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Epoxy Resins

Curing of Epoxy Resins:
Configurational Structure and Reactivity of Stereoisomers in the Model Reaction of Diglycidylaniline with N-Methylaniline

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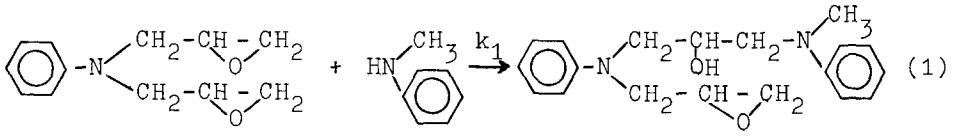
Summary

The course of the model reaction of diglycidylaniline (DGA) with N-methylaniline (NMA) was followed by HPCL. By reversed phase HPCL, good separation of all reaction products and of their stereoisomers was achieved. By analysis of NMR and IR spectra, the configurational structure of the diadduct of DGA with NMA was determined. It is demonstrated that the reactivity of the reaction components is affected by their configurational structure.

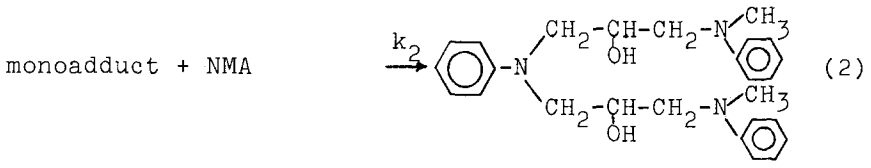
Introduction

The mechanism and kinetics of curing of epoxy resins based on N,N'-tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) with aromatic amines are conveniently studied by means of model systems diglycidylaniline (DGA) - monofunctional amine, e.g. N-methylaniline (NMA). The addition of NMA to DGA is the primary reaction which proceeds in two steps:



(1)

DGA NMA monoadduct (M)



(2)

diadduct (D)

The reaction products can then further react with DGA (etherification). The presence of the monoadduct and diadduct was previously proved by high performance liquid chromatography (HPLC) analysis of the reaction mixture 2-methyl-DGA+NMA (1).

DGA, the monoadduct and diadduct each contain two asymmetric carbon atoms, and therefore all these compounds can be present in the form of stereoisomers. Resolved bands of both stereoisomers have been detected in the ^{13}C NMR spectrum of the diadduct DGA + NMA (2).

In this paper the course of the model reaction DGA + NMA was followed by HPLC. The products were identified by NMR, IR and mass spectroscopy, with attention focussed on the configurational structure of the reaction products, and on the possible effect of the configurational structure of the reaction components on their reactivity. A detailed study of the mechanism and reaction kinetics will be presented in a subsequent communication.

Experimental

Synthesis of DGA: Aniline (186.2 g), epichlorohydrine (407 g), methyl isobutyl ketone (200 g) and water (36 g) were stirred at 80°C for 7 h. The temperature was lowered to 50°C, 480 g 50 % aq. NaOH was added during 1 h and the mixture was kept at 50°C for 8 h. Water (500 g) was then added and saturated NaCl solution was separated. The organic phase was washed three times with 150 g 5 % NaCl and the solvent was distilled off at 1330 Pa at 120°C. The yield of the crude product with the epoxy equivalent 110 g/mol was 98%. This product was purified by repeated distillation at 1330 Pa (b.p.172-4°C). The purified product had an epoxy equivalent 102.8 g/mol (theory 102.5 g/mol) and 0.08% Cl. The content of epoxy groups was determined by addition of HCl in pyridine medium and reverse titration of the HCl excess. The HPLC purity was 100 %.

The purity of NMA was 99 % by gas chromatography. The reaction of the mixtures DGA:NMA=1.7:1,1:1 and 1:2 was performed at 100°C in a series of sealed ampoules, and interrupted by immersion of the ampoule into a bath of 0°C at the given time.

The reaction kinetics was followed by HPLC, using the chromatograph HP 1084 B (Hewlett-Packard, USA), with a glass column 150×3mm ID filled with the reverse phase 5 µm octadecyl-silica SEPARON Si C_{18} (Laboratory Instruments, Prague). The methanol-water gradient was used for elution, with UV detection at 254 nm. 5 µl samples of the reaction mixtures in the form of ~0.2% methanol solution were injected.

