Influence of the reaction mechanism on network formation in amine-cured *N,N*-diglycidylamine epoxy resins

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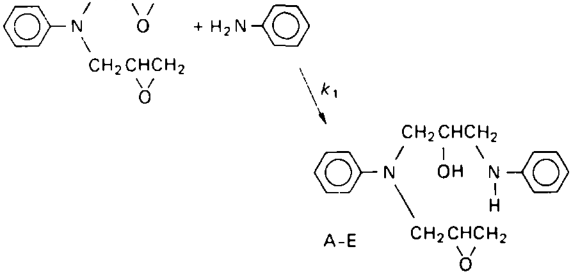
Epoxides based on diglycidylaniline (DGA) derivatives, i.e. DGA and *N,N,N',N'*-tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM), and diglycidylether of bisphenol A (DGEBA) were cured with diaminodiphenylmethane (DDM). The critical ratio of functional groups, necessary for the gelation of non-stoichiometric systems, was determined in bulk and in dilute solutions and the influence of cyclization and reactivity of functional groups on network formation was investigated. The theory of branching processes used in the treatment of the structure build-up in DGEBA–amine systems was modified to include a more complicated mechanism of the reaction of DGA with amines. The theoretical prediction fits the experimental data on network formation.

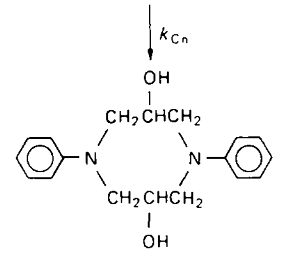
(Keywords: epoxy resins; network formation; reaction mechanism)

INTRODUCTION

The formation and structure of epoxy–amine networks depend on the mechanism of the curing reaction; different reaction mechanisms lead to dissimilar network structures. This is the case in the curing of two types of epoxies based on diglycidyl ether of bisphenol A (DGEBA) and on derivatives of diglycidylaniline (DGA), e.g. *N,N,N',N'*-tetraglycidyldiaminodiphenylmethane (TGDDM). The difference in the curing of these two types of epoxides with amines is that only in DGA–amine systems there exists cyclization and a dependent reactivity of the epoxy groups[1-4].

In contrast to the curing of DGEBA, small rings arise during the reaction of DGA with aniline. The content of the eight-membered ring I was found to be quite high[5]. Formation of intramolecular bonds during the cure of polyfunctional systems brings about a decrease in the effective functionality of reagents, resulting in a delay of gelation and a decrease in the crosslinking density. This is manifested, for instance, by a higher critical conversion, i.e. the conversion at the gel point, and a lower value of the critical molar ratio of functional groups necessary for gelation[6].





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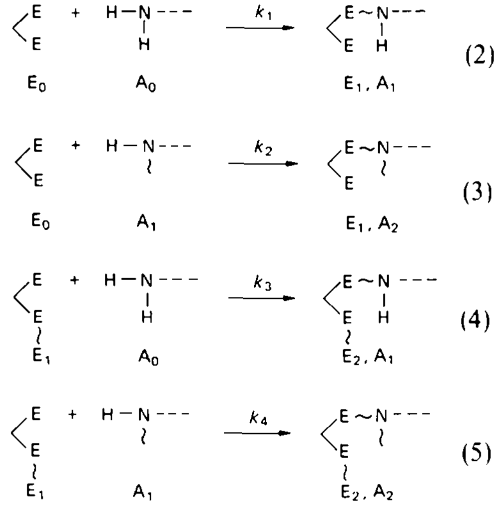
The reactivity of functional groups in a DGA–polyamine system determines the relative rates of reactions leading to chain extension [reactions (2) and (4)] or to branching and crosslinking [reactions (3) and (4)][4].



where E is an epoxy group, $<^{E}_{E}$ is DGA, E~ and N~ are reacted epoxy and amino groups, respectively, N--- is

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a connection through a sequence of bonds to another amino group, A_i, E_i are the amine and diepoxide units with i reacted functionalities, and k_i is the corresponding rate constant.

