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Epoxy resins with cyclic carbonate structures

Model studies for amine curing

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Summary

In this paper a mechanism of the reaction of 4-phenoxymethyl 1.3-dioxolan-2-one (PMD) with amines is suggested. The effect of PMD on the reaction of phenyl glycidyl ether (PGE) with amines was investigated as a model for epoxy resins modified by carbon dioxide. Reaction products were described by HPLC, spectroscopic methods and titration.

Introduction

The reaction of the glycidyl group of epoxy resins with carbon dioxide leads to products containing cyclic carbonate structures. Recently we reported some results concerning the model reactions of such modified epoxies with amines (1).

As a model for epoxies derived from the diglycidyl ether of bisphenol A, phenyl glycidyl ether (PGE) is usually used. Therefore, the corresponding cyclic carbonate 4-phenoxymethyl 1.3-dioxolan-2-one (PMD) was selected as model compound. Using the well-known reactions of epoxies with amines, we investigated the reactions of this cyclic carbonate and mixtures of both the glycidyl ether and the carbonate with primary and secondary aliphatic amines. These investigations were compared to results found by ROKICKI et al. (2-4) who cured modified epoxy resins by polyamines.

The reaction products were analyzed by high performance liquid chromatography (HPLC) and spectroscopic methods.

Experimental Part

Phenyl glycidyl ether was prepared according to (16); b.p. 96...98 °C/0.4 kPa.

4-Phenoxymethyl-1.3-dioxolan-2-one was prepared according to (5) from phenyl glycidyl ether and carbon dioxide, purified by recrystallization from ethanol and washed by ether; m.p. 97 °C.

Benzylcarbamic acid (2-hydroxy-3-phenoxyprop-1-yl)ester was prepared as described in (1).

1-Benzylamino-3-phenoxy propan-2-ol: 12 ml benzyl amine were dissolved in 20 ml methanol and 10 ml phenyl glycidyl ether were added. After refluxing for 2 hours the solvent was separated by distillation and the product was recrystallized from ethyl acetate; yield: 95%; m.p. 67 °C; N(calc.): 5.45%, N(found): 5.35%; m.p. 72 °C.

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3-Benzyl-5-phenoxymethyl 1.3-oxazolidin-2-one: 0.4 g hexachloro dimethylcarbonate (triphosgene) was dissolved in 2 ml ether. A solution of 3 g 1-benzylamino-3-phenoxypropan-2-ol in 10 ml acetonitrile was added and the hydrochloride of the amino alcohol precipitated. After evaporating the solvent the product was washed with ether, resolved in acetonitrile and precipitated in water; yield: 0.8 g (75%); m.p. 80°C; N(calc.): 4.95%, N(found): 4.89%; m.p. 86 °C.

Amines were dried with KOH pellets and distilled.

Kinetic measurements were carried out in a thermostated three-necked flask equipped with a thermometer, magnetic stirrer and reflux condenser.

HPLC samples were run with apparatures from KNAUER (Wiss. Gerätebau KG, F.R.G.); column 250 · 4 mm LiChrosorb RP-18, 7.8 µm; eluent: acetonitrile-water 30:70 to 100:0 linear; flow: 1.8 ml/min; detection: UV 263 nm; samples: 5% solution in acetonitrile.

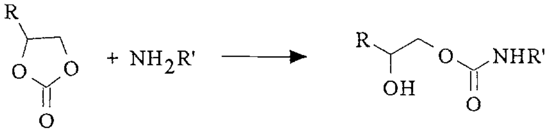
IR spectra were measured with a NICOLET FTIR spectrometer 205. Samples were prepared in chloroform (0.1 mm) or measured in substance (0.025 mm).

^{13}C-NMR spectra were performed on a VARIAN 300 XL spectrometer at 75,4 MHz using acetone or acetonitrile as a solvent and tetramethyl silane (TMS) as an internal standard.

