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Mechanism and Kinetics of Curing of Epoxides Based on Diglycidylamine with Aromatic Amines. 2. The Reaction between Diglycidylaniline and Aniline[†]

Libor Matějka* and Karen Dušek

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences,
162 06 Prague 6, Czechoslovakia.
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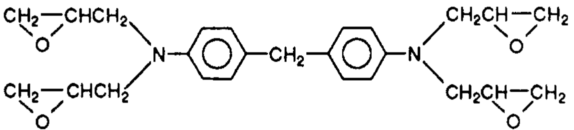
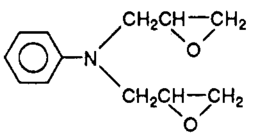
ABSTRACT: The mechanism of curing of epoxide resins based on diglycidylamine with polyfunctional aromatic amines was studied by using the model system diglycidylaniline–aniline. The rate constants of the particular partial reactions were determined by means of HPLC and GPC. Specific features of the mechanism of reaction of diglycidylamine epoxides with amines, i.e., the mutual dependence of reactivities of functional groups, the positive substitution effect of epoxy groups in diepoxide, and a considerable tendency to cyclization, are discussed using results of the first[1] and second (this) part of the study. The kinetic description of the addition reaction was carried out by means of a scheme with four kinetic equations, taking into consideration the dependence of reactivities of epoxy groups in diglycidylaniline and hydrogen atoms in the primary or secondary amino groups. Along with the intermolecular addition also the intramolecular one takes place. Formation of eight-membered "nitrogen" rings at the beginning of the reaction was proven.

Introduction

Curing of epoxides with amines with participation of polyfunctional components leads to the formation of cross-linked products, the structures of which greatly depend on the mechanism and kinetics of the reaction. A theoretical description of network formation and development of network structure during curing is possible by means of the theory of branching processes. So far, cross-linking of the diglycidyl ether of bisphenol A (DGEBA) has been theoretically worked out. The system was characterized by a very simple reaction mechanism and a good agreement with experimental values of the structural parameters, critical conversion, and gel fraction was obtained.[2] However, substantial deviations of the experimental results from the theory were found by applying the same simple kinetic scheme for curing of epoxy resins bis[(diglycidylamino)phenyl]methane (tetraglycidyldiaminodiphenylmethane, (TGDDM) or diglycidylaniline (DGA) with amines.[3] Consequently, a determination of the reaction mechanism of this system is necessary.

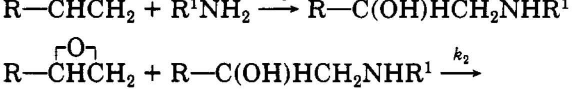


TGDDM

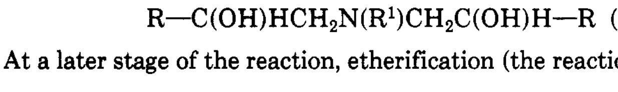


DGA

In the absence of catalyst the basic reaction of the system is the addition of the primary and secondary amino groups of the polyamine to the epoxy group:



$$\mathrm{R{-}\overset{\ulcorner O \urcorner}{CHCH_2} + R^1NH_2 \xrightarrow{k_1} R{-}C(OH)HCH_2NHR^1} \qquad (1)$$

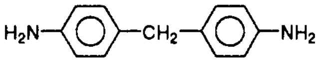


$$\mathrm{R{-}\overset{\ulcorner O \urcorner}{CHCH_2} + R{-}C(OH)HCH_2NHR^1 \xrightarrow{k_2} R{-}C(OH)HCH_2N(R^1)CH_2C(OH)H{-}R} \qquad (2)$$

At a later stage of the reaction, etherification (the reaction between epoxide and the OH group of the forming products) becomes operative.

In part 1[1] we discussed the mechanism of the model reaction of DGA (E) with secondary amines, i.e., *N*-methylaniline (NMA) and 1-anilino-3-phenoxy-2-propanol (S). Low molecular weight products are formed during this reaction; higher molecular weight components arise only by etherification, which makes possible a relatively simple analysis of the system. On the other hand, secondary amine is too simplified a model for curing epoxide resins with polyfunctional amines.

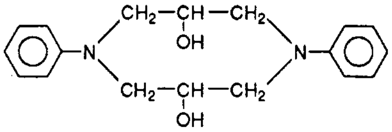
In this part of the study we report results of the investigation of a more complicated difunctional system, DGA with a primary amine—aniline. In such a case a linear polymer is formed, and etherification brings about cross-linking of the system. From the kinetic viewpoint, the bifunctional system DGA–aniline is a suitable model of polyfunctional systems, such as TGDDM and diaminodiphenylmethane (DDM).



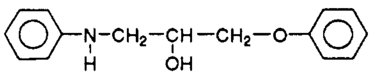
DDM

Experimental Section

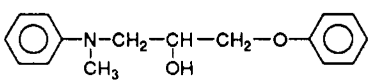
DGA was prepared by a reaction of aniline with epichlorohydrin.[4] Aniline was redistilled at reduced pressure; its purity was 99.9%. Cyclic product I was isolated in the crystalline form from a 20% solution of an equimolar reaction mixture DGA–aniline in toluene, heated to 135 °C for 9 days.[5] Tertiary amine, 1-(*N*-methylaniline)-3-phenoxy-2-propanol (T), was prepared by a reaction between phenylglycidyl ether and *N*-methylaniline.[1] Secondary amine, 1-anilino-3-phenoxy-2-propanol (S), was prepared by a reaction of phenyl glycidyl ether with aniline in excess.[1]



