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Curing of Epoxide Resins by Anhydrides of Dicarboxylic Acids: Model Reactions

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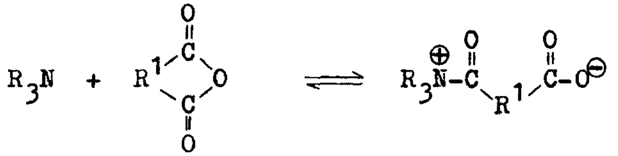
Summary

The kinetics of the polyaddition reaction of epoxy resins were studied using the model system phenyl glycidyl ether, phthalic anhydride, tertiary amine. N,N-dimethylbenzylamine and N,N-dimethylaniline were used as tertiary amines. Furthermore the influence of phenol and benzoic acid was investigated. The oligomer products were separated by high pressure liquid chromatography. A reaction scheme of the copolyaddition and the structure of the products were proposed.

Introduction

The curing of epoxide resins by cyclic anhydrides of dicarboxylic acids is of great technical importance. The kinetics and the mechanism of the copolyaddition of epoxides with acid anhydrides have been studied in length in many laboratories. Recent reviews were published by Luston and Vass (1) and by us (2).

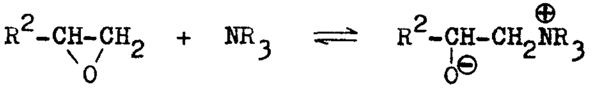
There are different conceptions of the initiation steps. Originally the anhydride was believed to undergo a nucleophilic attack by the tertiary amine (Fischer (3)) and the resulting quaternary ammonium salt zwitterion initiates the polyaddition.



$$R_3N + R^1(CO)_2O \rightleftharpoons R_3\overset{\oplus}{N}-\overset{O}{\overset{\|}{C}}-R^1-\overset{O}{\overset{\|}{C}}-O^{\ominus} \qquad (1)$$

This mechanism was modified in the presence of proton-donating compounds by Tanaka and Kakiuchi (4) and Feltzin et al. (5). They explained the activation of tertiary amine by the proton-donating compound.

Matejka et al. (6) suggested a reaction mechanism for the initiation step in which the tertiary amine reacts with the epoxy group, giving rise to a zwitterion. This way is the critical reaction step of epoxide polymerization.



$$R^2-\underset{\diagdown O \diagup}{CH-CH_2} + NR_3 \rightleftharpoons R^2-\underset{|\\ O^{\ominus}}{CH}-CH_2\overset{\oplus}{N}R_3 \qquad (2)$$

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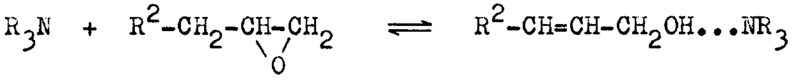
According to a later article by Tanaka and Kakiuchi (7), and also by Luston and Manasek (8), the proton donor may be formed during the reaction by isomerization of the epoxides to a derivative of allyl alcohol.



$$R_3N + R^2\text{-}CH_2\text{-}\underset{\diagdown O \diagup}{CH\text{-}CH_2} \rightleftharpoons R^2\text{-}CH{=}CH\text{-}CH_2OH\cdots NR_3 \qquad (3)$$

The study of the mechanism is usually based on reaction kinetics. The results differ to a large extent. So the kinetics have been variously interpreted from first order to fourth order, as shown in (1).

This paper will deal with the copolyaddition of phenyl glycidyl ether with phthalic anhydride using N,N-dimethylbenzylamine and N,N-dimethylaniline as catalysts. The reaction was studied by chemical titration of functional groups and by liquid chromatography.

Experimental

Phenyl glycidyl ether (1-phenoxy-2,3-epoxypropane) was prepared from epichlorohydrin and phenol with an aqueous solution of sodium hydroxide (b. p. 96 - 98 °C / 0,4 kPa). Phthalic anhydride was purified by crystallization from dry benzene (m. p. 131 °C). The tertiary amines were dried with potassium hydroxide pellets, purified with phenylisocyanate and distilled under reduced pressure. Benzoic acid-2-hydroxy-3-phenoxypropylester was prepared from phenyl glycidyl ether and benzoic acid (m. p. 51 °C) as a test substance.

