Investigations on the Curing of Epoxy Resins with Hexahydrophthalic Anhydride

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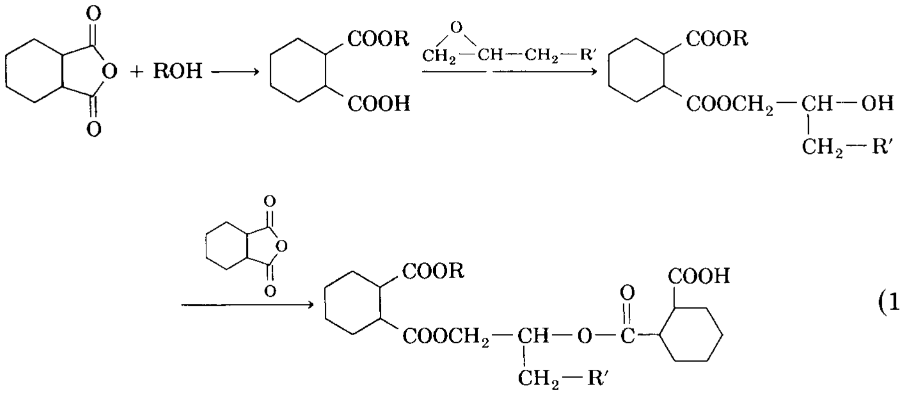
Synopsis

The bifunctional epoxides bisphenol A diglycidyl ether (BADGE) and hexahydrophthalic diglycidyl ester (HHDGE) as well as the monoepoxides phenyl glycidyl ether (PGE) and cyclohexane carboxylic acid glycidyl ester (CHGE) were cured with hexahydrophthalic anhydride (HHPA) in the presence of benzyldimethylamine (BDMA) or 1-methylimidazole (1-MI) as catalysts at 100–140°C. Investigations of the curing kinetics gave sigmoidal-shaped curves with marked induction periods. IR analysis of the cured products revealed that the propagation proceeds not only by the esterification reaction of epoxide with anhydride but also by chain anhydride formation by the reaction of carboxylate with anhydride groups. ^{13}C-NMR investigations of the soluble polymers showed that most of the peaks resulting from double bonds could not be assigned to structures formed by initiation reactions that had previously been proposed for the anhydride curing of epoxides. In analogy to a postulated mechanism for the decarboxylation condensation of HHPA alone in the presence of tertiary amines, it is proposed that an isomerization product of HHPA is one of the molecules that initiate the curing reaction.

INTRODUCTION

The curing of epoxy resins with cyclic anhydrides is an important process for the fabrication of electrical insulating materials. The mechanism of this reaction has been intensively studied during the last years.[1-18] The noncatalyzed polymerization is now quite well understood.[1,2,11,12,17] It is started by the reaction of anhydride groups with hydroxyl groups that are present in the reaction mixture (as part of the epoxy resin) to generate a monoester and a carboxylic acid group. The carboxylic acid group then reacts with the epoxide to form a diester with a hydroxyl group, which in turn reacts with another anhydride:



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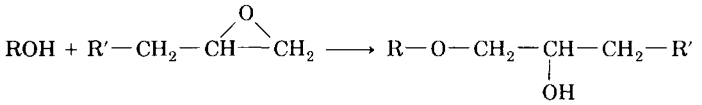
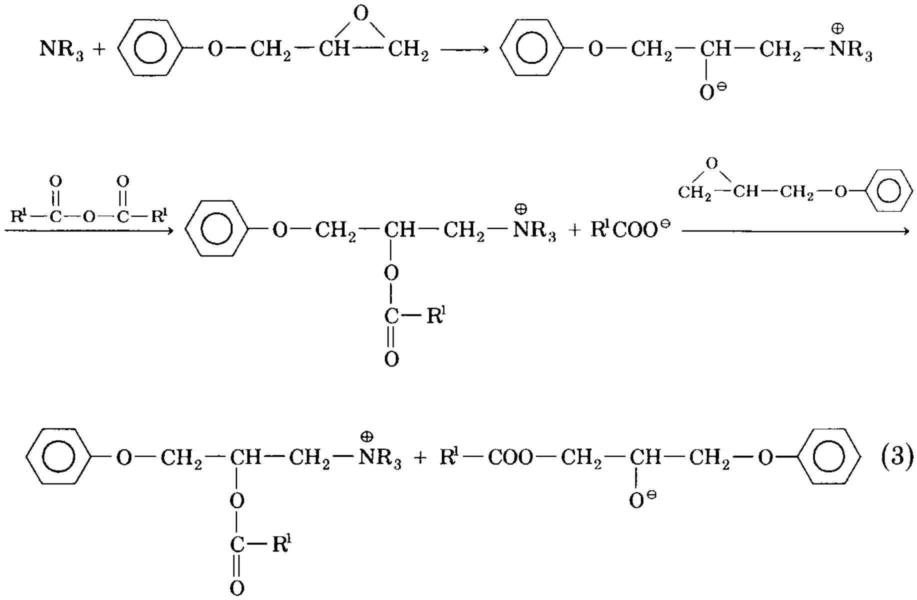
As a side reaction, ether formation by the reaction of OH groups with epoxy groups was found.[1,2,11,12]



$$\mathrm{ROH} + \mathrm{R'{-}CH_2{-}\overset{\;O\;}{CH{-}CH_2}} \longrightarrow \mathrm{R{-}O{-}CH_2{-}\underset{OH}{CH}{-}CH_2{-}R'} \qquad (2)$$

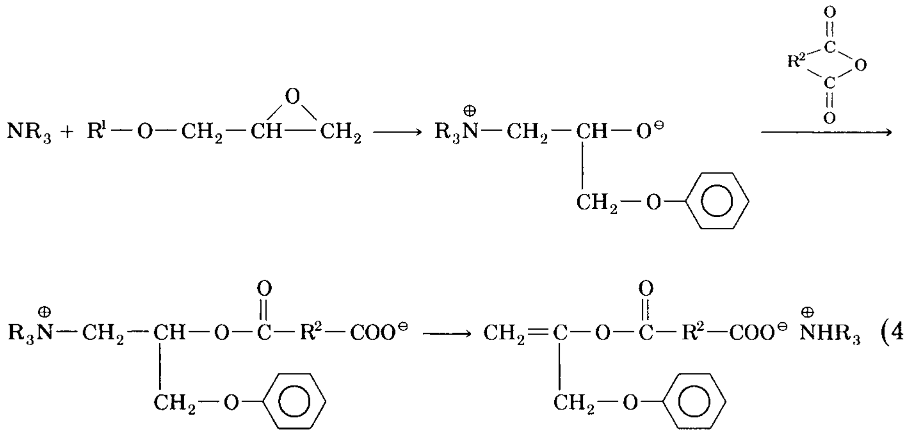
The situation is not as clear when tertiary amines are used as catalysts. In the case of technical epoxy resins, the reaction might be initiated by complex formation of an amine with a proton donor and proceed in a similar way as above, the active centers being the carboxylate and hydroxylate anions.[3,13]

In the absence of proton donors, however (i.e., if pure monomeric epoxides without OH groups and pure anhydrides are used), the amine must react either with the anhydride[7] or the epoxide[15] to initiate the polymerization. The second possibility, the complex formation of a tertiary amine with an epoxide, was detected by Matejka et al.[15] by NMR investigations of model compounds. The following initiation mechanism was postulated[15]:



(3)

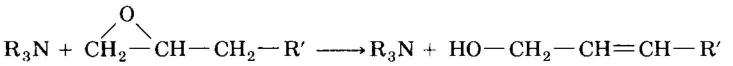
The authors found that the tertiary amine was irreversibly bound to the epoxide. For the reaction of monoepoxides with cyclic anhydrides, this would mean that no termination or transfer reactions occur and that only the catalyst concentration determines the resulting molecular weight of the polymer. Thus, each polymer chain would contain a quarternary ammonium ion at one end. From investigations of the oligomers formed by the reaction of phenylglycidyl ether with phthalic anhydride, Fedtke and Domaratius[16] suggested the following modification of the initiation mechanism described above:



(4)

This mechanism involves the release of the tertiary amine from the epoxide by formation of an ammonium ion and a double bond at the end of the polymer chain.

Another possibility of initiation by double bond formation was described by Tanaka and Kakiuchi[5]:



$$R_3N + \overset{O}{CH_2-CH}-CH_2-R' \longrightarrow R_3N + HO-CH_2-CH{=}CH-R' \qquad (5)$$

Under the influence of the tertiary amine, the epoxide might isomerize to the allyl alcohol, which can start the polymerization by the reaction with an epoxide or an anhydride molecule.

However, although these authors found some indications of double bond formation in the resulting polymers, an unambiguous identification of the structures given in (4) or (5) has not been made. In contrast to this, Matejka et al.[15] did not detect any double bonds during their investigations. So, the initiation mechanism remains still obscure, and further investigations are necessary to settle these questions.

This paper describes studies on the curing of diglycidyl ethers and esters, and of the model compounds phenyl glycidyl ether and cyclohexane glycidyl ester, with hexahydrophthalic anhydride (Table I).

