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Network build-up by initiated polyreaction

4. Derivation of postgel parameters for postetherification in diamine-diepoxide curing

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SUMMARY

The theoretical treatment of network formation in diamine-diepoxide curing under participation of etherification of excess epoxide groups, which is based on the combination of kinetic and statistical methods, has been extended to cover postgel parameters. Within the ring-free approximation, this treatment is rigorous. Relations have been derived for the extinction probabilities, sol fractions and concentrations of elastically active network chains. In the system under consideration, various definitions of an elastically active network chain are possible.

INTRODUCTION

In Part 1 of this series (1), it has been shown that the application of a branching theory based on statistical (Markovian) network build-up from units is not rigorous and in the case of initiated reactions may lead to serious deviations from the correct solution obtained by the kinetic method. It has also been shown that a considerable simplification can be reached if the system contains monomers in which the reactivity of functional groups is independent.

The reason of the divergence of results obtained by the statistical and kinetic methods is that the statistical generation from units is always a Markovian process and in the case of linear chains one gets a most probable or pseudo most probable degree-of-polymerization distribution. However, the process is correctly described by an infinite set of deterministic differential equantions of chemical kinetics, which yield a non-Markovian distribution. For the case of a monomer with two polymerizable groups participating in an initiated polymerization process of the living polymerization type, the gel point conversion was shown to be larger by up to 50% compared to the approximate statistical build-up from units.

In Part 3 (2) the rigorous solution was compared with that obtained by the fragment method of Williams. In this approach, the network is built up from fragments larger than monomer units. The fragment distribution was obtained by solving a finite number of differential equations of chemical kinetics. By increasing the fragment size, the results converged to the rigorous solution obtained by the kinetic method.

Part 2 (3) deals with the application of the kinetic method to network build-up in a diepoxide-diamine system where the excess epoxy groups can form polyether sequences. The hydroxyl groups formed in the amine-epoxy addition steps serve as initiators for a step growth of a polyether chain. Therefore, this process was treated by the kinetic method. It was assumed that the etherification starts only after all amine hydrogens had reacted.

Because the reactivities of the epoxy groups in diepoxide and of the

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amino groups in diamine are independent, the connections between them were cut and the points of cut were labelled **e** and **a**, respectively. Thus, diepoxide was split into two monofunctional fragments and diamine was split into two bifunctional fragments. In the second step, the etherification reaction was described by the kinetic differential equations which have been converted into a differential equation of the generating function for the degree of polymerization distribution of the amine-polyepoxy adducts (called clusters). This equation was then solved (3). The distribution of these clusters and unreacted monoepoxy fragments bearing labelled points of cut served as initial components for the third step in which the **e** + **e** and **a** + **a** labelled points were recombined using the statistical approach. For details see Ref. 3.

In this contribution, the distribution obtained in the second step has been utilized for derivation of the postgel parameters such as the extinction probabilities, sol fraction and concentration of elastically active network chains.

THEORY

The probability generating function (pgf) for the number of bonds issuing from the amine-polyepoxy clusters $F_{OC}(z)$ and from monoepoxide fragments $F_{OE}(z)$ is as follows (3)

$$F_{OC}(\underline{z}) = z_{CaC}\, g(z_E) \tag{1}$$

$$F_{OE}(\underline{z}) = \phi_1 z_{EeC} + \phi_2 z_{EeE} \tag{2}$$

where

$$z_E = \phi_1 z_{CeC} + \phi_2 z_{CeE} \tag{3}$$

and

$$g(z_E) = z_E^2 \exp[(z_E - 1)\rho\alpha_{ETH}] \tag{4}$$

In these equations, ρ is the molar ratio of excess epoxy groups to initial amino groups: $\rho = ([E]_0 - 2[A]_0)/[A]_0 = r_E - 2$; $r_E = [E]_0/[A]_0$ in contrast to $r_A = 2[A]_0/[E]_0$ used previously, e.g. in Ref. 4; $[E]_0$ and $[A]_0$ are the initial molar concentrations of epoxide and amine, respectively.
The quantities ϕ_1 and ϕ_2 are probabilities that an **e** - **e** bond (denoted below as **e**) extends to an epoxy group bound in cluster and an epoxy fragment bearing unreacted epoxy group, respectively. It is easy to see that

$$\phi_1 = \alpha_E\,, \qquad \phi_2 = 1 - \alpha_E \tag{5}$$

where α_E is the total conversion of epoxy groups and the relation between α_E and the conversion of excess epoxy groups in the etherification reaction, α_{ETH}, is (3)

$$\alpha_E = (\alpha_{ETH}\rho + 2)/r_E$$

The notation of the pgf variables **z** is as follows: CaC means that a bond extends from a cluster to a cluster via a **a** - **a** bond, i.e. by coupling two points labelled **a**; CeC means a bond extending from cluster to cluster via an **e** - **e** bond; EeC and EeE mean bonds extending via an **e** - **e** bond to a cluster or an epoxy fragment, respectively.

