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Reaction of cyclic carbonates with amines: Linear telechelic oligomers

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Dedicated to Professor H.-J. Cantow on the occasion of his 70th birthday

Summary

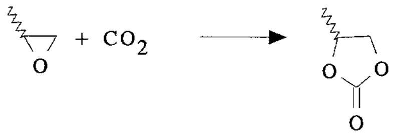
The oligomerization of bisphenol A diglycidyl ether partially and fully modified by carbon dioxide with amines has been studied. The synthesis of prepolymers containing reactive amino and cyclic carbonate groups is described. The reactions have been investigated using chromatography and IR spectroscopy.

Introduction

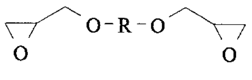
Recently (1,2) we reported some results of model studies of the reaction of epoxy resins modified by carbon dioxide. In this article the formation of linear oligomers and polymers based on the reaction of cyclic carbonate and epoxy structures with amines will be described.

Epoxy resins have been used for the preparation of linear polymers, networks, laminates etc. for many years. Some properties of the products can be changed modifying the resin or the hardener. One way to get resins or curing agents with low vapour pressure, low viscosity, low melting point and good solubility is to synthezise telechelic prepolymers. Another advantage of using prepolymers is the decrease of shrinkage and the fact that a lot of reaction heat arises before curing.

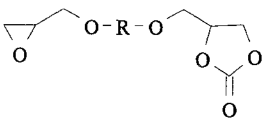
A very important group of epoxy resin intermediates are deriven from the diglycidyl ether of bisphenol A (BADGE) and its advancement products. The reaction of an oxirane group with carbon dioxide gives rise to cyclic carbonate structures (1.3-dioxolan-2-ones).



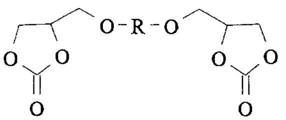
Using this modification reaction BADGE (I) and mixtures with its cyclic carbonates, (II,III) were converted with aliphatic and aromatic amines to give telechelic oligomers and polymers.



I

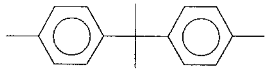


II



III

R =



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The course of these reactions was followed by titration of the functional groups and by IR spectroscopy. The products obtained were analyzed by HPLC, GPC and IR spectroscopy.

Experimental

Chemicals

The diglycidyl ether of bisphenol A (I) was obtained by recrystallization of the commercial epoxy resin EPILOX A17-01 (Leuna AG, F.R.G.) from acetone/methanol (m.p. 42-43° C; content of epoxy: 5.82 mmol/g (found), 5.88 mmol/g (calc.)).

Bisphenol A bis[(2-oxo-1.3-dioxolan-4-yl)-methyl]ether (III) was prepared by addition of carbon dioxide to I according to (3). 50 g I, 0.7 g triphenyl phosphane and 0.3 g KI were melted. Carbon dioxide was let through by strongly stirring the melt at 130° C until the beginning of crystallization of III. The product was recrystallized twice from ethyl acetate (m.p. 172-174° C; yield: 60 %) calc.: C 64.51,H 5.65; found: C 64.58,H 5.72.

Modified resins were prepared in the same manner; the reaction was stopped at the desired grade of conversion. The viscous oil was strained off the settled salt. The content of epoxy was ascertained by titration; the content of carbonate was determined using IR spectroscopy.

All diamines used at least 99% quality were purchased: xylylene diamine (XDA/Aldrich), piperazine (Aldrich), 1.8- diamino 3.6-dioxaoctane (DADO/Merck-Schuchardt), N.N'-dibenzyl ethylene diamine (DED/Merck-Schuchardt), hexamethylene diamine (HMDA/Riedel-de Haen). Monoamines were dried with KOH and distilled.

