

Curing Mechanism of Epoxides by Imidazoles

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Synopsis

The courses of the reactions of the epoxides with the various derivatives of imidazole in the concentration range 0.5–25 epox. weight eq./mol imidazole and in the temperature range 80–155°C were studied. All imidazoles form adducts with epoxides very quickly, namely the 1-substituted imidazole 1:1 adducts, in case of the 1,3-unsubstituted imidazoles the reaction continues to the 1:2 adducts. The polymerization effectiveness of the imidazoles falls in order 2-ethyl-4-methylimidazole (EMI) > 1-*n*-butylimidazole (BI) > 2-phenylimidazole (PI) > imidazole (I) \gg 1-vinylimidazole (VI) > benzimidazole (BZI). The effect of temperature, epoxide, and imidazole concentrations on the overall curing rate and the limiting conversion were investigated. In the concentration and temperature range studied the overall curing rate is directly proportional to the imidazole and epoxide concentrations and follows the Arrhenius ratio with similar values of the overall activation energy $E_a = 70$ to 79 kJ/mol for all active tested imidazoles in the studied concentration and temperature range.

INTRODUCTION

Owing to their extreme versatility, plastics based on epoxy resins find numerous uses worldwide. They are components of various construct composites, they are applied as adhesives, protective coatings, and covers. In the electrotechnical industry their application as materials for coating and encapsulation of electronic components is very important.

The properties of the cured epoxy resins depend on their composition, on the structure of the epoxy resin, and the curing agents and their ratios as well as on the conditions and the course of the curing process.

Some imidazoles are highly effective curing agents for curing of epoxy resins. Resins cured with imidazoles possess excellent resistance to chemicals and to oxidation reactions, have high thermal and shape resistance and good dielectric parameters.

There have been few attempts to investigate more profoundly the process occurring in the curing of epoxy resins with imidazole compounds in spite of the fact that using imidazoles as curing agents for epoxies has been known for about twenty years.

Farkas and Ströhm¹ were the first to study this problem seriously. They found the curing of epoxies with imidazoles to be a complex process beginning with addition of the carbon of the epoxy group to the nitrogen of the imidazole. Barton and Shepherd² postulated that the reaction involved the attack of the basic pyridine-type nitrogen, but no secondary pyrrole-type nitrogen as suggested by the first study.

They supported this theory by evidence of the same rates of reaction of the epoxides both with the original imidazole and with the 1:1 adduct of this imidazole and the epoxide. Both the authors^{1,2} noted the rate of the adduct

formation was higher than the rate of polymerization and therefore not overall rate determining. They suggested that the adducts of imidazoles with epoxides are the proper catalysts of polymerization of epoxides.

Active imidazoles are present throughout the course of curing, and overall curing rates (formation of polyethers) vary with imidazole structure even though all imidazoles form adducts rapidly. Ricciardi and his co-workers³ explain this discrepancy as the instability of adducts of imidazoles with epoxides. Parallel to the polymerization there occur cleavage of N—C bonds and the deprotonation of the carbon at the 2-position of imidazole and thus the imidazoles are regenerated.

A major pathway for the regeneration of the catalyst during the curing process is *N*-dealkylation of the imidazoles via substitution process and concomitant formation of ethers. The second route is the reformation of imidazole or adduct with only one substituted nitrogen by β -elimination of a *N*-substituent from either the adduct or the polymer accompanied by production of ketones and eventually double bonds. The elimination can occur at any stage of the curing, and proton abstraction may take place through an intermolecular or intramolecular mechanism.

For the studies of imidazole curing, 2-ethyl-4(5)methylimidazole (EMI) and 1-methylimidazole (1-MI), 2-methylimidazole (2-MI), and 1,2-dimethylimidazole (1,2-DMI) as representative curing agents and phenylglycidylether (PGE) and diglycidylether of bisphenol A (DGEBA) as epoxide were utilized.

In this paper the reactions of derivatives of imidazoles with epoxides were studied. Also the curing efficiency of imidazole and the effect of the temperature and the concentration of the catalyst or monomer on the curing process were investigated.

EXPERIMENTAL

All imidazoles and epoxides used are commercial products and they were used as received.

Imidazole (99%), 1-vinylimidazole (98%), and 2-phenylimidazole (98%) were obtained from Merck-Schuchard; 4,5-benzimidazole (98%) and 2-ethyl-4(5)-methylimidazole (97%) were obtained from Aldrich-Europe, Janssen Chimica Div., and 1-*n*-butylimidazole (purum) from Fluka AG.