The polymerization was carried out in a three necked flask equipped with a thermometer, magnetic stirrer and reflux condenser in an argon atmosphere.

Epoxide values were determined by a titrimetric method according to Durbetaki (9). Acid anhydride was determined by a titrimetric method with NaOH and $NaOCH_3$. The reaction mixtures were analyzed by reverse-phase high pressure liquid chromatography with gradient elution in a self constructed instrument which was illustrated in (10). The column was packed with LiChrosorb RP-18 (Merck) phase. The reaction mixtures were diluted with acetonitrile and eluted in a gradient consisting of acetonitrile - water.

Results and Discussion

Polyaddition in a solution of o-dichlorobenzene was used for the kinetic investigations. The conversion curves has a sigmoidal shape with an induction period (Fig. 1). The induction period is shorter when temperature and concentration of the reactants are increased. The induction period can be explained by the gradual increase in concentration of the active centres. The course of the reaction outside the induction period may be described by the following equation:

$$-\frac{dc_{epoxide}}{dt} = k_{exp} \cdot c_{epoxide} \qquad (4)$$

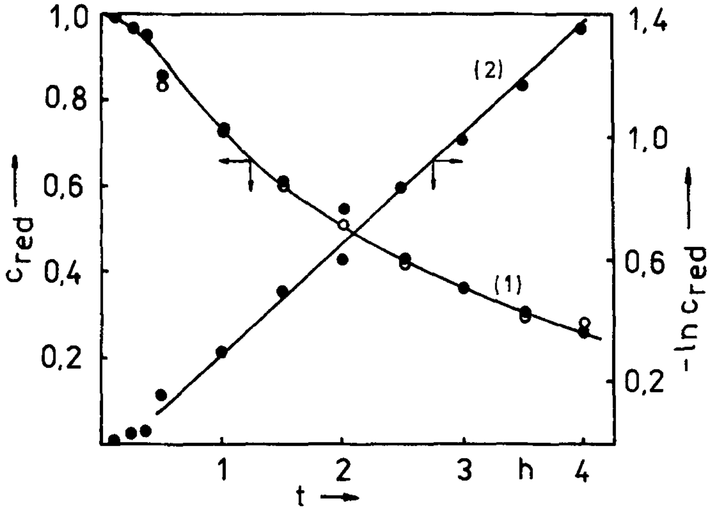


Fig.1 Copolyaddition of phenyl glycidyl ether (0,1 mole/liter) with phthalic anhydride (1,0 mole/liter) catalyzed by N,N-dimethylbenzylamine (0,05 mole/liter) in o-dichlorobenzene at 373 K (100 °C): (1) conversion curves of epoxide (●) and anhydride (O); (2) first order graph,

where k_{exp} is the experimental rate constant of the reaction. It was found that there was almost no difference in decreases of the concentrations between epoxide and anhydride. The reaction course is selective. The equimolar loss of anhydride and epoxide can be explained as alternating reaction, that corresponds well with literature (3,4,5,8). We established that kinetic equations described by Luston and Manasek (8) are also valid for the system phenyl glycidyl ether, phthalic anhydride and tertiary amine.

Furthermore we have considered the effect of benzoic acid and phenol on the reaction between phenyl glycidyl ether and phthalic anhydride catalyzed by N,N-dimethylbenzylamine. The effect of proton-donating compounds is very important because in technical epoxy resins a proton donor is always present, on the one hand as a secundary hydroxyl group, on the other hand as a carboxyl group by partially solvolyse of the acid anhydride.

The course of the reaction between phenyl glycidyl ether and phthalic anhydride catalyzed by N,N-dimethylbenzylamine in the presence of phenol or benzoic acid can be correlated with kinetic equations for reactions of the first order. The influence of proton donors on the rate constant is presented in Table 1. It is obvious that the proton-donating compounds have an accelerating effect. The influence of benzoic acid is greater than that of phenol.

For further characterization of the reaction course, it appeared to be necessary to use liquid chromatography as an analytical method.

