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Catalyzation

Polymerization of p-Cresyl Glycidyl Ether Catalyzed by Imidazoles.

2. Polymerization Catalyzed "in situ" (1)

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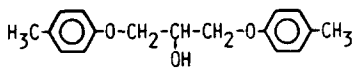
Summary.

The clear dependence between the age of mixtures of p-cresyl glycidyl ether and imidazoles and their subsequent rates of polymerization at elevated temperatures show that low molecular weight products formed by the reaction of p-cresyl glycidyl ether with imidazoles catalyze the polymerization of p-cresyl glycidyl ether much more efficiently than imidazoles by themselves.

Especially in the reaction mixture of p-cresyl glycidyl ether with 1-methyl imidazole is 1,3-bis(4-methylphenoxy)-propanol-2



in high yield formed. This product is one of the most responsible for the acceleration of the polymerization in aged mixtures since it was found to accelerate considerably the polymerization of p-cresyl glycidyl ether when used as a cocatalyst with imidazoles.

The isopropanol derivative accelerates the polymerization more efficiently than isopropanol.

On the other hand, the isopropanol derivative is formed only to an insignificant extent when 2-ethyl,4-methylimidazole is used instead of 1-methylimidazole.

Introduction.

In their fundamental work about the curing of epoxides by 2-ethyl,4-methylimidazole A.Farkas and P.F.Strohm (2) suggested that the true catalytic species is not imidazole itself but an addition product thereof.

J.M.Barton and P.M. Shepherd (3) supposed that the unreacted 2-ethyl,4-methylimidazole and the glycidyl ether - imidazole 1 : 1 adduct show the same reactivity towards the epoxide group. Notwithstanding, the adduct was applied as a good harde-

ning agent (4).

The investigations carried out in Part I of this work (1) indicate that during the polymerization of p-cresyl glycidyl ether catalyzed by 1-methylimidazole, the true catalyst is formed primarily in the starting stage of the reaction. This tendency could not be detected so clearly when the polymerization was catalyzed by 2-ethyl,4-methylimidazole.

The question arise what are the species catalyzing the polymerization of p-cresyl glycidyl ether in the presence of imidazoles more effectively than imidazoles themselves.

The following points were investigated :
- the influence of the age of mixtures of p-cresyl glycidyl ether and imidazole at 25°C (i.e. the time in which the catalytic adduct is formed) on the subsequent polymerization at elevated temperatures,
- the nature of a major compound formed in p-cresyl glycidyl ether - imidazole mixtures and its respective influence on the p-cresyl glycidyl ether polymerization.

Experimental.

The chemicals and experimental conditions for polymerizations, gel permeation chromatography (GPC) and differential scanning calorimetry (DSC) were described in Part I of this work (1).

1,3-Bis(4-methylphenoxy)-propanol-2 prepared by adding p-cresol to p-cresyl glycidyl ether was used to check the analytical data of this derivative prepared by the reaction of p-cresyl glycidyl ether with 1-methylimidazole.

The procedure was the following :
An equimolar mixture of p-cresyl glycidyl ether and p-cresol and 1 w.-% tetramethyl ammonium chloride were reacted at 140°C for 5 hours. Afterwards the crude product was recrystallized twice from cyclohexane and dried in vacuum. The purity of the product was 99.5 %, the yield was 87 %, m.p. 83°C, elemental analysis :

	C	H
found :	74.65 %	7.48 %
calc. :	74.98 %	7.40 %

The High Pressure Liquid Chromatography (HPLC) measurements were performed on a Varian Liquidchromatograph 5000 equipped with a Varian Injection Automat 8055, Kratos Detector Spectroflow 773 and Varian Data System CDS 401.

The separations were carried out in a Nucleosil 10 C 18 column (Macherey & Nagel) with a solvent gradient water-acetonitrile, flow rate 1.5 ml/min., pressure 80 bar, temperature 55°C.

Results and discussion.