Phenylglycidylether (PGE) is a product of Koch-Light ($\geq 99\%$). Epoxide resins ChS Epoxy 15 (E 15) and ChS Epoxy 1/8 (E 1/8) with epoxide equivalent weight 188–200 and 300–370, respectively, corresponding to 72–79%, respectively, 18–25% the diglycidyl ether of bisphenol A (DGEBA) were delivered by Spolchemie, CSSR.

The course of reactions of epoxides with imidazoles was studied by differential scanning calorimetry (DSC) under isothermal conditions in the range 80–155°C and dynamic measurement samples were scanned at a heating rate of 10°C/min. from 20°C to 360°C. The instrument used was Perkins-Elmer 990 thermal analyzer with the DSC cell, operating in a nitrogen atmosphere.

RESULTS AND DISCUSSIONS

The reactions of imidazoles with epoxides were investigated in the concentration range 0.5 to 25 mole of PGE (or epoxy weight equivalent, ewe, in case of E 15) for each mole of imidazole.

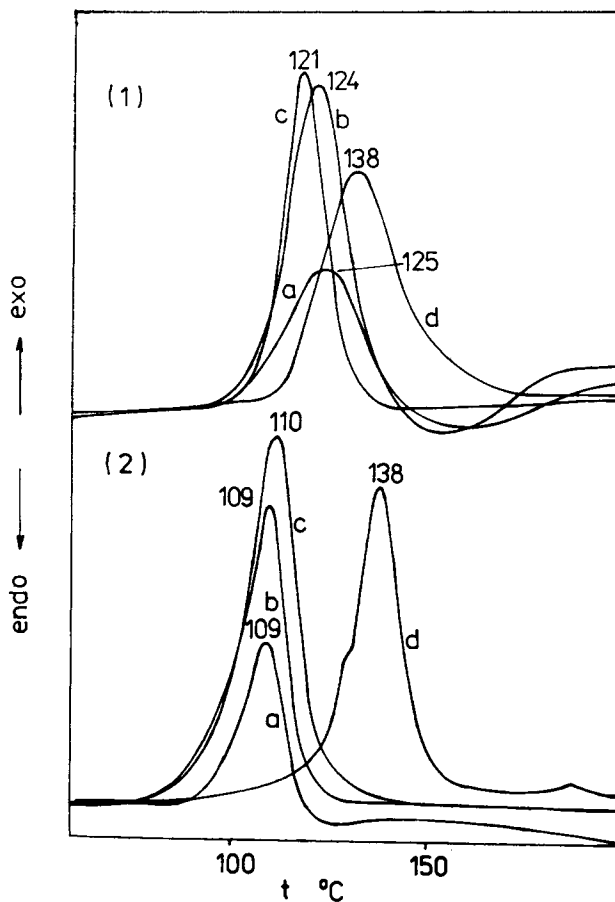


Fig. 1. DSC thermograms of the reaction of PGE with BI(1) and PI(2) at various PGE/imidazole mol/mol ratios: a) 1 : 2; b) 1 : 1; c) 2 : 1; d) 10 : 1. Heating rate 10°/min.

TABLE I
Overall Heat Output From the Reactions of Imidazoles with PGE in kJ/g From the Dynamic DSC Measurements

	PGE/imidazole mol/mol		Polymerization 10 : 1
	1 : 1	2 : 1	
I	442	487	438
EMI	248	381	331
PI	268	351	335
BZI	232	376	268
BI	316	285	360
VI	327	168	295