EXPERIMENTAL

Hexahydrophthalic diglycidyl ester (HHDGE) was a distilled Ciba-Geigy product with an epoxy content of 6.82 mol/kg and an hydroxyl content of 0.1 mol/kg (purity 98.5% by GC). Bisphenol-A-diglycidyl ether (BADGE) was crystalline with a melting point of 41–42°C (purity > 99.9% by GC). Cyclohexane carboxylic acid glycidyl ester was prepared as described by Hao and Mleziva[19] and distilled three times at reduced pressure (purity 98% by GC). Hexahydrophthalic anhydride (HHPA) was distilled at reduced pressure. The freshly distilled product contained less than 0.1% acid. Benzyldimethylamine

(BDMA) and 1-methylimidazole (1-MI) were distilled at reduced pressure (purity > 99.5% by GC).

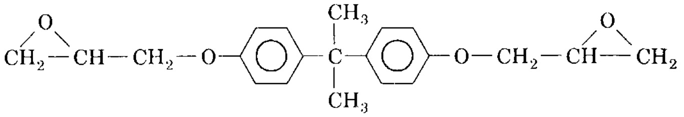
For the kinetic investigations, ampoules containing the reaction mixture were placed into an oil bath preheated to 100°C. At certain time intervals, two samples were removed and cooled quickly to 0°C. The epoxy content of the sample was titrated with 0.1*N* $HClO_4$ after addition of tetraethyl ammonium bromide. The sum of anhydride and acid groups was titrated with 0.1*N* Na-methylate in methanol. Carboxylic acid groups were titrated with 0.1*N* tripropylamine in acetone.

The polymerizations of phenyl glycidyl ether (PGE) and cyclohexane carboxylic acid glycidyl ester (CHGE) with HHPA and BDMA or 1-MI as catalysts were carried out in bulk or toluene solution in a nitrogen atmosphere. The polymers were reprecipitated from toluene/methanol, isolated by centrifugation and dried *in vacuo*.

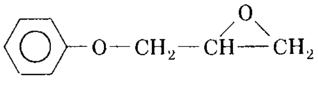
For the hydrolysis experiment, 10 g of the PGE/HHPA copolymer was dissolved in 30 mL THF and 50 mL of 1*N* NaOH were added. The resulting two-phase system was heated under reflux for 1 h. Then the two phases were separated. The aqueous phase was extracted two times with THF, the combined organic phases were washed with water, dried, and concentrated

TABLE I
Monomers and Catalysts Used for the Curing Experiments of Epoxides with HHPA

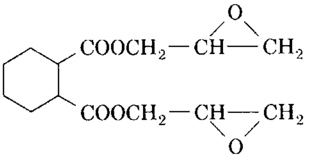
Epoxides



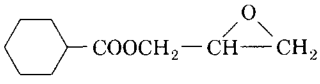
Bisphenol-A-diglycidyl ether (BADGE)



Phenyl glycidyl ether (PGE)

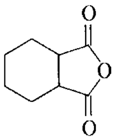


Hexahydrophthalic diglycidyl ester
(HHDGE)



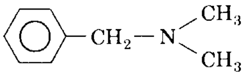
Cyclohexane carboxylic
Acid glycidyl ester (CHGE)

Anhydride

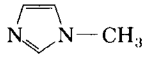


Hexahydrophthalic anhydride (HHPA)

Catalysts



Benzyldimethylamine (BDMA)



1-Methylimidazole (1-MI)

in vacuo. The residue was dissolved in toluene and precipitated with methanol. Yield: 1.4 g, white powder.

The reactions of HHPA with 0.16–1% of BDMA or 1-MI were carried out in bulk at 100 or 140°C in a nitrogen atmosphere. After 3–5 h, the reaction mixtures were analyzed by GPC and ^{13}C-NMR spectroscopy. For the isolation of the main product with a molecular weight of ~ 270, HHPA was heated to 140°C in the presence of 10% of BDMA in a nitrogen atmosphere. After 3 h, the reaction was stopped. The residual starting material was removed by distillation in a Kugelrohr apparatus. Recrystallization of the dry residue from THF/hexane gave 1.3 g of a product with mp 167°C (mixture of cis and trans isomers). After two further recrystallizations pure trans isomer of structure I was obtained with a melting point of 192°C.

MICROANAL: C, 68.2% (68.2%); H, 7.71% (7.58%). ^{13}C-NMR: δ = 179, 173, 163, 127, 85, 42, 40, 20–30 ppm.

IR spectra were recorded on a Nicolet 20 SX-FT-IR spectrometer. Samples were prepared either as thin films on KBr disks, as KBr pills or as solutions in CCl_4 (2%). The ^{13}C-NMR spectra were recorded on a Bruker SY 100 WP or AM-300 instrument.

Molecular weights were determined by GPC on a Waters liquid chromatograph equipped with an RI detector. Three columns (7 × 300 mm) filled with ultra Styragel of pore sizes 1000, 500, and 100 Å were connected in series and calibrated by a polystyrene standard.

The content of double bonds was measured by hydrogenation in dimethylacetamide with a catalyst of 10% palladium on coal.

RESULTS AND DISCUSSION

Kinetics

Mixtures of pure epoxy compounds (BADGE or PGE) with pure HHPA without a catalyst showed no reaction during a period of 24 h at 100°C. Thus, a catalyst (acid or base) is necessary to initiate the curing of pure epoxides with anhydrides.

The kinetic experiments were then carried out with two different catalysts, namely, benzyldimethylamine (BDMA) or 1-methylimidazole (1-MI) at 100°C in bulk. The results are shown in Figures 1 and 2. Sigmoidal curves are obtained in each case with more or less marked induction periods. Epoxide and anhydride consumptions are parallel which indicates that the reactions of the two groups are alternating. An etherification due to the homopolymerization of epoxy groups cannot be detected by these experiments. This agrees with the results obtained by Tanaka and Kakiuchi,[4] Fischer,[7] and Luston et al.[18]

Polymerization of Monoepoxides with HHPA

Polymerizations of the monoepoxides with HHPA were carried out under various conditions, as shown in Tables II and III. The soluble products were

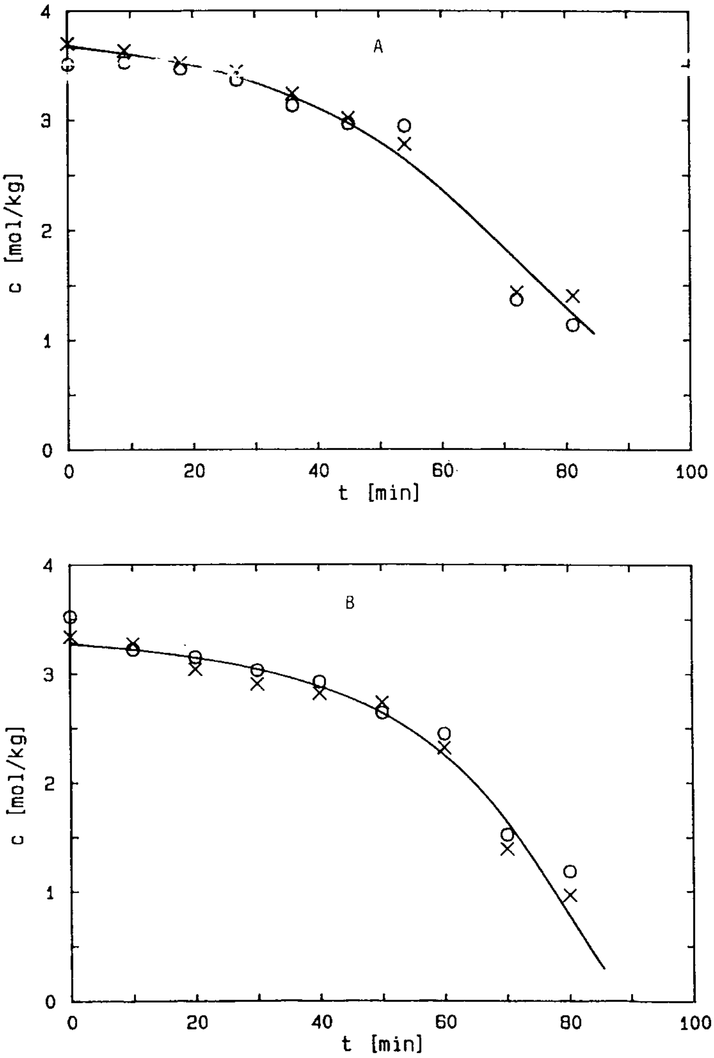


Fig. 1. Curing kinetics of diglycidyl ethers and esters with HHPA at 100°C in bulk: (a) HHDGE, catalyst 0.5% (w/w) BDMA, (b) HHDGE, 0.33% 1-MI, (c) BADGE, 0.25% BDMA, (d) BADGE, 0.16% 1-MI; (○) epoxy groups; (×) anhydride groups.

colorless to yellow amorphous substances with glass transitions of 30–40°C. The molecular weights ($\overline{M}_n$) were in the range of 2000–3600 (see Tables II and III). Typical GPC curves are shown in Figures 3(a) and (b). In the most cases, two peaks or a peak with a shoulder are observed. A clear dependence of molecular weights on the concentration or type of catalyst cannot be found. In the case of CGE, slightly better results were obtained with low concentrations of BDMA at 100–140°C, whereas the polymerization of PGE and HHPA gave higher molecular weights in the presence of 1-MI.

