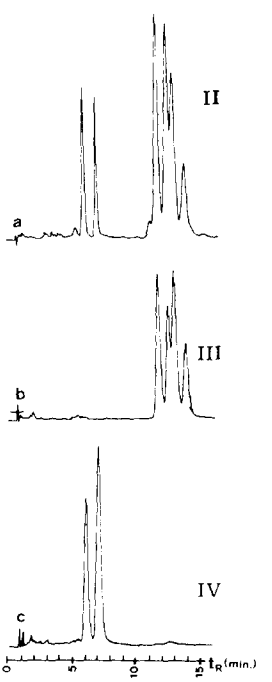


Fig. 2 - HPLC - Identification of different components in heat treated (I)

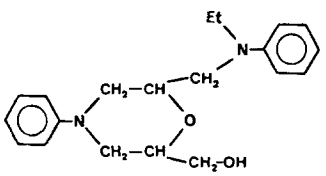
CH_2 peaks, attributed to alcoholic functions. On the other hand, all the peaks in the ether region between 70 and 80 ppm are CH groups, except the peaks at 76.3 and 75 ppm.

Deuterium substitution in alcoholic functions

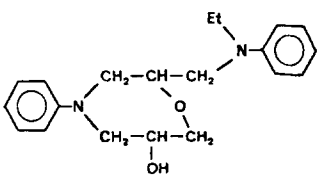
By addition of D_2O to the $CDCl_3$ solution of (III) and shaking, hydrogen atoms of hydroxyl groups were replaced by deuterium, and carbons bonded to these groups give shifted peaks in the ^{13}C NMR spectrum. With reference to the preceeding results, this experiment confirms that the peaks at 63 and 64 ppm can be attributed to $-CH_2OH$ groups. But it also shows that two other peaks, belonging to CH groups, are also shifted, and can thus be attributed to secondary alcoholic functions.

Discussion

Previous results point out the presence in (III) of -CHOH, as well as $-CH_2OH$ groups, and of $-CH_2-O-$, as well as $>CH-O-$ groups. They suggest accordingly that the Sorokin type synthesis does not lead exclusively to the 6-membered ether (IIIa), but also to a certain proportion of 7-membered structure (IIIb), already assumed by Matejka et al. (1).



(IIIa)



(IIIb)

Since it also contains two asymetric carbons, structure (IIIb) can contribute, as well as (IIIa), to the multiplicity of peaks observed in the HPLC chromatogram of (III) (fig. 2b).

Since all the peaks of the NMR spectrum of (III) are parts of the spectrum of (II), it is possible to come to a similar conclusion for the latter compound, that is to say, it is possible for the model (I) to generate by heat treatment a sizeable proportion of 7-membered cyclisation products, as well as 6-membered ones.

3. Identification of other components of (II) - Evidence of a novel cyclic structure

The HPLC chromatogram of (II), besides a peak grouping near 12 mn related to cyclic ethers, comprises also two peaks of nearly equal intensity around 7 mn (fig. 2a). Fraction (IV), corresponding to both latter peaks, was isolated by repetitive analytical HPLC. Its HPLC chromatogram is reported on fig. 2c, and confirms the purity of this fraction.

The ^{13}C NMR spectrum of (IV) (fig. 3c), when compared with those of (I) (fig. 3d) and (II) (fig. 3b), shows respectively the absence of glycidyl groups (no peaks at 45, 51 and 54 ppm), and of any peak in the ether region (70-80 ppm range). The reaction path leading from (I) to (IV) thus consumes epoxy groups, but very likely does not affect hydroxyl functions (no ether formation) and cannot be

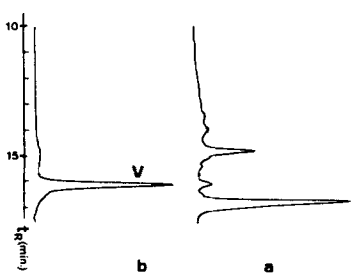


Fig. 4 - GPC
Effect of heat treatment of EGA
a) EGA after 24 h at 200°C
b) (V)

an epoxy-epoxy reaction (no or little molar weight change). So the hypothesis was made that this reaction concerns only one epoxy group, and possibly the non-functional part of the molecule.