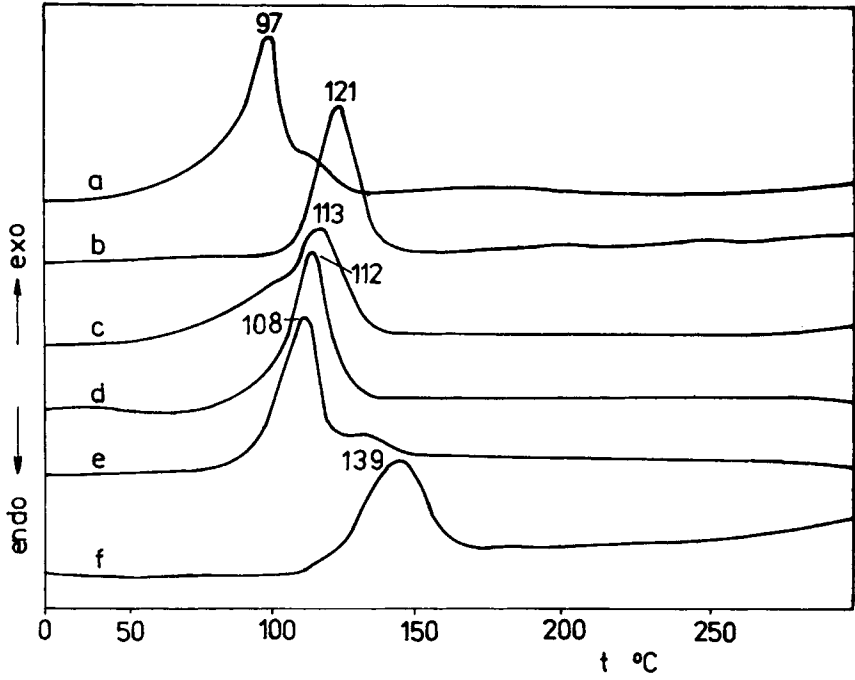


Fig. 2. DSC thermograms of the reaction PGE with the various derivatives of imidazole, PGE/imidazole = 2 : 1 mol/mol: a) I; b) BI; c) EMI; d) PI; e) BZI; f) VI. Heating rate 10°/min.

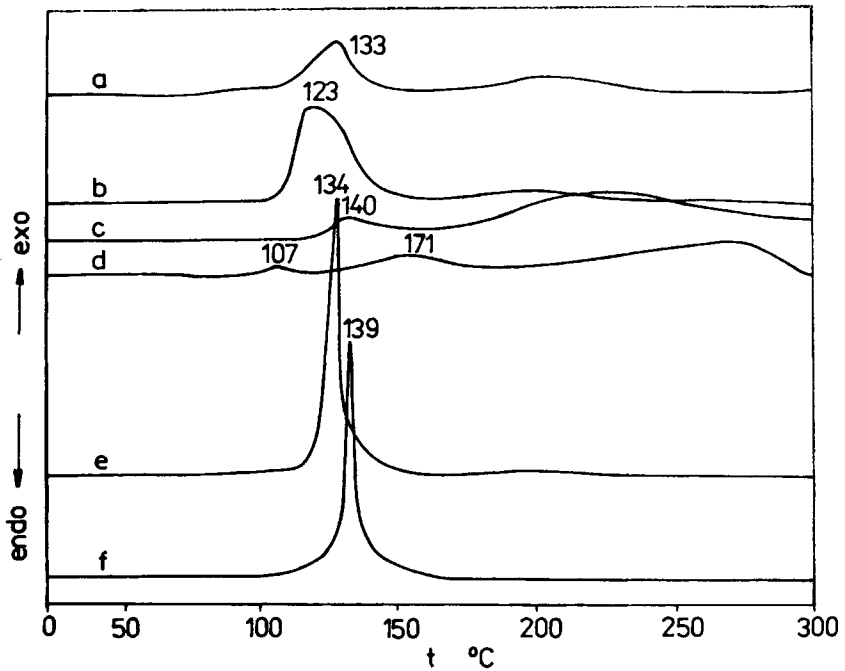


Fig. 3. DSC thermograms of the polymerization of the epoxy resin E 15 with the various derivatives of imidazole at the ratio of the component 10 ewe resin/1 mol catalyst: a) I; b) BI; c) VI; d) BZI; e) EMI; f) PI. Heating rate 10°/min.

In the mixtures where the ratio of the epoxy groups to the nitrogens of imidazoles is 0.5–2.0 (in nearly equimolar mixtures) only addition reactions occur. In that concentration range the total heat output of the reaction PGE with 1-*n*-butylimidazole (BI) or 1-vinylimidazole (VI) is highest when the ratio PGE to imidazole is 1 : 1. On the other hand, when PGE reacts with imidazole (I), 2-phenylimidazole (PI), benzimidazole (BZI), or 2-ethyl-4-methylimidazole (EMI) the total heat output increases with the quantity of PGE in the same concentration range (Fig. 1, Table I).