A. The "pre-history" of the polymerization mixture.

It is known that polymerization of epoxides with imidazoles can start at room temperature. Nevertheless, it seems worth to be known how the ageing of the polymerization composition at room temperature influences the rate of p-cresyl glycidyl ether polymerization at elevated temperatures. The differences between the polymerization rates of "fresh" and "older" compositions with 1-methylimidazole and 2-ethyl,4-methylimidazole (EMI) are mostly significant. Fig. 1 illustrates how the polymerization is influenced by the ageing of p-cresyl glycidyl ether with 8 mole % 1-methylimidazole at 25°C. Curve 1 shows the dependence of the conversion on the ageing time. The polymerization rate at room temperature is very low with a slight accelerating tendency. A substantial increase of the polymerization rate with increasing age of a composition can be detected when samples of this composition are taken for subsequent polymerizations for 10 (curve 2), 30 (curve 3) and 60 (curve 4) minutes at 100°C. Besides, it is apparent that the increase of the polymerization rate is not simply additive to the corresponding polymerization rate at 25°C. An even stronger accelerating effect has been detected in the case of p-cresyl glycidyl ether polymerization catalyzed by EMI. Results of this system are shown in Fig. 2. Selected data are given in Table 1.

In agreement with the results above, there was observed a strong desrease of the polymerization peak temperature T_{max} (DSC values) and of the time necessary to complete the polymerization t_{max} (under isothermal conditions at 110°C) with the ageing time at 25°C of the mixture (Fig. 3)

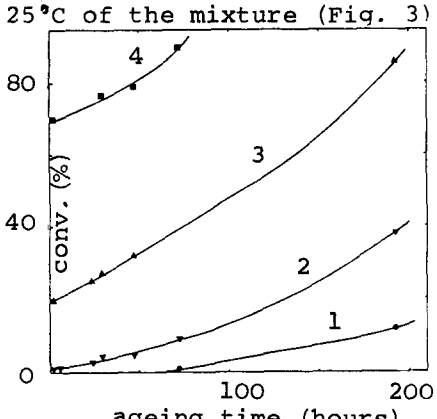


Fig.1. Conversion vs. time of the polymerization with 8 mole % 1-methylimidazole.Curve 1:at 25 C, 2-4 :ageing at 25° (the time on the abscissa) followed by the polym. at 100°C: 2 (10),3(30),4(60 min.)

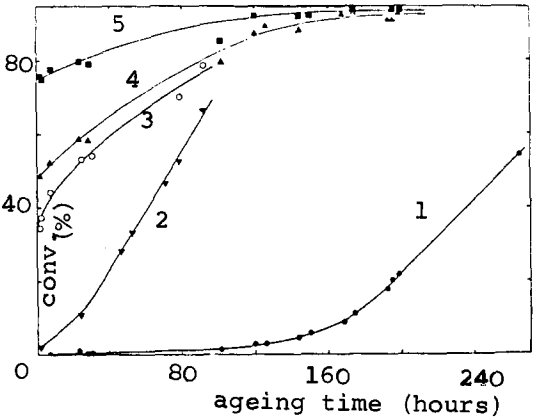


Fig. 2.Conversion vs. time of the polymerization with 8 mole % EMI. Curve 1 : at 25°C, 2 - 5 :ageing at 25°C (the time on the abscissa) followed by the polym. at 100°C : 2(10),3(20),4(30),5(60 minutes).

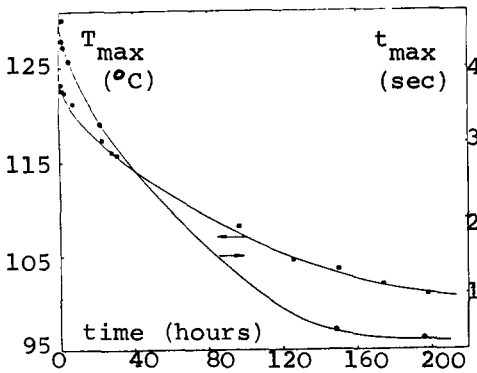


Fig.3.Dependence of the polym. peak-temperature T_{max} and the time necessary to complete the polymerization t_{max} on the ageing time (8 mole % EMI at 25°C (DSC measurements).