For some of the polymers, the content of unsaturation was determined by hydrogenation in the presence of a Pd catalyst. Concentrations of < 0.1–0.2

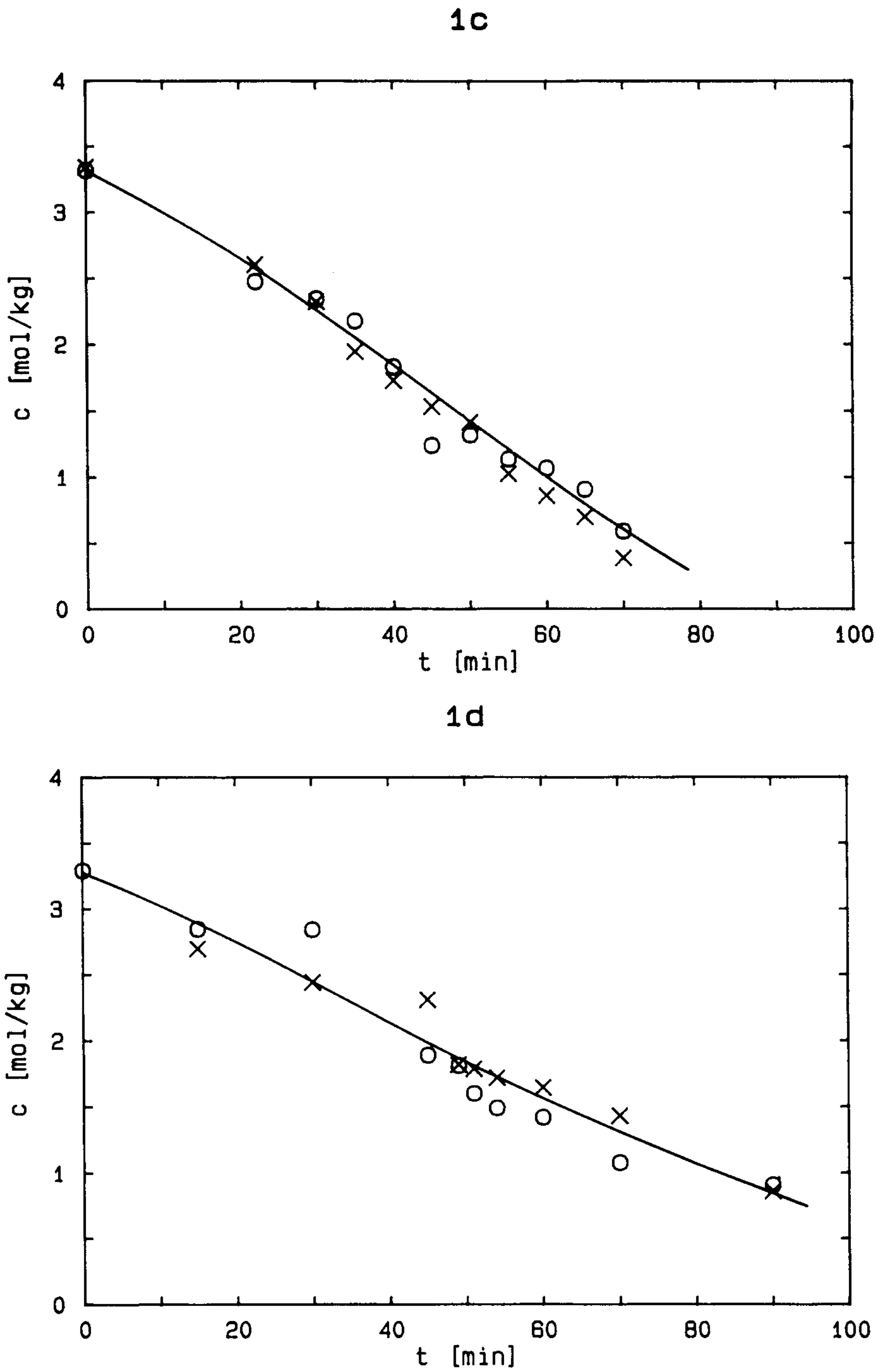


Fig. 1. (*Continued from the previous page.*)

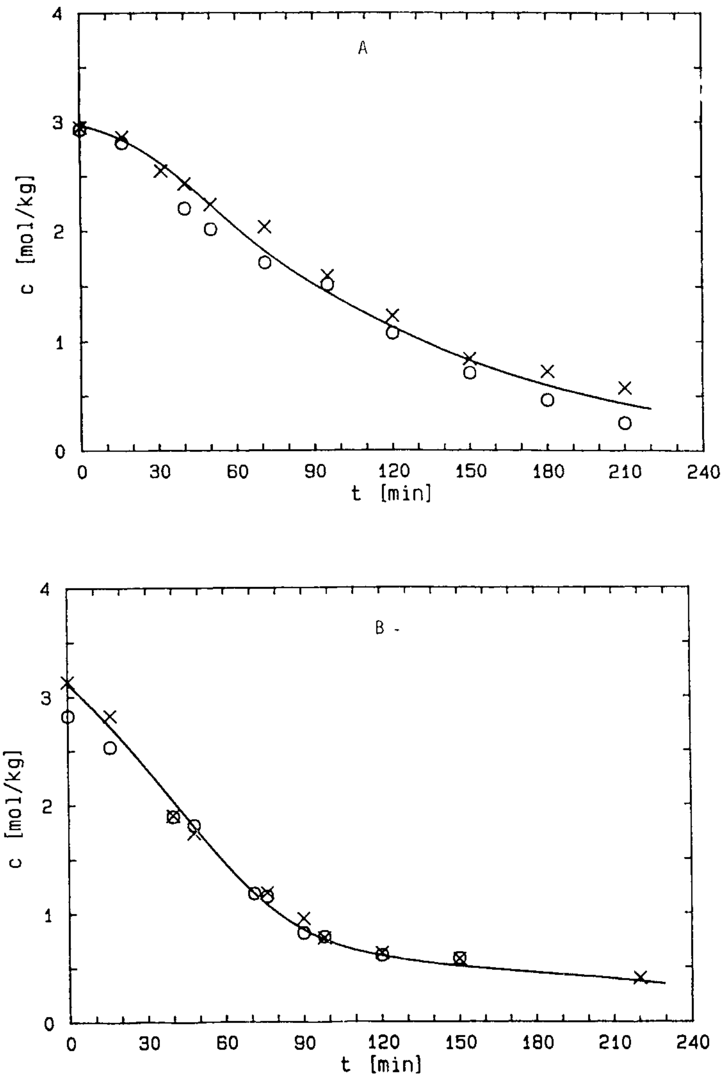


Fig. 2. Curing kinetics of glycidyl ethers and esters with HHPA at 100°C in bulk: (a) CHGE, 0.25% BDMA; (b) CHGE, 0.25% 1-MI; (c) PGE, 0.25% BDMA; (d) PGE, 0.16% 1-MI; (○) epoxy groups; (×) anhydride groups.

mmol/g were found which corresponds to < 1.5–3% with regard to monomer concentration.

IR Spectra

Typical IR spectra of soluble and unsoluble polymers are shown in Figures 4 and 5. The crosslinked products from the polymerization of HHDGE and BADGE with HHPA [figs. 4(a) and (b)] show a distinct shoulder at 1800 cm^{-1}

