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Oligomerization of phenyl glycidyl ether in the presence of $ZnCl_2$

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Summary

In the presence of $ZnCl_2$ phenyl glycidyl ether reacts to different products owing to the ring-opening reaction of the oxirane and the cleavage of the ether bond. Using HPLC and off-line mass spectrometry most of the reaction products could be identified.

A reaction scheme and the supposed reaction mechanism were described involving the formation of chlorine - containing oligomers and low molecular weight by - products resulting from the cleavage of the ether bond of the monomer. Conclusions were drawn for original polyfunctional epoxy resin systems.

Introduction

The homopolymerization of epoxides plays an important role in connection with the curing reactions of epoxy resins. To date a variety of papers have been published dealing with the oligomerization of glycidyl ethers in the presence of tertiary amines. Less information, however, is known about Lewis-acids as initiators of oligomerization.

Hence the present paper deals with the oligomerization of phenyl glycidyl ether as a model compound in the presence of $ZnCl_2$ as a well-known example of a Lewis acid. The primary task consists in the identification of the reaction products including the structure of the resulting oligomers.

The mechanism of the reaction between glycidyl ethers and catalysts of the Lewis acid-type is rather complicated because it depends on the catalyst structure and the reaction conditions. Therefore the full elucidation of the mechanism is not yet clear.

Lewis acids and their complexes catalyse the cationic polymerization of epoxides (1). With different structures of the catalysts, often different products can be formed. Transfer reactions and terminating reactions can be the reasons for these differences. Both chainformed polymers and cyclic oligomers may be the reaction products. The ratio of these different types of reaction products depends on several factors
- steric effects
- functional groups
- reaction conditions (temperature, pressure, concentrations).

Essentially the starting reaction is described as an electro-

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philic attack of the Lewis acid on the oxygen of the epoxide ring. Some of the various results concerning the investigation of the advancement reactions should be mentioned.

Worsfold and Eastham (2) investigated the cationic polymerization of ethylene oxide in the presence of $SnCl_4$ and BF_3-ethylether complex. With $SnCl_4$ as the catalyst polymers with $\bar{M}W$ = 5000, dioxane and a small amount of 2-methyl-1,3-dioxolane were formed. A cyclic oxonium ion acts as the propagation centre. The formation of dioxane and the chain growth are competitive reactions of the growing chain end. Subsequent chain termination occurs by scission of the catalyst. Chloride ions which have split off orientate to the cationic chain end. Chain transfer reactions could not be observed. Quite another reaction occurs in the presence of BF_3-ethylether complex. Reversible transfer reactions lead to an equilibration between polymerization and depolymerization. As a result of the latter reaction large amounts of dioxane were formed. The resulting polymeric products posses the MW = 700. Stolarzewicz and Jedlinski (3) found a mechanism with a parallel ring opening and attack on the monomer. Estrin and Entelis (4) polymerized epichlorohydrin in the presence of BF_3 and proposed a mechanism with chain transfer, cyclization and regeneration of the active centre at the same stage of the process. The terminating reaction includes the transfer of a fluoride ion to the cationic chain end, the formation of hydroxylic groups and double bonds. $FeCl_3$ may also act as a Lewis acid-catalyst (5). Since no polymers of propylene oxide could be found the authors proposed a coordination mechanism with an alkoxide as the catalyst proper ($ClFe(OR)_2$). Lidarshik (6) found isotactic polymers of phenyl glycidyl ether in the presence of trialkoxylaluminium and $ZnCl_2$. Kern (7) proposed a quite another mechanism with the elimination of a hydride ion to form the cation. This is possibly solvated by monomer molecules. Other authors discussed the cocatalytic influences of water and other proton donors on the polymerization reaction.

Experimental

Chemicals: Phenyl glycidyl ether (PGE) was distilled at reduced pressure and the purity was determined by HPLC. No phenol or other impurities could be found. The absence of remaining water was determined by IR-spectroscopy. $ZnCl_2$ was supplied in a commercial grade of purity and stored in a desiccator.

Analysis: Samples of the reaction mixture were analyzed using epoxide titration, HPLC and mass spectrometry.

Determination of the epoxide content was carried out by the direct titration method with tetraethylammoniumbromide and perchloric acid at room temperature.