If the reactivity of functional groups in a monomer unit decreases with the degree of substitution (number of reacted functional groups), this is referred to as a negative substitution effect. Such slowing down of the reactions of partially substituted functional groups resulting in branching [e.g. reactions (3) and (5)], brings about a delay in gelation. Thus, the substitution effect in the amino group, ρ, is defined as the ratio of the rate constants for the reaction of the secondary and primary amino groups with an epoxy group ($\rho = k_2/k_1$). The substitution effect of the epoxy groups in the diepoxide unit, σ, is represented by the ratio of the rate constants for the reaction of the diepoxide unit with one and no reacted epoxy group ($\sigma = k_3/k_1$). In the rate equations, concentrations of molecules (not functional groups) are used and the values of rate constants depend on the number of functional groups in the molecule. The primary amine or diepoxide (k_1) contain two functional groups and the secondary amine (k_2) or a monosubstituted diepoxide (k_3) only one group. Therefore, the ideal value of ratios of rate constants at which all functional groups have the same reactivity is 1/2. This is the case of epoxy groups in DGEBA. It is known that the substitution effect in the amino group is usually negative[7], i.e. $\rho < 0.5$, and the substitution effect of the epoxy groups in DGA is positive[3,4], $\sigma > 0.5$.

Structure build-up is treated using a theory of network formation. The theory gives information on, e.g. the molecular weight of the polymer in a pregel stage, the conversion at the gel point, the fraction of gel and the concentration of elastically active chains in the network. The most common theories are based on the graph-like model and statistical or kinetic methods are employed to treat the build-up of structures[8]. The kinetic treatment is exact unless space correlations are operative, e.g. cyclization or excluded volume effects; however, structural information on the gel is then very limited. On the other hand, the statistical methods—theory of branching processes (TBP)— of generation of macromolecular structures from structural fragments are efficient even for complex systems and provide information on the gel structure. Several theories were developed to treat epoxy–amine systems: DGEBA–DDM[9], TGDDM–amine[10–12]. The theories do not take into account cyclization and the dependent reactivity of epoxy groups in *N,N*-diglycidylamines.

In this paper, the build-up of the DGEBA-diaminodiphenylmethane (DDM), DGA–DDM and TGDDM–DDM networks was investigated and characterized by the critical ratio of functional groups, r_c, and by the critical conversion. The theory (TBP) used for DGEBA systems was modified to be applicable to TGDDM–amine networks and an analysis was performed to determine the effect of cyclization and reactivity of functional groups on network structure.

EXPERIMENTAL

The synthesis of DGA and TGDDM has been described previously[6,13]. The purity of DGA was 99.9% according to high performance liquid chromatography (h.p.l.c.) and the composition of the tetrafunctional resin was (h.p.l.c.)[14]: 93.0% TGDDM; 2.4% dimer of TGDDM; 1.5% monochlorohydrin of TGDDM; 1.0% monochlorohydrin of a TGDDM compound with one epoxy group involved in the ring structure; and ~2% of unidentified impurities.

The DGEBA was purified by recrystallization from a 4:1 methanol:acetone mixture. The epoxy equivalent (171 g mol^{-1}), corresponding to 99.4% purity, was determined by titration. The DDM was recrystallized from toluene yielding a product with 99.5% purity (gas chromatography). Aniline was distilled at reduced pressure (99.9%, gas chromatography).

The preparation of non-stoichiometric networks DGEBA–DDM, DGA–DDM and TGDDM–DDM with excess amine in bulk or in solution was carried out by heating the reaction mixture to 130–140°C for 2–7 days. Diethylene glycol dimethylether (DEGDME) was used as diluent. A series of samples with various ratios of functional groups r ($= C_A/C_E$) were prepared and subsequently extracted with dimethylformamide (C_A and C_E are the respective concentrations of the amine NH groups and the epoxy groups). The critical molar ratio r_c corresponding to the composition of the critical non-stoichiometric network was determined by solubility measurements as the midpoint between the last sample containing the gel and the first fully soluble sample. The critical ratio was determined with an accuracy of $r_c \pm 0.05$.

