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J. Bauer[a]; M. Bauer[a]
[a] Institute of Polymer Chemistry "Erich Correns" Academy of Sciences of the GDR, Teltow, German Democratic Republic

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KINETIC STRUCTURAL MODEL FOR THE NETWORK BUILD-UP DURING THE REACTION OF CYANIC ACID ESTERS WITH GLYCIDYL ETHERS

J. BAUER* and M. BAUER

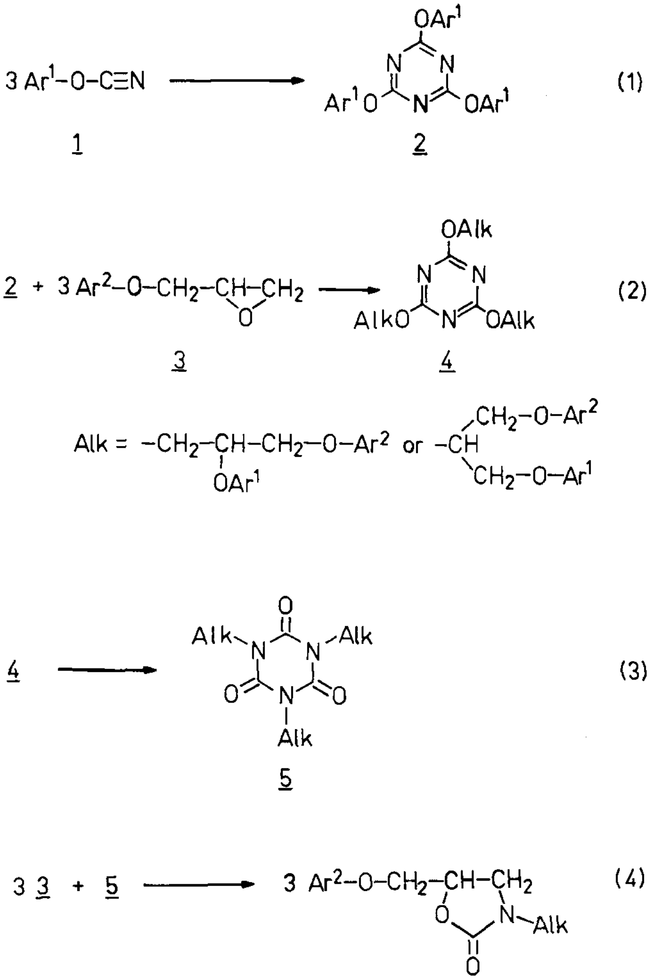
Institute of Polymer Chemistry "Erich Correns"
Academy of Sciences of the GDR
Kantstrasse 55, Teltow 1530, German Democratic Republic

ABSTRACT

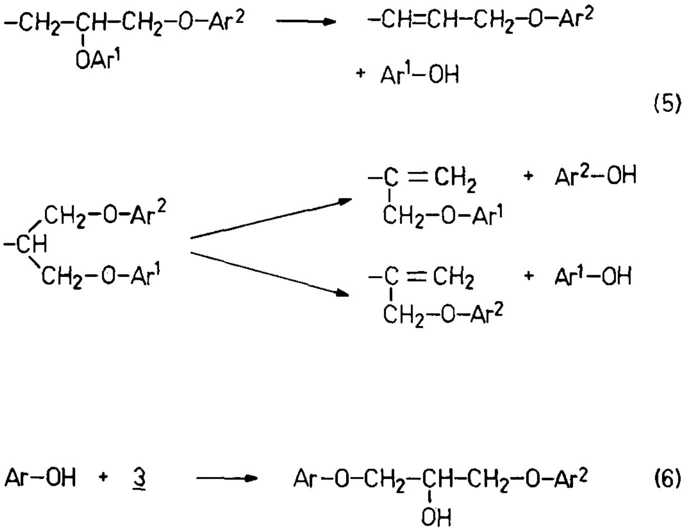
A kinetic structural model is developed to describe the reaction of difunctional aromatic cyanic acid esters with aromatic bisglycidyl ethers. Based on the main reactions found—trimerization of the cyanate groups, insertion of glycidyl ethers into the cyanurate, isomerization into isocyanurates, build-up of oxazolidinones, phenol abstraction, and phenol-glycidyl ether addition—the reaction kinetics were modeled by a system of differential equations. The resulting concentrations of the possible structural elements were combined with the help of cascade formalism to describe the statistics of the network build-up. The approach is illustrated by discussing the influence of the several reaction steps on the gelation behavior and the network structure. It was found that a broad spectrum of possible structural compositions can be simulated, especially near the equimolar initial ratio of cyanate to epoxy groups.

INTRODUCTION

The reaction of aromatic cyanic acid esters and glycidyl ethers in bulk without any additional catalysts was found to consist of six main steps [1] which are illustrated in Scheme 1.