Table 1
Influence of proton-donating compounds (PD) on the value of k_{exp} for copolyaddition for phenyl glycidyl ether (1,0 mole/liter) with phthalic anhydride (1,0 mole/liter) catalyzed by N,N-dimethylbenzylamine (0,05 mole/liter) in o-dichlorobenzene at 373 K.

proton-donating compound	c_{PD} mole/liter	$k_{exp} \cdot 10^5$ sec^{-1}
-	-	10,0
phenol	0,1	10,6
benzoic acid	0,05	20,8
benzoic acid	0,1	26,9

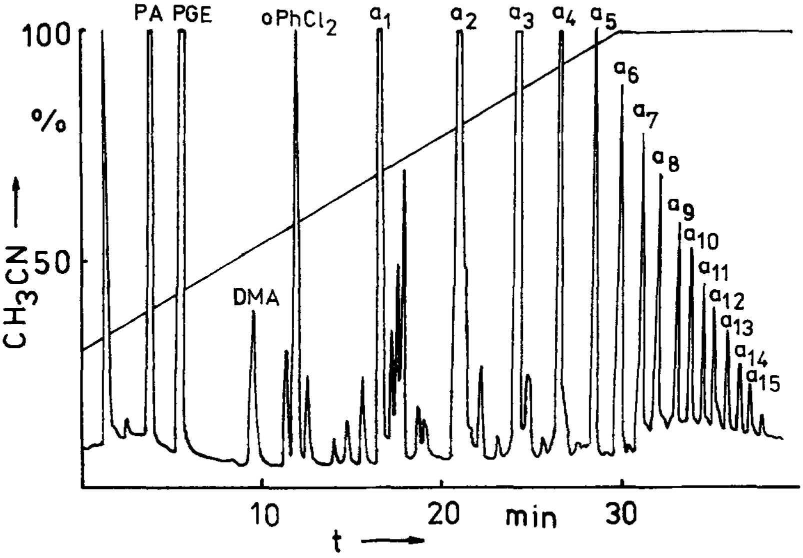
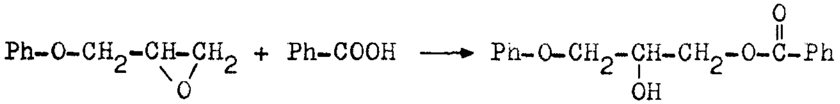


Fig.2 Chromatogram of the reaction mixture of phenyl glycidyl ether (PGE), phthalic anhydride (PA), o-dichlorobenzene ($oPhCl_2$), N,N-dimethylaniline (DMA) (ratio: 1:1:1:0,2) at 423 K (150 °C); reaction time: 6 h; conversion of epoxide: 69 %.

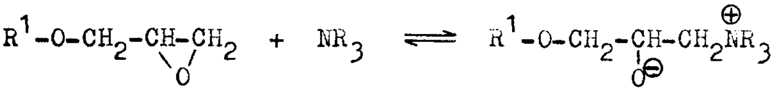
In a previous paper (2), it was shown that the reaction of phenyl glycidyl ether with phthalic anhydride catalyzed by N,N-dimethylaniline was suitable for analysis by liquid chromatography. A typical chromatogram is shown in Fig. 2.

A wide product spectrum is formed with a clear oligomer distribution (a_1 - a_{15}). Analogous distributions were also formed at nonequimolar ratio, excess of anhydride or epoxide and various concentrations of tertiary amine. In comparison with the reaction products of phenyl glycidyl ether with N,N-dimethylaniline, we are sure that no decomposition of the glycidyl ether (11) appears. It was not possible to directly compare the oligomer products of phenyl glycidyl ether and N,N-dimethylbenzylamine with the reaction products of the systems phenyl glycidyl ether, phthalic anhydride catalyzed by N,N-dimethylbenzylamine, because these oligomers could not be analyzed by liquid chromatography. According to these results, it can be supposed that the epoxide homopolymerization is effectively suppressed. By product distribution research in presence of proton donors (2) we demonstrated that different types of oligomers are formed. In addition to the oligomers initiated by tertiary amine, oligomer products were formed by the influence of proton donors. In the presence of benzoic acid, a primary initiation compound (Eq. (5)) was identified by comparing the retention time with those of an authentic sample (benzoic acid-2-hydroxy-3-phenoxypropylester) at the beginning of the reaction.