Oligomers from III and diamines in solution

8.568 g (20mmol) III and 20 mmol of the diamine were dissolved in 20 ml of dried dimethyl sulphoxide and stirred at 75° C until there were no change in the absorption of carbonyl groups in the IR spectra. The solution was given in 500 ml cold stirred water, after drying the product was dissolved in tetrahydrofurane, precipitated in water and dried again.

HMDA: reaction time 42 hours, yield 92%
$(C_{29}H_{40}N_2O_8)_n$ calc. C 63.95 H 7.40 N 5.14, found C 63.63 H 7.38 N 4.93
XDA: reaction time 96 h, yield 90%
$(C_{31}H_{36}N_2O_8)_n$ calc. C 65.94 H 6.43 N 4.96, found C 64.07 H 7.00 N 4.73
DADO: reaction time 72 h, yield 78%
$(C_{29}H_{40}N_2O_{10})_n$ calc. C 60.40 H 6.99 N 4.86, found C 59.17 H 7.24 N 4.62
Piperazine: reaction time 96 h, yield 84%
$(C_{27}H_{34}N_2O_8)_n$ calc. C 63.01 H 6.66 N 5.44, found C 62.85 H 6.70 N 5.31

Oligomers from mixtures of I, II and III and aliphatic amines

About 3 g of the modified resin was dissolved in 5 ml of DMSO, the calculated amount of the amine was added and the mixture was stirred for 10 hours at 80°C. The products were processed as described above.

Oligomers from mixtures of I, II and III and aromatic amines

About 3 g of the modified resin was mixed in bulk with the calculated amount of the amine. After a reaction time of 10 hours at 80°C the temperature was increased up to 110°C until the complete conversion of the epoxy.

Analysis

HPLC samples were run with equipments from KNAUER (Wiss. Gerätebau KG, F.R.G.); column: LiChrosorb RP-18, 7.8 µm; eluent: acetonitrile/water 40 : 60 to 100 : 0 linear; flow 1.2 ml/min; detection 263 nm; samples: 5% solution in acetonitrile.

IR spectra were measured with a NICOLET FTIR spectrometer 205. Samples were prepared as solutions in chloroform or in mixtures of chloroform and methanol.

VPO: molecular weights were ascertained using the VPO apparatus from KNAUER with tetrahydrofurane as a solvent at 45 °C.

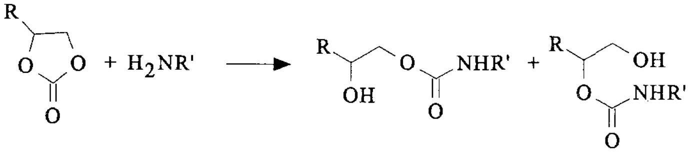
GPC samples were run with apparatuses from KNAUER; two columns LiChrogel(100 - 20000/100 - 5000 g/mol polystyrene in tetrahydrofurane); solvent: THF; detection: RI/viscosity dual; calibrated using polystyrene standards.

Titration: epoxy (potentiometric $HBr/AgNO_3$), amine ($HClO_4$ in acetic acid).

Results and Discussion

Oligomerization of bifunctional epoxies with amines containing two NH-bonds (primary monoamines, secondary diamines) was described by KLEE et al. (4, 5, 9). The addition of the diglycidylether of bisphenol A (BADGE, I) with such amines gives rise to polymeric amino alcohols and epoxy or NH_2-terminated oligomers. We reacted BADGE partially and fully modified by carbon dioxide with bifunctional amines.

Cyclic carbonates react with primary and secondary aliphatic amines to give β-hydroxy urethanes. There are two isomeric structures (1,6):



We found a time law containing an uncatalyzed and an autocatalyzed term (1,2):

$$-dc/dt = k_1 \cdot c \cdot a^3 + k_2 \cdot c \cdot a^2 \cdot [OH] \qquad \text{Eq. 1}$$

c = concentration of carbonate
a = concentration of amine
[OH] = concentration of hydroxyl groups

The high reaction order and the low apparent parameters of activation (about 20 kJ/mol) point at association equilibra before the reaction.