RESULTS AND DISCUSSION

Theory

Network formation is characterized by critical parameters, such as critical conversion, α_c, or critical molar ratio of functional groups, r_c. In the case of epoxy–amine networks, the critical ratio is defined as the ratio of molar concentrations of amine hydrogens to epoxy groups, at which the gel is just formed at complete conversion of the minority groups. The following conditions for the gel point are applicable, if the reactivities of all groups in polyepoxide and polyamine are equal and independent:

$$(\alpha_A)_C(\alpha_E)_C = [(f_A - 1)(f_E - 1)]^{-1} \qquad (6)$$

where $(\alpha_A)_C$ and $(\alpha_E)_C$ are the critical conversions of the amino NH groups and the epoxy groups, respectively, and f_A, f_E are the respective functionalities of the amine and the epoxide. For a random alternating reaction of an epoxide with an amine we have:

$$r = C_A/C_E = \alpha_E/\alpha_A \qquad (7)$$

For the critical non-stoichiometric network $[(\alpha_E)_C = 1, (\alpha_A)_C = 1/r_C]$ expression (6) reads:

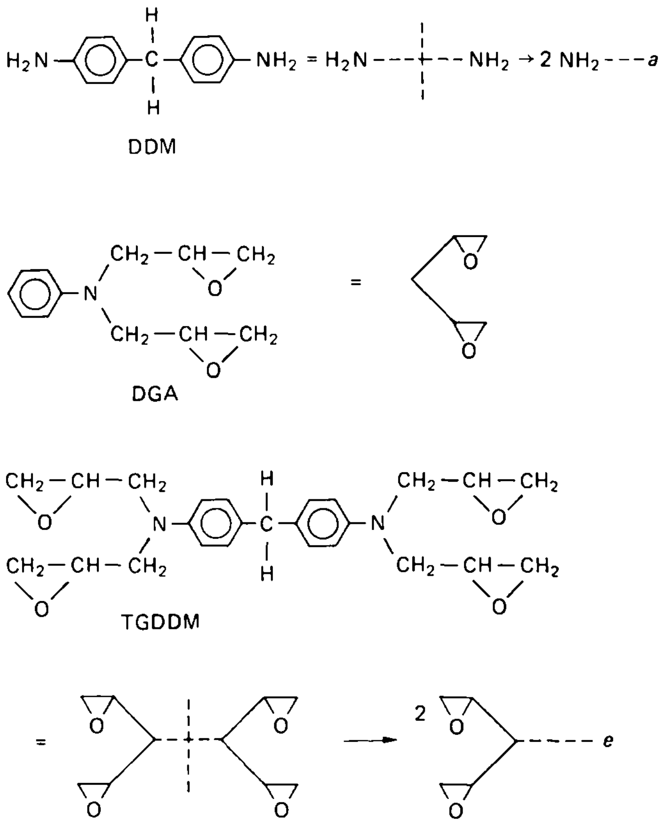
$$r_C = (f_A - 1)(f_E - 1) \qquad (8)$$

Consequently, the critical ratios for systems containing a tetrafunctional amine and a bi- or tetrafunctional epoxide are $r_C = 3$ and 9, respectively, in the case of the ideal random reaction.

Our systems do not comply with these simple assumptions and therefore a more general TBP was used[8]. The initial composition of the system and the reaction mechanism are the main input parameters for the theory. The reaction mechanism of DGEBA with

Table 1 Critical molar ratios r_c for network formation of the DGEBA–DDM, DGA–DDM and TGDDM–DDM systems in bulk

	Theory				
			With cyclization		
	Random	Without cyclization	$T = 100°C$	$T = 140°C$	Experiment ($T = 140°C$)
DGEBA–DDM	3	2.56	–	–	2.61
DGA–DDM	3	2.74	2.39	2.26	2.20 2.25
TGDDM–DDM	9	7.79	6.56	6.04	5.50

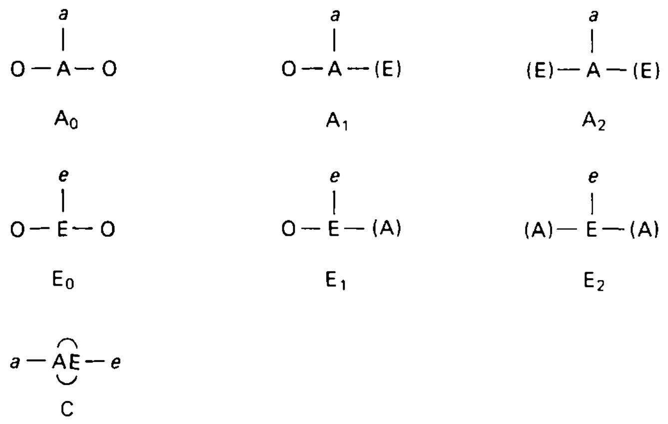


Scheme 1 Note, the labels *a* and *e* must be recombined ($e + e \rightarrow ee$, $a - a \rightarrow aa$) to reform the connections in DDM and TGDDM molecules, respectively (see Appendix)

DDM is quite simple, since practically no cyclization and etherification occur (at least at $r > 1$), and the reactivities of the epoxy groups are independent[9]. A negative substitution effect in the amino group ($\rho = 0.2$) was used[15,16] in the calculation. The decrease in r_c because of the negative substitution effect is compared with the random case in *Table 1*.