The conversion was followed by evaluation of the relations of infrared absorption of the carbonyl groups at 1805 cm^{-1} (carbonate) and 1720 cm^{-1} (secondary urethane) and the epoxy at 917 cm^{-1}. Furthermore, the reaction was followed by titration with $HClO_4$ (amine) or $HBr/AgNO_3$ (epoxy). The relation between carbonate, epoxy and urethane was partially observed by HPLC.

Results and Discussion

At temperatures below 100 °C cyclic 1.2-alkylene carbonates (1.3-dioxolan-2-ones) react with aliphatic amines forming β-hydroxy urethanes ((6); Eq. (1)).



(1)

1

In our investigations 4-phenoxymethyl 1.3-dioxolan-2-one (PMD; 1, R- = Ph-O-CH_2-) was reacted with several primary and secondary aliphatic amines in substance and in several solvents. We found a rapid reaction with primary amines. The reactivity of secondary amines depends on whether cyclic amines (piperidine) or methyl substituted amines (benzyl methyl amine) on the one side or higher dialkylamines (diethyl, di-n-butyl or di-tert-butyl amine) on the other side are used. The first group is comparable to primary amines, the latter is almost not reactive at all. ARNETT et al. (7) observed an equal behaviour in the aminolysis of lactates. The reactions are, obviously, sterically hindered (Fig. 1).

A consequence of this is that polyamines (dipropylene triamine, triethylene tetramine) only form secondary β-hydroxy urethane structures. In this case absorbtion is observed only at 1720 cm^{-1}; no absorbtion of the tertiary urethane structure (1690 cm^{-1}) is to be seen. This effect is very important for ascertaining the functionality of curing epoxy resins containing cyclic carbonate structures by polyamines.

The reaction of PMD with primary amines may be described by a time law containing an uncatalysed and an autocatalysed reaction ((1); Eq. (2)).

$$-dc/dt = k_1 \cdot c \cdot a^p + k_2 \cdot c \cdot a^q \cdot [OH] \tag{2}$$

c - concentration of carbonate
a - concentration of amine
[OH] - concentation of hydroxyl groups

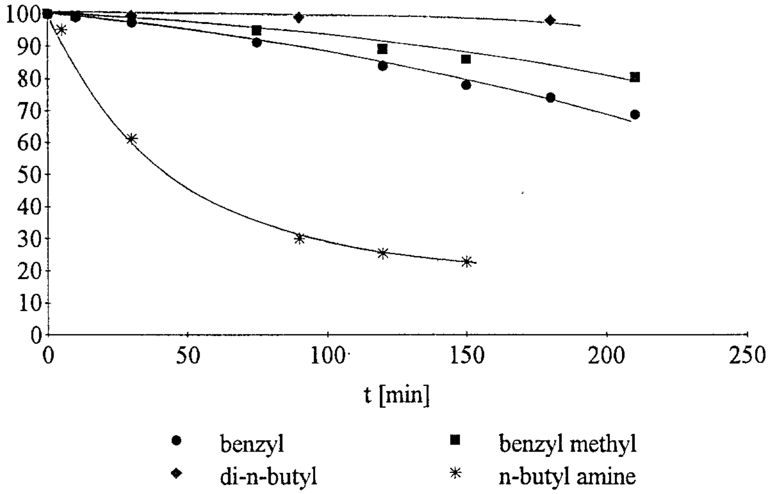


Fig. 1: Course of the reaction of PMD with several amines
c_0= 1 mol/l in anisole 50 °C

