2902 *Macromolecules* **1989**, *22*, 2902-2910

Mechanism and Kinetics of Curing of Epoxides Based on Diglycidylamine with Aromatic Amines. 1. The Reaction of Diglycidylaniline with Secondary Amines†

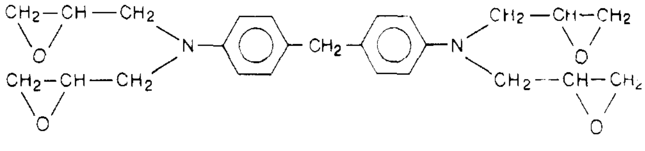
Libor Matějka* and Karel Dušek

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia. *Received August 10, 1988; Revised Manuscript Received December 12, 1988*

ABSTRACT: The reaction mechanism of curing of epoxides based on glycidylamine with aromatic amines was studied by using model systems. In this paper, the reaction of bifunctional diglycidylaniline with secondary amines, *N*-methylaniline and 1-anilino-3-phenoxy-2-propanol, was studied by means of HPLC. The reaction products were isolated by preparative HPLC and identified. The rate constants of the individual partial reactions—addition, etherification, and cyclization—were determined, including the constants for individual stereoisomers. The reactivities of epoxy groups in diglycidylaniline are interdependent. After one functional group in the molecule has reacted, the other epoxy group is activated and reacts faster. With epoxide in excess and after all amine groups are consumed, intra- and intermolecular etherification becomes operative and six- and seven-membered rings arising by intramolecular etherification become the main reaction products. The reaction with primary amines and a general discussion of the reaction mechanism are dealt with in part 2.

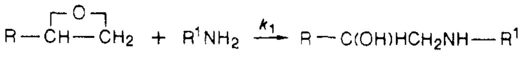
Introduction

The most common procedure of curing epoxy resins is a reaction with polyfunctional amines. In particular, the kinetics of the reaction of epoxides based on diglycidyl ether of bisphenol A (DGEBA) have been studied in detail.[1] Lately, attention has been concentrated on the reaction of diglycidylamine derivatives used in the preparation of high-performance composites, especially on the tetrafunctional epoxide bis[(diglycidylamino)phenyl]methane (*N,N,N′,N′*-tetraglycidyldiaminodiphenylmethane, TGDDM). In this paper the reaction of a model system, N,N-diglycidylaniline, with a monoamine is studied.

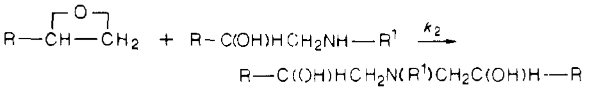


TGDDM

It is known that in the reaction between epoxides and amines the addition occurring in two stages is the most important:

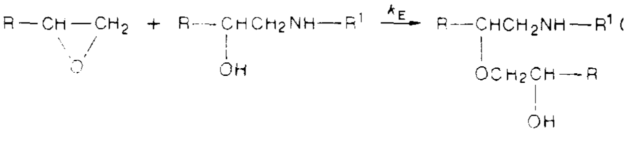


$$\mathrm{R{-}\overset{\frown O \frown}{CH{-}CH_2}} + \mathrm{R^1NH_2} \xrightarrow{k_1} \mathrm{R{-}C(OH)HCH_2NH{-}R^1} \qquad (1)$$



$$\mathrm{R{-}\overset{\frown O \frown}{CH{-}CH_2}} + \mathrm{R{-}C(OH)HCH_2NH{-}R^1} \xrightarrow{k_2} \mathrm{R{-}C(OH)HCH_2N(R^1)CH_2C(OH)H{-}R} \qquad (2)$$

According to the type of the epoxide–amine system, some other reactions also become operative to various extents: etherification, i.e., reaction between epoxide and the OH group of the forming addition products



$$\mathrm{R{-}\underset{\diagdown O \diagup}{CH{-}CH_2}} + \mathrm{R{-}\underset{OH}{\underset{|}{C}}HCH_2NH{-}R^1} \xrightarrow{k_E} \mathrm{R{-}\underset{OCH_2\underset{OH}{\underset{|}{C}}H{-}R}{\underset{|}{C}}HCH_2NH{-}R^1} \qquad (3)$$

homopolymerization, i.e., the anionic or cationic polymerization of epoxides, initiated by an interaction of epoxide with tertiary amine or a Lewis acid, occasionally also in the presence of a proton donor. The mechanism of both polyetherification and homopolymerization is rather complicated, and various oligomeric structures are formed depending on reaction conditions.[1-4]

The overall mechanism of the reaction between epoxide and amines involves the formation of various donor–acceptor complexes, -OH...O- -OH...N- -OH...OH-, etc., the formation of which affects the reaction kinetics. The OH groups arising during the reaction and the corresponding associates are the cause underlying the autocatalytic course or the retardation of the reaction in its final stage.[1,5-7]

In the case of polyfunctional components, the reaction mechanism and kinetics determine to a great extent the structure of the forming network. The relative rates of particular partial reactions play an especially important role. The reactivity of both epoxy groups in DGEBA is the same and is independent, similar to the reactivity of amino groups in diamines in most cases, if the amino groups are separated by a sufficient distance.[8,9] On the contrary, the reactivity of hydrogen atoms in the primary amino group and in the secondary amino group formed in the reaction is different in most cases. The ratio of rate constants of the reaction of the secondary and primary amino group with epoxide, ρ ($=k_2/k_1$) (cf. eq 1 and 2), the so-called substitution effect in the amino group, becomes a very important kinetic parameter. In an ideal case (the same reactivity of the hydrogen atoms of the primary and secondary amino group), $\rho = 1$, if the rate constants are related to the hydrogen of the amino group. In this paper, the rate constants are related to the molecule and $\rho = {}^1/_2$ in an ideal case, because the primary amino group contains two hydrogen atoms. The definition of the rate constants is not always given in the original literature and therefore one may find incorrect data for the substitution effect. Usually, the secondary amino group is less reactive than the primary one owing to the steric hindrances. The substitution effect is negative ($\rho < 0.5$), its value depends on the structure of the amines and is lower for the amines with a sterically hindered functional group.[10-12] Generally, aromatic amines show a more negative substitution effect ($\rho = 0.15$–0.25) than aliphatic amines ($\rho = 0.3$–0.5),[1] in which the hydrogen atoms of the amino group possess an almost identical reactivity. The ratio of rate constants seems to depend also on the solvent.[13]

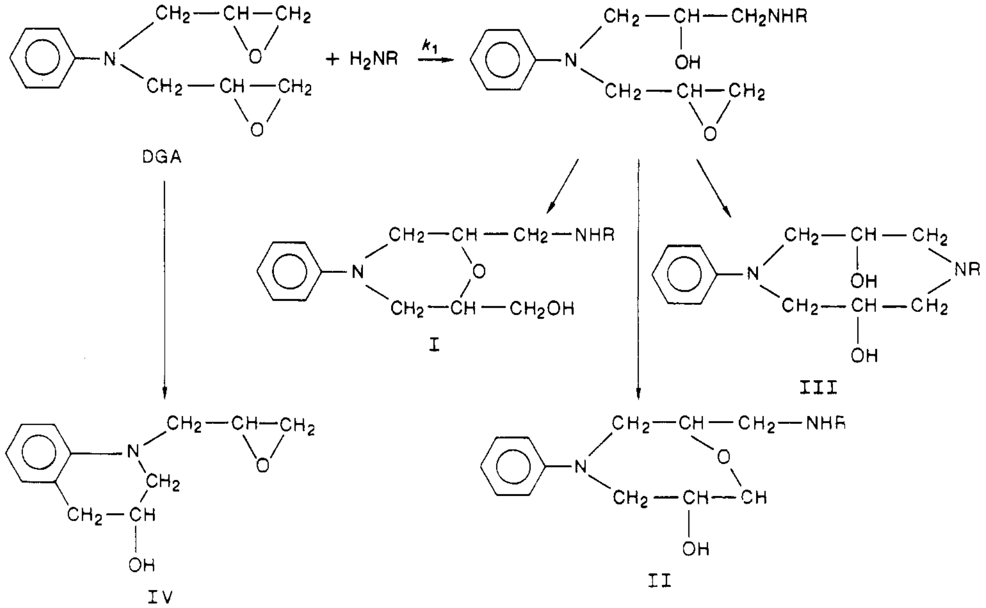
Etherification and homopolymerization are operative in the presence of catalysts, such as BF_3–amine, Monuron (Du Pont) (i.e., (chlorophenyl)dimethylurea), and tertiary amines.[14-18] The tendency of a system to etherify depends

---

† Dedicated to Professor O. Wichterle on the occasion of his 75th birthday.

