

Polymerization of *p*-Cresyl Glycidyl Ether Catalyzed by Imidazoles I. The Influence of the Imidazole Concentration, the Reaction Temperature, and the Presence of Isopropanol on the Polymerization

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Synopsis

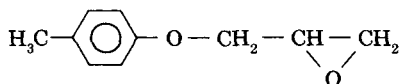
The polymerization of *p*-cresyl glycidyl ether catalyzed by imidazoles has been investigated as a model reaction for the polymerization of technical epoxy resins. The dependence of oligomer yield on time, temperature, and imidazole concentration, the distribution of the polymerization degrees, and the influence of isopropanol have been studied. The reaction rate and the average degree of polymerization are affected by the presence or absence of a secondary nitrogen on the imidazole, i.e., different results are obtained when 2-ethyl, 4-methyl imidazole (EMI) or 1-methyl imidazole (1-MIA) are used. 1-MIA seems to be a "precursor" of the catalyst rather than a catalyst by itself. The comparisons of CGE polymerizations catalyzed by 1-MIA in the absence and presence of isopropanol show only quantitative differences: The polymerization in the presence of isopropanol is faster, and the average degree of polymerization is shifted to higher values. The activation energies of CGE polymerizations catalyzed by different imidazoles have been determined.

INTRODUCTION

Among different epoxy polymerization catalysts, imidazoles proved to be good crosslinking agents for technical epoxy resins. Some efforts were made to ascertain not only the nature of the reaction¹⁻³ but also to create a kinetic model of this polymerization reaction⁴ and to determine the influence of the curing conditions on the mechanical behavior of crosslinked resins.⁵

Contrary to publications describing the influence of hydrogen donors (water, alcohols) on the polymerization of glycidyl ethers catalyzed by tertiary amines,⁶⁻⁸ no analogous investigations were made with imidazoles.

It was the aim of this work to study the course of the epoxide polymerization catalyzed by imidazoles and the influence of the polymerization conditions on the polymer characteristics. Since the analysis of crosslinked polymers prepared from technical resins is too difficult, polymerizations of a mono glycidyl ether [*p*-(2,3-epoxypropyloxy) phenyl] methane (or *p*-cresyl glycidyl ether)



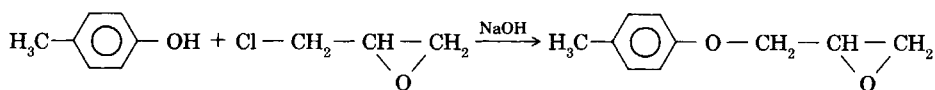
as a model monomer (leading to linear, well-soluble oligomers) were performed.

The structure of this monomer is an approximation to 2,2-bis[*p*-(2,3-epoxypropyloxy) phenyl] propane (or diglycidyl ether of bisphenol A), and the reactions were carried out according to technical polymerization conditions of epoxy resins, especially regarding the purity and concentrations of imidazoles and the polymerization temperatures.

The molecular weight distribution was determined by gel permeation chromatography (GPC). This method is very suitable for the separation of low molecular weight epoxy oligomers.⁹⁻¹³ Activation energies of the polymerizations were measured by differential scanning calorimetry (DSC).

EXPERIMENTAL

p-Cresyl glycidyl ether (CGE) was synthesized from *p*-cresol and epichlorhydrin via the following scheme:



Procedure

To a mixture of 262 g epichlorhydrin and 103 g *p*-cresol at 50°C, was added 37.25 g solid NaOH for 60 min. The white suspension was stirred for 7 h at 50°C. After stirring another 10 h at 20°C the suspension was filtered off, the solution was diluted with 70 mL acetone and the rest of NaCl was filtered off. The raw product was purified by distillation. The main fraction is CGE with a boiling point of 79°C/0.03 Torr. The yield was 73% with a purity of 99%.

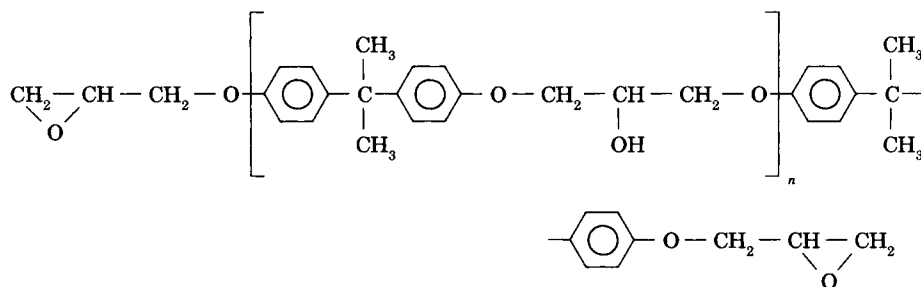
Materials

1-Methyl imidazole (1-MIA), product of Fluka, Switzerland, purity 99.5%; 2-methyl imidazole (2-MIA), product of Fluka, Switzerland, purity 98.5%; 4(5)-methyl imidazole (4/5-MIA), product of Fluka, Switzerland, purity 98.5%; 2-ethyl, 4-methyl imidazole (EMI), product of Aldrich Chemical Co., purity 97%; 2-phenyl imidazole (2-PhIA), product of Merck-Schuchardt, Germany, purity 98%.