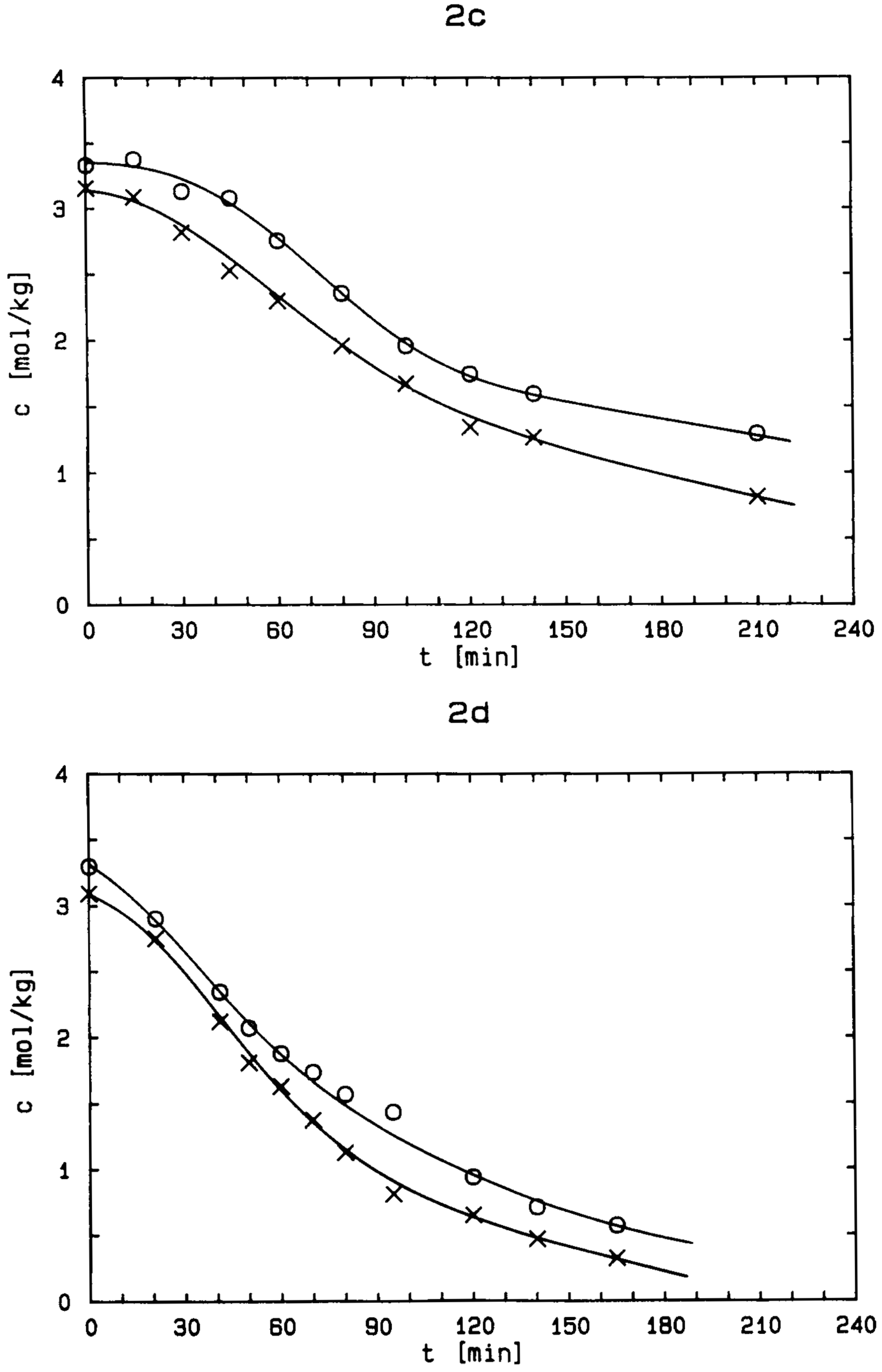


Fig. 2. (*Continued from the previous page.*)

TABLE II
Polymerizations of CHGE and HHPA (1:1 mol/mol), Reaction Conditions and Analytical Results

Catalyst	Reaction conditions	$\overline{M}_n$	$\overline{M}_w$	Content of unsaturation
BDMA 0.25% (w/w) = 0.3 mol%	5 h, 100°C, bulk	2860	3910	< 0.1 mmol/g (< 1.5%)
BDMA 1% (w/w) = 1.2 mol%	5 h, 100°C, bulk	2550	3520	
BDMA 0.25% (w/w) = 0.3 mol%	3 h, 140°C, bulk	2820	4580	
BDMA 1% (w/w) = 1.2 mol%	3 h, 140°C, bulk	2680	4030	0.1 mmol/g (1.5%)
1-MI 0.16% (w/w) = 0.3 mol%	5 h, 100°C, bulk	2010	3530	0.1 mmol/g (< 1.5%)
1-MI 0.6% (w/w) = 1.2 mol%	5 h, 100°C, bulk	2390	3450	
1-MI 0.16% (w/w) = 0.3 mol%	3 h, 140°C, bulk	2770	5250	
1-MI 0.6% (w/w) = 1.2 mol%	3 h, 140°C, bulk	2580	4190	0.1 mmol/g (1.5%)

TABLE III
Polymerizations of PGE and HHPA (1 : 1 mol/mol), Reaction Conditions and Analytical Results

Catalyst	Reaction conditions	$\overline{M}_n$	$\overline{M}_w$	Content of unsaturation
BDMA 0.25% (w/w) = 0.3 mol%	5 h, 100°C, bulk	2700	3750	0.1–0.2 mmol/g (1.5–3%)
BDMA 1% (w/w) = 1.2 mol%	5 h, 100°C, bulk	2150	2950	
BDMA 0.25% (w/w) = 0.3 mol%	3 h, 140°C, bulk	2310	3340	
BDMA 1% (w/w) = 1.2 mol%	3 h, 140°C, bulk	2120	3010	0.2 mmol/g (3%)
BDMA, 1.2 mol%	5 h, 100°C, 50% toluene	2340	3040	
1-MI 0.16% (w/w) = 0.3 mol%	5 h, 100°C, bulk	2860	4210	< 0.1 mmol/g (< 1.5%)
1-MI 0.61% (w/w) = 1.2 mol %	5 h, 100°C, bulk	3600	9060	
1-MI 0.16% (w/w) = 0.3 mol%	3 h, 140°C, bulk	3400	6220	
1-MI 0.61% (w/w) = 1.2 mol%	3 h, 140°C, bulk	3480	4750	0.2 mmol/g (3%)
1-MI, 1.2 mol%	5 h, 100°C, 50% toluene	2800	3550	

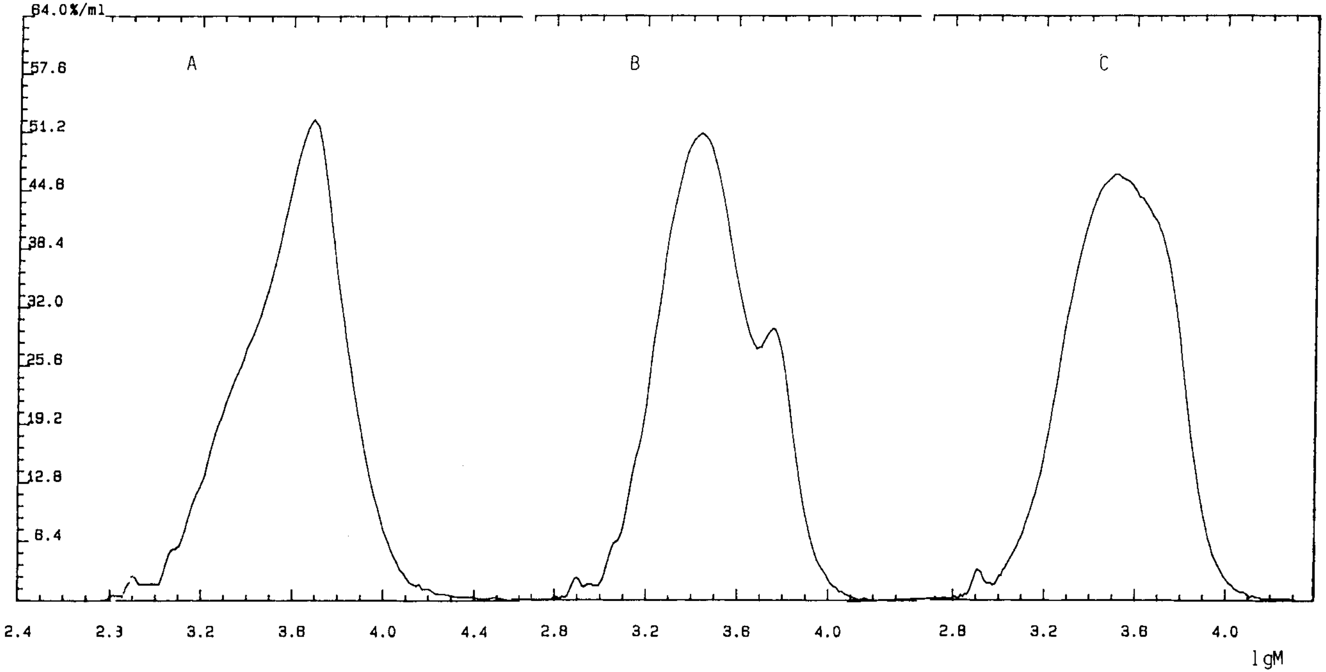


Fig. 3. GPC of PGE/HHPA-polyesters: (a) catalyst 0.6% 1-MI; reaction temperature 140°C; (b) catalyst 0.25% BDMA, reaction temperature 100°C; (c) after hydrolysis with 1*N* NaOH.