The products corresponding to the peaks 5,6 of the chromatogram in Fig.1 were isolated from the reaction mixture DGA:NMA=1:3 heated to 75°C for 24 h by means of a preparative chromatograph consisting of a pump LC-XPD (Pye Unicam, GB), Variscan detector (Varian, USA), recorder A 25 (Varian, USA) and the column LS Prep. 300×17 mm ID (Institute of Chemical Technology, Prague, ČSSR) filled with the reverse phase 8 µm octadecyl-silica Silasorb C_{18} (Lachema Brno, ČSSR). Methanol/water (70/30, v/v) was used as the mobile phase, at flow rate 600 ml/h. The sample was diluted with acetone (50 % solution) and injected at 300 µl portions. Fraction 1 (peak 5) was obtained with purity > 95 %, fraction 2 (peak 6) after two-fold separation with purity > 90 %. For the NMR measurements the fractions were further purified by extraction with C_6D_6 and crystallization; by NMR analysis, each fraction then contained < 2% of the other isomer.

^1H NMR spectra were measured on the PS-100 (JEOL) spectro-

meter at 100 MHz, using approximately 10 % solutions in C_6D_6, with TMS as internal standard. ^{13}C NMR spectra were measured on the spectrometer XL-200 (Varian) at 50 MHz, (90° pulse, sweep width 10 kHz, at 0.8s, pulse repetition rate 6s) using approximately 30 % solutions v/v in C_6D_6 and the C_6D_6 triplet (128.5 ppm) for chemical shift calibration.

Infrared spectra of the neat samples were measured on the spectrometer Perkin-Elmer 580B connected on-line with the multichannel analyzer Tracor-Northern TN-4000.

Results and Discussion

Representative HPLC chromatograms of some reaction mixtures are shown in Fig.1. The stoichiometric mixture, i.e. with DGA:NMA=1:2, exhibits 6 peaks (Fig.1a), the mixture with excess epoxide, DGA:NMA=1.7:1, shows additional four peaks (Fig.1b). The peaks 1 and 2 are assigned to NMA and DGA, respectively; 7-10 are assumed to correspond to ethers (they increase in systems with excess epoxide after consumption of the amine). By mass spectrometry, the peaks 3,4 were shown to correspond to the monoadduct (NMA.DGA), the peaks 5,6 to the diadduct (2NMA.DGA). The system with excess NMA (DGA:NMA=1:3, 24 h at 75°C) gives only 3 peaks by HPLC, corresponding to peaks 1,5,6 in Fig.1. This system, as well as the fractions corresponding to peaks 5,6 separated by preparative chromatography, were analyzed by NMR spectroscopy.

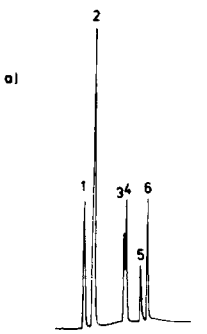


Fig.1. HPLC record of the reaction mixture DGA-NMA. a) DGA:NMA=1:1, $t_{reaction}$ = 7 h, T=90°C; b) DGA:NMA=1.7:1, $t_{reaction}$ = 28 h, T=100°C. 1 NMA; 2 DGA; 3,4 monoadduct; 5,6 diadduct; 7-10 ethers

^{13}C NMR spectra of the system with excess NMA (Fig. 2a and the corresponding fully coupled spectrum) indicate that besides unreacted NMA the product contains two types of -O-CH, four types of $N-CH_2$, four types of aromatic $N-C_1$ carbons, and does not contain $O-CH_2$ carbons and unreacted epoxy groups. Thus it was proved that the opening of the epoxide ring proceeds in agreement with the proposed mechanism (1), (2). Contrary to the ^{13}C NMR spectrum of DGA, and also of TGDDM, which both exhibit only very small splittings (<0.1ppm) of bands corresponding to the presence of stereoisomers, the spectrum of the diadduct is remarkable by the large shift differences in the group of OCH and especially of the NCH_2 bands. ^{13}C NMR spectra of the pure, chromatographically separated fractions 5 and 6, shown in Fig.2b,c

prove that these two fractions are chemically identical, that they both correspond to the structure of the diadduct (D) as shown in scheme (2), and therefore they can only differ by configurational structure (D_1,D_2, Fig.5). In analogy it may be assumed that also the doublet of the chromatographic peaks 3,4 correspond to the stereoisomers of the monoadduct, M_1 and M_2. In this connection it should be noted that also in the HPLC chromatograms, the doublet 5,6 exhibits a large splitting, the splitting of the doublet 3,4 is much smaller, and for the band of DGA under the given experimental conditions no splitting due to configurational structure is observable.