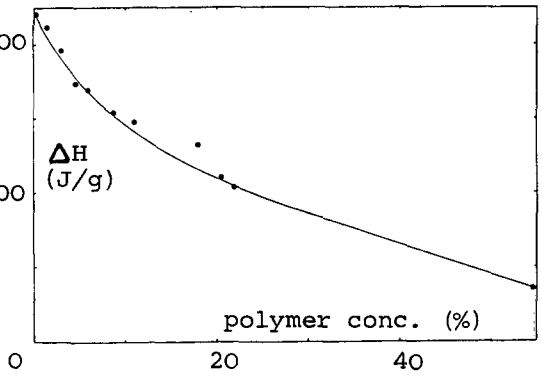


Fig.4. Dependence of the polym. enthalpy ΔH (8 mole % EMI) on the concentration of the polymer pre-formed during ageing at 25°C. (DSC measurements :5°C/min., 20-220°C).

Table 1. Polymerization rates of the fresh and aged p-cresyl glycidyl ether - imidazoles mixtures.

Catalyst	Rate of polymerization[1] in p-cresyl glycidyl ether - imidazole solutions (%/min.)	
	fresh	aged[2]
1-methyl-imidazole	0.10	1.20
2-ethyl,4-methylimidazole	0.15	6.60

1) determined from the polymerizations carried out at 100°C during 10 minutes
2) at 25°C for 90 hours

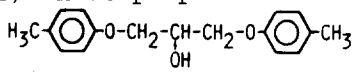
These results prove that the new catalytic and/or cocatalytic species, more active than imidazoles themselves, are formed. The aged compositions polymerize at lower temperatures and with higher rates than the freshly prepared ones. The new catalysts might have the character of dimers or even trimers as indicated by the presence of insignificant amounts of fractions with polymerization degrees 2 and 3 in aged mixtures (found by GPC). Fig. 4 shows an indirect proportionality between the enthalpy ΔH of the polymerization at 100°C and the concentration of the pre-formed oligomers. Parallely to formation of different adducts in systems p-cresyl glycidyl ether - imidazoles (during their ageing), which serve as catalysts for further chain propagation, chains are terminated, i.e. dead oligomers are formed. The dead oligomers cannot participate in the chain propagation which is exothermic. Their growing concentration must then lead to the decrease of the polymerization enthalpy ΔH of the subsequent polymerization at 100°C.

B. The cocatalysis with 1,3-bis(4-methylphenoxy)-propanol-2.

The results described in Part A show that polymerizations in the system p-cresyl glycidyl ether - imidazoles are self-accelerating. The acceleration of the polymerization is caused by a new powerful catalytic species formed during the ageing of the

p-cresyl glycidyl ether - imidazole compositions.
This hypothesis was still strengthened by finding of a compound formed in high yield in p-cresyl glycidyl ether - 1-methylimidazole mixtures.

From the p-cresyl glycidyl ether - 1-methylimidazole compositions reacted at higher temperatures and prepared in different glycidyl ether - imidazole molar ratios (1 : 2 to 4 : 1, heated at 100°C for 5 hours) an isopropanol derivative of the formula



has been isolated and analytically detected at relatively high concentrations. The data are summarized in Table 2.

Table 2. 1,3-bis(4-methylphenoxy)-propanol-2 content in the products of p-cresyl glycidyl ether : imidazole reaction.

p-cresyl glycidyl ether : imidazole[1] (molar ratio)	1,3-bis(4-methylphenoxy)-propanol-2 (weight %)		
	from p-cresyl glycidyl ether:1-methylimidazole		from p-cresyl glycidyl ether :2-ethyl-4-methylimidazole
	found[2]	isolated[3]	found[2]
1:2	13.0	14.2	0.1
1:1	16.5	14.7	0.2
2:1	18.0	17.1	0.5
4:1	21.5	13.5	1.5
12.5:1	19.3		

1) Heated 5 h./100°C, 2) HPLC, 3) 20 g mixture was separated on a column filled with 700 g silica-gel (Kieselgel 60 puriss. particle size 0.063-0.200 mm, Merck, Germany), solvent $CHCl_3$: methyl ethyl ketone = 5 : 1 (volume ratio) at 25°C.

Table 3. The analytical data of 1,3-bis(4-methylphenoxy)-propanol-2.