3 Ar¹–O–C≡N
1
OAr¹
Ar¹O
OAr¹
2
(1)
2 + 3 Ar²–O–CH₂–CH–CH₂
3
OAlk
AlkO
OAlk
4
(2)
Alk = –CH₂–CH–CH₂–O–Ar² or –CH
OAr¹
CH₂–O–Ar²
CH₂–O–Ar¹
4
Alk
Alk
Alk
5
(3)
3 3 + 5
3 Ar²–O–CH₂–CH–CH₂
N–Alk
(4)



$$-CH_2-\underset{OAr^1}{CH}-CH_2-O-Ar^2 \longrightarrow -CH{=}CH-CH_2-O-Ar^2 + Ar^1-OH \quad (5)$$

$$-CH(CH_2-O-Ar^2)(CH_2-O-Ar^1) \longrightarrow -\underset{CH_2-O-Ar^1}{C}{=}CH_2 + Ar^2-OH$$

$$-CH(CH_2-O-Ar^2)(CH_2-O-Ar^1) \longrightarrow -\underset{CH_2-O-Ar^2}{C}{=}CH_2 + Ar^1-OH$$

$$Ar-OH + \underline{3} \longrightarrow Ar-O-CH_2-\underset{OH}{CH}-CH_2-O-Ar^2 \quad (6)$$

SCHEME 1.

Bauer et al. [2] showed that the gelation behavior resulting from the reaction of difunctional aromatic cyanic acid esters with difunctional glycidyl ethers is determined by Reactions (1), (2), and (5) only. The abstraction reaction (5) plays an especially important role by producing different types of substituted triazines, which shift the critical OCN conversion to higher values.

The aim of the present paper is to introduce a kinetic/structural model based on the whole of Scheme 1 (Reactions 1–6) for difunctional monomers. The approach is illustrated by studying the resulting postgel behavior and discussing the broad spectrum of possible network structures which result on solving the model equations with different kinetic reaction constants.

KINETIC MODEL

The different structural elements present during the reaction according to Scheme 1 are shown in Fig. 1. C, E, and H denote unreacted cyanate,

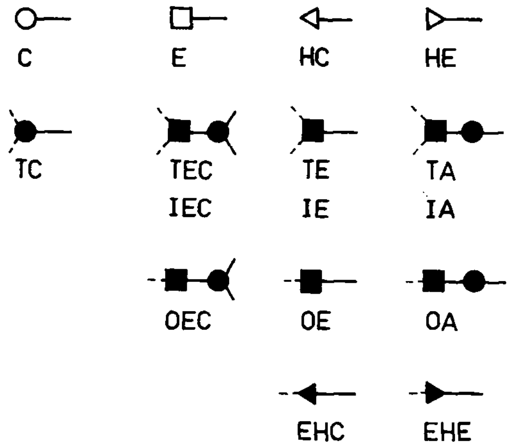


FIG. 1. Structural elements present during the reaction of cyanic acid esters with glycidyl ethers.

epoxy, and hydroxyl groups; T, I, and O are abbreviations for the different substituted triazine, isocyanurate, and oxazolidinone bridges, and EH stands for the addition product of a phenolic and an epoxy group. A model network built up from these units is illustrated in Fig. 2.

The relations between the structural elements can be formulated as in Scheme 2, where TEC, IEC, and OEC denote triazine, isocyanurate, and oxazolidinone structures with connections to the aromatic moieties Ar^2 of an epoxy and Ar^1 of a cyanate unit. TE, IE, and OE result from the abstraction of Ar^1 in TEC, IEC, and OEC, and have a connection to the aromatic moiety Ar^2 of an epoxy unit, and TA, IA, and OA are the analogous structural units with aliphatic bridges between triazine, isocyanurate, or oxazolidinone and the aromatic moiety Ar^1.

The rates of the six reactions, (1)–(6), can be formulated by using their ratios of rate constants relative to the trimerization.

(1) Trimerization of cyanate groups:

$$R_1 = 3[C][H]. \tag{7}$$

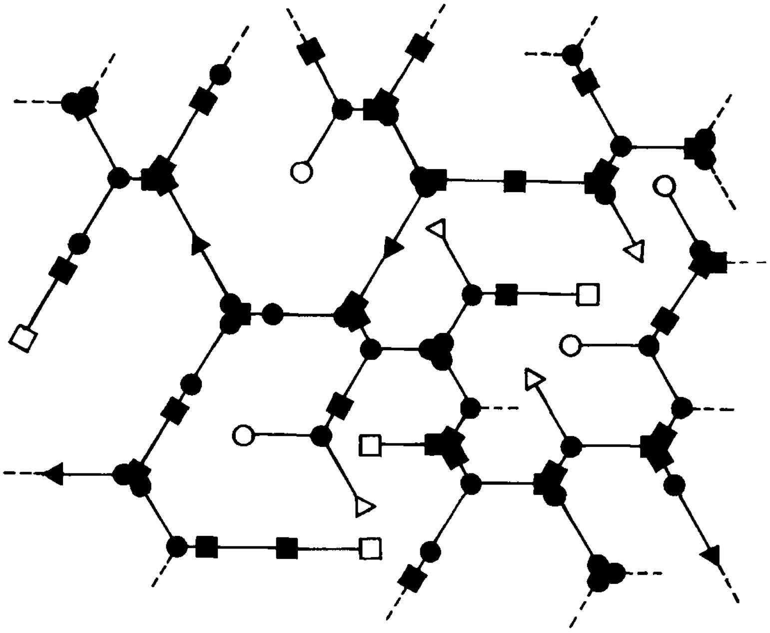


FIG. 2. Network formed by structural elements shown in Fig. 1.

The trimerization of cyanates is catalyzed by hydroxyl groups, as shown by Bauer et al. [3].