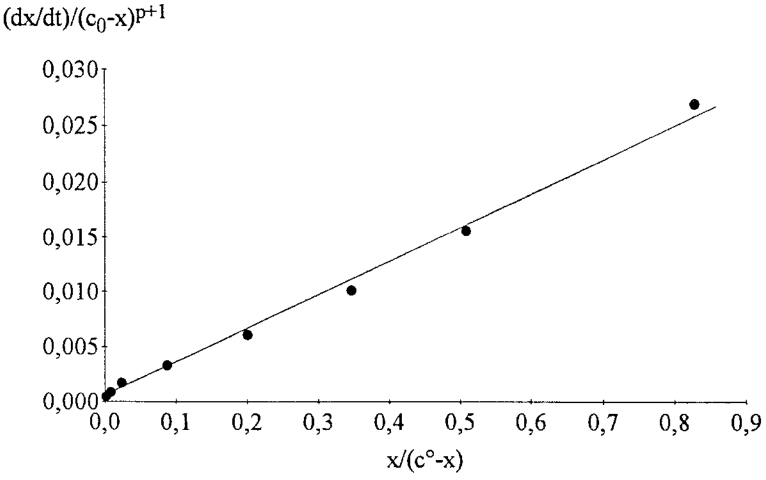


Fig. 2: Linear fit of the reaction of PMD with benzyl amine
c_0 = 0.8 mol/l in toluene, 65 °C
p = 3; q = 2

Its linearized shape (Eq. (3)) shows a fairly good fit for p=2.5...3 and q=2 (Fig.2). The apparent parameters of activation (Tab. 1) are ascertained from k_1 and k_2 of the reaction of PMD and benzyl amine in anisole. From these values and the high reaction order, it must be concluded that there is an association equilibrium.

$$\frac{dx/dt}{(c_0-x)^{p+1}} = k_1 + k_2 \cdot (c_0-x)^{q-p} \cdot x \qquad (3)$$

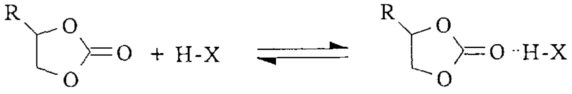
x - extent of reaction
$c_0 = a_0$
$[OH]_0 = 0$

Tab. 1: Activation parameters of the reaction PMD/benzyl amine in anisole

T [°C]	k_1 [l^3/mol^{3}min]	k_2 [l^3/mol^{3}min]
50	0.00089	0.0129
57	0.0012	0.0155
65	0.0014	0.0144
74	0.00142	0.0205
80	0.00158	0.0273
E_A [kJ/mol]	16.3	21.6
$H^{=}$ [kJ/mol]	13.5	18.8
$S^{=}$ [J/molK]	- 260	- 224

STROGANOW et al. (8) suggested such a mechanism without taking account of the catalytic effect of hydroxyl groups.

There is a variety of possible associates. Using IR spectroscopy a shift in the maximum absorbtion of the carbonyl group to higher wavelengths can be observed if either an amine or an alcohol is added. This can be explained by the formation of associates (Eq. (4)).



(4)

-X = -NHR', -OR''

2

Comparing the IR spectrum of a mixture of benzyl amine and propan-2-ol to the spectra of the pure components the formation of mixed associates in addition to the association of both components can be shown. In addition to the shift of the maxima of absorbtion to higher wavelengths there is a strong shoulder at 3150 cm^{-1}.

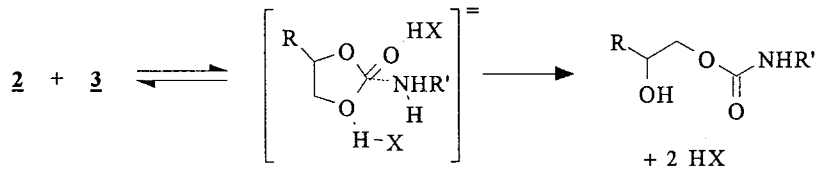
Therefore, the mechanism suggested by STROGANOW et al.(8) should be enlarged by Eq. (6).

$$2\,R'NH_2 \rightleftharpoons R'NH\text{-}H\cdots NH_2R' \qquad (5a)$$

3a

$$R'NH_2 + R''OH \rightleftharpoons R'NH\text{-}H\cdots OHR'' \qquad (5b)$$

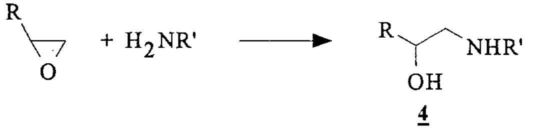
3b



(6)

-X = -NHR', -OR''

To investigate the effect of 1.3-dioxolan-2-one structures on the curing of epoxy resins, the reaction of epoxy and amines was followed in the presence of PMD. Phenyl glycidyl ether (PGE) is able to react twice with primary amines ((9); Eq. (7), (8)).