	1,3-bis(methylphenoxy)-propanol-2	
	of p-cresyl glycidyl ether : 1-methylimidazole mixture	model compound
melting point (°C)	82.5	83.0
elemental analysis (%)	C: 74.40, H: 7.65	C: 74.65, H : 7.48
NMR (δ, ppm)	CH_3:2.30, CH_2 :4.10, OH^-:4.36, Ø :6.84 & 7.10	identical
MS (molecular weight, fragments)	272 (164,147,121, 108, 91, 65)	identical

The structure of the isopropanol derivative was confirmed by comparison of the analytical data of the compound isolated from the p-cresyl glycidyl ether - 1-methylimidazole mixtures with those of the model compound (Experimental, Table 3).
The HPLC diagram of one of the compositions (molar ratio 1 : 1) is shown in Fig. 5. Compositions of p-cresyl glycidyl ether - EMI in molar ratios 1 : 2 to 4 : 1 were also analyzed by HPLC. In these cases much lower concentrations of the isopropanol derivative are obtained. The results are shown in Table 2 and in the GPC curve of Fig. 6.
These results are in a good agreement with the different consistencies of compositions p-cresyl glycidyl ether with EMI and with 1-methylimidazole : the compositions p-cresyl glycidyl ether - EMI have a much higher viscosity than p-cresyl glycidyl ether - 1-methylimidazole, i.e. higher molecular weight products (1) are formed in the p-cresyl glycidyl ether - EMI compositions. The presence of the isopropanol derivative decreases the acti-

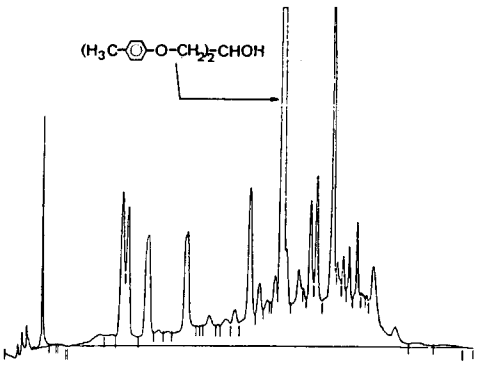


Fig. 5. HPLC of the equimolar mixture p-cresyl glycidyl ether - 1-methylimidazole heated at 100°C for 5 hours. The mixture contains 16.5 weight % 1,3-bis(4-methylphenoxy)-propanol-2.

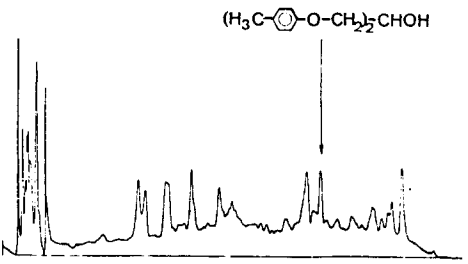


Fig. 6. HPLC of the equimolar mixture p-cresyl glycidyl ether - EMI heated at 100°C for 5 hours. The mixture contains 0.2 weight % 1,3-bis(4-methylphenoxy)-propanol-2.

vation energy E_a and strongly increases the polymerization rate of p-cresyl glycidyl ether catalyzed by imidazoles, especially with 1-methylimidazole.
Fig. 7 shows the Arrhenius diagrams of p-cresyl glycidyl ether polymerized with 8 mole % 1-methylimidazole and with two different alcohols, isopropanol and 1,3-bis(4-methylphenoxy)-propanol-2, both 7.5 mole %. The half-life times $t_{1/2}$ of the isothermal DSC curves are measures of the polymerization rates. The influence of the isopropanol derivative (curve 3) is much stronger than that of isopropanol (curve 2).
The differences in E_a are less significant than in the polymerization rates (Table 4), nevertheless there seems to be an inverse proportionality between the polymerization rate and the activation energy E_a.

Table 4. Activation energies E_a of the polymerization of p-cresyl glycidyl ether.

System	Catalyst	E_a (kJ/mole)	Ref.
1	8 mole % 1-methylimidazole	74.7	1
2	8 mole % 1-methylimidazole + 7.5 mole % isopropanol	70.8	1
3	8 mole % 1-methylimidazole + 7.5 mole % ID*)	65.1	this work

*) 1,3-bis(methylphenoxy)-propanol-2

The dependence of the polymerization on the temperature in the presence of alcohols is weaker, probably because of increasing initiation efficiency of the imidazoles.