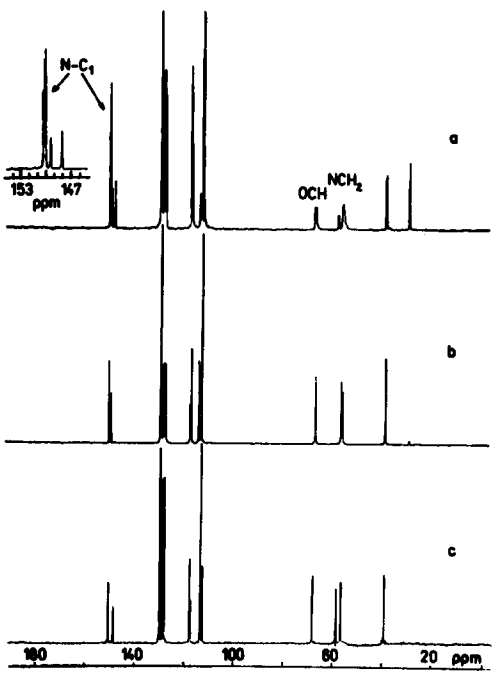


Fig.2. ^{13}C NMR spectra (solvent C_6D_6): a) DGA: :NMA=1:3, 24 h at 75°C; b,c) HPLC fractions 5 (diadduct D_1) and 6 (diadduct D_2), respectively isolated from a) by preparative chromatography

The fractions 5 and 6 differ very remarkably in their ^1H NMR spectra (Fig.3a,b). In the spectrum of the fraction 5 the bands of all NCH_2 protons coincide in a relatively narrow range, around 3 ppm, while the spectrum of the fraction 6 exhibits in this range a relatively narrow unresolved multiplet of one type of NCH_2 groups, and a very broad multiplet corresponding to the AB part of an ABX spectrum (3) for another type of NCH_2 groups, with $\delta_{AB} \doteq 0.8$ ppm, and a large difference of coupling constants, $J_{AX} \doteq 9.5$ Hz, $J_{BX} \doteq 2.5$ Hz.

IR spectra of the separated fractions 5 and 6 (Fig.4) exhibit striking similarity - they differ only by the ratio of intensities of some bands in the range 1050-1300 cm^{-1}. In dilute solution in CCl_4 (0.001 M) where intermolecular hydrogen bonds are broken, bands of intramolecular hydrogen bonds are observed in the range 3000-3600 cm^{-1} for both isomers.

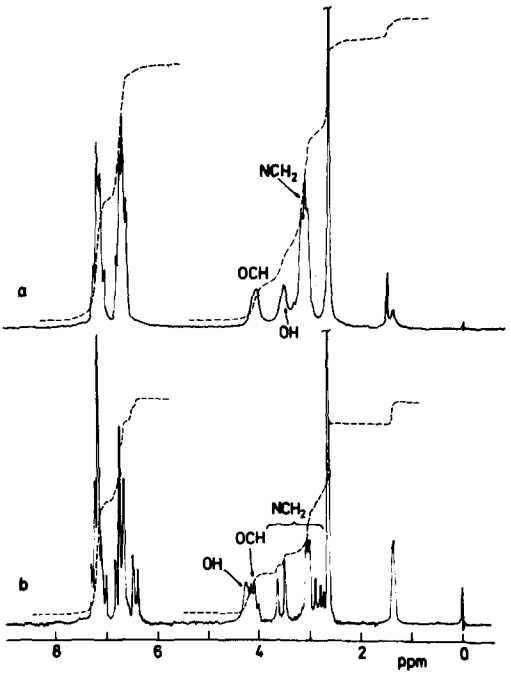


Fig.3. ^{1}H NMR spectra of a) diadduct D_1; b) diadduct D_2 (10 % w/v solutions in C_6D_6)

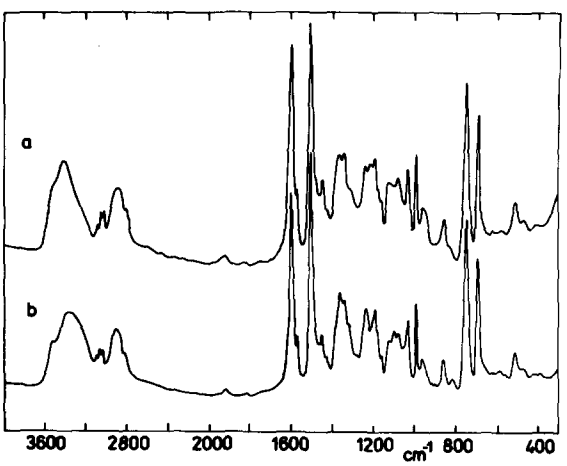
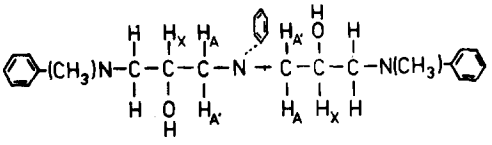
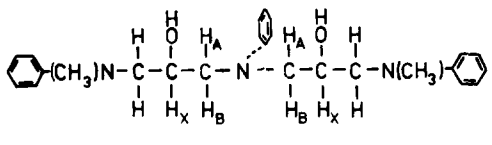