In this paper a theory has been derived to describe network formation in the more complicated DGA–DDM and TGDDM–DDM systems. We assumed the validity of a reaction mechanism based on the kinetic scheme and used the rate constants determined previously with model systems[3,4]. Four rate constants for the intermolecular addition reactions [eqs (2)–(5)] and one rate constant for cyclization to form the eight-membered ring I [eq. (1)] characterize the reaction mechanism. Etherification was not included in this simplified model, because only networks prepared with excess amine were taken into account.

The statistical approach employs structural units to build up polymer structures. Since the reactivity of the amino groups in DDM and of the remote epoxy groups in TGDDM are independent, the TGDDM and DDM molecules can be cut into two independent parts[17]. The cut is indicated by labels *a* and *e*. The structural fragments were obtained as shown in *Schemes 1* and *2*. Amine and epoxy units are present in the reaction system in different reaction states depending on the conversion of functional groups (*Scheme 2*). In addition to the epoxy and amine units, the cyclic fragment C was also used as a building unit in order to include the cyclization. Consequently, the system TGDDM–DDM was built up using the structural units shown in *Scheme 2*. The time evolution of fractions of these fragments is given by equations (A12)–(A18) in the Appendix. The generation of polymer structures from the structural fragments and the condition for gel formation are given in the Appendix.



Scheme 2 Note, A_0, A_1, A_2, E_0, E_1 and E_2 represent the reaction states of the units, i.e. the amine and diepoxide units with zero, one or two reacted functionalities, respectively; C is the eight-membered cycle; (E) and -(A) indicate that the given functionality has reacted with an epoxide or amine, respectively; 0 is an unreacted amine hydrogen or epoxy group

This theoretical approach involves the following approximations: the statistical approach does not take into account long-range stochastic correlations. It is known[18] that the results of the statistical and rigorous kinetic methods differ in the case of a strong substitution effect, e.g. in initiated reactions. Two functional groups with interdependent reactivities may therefore result in deviations from the theory in our system; long-range cyclization is neglected. Only the cyclization leading to small eight-membered rings is included; etherification was not taken into account because it was absent.

