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Oligomerization of N-ethylglycidyl aniline induced by tertiary amines

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Summary

The homopolymerization of N-ethylglycidyl aniline in the presence of N,N-dimethylbenzyl amine was determined by HPLC and titrimetric methods. A product spectrum of oligomer distribution was observed. It was clearly demonstrated that the formation of this oligomer distribution was only possible in the presence of moisture. Furthermore, the formation of N-ethyl-N-propane-2,3-diol aniline was identified.

Introduction

Phenyl glycidyl ether (PGE) has been found to exhibit different types of oligomers. The formation of these oligomers occurs only in the presence of initiators such as tertiary amines or catalysts of the Lewis acid-type. We have investigated these oligomerizations and the resulting reaction mechanisms induced by tertiary amines recently (1).

Nowadays, epoxy resins based on glycidyl anilines are of great technical importance. Tetraglycidyl-4,4'-diaminodiphenyl methane (MY 720, CIBA-GEYGY) cured with diaminodiphenyl sulfone (DDS) is widely used in space programmes, oceanography and supersonic flight (2). Much information is available concerning the structure/properties relationships of such commercial grade crosslinking materials. However, very little has been reported about the elementary steps of glycidyl aniline ring opening reactions.

Using our results obtained from the oligomerization of glycidyl ethers, we tried to investigate analogous reactions using N-ethylglycidyl aniline (N-EGA) and N,N-dimethylbenzyl amine (DMBA) as model compounds, thereby drawing a comparative analysis of both systems.

Experimental

N-EGA was prepared from 2 moles of N-ethylaniline, 2.2 moles epichlorohydrin and 300 ml toluene. The reaction mixture was stirred at 80 °C for 7 h. The temperature was lowered to 50 °C, 2.1 moles 50 % aq. NaOH was added for 1 h during which the temperature of the reaction mixture was kept between 50 and 60 °C. Finally the mixture was stirred at 50 °C for 8 h, after which 300 ml water was added and the organic phase separated. The organic phase was dried with Na_2SO_4 and the solvent distil-

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*To whom offprint requests should be sent led off. The product was purified by distillation at 0.27 kPa (b.p. 136,5 °C) and had an epoxy equivalent of 178.9 (theory 177.0). The determination of epoxy groups was carried out by a titrimetric method according to Durbetaki (3). The HPLC purity was 98 %.

N-Ethyl-N-propane-2,3-diol aniline was prepared as a test substance: 0.06 mole N-EGA, 3 g wofatit KPS (ionexchange resin of VEB Chemiekombinat Bitterfeld, GDR) and 150 ml water were stirred at 80 °C for 24 h. The mixture was filtered and the water was distilled off. The HPLC purity was 100 %.

Purification of DMBA: 300 ml DMBA and 100 g KOH were heated for 5 h under reflux. The mixture was distilled. The distillate was mixed with 5 ml pure phenyl isocyanate and heated under reflux for 5 h. Finally the mixture was distilled (b.p. 190 °C). The chromatogram (Fig. 2) was obtained using the following equipment (4):

column	250 x 4 mm; LiChrosorb RP-18 (5 um)
eluent	CH_3CN : H_2O = 30 : 70 (volume-%) to 100 : 0 (volume-%) in 25 min
flow	1,8 ml min^{-1}
detection	UV 254 nm
sample	10 μl (5 w-% solution in acetonitrile)

Results and Discussion

We observed no reaction after heating 1 mole of N-EGA at 150 °C for 10 h.

Maintaining the same reaction conditions, the process was repeated, this time in the presence of 5 mole-% DMBA. A reaction was found to occur (Fig. 1).