0024-9297/89/2222-2902$01.50/0

Scheme I



on the character of the amine and on temperature[14,19,20] and increases with the initial ratio epoxide/amine. These reactions can be neglected in a noncatalyzed stoichiometric mixtures of DGEBA with aliphatic amines at $T < 150$ °C.[1,5,21,22] Only if epoxide is present in excess does etherification become operative after all amine groups have been consumed.[21] Tertiary amine arising by reaction 2 has a catalytic effect in this case. For the reaction of DGEBA with aromatic amines it has been reported that etherification again appears only after amine has been consumed[23] or does not appear at all, even with epoxide in excess.[1,14,17,24]

The reactions reported above can occur also intramolecularly, with formation of rings. However, in the case of the reaction between DGEBA and primary amines, no cyclization takes place, due to the rigidity of the DGEBA molecule.[25-27] The reaction of DGEBA with flexible poly(oxypropylene) polyamines (Jeffamines), in which cyclization was observed, is an exception.[28] Cyclization occurs, however, in the case of aromatic ortho diglycidyl derivatives.[29,30]

The mechanism of the reaction between epoxides of the diglycidylamine type, e.g., of diglycidylaniline (DGA) or TGDDM, with amines has its own peculiar features.[31] A special feature of such epoxides is the presence of the tertiary amino group in the epoxide molecule and the steric proximity of two epoxy groups.

The existence of a catalytic center directly in the epoxide molecule results in a stronger tendency toward etherification also in the reaction with aromatic amines.[14,32-34] Most authors refer to a paper by Gupta et al.[32] and give the ratio of rate constants of etherification and addition as $k_E/k_1 = 0.1$. In this paper, however, the rate of etherification in the TGDDM-bis(aminophenyl) sulfone (DDS) system was affected by vitrification of the system.

Due to the steric proximity of the epoxy groups of diglycidylamine it is probable that the reactivities of these epoxy groups will affect each other. In such a case the kinetic course of the reaction cannot be characterized merely by using the rate constants k_1 and k_2 (cf. eq 1 and 2), but a more complicated kinetic scheme involving several rate constants ought to be considered.[27]

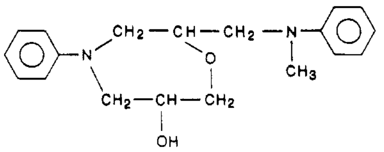
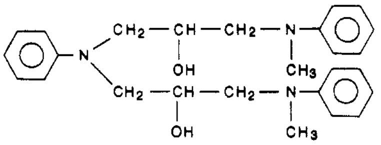
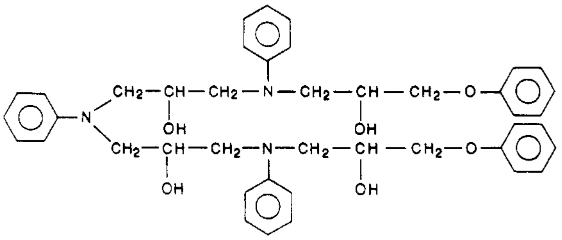
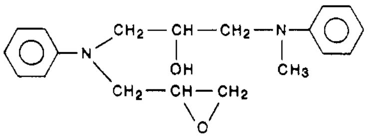
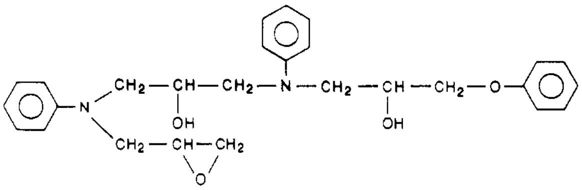
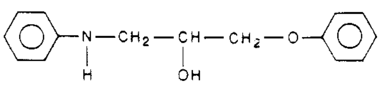
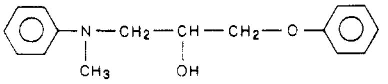
The proximity of both epoxy groups also has as a consequence a higher probability of cyclization.[14,27,33,35-41] The formation of a morpholine ring (I),[38] seven-membered ring (II),[39] and eight-membered ring (III)[39,41] (Scheme I) has been shown. Morgan[33] estimates that 75% of epoxide–OH reactions and epoxide–secondary amine reactions in the system TGDDM-DDS occur intramolecularly. Recently, a ring of the tetrahydroquinoline type (IV) was found to be formed by a reaction between the epoxy group and the hydrogen atom of the aromatic ring in the ortho position, taking place at $T > 150$ °C.[38,40]

Due to the presence of an asymmetrical carbon atom in the glycidyl group, epoxides are a mixture of stereoisomers, which usually cannot be distinguished. Stereoisomers of the products formed, however, can be discerned by means of liquid chromatography (HPLC) and NMR spectroscopy.[11,14,23,34,37,42]

Differential scanning calorimetry (DSC) is the analytical method most often used to follow curing of epoxides with amines.[43] Evaluation of data is based on the assumption that the heat released in an exothermic reaction is proportional to the overall conversion. However, the heats of individual partial reactions may differ and the overall thermal effect is not proportional to conversion but depends upon the extent of partial reactions. Spectral methods-NMR,[23,44] IR,[44] and to some extent UV[45]—give more experimental data and are more suitable for the study of the reaction mechanism, especially in the pregel stage. The interpretation of data, however, is a difficult problem. On the contrary, the interpretation of chromatographic analysis—HPLC and GPC—is more straightforward and unambiguous. These methods cannot be used beyond the gel point, but they are of great importance for a study of reactions of low molecular weight models. In this case they give direct information about all reaction species in the system.

This study is concerned with an investigation of the mechanism and kinetics of a reaction between epoxide based on diglycidylamine and aromatic amines by using model systems and the HPLC and GPC methods. Part 1 of the study deals with the reaction of DGA with monofunctional secondary amines, i.e., N-methylaniline (NMA) and 1-anilino-3-phenoxy-2-propanol (S). The advantage of this model system is that mainly low molecular weight compounds are formed which are well separable by HPLC. In part 2[46] the reaction between DGA and a primary amine—aniline—is reported. The study has had as its objective obtaining kinetic parameters, particularly the relative rates and the extent of the individual partial

Table I
Reaction Models Used and Products of the Reaction of DGA with Secondary Amines

	chemical formula	
C		cycle formed at the reaction DGA + NMA
D (D_I, D_{II})[a]		diadduct of the reaction DGA + NMA
D_s		diadduct of the reaction DGA + S
M (M_I, M_{II})[a]		monoadduct of the reaction DGA + NMA
M_s		monoadduct of the reaction DGA + S
S		model of a secondary amine
T		model of reaction products

[a] Stereoisomers (I = *dd,ll*; II = *d,l*; cf. ref 34).

reactions, i.e., addition, etherification, and cyclization, which characterize the reaction mechanism and determine the network structure in real systems. Although both etherification and cyclization already have been proved in the reaction of DGA derivatives, no quantitative experimental data exist. They are, however, necessary for a theoretical description of network formation.

Experimental Section

Diglycidylaniline (DGA) was prepared by reacting aniline with epichlorohydrin and by a subsequent dehydrochlorination with an aqueous NaOH solution. The synthesis, isolation, and purification procedures have been described in ref 34. According to HPLC, the purity of DGA is 99.9%. *N*-Methylaniline (NMA) (99%) was used as received (Fluka).