(7)

(8)

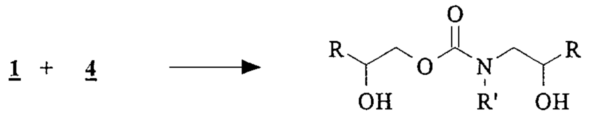
The reaction with secondary amines (Eq. (7) only; H=R') can be described by the time law ((10-14); Eq. (9)).

$$-de/dt = k_3 \cdot e \cdot a^r + k_4 \cdot e \cdot a^s \cdot [OH] \qquad (9)$$

e - concentration of epoxy
$r = 0.5 \ldots 1$; $s = 0.5 \ldots 1$ (10-14)

Without carbonate the reaction proceeds with a distinctive induction period. In the presence of PMD the induction period decreases. The same effect was observed when β-hydroxy urethane was added to a mixture of PGE and amine. It can be concluded that the accelerating effect is based on the rapid formation of hydroxyl groups (Fig. 3).

Using primary amines the corresponding amino alcohol 4 (Eq. (7)) is able to react with unconverted carbonate to form tertiary urethane structures (Eq. (10)). This product is detected using HPLC as well as ^{13}C-NMR and IR spectroscopy in reaction mixtures with a high content of carbonate and in the reaction of the amino alcohol 4 with PMD. The low reactivity of secondary amines seems to be compensated by the vicinity of a hydroxyl group.



5

(10)

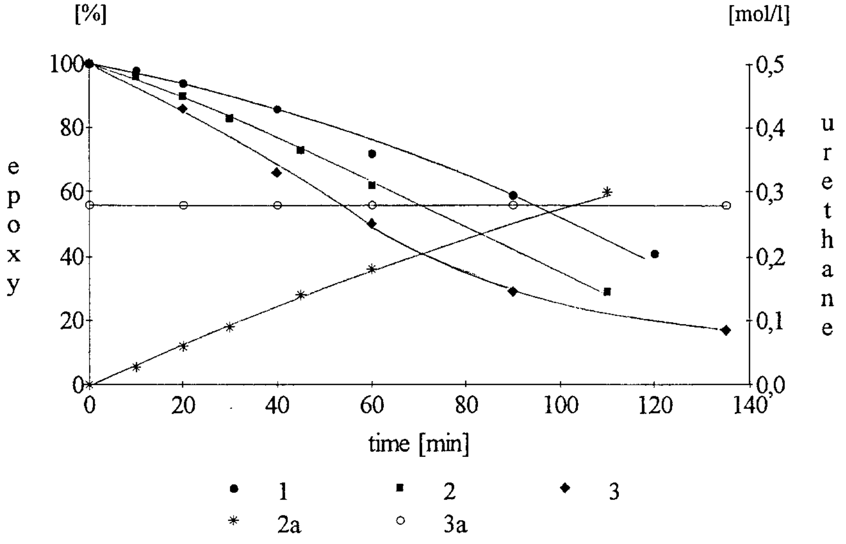


Fig. 3: Course of the reaction of PGE with benzyl methyl amine

1 - pure
2 - with 9 % PMD
3 - with 17 % β-hydroxy urethane
2a - formation of β-hydroxy urethane in 2
3a - content of β-hydroxy urethane in 3

The tertiary urethane formed 5 is able to split off phenoxypropan-2.3-diol at low temperatures (below 80°C). In this reaction the substituted 1.3-oxazolidin-2-one is formed (Eq. (11)). The formation of 1.3-oxazolidin-2-ones from cyclic carbonates and amino alcohols at high temperatures (about 150°C) was recently described in a patent (15). This structure should be formed also in the curing of epoxy resins modified by carbon dioxide with polyamines.