Using bifunctional compounds it is possible to synthesize oligomers. The biscarbonate derived from the diglycidyl ether of bisphenol A (III) melts at 172-174° C and is not very soluble in many solvents. Converting III with bifunctional amines in the melt oligomer products are formed. Due to the high reaction temperature side reactions occur. Thus the urethane formed reacts with amines to give urea structures (1). Furthermore, carbon dioxide is split off and the epoxy formed is able to react.

In strongly polar solvents (dimethyl sulphoxide) III can be reacted with diamines at lower temperatures (60-80 °C). Polymers are formed with relatively low molecular weights. Fig. 1 shows a typical gel permeation chromatogram of these products. The relation $M_w/M_n = 2$ is typical of linear polymers obtained by polyaddition at complete conversion (7). The values found lie in this range.

Oligomer β-hydroxy urethanes were obtained from III and hexamethylene diamine (HMDA), xylylene diamine (XDA), 1.8- diamino 3.6-dioxaoctane (DADO) and piperazine.

Many secondary diamines (N.N'-dibenzyl ethylene diamine; DED) almost do not react because of steric hinderance (2).

Low molecular weights result from the high reaction order of the amine. Reaching high conversion the concentration of the amine decreases and the reaction slowes down.

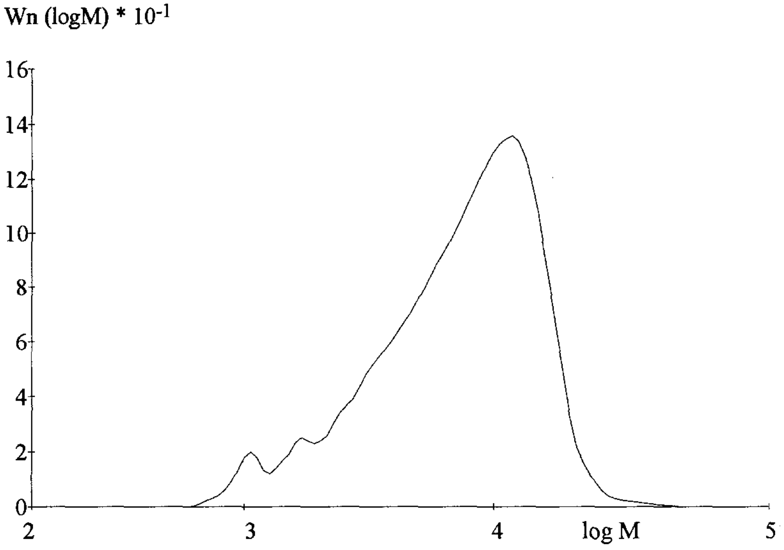


Fig. 1: GPC of the oligomer from **III** and HMDA

Tab. 1: Molecular weights of oligomer β-hydroxy urethanes (in g/mol)

Amine	VPO M_n	GPC M_n	GPC M_w	$M_w : M_n$
HMDA	7500	7700	12000	1.6
XDA	2400	3290	7730	2.35
DADO	2800	3170	7000	2.2
Piperazine	3300	3500	7200	2.1

Using an excess of diamine NH_2-terminated oligomers can be obtained in shorter reaction times (Tab. 2). Precipitating the products in water the lowest oligomers do not precipitate completely. The yield decreases and the molecular weight of the product is higher as it is calculated according to Eq. 2 (8).

$$M_n = (r \cdot M_1 + M_2)/(1 - r) \qquad r = c/a \qquad \text{Eq. 2}$$

The oligomer β-hydroxy urethanes obtained from **III** and secondary diamines can be converted with BADGE to products with higher molecular weights. Fig. 2 shows the gel permeation chromatograms of the oligomer urethane and the oligomer obtained by its further reaction with BADGE.

If a primary diamine is reacted with **III**, the oligomers can be cured by BADGE.