It follows from those reactions that the formation of the 1 : 1 adduct of the imidazole and epoxide prevails when imidazole has a substituent at the nitrogen (1-substituted imidazole). In cases where the imidazoles are unsubstituted at the nitrogen, 1 : 1 adducts form at first, and the reaction continues up to 1 : 2 adducts of imidazole and epoxide (with an excess of epoxide). The maximal rates of the formation 1 : 1 and 1 : 2 adducts PGE with PI are similar, which is in conformity with the results of the above mentioned authors^{2,3} acquired in studying the reaction of epoxides with EMI.

Temperatures at which the additions begin (the onset of exotherm) and temperatures at which the most energy was given off (the peak of exotherm), as well as the total heat outputs for the reaction depend on the derivative of imidazole used (Fig. 2). The same dependence is valid for the polymerization (Fig. 3).

The polymerization of epoxides by imidazoles was investigated at temperatures from 80°C to 155°C in the concentration range of the epoxide 0.1–6.2 ewe/L and imidazole 0.025–0.950 mol/L.

The differences in the effectiveness of the various derivatives of imidazoles under the concentration conditions corresponding to the polymerization were more evident.

It follows from the comparison of the course of the polymerization of E 15 in the ratio of the imidazole to equivalents of epoxide 1 : 10 that the adducts

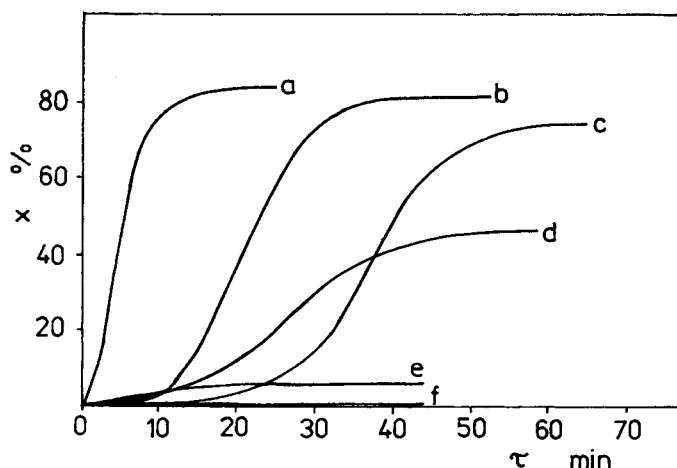


Fig. 4. Dependence of conversion x in the isotherm polymerization E 15 with various imidazoles in percent of the total heat output determined with dynamic DSC measurement at 90°C and the ratio of the component 10 ewe resin/1 mol catalyst on time: a) EMI; b) BI; c) PI; d) I; e) BZI; f) VI.

with EMI possess the highest effectiveness for polymerization of the epoxides. The adducts with BI and PI are also very effective. Polymerization by initiation with these imidazoles occurs at temperatures below 100°C. The polymerization effectiveness of the unsubstituted imidazole is about half. Adducts with BZI or VI are inactive under the same conditions (Fig. 3). The reduced polymerization activity of the BZI is probably caused by steric hindrances owing to the substitution of the imidazole at the 4 and also 5 position and in case of the VI it accounts for the lowering of its concentration by its parallel vinyl polymerization.^{5,6}

The differences in polymerization effectiveness fall quickly with higher temperature and at temperatures above 120°C the course of polymerization is practically the same. This fact supports the idea that the main factor determining the polymerization effectiveness of the imidazoles is the ability of their adducts with epoxide to initiate the polymerization, and that the initiation is the step determining the overall rate of the polymerization.

The inactivity of the BZI or VI adducts at temperatures below 100°C and their nearly identical curing effectiveness as the most active adducts of imidazoles at temperatures above 120°C makes it possible to utilize them for the preparation of epoxy compositions with relatively long shelf life and workability at room temperature. There are known imidazole mixtures, the catalytic activity of which is maintained in a latent form with the bonding of the imidazoles with a heat-labile group that can block the active site. For example, the complexes of the imidazole with inorganic salts⁷ or quaternary 1,3-dialkylimidazolium salts,⁸ can be cleaved at temperatures around 200°C and produce active imidazoles capable of initiating the polymerization of the epoxides. But those temperatures (which are substantially higher compared to about 150°C necessary for the perfect curing of compositions with the BZI or VI adducts) are too high for many applications. Besides, the metal, halide, or other ions remain in compositions, which is often inadvisable, especially for microelectronics applications.