Effect of cyclization

The extent of cyclization in a DGA–amine system

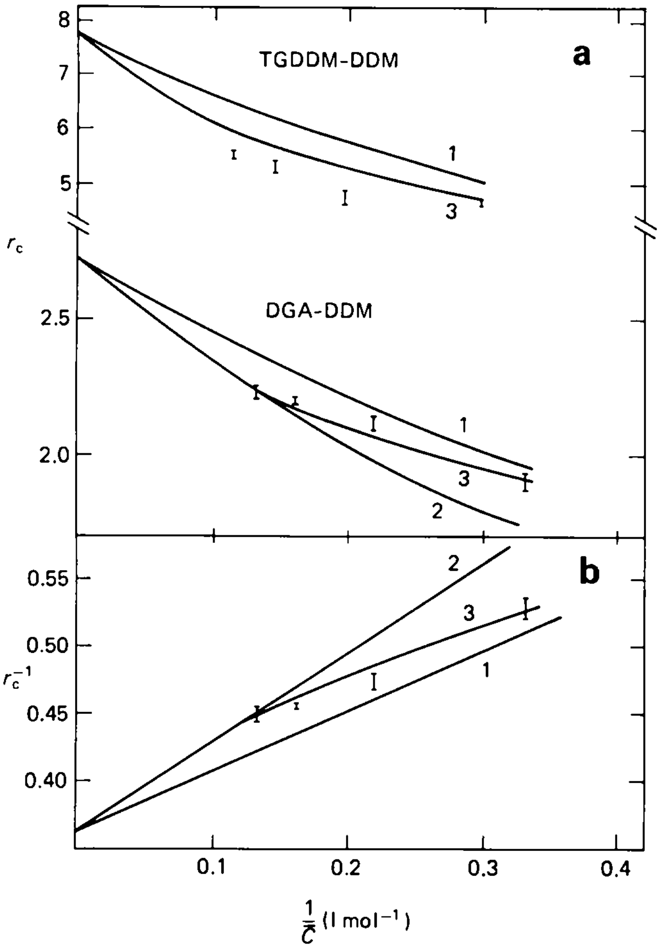


Figure 1 Critical ratio of functional groups, r_c ($= C_A/C_E$), in the formation of DGA-DDM and TGDDM-DDM networks (a) and the reciprocal value, r_c^{-1}, for DGA-DDM networks (b) as a function of dilution. The initial concentrations of the amino NH and the epoxy groups are C_A and C_E, respectively. Bars are experimental data. Curves 1-3 are the theoretical dependences: 1, rate constants determined at 100°C; 2, influence of temperature taken into account, $b_T = 1.49$ (ref. 5); 3, influence of temperature and association taken into account, b_{AS} (in DEGDME) = 0.55 (ref. 5)

increases with increasing dilution ($1/\bar{C}$) of the reaction mixture with an inert solvent[5] [$\bar{C} = (C_A/2) + (C_E/2)$]. Consequently, the critical ratio r_C of the DGA-DDM network also decreases with dilution due to more pronounced cyclization (*Figure 1*). Our theory reveals that the dependence of r_C^{-1} on dilution $1/\bar{C}$ should be linear (*Figure 1b*, curve 1). This finding makes it possible to extrapolate to zero dilution and determine the extrapolated value $(r_C)_{ext}$ which is an important parameter characterizing the formation of the network.

Effect of the reactivity of functional groups

The effect of the dependent reactivity of functional groups was considered in the absence of cyclization. *Table 1* shows that the theory predicts lower values of r_C in comparison with the ideal network. In this work, gelation was also characterized by the geometric average of the critical conversions of functional groups, $P = [(\alpha_A)_C(\alpha_E)_C]^{1/2}$ [cf. eq. (6)] calculated theoretically. *Figure 2* shows a comparison of the systems DGEBA-DDM and DGA-DDM with a network formed by a random reaction. The theory reveals higher values of P for the DGEBA-DDM system and a lower value for the stoichiometric DGA-DDM system compared to the ideal random case. The ideal value is 0.577. The delay in gelation in the DGEBA-DDM network is brought about by a negative substitution effect in the amino group of DDM. The formation of linear sequences by a reaction of primary amino groups [reactions (2) and (4)] is preferred over the reaction of secondary amino groups leading to branching [reactions (3) and (5)].

The different behaviour of the DGA-DDM system in contrast to DGEBA is given by the fact that the reactivities of the epoxy groups in DGA are interdependent (positive substitution effect). It is obvious from *Figure 2* that the parameter P depends on the composition of the system characterized by r and increases with increasing excess of amine. The stoichiometric network ($r = 1$) has a lower P value and the critical non-stoichiometric network ($r = r_C$) has a higher value compared to the random case. This theoretical conclusion may be explained as follows: both the negative substitution effect in the amino group and the positive one of the epoxy groups in DGA are operative in the stoichiometric system. A stronger influence of the positive effect in DGA results in the preference of branching over chain extension and the gelation sets in earlier. However, the critical conversion of the critical non-stoichiometric network with excess amine is not affected by the reactivity of epoxy groups since all minority (epoxy) groups have already reacted at the gel point [$(\alpha_E)_C = 1$]. Therefore, only the negative substitution effect in the amino group determines the critical state leading to an increase in critical conversion or a decrease in the critical ratio compared to the random reaction (cf. *Table 1*). One can conclude that the influence of the substitution effect on the critical parameters decreases with increasing conversion of the corresponding functional group and vanishes at its complete conversion.