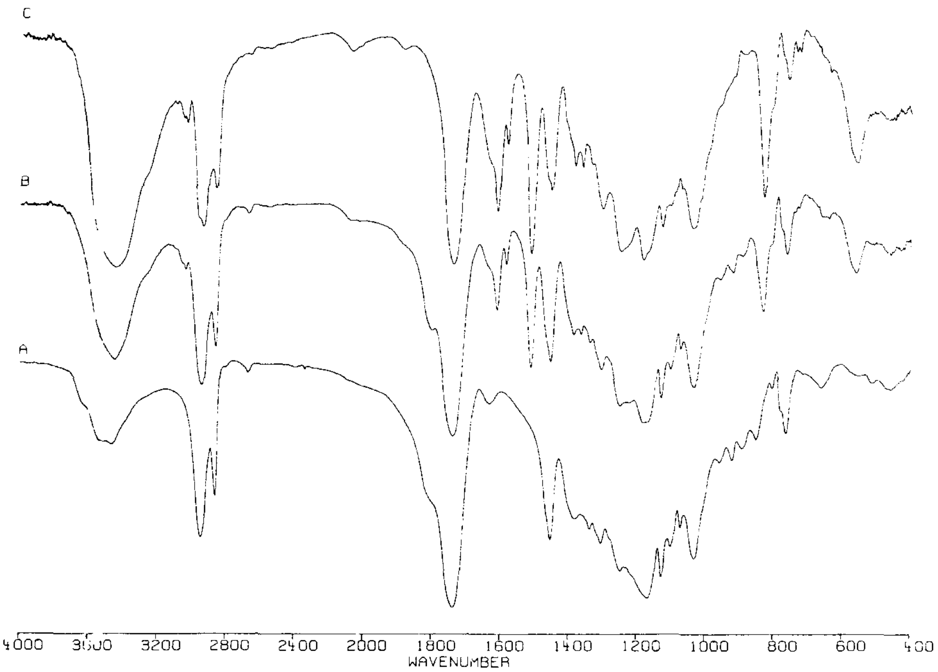
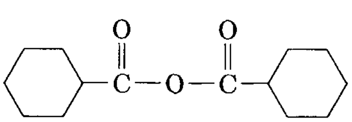


Fig. 4. IR spectra of crosslinked products from the curing of diglycidyl ethers and esters with HHPA (KBr pills): (a) HHDGE, catalyst 0.6% 1-MI (w/w) reaction at 140°C, N_2 atmosphere; (b) BADGE, catalyst 0.6% 1-MI, reaction at 140°C, N_2 atmosphere; (c) BADGE, catalyst 0.6% 1-MI, reaction at 140°C in air.

besides the ester band at 1740 cm^{-1}. This shoulder resolves to a separate band in the case of the polymers from CHGE or PGE with HHPA [figs. 5(a) and (b)], probably because of the different preparation techniques for soluble and unsoluble polymers (films on KBr disks or KBr pills). Interestingly, no or only a very weak shoulder at 1800 cm^{-1} can be observed, if the polymerizations are carried out under normal atmosphere, without taking care to prevent humidity [Fig 4(c)]. Such a side band at 1800 cm^{-1} has not been described before for products obtained by the curing of epoxides with anhydrides. Its intensity varies slightly with the type and concentration of the catalyst used. If the polymerizations are carried out with 0.6% (w/w) 1-MI, for example, the band is weaker than with 0.15% 1-MI or with BDMA (Fig. 6).

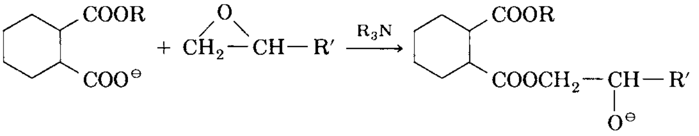
This band has to be assigned to an anhydride structure, however *not* to the monomer HHPA. The latter compound has two bands at 1860 and 1790 cm^{-1}, the normal absorptions for *cyclic* anhydrides. Open chain anhydrides, in contrast, have two absorptions at about 1820–1800 and 1760–1740 cm^{-1}.[20] Cyclohexane carboxylic acid anhydride



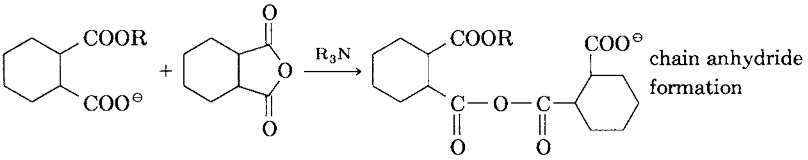
shows two absorptions at 1795 and 1733 cm^{-1} (in $CHCl_3$), the band with higher frequency being stronger.[21]

A similar structure seems to be present in the epoxide–anhydride copolymers. The lower absorption at 1733 cm^{-1}, of course, must be hidden by the strong ester absorption. A proof of the presence of such an anhydride group was obtained by hydrolyzing the polymer with 1*N* NaOH. After the hydrolysis, a product was obtained in about 14% yield, which showed an intact polyester structure [Fig. 5(c)], but no band at 1800 cm^{-1}. This polymer had a slightly higher average molecular weight than the educt [$\overline{M}_n = 2740$ instead of 2590, Fig. 3(c)]. It represents only a rather small fraction of the starting polymer, the rest of the hydrolysis fragments being too small to be isolated by precipitation with methanol. Titration of the polymers gave anhydride concentrations of 0.15–0.5 mol/kg, which corresponds to about 2–7.5% of anhydride groups with respect to ester groups.

The chain anhydride formation apparently is a side reaction of the normal esterification. The carboxylate end group of the growing chain does not only react with an epoxide to give an ester, but also with another anhydride, so that chain anhydride groups are incorporated into the polymer:

 (6)

esterification

 (7)

chain anhydride formation

This reaction, however, proceeds in noticeable amounts only when pure monomers are used and care is taken to prevent humidity. If higher concentrations of (acidic) impurities are present, the parallel reaction, the esterification, is probably so much accelerated that chain anhydride formation becomes negligible.

^{13}C-NMR Spectra

The ^{13}C-NMR spectrum of a PGE/HHPA polyester that was formed by a reaction at 100°C with 0.25% BDMA as catalyst is shown in Figure 7(a). The main peaks can be assigned to the known polyester structure. In addition, some smaller peaks are observed that indicate the presence of noticeable amounts of side reactions. Products resulting from polymerizations at 140°C with higher amounts of catalyst have more complicated spectra as shown in Figure 7(b). In the regions 20–50 ppm and 170–175 ppm, we observe a doubling of the main peaks. The "new" peaks at 25, 28.5, 44.5 and 174.5 ppm have to be assigned to the *trans*-hexahydrophthalic ester,[22] whereas the starting material was *cis*-hexahydrophthalic anhydride.

The amount of *trans*-isomer formed during the polymerization depends on the reaction temperature and the type and concentration of the catalyst used.

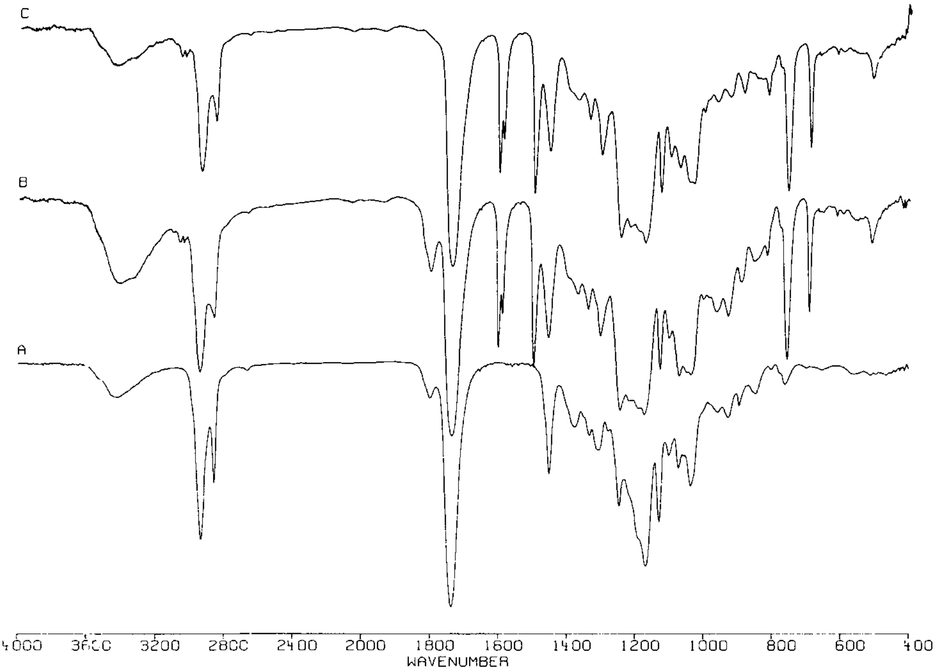


Fig. 5. IR spectra of polymers from the curing of glycidyl ethers and esters with HHPA (films on KBr disks): (a) CHGE, catalyst 0.25% BDMA, reaction temperature 100°C, N_2 atmosphere; (b) PGE, catalyst 0.25% BDMA, reaction temperature 100°C, N_2 atmosphere; (c) b) after hydrolysis with 1*N* NaOH.

High temperatures and high catalyst concentrations increase the isomerization rate. 1-MI catalyzes the isomerization more than BDMA. In the presence of 1% BDMA at 140°C, for example, about 20% of the ester is converted. The same molar concentration of 1-MI (0.6% w/w), under the same conditions, causes the isomerization of about 50% of the ester to the transform [Fig. 7(b)].

The small peaks from other side reactions observed in Figure 7(a) could be resolved by recording ^{13}C-NMR spectra on a 300 MHz NMR spectrometer with about 28000 scans, as shown in Figures 8 and 9. In the carboxyl region (165–180 ppm), several peaks could be due to the chain anhydride group detected by IR spectroscopy, but it is impossible to make exact assignments.

Ether groups which would result from a homopolymerization of the epoxide groups are not observed in the PGE/HHPA polymer (Fig. 9) as there are no peaks between 70 and 80 ppm, where absorptions of $C—O—C—$ groups are expected. The CHGE/HHPA polymer (Fig. 8) has three small peaks in this region which in fact indicate the formation of very small amounts of ether groups ($\leq 5\%$).