I



S



T

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

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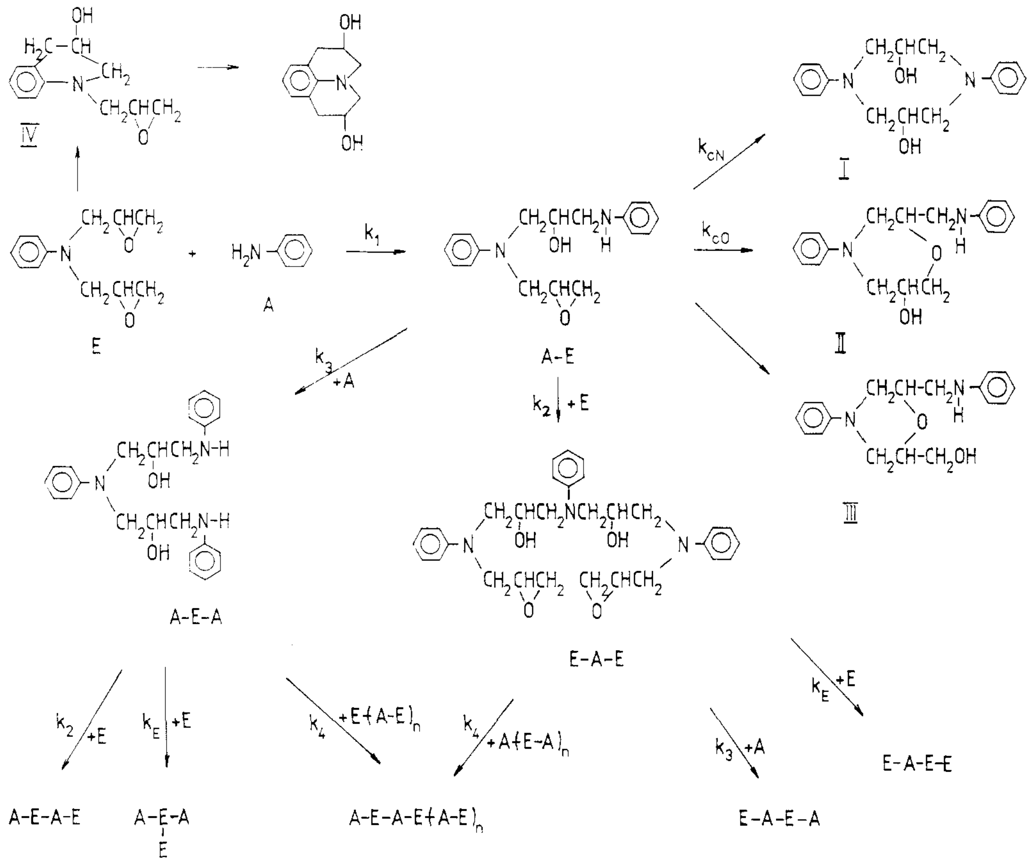
Scheme I



For the investigation of the mechanism and kinetic course, the reactions were carried out in sealed ampules under nitrogen in bulk at 100 °C. Cyclization reaction was studied also in toluene solution at 140 °C. The reaction was stopped by cooling the sample. In each experiment a series of samples was prepared which differed in the reaction time. The samples were analyzed by GPC and HPLC.

GPC. A chromatograph built in IMC CSAS was provided with four stainless steel columns connected in series, 8 × 1200 mm in size, packed with the styrene–divinylbenzene copolymer S-Gel 832, particle size 32–40 μm (IMC CSAS). This packing possesses a high selectivity in the oligomeric range and has the exclusion limit of *c* 1200 molecular weight units. THF was the eluent; the flow rate was 0.4 mL/min. Detection was made by means of a differential refractometer Waters R-403 (Waters). The samples were injected into the separation system in the form of a *c* 2% solution in THF in an amount of 0.35 mL.

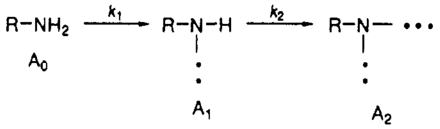
HPLC (cf. ref 1). A liquid chromatograph HP 1084B (Hewlett-Packard) with a column packed with the reverse-phase Separon C18 was used. The samples were injected in the form of a solution in methanol and analyzed by gradient elution in the methanol–water system. A UV detector at a wavelength of 254 nm was used for detection. Mass spectra were recorded with an AEI MS 902 apparatus.

Results and Discussion

In the reaction of DGA (E) with difunctional aniline (A) a linear polymer and cyclic products are formed. By a gradual alternating polyaddition, adducts A–E, A–E–A, E–A–E, etc. arise, cf. Scheme I. Cyclic products formed from adducts larger than A–E are not given in the scheme.

The reaction of the amino group can be characterized by Scheme II. The relative reactivity of hydrogen atoms in the primary and the secondary amino group is given by the ratio of rate constants for the reaction of corresponding amino groups with an epoxy group, a so-called substitution effect ρ ($=k_2/k_1$) (cf. eq 1 and 2). The rate constants are related to the concentration of the primary or secondary amine and diepoxide, respectively. In an ideal case of the same reactivity of hydrogens in both amino groups, $\rho = {}^1/_2$, because the primary amino group contains two hydrogen atoms in contrast to the secondary group and $k_1 = 2k_2$.

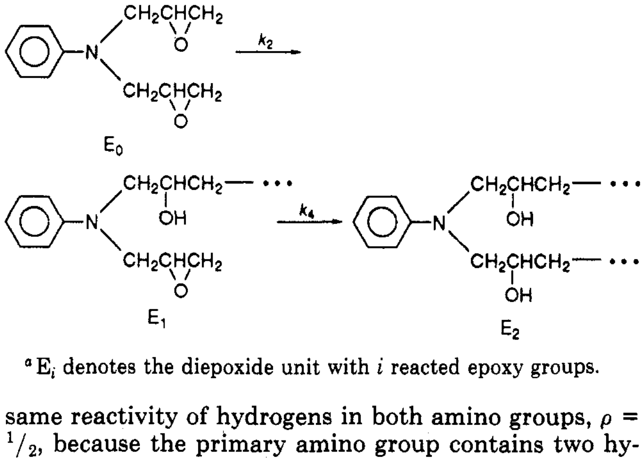
Scheme II[a]



$$\mathrm{R{-}NH_2} \xrightarrow{k_1} \mathrm{R{-}\underset{\vdots}{\underset{|}{N}}{-}H} \xrightarrow{k_2} \mathrm{R{-}\underset{\vdots}{\underset{|}{N}}{-}\cdots}$$

[a] A_i denotes the amino group with i reacted hydrogen atoms.