Tab. 2: Molecular weights of NH_2-terminated oligomers of III and HMDA

C : NH_2	M_n [g/mol]	M_n [g/mol] calc.	reaction time [hr.]	yield [%]
1 : 1	7700		42	92
1 : 1,1	5400	5556	24	79
1 : 1,25	3300	2292	18	66
1 : 1,5	2000	1204	12	62

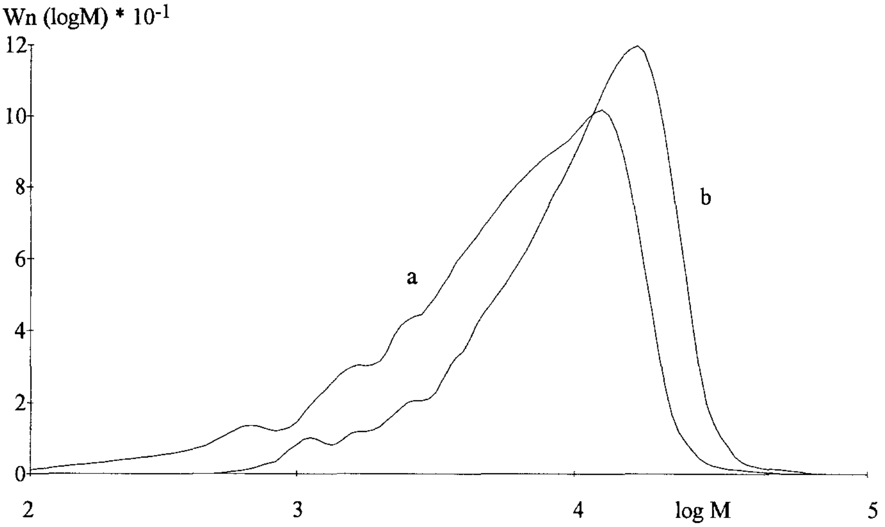
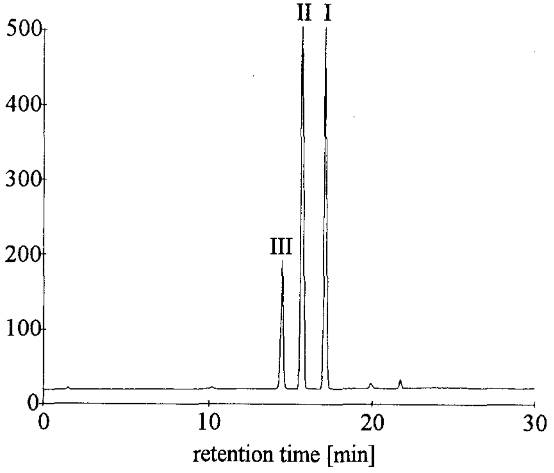


Fig. 2: GPC of an oligomer (**IV**) from **III** and piperazine (1 : 1.165; **a**) and the product from **IV** and BADGE (1 : 1; **b**)

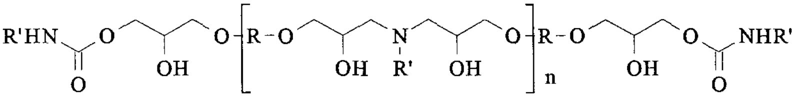


Using a suitable system of catalyst (3) resins with each of the desired level of carbonate structures can be synthesized, if carbon dioxide was led through the melt of BADGE. **I**, **II** and **III** are present in statistic distribution. Fig. 3 shows a chromatogram of the product containing 40 mol% carbonate. The resins are high viscous oils at room temperature or may be homogenized by little warming if partially crystallization occurs at high or very low contents of carbonate structures.

