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Reactions

Cyclization in the Reaction Between Diglycidylaniline and Amine

L. Matějka*, M. Tkaczyk, S. Pokorný, and K. Dušek

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences,
CS-162 06 Prague 6, Czechoslovakia

Summary

The reaction of diglycidylaniline (DGA) and N-methylaniline (NMA) was investigated by means of HPLC, and the products were identified by mass spectrometry. A number of cyclic products is formed. An eight-membered ring formed by the intramolecular reaction of the secondary amino group and the epoxy group in the DGA-aniline monoadduct is the main cyclic product. The monoadduct DGA-NMA yields a seven-membered ring by internal etherification only after the amine has been consumed.

Introduction

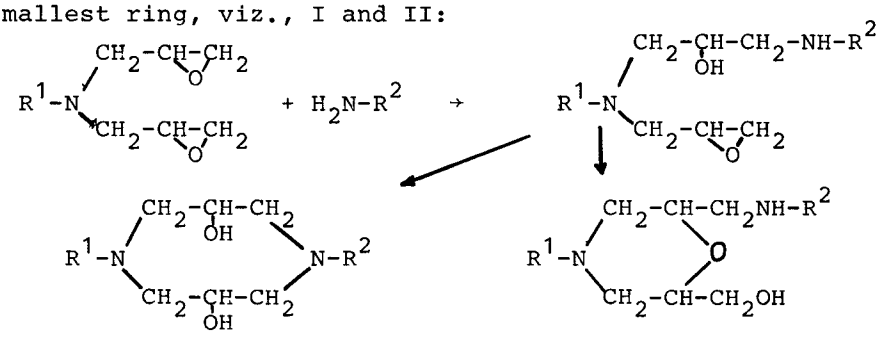
Cyclization plays an important role in network formation: it affects rheological properties of the reacting system, displaces the gel point towards higher conversions and decreases the crosslinking density of the network. In the case of diepoxides based on diglycidyl ethers of Bisphenol A (DGEBA) cured with amines, the cyclization is negligible (1-3), as indicated by the independence of critical conversion (critical molar ratio) at gelation of dilution (1,3) and by the good agreement of post-gelation parameters (sol fraction, concentration of elastically active chains, etc.) with the assumed negligible cyclization (1,4-7). This is due to the fact that the formation of the smallest possible ring, e.g. by a reaction of two epoxide groups of DGEBA with one primary amino group, is very unlikely with respect to the necessary conformational rearrangement.

On the contrary, with nitrogen-containing polyepoxides based on N,N-diglycidyl amines - N,N-diglycidylaniline (DGA) and N,N,N´,N´-tetraglycidyl-4,4´-diaminodiphenylmethane (TGDDM) - cyclization becomes much more probable due to the steric closeness of glycidyl groups. A pronounced cyclization is indicated, e.g., by a strong dependence of the critical molar ratio at gelation on the concentration of diluent observed for DGA and TGDDM (3). Also, the occurrence of a product consisting of one molecule of DGA and one molecule of amine, but not containing the epoxide group, detected in the reaction mixture of DGA with secondary amine (8), suggests an intramolecular reaction (morpholine structure is assumed). The presence of morpholine rings (II) is also inferred from the position of some signals in ^{13}C-NMR (9). For the system TGDDM - 4,4´-diaminodiphenyl sulfone (DDS) the formation of cyclic ethers is deduced from the displacement of the IR absorption of the ether group (10).

* To whom offprint requests should be sent

Morgan (11,12) assumes that in the products of the reaction TGDDM+DDS, up to 75% bonds formed are involved in cycles.

On summarizing the findings reported in the literature, one may expect formation of two cyclic structures with the smallest ring, viz., I and II:



I II

Up to now, however, there has been no direct evidence of formation of such cyclic products.

In this study we briefly report the results of an investigation of cyclization in the systems DGA-N-methylaniline (NMA) and DGA-aniline. The reaction products were separated by means of HPLC, and identified by mass spectrometry.

Experimental

The reaction between DGA (99.9%, preparation reported in ref. 13) and NMA (99%) or aniline (99.9%) proceeded in sealed ampoules under nitrogen at 100°C in bulk or at 140°C in toluene solution. The samples were analyzed by means of liquid chromatography (HPLC).