These small concentrations of side reactions from chain anhydride formation or etherification (in the case of CHGE/HHPA) could, of course, not be noticed by carrying out the kinetic experiments described in the first section. The extent of these reactions still lies within the experimental error of the titration experiments.

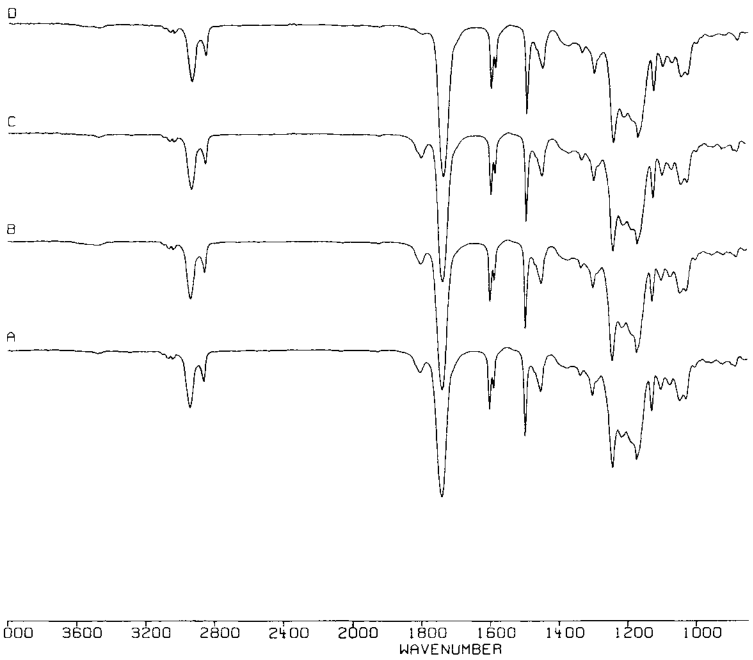
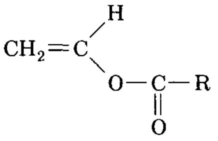
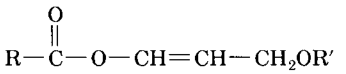


Fig. 6. IR spectra of PGE/HHPA polyesters, solutions in CCl_4 (0.2%): (a) catalyst 0.25% BDMA, reaction temperature 140°C; (b) catalyst 1% BDMA, reaction temperature 140°C; (c) 0.16% 1-MI, 100°C; (d) 0.6% 1-MI, 100°C.

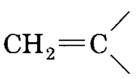
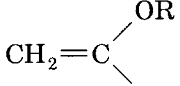
In the region 80–160 ppm, several small peaks resulting form double bonds can be detected. The PGE/HHPA polyester (Fig. 9) has a very small peak at 85 ppm which may be assigned to the polarized double bond



postulated in mechanism (4) by Fedke and Domaratius.[16] This peak is not observed in Figure 8, i.e., in the copolymer from CHGE and HHPA. But there are other peaks in this region which are common to both polymers. The peak at 110–112 ppm, for example, appear in both spectra and could be due to the other polarized double bond



$$R{-}\overset{\overset{\large O}{\|}}{C}{-}O{-}CH{=}CH{-}CH_2OR'$$

described in (5).[5] The undecoupled spectra, however, show that these peaks are triplets and belong to structures  (but *not* ). So, there is no evidence for initiation mechanism (5). A rather strong peak is also

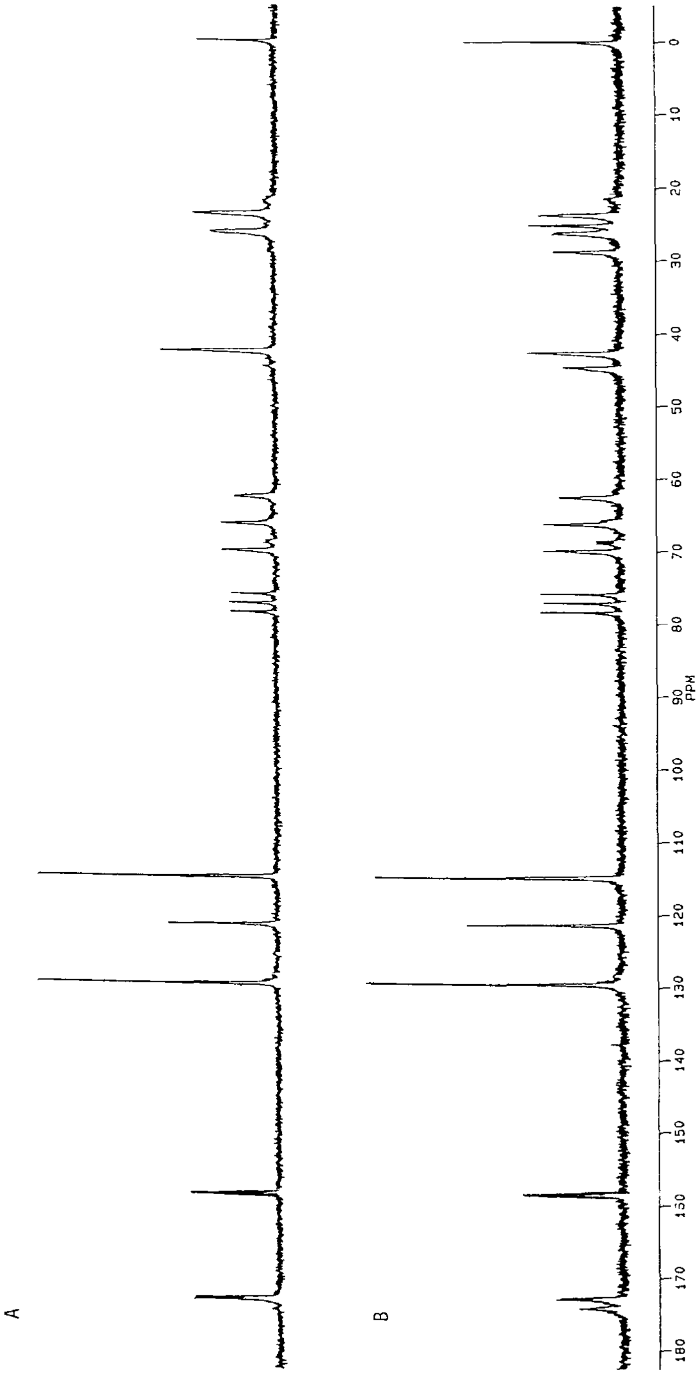


Fig. 7. ^{13}C-NMR spectra of PGE/HHPA polyesters (30% solutions in $CDCl_3$): (a) catalyst 0.16% 1-MI, reaction at 100°C; (b) catalyst 0.6% 1-MI, reaction at 140°C.

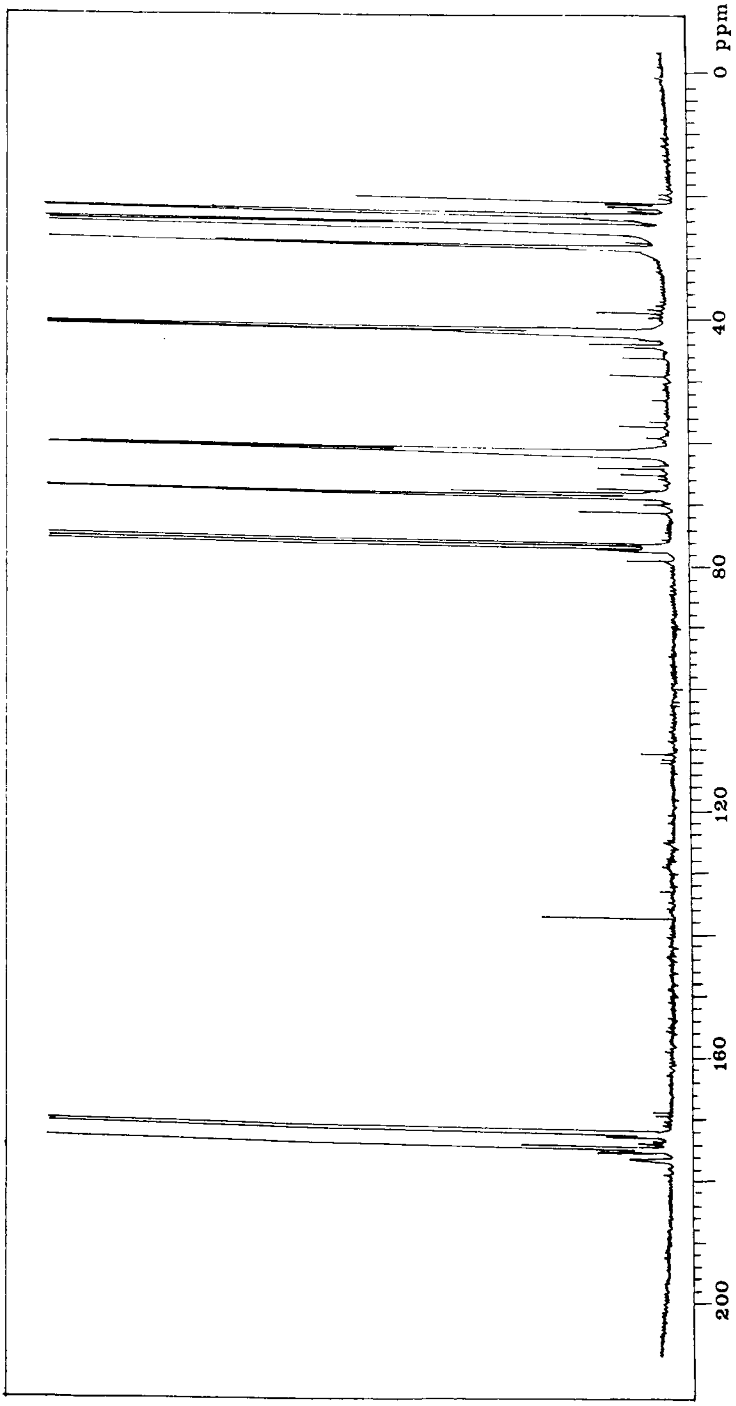


Fig. 8. ^{13}C-NMR spectra of a CHGE/HHPA polyester (reaction at 100°C, 0.25% BDMA as catalyst).