The ratios between the conversions c in the presence of the imidazole (1-methylimidazole or EMI) and the isopropanol derivative, c_{IA}, (8 mole % imidazole + 7.5 mole % 1,3-bis(4-methylphenoxy)-propanol-2), and conversions in the presence of

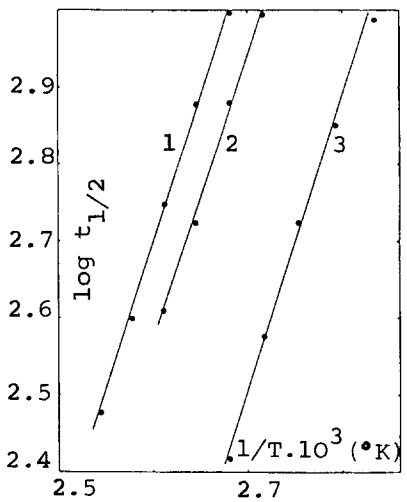


Fig. 7. Arrhenius plots of p-cresyl glycidyl ether polymerizations : curve 1 : with 8 mole % 1-methylimidazole , curve 2 : with 8 mole % 1-methylimidazole + 7.5 mole % isopropanol , curve 3 : with 8 mole % 1-methylimidazole + 7.5 mole % 1,3-bis(4-methylphenoxy)-propanol-2 (concentrations related to p-cresyl glycidyl ether).

imidazole alone, c_I, (8 mole %), at different polymerization times and temperatures show a substantial increase of the polymerization rates in the presence of the isopropanol derivative, especially with 1-methylimidazole.
The values of c_{IA}/c_I in Table 5 for lower temperatures and/or shorter polymerization times are not given because of the difficulties encountered at very low polymerization rates and because of bad reproducibilities with imidazoles in the absence of the isopropanol derivative.

The higher c_{IA}/c_I values in the system with 1-methylimidazole are observed at shorter polymerization times and/or at lower temperatures.These differencies might be indicative for different starting mechanisms in the presence and absence of 1,3-bis(4-methylphenoxy)-propanol-2 :
When p-cresyl glycidyl ether is polymerized with 1-methylimidazole alone, the catalyst must be formed first. The formation of the catalyst is time and temperature dependent. On the other hand, the isopropanol derivative as a cocatalyst can activate more efficiently the system p-cresyl glycidyl ether - 1-methylimidazole. This activation definitely leads to faster polymerization rates than the one without 1,3-bis(4-methylphenoxy)-propanol-2.

Table 5. The influence of 1,3-bis(methylphenoxy)-propanol-2 on the polymerization of p-cresyl glycidyl ether catalyzed by 1-methylimidazole and 2-ethyl,4-methylmidazole.[1)]

Catalyst	Polym. temp. (°C)	c_{IA}/c_I[2)] at the polymerization times (min.) : 10	20	30
1-methyl-imidazole	100	5.74	2.37	1.67
	90	6.11	6.00	4.29
	80			9.32
2-ethyl,4-methylimi-dazole	100	3.28	1.30	1.22

1) concentrations of the imidazoles are 8 mole %, concentration of the isopropanol derivative is 7.5 mole %,
2) c_{IA} is the conversion achieved with the isopropanol derivative, c_I is the conversion achieved without it.

These conclusions are coherent with those made for the influence of isopropanol on the polymerization of p-cresyl glycidyl ether catalyzed by 1-methylimidazole (1).
The polymerization catalyzed by EMI is less influenced by 1,3-bis(4-methylphenoxy)-propanol-2. It might be connected with lower yields of the isopropanol derivative formed in p-cresyl glycidyl ether mixtures with EMI than in those with 1-methylimidazole, i.e. with starting mechanism which is in p-cresyl glycidyl ether - EMI less alcohol dependent than in p-cresyl glycidyl ether - 1-methylimidazole.
However, the time dependence of c_{IA}/c_I has the same tendency as in the case of the polymerization catalyzed by 1-methylimidazole. In the case of EMI other structures - formed at the beginning of the reaction - than the particular isopropanol derivative, seem to be responsible for the acceleration. The investigation of their structures need further analytical work.

References.

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