Secondary amine 1-anilino-3-phenoxy-2-propanol (S) (see Table I) was prepared by heating phenyl glycidyl ether (PGE) with aniline in excess (mole ratio 1:10) at 100 °C for 5 h. Aniline in excess was then removed by distillation at T = 75 °C and pressure 16 Torr. According to HPLC, the purity of the product S was 95%. The sample contains 5% of disubstituted aniline. Tertiary amine 1-(*N*-methylanilino)-3-phenoxy-2-propanol (T) (see Table I) was prepared by heating a stoichiometric reaction mixture of PGE and NMA at 110 °C for 7 h. The purity of T was 97.9% (HPLC).

In the investigation of kinetics the reactions were carried out in sealed ampules under nitrogen in bulk and in toluene or triethylene glycol dimethyl ether solutions at 100 °C. The reaction was stopped by cooling the sample to -40 °C. In each experiment a series of samples differing in the reaction time was prepared. The samples were analyzed by HPLC using a chemically bonded reverse phase.

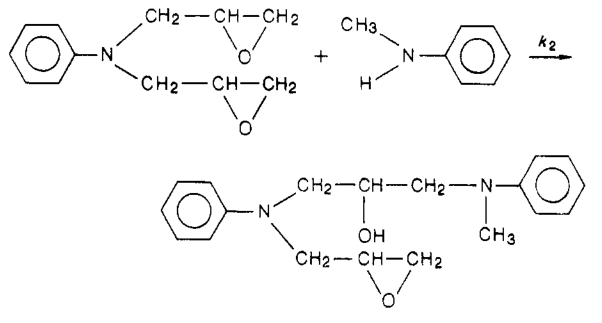
Some compounds were isolated from the products of the bulk reaction and identified by NMR and mass spectrometry. The seven-membered ring C (see Table I) was obtained from the reaction mixture DGA:NMA = 2:1 heated to 100 °C for 35 h by repeated separation by analytical HPLC. Stereoisomers of the mono- and diadduct of the reaction between DGA and NMA (M_I, M_{II} or D_I, D_{II}) (see Table I) and the mono- and diadduct of the reaction between DGA and S (M_s or D_s) (see Table I) were isolated by preparative chromatography. Monoadducts M_I, M_{II} were isolated from the reaction mixture DGA:NMA = 1.5:1 heated to 100 °C for 4 h; diadducts D_I, D_{II} were isolated from the mixture DGA:MMA = 1:3 heated to 75 °C for 24 h. Both isomers of the monoadduct M_s and diadduct D_s were obtained from the reaction mixture DGA:S = 2:1 heated to 100 °C for 15 h. The isolation using preparative chromatography has been described elsewhere.[34]

HPLC. The liquid chromatograph HP 1084 B (Hewlett-Packard) was provided with a glass column, 3 × 150 mm in size, packed with the reverse-phase Separon C18, particle size 7 μm (Laboratory Instruments, Czechoslovakia). A combination of isocratic and gradient elution in the methanol–water system was used. The injected amount was about 5 μL of the sample in the form of a *c* 0.2% solution in methanol. A built-in UV detector and the wavelength 254 nm were used for detection. For the quantitative calibration, the extinction coefficients at 254 nm of the starting components and some intermediates isolated from the reaction mixture were determined.

Mass spectra were recorded with an AEI MS 902 apparatus at direct inlet and at the source temperature 200 °C, ionization energy 60 eV, emission 100 mA, and acceleration voltage 6 kV.

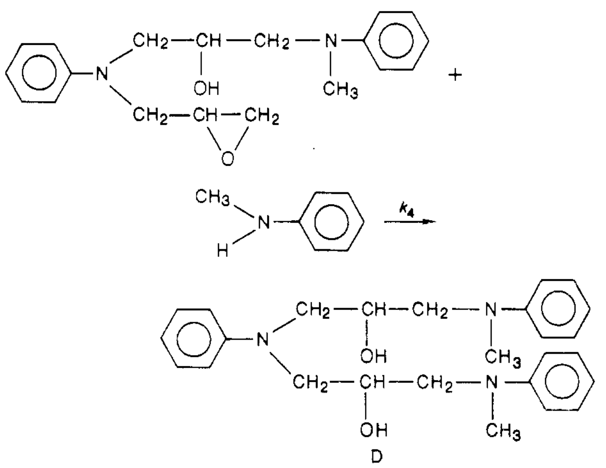
Results and Discussion

Addition. 1. Reaction of *N*,*N*-Diglycidylaniline with *N*-Methylaniline. The reaction of DGA with monofunctional amine NMA proceeds with formation of the monoadduct (M) and the diadduct (D).[34,37] The rate constants of the two partial reactions of secondary amine with diepoxide are denoted k_2, k_4.



(4)

M



(5)

D

Using HPLC, it is possible to observe the formation of stereoisomers of the monoadduct M_I, M_{II} and of the diadduct D_I, D_{II}. In Figure 1 they are characterized by chromatographic peaks 3, 4 and 5, 6, respectively. Isomers of both adducts were isolated by means of preparative HPLC and identified. NMR analysis was used to determine the configurational structure of the diadduct.[34] It was found that the isomer D_I has two configurations *RR* (*d,d*) and *SS* (*l,l*) which cannot be distinguished by NMR, while the isomer D_{II} has the *d,l* configuration. Similar configurations are assumed for stereoisomers M_I, M_{II} and must also exist in the starting DGA (E_I and E_{II}). The individual isomers differ in their reactivity.[34]

In the stoichiometric mixture of DGA and NMA and with amine in excess only the addition reaction takes place, because isomers M and D are the only reaction products (cf. Figure 2a).

From the dependence of the initial rate v_0 on the initial concentration (toluene solution) of one reaction component at constant concentration of the other component, partial reaction orders with respect to epoxide (ϵ) and amine (β) were determined for the initial stage: $\epsilon = 1.1 \pm 0.2$, $\beta = 2.2 \pm 0.2$. Consequently, for the initial stage the kinetic relation (cf. ref 1) $v_0 = k[E]_0[A]_0^2$ is valid, $[E]_0$ and $[A]_0$ being the initial concentrations of epoxide and amine, respectively, and k being the rate constant.

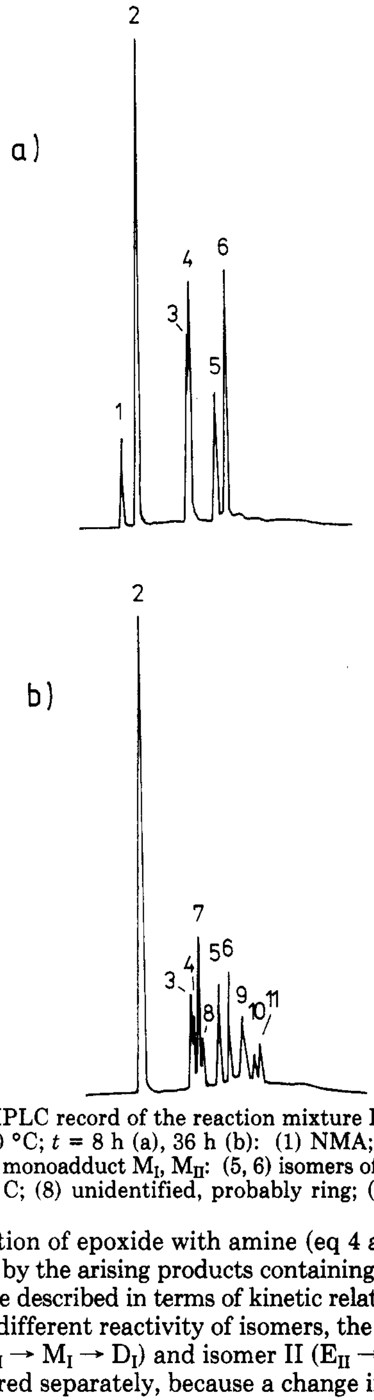


Figure 1. HPLC record of the reaction mixture DGA:NMA = 2:1. T = 100 °C; t = 8 h (a), 36 h (b): (1) NMA; (2) DGA; (3, 4) isomers of monoadduct M_I, M_{II}; (5, 6) isomers of diadduct D_I, D_{II}; (7) ring C; (8) unidentified, probably ring; (9–11) ethers.