Comparison of experiment with theory

The experimental values of critical ratios in bulk or in a diluted system are given in *Table 1* and *Figure 1*. The results reveal good agreement between experiment and theory in the case of the DGEBA-DDM network. However, deviation from theory was found for the DGA-DDM system. It is obvious that the theoretical dependence of r_C on dilution (*Figure 1*, curve 1) does not fit the experimental data. The theoretical values of r_C are too high (cf. *Table 1*, *Figure 1*) indicating that the theory

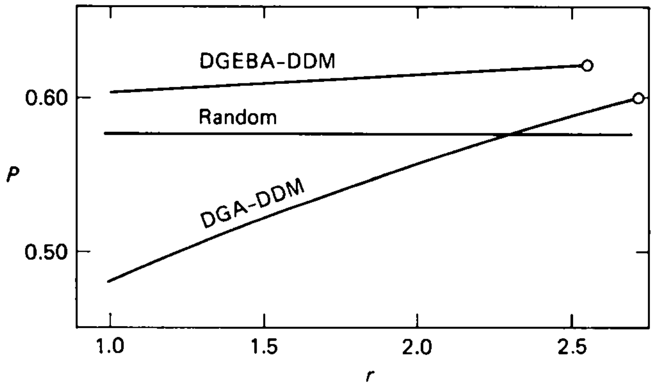


Figure 2 Parameter $P = \{[(\alpha_A)_C(\alpha_E)_C]^{1/2}\}$ for the formation of epoxy-amine networks as a function of the initial composition of the reaction system $r = C_A/C_E$ (without cyclization). ○, Critical ratio

predicts a lower extent of cyclization when the rate constants determined on model systems at 100°C are used. However, the networks were prepared at 140°C and the relative extent of cyclization increases with increasing temperature[5,12]. The ratio of rate constants for intra- and intermolecular reactions was therefore multiplied by an empirical parameter (b_T) which yielded the best fit for the content of cycles in the model reaction at 140°C[5]. In this case, the theoretical (curve 2) and experimental values of r_c agreed for the reaction in bulk (cf. *Figure 1*, *Table 1*).

To explain the deviation of the theory from the experimental dependence of r_C on dilution, we assumed association of reaction products with OH groups in non-polar solvents. It was concluded that this association suppresses cyclization[5]. Association in diluted systems, resulting in an increase in the effective concentration of reagents, was taken into account by multiplying the rates of intermolecular reactions by the empirical parameter b_{AS}. *Figure 1* shows good agreement between experiment and theory provided the effects of temperature and association in the solvent are considered (curve 3).

One can see from *Figure 1b* (curve 3) that the plot r_C^{-1} *versus* $1/\bar{C}$ is not linear because of association in diluted systems. Consequently, a linear extrapolation of experimental data provides an incorrect value for $(r_C)_{ext}$.

Similar results were obtained for TGDDM DDM networks (*Figure 1*, *Table 1*). In this case, however, the network formation is also affected by functionality distribution in the epoxy resin. So far, this factor has not been included in the theoretical approach. As a result of this distribution the experimental r_C value deviates from theory.

CONCLUSIONS

The theory of branching processes was modified by including cyclization and a complex reaction mechanism determined earlier[3,4], to describe curing of DGA and TGDDM with amines. The effects of cyclization, reactivity of functional groups and molar composition of reagents on the formation of DGEBA-DDM, DGA-DDM and TGDDM DDM networks was predicted theoretically.

The cyclization in DGA DDM networks results in a delay of gelation, i.e. in decreasing critical molar ratio r_C. The positive substitution effect of the epoxy groups in DGA, i.e. a faster reaction of the monosubstituted diepoxide unit compared to free DGA, brings about a preferential branching leading to lower critical conversion of the stoichiometric DGA DDM network. On the contrary, gelation is delayed in networks with a high excess of amine. The epoxy groups are fully reacted in this case and only the negative substitution effect in an amino group is operative. The epoxy groups in DGEBA are independent and the effect of an amino group therefore governs the formation of the DGEBA-DDM network, resulting in a delay of the gelation under all circumstances. Agreement between theory and experiment was found.

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APPENDIX

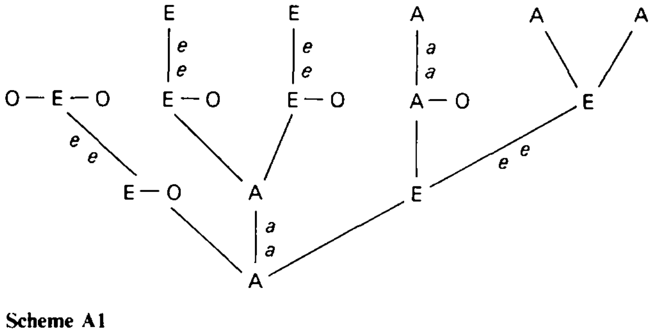
The TBP was used for analysing theoretically the formation of DGA-DDM and TGDDM-DDM networks.