Fig. 3: HPLC of a modified resin containing 40 mol% carbonate

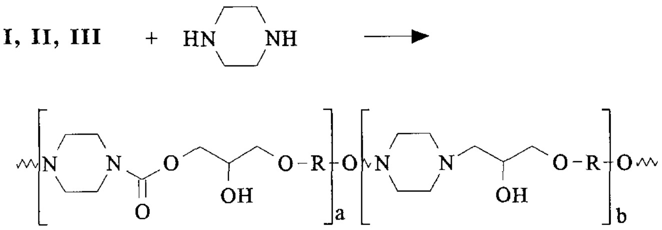
Partially modified BADGE (containing II and III) can be reacted with amines without a solvent or in DMSO dependent on the content of carbonate structures at 20 ... 100 °C. Linear products are formed with primary monoamines and secondary diamines. Using primary amines (benzyl amine, butyl amine), oligomer amino alcohols containing β-hydroxy urethane stuctures on the chain end are obtained. The molecular weight depends on the content of carbonate.

I, II, III + H_2NR' ⟶



R' = alkyl

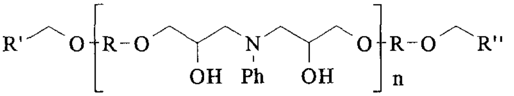
If a secondary diamine is used polymers containing amino alcohol and β-hydroxy urethane structures are hold.



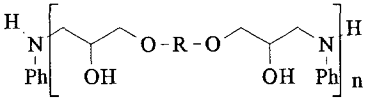
Using aliphatic amines the molecular weight is higher than it was calculated because of etherification of epoxy and hydroxy groups.

Aromatic amines almost do not react with cyclic carbonates at temperatures below 100 °C (1).

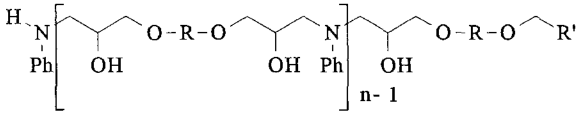
I, II, III + H_2NPh ⟶



IV



V



VI

It is possible to synthesize oligomer amino alcohols containing cyclic carbonate structures at the chain end if an aromatic amine (aniline) is converted with the epoxy groups of the modified resin.

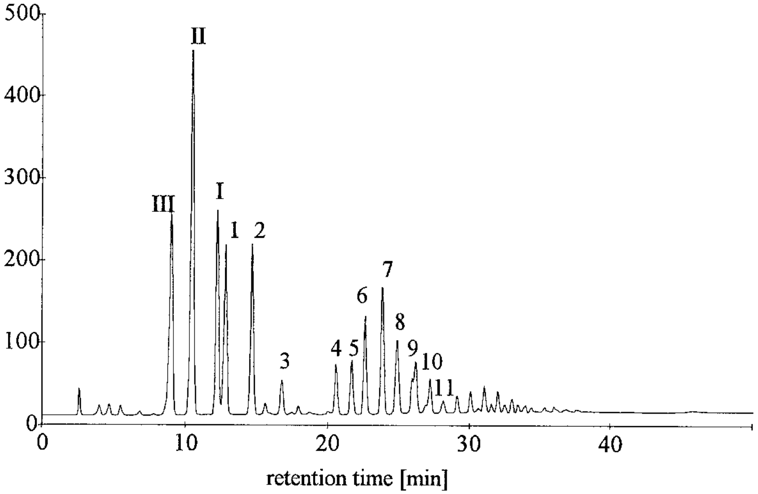


Fig. 4: HPLC of the oligomers from a modified epoxy resin (40 mol% carbonate) and aniline, epoxy : amine = 1:1,5

The oligomerization of the modified resin with aromatic amines can be observed by HPLC. Fig. 4 shows a chromatogram of the reaction product of a resin containing 40 mol% carbonate and aniline. The products of the reaction of **I** with aniline are categorized according to (5). The other products are assigned varying the relation between the resin and the amine. There is an erythro and a threo form of tertiary amino alcohols (9). That is why two or more peaks occur from one compound.