(2) Insertion of an epoxy group:

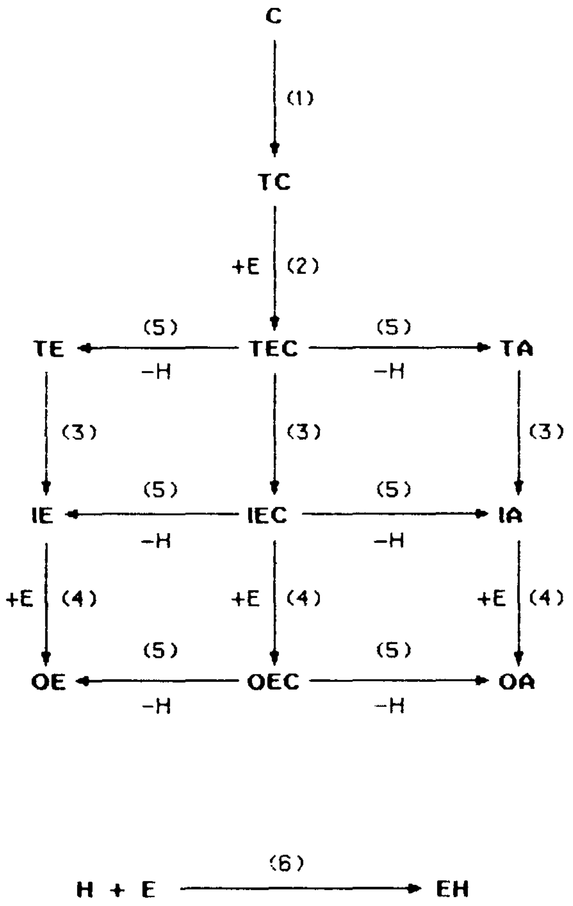
$$R_2 = k_2[E][TC]. \qquad (8)$$

The insertion reaction is assumed to follow bimolecular kinetics.

(3) Isomerization of aliphatic cyanurates to isocyanurates:

$$R_3 = 3k_3[E]F^3. \qquad (9)$$

The isomerization to isocyanurates is catalyzed by free epoxy groups [1]


C
(1)
TC
+E
(2)
(5)
(5)
TE
TEC
TA
-H
-H
(3)
(3)
(3)
(5)
(5)
IE
IEC
IA
-H
-H
+E
(4)
+E
(4)
+E
(4)
(5)
(5)
OE
OEC
OA
-H
-H
(6)
H + E
EH

SCHEME 2.

and is assumed to take place only for triple aliphatic substituted triazines. This fact is taken into account with the help of the statistical factor *F*, which is defined as

$$F = \frac{[\mathrm{TEC}] + [\mathrm{TE}] + [\mathrm{TA}]}{[\mathrm{TC}] + [\mathrm{TEC}] + [\mathrm{TE}] + [\mathrm{TA}]} \tag{10}$$

To obtain the isomerization rate of the possible structural elements, R_3 must be multiplied by [TEC], [TE], or [TA].

(4) Build-up of oxazolidinones:

$$R_4 = 3k_4[\mathrm{E}]. \tag{11}$$

The reaction rate of oxazolidinone build-up is R_4 multiplied by [IEC], [IE], or [IA].

(5) Generation of phenols:

$$R_5 = k_5[\mathrm{C}]. \tag{12}$$

The generation probability of a phenol including the aromatic moiety Ar^1 of a cyanate unit and resulting in a structure TE, IE, or OE from TEC, IEC, or OEC, respectively, is denoted by *a*. To determine the build-up rate of [TE], [IE], and [OE], R_5 must be multiplied by *a* and [TEC], [IEC], or [OEC] (analagous to $(1 - a)$ and [TEC], [IEC], or [OEC] for the build-up rate of [TA], [IA], and [OA]). The cyanate group acts as a catalyst.

(6) Addition of epoxy and hydroxyl groups:

$$R_6 = k_6[\mathrm{E}]. \tag{13}$$

The concentrations of HC and HE, the phenolic groups, which are connected with Ar^1 or Ar^2, must be multiplied by R_6 to give the reaction rate of the addition.

Based on Relations (7)–(13), a system of differential equations describing the kinetics of the formulated structural elements can be written as follows:

$$\frac{d}{dt}[\mathrm{C}] = -R_1,$$

$$\frac{d}{dt}[\mathrm{E}] = -R_2 - R_4([\mathrm{IEC}] + [\mathrm{IE}] + [\mathrm{IA}]) - R_6([\mathrm{HC}] + [\mathrm{HE}]),$$