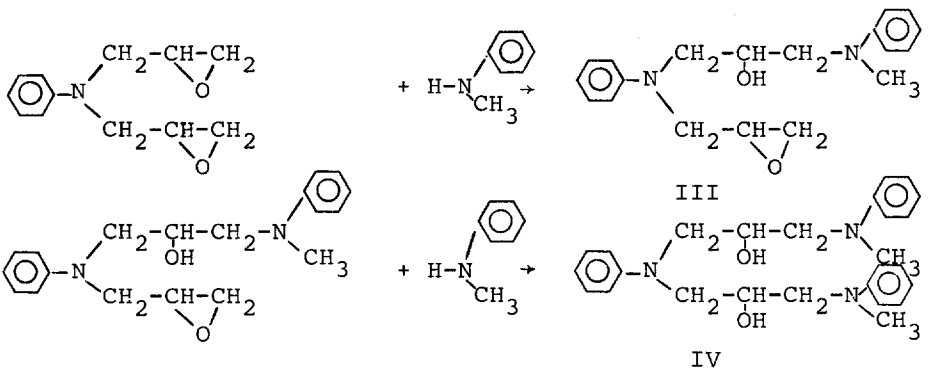
The liquid chromatograph HP 1084 B (Hewlett-Packard,USA) was provided with a glass separation column, 3x150 mm in size, packed with the reverse phase Separon S_{18}, particle size 7 μm (Laboratory Instruments, Czechoslovakia). A combination of isocratic and gradient elution in the system methanol-water was used. Samples in the form of c. 0.2% solutions in methanol were injected in an amount of 5 μl. A built-in UV detector was used for detection (wavelength 254 nm). Relevant separated substances were isolated by means of an automatic fraction collector which is part of the apparatus.

The samples were identified in an AEI MS 902 mass spectrometer, by direct inlet at the source temperature 200°C, ionization energy 60 eV, emission 100 mA and accelerating voltage 6 kV.

Results and Discussion

Reaction of diglycidylaniline (DGA) with N-methylaniline (NMA)

In the reaction of a stoichiometric mixture of DGA with NMA or with NMA in excess, only the monoadduct (III) and the diadduct (IV) are formed, according to the scheme:



III

IV

An analysis of the NMR spectra showed (13) that both these products are a mixture of stereoisomers which may be divided by means of HPLC. No other products are formed under such conditions, even if the reaction mixture has been diluted with an inert solvent. Thus, neither inter- nor intramolecular etherification takes place in this case.

However, with epoxide in excess and after NMA has been consumed, some further peaks corresponding to ethers appear in the chromatogram (Fig.1). The kinetic course of the reaction is illustrated by an example in Fig.2. It can be seen that the

Fig.1 HPLC record of reaction mixture in reaction between DGA and NMA in molar ration 2:1. T=100°C, $t_{reaction}$ = 36 h. Identification of peaks: t_e = 4.4 min - DGA, t_e = 8.1 and 8.3 min - stereoisomers III, t_e = 8.6 and 8.9 min - cyclics, t_e = 10.2 and 10.9 min - stereoisomers IV.

areas of some yet unidentified peaks (except DGA, NMA and stereoisomers III,IV), particularly of peaks with the retention time t_e = 8.6 and 8.9 min, reach a certain constant value and do not change any more. Their height increases with dilution of the system. We believe, therefore, that they correspond to cyclic products. By using multiple separation by means of HPLC,