In order to investigate such a hypothesis, a molecule was chosen to model it. This model is N-ethyl-N-glycidyl-aniline (EGA), the reactivity of which was studied during heat treatment at 200°C. The reaction was followed by GPC. The chromatogram obtained after 24h (fig. 4a) comprises essentially three peaks. The retention times of the last two are not very different (16.75 mn, which is exactly the same as that of EGA and corresponds to the main product, and 16.05 mn) ; the first one, on the contrary, appearing at 14.8 mn, corresponds to twice the molar weight of EGA. As we are interested only in intra-molecular processes and because a little difference in retention time does not necessarily imply an inter-molecular process (possibly being due to hydrodynamic volume alteration resulting from a mere structural modification, or alternatively from formation of functional groups, such as OH, able to be solvated by elution solvent THF), both peaks at 16.05 and 16.75 mn were separately isolated by preparative GPC.

By considering ^{13}C NMR spectra (fig. 5), the 16.75 mn peak is doubtless to be attributed to non-reacted EGA. On the other hand, fraction (V) corresponding to the 16.05 mn peak (fig. 4b) has a NMR spectrum (fig. 5b) showing the absence of epoxy groups, and a loss in symmetry for the aromatic ring (six peaks instead of four). By using a J-modulated pulse sequence, it can also be pointed out :

- in the aromatic region, the presence of two peaks assignable to quaternary C groups at 121.5 and 145.4 ppm, and of four peaks assignable to CH groups at 111.3, 116.6, 127.8 and 130.6 ppm ;
- in the aliphatic region, the presence of two peaks assignable to CH_2 groups at 37.9 and 55.7 ppm, and of one peak assignable to a CH group at 64.3 ppm.

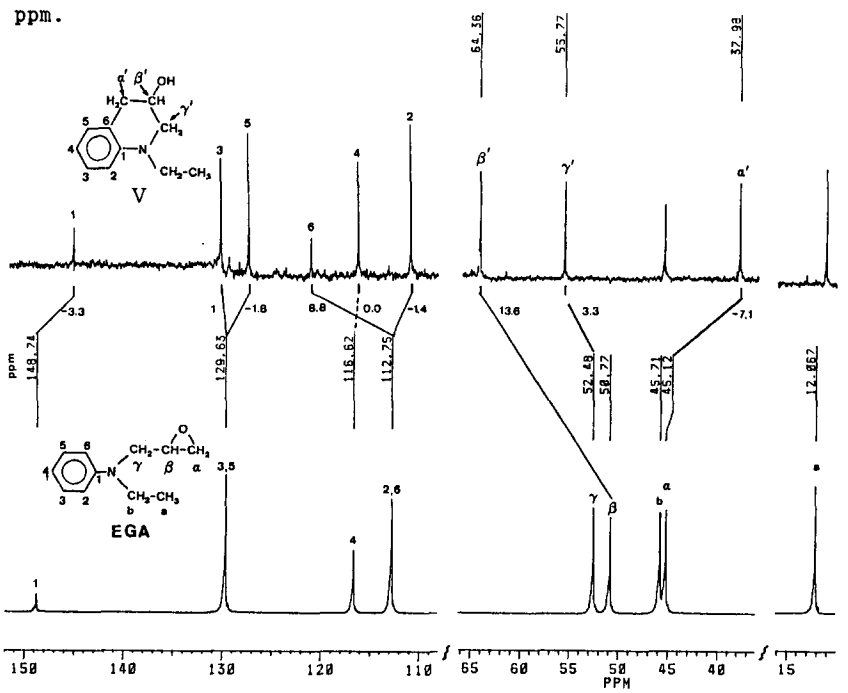
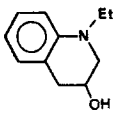


Fig. 5 - ^{13}C NMR - Intramolecular cyclisation of EGA

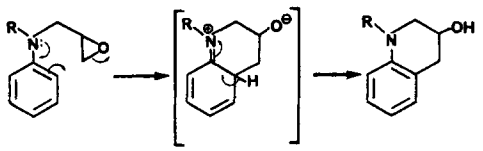
From all these data, it is possible to infer that the 1,2,3,4-tetrahydro 3-hydroxy quinoline structure given beside can very likely be assigned to (V).



(V)

Such an attribution is confirmed by recording the ^{13}C spectrum without proton decoupling, and also by an incremental chemical shifts calculation.

The N-glycidyl group thus demonstrates the capacity to react with the ortho-position of the aromatic ring, probably by the following mechanism :



Such a structure, although not previously proposed as a result of the reaction of glycidyl groups, has, however, been previously identified by Davies and Savige (4), when an aromatic secondary amine is reacted with epichlorohydrin at high temperature, probably as result of cyclisation of the intermediate chlorohydrin.

