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Amine Cured Epoxide Networks: Formation, Structure, and Properties[†]

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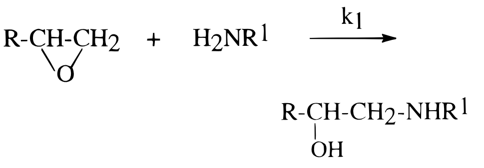
ABSTRACT: Various types of epoxide−amine networks based on diglycidyl ether of Bisphenol A (DGEBA), diglycidylaniline (DGA), or TGDDM were prepared, and the effect of the reaction mechanism on network formation, its structure, and properties was investigated. Structure evolution was followed, and fraction of the sol, equilibrium rubbery modulus, and glass transition temperature of nonstoichiometric networks were determined as a function of composition. Short-range cyclization was proved to be the main factor governing formation and structure of DGA-based networks, resulting in a nonnegligible sol fraction of the stoichiometric system. In contrast, the substitution effect in amine determines the structure evolution in the DGEBA−diamine networks. A theoretical model for formation of DGA−amine networks was developed, taking into account the full complexity of the reaction mechanism: cyclization, interdependent reactivity of epoxy and amine groups, homopolymerization by etherification, and ionic polymerization as well as formation of reactive intermediates. A reasonable agreement with experimental data in both amine and epoxide excess was obtained.

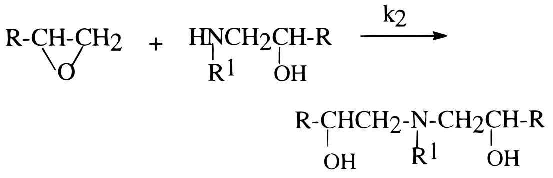
Introduction

Curing of epoxy resins is one of the most common procedures in synthesis of thermosetting materials. Because of their excellent mechanical and thermal properties, epoxide networks are used in a wide range of applications covering composite materials, adhesives, coatings, materials for encapsulation, etc. Polyfunctional amines, acid/anhydrides, polycarboxylic acids, or phenolics are usually employed as curing agents.[1] The epoxy−amine networks are the most widespread systems. They are based mainly on two types of resins: diglycidyl ether of Bisphenol A (DGEBA) and a diglycidylamine, e.g., *N*,*N*,*N*′,*N*′-tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM), used particularly in high-performance composites. They have been extensively studied and the results reviewed.[2] However, there is still lack of knowledge about relations between the reaction mechanism, network structure, and properties of the epoxy−amine networks.

The reaction mechanism of the system epoxide−amine involves several particular reactions: addition of amine to the epoxy group, homopolymerization of epoxide by etherification or ionic polymerization, cyclization, and various side transformation and degradation reactions.[1,3,4] In most cases addition of an amine is the strongly predominating reaction proceeding in two steps:



$$\underset{\diagdown O \diagup}{\mathrm{R{-}CH{-}CH_2}} + \mathrm{H_2NR^1} \xrightarrow{k_1} \mathrm{R{-}\underset{OH}{\underset{|}{CH}}{-}CH_2{-}NHR^1} \qquad (1)$$



$$\underset{\diagdown O \diagup}{\mathrm{R{-}CH{-}CH_2}} + \mathrm{H\underset{R^1}{\underset{|}{N}}CH_2\underset{OH}{\underset{|}{C}}H{-}R} \xrightarrow{k_2} \mathrm{R{-}\underset{OH}{\underset{|}{C}}HCH_2{-}\underset{R^1}{\underset{|}{N}}{-}CH_2\underset{OH}{\underset{|}{C}}H{-}R} \qquad (2)$$

The rate constants are related to the functional group, primary and secondary amine. For a random reaction, i.e., at the same reactivity of both hydrogens in the primary amine group, $k_2/k_1 = {}^1/_2$ because of two hydrogens in the primary amine in contrast to one in the secondary group. These rate ratios differ by a factor of 2 from some values given in the literature, where the rate constants are related to the hydrogen of the NH group (the ratio is equal to 1 in that case). Usually the hydrogen of the secondary amine reacts slower, $k_2/k_1 < {}^1/_2$, and amines show the so-called negative substitution effect ρ ($=k_2/k_1$), characterizing the dependence of reactivity of a functional group on the reaction state of a neighboring functionality. A detailed analysis of the substitution effects was given by Miller and Macosko.[5]

Scheme 1[a]

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

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

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

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

[a] A_i and E_i are respectively amine group and diepoxy unit with i reacted functionalities.

DGEBA-based epoxides show a simple mechanism in the reaction with an amine at stoichiometric composition or at excess amine, and the kinetics can be described by two rate constants. On the contrary, a more complex reaction mechanism was found in the case of epoxides based on diglycidylaniline (DGA). While reactivities of the epoxy groups in DGEBA are the same and independent, the epoxy groups in DGA exhibit a positive substitution effect.[6] As a result, at least four rate constants are necessary for description of the kinetics of the DGA−amine addition reaction (see Scheme 1). Homopolymerization of epoxides takes place mainly with excess of epoxide, at high temperature and in the

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[†] Dedicated to Prof. Karel Dušek to his 70th birthday.

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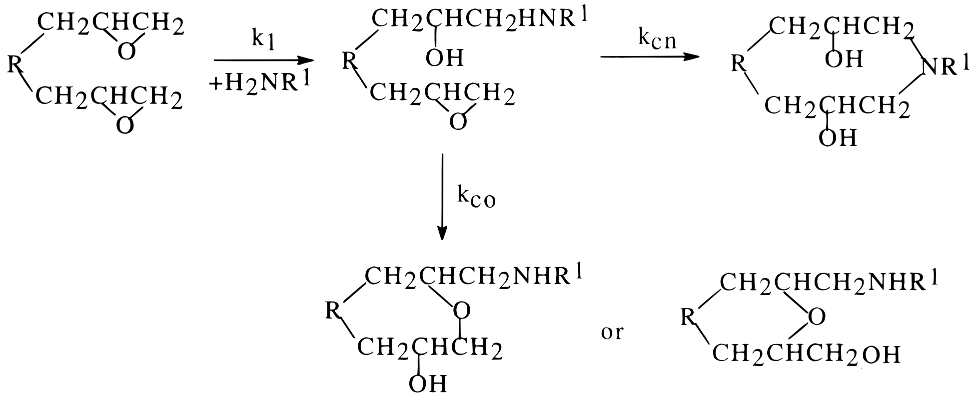
Scheme 2



presence of a catalyst. The polymerization is initiated by the OH group formed in situ in the reaction with amines—polyetherification—or by interaction with an ionic catalyst—ionic polymerization.[3,7,8] Due to the presence of nitrogen in the diepoxide, homopolymerization is more significant in DGA-based epoxides. Moreover, in contrast to DGEBA, an extensive cyclization forming small six- to eight-membered rings was detected in the reaction of DGA with amines[9,10] (Scheme 2) by intramolecular addition or etherification.