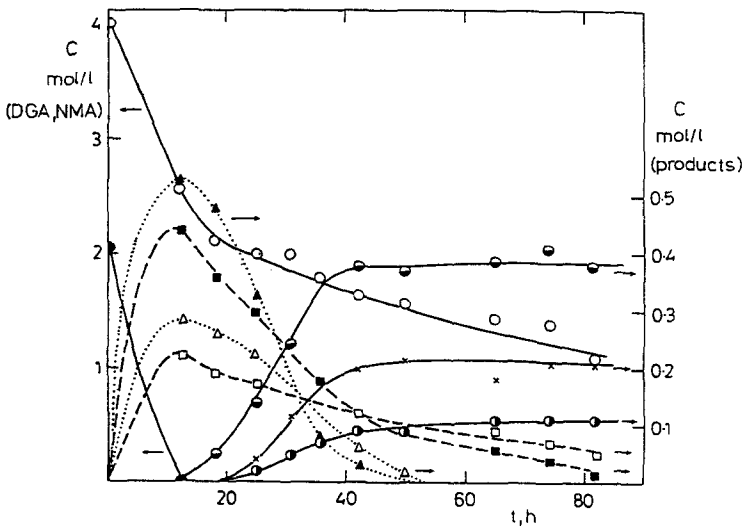
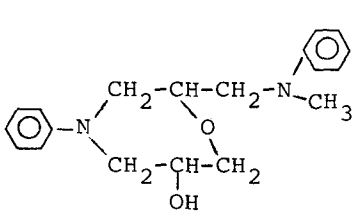
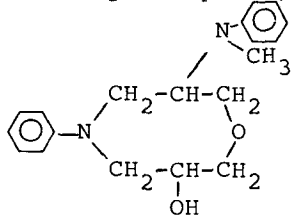


Fig.2 Kinetic course of reaction between DGA and NMA in molar ratio 2:1 at 100°C. O DGA, ● NMA,Δ ▲ ... stereoisomers III,□ ■ ---- stereoisomers IV, ◒ cycle with t_e = 8.6 min, ◑ product with t_e = 8.9 min, x ethers (summarily)

a fraction corresponding to the peak with t_e = 8.6 min was isolated and analyzed by mass spectrometry. The following fragmentary ions with the corresponding intensities relative to the most intensive peak were found in the mass spectrum: m/z 30 (100%), 43 (40%), 55 (35%), 57 (40%) 107 (10%), 114 (14%), 121 (50%), 178 (10%), 195 (12%) and 312 (6%). The existence of the molecular ion m/z 312 and the total fragmentation indicate that it is compound (V) (1-phenyl-3-hydroxy-6-phenyl-methylaminomethyl-1-aza-5-oxa-cycloheptane)



V



VI

An alternative interpretation, according to which this compound should have the structure of the morpholine ring II, is unlikely, due to the absence of the fragment m/z 31, i.e. of the ion CH_2OH. With all probability, the eight-membered ring VI can also be ruled out, due to the weak intensity of the fragment m/z 107 and to the absence of the ion m/z 205 which would arise after splitting-off of the ion $(HNCH_3-C_6H_5)^+$ (m/z = 107) from structure VI (the remaining fragment has m/z = 205). The compound corresponding to peak 8.9 has not yet been identified. Comparing peak areas, it can be estimated that under the given conditions and in the absence of the diluent, some 60-70% of etherification reactions take place intramolecularly. Fig.2 also shows that stereoisomers of the monoadduct III are consumed more quickly than those of diadduct IV, although the diadduct has two hydroxyl groups capable of etherification. This is obviously caused by the fact that the ring closure in the monoadduct (intramolecular etherfication) proceeds at a relatively higher rate than intermolecular etherification.

Reaction of N,N-diglycidylaniline (DGA) with aniline (A)

In the reaction of the bifunctional compounds DGA and A, an alternating polyaddition takes place with formation of linear products DGA-A, DGA-A-DGA, A-DGA-A etc.; moreover, cyclic products DGA-A, DGA-A-DGA-A may also be formed. An example of the chromatogram of the reaction mixture DGA+A is given in Fig.3.