Fig.4. Infrared spectra of a) diadduct D_1; b) diadduct D_2

Both stereoisomers of the diadduct, D_1 and D_2, schematically shown in Fig.5, have several single bonds, rotation about which can lead to the formation of a great number of conformers which are averaged in the resulting NMR spectrum. The differences of the ^1H NMR spectra of D_1 and D_2 are the result of their different symmetry given by the presence of two asymmetric carbon atoms. The isomer D_1 can exist in two configurations RR (d,d) and SS (l,l) which are however indistinguishable in the NMR spectra; the protons of the methylene group next to the central nitrogen atom become magnetically equivalent due to the conformer averaging. In D_2 the asymmetric carbons are not equivalent because they are mirror images one of the other (d,l) and the inequivalence of protons H_A, H_B is preserved even with conformer averaging. Based on ^1H NMR spectra fraction 6 can thus be identified with D_2, and fraction 5 with D_1. The great difference of



D_1



D_2

Fig.5.

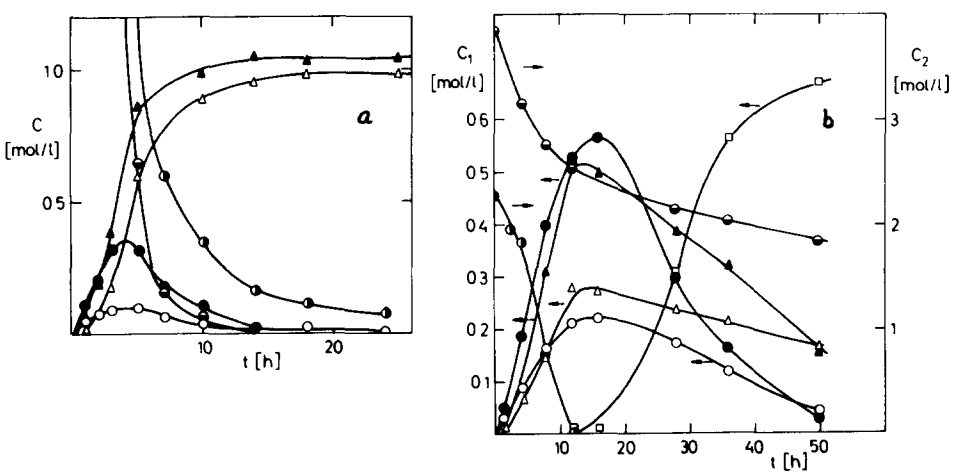


Fig.6. Time dependence of the concentration of reaction components and products during the reaction of DGA with NMA, T=100°C. a) DGA:NMA=1:2; b) DGA:NMA=1.7:1
◑ NMA, ◒ DGA, □ ethers, ○ monoadduct M_1, ● monoadduct M_2, △ diadduct D_1, ▲ diadduct D_2.
C_1 - concentration of monoadducts, diadducts and ethers;
C_2 - concentration of DGA and NMA

coupling constants J_{AX}, J_{BX} in D_2 is probably due to the preference of a conformer with a structure fixed by an intramolecular hydrogen bond.

The kinetics of the reaction in the stoichiometric mixture (molar ratio DGA:NMA = 1:2) and in the mixture with excess epoxide (DGA:NMA = 1.7:1) is shown in Fig.6. It can be seen that the monoadduct M_2, corresponding to the chromatographic peak 4, is generated more rapidly than M_1 (peak 3). Also in the second reaction step, the diadduct D_2 (peak 6) is formed more rapidly than D_1 (peak 5). Towards the end of the reaction, the population of the two diadduct isomers tends to equalization, because in DGA the stereoisomer ratio is 1:1 and change of configurational structure does not take place during the reaction.

Ethers which are formed at excess epoxide only appear after complete consumption of the amine (Fig.6b). The ethers were evaluated as a sum, assuming response equal to that of the diadducts. Therefore the graph presents only a qualitative picture of the course of the etherification. From Fig.6b it is evident that by etherification the monoadducts are consumed more rapidly than the diadducts. M_2 is consumed more rapidly than M_1, and similarly D_2 reacts faster than D_1.

The above results indicate considerable dependence of reactivity on the configurational structure of the reaction components.

References

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