Nonlinear polymerization and the network buildup is described by statistical or kinetic theories of network formation[2] predicting structure evolution and gelation as a function of conversion. Theoretical model for curing of DGEBA with diamines based on the theory of branching processes (TBP) was developed by Dušek et al.[11] Simple kinetics involving the addition reactions 1 and 2 was assumed, and the value of the substitution effect ρ in an amine was the only input parameter. The model properly predicts experimental molecular weights, gel point, sol fraction, and cross-linking density of networks produced with a stoichiometric or excess amount of amine.[12,13] Etherification was taken into account in subsequent statistical treatments.[14−17] However, for reactions with long-range correlation in time (substitution effect, initiation) and space (cyclization, excluded volume), statistical methods based on TBP are only approximate. A rigorous approach to treatment of an initiated type of polymerization like etherification is presented by the kinetic method used by Bokare and Gandhi[18] in the pregel stage or by combination of statistical and kinetic methods.[19,20] The combined approach was applied to homopolymerization assuming a reaction mechanism with initiation and formation of several oligomeric series.[21] Plausible adjustment and combination of rate constants gives a partial agreement with experimental critical conversions. Unfortunately, lack of input kinetic parameters prevented a reliable comparison of this approach with experiment. Riccardi and Williams,[22] however, showed that there are only small deviations between the combined and statistical model considering the directionality effect in the network buildup.

Formation of DGA-based epoxide networks, such as TGDDM−amine, was theoretically described by several authors[17,18,23] using a simple reaction mechanism neglecting cyclization and a dependent reactivity of epoxy groups. Zelenka et al.[24] assumed an adjustable apparent intermolecular conversion of minority groups to fit experimental data in order to implicitly consider the intramolecular reaction. Short-range cyclization and interdependent reactivity of functional groups was taken into account in our model.[25]

In the present paper, various epoxy−amine networks were investigated in order to find out relations between the reaction mechanism and buildup, structure, and final properties of stoichiometric and nonstoichiometric networks. DGEBA and diglycidylaniline-based epoxies, DGA and TGDDM, were cured with amines of various structure, both aromatic and aliphatic including flexible poly(oxypropylene)diamines (Jeffamine). The critical molar ratio of functional groups for network formation, sol fraction, equilibrium modulus, and glass transition temperatures were determined. The new theoretical model was developed for formation of DGA-based epoxy−amine networks. This model, contrary to previous ones, takes into account all the complexity of the reaction mechanism including cyclization, dependent substitution effects in both components, homopolymerization by etherification or ionic polymerization, and transformation reaction of epoxide. Statistical and combined (combination of statistical and kinetic methods) approaches were used. The theoretical prediction was compared with experimental data of the networks prepared with both amine and epoxide excess, and the main factors governing network formation were determined. A question is whether cross-linking of a complex polyfunctional system can be described by the reaction mechanism and kinetic parameters determined in simple model reactions and whether combined and approximate statistical methods are applicable in the system undergoing homopolymerization.

Experimental Section

Chemicals. The epoxides diglycidyl ether of Bisphenol A (DGEBA), *N,N'*-diglycidylaniline (DGA), and *N,N,N',N'*-tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) were obtained from SYNPO a.s. Pardubice; the corresponding epoxy equivalents were determined by titration and high-performance liquid chromatography (HPLC), E_E = 171,103.5, and 113. The following amines were used as curing agents: octane-1,8-diamine (OMDA), 4,4'-diaminodiphenylmethane (DDM), 4,4'-diaminodiphenyl sulfone (DDS), *N,N'*-dimethylethane-1,2-diamine (DMEDA), *N,N'*-dimethylhexane-1,6-diamine (DMHDA), aniline, *p*-toluidine (TDA), 1,2-phenylenediamine (1,2PDA), 1,3-phenylenediamine (1,3PDA), and 2,3,5,6-tetramethyl-1,4-phenylenediamine (TMPDA). The purity of amines was >99.5% (gas chromatography, HPLC). In addition, poly(oxypropylene)diamines, Jeffamine, with distribution of functionalities were used: D400 ($M_n = 395$, amine equivalent $E_{NH} = 105.5$, $f_n = 3.75$), D2000 ($M_n = 1970$, $E_{NH} = 505$, $f_n = 3.9$), and triamine T403 ($M_n = 427$, $E_{NH} = 78$, $f_n = 5.46$).

Network Preparation. The preparation of nonstoichiometric networks in bulk or in solution was carried out in molds by heating the reaction mixture to 130−150 °C for 2−7 days. The DGEBA-DDS networks and samples with a stoichiometric composition or excess of epoxide were cured at 170 °C. A series of samples with various ratios of functional groups, r_A ($=C_{NH}/C_{epoxy}$), were prepared and subsequently extracted with dimethylformamide and diethylene glycol dimethyl ether (DEGDME). The sol fraction was determined from the weight of a dry sample before and after extraction. The critical molar ratio, r_C, of functional groups for formation of nonstoichiometric network was determined by solubility measurements as the midpoint between the last sample containing the gel and the first soluble sample. Dependence of r_C on dilution was obtained by cross-linking in the presence of 20−60 vol % of an inert solvent DEGDME. Conversion of the epoxide groups was evaluated by near-infrared spectrometry using the band at 4530 cm^{-1}.

Dynamic Mechanical Analysis. A Rheometrics system 4 apparatus was used to determine structure evolution during network formation and to characterize dynamic mechanical properties of the cured networks. Evolution of the dynamic shear modulus during polymerization at 150 °C was measured using the plate and plate geometry by oscillatory shear deformation at 1 Hz frequency. Gelation was determined by following the decreasing loss factor, tan δ, during polymerization and its frequency dependence. The gel point corresponds to the time of the frequency-independent tan δ value according to the power law of viscoelastic behavior of the networks in the critical state.[26] Equilibrium rubbery shear modulus G_e of rectangular nonextracted samples was determined at temperatures $T \geq T_g + 30$ °C by stress relaxation to equilibrium. The glass transition was characterized by T_α, i.e., temperature at the maximum of the loss shear modulus $G''(T)$ at a frequency of 1 Hz.

Results and Discussion

1. Curing and Network Formation. The structure development and network formation during cure were followed by measurements of the dynamic storage modulus $G'(t)$ and loss factor, tan δ, evolution in cross-linking of epoxy−amine systems. The rate of gelation reflects the reaction rate and the reaction mechanism determining the conversion at the gel point which is affected by both the amine and epoxide type including functionality of the system. The results reveal that the rate of the network buildup decreases in the order of amines OMDA > DDM > DDS and epoxides TGDDM > DGEBA > DGA. The gel formation of the TGDDM−DDM network is faster compared to DGEBA and DGA epoxides due to a higher functionality and correspondingly lower critical conversion.