The polymerizations were carried out in bulk mixtures of the imidazoles in CGE in closed glass ampules immersed in a thermostated oil bath (precision $\pm 0.04^\circ\text{C}$). The reactions were interrupted by immersion of the ampules into a bath of -80°C for 15 min. Afterwards the polymerization mixtures were dissolved in tetrahydrofuran. 0.5% solutions were used for GPC separations on a Waters Liquid Chromatograph with two Zorbax PSM HPSEC 60-S columns (6.2×250 mm) connected in series and filled with silica microspheres with an approximative molecular weight range of $2 \times 10^2 - 2 \times 10^4$ (polystyrene standard): the flow rate was 0.5 mL/min, the absorbance was measured by the UV detector, Model 440, at 254 nm. The flow was controlled by a flowmeter of Phase Separation Ltd. (United King-

dom and United States). The GPC data were processed by the Waters Data Model.

An advanced epoxy resin, based on bisphenol A diglycidyl ether,



with an average molecular weight $MW = 950$ was used as a standard for GPC calibration.¹³ The resulting resolution curve is shown on Figure 1.

The GPC of the polymerization products of CGE when polymerized with 8 mol % of EMI 6 h at 100°C is shown on Figure 2. The peak no. 1 in Figure 2 corresponds to the unreacted monomeric CGE which shows an exclusion at about $MW = 159 - 165$ (CGE has $MW = 164$). The fractions 2, 3, 4, 5, etc., are eluted with molecular weight differences of 100–150 based on the standard in Figure 1. Sometimes shoulders indicate a possible overlapping of two CGE oligomer fractions with only slightly different retention times.

This may come from oligomers with incorporated imidazole. If the overlapping is within the limits of the molecular weight range of 100–150 for the distinct oligomers (e.g., fraction no. 5 on Fig. 2), such a fraction is consequently considered as a single one.

The 254-nm detection is very suitable for the glycidyl ethers but the imidazoles do not absorb in this UV range. The quantitative evaluation of the GPC diagrams was performed by the simplified assumption that all polymer fractions have equal molar extinction coefficients. The absorbances

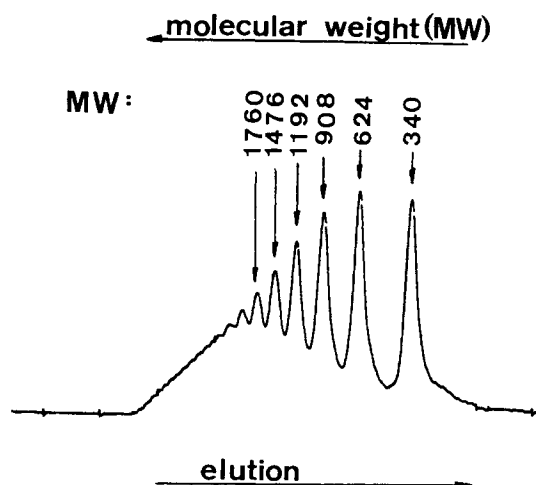


Fig. 1. GPC diagram of an advanced bisphenol A diglycidyl ether, average epoxy equivalent weight 425.

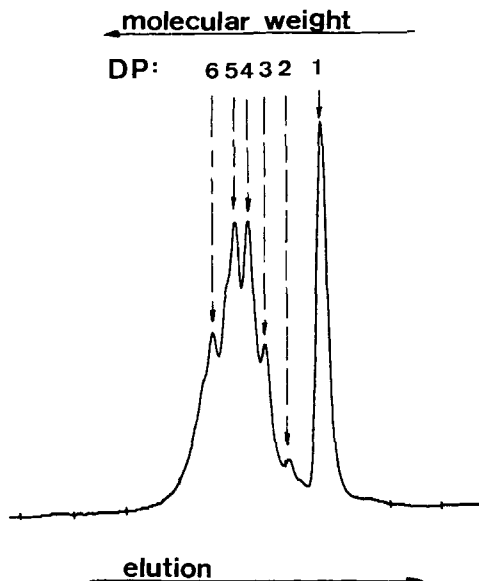


Fig. 2. GPC diagram of the polymerized CGE with 8 mol % EMI, 6 h/100°C.

of the initiator system (e.g., imidazoles with isopropanol) were subtracted from the peak areas at the corresponding elutions of the polymerized CGE.

DSC measurements were performed on the TA 3000-System of Mettler, Switzerland.

RESULTS AND DISCUSSION

Polymerizations in System CGE-Imidazoles

From the large group of the epoxide polymerization catalysts based on imidazoles 1-methyl imidazole (1-MIA) and 2-ethyl-4-methyl imidazole (EMI) were selected for the following investigations. The most convenient polymerization temperature was 100°C; some polymerizations were carried out in the temperature range 80–140°C. Monomer-oligomer conversions were determined by GPC of the polymerized CGE. The conversions and the compositions of the oligomers (in regard to their degrees of polymerizations) were followed as a function of the polymerization time.

Figure 3 shows the polymerization of CGE in presence of 2 mol % 1-MIA at 100°C. Curves 1–4 correspond to the decay of the monomer (curve 1) and to the increase of the oligomers with polymerization degrees 2–4 (curves 2–4). The highest conversion is about 15% and the highest degree of polymerization (DP) is 4.