Scheme III[a]



[a] E_i denotes the diepoxide unit with i reacted epoxy groups.

The reactivity of epoxy groups in diepoxide is mutually independent in the case of DGEBA. Therefore, ρ fully characterizes the kinetics of the system in the reaction between DGEBA and amine. For DGA or TGDDM it was found, however, that this ratio of rate constants (k_2/k_1) is not a constant for the given amine but that it may depend on the epoxide used.[6]

Unlike DGEBA, in the reaction of DGA with secondary amine, NMA, epoxy groups are not independent, and one

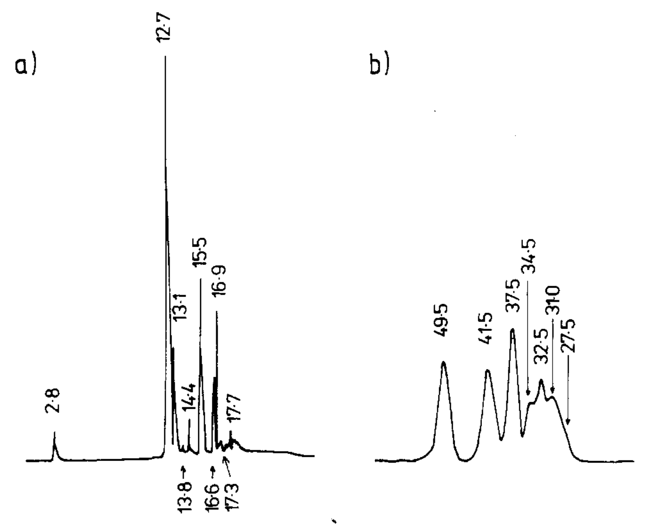


Figure 1. Chromatographic record of the equimolar mixture of DGA with aniline: T = 100 °C: (a) HPLC, t = 2 h; (b) GPC, t = 3 h. For identification of peaks see Table I.

has to consider whether the unit E_0 or E_1 is the reaction partner of the amine (cf. Scheme III). In an ideal case of the same reactivity of epoxy groups in DGA (E_0) and in the unit E_1, $k_4/k_2 = {}^1/_2$. In the reaction with NMA, DGA has a positive substitution effect:[1] $\kappa = k_4/k_2 = 1.5\text{–}8$.

Both substitution effects, ρ and κ, are mutually dependent, as can be seen from the results of gelation experiments.[6] Therefore, the system DGA–aniline cannot be adequately described by using only these two ratios of rate constants. It is obvious that four kinetic equations or three ratios of rate constants, $\rho = k_2/k_1$, $\kappa = k_4/k_2$, and $\sigma = k_3/k_1$, are needed for this purpose (cf. Scheme IV; the rate constants are related to A_i or E_i units). We assume

Scheme IV

$$A_0 + E_0 \xrightarrow{k_1} A_1 + E_1$$

$$A_1 + E_0 \xrightarrow{k_2} A_2 + E_1$$

$$A_0 + E_1 \xrightarrow{k_3} A_1 + E_2$$

$$A_1 + E_1 \xrightarrow{k_4} A_2 + E_2$$

the reactivity of functional groups to be independent of the molecular weight of the respective species. In the kinetic scheme we have neglected the different reactivity of isomers.

The reaction mixture DGA–aniline was analyzed by using HPLC combined with GPC (Figure 1). While HPLC made possible good separation in the region of the first several homologues of the forming series of oligomers, GPC provided valuable information about the presence of higher oligomers and polymers.

The individual stereoisomers of the low molecular weight reaction products can be distinguished by means of HPLC.[1]

In the GPC record we can distinguish the individual oligomeric reaction products up to $M \sim 1200$, which is the exclusion limit of the column system used. On the basis of calibration of the separation system by means of polystyrene fractions and bearing in mind the solvation of the amino group by the mobile phase (THF), oligomers with increasing molecular weight were assigned to chromatographic peaks, as shown in Table I.

In the initial stage of the reaction the main product is the adduct A–E (cf. Scheme I), which under the given separation conditions is reflected in chromatographic peaks having t_e = 15.5 min (HPLC) and 41.5 counts (GPC) (see Figure 1). In the reaction with aniline in excess peaks with t_e = 16.6 and 16.9 min are those most represented in HPLC. They increase and then decrease synchronously and most probably correspond to stereoisomers A–E–A. On the contrary, with epoxide in excess the pair of peaks with t_e = 17.3 and 17.7 min becomes accentuated, obviously corresponding to isomers E–A–E.

Table I
Assignment of Chromatographic Bands to Components of the Reaction Mixture of DGA with Aniline

HPLC[a]		GPC	
band, min	species	band, count	species
2.8	aniline	49.5	DGA, aniline
12.7	DGA	41.5	A–E, cycle I
13.1, 14.4	cycle I isomers	37.5	A–E–A, E–A–E
13.8	cycle ?	34.5	A–E–A–E
15.5	A–E	32.5	$(A\text{–}E)_2\text{–}A$, $(E\text{–}A)_2\text{–}E$
16.6, 16.9	A–E–A isomers	31.0	$(A\text{–}E)_3$
17.3, 17.7	E–A–E isomers	27.5	polymer (M > 1200)

[a] Experimental conditions for HPLC: gradient elution was used in the methanol–water system, starting with 70% and ending with 10% water.