The reaction of epoxide with amine (eq 4 and 5) is autocatalyzed by the arising products containing OH groups, and it can be described in terms of kinetic relations (6)–(8). Due to the different reactivity of isomers, the reactions of isomer I ($E_I \rightarrow M_I \rightarrow D_I$) and isomer II ($E_{II} \rightarrow M_{II} \rightarrow D_{II}$) are considered separately, because a change in configuration during the reaction is not possible. The experiments were carried out in toluene solutions.

$$-\mathrm{d}[E_i]/\mathrm{d}t = k'_{2i}[E_i][A]^2 + k_{2i}[E_i][A]([M] + 2[D]) \quad (6)$$

$$\mathrm{d}[M_i]/\mathrm{d}t = k'_{2i}[E_i][A]^2 + k_{2i}[E_i][A]([M] + 2[D]) - k'_{4i}[M_i][A]^2 - k_{4i}[M_i][A]([M] + 2[D]) \quad (7)$$

$$\mathrm{d}[D_i]/\mathrm{d}t = k'_{4i}[M_i][A]^2 + k_{4i}[M_i][A]([M] + 2[D]) \quad (8)$$

where [A], $[E_i]$, $[M_i]$, and $[D_i]$ are molar concentrations of NMA, isomers of DGA, monoadduct, and diadduct, respectively. The index i stands for the individual isomers I, II; k'_{2i}, k'_{4i}, k_{2i}, and k_{4i} are the rate constants of reactions 4 and 5 for the respective noncatalyzed and catalyzed reactions of the isomer i (I, II). The term ([M] + 2[D]) denotes the concentration of the catalyzing OH groups of the products. It should be born in mind, of course, that the catalytic activity of groups in stereoisomers need not be the same. In the term ([M] + 2[D]) the total concentrations of isomers are considered, which is a certain ap-

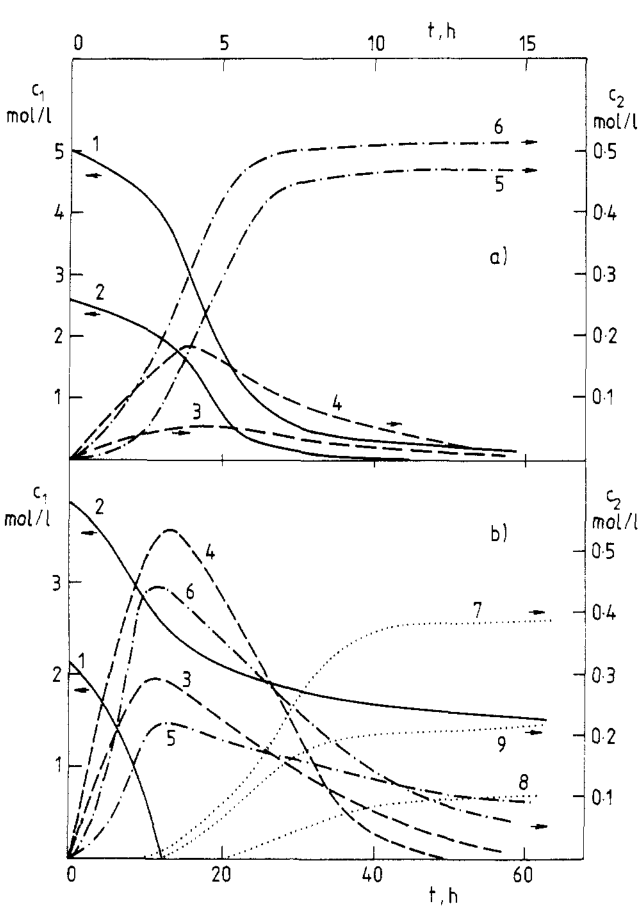


Figure 2. Time dependence of the concentration of the initial reaction components (c_1) and products (c_2) in the course of the reaction of DGA with NMA at 100 °C, (a) DGA:NMA = 1:2; (b) DGA:NMA = 1.7:1: (1) NMA; (2) DGA; (3) monoadduct M_I; (4) monoadduct M_{II}; (5) diadduct D_I; (6) diadduct D_{II}; (7) ring C; (8) ring; (9) ethers.

proximation. The isomers of DGA (E_I, E_{II}) cannot be distinguished by HPLC, and their content was therefore evaluated from the total DGA concentration (E), determined by HPLC, and from the material balance:

$$[E] = [E_I] + [E_{II}]$$

$$[E_I]_0 - [E_I] = [M_I] + [D_I], \qquad [E_{II}]_0 - [E_{II}] = [M_{II}] + [D_{II}]$$

$$[E_I]_0/[E_{II}]_0 = ([D_I]_\infty + [M_I]_\infty)/([D_{II}]_\infty + [M_{II}]_\infty)$$

where $[M_i]_\infty$ and $[D_i]_\infty$ are the concentrations of isomers of the mono and diadduct at the end of the reaction. The content of isomers M_i and D_i was determined directly by means of HPLC.

With respect to relation 6 the plot $(-d[E_i]/dt)/[E_i][A]^2$ versus $([M] + 2[D])/[A]$ should be linear. The intercept on the y-axis and the slope of the dependence give the rate constants of the noncatalyzed and catalyzed reaction, k'_{2i} and k_{2i} respectively, for isomer i (Figure 3a). Similarly, the rate constants k'_{4i} and k_{4i} can be determined from the relation for the formation of diadduct (8) as an intercept on the y-axis and the slope of the linear dependence $(d[D_i]/dt)/[M_i][A]^2$ versus $([M] + 2[D])/[A]$ (Figure 3b). The rate constants thus obtained are given in Table II.

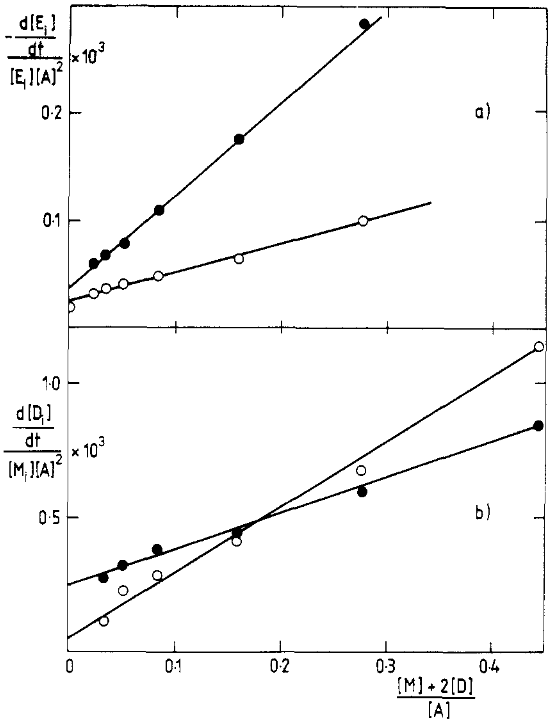


Figure 3. Kinetic dependence of the reaction of DGA with NMA at the molar ratio 1:2 at 100 °C. Plots on the basis of eq (a) 6 and (b) (8); (○) isomer I; (●) isomer II.

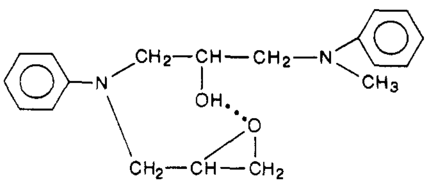
Table II
Rate Constants of the Reaction of DGA with Secondary Aromatic Amines at 100 °C in Bulk or in Toluene Solution[a]

rate const	amine NMA isomer I		amine NMA isomer II	amine S[b] isomer I		amine S[b] isomer II
Addition,[c] $k_i \times 10^3$ ($L^2\ mol^{-2}\ min^{-1}$)						
k'_2	0.03		0.04			
k_2	0.26		0.88		0.9[d]	
k'_4	0.05		0.25			
k_4	2.0		1.4		1.3[d]	
				0.73[e]	0.4[d,e]	0.22[e]
Etherification,[f] $k_i \times 10^3$ ($L^2\ mol^{-2}\ min^{-1}$)						
$k_{E1}{}^D$	0.02[g]	0.03[d]	0.04[g]			
$k_{E2}{}^D$	0.05[g]	0.10[d]	0.12[g]			
$k^*_{E1}{}^h$		0.014[d]				
Cyclization,[i] $k_i \times 10^3$ ($L\ mol^{-1}\ min^{-1}$)						
k_{c0}		0.15[d]				

[a] Rate constants are related to the molecule. [b] 1-Anilino-3-phenoxy-2-propanol (cf. Table I). [c] Cf. eq 4–8. [d] Total average value irrespective of isomers. [e] Reaction in triethylene glycol dimethyl ether. [f] See eq 13 and 14. [g] Rate constant obtained by computer simulation. [h] Rate constant is related to the OH group. [i] See eq 17.