Analytical HPLC-separations were obtained using Knauer HPLC-equipment. Chromatograms were achieved using 250 x 4 mm LiChrosorb RP-18 (5 µm) columns. Detection wavelength was 265 nm. Two mixed solvents were prepared in a gradient mode using glass distilled acetonitrile and distilled water. The mobile phase composition, sample volume, and other pertinent conditions are listed with the chromatogramm.

Preparative HPLC-separations were obtained using the apparatus described previously by us (8). Preparative columns (250 x 16 mm, LiChroprep RP-18 (5 - 20 µm)) were supplied from E. Merck, Darmstadt, F.R.G. The separation conditions were the same as for analytical runs but on a larger scale.

Mass spectra of HPLC-separated compounds were obtained using a MS 5986 mass spectrometer (Hewlett Packard).

Results and Discussion

In comparison with tertiary amines as polymerization catalysts $ZnCl_2$ causes a different consumption of phenyl glycidyl ether (Fig. 1).

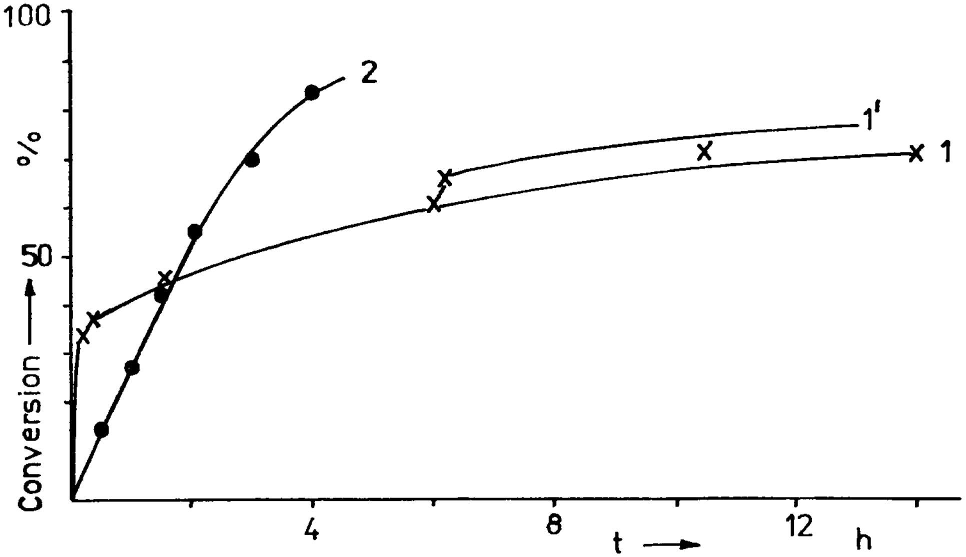


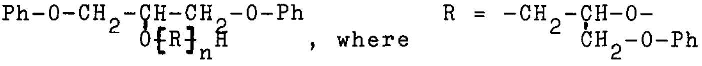
Fig. 1 Epoxide consumption in dependence on the catalyst type; PGE : catalyst = 1 : 0,1; temperature : 80 °C; (1) $ZnCl_2$; (2) $(C_2H_5)_3N$; (1') additional 5 mole-% $ZnCl_2$

Furthermore it has been found that with $ZnCl_2$ as catalyst the conversion of phenyl glycidyl ether is limited. This limit depends on the concentration of $ZnCl_2$ in the reaction mixture. It is remarkable that a subsequent addition of 5 mole-% $ZnCl_2$ again causes a definite acceleration of the epoxide consumption followed by a course of the conversion curve analogous to the course of the former one. This seems to be due to the quantitative consumption of $ZnCl_2$ and diminishing catalytic properties.

By means of analytical HPLC a variety of products were detected. Partial amounts of these products show an oligomer-like distribution. Hence a joint structure of these products can be assumed (Fig. 2).

Identification of the primary products could be achieved by the chromatographic comparison with samples of known compositions. This was possible by using the results of our laboratory of glycidyl ether reactions in the presence of tertiary amines as accelerators (9) - (11). Some of the identified products of these reactions could be found in the reaction product mixture shown above.