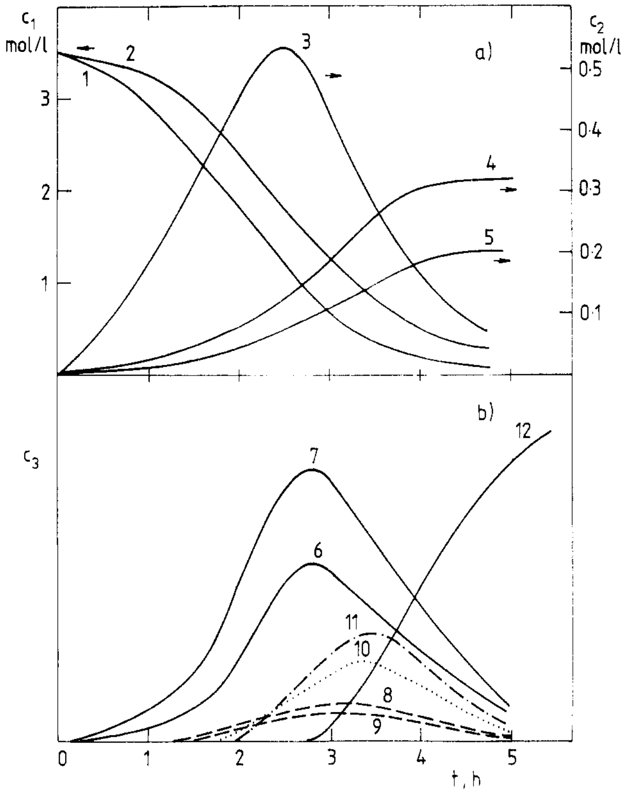


Figure 2. Kinetic course of the reaction of DGA with aniline at molar ratio 1:1; T = 100 °C: (a) concentrations of DGA, aniline (C_1), adduct A–E, and cycles (C_2); (b) relative concentrations of higher oligomers (C_3) (1) aniline, (2) DGA, (3) A–E, (4 and 5) isomers of cycle I (peaks at 13.1 and 14.4 min in HPLC), (6 and 7) isomers of A–E–A, (8 and 9) isomers of E–A–E, (10) $(A\text{–}E)_2$, (11) $(A\text{–}E)_2\text{–}A$, (12) polymer (M > 1200).

The kinetic course of the reaction between DGA and aniline at various stoichiometric ratios is shown in Figures 2–4. The individual figures are divided into two parts, (a) and (b), to obtain a better-arranged picture, with the initial compounds and the first products shown in (a) and other oligomers in (b). One can see the gradual formation of higher oligomers typical of a stepwise addition reaction. A striking feature is a considerably higher content of the product A–E–A (curves 6 and 7) compared with E–A–E (curves 8 and 9), which is formed to a larger extent only

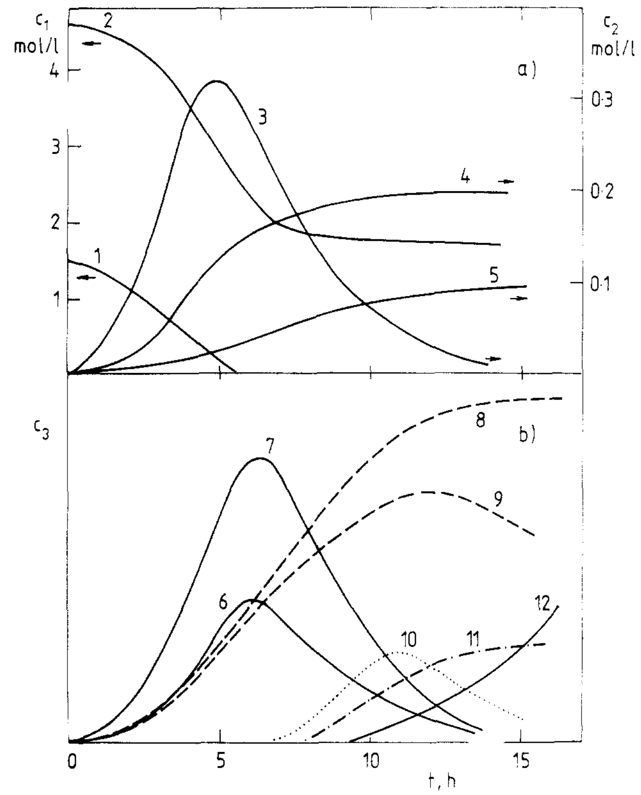


Figure 3. Kinetic course of the reaction of DGA with aniline at molar ratio 3:1, $T = 100$ °C. See Figure 2.

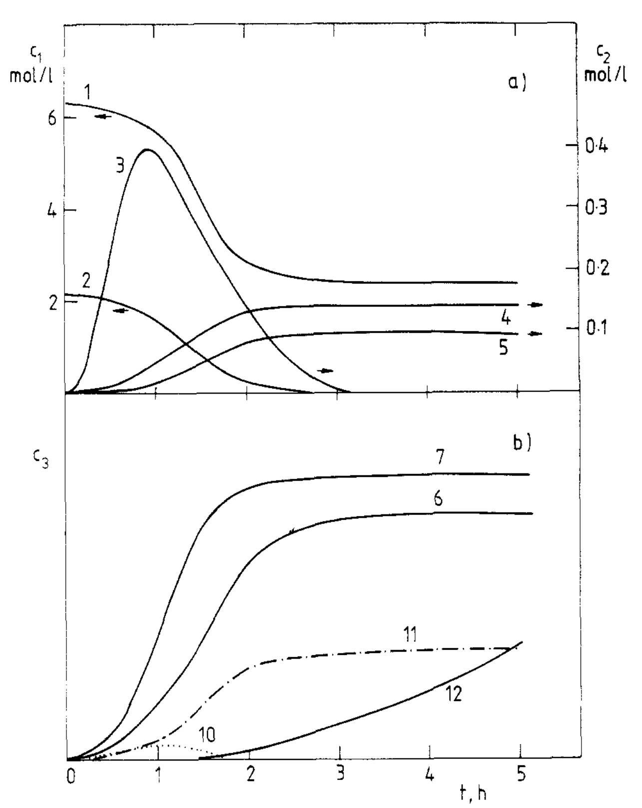


Figure 4. Kinetic course of the reaction of DGA with aniline at molar ratio 1:3, $T = 100$ °C. See Figure 2.

with epoxide in excess (Figure 3).