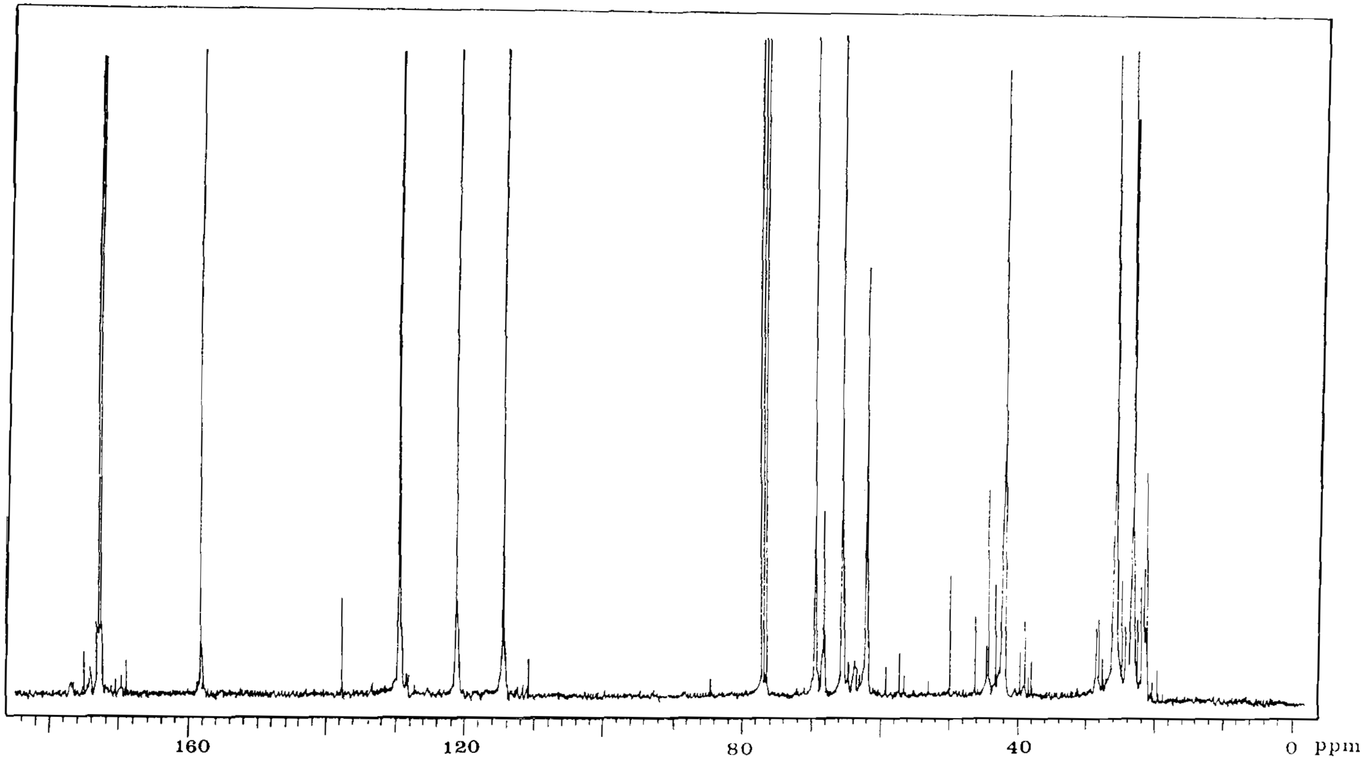


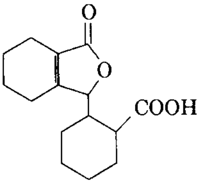
Fig. 9. ^{13}C-NMR spectra of a PGE/HHPA polyester (reaction at 100°C, BDMA as catalyst).

observed at 138 ppm in both spectra (Figs. 8 and 9) which are not explained by the initiation reactions described above.

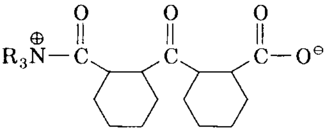
It appears from these spectra that the polymerization mechanism of epoxides with HHPA is rather complicated and that not only one, but several initiation and side reactions happen, which cannot easily be identified.

Reaction of HHPA with Tertiary Amines

The chain anhydride formation, the inversion of the *cis*-hexahydrophthalic ester to the transform and several smaller side peaks in the aliphatic region of the ^{13}C-NMR spectra led to the conclusion that the HHPA rather than the epoxide might be responsible for the side reactions occurring during the polymerizations. This assumption was also confirmed by comparative studies on the polymerization of PGE with phthalic anhydride, which gave much purer polyesters with higher molecular weights (to be published). From the literature, it is known that HHPA can decarboxylate in the presence of tertiary amines. Bayer et al.[23] identified the unsaturated lactone of structure I as reaction product:



I

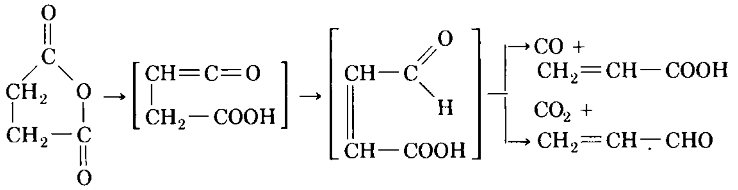


II

This product is formed by the reaction of two HHPA molecules with loss of one molecule of carbon dioxide. Under slightly different conditions, Fedtke et al.[24] obtained oligoketones of structure II as decarboxylation products.

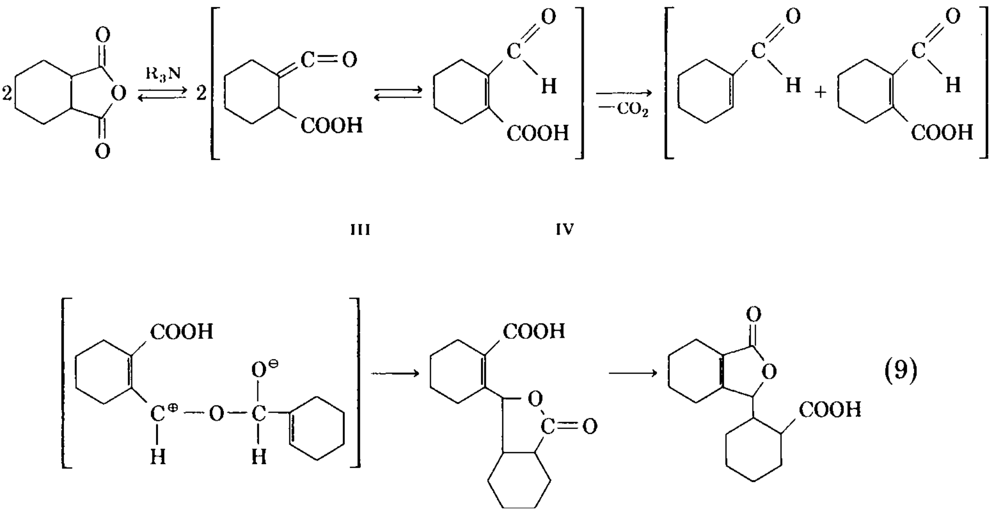
We carried out the reaction of HHPA with BDMA or 1-MI under the same conditions as the polymerizations of epoxides with HHPA, i.e., at 100 or 140°C with 0.16–1% of tertiary amine. After the end of the reaction, GPC indicated the formation of 10–20% of a product with a molecular weight of about 270 and very small amounts of higher oligomers. IR and ^{13}C-NMR spectra of the reaction mixture showed the presence of several products with carboxylic acid groups. Ketone structures with chemical shifts of > 200 ppm could not be detected in the ^{13}C-NMR spectra. The main product with a molecular weight of 264 was isolated and identified as the lactone of structure I (mixture of cis and trans isomers). The structures of the other side products could, however, not be revealed unambiguously.