A higher catalyst concentration increases both the polymerization rate and the DP of the oligomers. This is represented in Figure 4, which shows the CGE polymerization with 8 mol % 1-MIA. The meaning of the curves is identical to those in Figure 3. The highest DP value is 5. From comparison of Figures 3 and 4 it follows that the highest conversion and the corresponding reaction time necessary to achieve it are dependent on the 1-MIA concentration. Thus, for instance, with 2 mol % 1-MIA a conversion of 15%

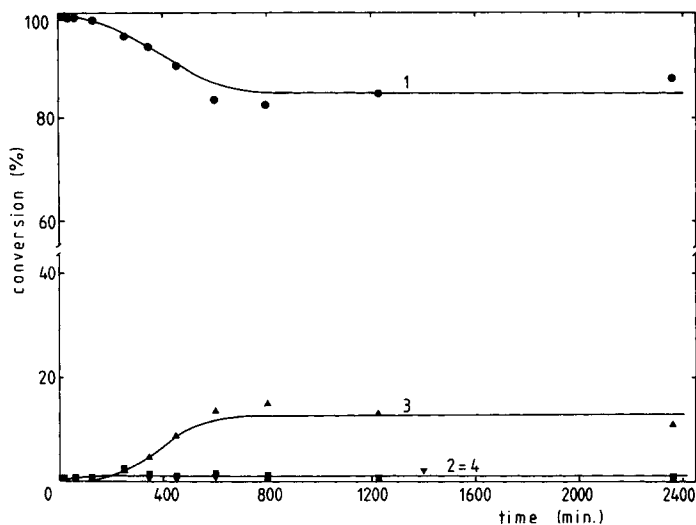


Fig. 3. Conversion vs. time dependence of CGE polymerized with 2 mol % 1-MIA at 100°C: (1) monomeric CGE; (2-4) dimer-tetramer.

is achieved in about 800 min and with 8 mol % 1-MIA the conversion is 96.5 % in 200 min.

Table I summarizes the maximal conversions at concentrations of 1-8 mol % 1-MIA. By comparison of the conversion-time dependencies of the polymerizations with 1-MIA on Figure 4 and EMI on Figure 5, both at a concentration of 8 mol %, the differences become evident:

—The polymerization catalyzed by EMI (Fig. 5, curve 1) is faster than that catalyzed by 1-MIA (Fig. 4, curve 1).

—The polymerization catalyzed by 1-MIA is accelerated, which becomes apparent from the S-shape of curve 1 on Figure 4 during the first 100 min

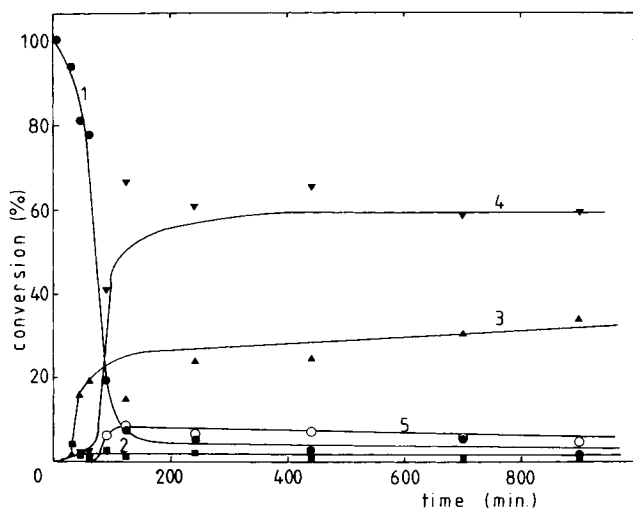


Fig. 4. Conversion vs. time dependence of CGE polymerized with 8 mol % 1-MIA at 100°C. The meaning of the curves is identical with those in Figure 3.

TABLE I
Maximal Conversions Obtained by Polymerization of CGE Polymerization
Catalyzed by 1-MIA^a

1-MIA concn (mol %)	Conversion (%)
1	8
2	15
4	86
6	96
8	96.5

^a Polymerizations were carried out at 100°C for at least 600 min.

of the polymerization. The polymerization of CGE catalyzed by EMI does not show this behavior.

—In polymerizations catalyzed by EMI higher molecular weight oligomers are formed than with 1-MIA. The highest degree of polymerization with EMI is 6 while with 1-MIA it is 5.

The average degree of polymerization \overline{DP} is dependent on the catalyst concentration. The curves 1 and 2 on Figure 6 show the \overline{DP} dependencies on the polymerization time for 2 and 8 mol % 1-MIA. Curve 3 in Figure 6 shows the \overline{DP} vs. time dependence when the CGE polymerization is catalyzed by 8 mol % 1-MIA with addition of 7.5 mol % isopropanol. This particular case is discussed below. A higher 1-MIA concentration causes a faster \overline{DP} increase and yields a higher final \overline{DP} . This tendency is fully confirmed by detailed investigations of the conversion and \overline{DP} dependencies on the catalyst concentration in the whole range of 1–8 mol %. Figure 7 shows the dependence of the CGE monomer-oligomer conversion on the 1-MIA concentration at different temperatures.