A different kinetic course can be observed in the case of products characterized by HPLC peaks with $t_e = 13.1$, 14.4 (curves 4 and 5), and 13.8 min. They attain the highest concentration, but unlike the oligomers they are not consumed, or are consumed very slowly. These products were isolated and identified by mass spectrometry. It was proved that the peak with $t_e = 13.1$ min corresponded to the cyclic product I (1,5-diphenyl-3,7-dihydroxy-1,5-diazacyclooctane)[5,7] and the product eluting at $t_e = 14.4$ min belonged to its isomer. Attias et al.[8] also have shown by NMR analysis the existence of two stereoisomers of this cyclic compound. The product corresponding to the peak with $t_e = 13.8$ min was not isolated in the pure form. However, from the mass spectrum analysis, a structure of a seven-membered ring containing the primary OH group is likely. Both hydrogen atoms of the amino group are reacted in these cyclics and therefore they cannot be consumed by the addition reaction like linear oligomers. Their concentration increases during the reaction to a maximum, and the loss—if any—due to the etherification of the OH group is much slower.

Addition

The addition reaction is autocatalyzed with hydroxylic groups of the arising products, as documented by the shape of kinetic curves of DGA and aniline in Figures 2–4. The reaction can be expressed by two terms for the noncatalyzed and catalyzed reaction, respectively.[1] The rate constant of the noncatalyzed reaction k_1 (cf. Schemes I and IV) was determined from the rate of consumption of aniline (A) at the beginning of the reaction using the kinetic equation

$$-(\mathrm{d}[\mathrm{A}]_0/\mathrm{d}t)_{t\to 0} = k_1'[\mathrm{A}]_0^2[\mathrm{E}]_0 \qquad (3)$$

in which $[\mathrm{A}]_0$ and $[\mathrm{E}]_0$ are the initial concentrations of aniline and DGA, respectively.

To rule out complications connected with autocatalysis in further kinetic studies, we investigated the reaction of DGA with aniline in the presence of alcohol. In this case the noncatalyzed reaction can be neglected. The kinetic results can, however, be affected by the alcohol used, because the catalytic activity depends on its acidity.[9] For this reason, we used amino alcohol 1-(*N*-methylanilino)-3-phenoxy-2-propanol (T), which models products arising during the reaction. When evaluating the kinetics, the effect of the different reactivity of isomers was neglected,[1] because in most cases the chromatographic record does not make possible a quantitative determination of the individual isomers in a complicated mixture of oligomers.

In the initial stage of the reaction, when esterification is negligible and only the lowest oligomers A–E and A–E–A are present, the following relations are approximately valid for units with a secondary amino group (A_1) or for a diepoxide unit with one reacted functional group (E_1) (cf. Schemes I–III):

$$[\mathrm{A}_1] = [\mathrm{A{-}E}] + 2[\mathrm{A{-}E{-}A}], \quad [\mathrm{E}_1] = [\mathrm{A{-}E}]$$

where $[\mathrm{A}_1]$ and $[\mathrm{E}_1]$ are the concentrations of units A_1 and E_1, respectively, and [A–E] and [A–E–A] denote the concentrations of products A–E and A–E–A.

The kinetic course in this stage of the reaction can be described by (cf. Scheme IV)

$$-(\mathrm{d}[\mathrm{E}_0]/\mathrm{d}t) = k_1[\mathrm{A}_0][\mathrm{E}_0][\mathrm{H}] + k_2[\mathrm{A}_1][\mathrm{E}_0][\mathrm{H}] \qquad (4)$$

$$-(\mathrm{d}[\mathrm{A}_0]/\mathrm{d}t) = k_1[\mathrm{A}_0][\mathrm{E}_0][\mathrm{H}] + k_3[\mathrm{E}_1][\mathrm{A}_0][\mathrm{H}] \qquad (5)$$

where $[\mathrm{E}_0]$ and $[\mathrm{A}_0]$ are the concentrations of units E_0 and A_0, respectively, [H] ($=[\mathrm{T}]_0 + [\mathrm{A}_1] + 2[\mathrm{C_N}]$) is the concentration of OH groups, $[\mathrm{C_N}]$ is the concentration of the eight-membered "nitrogen" ring I containing two OH groups, and $[\mathrm{T}]_0$ is the initial concentration of amino alcohol T.

By means of relations 4 and 5, we determined the rate constants k_1, k_2, and k_3 from Scheme IV using linear plots $-(\mathrm{d}[\mathrm{E}_0]/\mathrm{d}t)/[\mathrm{A}_0][\mathrm{E}_0][\mathrm{H}]$ versus $[\mathrm{A}_1]/[\mathrm{A}_0]$ and $-(\mathrm{d}[\mathrm{A}_0]/\mathrm{d}t)/[\mathrm{A}_0][\mathrm{E}_0][\mathrm{H}]$ versus $[\mathrm{E}_1]/[\mathrm{E}_0]$. The constant k_1 was

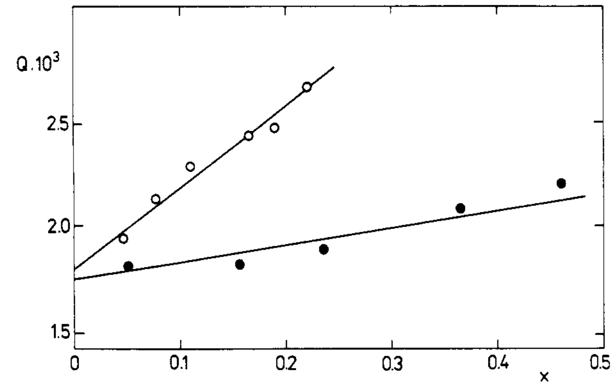


Figure 5. Kinetic course of the reaction between DGA and aniline in the presence of the amino alcohol 1-(*N*-methylanilino)-3-phenoxy-2-propanol at 100 °C: (○) $Q = -(d[A_0]/dt)/[A_0][E_0][H]$, $x = [E_1]/[E_0]$; (●) $Q = -(d[E_0]/dt)/[A_0][E_0][H]$, $x = [A_1]/[A_0]$.