The structural units (fragments) of the system described in *Scheme 2*, A_i, E_i and C, are combined anew at any moment of the reaction to form tree-like structures containing small rings within the building units. Each unit can be chosen as a root of the tree (zeroth generation) and other connected units occur in higher generations (*Scheme A1*). Only alternating connections of amine and epoxy units were taken into account. Etherification was not considered. The fragments of TGDDM and DDM are connected via combination of *a* and *e* labels, respectively (*Schemes 1* and *A1*). *Scheme A1* shows an example of a tree in the TGDDM DDM system.

The number of bonds issuing from a unit is given by the probability generating function (p.g.f.). The p.g.f. for a unit in the root is as follows:

$$F_0(z) = n_A(a_0 + a_1 z_{AE} + a_2 z_{AE}^2) z_{AA} + n_E(e_0 + e_1 z_{EA} + e_2 z_{EA}^2) z_{EE} + n_C z_{AA} z_{EE} \quad (A1)$$

where $n_A = \sum_i A_i/(\sum_i A_i + \sum_i E_i + C)$, $n_E = \sum_i E_i/(\sum_i A_i + \sum_i E_i + C)$ and $n_C = C/(\sum_i A_i + \sum_i E_j + C)$ are mole fractions of the amine, epoxy and cyclic units, respectively; A_j, E_i are amine and epoxy units with *i* reacted functionalities; a_i, e_i are fractions of the A_i and E_i units, respectively; and *z* is a dummy variable. Subscripts of *z* indicate the direction of a bond; thus z_{AE} and z_{EA} indicate a bond



Scheme A1

from unit A to E and from unit E to A, respectively, z_{AA} and z_{EE} indicate a connection between A fragments and E fragments, respectively, via connection of $a+a$ and $e+e$ labels, i.e. a connection of two independent parts of DDM and TGDDM, respectively.

The p.g.f.s for units already connected by a bond, i.e. for units in higher generations, are derived from $F_0(z)$:

$$F_{IJ}(z) = F_{OJ}^{JI}(z)/F_{OJ}^{JI}(1) \qquad \text{(A2)}$$

where $F_{IJ}(z)$ is the p.g.f. for unit J bonded to unit I in a previous generation:

$$F_{OJ}^{JI}(z) = \partial F_{OJ}/\partial z_{JI} \qquad \text{(A3)}$$

Thus, the p.g.f.s for A and E units bonded with a unit in the preceding generation are:

$$F_{EA}(z) = (a_1 + 2a_2 z_{AE}) z_{AA}/(a_1 + 2a_2) \qquad \text{(A4)}$$

$$F_{EE}(z) = [n_E(e_0 + e_1 z_{EA} + e_2 z_{EA}^2) + n_C z_{AA}]/(n_E + n_C) \qquad \text{(A5)}$$

$$F_{AA}(z) = [n_A(a_0 + a_1 z_{AE} + a_2 z_{AE}^2) + n_C z_{EE}]/(n_A + n_C) \qquad \text{(A6)}$$

$$F_{AE} = (e_1 + 2e_2 z_{EA}) z_{EE}/(e_1 + 2e_2) \qquad \text{(A7)}$$

The condition for the gel point reads

$$|\delta_I^J - F_{IJ}^{KL}| = 0 \qquad \text{(A8)}$$

where δ_I^J is Kronecker's δ ($\delta_I^J = 0$ for $I \neq J$ and $\delta_I^J = 1$ for $I = J$), F_{IJ}^{KL} are elements of a 4 × 4 matrix $|F_{IJ}^{KL}|$ of derivatives of the four p.g.f.s F_{IJ} with respect to the four directions z_{KL}. The gel condition for the TGDDM–DDM system reads:

$$\begin{aligned} 1 &- \frac{2a_2}{a_1 + 2a_2}\left[\frac{2e_2}{e_1 + 2e_2} + \frac{n_E}{n_E + n_C}(e_1 + 2e_2)\right] \\ &- \frac{n_A}{n_A + n_C}(a_1 + 2a_2)\left[\frac{n_E}{n_E + n_C}(e_1 + 2e_2)\right. \\ &\left. + \frac{n_C}{n_E + n_C} + \frac{2e_2}{e_1 + 2e_2}\right] - \frac{n_C}{n_A + n_C}\left[\frac{n_E}{n_E + n_C}(e_1 + 2e_2)\right. \\ &\left. + \frac{n_C}{n_E + n_C}\left(1 - \frac{2e_2}{e_1 + 2e_2} \times \frac{2a_2}{a_1 + 2a_2}\right)\right] = 0 \qquad \text{(A9)} \end{aligned}$$