Polymerizations were carried out at 80°C, 100°C, 120°C, and 140°C for 3 h. There is a clear dependence of the conversion on the polymerization temperature; the dependence on the 1-MIA concentration is even more

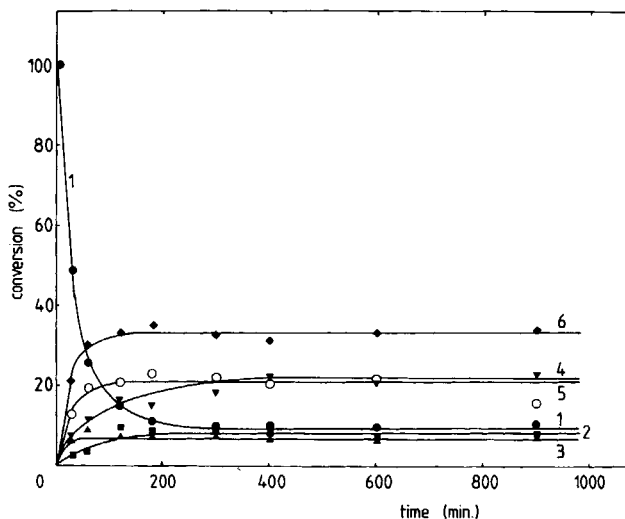


Fig. 5. Conversion vs. time dependence of CGE polymerized with 8 mol % EMI at 100°C. The meaning of the curves is identical with those in Figure 3.

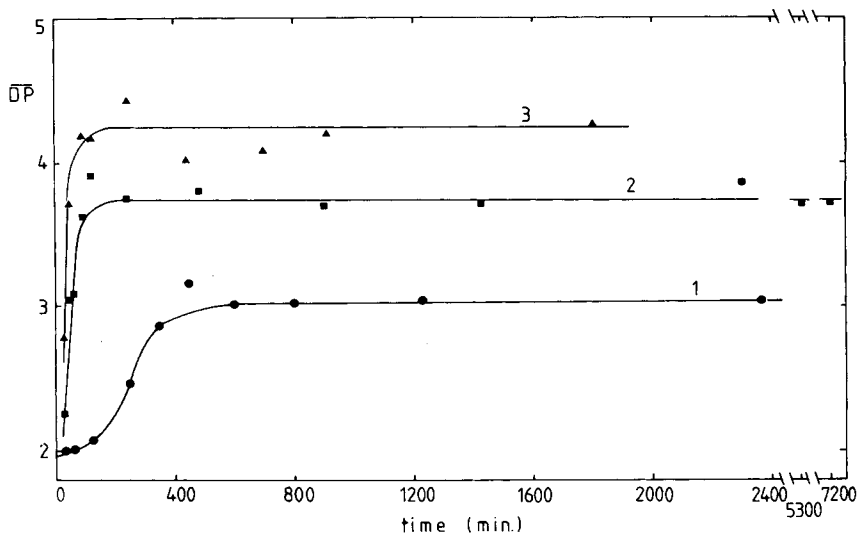


Fig. 6. \overline{DP} vs. polymerization time, polymerized at 100°C: (1) 2 mol % 1-MIA; (2) 8 mol % 1-MIA; (3) 8 mol % 1-MIA + 7.5 mol % IP.

pronounced. The dependence of the average degree of the polymerization \overline{DP} on the 1-MIA concentration is plotted on Figure 8, curve 1. The differences of \overline{DP} due to the polymerization temperatures are small and in the limits of standard deviations (marked as vertical bars).

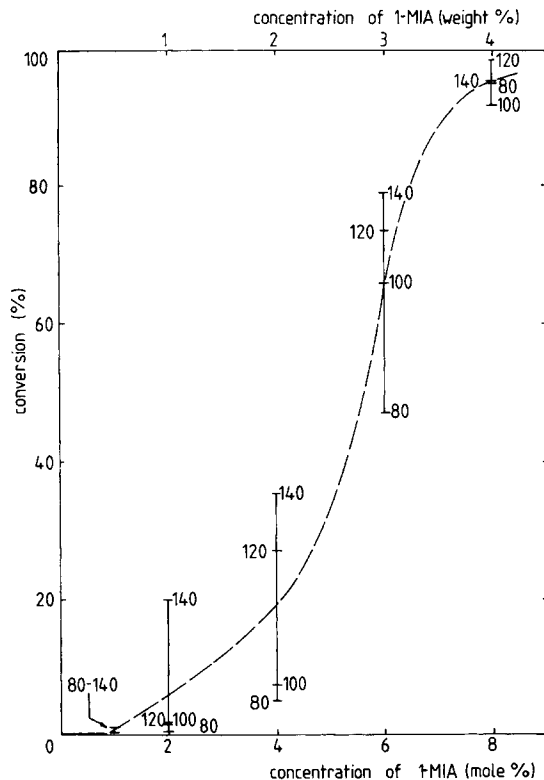


Fig. 7. Conversion vs. 1-MIA concentration of CGE polymerization. Polymerized 3 h at 80°C, 100°C, 120°C, and 140°C.