The mechanism of the decarboxylation condensation reaction which leads to lactone I can be explained on the basis of a reaction sequence which has been postulated by Brown and Ritchie[25] for the pyrolysis of cyclic anhydrides. According to these authors, the first step for the decarboxylation of anhydrides having an α-hydrogen atom is the formation of a keten and a carboxylic acid. In the case of cyclic anhydrides of dibasic acids, this yields an intermediate open-chain "keten acid," undergoing further reaction as a single molecule. For the pyrolysis of succinic anhydride, the following mechanism was proposed[25]:



(8)

In analogy to this mechanism, the formation of lactone I from HHPA can be formulated as follows:

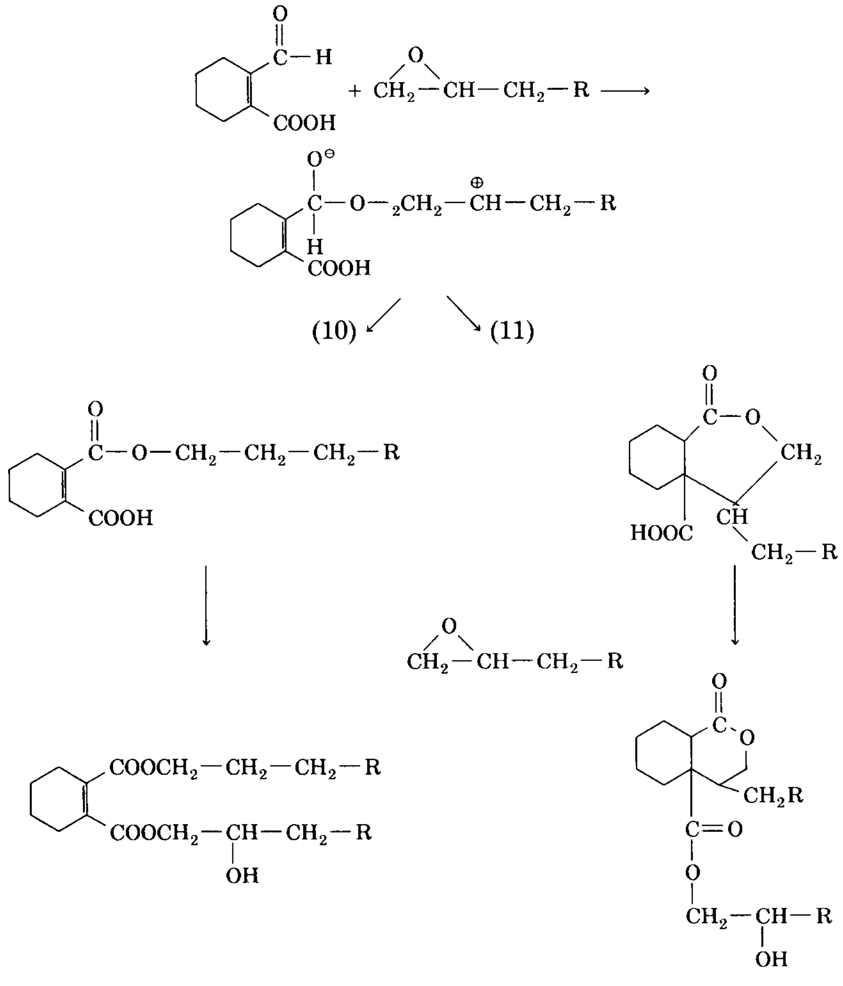


III IV

I

(9)

If this reaction also occurred during curing of epoxides with HHPA the formed product of structure I would act as additional initiator molecule. This would then account for the low molecular weights obtained in the polymerization experiments described above. However, weight loss during polymerizations is too small to indicate any decarboxylation reactions, and the ^{13}C-NMR spectra of the polymers (Figs. 8 and 9) do not show any derivatives of structure I. The high quantities of *trans*-hexahydrophthalic derivatives in the polymers formed at higher temperatures, nevertheless, can only be explained by the assumption that a reversible isomerization reaction of HHPA to structures III and IV occurs. These isomerization products might also react with epoxides to yield components which could function as polymerization initiators. Two initiation reactions may be postulated in analogy to mechanism (9):



Evidence for structure V with the symmetrical double bond is given by the presence of a peak at 138 ppm in the ^{13}C-NMR spectra of the polymers (Figs. 8 and 9). Structure VI should have a singlet of the C atom adjacent to the ester group at 50–60 ppm, a region where in fact several small peaks are observed.

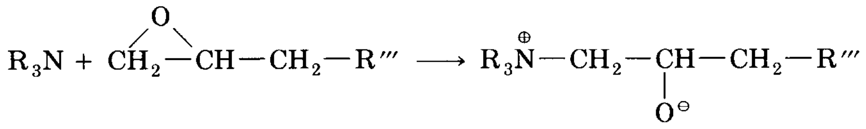
These two reactions proposed here are, of course, speculations and there are still several side peaks in the ^{13}C-NMR spectra which cannot be assigned [as, for example, the signals at ~ 110 ppm (Figs. 8 and 9)], but there is strong evidence that the isomerization of HHPA to structures III and IV, which proceeds so easily in the presence of tertiary amines, plays an important role during the copolymerization of epoxides with HHPA.

CONCLUSIONS

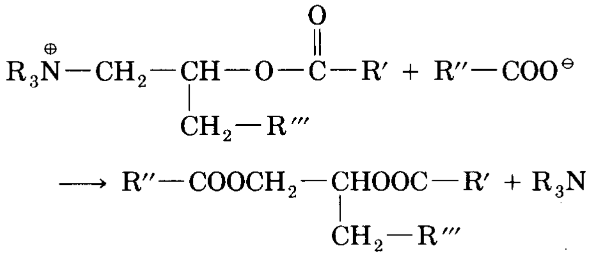
The investigations presented here have shown that the curing reaction of epoxides with anhydrides is more complicated as assumed up to now. Above all, it has become evident that the type of the anhydride used plays an important role for the polymerization mechanism. Specially the cycloaliphatic anhydride HHPA seems to undergo a lot of side reactions, which are responsible for most of the unexpected effects observed during our studies. The results may be summarized as follows:

1. The initiation mechanism (4) proposed by Matejka et al.[15] is not the only initiation reaction occurring during the polymerization of epoxides with HHPA, as indicated by the low molecular weights, the induction period and the ^{13}C-NMR spectra. As most of the GPC curves of the polymers from PGE or CHGE with HHPA show a double peak or a peak with a shoulder, it might be assumed that one of the transfer reactions is the condensation of two polymer chains under release of the tertiary amine that was bound to the epoxide:

Initiation:



Transfer:

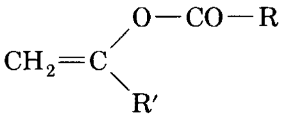


$$R_3\overset{\oplus}{N}-CH_2-\underset{\underset{\displaystyle CH_2-R'''}{|}}{CH}-O-\overset{\overset{\displaystyle O}{\|}}{C}-R' + R''-COO^{\ominus}$$

$$\longrightarrow R''-COOCH_2-\underset{\underset{\displaystyle CH_2-R'''}{|}}{CH}OOC-R' + R_3N$$

2. The initiation mechanism described by Tanaka and Kakuichi[5] (5) does not occur during the polymerizations of epoxides with HHPA. The ^{13}C-NMR spectra do not give any evidence of unsaturated compounds of the structure $RO-CH_2-CH=CH-R'$.

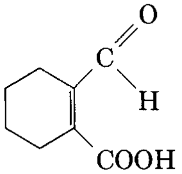
3. The mechanism described by Fedtke and Domaratius[16] (4) is not observed for the copolymerizations of CHGE and HHPA, because no signal exists in the ^{13}C-NMR spectra that may be assigned to a polarized double bond



The copolymer of PGE and HHPA, however, shows a very small peak at 85 ppm, which might be due to the structure described above, but there are a lot of other side peaks common to both systems (PGE/HHPA and CHGE/HHPA) which indicate the presence of several other initiation mechanisms.

4. In analogy to the reaction of HHPA with tertiary amines, which is caused by an isomerization of the anhydride, it is proposed that the molecule of

structure IV


IV

is one of the initiator molecules which might react with epoxides in several ways. Two of these initiation reactions are postulated in (10) and (11).

5. The propagation does not only proceed by the esterification reaction of carboxylate with epoxide groups as shown in reaction (6), but also by a chain anhydride formation caused by the reaction of carboxylate groups with HHPA (7). About 2–8% of chain anhydride is found in the copolymers from PGE or CHGE with HHPA, if the reactions are carried out under nitrogen and pure compounds are used. The reaction is, however, suppressed if no care is taken to avoid humidity.

6. An etherification resulting from the homopolymerization of epoxides (3) is not observed for the copolymers from PGE and HHPA. The CHGE/HHPA copolymers, in contrast, contain small amounts of ether groups ($\leq$ 5%).

7. If the polymerizations are carried out at higher temperatures (140°C) in the presence of larger concentrations of tertiary amines (0.6–1%), a part of the formed polyesters is found to be in the transform, whereas the starting material was *cis*-HHPA. The isomerization occurs to a higher extent (up to 50%) in the presence of 1-MI than with BDMA as catalyst.

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