$$\begin{aligned}
\frac{d}{dt}\,[\mathrm{TC}] &= R_1 - R_2,\\
\frac{d}{dt}\,[\mathrm{TEC}] &= R_2 - (R_3 + R_5)[\mathrm{TEC}],\\
\frac{d}{dt}\,[\mathrm{TE}] &= R_5[\mathrm{TEC}]a - R_3[\mathrm{TE}],\\
\frac{d}{dt}\,[\mathrm{TA}] &= R_5[\mathrm{TEC}](1 - a) - R_3[\mathrm{TA}],\\
\frac{d}{dt}\,[\mathrm{IEC}] &= R_3[\mathrm{TEC}] - (R_4 + R_5)[\mathrm{IEC}],\\
\frac{d}{dt}\,[\mathrm{IE}] &= R_3[\mathrm{TE}] + R_5[\mathrm{IEC}]a - R_4[\mathrm{IE}],\\
\frac{d}{dt}\,[\mathrm{IA}] &= R_3[\mathrm{TA}] + R_5[\mathrm{IEC}](1 - a) - R_4[\mathrm{IA}], \qquad (14)\\
\frac{d}{dt}\,[\mathrm{OEC}] &= R_4[\mathrm{IEC}] - R_5[\mathrm{OEC}],\\
\frac{d}{dt}\,[\mathrm{OE}] &= R_4[\mathrm{IE}] + R_5[\mathrm{OEC}]a,\\
\frac{d}{dt}\,[\mathrm{OA}] &= R_4[\mathrm{IA}] + R_5[\mathrm{OEC}](1 - a),\\
\frac{d}{dt}\,[\mathrm{HC}] &= R_5([\mathrm{TEC}] + [\mathrm{IEC}] + [\mathrm{OEC}])a - R_6[\mathrm{HC}],\\
\frac{d}{dt}\,[\mathrm{HE}] &= R_5([\mathrm{TEC}] + [\mathrm{IEC}] + [\mathrm{OEC}])(1 - a) - R_6[\mathrm{HE}],\\
\frac{d}{dt}\,[\mathrm{EHC}] &= R_6[\mathrm{HC}],\\
\frac{d}{dt}\,[\mathrm{EHE}] &= R_6[\mathrm{HE}].
\end{aligned}$$

The initial values of the concentrations are denoted by the subscript zero. This system of 16 ordinary differential equations was numerically solved by using a 5th-order Runge/Kutta/Fehlberg procedure.

CASCADE FORMALISM

The cascade formalism was introduced by Gordon and coworkers [5–9] and successfully used by Dusek [10] in studying the cure of epoxy resins. It describes the polymer molecules as rooted trees which were generated by the so-called probability generating functions for the number of bonds issuing from the monomeric units in the root and the succeeding generations.

The reaction of difunctional aromatic cyanic acid esters with bisglycidyl ethers in bulk was shown not to be influenced by substitution effects or additional intramolecular macrocyclizations [2, 4]. Under these conditions, the following probability generating functions for the root describe the structures build-up from the structural elements defined above:

$$\begin{aligned}
F_{0C}(z) &= [1 - \alpha_C + \alpha_C(x_{CT}z_T + x_{CI}z_I + x_{CO}z_O + x_{CE}z_E)]^2,\\
F_{0E}(z) &= [1 - \alpha_E + \alpha_E(x_{ET}z_T + x_{EI}z_I + x_{EO}z_O + x_{EE}z_E\\
&\quad + x_{EC}z_C)]^2,\\
F_{0T}(z) &= [x_{TC}z_C + x_{TE}z_E + x_{TEC}z_Cz_E]^3, \qquad (15)\\
F_{0I}(z) &= [x_{IC}z_C + x_{IE}z_E + x_{IEC}z_Cz_E]^3,\\
F_{0O}(z) &= z_E[x_{OC}z_C + x_{OE}z_E + x_{OEC}z_Cz_E].
\end{aligned}$$

The units resulting from the difunctional cyanic acid ester and glycidylether monomers are denoted by the indices C and E, and the triazine, isocyanurate, and oxazolidinone bridges by T, I, and O. The dummy variables z, through which operations with the generating functions are performed, indicate the connections between these units. The probabilities of finding the different structural elements are defined by the following formulas:

$$\begin{aligned}
A_C &= [TC] + [TEC] + [TA] + [IEC] + [IA] + [OEC]\\
&\quad + [OA] + [EHC],\\
A_E &= [TEC] + [TE] + [IEC] + [IE] + 2[OEC] + 2[OE]\\
&\quad + [OA] + [EHC] + 2[EHE],\\
A_T &= [TC] + [TEC] + [TE] + [TA],\\
A_I &= [IE] + [IEC] + [IA],\\
A_O &= [OE] + [OEC] + [OA],
\end{aligned}$$

$$
\begin{aligned}
x_{CT} &= ([TC] + [TEC] + [TA])/A_C, \\
x_{CI} &= ([IEC] + [IA])/A_C, \\
x_{CO} &= ([OEC] + [OA])/A_C, \\
x_{CE} &= [EHC]/A_C, \\
x_{ET} &= ([TEC] + [TE])/A_E, \\
x_{EI} &= ([IEC] + [IE])/A_E, \\
x_{EO} &= (2[OEC] + 2[OE] + [OA])/A_E, \\
x_{EE} &= 2[EHE]/A_E, \\
x_{EC} &= [EHC]/A_E, \\
x_{TC} &= ([TC] + [TA])/A_T, \\
x_{TE} &= [TE]/A_T, \\
x_{TEC} &= [TEC]/A_T, \\
x_{IC} &= [IA]/A_I, \\
x_{IE} &= [IE]/A_I, \\
x_{IEC} &= [IEC]/A_I, \\
x_{OC} &= [OA]/A_O, \\
x_{OE} &= [OE]/A_O, \\
x_{OEC} &= [OEC]/A_O.
\end{aligned}
\tag{16}
$$