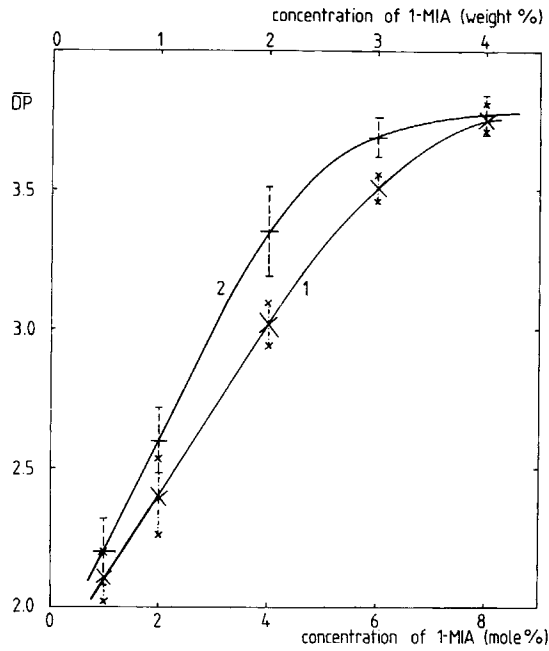


Fig. 8. Average degree of polymerization \overline{DP} vs. 1-MIA concentration, in 3 h polymerization at 80°C, 100°C, 120°C, and 140°C: (---) standard deviations over the whole temperature range; (1) polymerization catalyzed by 1-MIA; (2) polymerization catalyzed by 1-MIA with 7.5 mol % IP.

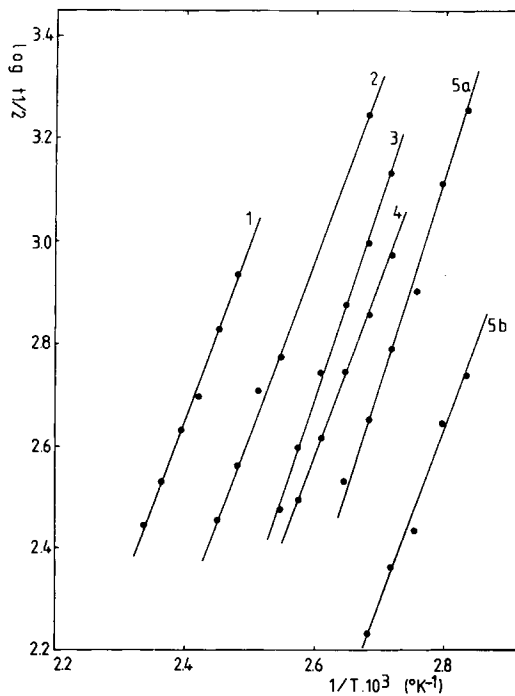


Fig. 9. Arrhenius diagrams of CGE polymerizations with different imidazoles: (1) 2-PhIA; (2) 2-MIA; (3) 1-MIA; (4) EMI, (5a, 5b) 4/5-MIA.

TABLE II
Activation Energies of the CGE Polymerizations Catalyzed by Imidazoles

No.	Imidazole derivative	Concentration (mol %)	Temperature range (°C)	Activation energy E_a		Remarks
				(kcal/mol)	(kJ/mol)	
1	2-PhIA	2	130-155	15.7	65.5	Low solubility in CGE
2	2-MIA	2	100-135	15.7	65.7	
3	1-MIA	8	90-120	17.9	74.7	
4	EMI	8	85-115	15.7	65.7	
5	4/5-MIA	8	80-105	19.2	80.3 ^a	
	1-MIA + IP ^c	8 + 7.5 ^d	90-120	15.9	66.5 ^b	Two DSC peaks ^{a,b}
				16.8	70.0	See Part 2

^a Insignificant.

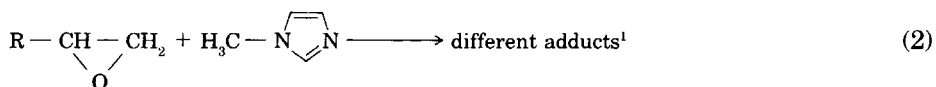
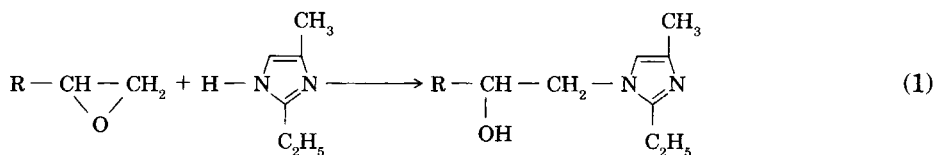
^b Prominent.

^c IP = isopropanol.

^d 7.5 mol % IP.

The activation energies E_a of CGE polymerizations catalyzed by 2-PhIA, 2-MIA, 1-MIA, EMI, and 4/5-MIA were determined from the half-life times of the isothermal DSC curves. The E_a values show (Fig. 9, Table II) small differences in relation to the substitution at the imidazole nitrogen. Polymerizations catalyzed by imidazoles with a secondary amine structure (four compounds) have an E_a of about 2 kcal/mol (8.8 kJ/mol) lower than those catalyzed by 1-MIA, which has only tertiary amine nitrogen.

The differences in E_a and in conversion/time dependencies between CGE polymerizations catalyzed by EMI and 1-MIA suggest the possibility of different starting mechanisms when glycidyl ethers are polymerized by imidazoles with or without secondary amines. The difference might be attributed to the readiness of CGE to react with the secondary amine of EMI or the tertiary amine of 1-MIA:



Farkas and Strohm³ found that phenyl glycidyl ether with EMI form 1:1 (1) and 2:1 adducts which are the first stages of the chain propagation reaction. According to this scheme, EMI is supposed to be incorporated into the polymer molecule.