(5)

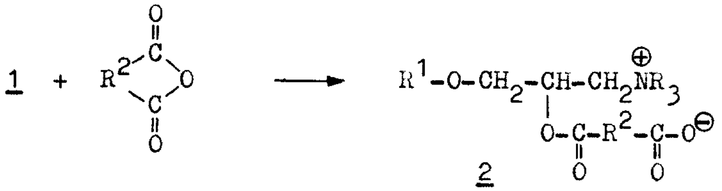
Ester, carboxyl and hydroxyl groups and also unsaturated bonds were found by investigations of the oligomers with spectroscopic methods. According to newer papers (12,13) concerning epoxide polymerization, an amine-catalyzed isomerization of epoxy groups to a derivative of ally alcohol was not confirmed. With reference to the different viewpoints in the literature using the results obtained, we suggest the following reaction mechanism.

Initiation involves the reaction of the tertiary amine with the epoxy group, giving rise to a zwitterion that contains a quaternary nitrogen atom and an alkoxide anion.


(6)

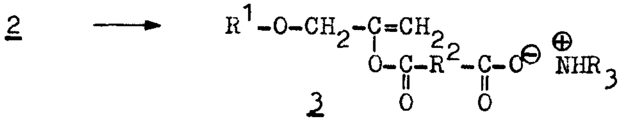
1

This zwitterion can react with acid anhydride or epoxide. The zwitterion reacts much faster with acid anhydride than epoxide. So reaction with acid anhydride will take place.


(7)

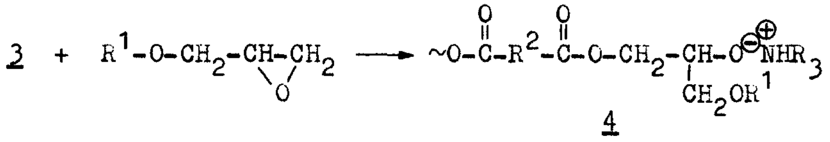
2

The anionic active centre is formed by a reaction within structure 2 under formation of an unsaturated bond.



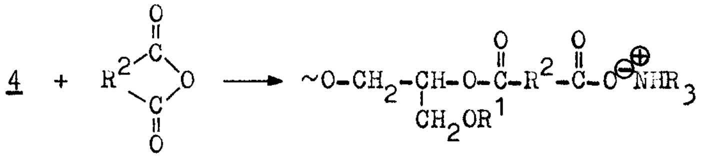
$$\underline{2} \longrightarrow \begin{array}{l} R^1\text{-O-CH}_2\text{-}\underset{|}{C}\text{=CH}_2 \\ \qquad\qquad\quad \text{O-}\underset{\|}{\overset{}{C}}\text{-}R^2\text{-}\underset{\|}{C}\text{-O}^{\ominus}\ \overset{\oplus}{N}HR_3 \\ \underline{3} \qquad\qquad\quad\ \ \text{O} \qquad\quad \text{O} \end{array} \qquad (8)$$

The propagation steps are as follows:



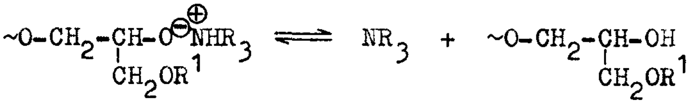
$$\underline{3} + R^1\text{-O-CH}_2\text{-}\underset{\diagdown O \diagup}{\text{CH-CH}_2} \longrightarrow \sim\text{O-}\overset{O}{\overset{\|}{C}}\text{-}R^2\text{-}\overset{O}{\overset{\|}{C}}\text{-O-CH}_2\text{-}\underset{CH_2OR^1}{\underset{|}{CH}}\text{-}O^{\ominus}\overset{\oplus}{N}HR_3 \qquad (9)$$