Oligomers from BADGE and aniline have relatively high glass transition temperatures. That is why it is nessesary to increase the temperature beyond 100°C to get complete conversion of the epoxy. At this temperature the carbonate split off carbon dioxide to give epoxy groups. To get prepolymers without epoxy structures an excess of amine is nessesary. The products than contain carbonate and amine groups at the chain end. The molecular weight can be influenced by the content of carbonate and the initial relation between epoxy and amine.

Tab. 3: Peaks of the chromatogram (Fig. 4)

Peak	Formula	n	R'	R"
1	**VI**	1	carbonate	
2	**VI**	1	epoxy	
3	**V**	1		
4, 5	**IV**	1	carbonate	carbonate
6, 7	**IV**	1	carbonate	epoxy
7, 8	**VI**	2	carbonate	
8, 9	**IV**	1	epoxy	epoxy
9, 10	**VI**	2	epoxy	
10, 11	**V**	2		

The oligomers contain reactive carbonate groups and can be added with aliphatic diamines. Fig. 5 shows IR spectra of the product from an epoxy resin containing 40 mol% carbonate structures with aniline and the product of this prepolymer with hexamethylene diamine.

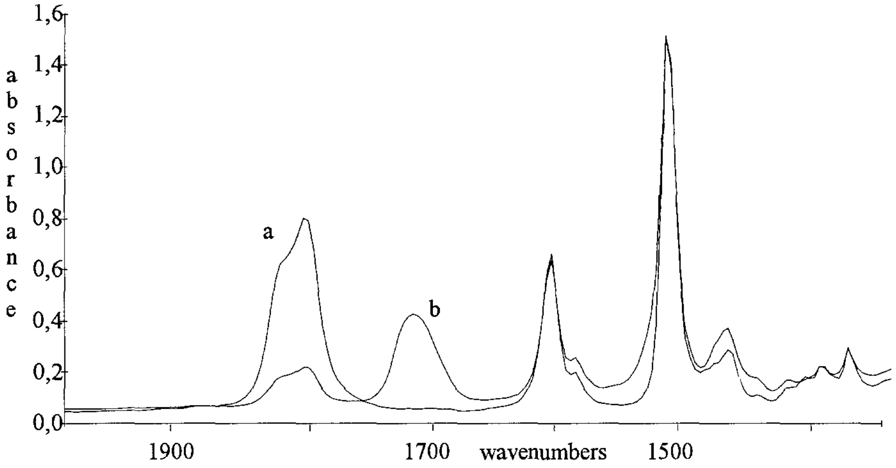


Fig. 5: IR spectrum of the oligomer from a modified resin (40 mol% cyclic carbonate) and aniline, epoxy : amine = 1:1,1 (a) and its product with HMDA (b)

Acknowledgements

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References

1. Th. BÜRGEL, M. FEDTKE, Polym. Bull. 27 (1991), 171
2. Th. BÜRGEL, M. FEDTKE, Polym. Bull. in press
3. G. BRINDÖPKE, M. MARTEN, DE 35 29 263 (1987)
4. J. KLEE, H.-H. HÖRHOLD, J. RADDATZ, Acta Polymerica, 41 (1990), 557
5. J. KLEE, H.-H. HÖRHOLD, W. TÄNZER,
   Crosslinked Epoxies, W. de Gruyter & Co. Berlin, New York (1987), 47
6. M. M. BAIZER, J. R. CLARK, E. SMITH, J. Org. Chem. 22 (1957), 1706
7. P. J. FLORY, Principles of Polymer Chemistry, Cornell Univ. Press Ithaca, USA, 1953, 71
8. H.-G. ELIAS, Makromoleküle, Hüthig und Wepf Verlag Basel, Heidelberg, New York, 1981
9. J. KLEE, H.-H. HÖROLD, W. TÄNZER, M. FEDTKE, Angew. Makromol. Chem. 147 (1987), 71

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