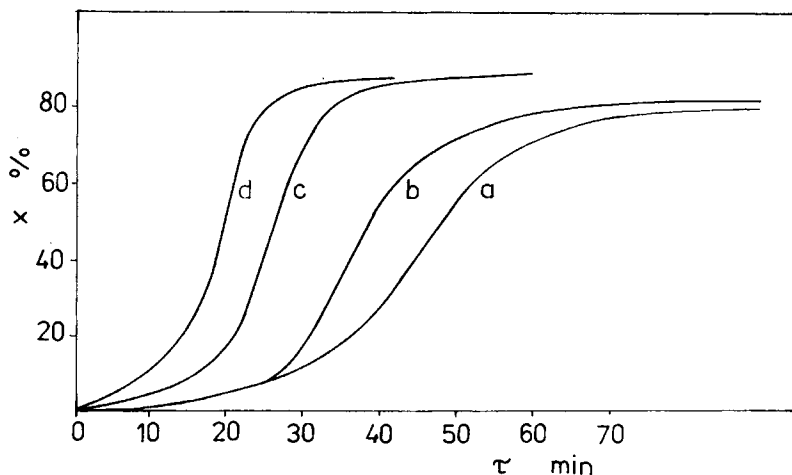


Fig. 5. Dependence of conversion x in the isotherm polymerization E 15 with PI in percent of the total heat output determined with dynamic DSC measurement at 90°C and the various concentrations of catalyst on time: a) 0.24 mol/L; b) 0.32 mol/L; c) 0.40 mol/L; d) 0.53 mol/L.

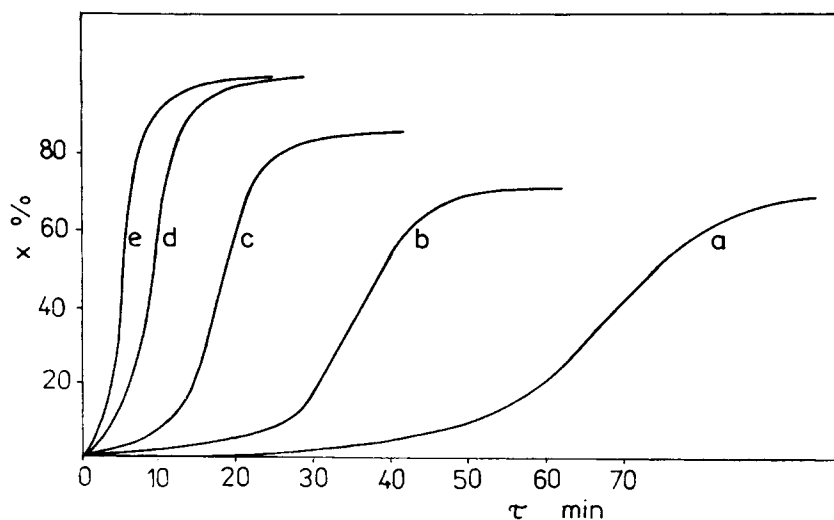


Fig. 6. Dependence of conversion x in the isotherm polymerization E 15 with PI in percent of the total heat output determined with dynamic DSC measurement at various temperatures and concentration of catalyst 0.32 mol/L on time: a) 80°C; b) 90°C; c) 100°C; d) 110°C; e) 120°C.

The isothermal course of cure of epoxides catalyzed with various imidazoles and its dependence on time was measured by means of the heat output. The fractional conversion was defined as the ratio of the heat flow at a given time to the total heat output determined from the dynamic DSC scan.

After an induction period, conversion is directly proportional to time. Then the reaction rate drops and the conversion approximates to the limiting value in the last period. A similar course was stated by Tanaka⁹ who investigated