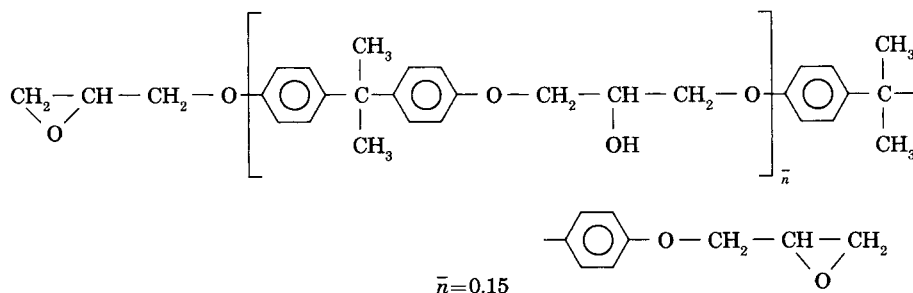
Ricciardi et al.¹ isolated seven adducts resulting from the reaction of phenyl glycidyl ether with 1-MIA (2), most of them with unexpected structures, for instance, four were different adducts of phenyl glycidyl ether to demethylated 1-MIA. Only one structure, the 1-MIA:phenyl glycidyl ether (1:1)-adduct (isolated only as hydrochloride) confirms the usual concepts of glycidyl ether polymerization catalyzed by 1-MIA. Ricciardi, furthermore, showed that imidazole is regenerated during the curing process mostly by cleavage of the 3-N—C bond. The N—C cleavage might lead to demethylated products as well as to the regenerated 1-MIA. For this reaction, which is essential for the further glycidyl ether polymerization, higher temperatures¹ are necessary.

On the other hand, the formation of the glycidyl ether-EMI (1:1)-adduct¹ could be less temperature dependent and of higher stability. This adduct is claimed to be the "true" catalyst of the glycidyl ether polymerization catalyzed by EMI. The differences in E_a shown above could be interpreted in terms of a higher temperature dependence of the formation of the catalytic species from 1-MIA vs. smaller ones from EMI or other imidazoles with a secondary amine structure.

The chain propagation steps from the adducts generated by the reactions (1) and (2) might involve different mechanisms and hence even more intermediates. Unfortunately, there are no data available on the basis of which it would be possible to decide whether the propagation reactions are also important for the differences between the polymerization catalyzed by EMI and 1-MIA.

Polymerizations Catalyzed by 1-MIA in the Presence of Isopropanol (IP)

The cocatalytic activity of alcohols on the polymerization of epoxy compounds by tertiary amines is well known. Some of the work is dedicated to the interpretation of the mechanism of these polymerizations.^{7,8,10} However, no investigations on imidazole catalyzed polymerizations of model epoxy compounds are known heretofore, although all technical epoxy resins contain a certain amount of hydroxyl groups. Since the ratio of the epoxy to the hydroxyl groups in a technical resin of the formula



is 1:0.075, it was obvious to carry out the model polymerizations of CGE with 1-MIA in the presence of IP in the molar ratios of CGE:IP mentioned above. Isopropanol represents the repeating unit in the resin which is actually isopropanol derivative.

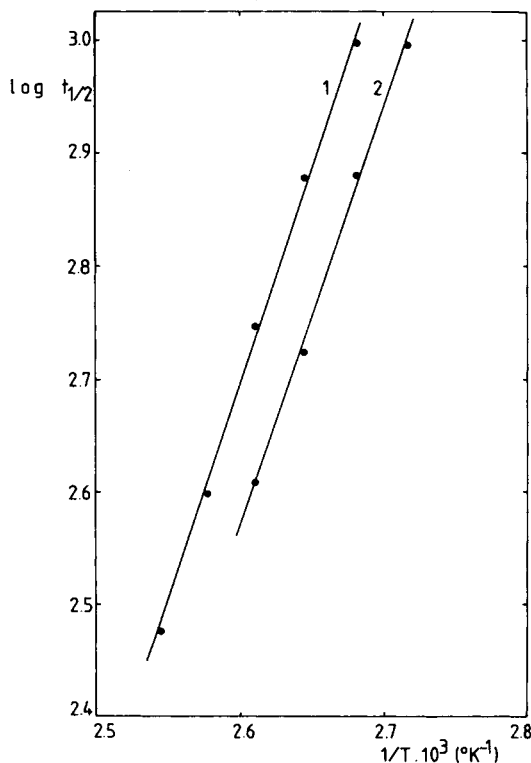


Fig. 10. Arrhenius diagrams of CGE polymerizations: (1) 8 mol % 1-MIA; (2) 8 mol % 1-MIA + 7.5 mol % IP.

The polymerizations were performed in bulk mixtures of CGE with 7.5 mol % IP and different contents of 1-MIA, both related to the amount of CGE. The half-life times of the isothermal polymerizations (DSC measurements), at different temperatures shown in Figure 10 demonstrate that CGE polymerizes much faster in the presence of IP (curve 2) than without IP (curve 1).