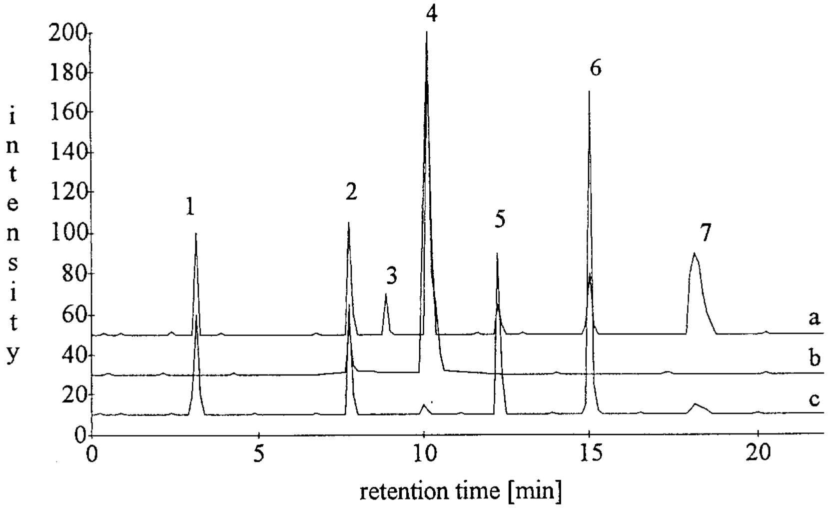


Fig. 4: HPLChromatograms

a - PGE/PMD/benzyl amine =
1:1:1.5
b - PMD/benzyl amine = 1:1
c - PMD/4 = 1:1

1 - phenoxypropane-2.3-diol
2 - PMD
3 - PGE
4 - secondary urethane
5 - 1.3-oxazolidin-2-one
6 - tertiary urethane
7 - amino alcohol

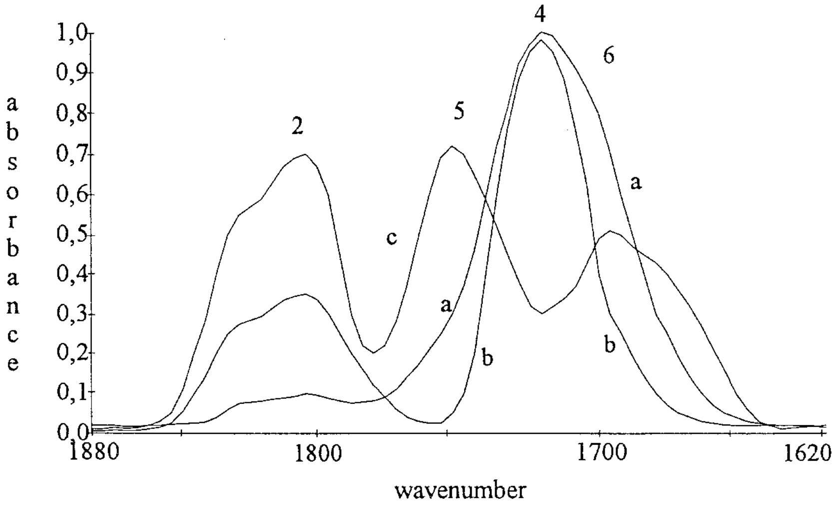
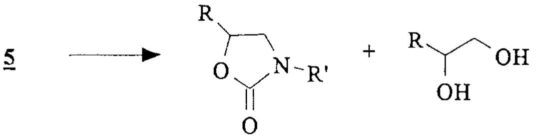


Fig. 5: IR spectra (range)



(11)

Fig. 4 and 5 shows chromatograms and IR spectra of the system PGE/PMD/benzyl amine compared to the systems PMD/4 and PMD/benzyl amine.

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