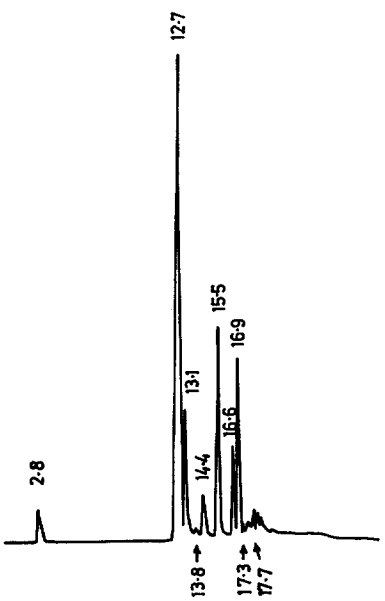


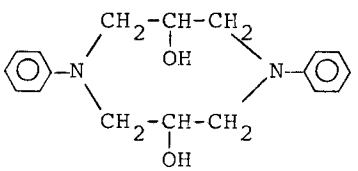
Fig.3 HPLC record of equimolar reaction mixture of DGA with aniline (A)
T = 100°C, $t_{reaction}$ = 2h;
Identification of peaks:
t_e = 2.8 min - aniline,
t_e = 12.7 min - DGA,
t_e = 13.1, 13.8 and 14.4 min - cyclics, t_e = 15.5 min product DGA-A, 16.6 and 16.9 min - stereoisomers of A-DGA-A,
t_e = 17.3 and 17.7 min - stereoisomers of DGA-A-DGA.

The individual peaks of lower oligomers were assigned on the basis of experiments involving various molar ratios of epoxide and amine groups until complete conversion of minority

groups. We have found that the peak with t_e = 15.5 min obviously belongs to the acyclic product DGA-A, peaks with t_e = 16.6 and 16.9 min are probably those of the stereoisomers A-DCA-A, and peaks with t_e = 17.3 and 17.7 probably represent the stereoisomers DGA-A-DGA. Since the peaks with t_e = 13.1, 13.8 and 14.4 min reach a constant height during the reaction, it is assumed that they correspond to cyclic products which contain neither secondary nor primary amino groups, nor epoxy groups able to react.

A very important finding is that the compound corresponding to the peak with t_e = 13.1 min could be isolated in the crystalline form (yield 10%) from the reaction mixture composed of the equimolar mixture of DGA with A in 80% toluene, heated to 135°C for nine days.

The recrystallized product was identified by mass spectrometry. The spectrum has the following fragmentation: m/z 77 (42%), 91 (47%), 105 (82%), 120 (100%), 148 (42%), 253 (60%), 280 (12%), 298 (80%). The existence, and particularly the intensity of molecular ion m/z 298 suggest that we have here a compound with closed cyclic structure. The absence of the fragmentation ion m/z 31 almost excludes the presence of the group $-CH_2OH$. After deuteration with D_2O, ions m/z 298 $(M)^+$, 299 $(M+1)^+$ and 300 $(M+2)^+$ were obtained. This suggests the presence of two labile hydrogen atoms from OH groups which may be replaced with deuterium. The fragmentation ions $(M-H_2O)^+$ and $(M-CH_2CH_2OH)^+$ with the respective m/z 280 and 253, which are formed by the splitting-off of H_2O and CH_2CH_2OH, respectively, from M, increase only by one mass unit after the deuteration. In the case of the acyclic oligomer DGA-A with two labile hydrogen atoms on the OH and NH groups, the fragment m/z 253 may arise only by the splitting-off of the epoxy group, then, of course, there would be an increase by two mass units after the deuteration. This evidences the cyclic structure. Purity of the product is 98-99% (GPC), m.p. = 193-196°C. Analysis allows us to assign structure VII (1,5-diphenyl-3,7-dihydroxy-1,5--diazacyclooctane) to the product with t_e = 13.1 min. Chemical analysis shows 72.4% C, 7.4% H and 9.1% N (theory 72.48% C, 7.38% H and 9.40% N).



VII

The course of the reaction between DGA and A (Fig.4) at various molar ratios shows that the cyclic product VII is formed immediately at the beginning of the reaction. This takes place also with amine in excess; however, the formation of the linear oligomer A-DGA-A is preferred. The formation of the cyclic product VII remains pronounced also with epoxy groups in excess. Under given conditions etherification is slower by an order of magnitude than the addition amine-epo-