Table II
Rate Constants $k_i \times 10^3$ of the Reaction between Diglycidylaniline and Aniline at T = 100 °C

addition,[a] $L^2/mol^{-2}/min^{-1}$					cyclization,[b] $L/mol^{-1}/min^{-1}$,
k'_1	k_1	k_2	k_3	k_4[c]	k_{cN}
0.08	1.8	0.8	4.0	1.0	2.5

[a] See Scheme IV. [b] See eq 7; formation of ring I. [c] Determined by means of computer simulation.

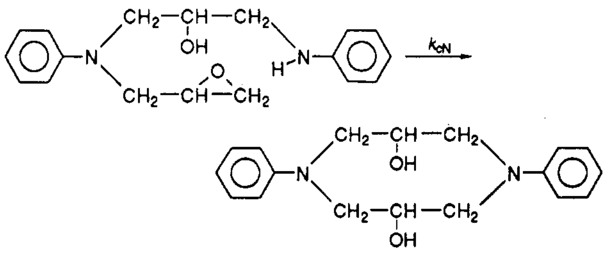
obtained as an intercept on the y-axis in both plots; the constants k_2 and k_3 were determined as the slopes of the first and second plot, respectively (see Figure 5). The results are summarized in Table II.

In order to determine the constant k_4 (Scheme IV), it would be necessary to follow the kinetics of the reaction DGA–aniline to a high conversion and to determine the higher oligomers. This is difficult, however. Therefore, k_4 was evaluated by means of computer simulation, looking for the value that gives the best fit with experimental data. The results reveal that the secondary amine 1-anilino-3-phenoxy-2-propanol (S) is a good model for the monosubstituted aniline as follows from the comparison of values of k_2 and k_4 for S and aniline (cf. Tables I and II in ref 1).

Due to the positive substitution effect of epoxy groups, the fastest addition step is the reaction of the primary amino group with monosubstituted DGA: $A_0 + E_1 \rightarrow (k_3)$ A–E–···. This explains the experimentally observed much higher content of the product A–E–A in the reaction mixture, compared with E–A–E formed by the reaction $E_0 + A_1 \rightarrow (k_2)$ E–A–··· (cf. Figure 2). As $k_3 > k_2$, E–A–E is formed more slowly but is consumed more quickly (cf. Scheme I). The reaction of two substituted units $A_1 + E_1 \rightarrow (k_4)$ ···–A–E–··· is fast in the simple model system DGA–NMA, but in a sterically more hindered system, DGA–S or DGA–aniline, this reaction is slowed down.[1] This finding shows that the results obtained by an investigation of a simple model system cannot always be applied to real systems in a simple way.

Cyclization

Figures 2–4 demonstrate the fast formation of isomers of the eight-membered ring (I) (curves 4 and 5). These "nitrogen" cyclics which involve two nitrogen atoms in the ring are formed from the adduct A–E by an intramolecular reaction between the epoxy group and the secondary amino group. Both isomers of ring I are formed in the initial stage of the reaction, unlike the "ether" rings, e.g., the seven-membered ring 4-phenyl-2-[(*N*-methylanilino)-methyl]-1-oxa-5-aza-cycloheptanol (II) or the morpholine product (III) which contain in the ring an oxygen atom (cf. Scheme I). "Ether" cyclics are formed in the case of the reaction between DGA and NMA by an intramolecular etherification only after amine has been consumed.[1] Tetrahydroquinoline type cycle IV (Scheme I) described by Reyx and Costes[10] and by Attias et al.[11] was not detected under our experimental conditions.



(6)

I

In mixtures DGA–aniline at molar ratios 3:1, 1:1, and 1:3 the content of ring I formed in the reaction is approximately 20, 15, and 10%, respectively, with respect to the concentration of the minority component in the initial reaction mixture. The smallest relative amount of ring I is formed in the mixture with aniline in excess (see Figure 4). In this case the preferred reaction is that of the epoxy group of the adduct A–E with the primary amino group of aniline to form the linear A–E–A. The content of the ring increases if the initial system is diluted with an inert solvent. About 25% of cycles were determined in the 20% toluene solution of the stoichiometric reaction mixture.

Cyclization is catalyzed by OH groups and the formation of ring I obeys the kinetic relation

$$d[C_N]/dt = k_{cN}[A\text{–}E][H] \tag{7}$$

Here, $[C_N]$ and k_{cN} respectively are the total concentration of isomers of "nitrogen" ring I and the rate constant of their formation; [H] is the concentration OH groups.

In the case of an intermolecular addition reaction to form linear oligomers, the local intramolecular catalysis by the OH group in a monosubstituted diepoxide is operative.[1] This is manifested by the positive substitution effect of epoxy groups in DGA. For elucidation of the kinetics of ring formation, the effect of dilution has been examined. If only the intramolecular catalysis is operative then $d[C_N]/dt = k_{cN}[A\text{–}E]$ holds, whereas for intermolecular catalysis eq 7 holds. The relative amount of the cycle calculated for k_{cN} determined in the bulk would increase in the stoichiometric mixture by passing from the bulk to 20% solution from 15% to, respectively, 60% (intramolecular catalysis) and 37% (intermolecular catalysis, eq 7). The experimental value is 25%. Therefore the intermolecular catalysis seems to be dominant; moreover, the possible association in a nonpolar solvent (toluene) seems to favor the intermolecular reaction over the intramolecular one.