These probabilities can be calculated by using the solution of the system of kinetic differential equations (14). In the same way, the conversions of the functional groups C and E are found to be

$$\alpha_C = A_C/([C]_0 + [HC]_0), \tag{17}$$

$$\alpha_E = A_{E/([E]_0} + [HE]_0).$$

In the case of equal and independent reactivities of all functional groups, the generating functions of the first, second, etc. generations with respect to the root are all equal. They are defined by the normalized derivatives of the generating functions of the root:

$$F_1(z) = F_0'(z)/F_0'(1). \tag{18}$$

Thus, for the system under consideration,

$$F_{1C}(z) = 1 - \alpha_C + \alpha_C(x_{CT}z_T + x_{CI}z_I + x_{CO}z_O + x_{CE}z_E),$$

$$F_{1E}(z) = 1 - \alpha_E + \alpha_E(x_{ET}z_T + x_{EI}z_I + x_{EO}z_O + x_{EE}z_E + x_{EC}z_C), \tag{19}$$

$$F_{1T}(z) = [x_{TC}z_C + x_{TE}z_E + x_{TEC}z_Cz_E]^2 \frac{[x_{TC} + x_{TE} + x_{TEC}(z_C + z_E)]}{1 + x_{TEC}},$$

$$F_{1I}(z) = [x_{IC}z_C + x_{IE}z_E + x_{IEC}z_Cz_E]^2 \frac{[x_{IC} + x_{IE} + x_{IEC}(z_C + z_E)]}{1 + x_{IEC}},$$

$$F_{1O}(z) = \frac{z_E(2x_{OE} + 2x_{OEC}z_C + x_{OEC}z_E + x_{OC}) + x_{OC}z_C}{(2 + x_{OEC})}.$$

The gelation condition in terms of the cascade formalism has the form:

$$\det\,[\delta_i^j - F_{1i}^j] = 0, \quad i, j = C, E, T, I, O, \tag{20}$$

With the Kronecker delta δ equal to 1 if $i = j$ and to zero otherwise. The partial derivatives $F_{1i}^j = F_{1i}^j(1) = \partial F_{1i}(z)/\partial z_j$ for $z = 1$ are given by

$$F_{1C}^{C} = 0, \quad F_{1C}^{E} = \alpha_C x_{CE}, \quad F_{1C}^{T} = \alpha_C x_{CT}, \quad F_{1C}^{I} = \alpha_C x_{CI},$$
$$F_{1C}^{O} = \alpha_C x_{CO};$$

$$F_{1E}^{C} = \alpha_E x_{EC}, \quad F_{1E}^{E} = \alpha_E x_{EE}, \quad F_{1E}^{T} = \alpha_E x_{ET}, \quad F_{1E}^{I} = \alpha_E x_{EI},$$
$$F_{1E}^{O} = \alpha_E x_{EO};$$

$$F_{1T}^{C} = 2(x_{TC} + x_{TEC}) + \frac{x_{TEC}}{1 + x_{TEC}} \quad F_{1T}^{E} = 2(x_{TE} + x_{TEC})$$
$$+ \frac{x_{TEC}}{1 + x_{TEC}}, \quad F_{1T}^{T} = 0, \quad F_{1T}^{I} = 0, \quad F_{1T}^{O} = 0; \qquad (21)$$

$$F_{1I}^{C} = 2(x_{IC} + x_{IEC}) + \frac{x_{IEC}}{1 + x_{IEC}}, \quad F_{1I}^{E} = 2(x_{IE} + x_{IEC}) +$$
$$+ \frac{x_{IEC}}{1 + x_{IEC}}, \quad F_{1I}^{T} = 0, \quad F_{1I}^{I} = 0, \quad F_{1I}^{O} = 0;$$

$$F_{1O}^{C} = \frac{2x_{OEC} + x_{OC}}{2 + x_{OEC}}, \quad F_{1O}^{E} = \frac{2 + 2x_{OEC} - x_{OC}}{2 + x_{OEC}},$$
$$F_{1O}^{T} = 0, \quad F_{1O}^{I} = 0, \quad F_{1O}^{O} = 0.$$

The special case in which no isocyanurates, oxazolidinones, and epoxide-hydroxyl adducts are formed ($k_3 = k_4 = k_6 = 0$) has been treated elsewhere [2].

The extinction probabilities, v, which describe the probability that a bond has no continuation to infinity, can be evaluated by solving the following system of nonlinear equations:

$$v_i = F_{1i}(v_j), \qquad i, j = \mathrm{C, E, T, I, O}, \qquad (22)$$

by a numerical iteration process using Eqs. (21).