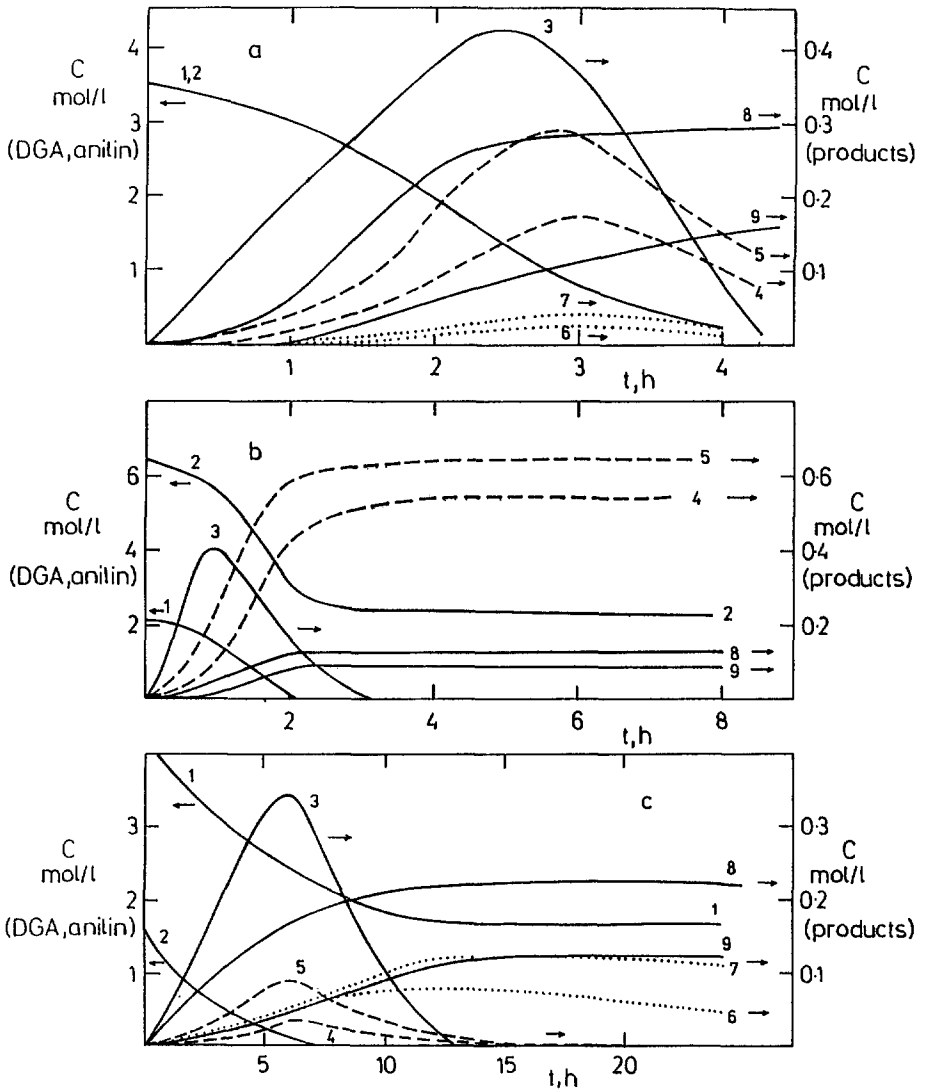


Fig.4 Kinetic course of reaction between DGA and aniline at molar ratio: a) DGA:aniline = 1:1, b) DGA:aniline = 1:3, c) DGA:aniline 3:1 T = 100°C, 1 DGA, 2 aniline, 3 product DGA-A, 4,5---isomers A-DGA-A, 6,7 ... isomers DGA-A-DGA, 8 cycle VII, 9 --- cycle with t_e = 14.4 min

xide, so that the formation of polyethers does not interfere. The relative content of the cyclic product VII and of the assumed cyclic products with t_e = 13.8 and 14.4 min increases with increasing dilution of the reacting system with an inert

solvent (toluene). This fact also indicates that they arise by an intramolecular reaction.

Conclusion

The results reported above show that a pronounced cyclization in the reaction of N,N-diglycidylamines or of their polyfunctional analogs is indeed their specific feature. This special feature should be considered in correlations between the structure and properties of cured systems.

The internal cyclization by a reaction of the epoxy and NH groups of the monoadduct DGA-A giving rise to the eight-memebered N-ring VII is very fast. On the contrary, etherification by a reaction between the epoxy and OH group accompanied by formation of the O-ring V is much slower and takes place only after the amino groups have reacted.

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