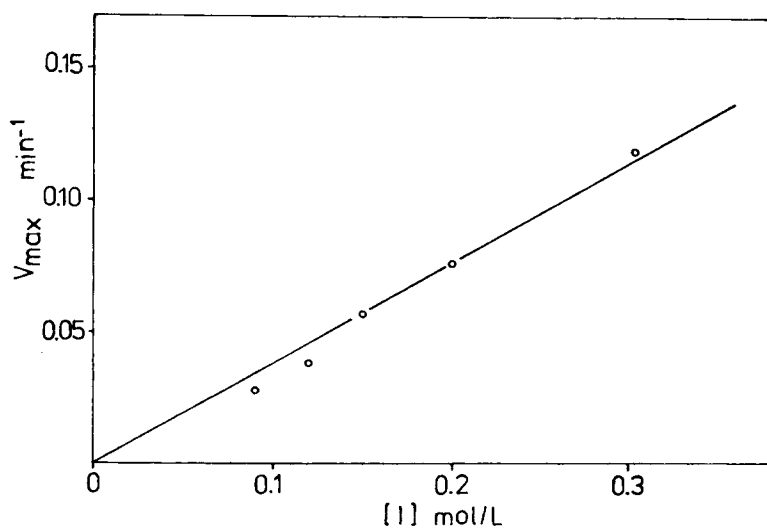


Fig. 7. Dependence of the relative maximal rate V_{max} of the isotherm polymerization E 15 with PI at 90°C on the concentration of catalyst. V_{max} is defined as the max. heat output in time related to the total heat output determined with dynamic DSC measurement.

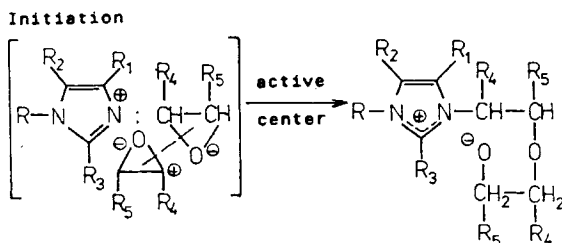
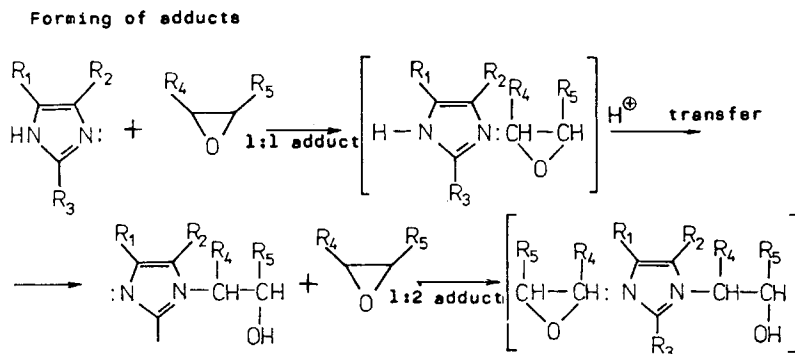
polymerization of PGE with tertiary amines, as well as Ricciardi⁴ who studied the polymerization of PGE with 1-MI, 2-MI, and 1,2-DMI. The induction period and the overall polymerization rate are dependent on temperature and the catalyst concentration and its effectiveness. This follows from the course of the polymerizations of E 15 with the various imidazoles at the same ratio of imidazole (mol) to epoxide (ewe) (Fig. 4) and the polymerization of E 15 with PI at various concentrations (Fig. 5) and temperatures (Fig. 6). The higher the temperature and the concentration or the effectiveness of the catalyst, the shorter is the induction period and the higher is the rate.

In the concentration range studied, the polymerization rate is directly proportional to the catalyst and the epoxide concentrations. This is seen in the polymerization of E 15 with various concentrations of PI (Fig. 7) and in the polymerization of E 15 in dibutylphthalate in various concentrations with BI (Fig. 8).

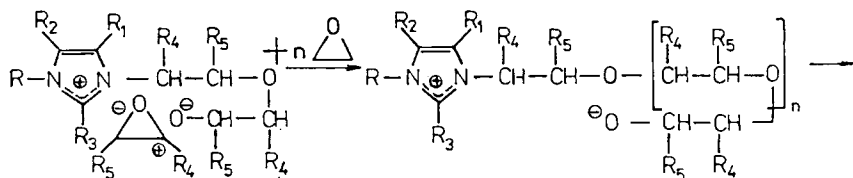
The overall activation energy for curing with the active imidazoles EMI, PI, and BI is 70–79 kJ/mol and it is nearly independent on the epoxide equivalent weight of the resin and catalyst used (Fig. 9).

The temperature at which the curing begins and temperature at which the most energy was given off, decreases with higher concentrations of imidazole (Fig. 10). At higher concentrations, dwells corresponding to forming of the adduct are visible.