The stoichiometric epoxy−amine networks under study could be divided into three groups according to the course of curing at 150 °C: (1) DGEBA−aliphatic amine (OMDA). Vitrification does not occur at curing temperature, and the network is fully cured in the rubbery state. (2) DGEBA or DGA−aromatic amine (DDM, DDS). The growing polymer forms the network, and after a shorter or longer postgel curing, it undergoes the glass transition. The reaction becomes diffusion-controlled and remarkably slowed. The final conversion depends on the onset of vitrification, and the full curing at 150 °C is suppressed or takes a long time. (3) TGDDM−aromatic amine (DDM, DDS). The polymer vitrifies at 150 °C in a close neighborhood of the gel point, and the conversion is low at this temperature.

2. Structure of Nonstoichiometric Networks. An ideal network without defects is formed in the alternating random reaction at full conversion of a stoichiometric mixture of reagents. All reactants are incorporated in the network, and the sol fraction, w_s, is zero. Real networks often exhibit $w_s > 0$ because of incomplete conversion, nonstoichiometric composition, distribution of functionality of the reactants, etc. A nonrandom reaction mechanism and side reactions can also result in the formation of a network with defects and affect the structure of the network, including sol fraction. Therefore, not only an accurate initial composition but also control of the reaction mechanism is necessary in order to eliminate the deleterious influences in the network formation and to achieve a network with the desired structure and properties. The effect of the reaction kinetics and mechanism on network structure is most remarkable in "imperfect" networks which are produced (a) at incomplete conversion or (b) at a stoichiometric imbalance of reagents. We have chosen the second way of introducing defects in a network and studied the influence of the reaction mechanism on the buildup and structure of nonstoichiometric networks cured to complete conversion of minority groups. The composition of an epoxide (E)−amine (A) system was characterized by the ratio of concentrations of the functional groups, NH and epoxy: $r_A = C_A/C_E$ or $r_E = 1/r_A$.

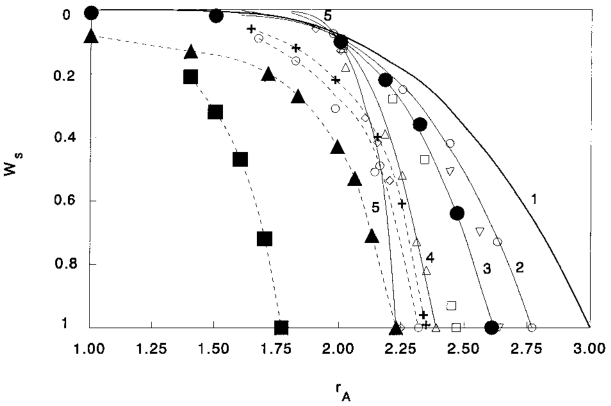


Figure 1. Sol fraction, w_s, of nonstoichiometric networks as a function of composition r_A: 1, theoretical curve for random reaction ($\rho = 0.5$); 2−5, theoretical curves for $\rho = 0.32$, 0.22, 0.10, and 0.05, respectively. Experimental: ●, DGEBA−DDM; ▲, DGA−DDM; ■, TGDDM−aniline; ○, DGEBA−OMDA; △, DGEBA−DDS; ◇, DGEBA−TMPDA; ▽, DGEBA−1,3PDA; □, DGEBA−1,2PDA; +, DGEBA−D400; ○, DGEBA−D2000. (− − −) Eye guide.

Figure 1 shows the effect of the type of epoxide and amine and the ratio of reagents r_A in excess of amine on the network buildup characterized by fraction of the sol. The sol fraction of the epoxide−amine networks increases with increasing stoichiometric imbalance of the system, and finally, no gel is formed ($w_s = 1$) at the critical mole ratio of reagents $(r_A)_C$. For the random alternating reaction of an epoxide with an amine, the epoxy groups are completely reacted ($\alpha_E = 1$) at excess amine. The following relations hold:[27]

$$(\alpha_A)_C(\alpha_E)_C = 1/[(f_A - 1)(f_E - 1)] \tag{3}$$

$$r_A = C_A/C_E = \alpha_E/\alpha_A = 1/\alpha_A \tag{4}$$

$$(r_A)_C = (f_A - 1)(f_E - 1) \tag{5}$$

where $(\alpha_E)_C$ and $(\alpha_A)_C$ are the conversions of the epoxy groups and NH functionalities at the gel point, and f_A and f_E are weight-average functionalities of the amine and epoxide, respectively.

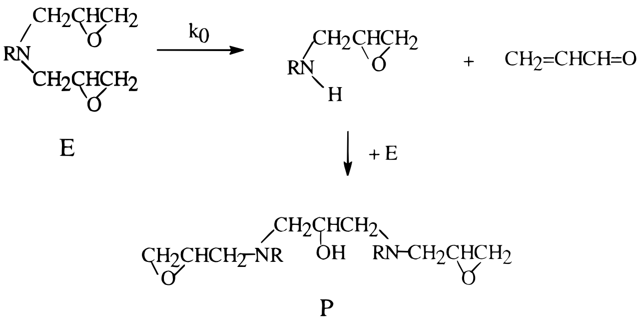
The critical mole ratio of functional groups, $(r_A)_C$, is a very important parameter for characterizing the formation of a network. In the case of the alternating random reaction of statistically equivalent systems diepoxide−tetrafunctional diamine or tetraepoxide−bifunctional monoamine, the critical ratio is $r_C = 3$ (cf. eq 5) as shown by the theoretical curve 1 in Figure 1. The experimental data in Figure 1 deviate from the theory for the random system ($\rho = 0.5$), the sol fractions being higher for a given ratio r_A and the critical value $(r_A)_C$ lower than the theoretical ones. The deviations are most striking in the critical area near the point of gelation. The full-points data reveal a different structure of networks formed from three types of epoxides: DGEBA−DDM (●), DGA−DDM (▲), and TGDDM−aniline (■). While the sol fractions of DGEBA networks closely approach the ideal curve at a low imbalance, $r_A < 2$, the DGA-based networks differ significantly from theory even in the near-stoichiometric composition, exhibiting a relatively high sol fraction at $r_A = 1$. Experimental deviations from the curve 1 and differences between DGEBA−amine and DGA or TGDDM−amine networks reflect the different reaction mechanism of curing of both types of epoxides.

In nonstoichiometric networks with epoxide in excess the sol fraction does not increase at complete conversion of epoxy groups because of homopolymerization; however, the reaction at a sufficiently high temperature necessary to reach complete conversion usually results in polymer degradation[4] competing with network formation and deteriorating the network structure.