The oligomers 7, 9, 11, 13 have the general formula I



$$Ph-O-CH_2-\underset{O\{R\}_nH}{CH}-CH_2-O-Ph \quad , \text{ where} \quad R = -CH_2-\underset{CH_2-O-Ph}{CH}-O-$$

and are the so-called types B PGE-oligomers. Cyclic products and oligomers of similar structures which are formed in the presence of tertiary amines could not be found (11).

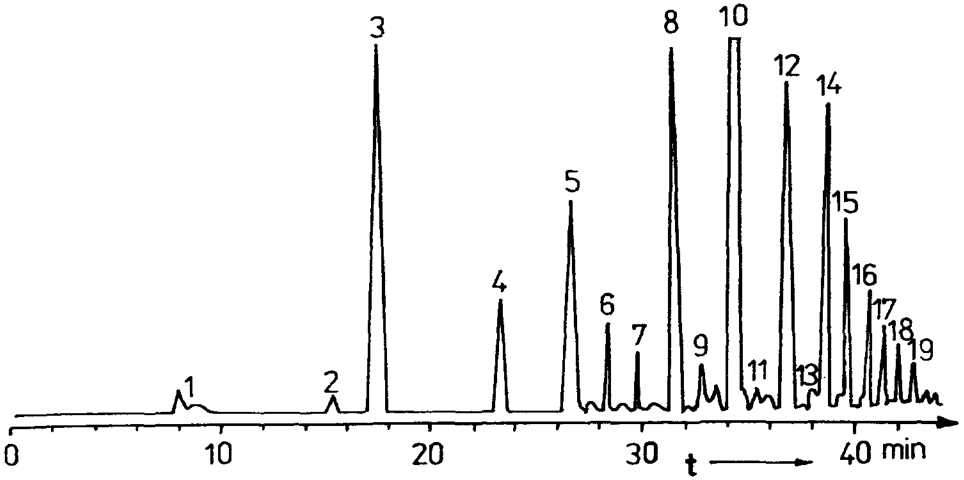
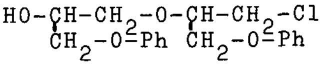


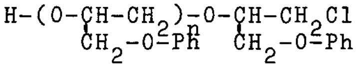
Fig. 2 Reaction products of PGE with $ZnCl_2$; PGE : $ZnCl_2$ = 1 : 0,1; temperature = 100 °C; HPLC-conditions $CH_3CN : H_2O$ = 30 : 70 to 100 : 0 in 40 min, solvent flow = 1,8 ml/min, sample concentration = 5 wt.-%, sample volume = 10 µl; reaction products : 1 phenol, 2 phenoxyacetone, 3 PGE, 4 1,3-diphenoxy propanole, 6 unknown, 7, 9, 11, 13 oligomers originating from 4 and PGE (general formula I), 5, 8, 10, 12 14 ... 19 oligomers of the general formula II

The presence of 1,3-diphenoxy propanole could be further confirmed by using mass spectrometry. For this purpose the reaction product mixture under consideration was separated by preparative HPLC. Almost the same quality of separation could be achieved. The solvent was removed at reduced pressure (T = 60 °C) to gain the pure compounds. We paid most attention to the peak 5 of Fig. 2. By mass spectrometry of the separated compound the following structure could be determined:



$$HO-\underset{CH_2-O-Ph}{CH}-CH_2-O-\underset{CH_2-O-Ph}{CH}-CH_2-Cl$$

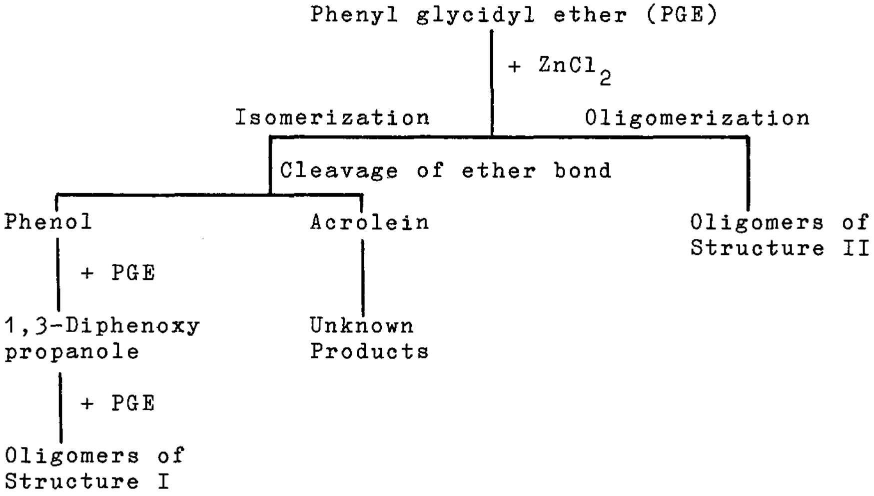
This compound is a part of the distributed oligomers shown in Fig. 2 (peaks 5, 8, 10, 12, 14 ... 19). Hence it can be assumed that the following oligomers in this range can be represented by the general formula II:



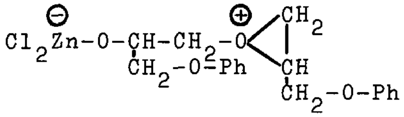
$$\mathrm{H{-}(O{-}\underset{CH_2{-}O{-}Ph}{CH}{-}CH_2)_n{-}O{-}\underset{CH_2{-}O{-}Ph}{CH}{-}CH_2Cl}$$

Peak 6 is the only product of this reaction remaining.

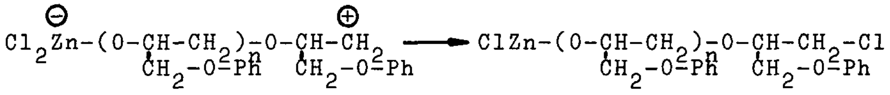
Concluding from these results we propose the following reaction scheme:



According to the reaction mechanism for the conversion of p-chlorophenyl glycidyl ether in the presence of $SnCl_4$ (3) it can be assumed that in the case of the forming of type II oligomers a product with the following structure is the most significant:

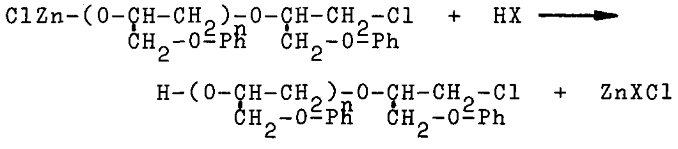


Chain terminating reaction occurs by transfer of a chloride ion to the cationic chain end:



$$\overset{\ominus}{\mathrm{Cl_2Zn}}\mathrm{{-}(O{-}\underset{CH_2{-}O{-}Ph}{CH}{-}CH_2)_n{-}O{-}\underset{CH_2{-}O{-}Ph}{CH}{-}\overset{\oplus}{CH_2}} \longrightarrow \mathrm{ClZn{-}(O{-}\underset{CH_2{-}O{-}Ph}{CH}{-}CH_2)_n{-}O{-}\underset{CH_2{-}O{-}Ph}{CH}{-}CH_2{-}Cl}$$

By attack of a proton donor scission of the ZnCl-group occurs and hydroxylic groups will be formed.



$$\mathrm{ClZn{-}(O{-}\underset{CH_2{-}O{-}Ph}{CH}{-}CH_2)_n{-}O{-}\underset{CH_2{-}O{-}Ph}{CH}{-}CH_2{-}Cl} + \mathrm{HX} \longrightarrow$$
$$\mathrm{H{-}(O{-}\underset{CH_2{-}O{-}Ph}{CH}{-}CH_2)_n{-}O{-}\underset{CH_2{-}O{-}Ph}{CH}{-}CH_2{-}Cl} + \mathrm{ZnXCl}$$

It is probable that water acts as a proton donor because of the hygroscopic properties of $ZnCl_2$.

Conclusions

In the presence of $ZnCl_2$ the conversion of phenyl glycidyl ether, leads to the formation of different products owing to the bond cleavage of the oxirane ring and the ether bond of the monomer.

Using HPLC and mass spectrometry chlorine-containing oligomers and various by-products could be identified, indicating that in original polyfunctional resin systems chlorine would be incorporated by covalent bonding, and several low molecular weight reaction products would be incorporated, however, they may react to further products.

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