The activation energy of the polymerization E_a in the presence of IP is only about 4 kJ/mol lower (70 kJ/mol) than E_a determined in the reaction without the secondary alcohol (Table II). The comparison of the conversion-time dependencies for the system with (Fig. 11) and without IP (Fig. 4) shows the accelerating effect of IP on the polymerization:

(a) The CGE consumption is faster in the presence of IP (curves 1 on Figs. 11 and 4),

(b) In the presence of IP an additional oligomer fraction ($DP = 6$) is formed; thus a higher \overline{DP} is obtained (curve 3 vs. curve 2 in Fig. 6).

On the other hand, the conversion curves in both cases show similarities in the accelerating disappearance of CGE. The influence of the 1-MIA concentration on the conversion, the average polymerization degree \overline{DP} , and the distribution of the oligomer fractions in the polymerization of CGE catalyzed by 1-MIA + IP was also investigated. The polymerizations were carried out at temperatures 80°C, 100°C, 120°C, and 140°C for 3 h with constant concentration of IP (7.5 mol %).

Figure 12 shows the conversion in function of 1-MIA concentration in the presence of IP in the temperature range 80–140°C as a S-form curve, similar to those obtained in the experiments without IP (cf. Fig. 7). The conversion strongly increases between 2 and 6 mol % 1-MIA. The temperature dependence also increases significantly between 2 and 4 mol % 1-MIA. It seems that the polymerizations are less temperature dependent at temperatures higher than 100°C and 1-MIA concentrations higher than 4 mol %.

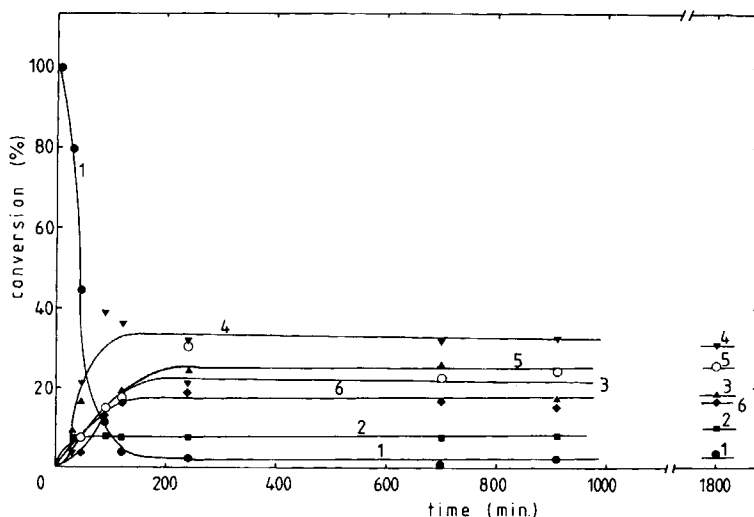


Fig. 11. Conversion vs. polymerization time of CGE polymerized with 8 mol % 1-MIA and 7.5 mol % IP at 100°C: (1) monomeric CGE; (2–6) di-hexamer.

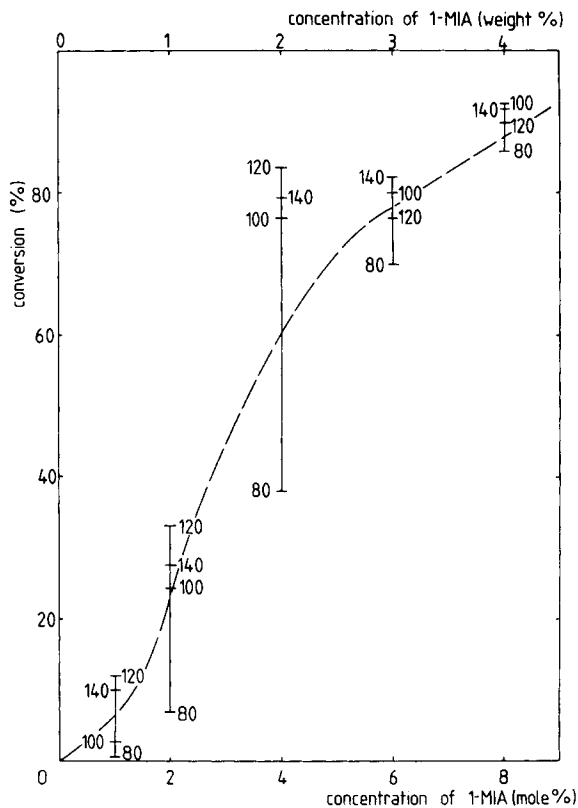


Fig. 12. Conversion vs. 1-MIA concentration of CGE polymerized in the presence of 7.5 mol % IP. Polymerizations were performed at 80°C, 100°C, 120°C, and 140°C. Polymerization time 3 h.

The average polymerization degree \overline{DP} of the polymers (calculated from the GPC data) synthesized in the presence of IP increases with the 1-MIA concentration (Fig. 8, curve 2), again as in the polymerizations in the absence of IP (Fig. 8, curve 1). The dependence in Figure 8, curve 2, as compared to theirs in curve 1, is shifted to higher \overline{DP} values. The dependence of \overline{DP} on the polymerization temperature at constant 1-MIA and IP concentrations is in the limits of relatively insignificant standard deviations.

Figure 13 shows the oligomer composition, for CGE polymerized at 80°C, 100°C, 120°C, and 140°C for 3 h in the presence of 7.5 mol % IP and different 1-MIA concentrations. The numbers near the curves indicate the DP values. Each point represents an average of values obtained over the whole temperature range.