Differences in the network buildup and structure can be predicted theoretically, taking into account the relevant theoretical model of the network formation involving the complex reaction mechanism of the epoxy−amine system. By comparing experiment with theory, the effects governing the network formation and structure differences in various networks can be determined and quantified.

3. Theoretical Model for Formation of DGA−Amine Networks. Our theoretical statistical model developed earlier[25] for the DGA−amine networks took into account short-range cyclization by intramolecular addition (Scheme 2, rate constant k_{CN}) and the interdependent reactivity of epoxy and amine groups in addition reactions (Scheme 1, k_1−k_4, and k_1', k_2' for an autocatalyzed reaction and that catalyzed with a tertiary amine[6]). The model properly described formation of networks with amine in excess. For a general description of the networks including those with epoxide excess, full complexity of the reaction mechanism was taken into account in the presented modified model in which homopolymerization by etherification (k_E) and ionic polymerization was considered. The ionic homopolymerization includes initiation (k_i), propagation (k_p) under formation of several oligomeric series,[8] and transfer (k_{tr}) followed by termination (k_T). The formation of reactive intermediates and the OH-containing diepoxide P (Scheme 3, k_0) were also taken into account.[8,28] Decisive is inclusion of the intramolecular etherification (Scheme 2, k_{CO}) which is the predominant reaction at epoxide excess.[28]

Scheme 3



The input parameters of the theory were the rate constants determined experimentally using model reactions[6,8,28]: $k_0 = 4 \times 10^{-5}$ L mol^{-1} min^{-1}, $k_1 = 1.2 \times 10^{-2}$ L^2 mol^{-2} min^{-1}, $k_2 = 5.2 \times 10^{-3}$ L^2 mol^{-2} min^{-1}, $k_3 = 2.6 \times 10^{-2}$ L^2 mol^{-2} min^{-1}, $k_4 = 2.6 \times 10^{-3}$ L^2 mol^{-2} min^{-1}, $k_1' = 5.2 \times 10^{-4}$ L^2 mol^{-2} min^{-1}, $k_2' = 2.3 \times 10^{-4}$ L^2 mol^{-2} min^{-1}, $k_{CN} = 2.4 \times 10^{-2}$ L mol^{-1} min^{-1}, $k_{CO} = 1.5 \times 10^{-3}$ L mol^{-1} min^{-1}, $k_E = 1 \times 10^{-5}$ L^2 mol^{-2} min^{-1}, $k_i = 5 \times 10^{-6}$ L mol^{-1} min^{-1}, $k_p = 4 \times 10^{-4}$ L^2 mol^{-2} min^{-1}, $k_{tr} = 1 \times 10^{-3}$ L^2 mol^{-2} min^{-1}, $k_T = 4 \times 10^{-5}$ L^1 mol^{-1} min^{-1}, which are valid for $T = 140$ °C. The rate constants for addition reactions and cyclization were determined at 100 °C, and the corresponding activation energies were used for data recalculation: 60 kJ/mol[29] for addition reactions (k_1−k_4 and k'_1, k'_2), 73 kJ/mol for cyclization (k_{CN}, k_{CO}).[30] The rate constants were expressed from rate equations including concentration of the catalyst: OH groups or a tertiary amine.[6,8]

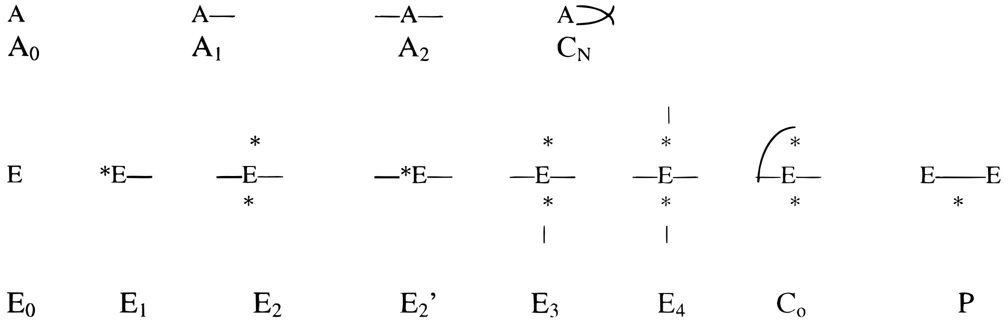
These rate constants (calculated for 100 °C) were already used to predict formation of linear bi-bifunctional polymer of DGA and aniline.[31] The theoretical model fits the experimental data of the molecular weight evolution; however, the rate constant k_4 (Scheme 1) was found to be lower by a factor 2.5 compared to the value obtained in the simple model reaction. It is assumed that the reaction of fully substituted reagents (substituted epoxide and amine units $E_1 + A_1$ in Scheme 1) is sterically hindered in polyfunctional systems, which is not properly modeled in simple model reactions. The value k_4 obtained for the bifunctional model was used in the model for network formation. No adjustable parameters were employed.

Network formation was treated using the described reaction mechanism by both the statistical model and the more rigorous method based on combination of kinetic and statistical approaches. The combined model consists of a kinetic generation of linear clusters which are in the next step recombined using a statistical method to form a network. The approach is based on the assumption that there are groups in a polyfunctional monomer that can react independently of the state of other groups. In this case, a tetrafunctional monomer with two independent bifunctional units can be split into two bifunctional monomers whose linear polymerization can be kinetically solved. The model is described elsewhere and is available on request.

3.1. Statistical Method. The statistical approach of the theory of network formation based on TBP employs structural units in various reaction states to build up polymer structure at any moment of the reaction. The model for description of the DGA−diamine network used tetrafunctional diepoxide units E_i to take into account homopolymerization and bifunctional amine fragments A_j (with one NH_2 group) because amine groups in a diamine are independent (Scheme 4).

The full structure description including all reaction states of intermediates P and ionic species is given elsewhere.[28]

Scheme 4[a]



[a] A_i and E_i represent the rection states of units with *i* reacted functionalities; C_N, C_O are corresponding 8- and 7- or 6-membered cycles (see Scheme 2); P is the reactive intermediate product (see Scheme 3). (—) Reacted functionality (NH or epoxy group), (*) OH group formed in situ or O^- group formed by anionic initiation, (—*) reacted OH or O^- groups.