Coming back to (IV), viz. the non-ether fraction of (II), it is possible to establish a clear correspondence between all unassigned resonances of its ^{13}C NMR spectrum (aliphatic part ; fig. 3c) with the three characteristic bands α', β', γ', of (V) spectrum (fig. 5b). The band α' situated near 38 ppm, very characteristic by its appearance at relatively high field, is especially worthy of note from this viewpoint. Splitting of bands in the spectrum of (IV), as well as the presence of two peaks in its HPLC chromatogram (fig. 2c), can be considered as a normal consequence of the presence of two asymmetric carbons in the inferred structure of (IV). Quantitative ^{13}C NMR analysis indicates a proportion of (IV) in (II) amounting to as much as 20%.

Further evidence of the importance of that reaction is given by analysis of the soluble fraction of heat treated TGDDM resin without hardener (3 h at 200°C) by ^{13}C NMR spectroscopy. The spectrum (fig. 6) only comprises bands resulting from that mechanism, in addition to residual epoxy resonances.

This result is to be compared to those of Mones et al. (2), who observed during TGDDM heat treatment an increase, in FT/IR spectra, of hydroxyl absorption bands, much stronger than that of the ether bands. This phenomenon, attributed by the authors to a radical reaction taking place between two epoxy groups, can also be interpreted by the OH-forming cyclisation mechanism here described.

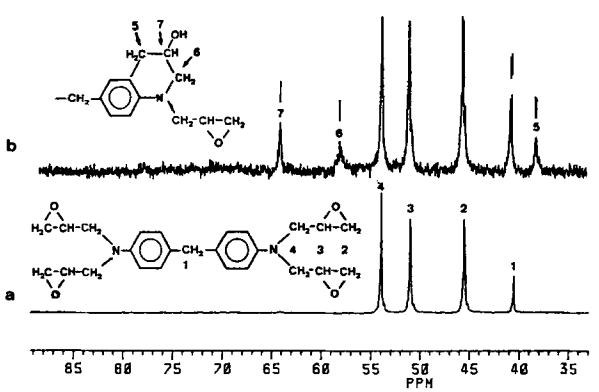


Fig. 6 - Effect of heat treatment of TGDDM on ^{13}C NMR spectra
a) TGDDM
b) Soluble fraction of TGDDM after 3 h at 200°C

Conclusion

By using model compounds, this study of the intramolecular processes taking place after first step of reaction between bis-(N-glycidyl) amines and aromatic amines first demonstrates that these processes are actually able to occur. But various cyclic structures can result from them. Morpholine, and also 7-membered cyclic ethers, already proposed by other authors, were effectively detected and characterized. But another non-ether cyclic product can also be formed by a reaction taking place between an aromatic ring and the N-glycidyl group directly bonded to it. The latter reaction has not yet been described for those systems. All detected structures can be affected by configurational isomerism, and were well characterized by ^{13}C NMR spectroscopy.

Experimental

Analyses and measurements

HPLC - Liquid chromatograph model 5020 (Varian). Column : RP-Select B (Merck) ; length 12.5 cm. Chromatographic conditions : flow rate 1 ml/mn ; detection : UV 254 nm ; elution solvent : acetonitrile/water 45:55 V/V.

GPC - Analytical conditions : column PL-Gel, porosity 100 A, particle diameter 5 µm, length 600 mm, diameter 10 mm (Polymer Laboratories). Detection : differential refractometer IOTA (Jobin-Yvon). Flow rate 1 ml/mn.
Preparative conditions : column PL-Gel, porosity 100 A, particle diameter 10 µm, length 600 mm, diameter 25 mm (Polymer Laboratories). Flow rate 10 ml/mn. Injection : 2 ml of 1-3 % solution.

^{13}C NMR - Spectrometer AM 300 (Bruker), ^{13}C frequency 75.4 MHz. Solutions in acetone-d_6, with TMS as internal reference.

Syntheses

(III) * "True" morpholine (still containing some 7-membered cyclic ethers): Sorokin method (3) was applied to (I) in the following way : (I) (0.5 g), dissolved in 7 ml of a 0.05 M solution of sodium n-butoxide in n-butanol, was heated at 60°C for 3 h. After cooling, water washing, and distillation under reduced pressure of the organic phase, the obtained product was purified by preparative GPC.

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