In the reaction between diepoxide and secondary amine the ratio of the rate constants k_4/k_2 indicates the substitution effect of epoxy groups in diepoxide. The rate constants are related to the molecule and not to the functional group (cf. eq 4–8). Therefore, at the same reactivity of epoxy groups in the monoadduct and in DGA $\kappa = k_4/k_2 = 1/2$, because of two functional groups in DGA. This is indeed so with DGEBA, but it can be seen in Table II that in the case of DGA a positive substitution effect becomes operative. After one epoxy group has reacted the other becomes activated and reacts much more quickly. $\kappa = 1.5–8$, taking into consideration a catalyzed or a noncatalyzed reaction of isomer I or II. This effect can be explained by the steric proximity of the two epoxy groups and by the local catalysis of the reaction, i.e., by the activation of the epoxy group of the monoadduct by the adjacent hydroxyl group.

On the contrary, Grenier-Loustalot et al.[35] mention a lower reactivity of the second epoxy group in DGA after the first one has reacted, i.e., the negative substitution effect. This



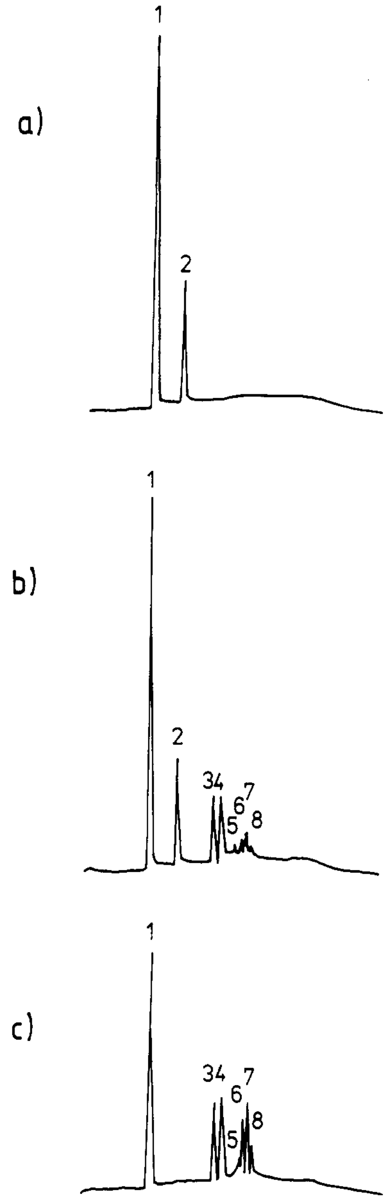


Figure 4. HPLC record of the reaction mixture DGA-1-anilino-3-phenoxy-2-propanol (S). $T = 100$ °C; $t = 0$ (a), 2 h (b), 16 h (c): (1) DGA; (2) S; (3, 4) isomers M_s; (5–8) isomers D_s. Experimental conditions: gradient elution, methanol–water starting with 55% and ending with 10% water.

conclusion was derived from the experimentally determined lower reactivity of the monoepoxide N-glycidyl-*N*-methylaniline (NNGMA) in comparison with DGA in the reaction with aniline. However, the model monoepoxide NNGMA does not contain the OH group, whose presence is the reason for the accelerating effect in the monoadduct.

Our results show that the reaction not catalyzed with OH groups is operative only in the initial stage, because the rate constants for the reaction catalyzed with OH groups are higher by an order of magnitude $k_j/k'_j = 5$–40). It can also be seen in Table II that isomer II is more reactive than isomer I, with the exception of the catalyzed formation of the diadduct (k_4).

2. Reaction between Diglycidylaniline and 1-Anilino-3-phenoxy-2-propanol. Steric conditions for the reaction between epoxide and the secondary amino group in NMA differ greatly from those of the reaction with the secondary amino group in forming intermediates during curing of real systems (cf. eq 2). Moreover, NMA contains no catalyzing OH group. For this reason, 1-anilino-3-phenoxy-2-propanol (S), a reaction product of aniline and phenyl glycidyl ether, is a more suitable model of a secondary amine. This model contains the OH group and steric conditions approach the real system.

In the reaction of the model S with DGA, products are formed which are characterized in HPLC by a doublet of synchronously arising bands 3 and 4 and by a symmetrical quadruplet 5–8 (cf. Figure 4). It has been shown by means of mass spectrometry that the doublet corresponds to isomers of the monoadduct M_s (see Table I). We assume that the quadruplet corresponds to four stereoisomers of the diadduct D_s (see Table I).

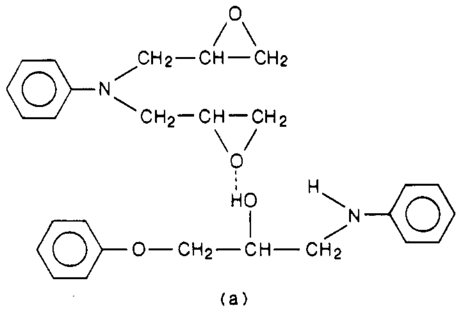
The presence of the hydroxyl in the amino alcohol S eliminates the autocatalytic course of the reaction, and the noncatalyzed term need not be considered. The reaction between S and DGA (E) can therefore be described in terms of

$$-(d[E]/dt) = k_2[E][S][H] \tag{9}$$

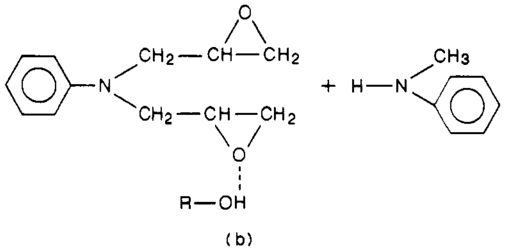
$$d[D_s]/dt = k_4[M_s][S][H] \tag{10}$$

where [E], [S], $[M_s]$, and $[D_s]$ respectively are the concentrations of DGA, amine S, monoadduct M_s, and diadduct D_s. [H] ($=2[S]_0 - [S]$) is the concentration of OH groups given by the initial content of amino alcohol $[S]_0$ and by the concentration of products arising by the reaction ($=[S]_0 - [S]$). With S present in high excess with respect to DGA, the term ([S][H]) is constant during the reaction, and on the basis of eq 9 the dependence $\ln([E]_0/[E])/([S][H])$ versus t is linear. $[E]_0$ is the initial concentration of DGA. The slope of the dependence gives the value of k_2. Also, the plot $(d[D_s]/dt)/([S][H])$ versus $[M_s]$ is linear according to relation 10; the slope gives the value of k_4 (cf. Table II). The reactions proceeded in bulk or in toluene solutions.