The number of bonds issuing from a diamine and diepoxide units is given by probability generating function (pgf).[2] The pgfs for units in the root are

$$F_{0A}(z) = (a_0 + a_1 z_E + a_2 {z_E}^2 + c_N {z_C}^2)^2 \qquad (6)$$

$$F_{0E}(z) = n_{EE}[e_0 + e_1(p_A z_A + p_E z_E) + e_2({p_A}^2 {z_A}^2 + p_A p_E z_A z_E + {p_E}^2 {z_E}^2) + e_2'(p_A z_A z_E + p_E {z_E}^2) + e_3(p_A {z_A}^2 z_E + p_E {z_E}^3) + e_4(p_A {z_A}^2 {z_E}^2 + p_E {z_E}^4) + c_O(p_A z_A z_C + p_E z_E z_C)] + n_{EP}[p_0 + p_1(p_A z_A + p_E z_E) + p_2({p_A}^2 {z_A}^2 + p_A p_E z_A z_E + {p_E}^2 {z_E}^2) + p_2'(p_A z_A z_E + p_E {z_E}^2) + p_3(p_A {z_A}^2 z_E + p_E {z_E}^3) + p_4(p_A {z_A}^2 {z_E}^2 + p_E {z_E}^4) + p_5(p_A {z_A}^2 {z_E}^3 + p_E {z_E}^5)] \qquad (7)$$

where a_i, e_i, and p_i are mole fractions of amine, diepoxide, and P units, respectively, with *i* reacted functionalities; c_N and c_O are fractions of the eight-membered and seven- or six-membered ring, respectively, n_{EE} and n_{EP} ($= 1 - n_{EE}$) are fractions of the diepoxide and P units; p_A and p_E are probabilities of epoxide–amine addition reaction and homopolymerization (etherification or ionic homopolymerization) given by corresponding rate constants and concentration of units; *z* is a dummy variable indicating direction of a bond, and hence z_A, z_E, and z_C indicate a bond issuing to unit A, E, or cyclic unit, respectively.

The pgfs of units in higher generations, i.e., those of already connected with a bond, are derived by differentiation from $F_O(z)$:[2]

$$F_{KL}(z) = F_{0L}^{LK}(z)/F_{0L}^{LK}(1)$$

where $F_{KL}(z)$ is the pgf for unit L bonded to unit K in a previous generation:

$$F_{0L}^{LK}(z) = \partial F_{0L}/\partial z_K$$

The distribution of units during the reaction was calculated using the complex kinetic scheme (Schemes 1–3 including homopolymerization[28]). The corresponding set of differential equations is given in ref 28, and the program is available from the author.

Condition for the point of gelation and statistical structure parameters, sol fraction w_s and concentration of elastically active chains ν_e, were calculated using the pgf formalism.[12]

Condition for gelation for instance is given by eq 8:

$$F_{EE}^{EE}(1) + F_{EA}^{AE}(1)[F_{AE}^{EA}(1)(1 - F_{EE}^{EE}(1)) + F_{EE}^{EA}(1)F_{AE}^{EE}(1)] = 1 \qquad (8)$$

4. Factors Governing Network Formation and Structure. 4.1. Different Reactivity of Functional Groups. a. DGEBA–Diamine Networks. The influence of the amine type and of the substitution effect in an amine on the sol fraction of the nonstoichiometric DGEBA–diamine networks is shown also in Figure 1. The theoretical curves 1–5 calculated under assumption of the simple alternating addition reaction correspond to $\rho = 0.5–0.05$. Because of a negative substitution effect, the reaction of primary amine is preferred to form linear chains. Branching and cross-linking through a reaction of a secondary amine group are delayed, and the gel point is shifted to a higher conversion or lower critical ratio, the sol fraction being higher for a given composition. At the composition $r_A = 1.97$, the sol fraction is independent of ρ, and at a lower excess of an amine, the influence of the negative substitution effect is just the opposite. The sol fraction is lower compared to the random case. The negative substitution effect leads to a relatively higher conversion of the monomer because of preference of the reaction of the primary amine group in the unreacted monomer to the reaction of secondary amine. As a result, long linear chains are formed with residing functional secondary amine groups. At a ratio $r_A < 2$, epoxy groups are available in the system to make a cross-link with the secondary amine even after all the primary amines have been consumed.

The experimental data points for DGEBA–diamine networks (open points) approach the theoretical curve 1 for the random reaction in the composition range $1 < r_A < 2$, as discussed above, with the exception of those cured with poly(oxypropylene)diamines D400 and D2000. Again, deviations from the random case and differences among various networks become significant at higher stoichiometric imbalance, $r_A > 2$. The figure reveals an increase in w_s for a given r_A and a decrease in the critical ratio $(r_A)_C$ in the series of amines: OMDA–1,3PDA–DDM–1,2PDA–DDS–TMPDA. This is an influence of different reactivities of amine groups. The ratio of rate constants ρ for the studied systems was determined from the corresponding critical ratios using TBP. Both $(r_A)_C$ and ρ are given in Table 1. The ρ values are somewhat lower than those given in the literature.[1,32] However, literature data show a scatter of results not

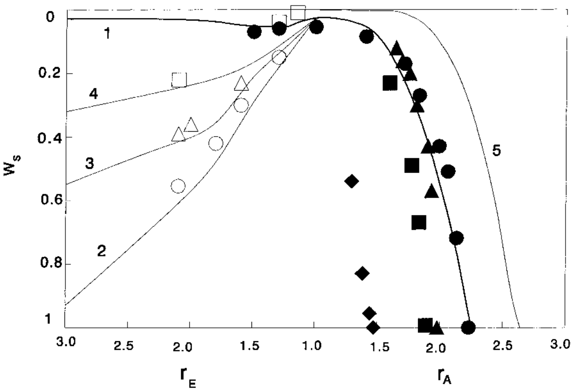


Figure 2. Sol fraction, w_s, of the DGA−diamine networks as a function of composition r_A and r_E: 1, theoretical model for DGA−DDM; 2−4, theory for $\alpha_{ET} = 0$, 0.35, and 0.65, respectively; 5, theory−without cyclization. Experimental: ●, DGA−DDM; ▲, DGA−DDS; ■, DGA−DDS, 20% diluent; ◆, DGA−TMPDA. Literature data:[24] ○, $\alpha_{ET} = 0$; △, $\alpha_{ET} = 0.35−0.38$; □, $\alpha_{ET} = 0.63−0.66$.