The sol fraction contains units issuing bonds with no infinite continuation and is, therefore, given by

$$w_s = n_C F_{0C}(v) + n_E F_{0E}(v) \qquad (23)$$

with the normalized molar fractions of the two components

$$n_C = ([C]_0 + [HC]_0), \qquad n_E = ([E]_0 + [HE]_0). \tag{24}$$

A chain in the gel is elastically active if the branching points at its end lead to at least three paths to infinity. The number, N_E, of elastically active network chains can be evaluated by using the generating functions T_0, in which the probability that a bond is formed is weighted by the probability for continuation to infinity:

$$\begin{aligned} T_{0T} &= (x_{TC}\vartheta_C + x_{TE}\vartheta_E + x_{TEC}\vartheta_C\vartheta_E)^3 = \sum_{i=0}^{6} t_{Ti}z^i, \\ T_{0I} &= (x_{IC}\vartheta_C + x_{IE}\vartheta_E + x_{IEC}\vartheta_C\vartheta_E)^3 = \sum_{i=0}^{6} t_{Ii}z^i, \\ T_{0O} &= \vartheta_E(x_{OC}\vartheta_C + x_{OE}\vartheta_E + x_{OEC}\vartheta_C\vartheta_E) = \sum_{i=0}^{3} t_{Oi}z^i, \end{aligned} \tag{25}$$

with

$$\vartheta_C = \nu_C + (1 - \nu_C)z,$$

$$\vartheta_E = \nu_E + (1 - \nu_E)z.$$

The coefficients t_{Ti}, t_{Ii}, and t_{Oi} of z^i are the fractions of triazine, isocyanurate, and oxazolidinone units from which issue i infinite paths. Therefore, the value of N_E is given by

$$N_E = \tfrac{1}{2}\sum_{i>3} i(\mathrm{A_I}^3 t_{Ii} + \mathrm{A_I}^3 t_{Ii} + A_O{}^3 t_{Oi}). \tag{26}$$

Rearranging Eqs. (25) leads to the coefficients t needed in Eq. (26):

$$\mathrm{A}_{0T} = x_{TC}\nu_C + x_{TE}\nu_E + x_{TEC}\nu_C\nu_E,$$

$$\mathrm{A}_{1T} = x_{TC}(1 - \nu_C) + x_{TE}(1 - \nu_E) + x_{TEC}[(1 - \nu_C)\nu_E + (1 - \nu_E)\nu_C],$$

$$\mathrm{A}_{2T} = x_{TEC}(1 - \nu_C)(1 - \nu_E),$$

$$\begin{aligned}
A_{0I} &= x_{IC}v_C + x_{IE}\nu_E + x_{IEC}\nu_C\nu_E \\
A_{1I} &= x_{IC}(1 - \nu_C) + x_{IE}(1 - \nu_E) + x_{IEC}[(1 - \nu_C)\nu_E + (1 - \nu_E)\nu_C], \\
A_{2I} &= x_{IEC}(1 - \nu_C)(1 - \nu_E), \qquad (27) \\
t_{T3} &= A_{1T}(6A_{0T}A_{2T} + A_{1T}{}^2), \\
t_{T4} &= 3A_{2T}(A_{0T}A_{2T} + A_{1T}{}^2), \\
t_{T5} &= 3A_{1T}A_{2T}{}^2, \\
t_{T6} &= A_{2T}{}^3, \\
t_{I3} &= A_{1I}(6A_{0I}A_{2I} + A_{1I}{}^2), \\
t_{I4} &= 3A_{2I}(A_{0I}A_{2I} + A_{1I}{}^2), \\
t_{I5} &= 3A_{1I}A_{2I}{}^2, \\
t_{I6} &= A_{2I}{}^3, \\
t_{O3} &= x_{OEC}(1 - \nu_C)(1 - \nu_E)^2.
\end{aligned}$$

RESULTS AND DISCUSSION

In order to study the behavior of the derived mathematical model, the system of kinetic differential equations (14) was solved for different values of the relative rate constants k_i (Table 1) and initial molar ratios $[C]_0$:$[E]_0$. The initial amount of phenolic hydroxyl groups needed to start the trimerization reaction [3] was fixed at 0.01. Furthermore, the ratio of the generations of phenols with an aromatic moiety resulting from a cyanate or an epoxide monomer, which was denoted by the parameter a, was taken as 0.67, where the possible phenol generations were assumed to have equal probabilities (see Scheme 1). The influence of a on the results was investigated in some preliminary calculations, and significant deviations were found only for the limiting cases $a = 0$ and $a = 1$.

TABLE 1. Relative Rate Constants Used for the Simulations

No.	k_2	k_3	k_4	k_5	k_6
1	0.2	1.0	1.0	3.0	1.0
2	0.2	1.0	1.0	3.0	0
3	0.2	0.01	1.0	3.0	1.0
4	2.0	1.0	1.0	3.0	1.0
5	2.0	1.0	1.0	3.0	0
6	2.0	0.01	1.0	3.0	1.0
7	0.2	1.0	1.0	0	1.0
8	0.2	0.01	1.0	0	1.0
9	2.0	1.0	1.0	0	1.0
10	2.0	0.01	1.0	0	1.0