A comparison between both models of secondary amines, i.e., NMA and S in the reaction with DGA reveals the following: The HPLC records show that the reaction with S is much faster than that with NMA in the initial stage due to the catalytic effect of the OH group (see Table II, cf. k_2 for S and k'_2 for NMA). However, the values of k_2 and k_4 for the reaction with NMA and with S, respectively, do not differ too much (see Table II). It implies that the intramolecular catalysis (a) in the case of S is about of the same efficiency as the intermolecular catalysis (b) in the reaction of NMA catalyzed by the products. It seems that a steric effect becomes operative. The reaction rate of DGA with S is the same or even higher than with NMA (cf. k_2 in Table II). However, the reaction rate of substituted diepoxide, monoadduct, with S is slower than that with NMA (cf. k_4 in Table II), obviously as a result of steric



(a)



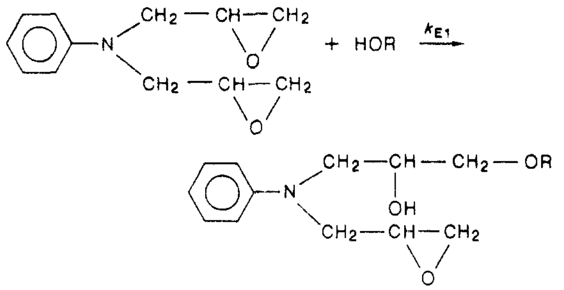
(b)

hindrance. Also, it should be born in mind that the interaction of the catalyzing hydroxyl in a product with the OH group of amino alcohol S competes with the activation of the epoxy group. Consequently, the epoxy groups of DGA show a smaller positive substitution effect, κ $(=k_4/k_2)$, in the reaction with S than with the simpler model NMA. For the average values of rate constants irrespective of isomers it holds that $\kappa_{\text{DGA-NMA}} \doteq 3$ and $\kappa_{\text{DGA-S}} \doteq 1.4$.

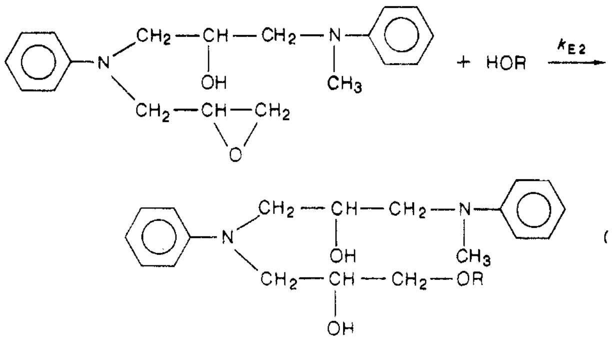
Also, the significance of the effect of a solvent on the reaction rate was studied. It was found that the reaction in an electron-donor solvent is considerably slower. The reaction of S with monoadduct M_S in triethylene glycol dimethyl ether was found to be about three times slower than in toluene. The rate constants k_{4I} and k_{4II} for both isomers M_{SI} and M_{SII} and the total average value k_4 irrespective of isomers are given in Table II.

Etherification. In the reaction between DGA and NMA and with epoxide in excess etherification takes place and the formation of both linear and cyclic products was observed (Figure 1b, chromatographic peaks 7–11). The reaction begins after almost the whole amount of amine has been consumed, as illustrated by Figure 2b.

Because of the dependence of the reactivities of epoxy groups in DGA, etherification in both unreacted DGA (rate constant k_{E1}) and diepoxide with one reacted functional group, e.g., the monoadduct (eq 12) or the ether (eq 12a) (rate constants k_{E2}, k'_{E2}), should be taken into account:

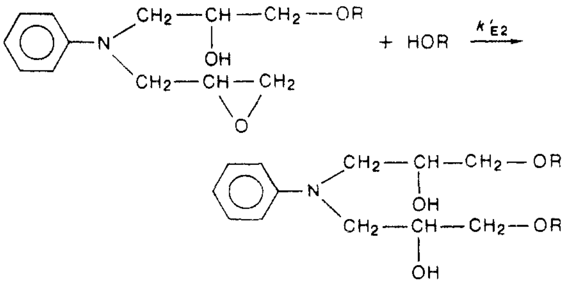


(11)



(12)

or



(12a)

where ROH is any reaction product containing an OH group, i.e., in the monoadduct or diadduct, or an ether. We assume the same values for the rate constants k_{E2} and k'_{E2}. The rate constants are related to the molecule. Consequently, taking into account the number of hydroxyls in the molecule and assuming the same reactivity of OH groups in the mono- and diadduct we have for the corresponding rate constants $k_{E1}{}^{M} = k_{E1}{}^{D}/2$ and $k_{E2}{}^{M} = k_{E2}{}^{D}/2$, where $k_{Ej}{}^{M}$ and $k_{Ej}{}^{D}$ are the rate constants for the etherification of an epoxy compound with M or D, respectively.

The course of the etherification has been investigated in the absence of solvent in a mixture of NMA and DGA in excess after all amine has reacted. The kinetics was evaluated by using eq 13 for the etherification of the diadduct by a reaction with epoxy groups in DGA (first term) and in the monoadduct (second term):

$$-\mathrm{d}[\mathrm{D}]/\mathrm{d}t = k_{E1}{}^{D}[\mathrm{D}][\mathrm{E}][\mathrm{N}] + k_{E2}{}^{D}[\mathrm{D}][\mathrm{M}][\mathrm{N}] \quad (13)$$

where [E], [M], [D] and [N] are the concentrations of DGA, monoadduct, diadduct, and the catalyzing tertiary amine, respectively. $[\mathrm{N}] = [\mathrm{E}]_0 + [\mathrm{A}]_0$; $[\mathrm{E}]_0$ and $[\mathrm{A}]_0$ are the initial concentrations of DGA and NMA, respectively.

The constants $k_{E1}{}^{D}$ and $k_{E2}{}^{D}$ (Table II) were obtained respectively as the intercept on the y-axis or as the slope of the linear dependence $(-\mathrm{d}[\mathrm{D}]/\mathrm{d}t)/[\mathrm{D}][\mathrm{E}][\mathrm{N}]$ versus $[\mathrm{M}]/[\mathrm{E}]$. Similarly to the addition of NMA, in the case of etherification the epoxy group was also found to be activated after the adjacent group in DGA had reacted; i.e., the reactivity of the epoxy group in the monoadduct was higher compared with that in DGA: γ $(=k_{E2}/k_{E1}) \doteq 3$. In the evaluation of the HPLC experimental data, we determined the average value of the rate constants irrespective of isomers (Table II). However, it is obvious in Figure 2b that isomer II is consumed by etherification more quickly than isomer I. Therefore, the values of the rate constants for different isomers k_{E1i} and k_{E2i} were determined by means of simulation on a computer. The decrease in the content of isomers M_I, M_{II}, D_I, and D_{II} by the etherification was calculated by using the values of rate constants k_{E1i} and k_{E2i} that provide the best fit of the experimental data (Table II). The rate constants of the reaction of isomer II were found to be two to three times higher than that of isomer I.

The relative rates of etherification and addition are characterized by the ratio of the corresponding rate constants for the reaction of the epoxy group in DGA: etherification (k_{E1}) and addition of NMA (k_2) $\mu^D = k_{E1}{}^{D}/k_2 = 0.06$, taking into account the total average values of the rate constants irrespective of isomers. Assuming the same reactivity of OH groups in M and D we have $\mu^M = k_{E1}{}^{M}/k_2 = 0.03$. Of course, the ratio of rates of the two reactions also depends on conversion and on the molar ratio of functional groups of the reaction components r $(=[\mathrm{A}]_0/2[\mathrm{E}]_0)$ (cf. ref 20). The addition reaction was described by eq 6, and for the rate of etherification of the diepoxide we obtain

$$-\mathrm{d}[\mathrm{E}]/\mathrm{d}t = k^*_{E1}[\mathrm{E}][\mathrm{H}][\mathrm{N}] \quad (14)$$

where [H] is the concentration of OH groups and k^*_{E1} is the rate constant related to the OH group. This rate constant was determined (a) in the reaction mixture of DGA with tertiary amine 1-(*N*-methylanilino)-3-phenoxy-2-propanol (T) (see Table I), which models products found in the addition reaction and initiates etherification, or (b) in a mixture of NMA and DGA in excess after all amine has reacted. In both cases the same values of the rate constant have been obtained (see Figure 5, Table II). Hence we can see that the effect of the possible difference in the basicity of tertiary amines, T, and mono- or the diadduct of the reaction between DGA and NMA on the rate of etherification is not pronounced. The ratio of the rates of consumption of diepoxide by etherification (v_E) and addition (v_A) obeys the relation

$$v_E/v_A = k^*_{E1}\alpha(1 + 2r\alpha)/\{2r(1 - \alpha)[k'_2(1 - \alpha) + k_2\alpha]\} \quad (15)$$