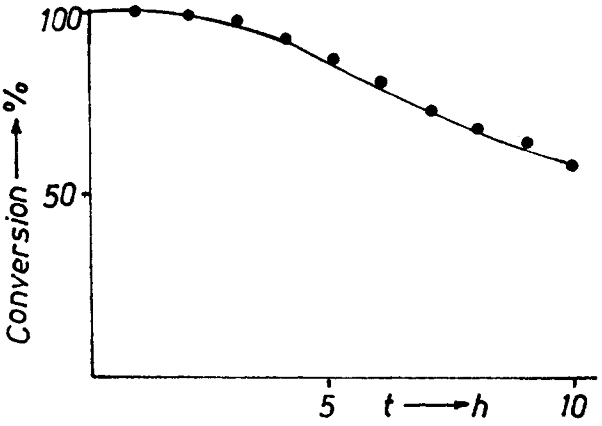
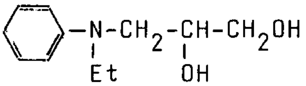


Fig. 1 Decrease of N-EGA vs. time in the presence of 5 mole-% DMBA; temperature = 150 °C

With the help of HPLC, a product spectrum of an oligomer distribution (peaks 1, 5, 6, 8, 9, 11) was observed (Fig. 2).

We identified peak 1 to be N-ethyl-N-propane-2,3-diol aniline 1



1

by the synthesis of this compound and comparison of the retention times.

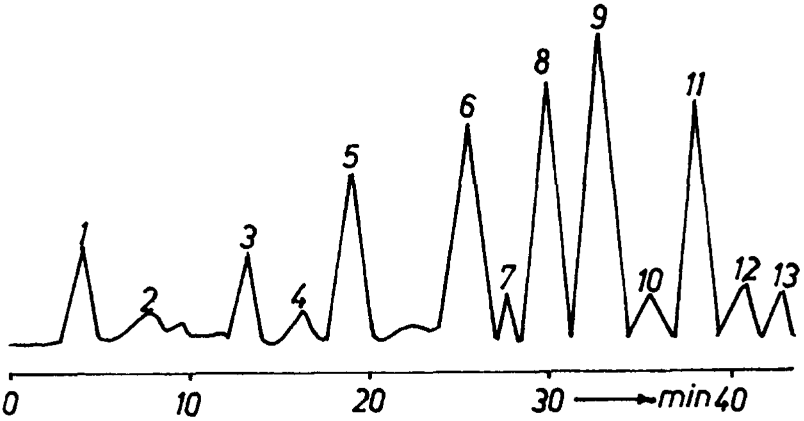
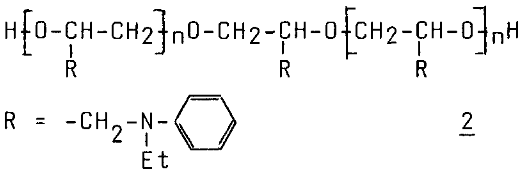


Fig. 2. HPLC chromatogram of the reaction according Fig. 1 after 10 h. HPLC-conditions see Experimental.

Peaks 5, 6, 8, 9 and 11 are considered to be oligomers, resulting from the reaction of 1 with N-EGA. These oligomers can be represented by the general structure 2



$$H\left[O-\underset{R}{CH}-CH_2\right]_nO-CH_2-\underset{R}{CH}-O\left[CH_2-\underset{R}{CH}-O\right]_nH$$

2

Peaks 2 and 3 represent DMBA and N-EGA respectively. Peaks 4, 7, 10, 12 and 13 were not identified and their concentrations were negligibly small. It is possible that these peaks represent another oligomer range.

An induction period was observed in the course of the reaction (Fig. 1). This is probably due to the gradual increase in concentration of OH-groups (active centres) (5).

Carrying out the reaction in the presence of Argon, we observed no oligomer formation. We therefore suppose that the formation of these oligomers can only occur in the presence of moisture. To support this supposition a few drops of water were added to the reaction mixture. There was a sharp increase in the HPLC peak intensities of the oligomers.

The reaction of PGE with DMBA results in the formation of three types of oligomers, which we designated as A, B and C (1). Comparing our results with those obtained from the system

PGE/DMBA, it was found out that the oligomer distribution (Fig. 2) corresponds to the analogous C-type oligomers in the PGE-DMBA reaction. In this case 1-phenoxy-propane-2,3-diol proved to be the starting compound.

The reaction of PGE with DMBA takes place already at temperatures lower than 100 °C. On the other hand the reaction of N-EGA with DMBA occurs only at temperatures above 100 °C.

The oligomerization of nitrogen containing epoxy compounds is much slower than that of ether-bridged epoxy compounds under the same reaction conditions. This is in agreement with the information obtained from literature (6).

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