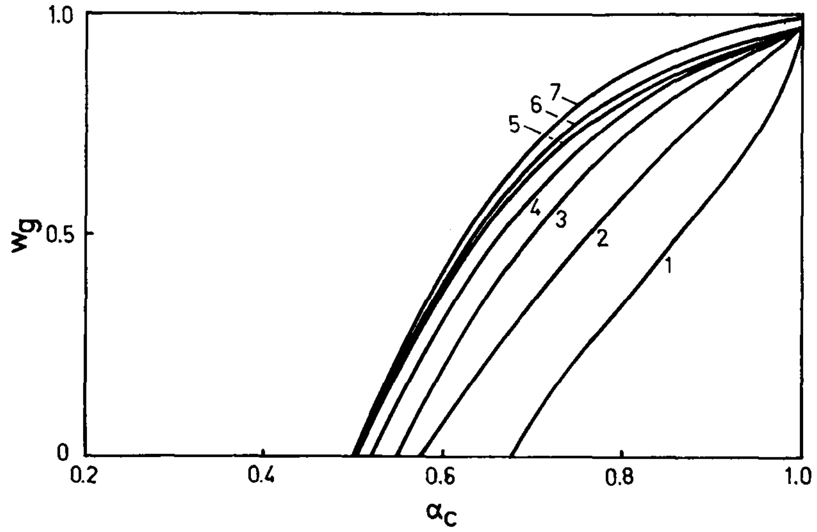


FIG. 3. Plot of gel content $w_g = 1 - w_s$ vs OCN conversion α_C for rate constant set No. 4 (Table 1) and varying $[C]_0$: (1) 0.3, (2) 0.4, (3) 0.5, (4) 0.6, (5) 0.7, (6) 0.8, (7) 0.9.

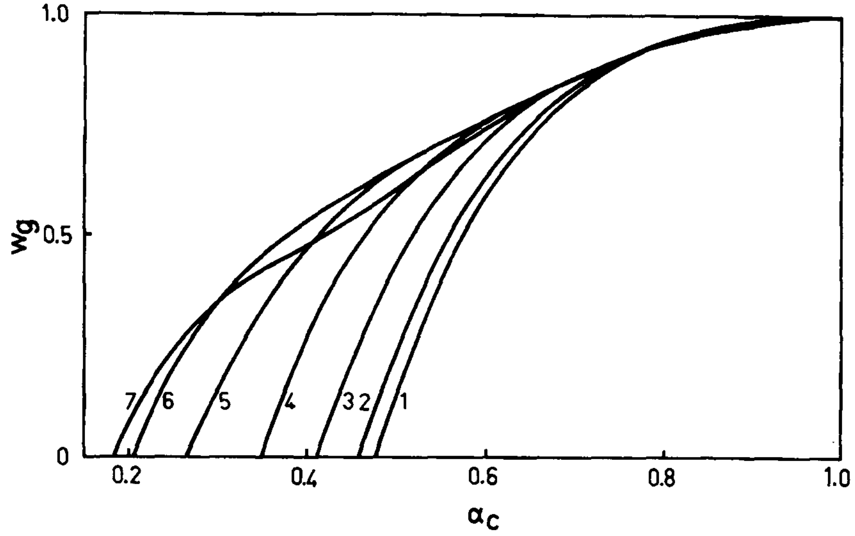


FIG. 4. Same as Fig. 3 for rate constant set No. 9 (Table 1).

The importance of the phenol generation reaction (12) for the gelation behavior is shown in Figs. 3 and 4. It can be seen that without any phenol generation, a rapid increase of the gel content for low cyanate conversions takes place. This effect becomes greater for the low initial epoxy contents because the formation of more than three-functional junction points (substituted triazines and isocyanurates) plays an important role in this region [2]. On the other hand, with an increasing amount of epoxy groups, an increasing part of these junctions can be rearranged into three-functional oxazolidinones, which results in gelation at higher conversions. Furthermore, for the same reasons, the number of elastically active network chains, N_E, increases with increasing initial cyanate content and decreases with increasing phenol generation reaction as can be seen in Fig. 5. For smaller relative insertion constants, the observed differences also become smaller.

The dependence of N_E at 99% conversion on the initial composition of the reaction mixture for different sets of the relative rate constants is

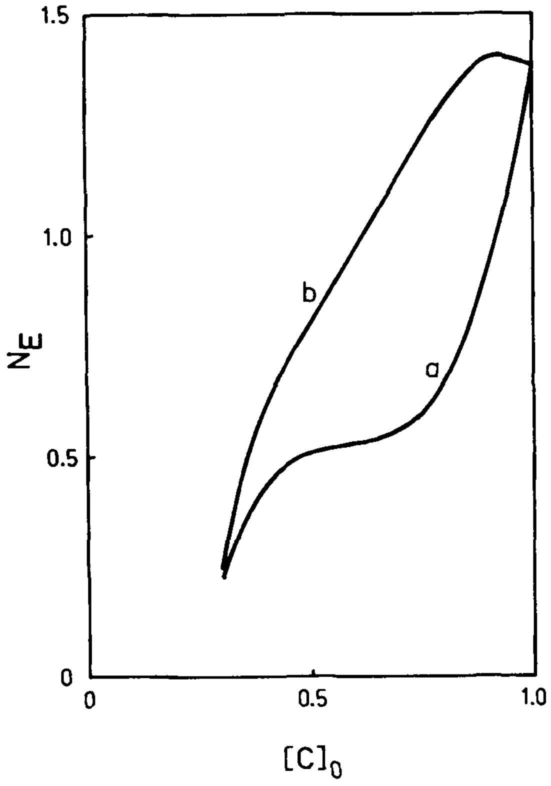


FIG. 5. Dependence of N_E at 99% conversion on initial cyanate content $[C]_0$ for reaction constants sets No. 4 (a) and 9 (b).

shown in Fig. 6. It can be seen that for $[C]_0$ ranging from 0.5 to 0.7, the influence of the rate constants on N_E is significantly higher than at a high excess of one functional group. On considering the reaction scheme, it becomes clear that in this region the chance for building up the different structures, especially those with epoxy units (substituted triazines, isocyanurates, oxazolidinones, and phenol adducts), passes through a maximum. The structural compositions resulting from the used sets of constants at equimolar initial concentrations $[C]_0 = [E]_0$ are illustrated in Fig.