The same approach was used to describe network formation in the system DGA–DDM. The absence of e–e connection (DGA is not split) is the only difference. The p.g.f. $F_0(z)$ in this case reads:

$$\begin{aligned} F_0(z) = {} & n_A(a_0 + a_1 z_{AE} + a_2 z_{AE}^2) z_{AA} \\ & + n_E(e_0 + e_1 z_{EA} + e_2 z_{EA}^2) + n_C z_{AA} \qquad \text{(A10)} \end{aligned}$$

The following gel condition was derived:

$$1 - \frac{2e_2}{e_1 + 2e_2}\left[\frac{2a_2}{a_1 + 2a_2} + \frac{n_A}{n_A + n_C}(a_1 + 2a_2)\right] = 0 \qquad \text{(A11)}$$

The distributions of units A_i, E_i and C, i.e. a_i, e_i and c, during the reaction were calculated using the kinetic scheme determined earlier[3,4] [cf. eqs (1)–(5) and differential equations (A12)–(A18)].

The epoxy–amine reaction is autocatalysed by the OH groups of reaction products. In addition, the rate equations contain terms that reflect the less effective catalysis by an amino group (A_0) (for details see refs 3 and 4).

$$\begin{aligned} d[E_0]/dt = {} & -[E_0][A_0](k_1'[A_0] + k_1[H]) \\ & - [E_0][A_1](k_2'[A_0] + k_2[H]) \qquad \text{(A12)} \end{aligned}$$

$$\begin{aligned} d[E_1]/dt = {} & [E_0][A_0](k_1'[A_0] + k_1[H]) \\ & + [E_0][A_1](k_2'[A_0] + k_2[H]) \\ & - [E_1][H](k_3[A_0] + k_4[A_1]) \\ & - k_{cn}[A\text{–}E]([H] + [A_0]/20) \qquad \text{(A13)} \end{aligned}$$

$$d[E_2]/dt = E_1[H](k_3[A_0] + k_4[A_1]) \qquad \text{(A14)}$$

$$\begin{aligned} d[A_0]/dt = {} & [E_0][A_0](k_1'[A_0] + k_1[H]) \\ & - k_3[A_0][E_1][H] \qquad \text{(A15)} \end{aligned}$$

$$\begin{aligned} d[A_1]/dt = {} & [E_0][A_0](k_1'[A_0] + k_1[H]) \\ & - [A_1][H](k_2[E_0] + k_4[E_1]) \\ & + k_3[A_0][E_1][H] \\ & - k_{cn}[A\text{–}E]([H] + [A_0]/20) \qquad \text{(A16)} \end{aligned}$$

$$d[A_2]/dt = A_1[H](k_2[E_0] + k_4[E_1]) \qquad \text{(A17)}$$

$$d[C]/dt = k_{cn}[A\text{–}E]([H] + [A_0]/20) \qquad \text{(A18)}$$

where k_1', k_2' are the rate constants of reactions (2) and (3), respectively, catalysed by an amino group; $[A_i][E_i]$ and [C] are the concentrations of the corresponding fragments, [H] and [A–E] are the concentrations of OH groups and of the A–E adduct, respectively. The term $[A_0]/20$ characterizes cyclization catalysed by A_0, which is 20 times slower than the catalysis by OH groups. The rate constants for the reaction at 100°C were determined previously[3,4]: $k_1 = 1.8 \times 10^{-3}$; $k_1' = 0.08 \times 10^{-3}$; $k_2 = 0.8 \times 10^{-3}$; $k_2' = 0.035 \times 10^{-3}$; $k_3 = 4.0 \times 10^{-3}$; $k_4 = 1.0 \times 10^{-3}$; $k_{cn} = 2.5 \times 10^{-3}$ l mol^{-1} min^{-1}.