only due to a different definition of rate constants (see Introduction) but also due to different techniques used to determine the substitution effect. The effect of temperature[33] and catalysis (autocatalytic and noncatalyzed reaction) on the ratio of rate constants is also mentioned and not always specified. The ρ values evaluated for amines in the DGEBA−diamine networks (DGEBA−OMDA, DGEBA−DDM, DGEBA−DDS, and DGEBA−TMPDA) were used for calculation of theoretical dependences of sol fractions in Figure 1, curves 2−5. The figure reveals a good fit of theoretical curves with experimental data of the corresponding networks. The results prove that the network formation and the structure characterized by the critical ratio and the sol fraction are influenced by factors leading to an increase in the negative substitution effect: (a) lowering of amine basicity (aromatic versus aliphatic amines or DDS versus DDM), (b) increasing steric hindrance on nitrogen atom of the diamine in the series 1,3PDA < 1,2PDA < TMPDA. A very strong substitution effect ($\rho = 0.06$) was found in the case of sterically hindered TMPDA. The influence of the amine structure on kinetics and the ratio of rate constants ρ was recently discussed in detail by Girard-Reydet et al.[32] They interpreted the relatively high negative substitution effect in DDS, proved also in our results, by a low number of stable configurations afforded by SO_2 group. However, the absolute value $\rho = 0.22$ for DGEBA−DDS was higher compared to ours. Also, Bidstrup−Macosko[34] and Riccardi−Williams[35] found the critical ratio $r_C = 2.50$ or 2.60 corresponding to $\rho = 0.17$ and 0.21, in contrast to our values, $r_C = 2.37$ and $\rho = 0.10$. On the other hand, Dobáš et al.[36] obtained $\rho = 0.11$ using kinetic measurements.

A relatively high sol fraction in the networks cross-linked with diamines D400 and D2000 even in the composition region $r_A < 2$ is a result of a cyclization reaction (see below) and of distribution of functionality in amines including monofunctional molecules.

b. DGA−Diamine Networks. DGA-based networks show larger deviations from the random reaction (see Figure 1). In particular, a relatively high sol fraction at $r_A < 2$ is typical of these systems. Prediction of the theoretical model and experimental data for the DGA−DDM networks with both an amine and epoxide excess are given in Figure 2. The models based on statistical and combined approaches yield the identical prediction at composition $r_A > 1$ and differ very slightly at $r_E > 1$ for given kinetic rate constants (relatively slow etherification with respect to addition, $k_E/k_{\text{addition}} \sim 0.004−0.0004$, and fast transfer in the ionic polymerization, $k_{tr}/k_p = 2.5$). According to the theory (curve 1), the sol fraction exhibits a local minimum at the stoichiometric composition ($w_s = 0.03$). In the networks with a high epoxide excess ($r_E > 2$), the sol fraction decreases to lower values; however, still $w_s > 0$. One can see that the model satisfactorily describes very complex formation of the DGA−DDM network characterized by the experimental sol fraction data points both at amine and epoxide excess (●). In addition, some more experimental data were taken from literature[24] for the networks with epoxide excess and various extents of homopolymerization (open points). The extent of etherification α_{ET} was calculated by the authors from the measured conversion of epoxy groups assuming that the etherification starts after consumption of all NH functionalities. The data roughly fit the theoretical prediction for the sol fraction at $\alpha_{ET} = 0$, 0.35, and 0.65 (curves 2−4), where α_{ET} was calculated in the same way as by Zelenka.[24]

Experimental data for other DGA−diamine networks in Figure 2 can be accounted for as follows. The more negative substitution effect in DDS (▲) and TMPDA (◆) with respect to DDM results in higher w_s and lower critical ratio of the corresponding networks. The shift of w_s curve to lower r_A for a dilute system DGA−DDS (■) is brought about by a higher extent of cyclization.

4.2. Cyclization. A comparison of theoretical prediction with experiment proves that DGA−diamine network formation is mainly affected by short-range cyclization. Theoretical curve 5 in Figure 2 describing a network without cyclics significantly deviates from the experimental data, and no sol fraction is predicted for the stoichiometric composition. Formation of cycles can account for a relatively high fraction of the sol in completely reacted stoichiometric networks and at epoxide excess. The OH-containing cycles (cf. Scheme 2) are gradually incorporated in the network by etherification reaction at epoxide excess, but due to a kinetically preferred intramolecular etherification,[6,28] there still remains a significant sol fraction of unbound cyclic products even at full conversion. Extent of cyclization was found to increase with increasing temperature because of higher activation energy with respect to intermolecular addition reaction.[30]

The intramolecular reaction diminishes the effective functionality of the system and gelation is shifted to a higher conversion or to a lower critical ratio. Because dilution promotes cyclization, the critical ratio decreases with increasing dilution $1/C$ (C is a concentration of functional groups)[25] as shown in Figure 3. The slope of the dependence $(r_A)_C$ vs $1/C$ characterizes a tendency to cyclization in the pregel stage. The critical ratio $(r_A)_C$ of the systems DGEBA−OMDA, DGEBA−DDM, and DGEBA−DDS is independent of dilution, thus revealing the absence of cyclization during the network formation in agreement with literature.[11] The DGEBA−aromatic amine is a stiff polymer preventing ring closure; however, even curing with a flexible aliphatic amine OMDA shows no cyclization. Only cross-linking with long flexible diamines D400 (curve 3), D2000, and T403 leads to an extensive cyclization, which is partly a reason for deviations of experiment from the theoretical prediction in Figure 1. In contrast, in the case of diglycidylamine

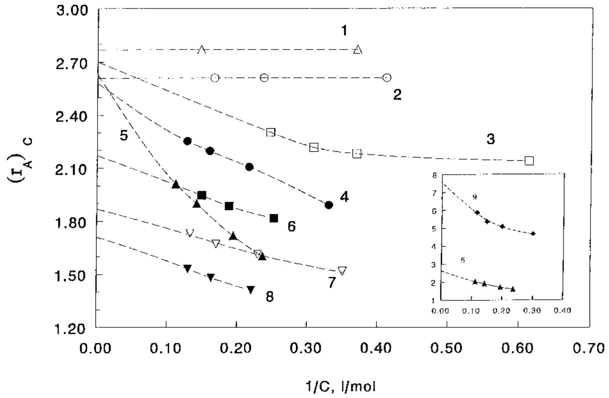
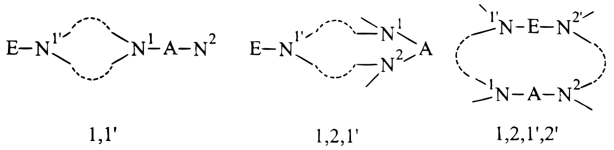


Figure 3. Critical molar ratio of functional groups $(r_A)_C$ as a function of dilution of the system during cross-linking, $C = ([NH] + [epoxy])/2$. 1, DGEBA−OMDA; 2, DGEBA−DDM; 3, DGEBA−D400; 4, DGA−DDM; 5, DGA−OMDA; 6, DGA−DDS; 7, TGDDM−aniline; 8, DGA−TMPDA; 9, TGDDM−DDM.