For the mechanism of the curing of the epoxides with the imidazoles as seen from previous studies^{1–3} and our results, the reaction scheme shown in Schemes (1)–(4) is suggested:

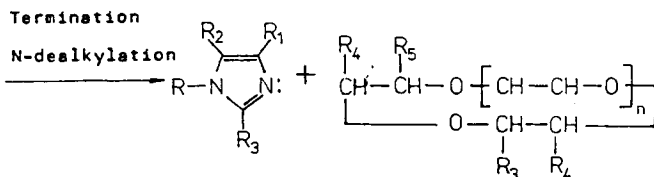


Propagation

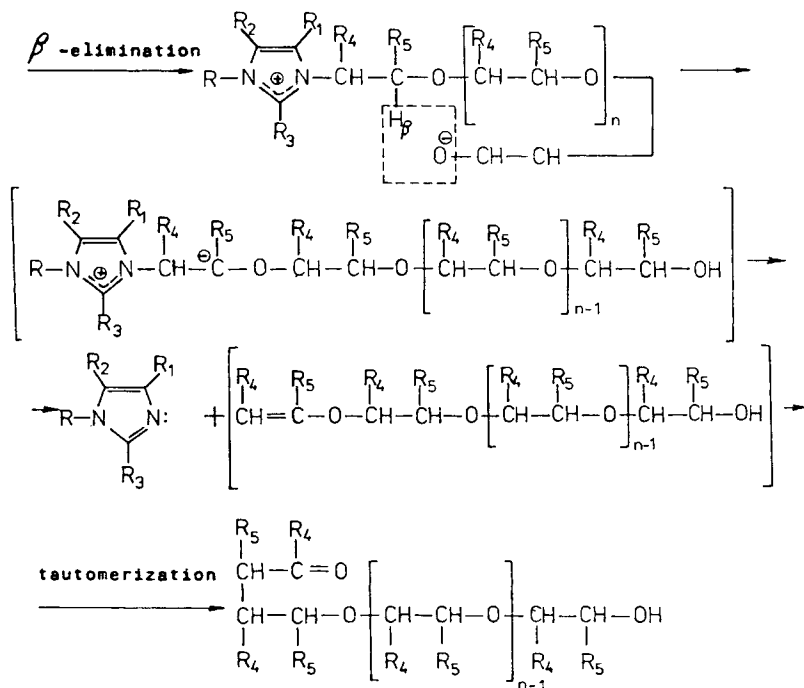


Scheme 3

The initiation occurs with an induction period. The 1:1 respective 1:2 adducts of the imidazole and the epoxide are formed quickly. In the presence of the excess epoxides, growth centers appear after the dissociation or the rearrangement of the formed adduct. The addition of a further molecule of epoxide to the growth center starts the propagation of the polymer.



Scheme 4 (a)



Scheme 4 (b)

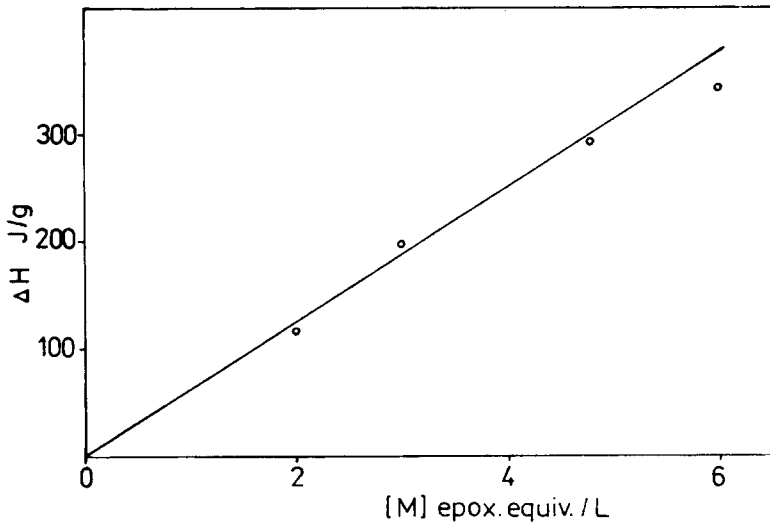


Fig. 8. Dependence of the total heat output in isotherm polymerization of E 15 in dibutylphthalate with BI at 100°C and the concentration of catalyst 0.27 mol/L on the concentration of resin.