The rate constant of formation of "nitrogen" rings determined by using relation 7 and given in Table II is higher by an order of magnitude than the corresponding constant for "ether" rings (cf. Table II and ref 1). The relative amount of "nitrogen" rings and linear oligomers formed (eq 10) in the initial stage of the reaction can be evaluated by using a relation for the intramolecular (eq 8) and intermolecular (eq 9) reaction of the adduct A–E. In these

$$-(d[A\text{–}E]/dt)_{intra} = k_{cN}[A\text{–}E][H] \tag{8}$$

$$-(d[A\text{–}E]/dt)_{inter} = [A\text{–}E][H]\{(k_2[E_0] + k_3[A_0]) + k_4([E_1] + [A_1])\} \tag{9}$$

$$d[cycle]/d[linear\ oligomer] = k_{cN}/\{(k_2[E_0] + k_3[A_0]) + k_4([E_1] + [A_1])\} \tag{10}$$

simplified equations the etherification, which is slower by an order of magnitude,[1] has been neglected. $[E_0]$ and $[E_1]$ respectively are the concentrations of diepoxide units with the unreacted and with one reacted epoxy group (cf. Scheme III); $[A_0]$, $[A_1]$, and $[A_2]$ are the concentrations of unreacted amine units and mono- and disubstituted amine units, respectively (cf. Scheme II); k_2, k_3, and k_4 are the rate constants of reactions between units $A_1 + E_0$, $A_0 + E_1$, and $A_1 + E_1$, respectively, from Scheme IV; and [H] $(=[H]_0 + [A_1] + 2[A_2])$ is the concentration of hydroxyls, where $[H]_0$ is the concentration of components containing the OH group at the beginning of the reaction.

Using eq 10, it is possible to explain the experimentally observed dependence of the extent of cyclization on the initial ratio of aniline and DGA. With increasing excess of aniline (A_0) the rate of formation of linear products increases, because $k_3 > k_2$ (cf. Table II), and the relative content of cyclics decreases. The relation also shows that the cyclization increases with dilution.

Conclusion

By summarizing the results of part 1 (ref 1) and of this study (part 2), we obtain a picture of the mechanism and kinetics of the reaction between DGA and aromatic amines, the reaction mechanism of DGA is much more complicated than that of the reaction of epoxides on the basis of DGEBA. Special features of the reaction of DGA are the mutual dependence of reactivities of all functional groups, the different reactivity of stereoisomers, a great tendency toward cyclization, and a more pronounced etherification.

A common feature of all systems is the autocatalytic course of the reaction as a result of the catalytic effect of the hydroxyl group of the products formed. Only in the initial stage the uncatalyzed reaction also becomes operative. In this case the assistance enabling the epoxide ring to be opened is provided by amines of the starting mixture. The rate constants of the reaction catalyzed with OH groups are higher by at least an order of magnitude.[1]

Stereoisomeric products are formed during the reaction between DGA and amines. The different reactivities of the isomers indicate an essential effect of configuration on the reaction rate. In the simple reaction system, DGA–NMA, isomer II, which has the *d,l* configuration, is the more reactive one. On the contrary, under sterically more demanding conditions, i.e., in the reaction of substituted units $(E_1 + A_1)$, e.g., of substituted DGA with NMA or S, isomer I with the configuration *d,d* or *l,l* reacts more quickly[1] (cf. $k_{2\mathrm{I}}$ and $k_{2\mathrm{II}}$ or $k_{4\mathrm{I}}$ and $k_{4\mathrm{II}}$ in ref 1).

The predominant reaction of the reaction mechanism in the system without any catalyst added is the amine addition to the epoxy group. The reactivities of the epoxy groups in DGA are mutually dependent and in the model reaction DGA–NMA a pronounced positive substitution effect was determined. The epoxy group in unit E_1 is more reactive than those in DGA (E_0). This means that after one epoxy group has reacted in DGA, the reactivity of the other is higher due to the intramolecular catalysis with the OH group formed in the reaction. However, the substitution effect of epoxy groups in DGA depends on the reaction partner. Reduction of this effect in some systems is due either to a larger steric hindrance in the reaction with the bulkier amine or to the presence of another OH group in the molecule which by the OH···OH interaction can compete with local catalysis.[1] The ratio of rate constants of the reaction of the epoxy groups in E_1 or E_0 with the primary amine aniline is $\sigma = k_3/k_1 = 2.2$ (cf. Scheme IV, Table II) and with the secondary amine NMA is $\kappa_{\mathrm{DGA-NMA}} = k_4/k_2 = 3$. The average rate constants k_4 and k_2, irrespective of isomers, were taken into account (cf. Scheme IV and ref 1). If, however, the more real model 1-anilino-3-phenoxy-2-propanol (S) is used, which is bulkier and contains an OH group, the substitution effect diminishes, $\kappa_{\mathrm{DGA-S}} = 1.4$.

Also in the case of the amino group the value of the substitution effect depends on the reaction partner and decreases in the reaction with substituted diepoxide, E_1, compared with that with unreacted DGA (E_0): $\rho = k_2/k_1 = 0.44$ and $\lambda = k_4/k_3 = 0.25$ (cf. Scheme IV, Table II). ρ and λ characterize the reaction of the amino group with respectively DGA and monosubstituted diepoxide.

Due to the interdependence of reactivities of all functional groups, the effect of the reaction partner on the reactivities of functional groups is taken into account in the kinetic Scheme IV. Four kinetic equations are used to describe the intermolecular reaction between the amino and epoxy groups.

Etherification is much slower than addition and the ratio of the corresponding rate constants is μ $(=k_{\mathrm{E1}}/k_2) = 0.03$–$0.06$.[1] k_{E1} is the rate constant of etherification of DGA. However, the participation of etherification in the overall reaction mechanism increases with conversion and with excess epoxide (cf. eq 15 and Figure 6 in ref 1). In the etherification too an increased rate of the reaction can be seen after one epoxy group in DGA has reacted; γ $(= k_{\mathrm{E2}}/k_{\mathrm{E1}}) = 3$,[1] where k_{E2} is the rate constant of etherification of monosubstituted diepoxide.