Scheme 5



derivatives (DGA, TGDDM), the critical ratio decreases with dilution, proving that cyclization is significant even when curing with aromatic amines. The high tendency to form cycles corresponding to the steep slope in Figure 3 was observed mainly in the DGA−OMDA network. Higher flexibility of aliphatic amine OMDA in comparison with DDM and DDS enables formation of two types of small cycles shown in Scheme 5. In addition to the smallest eight-membered ring of the type 1,1′, also the larger 17-membered ring 1,2,1′ could be formed by intramolecular reaction of DGA with both primary amine groups of the diamine. Another type of small cycles -1,2,1′,2′- is possible in TGDDM networks.

The extent of short-range cyclization is affected by the substitution effect in amine. The negative substitution effect makes slower the closure of the eight-membered ring by reaction of the secondary amine (see Scheme 2), and hence intermolecular reaction of the second epoxy group with a primary amine is preferred. As a result, the extent of cyclization decreases (cf. decrease in the slope in Figure 3) in the series of the networks DGA−DDM > DGA−DDS > DGA−TMPDA due to the decreasing relative rate of the secondary amine group in the corresponding diamines. This influence was also proved by comparing the cure of TGDDM with aniline and with bis-secondary amines, *N*,*N*′-dimethylhexane-1,6-diamine (DMHDA) and *N*,*N*′-dimethylethane-1,2-diamine (DMEDA), where the substitution effect is absent. The bis-secondary amines close the rings 1,2,1′ or 1,2,1′,2′ (DMHDA), and the tendency to cyclization is higher compared to TGDDM−aniline networks because of the substitution effect in aniline. Moreover, the extent of cyclization increases with the monomer functionality. A very steep dependence of r_C on dilution was found in the case of networks DGEBA−T403 and TGDDM−DDM (see details in Figure 3, where TGDDM−DDM is compared with DGA−OMDA).

The effect of cyclization could be eliminated by extrapolation of r_C values to zero dilution, $1/C \to 0$. For extrapolation, the dependence r_C^{-1} vs $1/C$ was used, which is linear according to the theoretical model.[25] The extrapolated critical ratio $(r_C)_{ext}$ (see Table 1) for DGA−DDM agrees with the theoretical critical ratio predicted for the reaction without cyclization in Figure 2 (curve 5). Because of elimination of the cyclization influence, $(r_C)_{ext}$ is determined mainly by different reactivity of functional groups. However, using a given diamine, the $(r_C)_{ext}$ values are lower for the DGA−diamine network than for the corresponding DGEBA−diamine system (cf. Table 1). It follows that ρ for a diamine is not a characteristic constant but depends on the reaction partner, epoxide, and its reaction state because of interdependence of the reactivities. Also, a dependence of ρ on temperature[33] or solvent[37] was reported.

Table 1. Parameters Characterizing Formation of Epoxide−Amine Networks

network	$(r_c)_{bulk}$	$(r_c)_{ext}$[a]	ρ[b]
DGBA−OMDA	2.77	2.77	0.32
DGEBA−DDM	2.61	2.61	0.22
DGEBA−DDS	2.37	2.37	0.10
DGEBA−1,3PDA	2.65	2.65	0.28
DGEBA−1,2PDA	2.48	2.48	0.16
DGEBA−TMPDA	2.22	2.22	0.06
DGEBA−D400	2.30	2.70	
DGEBA−D2000	2.32	2.78	
DGEBA−T403	3.91	4.30	
DGA−OMDA	2.00	2.63	
DGA−DDM	2.25	2.58	
DGA−DDS	1.96	2.17	
DGA−TMPDA	1.45	1.71	
TGDDM−DMEDA	2.50	2.65	
TGDDM−DMHDA	2.45	2.66	
TGDDM−aniline	1.73	1.87	
TGDDM−pTDA	1.69	1.85	
TGDDM−DDM	5.90	7.55	

[a] Value r_C extrapolated to $1/c \to 0$. [b] $\rho = k_2/k_1$, calculated from r_c, rate constants related to the functional group.

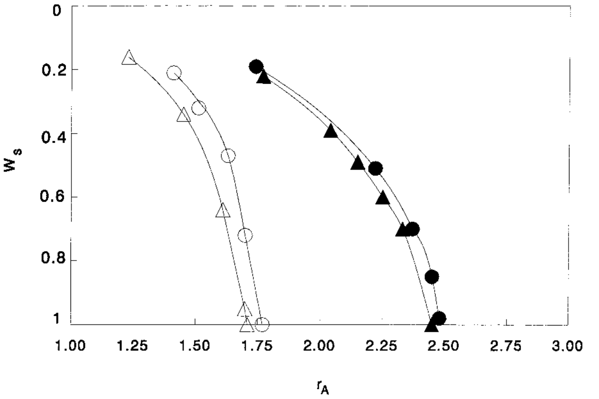


Figure 4. Sol fraction, w_s, of nonstoichiometric TGDDM−amine networks as a function of composition r_A: ○, aniline; △, pTDA; ●, DMEDA; ▲, DMHDA.

c. TGDDM−Amine Networks. A striking difference in network formation from TGDDM was found by using primary monoamines, aniline and *p*-toluidine (TDA), or bis-secondary diamines (DMHDA, DMEDA) (see Figure 4). The negative substitution effect in primary amines accounts for a higher sol fraction and lower critical ratios in the corresponding networks compared to those cured with bis-secondary amines, where the reactivities of the NH groups are independent.

4.3. Distribution of Functionality of Monomers. The networks formed from tetrafunctional epoxide TGDDM cured with bifunctional amines are the least perfect in Figure 1. The sol fraction in the TGDDM−

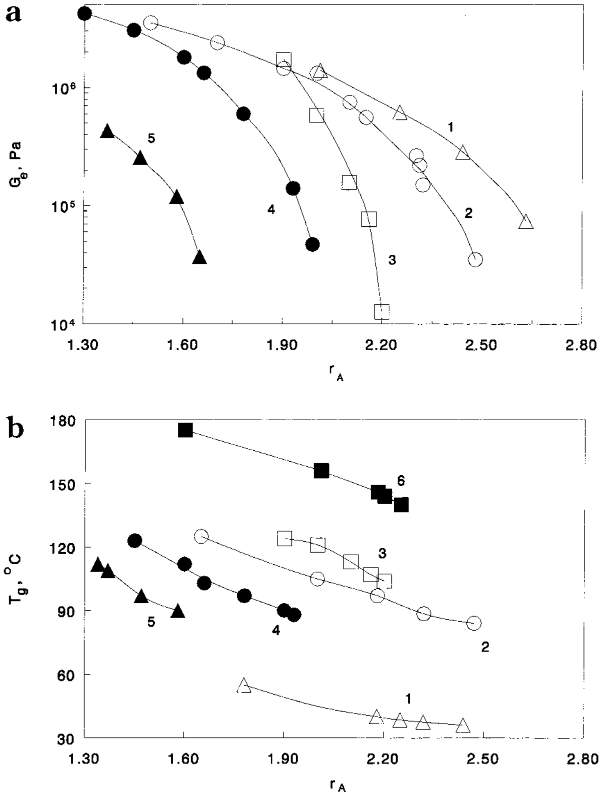


Figure 5. (a) Rubbery equilibrium shear modulus, G_e, and (b) glass transition temperature, T_g, of nonstoichiometric networks as a function of composition r_A: 1, DGEBA−OMDA; 2, DGEBA−DDM; 3, DGEBA−TMPDA; 4, DGA−DDM; 5, TGDDM−aniline; 6, DGEBA−DDS.