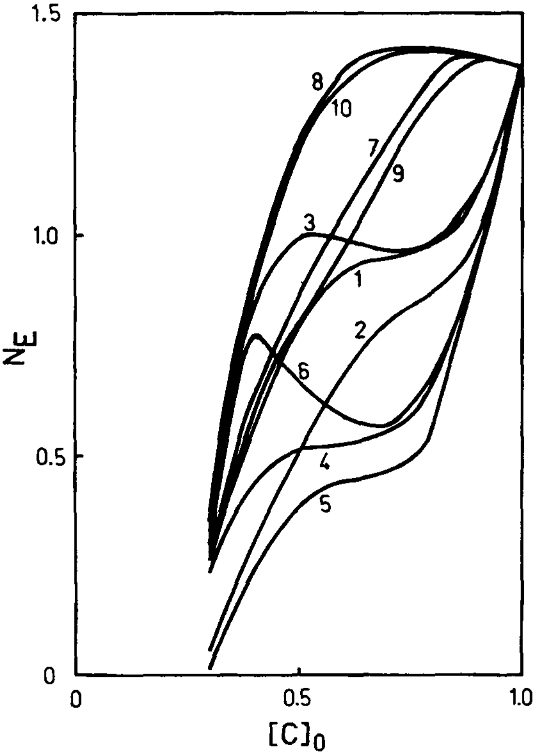


FIG. 6. Dependence of N_E at 99% conversion on initial cyanate content $[C]_0$ for different reaction constant sets (see Table 1).

7 to give a better understanding of the following discussion of the influence of the particular rate constants.

The importance of the epoxy-hydroxyl addition can be seen by comparing Curves 1 with 2 and 4 with 5 in Fig. 6. When the absence of addition is assumed ($k_6 = 0$), all the phenolic hydroxyl groups remain unreacted as dangling ends inside the network, which results in a decrease of N_E. The same effect appears at higher insertion constants k_2 if the phenol generating constant are unchanged (Curves 1 and 4, 2 and 5). There are not enough epoxy groups to link all the formed hydroxyls to the network via

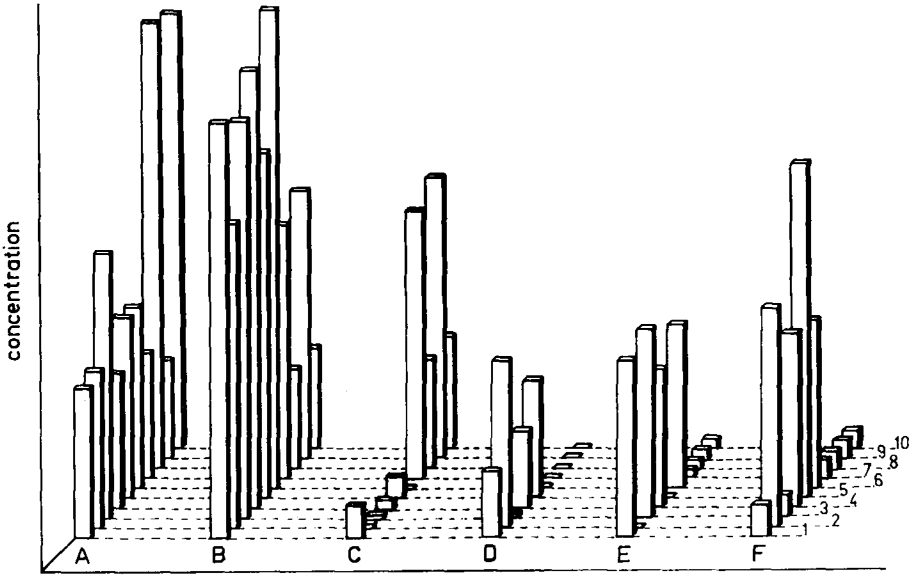


FIG. 7. Concentration of structural elements at 99% conversion for the reaction constant sets from Table 1 at the equimolar point $[C]_0 = [E]_0$. A: [TEC] + [IEC]. B: [TC] + [TE] + [TA] + [IE] + [IA]. C: [OEC]. D: [OE] + [OA]. E: [EHC] + [EHE]. F: [C] + [E] + [HC] + [HE].

propan-2-ols, so that the number of free ends increases. No such effect takes place if the phenol generating reaction is negligible, which can be noticed from Curves 7 and 9 or 8 and 10.

The key reaction for the build-up of oxazolidinones is the isomerization of alkoxy-substituted triazines into isocyanurates. A comparison of Curves 1 with 3 and 4 with 6 shows that only small amounts of oxazolidinones result from low isomerization constants. On the other hand, the formation of higher functionalized triazines becomes stronger and, therefore, N_E increases. Without phenol generation (Curves 7, 8 and 9, 10), the oxazolidinones become exclusively three-functional and act as additional junction points inside the network.

Summarizing all these facts, it is apparent that a broad spectrum of chemical and structural network compositions can be stimulated with the help of the derived model. The identification of the reaction constants for real chemical systems and some conclusions resulting from them will be the topic of a subsequent article.

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