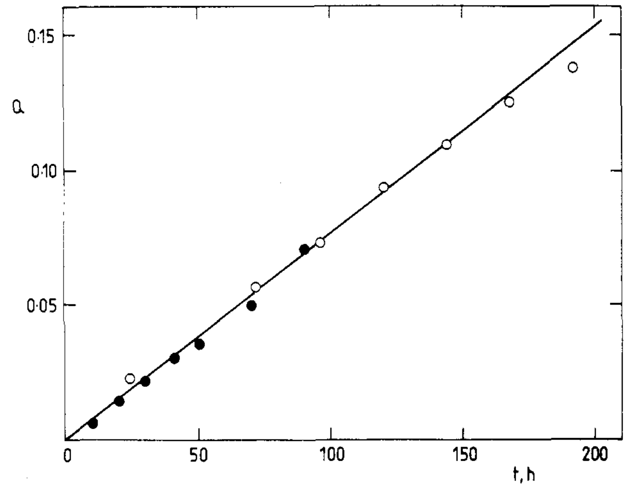


Figure 5. Kinetic dependence of etherification in the reaction between DGA (E) and NMA (A) after amine had reacted (○) or between DGA and 1-(*N*-methylanilino)-3-phenoxy-2-propanol (T) (●) at 100 °C: $Q = \ln([E]'_0/[E])/\{[A]_0([E]_0 + [A]_0)\}$ (○); $Q = \ln([E]_0/[E])/\{[T]_0([E]_0 + [T]_0)\}$ (●).

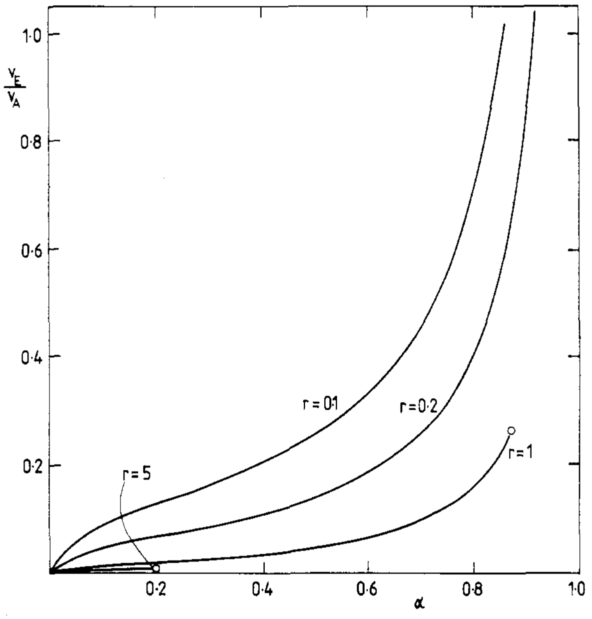


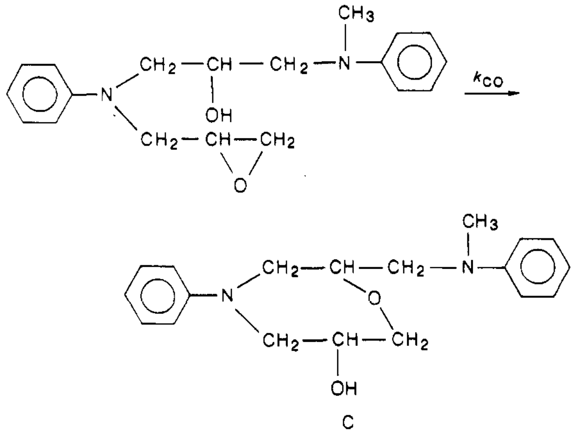
Figure 6. Theoretical dependence of the relative rate of decrease in DGA by etherification (v_E) and addition (v_A) in the reaction of DGA with NMA on the conversion of amine (α) and on the initial ratio of reaction components r (=[NMA]/2[DGA]); (○) end of the reaction due to the consumption of epoxide.

This expression was obtained from eq 14 ($v_E = -d[E]/dt$) and eq 6 ($v_A = -d([E_I] + [E_{II}])/dt$) by using the following substitution: $N = [E]_0 + \alpha[A]_0$; $[H] = [M] + 2[D] = \alpha[A]_0$; $[A] = (1 - \alpha)[A]_0$; $r = [A]_0/2[E]_0$; α is the conversion of the amine.

Etherification is initiated by addition, and therefore at the beginning of the reaction $v_E/v_A = 0$. With proceeding conversion the relative rate of etherification increases (cf. Figure 6), because the addition reaction component (amine with reactive hydrogen) is consumed while the amount of tertiary amine catalyzing the etherification increases. For instance, in a stoichiometric mixture ($r = 1$), etherification is slower than addition by a factor of 50 at the amine conversion $\alpha = 0.25$, while at the conversion 0.85 it is slower only by a factor of 4 or 5 ($v_E/v_A = 0.22$). Figure 6 shows that the extent of etherification increases with the excess of epoxide. In the stoichiometric mixture etherification can play a more pronounced role only at a very late stage of the reaction. With amine in excess it becomes completely negligible. However, if epoxide is present in excess the ratio of rates v_E/v_A for $r = 0.2$ or $r = 0.1$ is respectively 0.55 and 0.95 at the conversion $\alpha = 0.85$.

Because of etherification, unreacted amine remains in the stoichiometric reaction mixture (see Figure 6). Therefore, usually an excess of epoxide is used in the curing of polyfunctional systems to eliminate unreacted functionalities. The analysis shows that a 99% conversion of the amine would be accomplished only at a ~35% excess of epoxy groups.

Cyclization. Intramolecular etherification was shown to play an important part in the reaction beteen DGA and NMA. The main product of the reaction mixture with the epoxide in excess, corresponding to the chromatographic peak 7 in Figure 1b, was isolated by means of HPLC and identified by mass spectrometry.[39] It was found that this product is 4-phenyl-2-(*N*-methylanilinomethyl)-1-oxa-4-aza-6-cycloheptanol (C). On the basis of fragmentation of the mass spectrum, the structure of a six-membered morpholine ring (I) (see Scheme I) and the presence of a primary OH group were ruled out for this product. The seven-membered ring C arises by intramolecular etherification from the monoadduct. Attias et al.[38] have shown the presence of a product with the morpholine ring (I) in the reaction mixture of DGA and *N*-ethylaniline. It is possible that the unidentified peak 8 in Figure 1b corresponds to this cyclic product, R. We assume that intermolecular ethers having molar mass twice or several times as high as those cyclics are eluted at larger t_e in HPLC due to the reduced polarity (cf. Figure 1b, peaks 9–11). In the reaction in bulk the content of small rings is about 60–70% of all the ether products formed, in agreement with Morgan's estimate.[33] Our results reveal that the ring fraction increases with dilution of the initial reaction mixture. No loss of cyclic products due to the subsequent etherification of the OH group was observed in the reaction, as was the case with the mono- or diadduct. Etherification of these small rings either does not take place at all or is much slower than the corresponding reaction of the mono- and diadduct.



(16)

The apparent rate constant of formation of these cyclics containing ether oxygen in the ring, k_{c0} (cf. Table II), was determined according to the relation

$$d[C_0]/dt = k_{c0}[M][N] \qquad (17)$$

where $[C_0]$ is the concentration of the "ether" cyclics, including C and the product R corresponding to peak 8 in Figure 1b. It was found that the main ring C is formed from the isomer M_{II}. The slower decrease in M_I corresponds to the slower formation of R and one may assume that R arises from M_I.

The analysis reveals that the intramolecular etherification (cyclization) is faster than the intermolecular reaction, obviously due to the advantageous configuration of the monoadduct for the formation of a stable ring. This is in agreement with the experimental result. Figure 2b shows that both stereoisomers of the monoadduct are consumed by etherification more quickly than isomers of the diadduct. This is due to the fact that, while the diadduct may react only intermolecularly, in the case of the monoadduct a faster intramolecular etherification to form rings may also be considered.