The scattering of the values along the slopes at different temperatures is insignificant. The DP values of the oligomers formed are dependent on the catalyst concentration, while tetra- and pentamers are formed only if more than 2 mol % 1-MIA are added; dimers and trimers are formed even with 1 mol % 1-MIA.

By comparing the dependencies of the conversion (Fig. 12) and the polymer fractions according to DP values (Fig. 13) on the 1-MIA concentration, both with 7.5 mol % IP, it becomes evident that the concentrations of lower

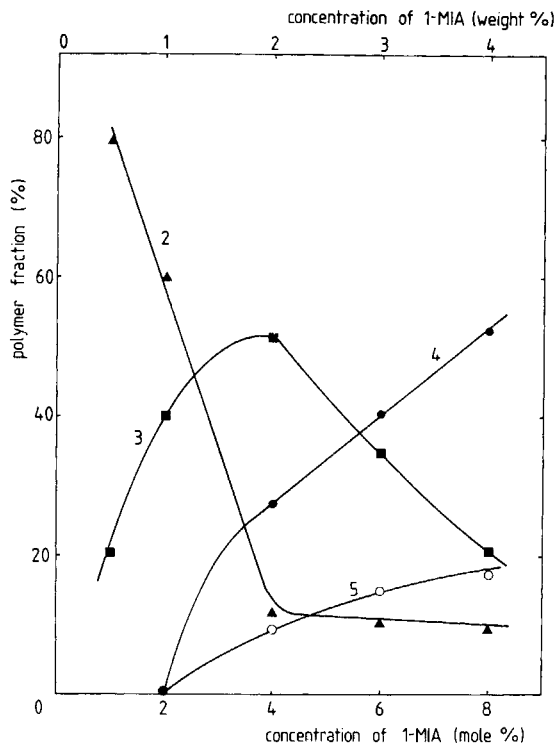


Fig. 13. Composition of the oligomers in % of the polymerization degrees DP in function of the 1-MIA concentration, in the presence of 7.5 mol % IP. The numbers close to the curves indicate the DP values. Each point represents an average of values obtained over the whole temperature range.

oligomers (DP = 2 and 3) are increasing much slower than the concentrations of the higher ones (DP = 4 and 5). Among the oligomers with DP = 2 and 3 there might be a considerable part of glycidyl ether-1-MIA (1:1)- and (2:1)-adducts or similar species (see Ref. 1) which could catalyze the chain growth reaction. Thus, rather the propagation (i.e., the formation of higher oligomers) than the initiation reaction is responsible for the faster polymerization at higher 1-MIA concentrations. The same dependence—as presented in Figure 13 for the presence of IP in Figure 13—is shown in the absence of IP in Figure 14.

Again, by comparing the dependencies of the conversion (Fig. 7) and polymer fractions according to DP values (Fig. 14) on the 1-MIA concentration—this time without IP—the same conclusions could be made regarding the influence of the initiation and propagation on the overall rate of polymerization.

Both Figures 13 and 14 show quite similar tendencies, i.e., the polymer composition changes according to the DP values. The small differences are of insignificant quantitative nature: The composition of the oligomers in the presence of IP is shifted to slightly higher DP values. We believe that

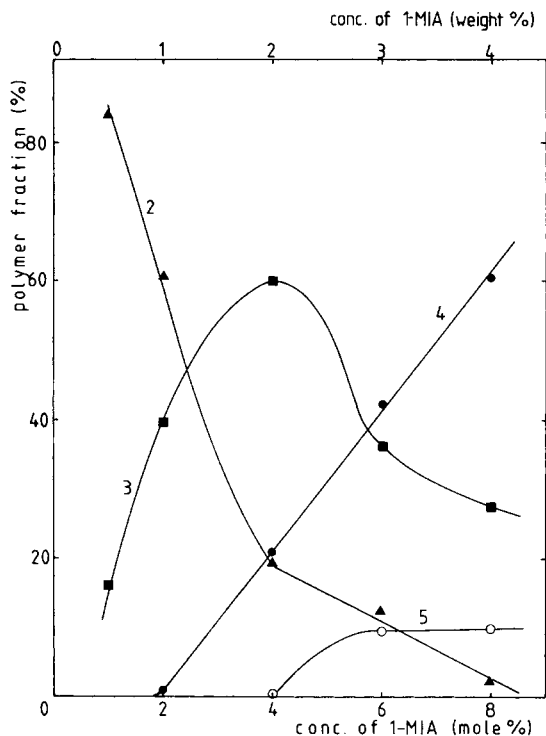


Fig. 14. As Figure 13, only in absence of IP.

this is caused by the higher polymerization rates in the presence of IP (Fig. 10).

During the polymerization of glycidyl ethers catalyzed by 1-MIA alone hydroxyl (or alcoholate) groups containing adducts are formed¹ (although most certainly unstable), probably already at the very beginning of the reaction. These hydroxyl groups then participate in the polymerization as cocatalysts with imidazole and lead to the accelerated monomer decay (Fig. 4).

Thus, the great similarities between the polymerizations of CGE catalyzed by 1-MIA, both in the presence and in the absence of IP are due to the hydroxyl (or alcoholate ion) groups acting as powerful cocatalysts.

The differences between the polymerizations in the presence and absence of IP seem to be caused only by the different concentrations of the hydroxyl groups in the system at the very early period of the polymerization.

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