$\underline{4}$

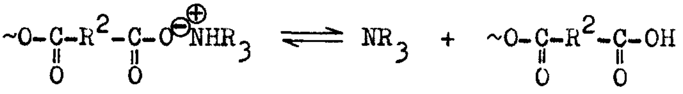


$$\underline{4} + R^2\langle\text{C(=O)-O-C(=O)}\rangle \longrightarrow \sim\text{O-CH}_2\text{-}\underset{CH_2OR^1}{\underset{|}{CH}}\text{-O-}\overset{O}{\overset{\|}{C}}\text{-}R^2\text{-}\overset{O}{\overset{\|}{C}}\text{-}O^{\ominus}\overset{\oplus}{N}HR_3 \qquad (10)$$

The chain grows by interchanging both propagation reactions. Termination steps occur by reversible decomposition of the active centres.



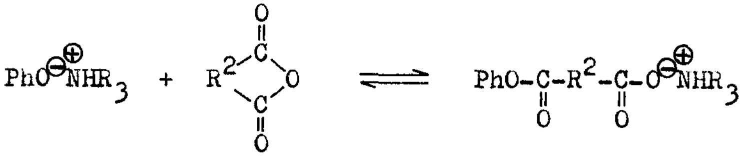
$$\sim\text{O-CH}_2\text{-}\underset{CH_2OR^1}{\underset{|}{CH}}\text{-}O^{\ominus}\overset{\oplus}{N}HR_3 \rightleftharpoons NR_3 + \sim\text{O-CH}_2\text{-}\underset{CH_2OR^1}{\underset{|}{CH}}\text{-OH} \qquad (11)$$



$$\sim\text{O-}\underset{O}{\underset{\|}{C}}\text{-}R^2\text{-}\underset{O}{\underset{\|}{C}}\text{-}O^{\ominus}\overset{\oplus}{N}HR_3 \rightleftharpoons NR_3 + \sim\text{O-}\underset{O}{\underset{\|}{C}}\text{-}R^2\text{-}\underset{O}{\underset{\|}{C}}\text{-OH} \qquad (12)$$

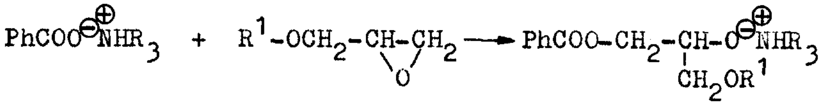
In presence of proton-donating compounds for the initiation, two different ways are possible. The active centres may arise by interaction of proton donor with amine as well as by initiation according to Eqs. (6) - (8). If the proton donor is benzoic acid or phenol, the following reactions can be given:

$$PhOH + NR_3 \rightleftharpoons PhO^{\ominus}\overset{\oplus}{N}HR_3 \qquad (13)$$



$$PhO^{\ominus}\overset{\oplus}{N}HR_3 + R^2\langle\text{C(=O)-O-C(=O)}\rangle \rightleftharpoons PhO\text{-}\underset{O}{\underset{\|}{C}}\text{-}R^2\text{-}\underset{O}{\underset{\|}{C}}\text{-}O^{\ominus}\overset{\oplus}{N}HR_3 \qquad (14)$$

$$PhCOOH + NR_3 \rightleftharpoons PhCOO^{\ominus}\overset{\oplus}{N}HR_3 \qquad (15)$$



$$PhCOO^{\ominus}\overset{\oplus}{N}HR_3 + R^1\text{-OCH}_2\text{-}\underset{\diagdown O \diagup}{\text{CH-CH}_2} \longrightarrow PhCOO\text{-CH}_2\text{-}\underset{CH_2OR^1}{\underset{|}{CH}}\text{-}O^{\ominus}\overset{\oplus}{N}HR_3 \qquad (16)$$

Propagation steps are also released by these complexes. The ratio of the two initiation steps is changed by acidity of the proton donor. The greater the interaction between tertiary amine and proton-donating compound, the lower the initiation by the tertiary amine only.

The effect of the tertiary amine as initiator as well as the influence of proton donors can be explained by the proposed reaction mechanism of the copolyaddition between glycidyl ethers and anhydrides of dicarboxylic acids. Our mechanism of initiation by aminoalcohols suggested in a previous paper (14) can be satifactorily explained by the bifunctional action of these compounds.

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