Conclusion

The study of model systems reveals that the reactivity of epoxy groups in DGA is interdependent. A pronounced positive substitution effect has been observed in the reaction with NMA, κ $(=k_4/k_2) = 1.5$–8, as well as in the etherification, γ $(k_{E2}/k_{E1}) \doteq 3$. This means that after one epoxy group in DGA has reacted with an amine, the adjacent epoxy group is activated by the hydroxyl formed, so that its reactivity is higher. The relative rates of the individual reaction steps depend, however, on the structure of the amine. Activation of the epoxy group is diminished in the reaction with the secondary amine, 1-anilino-3-phenoxy-2-propanol (S), which is sterically more hindered and moreover contains an OH group, $\kappa_{\text{DGA-S}} = 1.4$.

The etherification is relatively slow with respect to the addition, μ $(=k_{E1}/k_2) = 0.03$–0.06, but its relative extent and rate increase with increasing conversion and with excess of the epoxide. Due to etherification, 35% excess of the epoxy groups is necessary to reach a 99% conversion of the amine.

With epoxide in excess, the main reaction product is a seven-membered ring C, which has been isolated from the reaction mixture and identified. This ring arises by intramolecular etherification, which is faster than the intermolecular one.

Formation of stereoisomeric products of different reactivity has been proved.

The results are discussed in greater detail in connection with the reaction of DGA with primary amines in part 2,[46] which also contains the overall discussion of the reaction mechanism of DGA with aromatic amines.

Acknowledgment. We thank Dr. S. Pokorný for the chromatographic analysis of the reaction mixture.

Registry No. DGA, 32144-31-3; C, 104209-28-1; D, 96558-62-2; D_5, 119620-39-2; M, 104222-29-9; M_5, 119620-40-5; S, 16112-55-3; $H_3CNHC_6H_5$, 100-61-8.

References and Notes

(1) Rozenberg, V. A. Epoxy Resins and Composites. *Adv. Polym. Sci.* **1986**, *75*, 113.
(2) Eastham, A. M.; Darwent, B. de: B.; Beaubien, P. E. *Can. J. Chem.* **1951**, *29*, 575.
(3) Berger, J.; Lohse, F. *Eur. Polym. J.* **1985**, *21*, 435.
(4) Fedtke, M. *Makromol. Chem., Macromol. Symp.* **1987**, *7*, 153.
(5) Shechter, L.; Wynstra, J.; Kurkjy, R. P. *Ind. Eng. Chem.* **1956**, *48*, 94.
(6) Horie, K.; Hiura, H.; Sawada, M.; Mita, I.; Kambe, H. *J. Polym. Sci., Polym. Chem. Ed.* **1970**, *8*, 1357.
(7) Arutyunyan, Kh. A.; Tonoyan, A. O.; Davtyan, S. V.; Rozenberg, V. A. *Enikolopyan N.S. Dokl. AN SSSR* **1973**, *212*, 1128.
(8) Dobáš, .; Eichler, J. *Collect. Czech. Chem. Commun.* **1973**, *38*, 3279.
(9) Dušek, K. Epoxy Resins and Composites. *Adv. Polym. Sci.* **1986**, *1*, 78.
(10) Buckley, L.; Roylance, D. *Polym. Eng. Sci.* **1982**, *22*, 166.
(11) Johncock, P.; Porecha, L.; Tudgey, G. F. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 291.
(12) Duffy, J. V.; Hui, E.; Hartmann, B. *J. Appl. Polym. Sci.* **1987**, *33*, 2959.
(13) Buist, G. J.; Hagger, A. J.; Jones, J. R.; Barton, J. M.; Wright, W. *Polym. Commun.* **1988**, *29*, 5.
(14) Byrne, C.; Hagnauer, G. L.; Schneider, N. S.; Lenz, R. W. *Polym. Compos.* **1980**, *1*, 71.
(15) Morgan, R. J.; Walkup, C. M.; Hoheisl, T. H. *J. Appl. Polym. Sci.* **1985**, *30*, 289.
(16) Grenier-Loustalot, M. F.; Cazaux, F.; Grenier, P. *Makromol. Chem.* **1986**, *187*, 1855.
(17) Sabra, A.; Lam, T. M.; Pascault, J. P.; Grenier-Loustalot, M. F.; Grenier, P. *Polymer* **1987**, *28*, 1030.
(18) Barton, J. M. *Br. Polym. J.* **1986**, *18*, 44.
(19) Zukas, W. X.; Schneider, N. S.; MacKnight, W. J. *Polym. Mater. Sci. Eng.* **1983**, *49*, 588.
(20) Riccardi, C. C.; Williams, R. J. J. *J. Appl. Polym. Sci.* **1986**, *32*, 3445.
(21) Dušek, K.; Bleha, M.; Luňák, S. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2393.
(22) Morgan, R. J.; Kong, F. M.; Walkup, C. M. *Polymer* **1984**, *24*, 375.
(23) Grenier-Loustalot, M. F.; Grenier, P. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 4011.
(24) Bell, J. *J. Polym. Sci. Polym. Phys. Ed.* **1970**, 417.
(25) Ore, S.; Tjugum, O. G. *Acta Chem. Scand.* **1970**, *24*, 2397.
(26) Luňák, S.; Dušek, K. *J. Polym. Sci., Polym. Symp.* **1975**, *45*, 53.
(27) Matějka, L.; Dušek, K.; Dobáš, I. *Polym. Bull.* **1985**, *14*, 309.
(28) Dušek, K.; Ilavský, M.; Štokrová, Š.; Matějka, L.; Luňák, S. In *Crosslinked Epoxies*; Sedláček, B., Kahovec, J. Eds.; Walter de Gruyter Publ.: West Berlin, 1987; p 279.
(29) Hata, N.; Kumanotani, J. *J. Appl. Polym. Sci.* **1971**, *15*, 2371.
(30) Topolkaraev, V. A.; Oshmyan, V. G.; Nisichenko, V. P.; Zelenetskii, A. N.; Prut, E. V.; Berlin, A. A.; Enikolopyan, N. S. *Vysokomol. Soed.* **1979**, *A-21*, 1515.
(31) Dušek, K.; Matějka, L. *Polym. Mater. Sci. Eng.* **1987**, *56*, 356.
(32) Gupta, A.; Cizmecioglu, M.; Coulter, D.; Liang, R. H.; Yavrouian, A.; Tsay, F. D.; Moacanin, J. *J. Appl. Polym. Sci.* **1983**, *28*, 1011.
(33) Morgan, R. J. Epoxy Resins and Composites. *Adv. Polym. Sci.* **1985**, *1*, 72.
(34) Doskočilová, D.; Matějka, L.; Pokorný, S.; Březina, M.; Štokr, J.; Dobáš, I.; Dušek, K. *Polym. Bull.* **1985**, *14*, 123.
(35) Grenier-Loustalot, M. F.; Orozco, L.; Grenier, P. *Eur. Polym. J.* **1987**, *23*, 757.
(36) Bauer, R. S. *J. Polym. Sci.* **1967**, *A5*, 2192.
(37) Grenier-Loustalot, M. F.; Cazaux, F.; Berecoechea, J.; Grenier, P. *Eur. Polym. J.* **1984**, *20*, 1137.
(38) Attias, A. J.; Ancelle, J.; Bloch, B.; Laupretre, F. *Polym. Bull.* **1987**, *18*, 217.
(39) Matějka, L.; Tkaczyk, M.; Pokorný, S.; Dušek, K. *Polym. Bull.* **1986**, *15*, 389.
(40) Costes, B.; Reyx, D.; Platzer, N. *Makromol. Chem.* **1989**, *190*, 349.
(41) Reyx, D.; Costes, B.; Matějka, L.; Dušek, K. *Polym. Bull.* **1988**, *19*, 269.
(42) Hörhold, H. H.; Klee, N.; Flammersheim, H. J. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 113.
(43) Barton, J. M. Epoxy Resins and Composites. *Adv. Polym. Sci.* **1985**, *72*, 112.
(44) Mertzel, E.; Koenig, J. L. Epoxy Resins and Composites. *Adv. Polym. Sci.* **1985**, *72*, 75.
(45) Chin, I.-J.; Sung, Ch. S. P. *Macromolecules* **1984**, *17*, 2603.
(46) Matějka, L.; Dušek, K. *Macromolecules*, following paper in this issue.