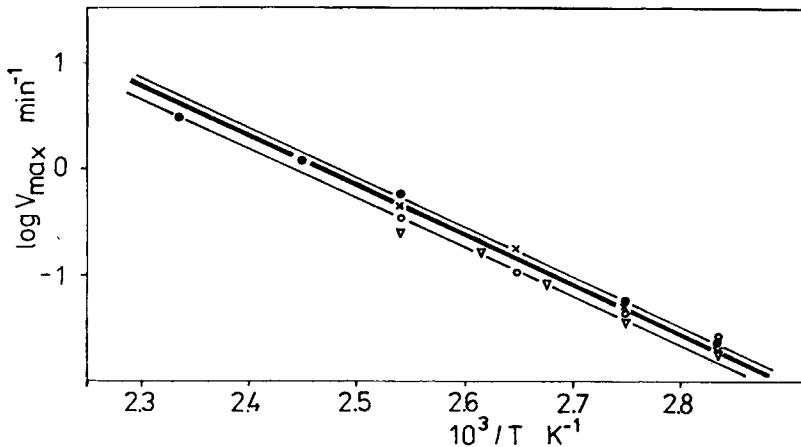


Fig. 9. Dependence of the relative maximal rate V_{\max} of isotherm polymerization of the epoxy resins at the concentration of catalyst 5 phr on temperature: (Δ) E 15 + BI; (\circ) E 15 + PI; (\times) E 1/8 + PI; (\bullet) E 1/8 + EMI.

The termination results from N -dealkylation or the β -elimination of an N substituent from the growing polymer. The formations of ethers or ketones and the regenerations of 1:1 adduct and, eventually, the imidazole are concomitant of the termination reactions and can occur at any stage of the curing.

CONCLUSION

The course of the curing of the epoxides with all the imidazoles used supports the conclusions of Ricciardi and co-workers.

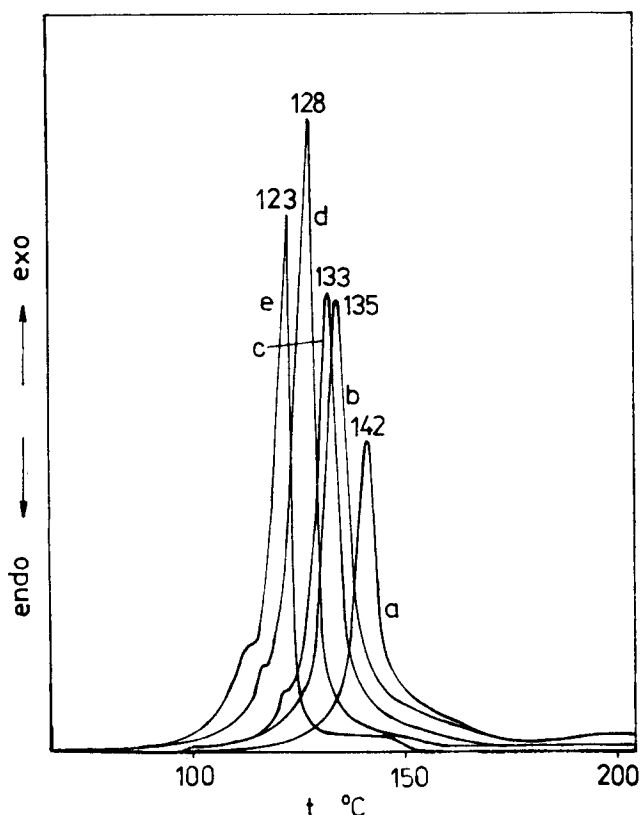


Fig. 10. DSC thermograms of the polymerization of resin E 15 with PI at various concentrations of catalyst: a) 0.24 mol/l; b) 0.32 mol/l; c) 0.40 mol/l; d) 0.53 mol/l; e) 0.80 mol/l. Heating rate $10^\circ/\text{min}$.

The polymerization effectiveness of imidazoles falls in the order 2-ethyl-4-methylimidazole (EMI) > 1-*n*-butylimidazole (BI) > 2-phenylimidazole (PI) > imidazole (I) \gg 1-vinylimidazole (VI) > benzimidazole (BZI) and is determined by the ability of the adduct of the epoxide with the imidazole to initiate the polymerization.

The overall polymerization rate is directly proportional to the imidazole and epoxide concentrations and follows the Arrhenius ratio with the similar values of the overall activation energy $E_a = 70\text{--}79$ kJ/mol for the all-tested active imidazoles in the studied concentration and temperature range.

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