In the reaction with amines, DGA shows a pronounced tendency toward the formation of small rings. As a result, "nitrogen" and "ether" cyclic products are formed, three of which (II and two isomers of I) were isolated and identified. "Nitrogen" rings, especially the eight-membered ring I, arise immediately in the beginning of the reaction by intramolecular addition, and the rate of their formation is comparable with the formation of linear oligomers (cf. Figures 2–4). The content of the rings depends on the molar ratio of the starting components and decreases with the excess of aniline due to the competitive intermolecular addition A–E with aniline (cf. Scheme I and eq 10). In a stoichiometric mixture in the reaction in bulk, the total content of both isomers of ring I is about 15% at the end of the reaction. The "ether" rings are formed by intramolecular etherification only at a later stage of the reaction when amine has reacted. Compared with intermolecular etherification, this cyclization is faster, and in the reaction in bulk small rings amount to 60–70% of all ether products formed.[1]

On the basis of the reaction mechanism determined by using model systems, one can describe the curing of polyfunctional systems. The results revealed that especially the formation of small cycles is substantial for the structure of the network TGDDM–DDM. The theory of network formation for this system must involve the complex kinetic scheme including cyclization and etherification.

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Registry No. DGA, 2095-06-9; (DGA)(aniline) (copolymer), 119391-54-7; aniline, 62-53-3.

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Charge Storage on a Conducting Polymer in Solution

M. J. Nowak,[†,‡] D. Spiegel,[†] S. Hotta,[§] A. J. Heeger,[*,⊥] and P. A. Pincus[‖]

Institute for Polymers and Organic Solids, University of California,
Santa Barbara, California 93106. Received October 24, 1988;
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ABSTRACT: Magnetic and optical studies of poly(3-hexylthienylene) (P3HT), doped in solution with NO$^+$PF$_6^-$ in both chloroform and in the more polar solvent methylene chloride (CH$_2$Cl$_2$), indicate a relatively small difference in the energy of polarons versus that of bipolarons and imply that the weak effective electron-electron Coulomb repulsion can be controlled by varying the solvent and/or the polymer concentration. As a result, we have observed unambiguous magnetic and optical signatures characteristic of polarons in P3HT in CH$_2$Cl$_2$ at the lowest doping levels. The relative fraction of polarons and bipolarons has been analyzed in the context of various proposed statistical models. A theoretical model is developed to include the effect (in such solutions) of ionic screening on the effective Coulomb interaction. This model is tested by adding salt to a dilute solution of doped polymer.

I. Introduction

In a nondegenerate ground state conjugated polymer such as polythiophene or its soluble alkyl derivates (Figure 1a), the fundamental nonlinear excitations and the dominant charge storage configurations are polarons and bipolarons.[1-4] The relative stability of these species depends on the relative strength of the electron-phonon and electron-electron interactions in the polymer. The doubly charged bipolaron is a bound state (resulting from the electron-phonon interaction) between two polarons. However, the repulsive Coulomb interaction favors the existence of two separated polarons. Hence, the energy of creation of two polarons may be comparable to that of a bipolaron.

In Figure 1b,c, we show the band diagrams with gap states and allowed optical transitions appropriate for a self-localized bipolaron and polaron, respectively.[1,3,4] Clearly, the two have distinguishing optical and magnetic signatures. A bipolaron with its two empty states in the gap carries a double-positive charge and is spinless. Two broad electronic transitions from the valence band to the gap states are expected with energies less than the interband transition. On the other hand, a polaron has one unpaired electron in its lower gap state, and hence, along with one positive charge, it has spin one-half. From Figure 1c, a polaron should display an additional subgap transition between two localized energy levels.

From these magnetic and spectroscopic signatures, studies of polythiophene and the poly(3-alkylthiophenes) have provided evidence that upon doping[1,6] or photoexcitation[7] charge is stored in spinless bipolarons. These results were obtained from measurements on the polymer in the form of solid-state films and powders and on the polymer in solution.[5-9]

There are reports by various groups,[10] however, that polarons are generated as well as bipolarons. This suggests a near degeneracy in the energy of two polarons versus a bipolaron, implying an equilibrium for the reaction

$$P^+ + P^+ \rightleftharpoons B^{2+}$$

Even in the case where bipolarons have the lowest creation energy, the entropy favors polarons so that a finite concentration of polarons can be expected. In this paper, we address this question with visible-near-IR spectroscopy and electron spin resonance data on the poly(3-hexylthienylene) system.[8,9]

The experimental results which we report here were carried out with poly(3-hexylthienylene) (P3HT) in a methylene chloride solution. By conducting the experiments in this more polar solvent than that used in previous work[9] (in chloroform), we find distinctly different behavior for the doped polymer in solution. For example, in the most dilute doping regime, our data indicate that charge storage is predominantly in polarons, in marked contrast with the low doping regime results of P3HT in chloroform. Only at higher doping levels in methylene chloride do we again observe the bipolaron as the dominant charge storage configuration. This implies an important solvent dependence to the polaron-bipolaron equilibrium described above.

By performing the experiments on a doped conducting polymer while it is in solution, it becomes possible to explore the effect of counterion screening on the interactions in the polymer. The effective on-chain Coulomb interaction between two polarons, although always repulsive, is strongly dependent on the extent to which the "bare" positive charge of the polaron is screened. To first order, this is determined by the proximity of its counterion. Second-order effects include the direct screening of the polarons by the solvent itself. This can be considered weak

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[†] Department of Physics.

[‡] Current address: Bell Communications Research, Red Bank, NJ 07701-7020.

[§] Permanent address: Central Research Laboratories, Matsushita Electric Industrial Co., Ltd., Moriguchi, Osaka 570, Japan.

[⊥] Department of Physics and Engineering Materials Department.

[‖] Engineering Materials Department.

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