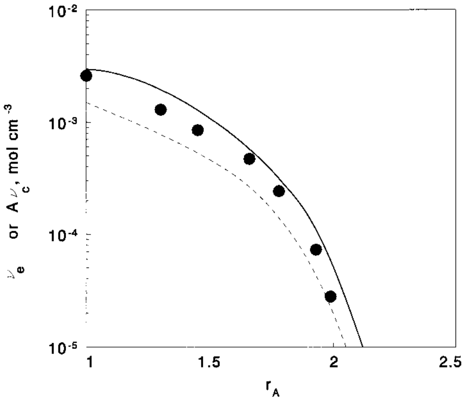


Figure 6. Cross-linking density of the DGA−DDM networks as a function of composition theory: (—) $A = 1$ (affine model), (- - -) $A = (f_e - 2)/f_e$ (phantom model), (●) experimental.

aniline network is much higher compared to the "statistically equivalent" model DGA−DDM. This is a result of distribution of functionality in TGDDM and the presence of a low-functional monomer. Hence, the system gels at a higher conversion and lower critical ratio.

Weight-average of functionality of TGDDM, $f_{Ew} = 3.65$, was determined by gelation experiments from the value of the critical ratio according to eq 9. TGDDM was cured with bifunctional bis-secondary amines DMEDA and DMHDA, and the critical ratios were extrapolated to zero dilution; $(r_A)_{C,ext}$ are given in Table 1.

$$(r_A)_{C,ext} = (f_{Ew} - 1)(f_A - 1) \qquad (5a)$$

$$f_{Ew} = (r_A)_{C,ext} + 1 \qquad (9)$$

The equation for random reaction could be used as there is no substitution effect in the bis-secondary amines, and the cyclization was eliminated by extrapolation to zero dilution. The substitution effect of epoxy groups does not affect the gelation point at amine excess (all epoxy groups are reacted), and homopolymerization can be neglected at this composition.[6,28]

5. Network Properties. Differences in the reaction mechanism and the network structure due to the type of reagents are reflected in properties of networks. We have measured the glass transition temperature and equilibrium rubbery modulus corresponding to cross-linking density of the networks. Both modulus and T_g decrease in Figure 5 with increasing imbalance of stoichiometry. The dependences of moduli (Figure 5a) closely resemble those of the sol fractions, revealing that the same factors are operative in controling the network cross-linking density. The influence of the reaction mechanism is crucial at a high stoichiometric imbalance. At amine excess, $r_A > 2$, the modulus decreases for a given composition in the series of networks DGEBA−OMDA > DGEBA−DDM > DGEBA−TMPDA with the increasing substitution effect of amine. Also, cyclization results in decreasing cross-linking density in the DGA−DDM network, and lower functionality accounts for the low modulus of the TGDDM−aniline network. T_g of various epoxide networks was successfully predicted by Bellenger et al.[38] using the DiMarzio approach to the effect of cross-linking density and assumption of additivity of molar contributions of constitutional units (copolymer effect). This approach can describe the results in Figure 5b by differences in the polymer backbone structure[39] in DGEBA-based networks due to high polarity (DGEBA−DDS), segment stiffness (DGEBA−TMPDA), and flexibility (DGEBA−OMDA). Fine structure differences because of the reaction mechanism do not significantly affect glass transition temperature.

Concentration of elastically active chains (cross-linking density) in the DGA−DDM network was calculated using the theoretical model and compared with experimental data in Figure 6. The experimental cross-linking density ν_e was obtained from the equilibrium shear modulus of the dry rubbery network measured at temperature $T \geq T_g + 30$ using the equation

$$\nu_e = G_e/w_g RT \qquad (10)$$

The ν_e value is assumed to be composed of contributions of permanent chemical cross-links ν_c and trapped entanglements ν_{ent}

$$\nu_e = A\nu_c + \nu_{ent} \qquad (11)$$

Front factor $A = 1$ for the affine network model with fully suppressed fluctuations of junctions of the Flory junction−fluctuation theory[40] where the contribution of entanglements is not taken into account, and $A = (f_e - 2)/f_e$ for the phantom network model with released fluctuations; f_e is the effective functionality of the cross-link.

A theoretical prediction of the concentration of elastically active chains, $A\nu_c$, for both the affine and phantom network model is given. Zelenka et al.[24] showed that the simple theory of network formation neglecting complexity of the reaction mechanism for the DGA-based networks can account for the experimental data assuming the apparent conversion as an adjustable parameter. Using the new model, a satisfactory agreement with theory is observed at excess of amine without necessity of adjusting the conversion. While the DGEBA-based networks roughly agree with the model of the affine network,[13,24] the DGA−DDM data fall between the limits for affine and phantom networks.

6. Conclusions. Investigation of nonstoichiometric epoxy−amine networks indicates that network formation and structure are strongly influenced by the reaction mechanism. The main factor governing formation of DGA-based networks is the extensive short-range cyclization. Formation of small cycles determined by model reactions was also evidenced in the network buildup. As a result, a slower gelation occurs compared to DGEBA-based networks, and a nonnegligible sol fraction of small cyclics appears even in the stoichiometric DGA−amine composition or at an epoxide excess. In contrast, the DGEBA−amine network formation and structure are mainly determined by the substitution effect in the amine; at a stoichiometric composition, the sol fraction approaches zero.

The theoretical model developed for DGA (TGDDM)−amine networks based on both statistical and combined approaches satisfactorily describes network formation in the whole composition range and predicts gelation, sol fraction, and cross-linking density. The model assumes full complexity of the reaction: cyclization, interdependent reactivity of functional groups, homopolymerization by etherification, and ionic polymerization as well as formation of reactive intermediates. In contrast to previous theoretical descriptions, predictions of the new model were compared with experimental data at both amine and epoxy excess. The results prove that the reaction kinetics determined in simple model systems is applicable in network formation. The reactivity of substituted units which is dependent on steric hindrance and decreases with increasing functionality of the system was successfully modeled using a bibifunctional system. The drawback of this model, however, is necessity of knowledge of many kinetic parameters for a studied system.

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