Five pgf's for the number of bonds extending from a unit (cluster or fragment) on generation g ($g > 0$) to a unit on generation $g+1$ correspond to the five variables $\underline{z}$. They are obtained by differentiation of pgf's (1) and (2):

$$F_{CaC}(\underline{z}) = g(z_E) \tag{6}$$

$$F_{CeC}(\underline{z}) = z_{CaC} g'(z_E)/g'(1) \tag{7}$$

$$F_{EeC}(\underline{z}) = z_{CaC} g'(z_E)/g'(1) \tag{8}$$

$$F_{EeE}(\underline{z}) = F_{CeE}(\underline{z}) = 1 \tag{9}$$

where $g'(z_E)$ is the derivative of $g(z_E)$ with respect to z_E; $g'(1)$ is its value for $z_E = 1$; F_{XyZ} is the pgf for the number of bonds extending to generation $g+1$ from a unit Z on generation g that is rooted on unit X in generation $g-1$ via an $y-y$ bond.

The derivatives of the pgf's (8)-(9) give the condition for the gel point which reads*

$$[6 + 8\rho\alpha_{ETH} + 2(\rho\alpha_{ETH})^2]/r_E = 1 \tag{10}$$

The Postgel State

The extinction probabilities v_{XyZ} for different bonds are obtained from the pgf's F_{XyZ} since $v_{XyZ} = F_{XyZ}(\underline{v})$. Thus,

$$v_{CaC} = v_e^2 \exp[(v_e - 1)\rho\alpha_{ETH}] = v_{aC} \tag{11}$$

$$v_{CeC} = v_{EeC} = \frac{v_{CaC} v_e \exp[(v_e - 1)\rho\alpha_{ETH}](2 + v_e\rho\alpha_{ETH})}{2 + \rho\alpha_{ETH}} = v_{eC} \tag{12}$$

$$v_{CeE} = v_{EeE} = 1 = v_{eE} \tag{13}$$

where

$$v_e = \phi_1 v_{eC} + \phi_2 v_{eE} = \phi_1 v_{eC} + \phi_2 \tag{14}$$

Since $v_{CeC} = v_{EeC}$ and $v_{CeE} = v_{EeE}$, only the type of the bond to generation $g-1$ matters but the type of the predecessor unit does not, so that only three extinction probabilities - v_{aC}, v_{eC} and v_{eE} - are necessary.

Sol Fraction

Only such units contribute to the sol fraction that issue exclusively bonds with finite continuation. One has to take into account that clusters have different weights depending on the number of epoxy fragments. Since Eq.(1) can be written in the form $F_{OC}(\underline{z}) = \sum_{i=2}^{\infty} n_i z_{aC} z_E^i$ (where n_i is the number fraction of clusters composed of i epoxy fragments) the weight fraction of the sol, w_s, can be written as

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*There is a printing error in Eq.28 of Ref.3 which has been corrected in Ref. 4 (Eq.87)

$$w_s = \frac{n_C \sum_{i=2}^{\infty} (M_A + i\, M_E)\, n_i\, v_{aC}\, v_e^i + (1 - n_C)\, M_E\, v_e}{n_C \sum_{i=2}^{\infty} (M_A + i\, M_E) n_i + M_E (1 - n_C)} \tag{15}$$

which can be transformed into

$$w_s = \frac{n_C\, v_{aC}\, [M_A g(v_e) + M_E\, v_e\, g'(v_e)] + (1 - n_C) M_E\, v_e}{n_C\, M_A + n_C M_E\, g'(1) + (1 - n_C) M_E} \tag{16}$$

where M_A and M_E are molecular weights of diamine and diepoxide fragments and n_C is the number fraction of clusters given by

$$n_C = 1/[1 + r_E(1 - \alpha_E)] = 1/(1 + \phi_2 r_E) \tag{17}$$

Using Eqs.(4),(11),(12) and (14) one gets

$$w_s = (M_A\, v_{aC}^2 + M_E\, v_e^2\, r_E)/(M_A + M_E\, r_E) \tag{18}$$

Number of Elastically Active Network Chains (EANC)

The number of EANC's per unit N_e is derived from the pgf $T_C(z)$ for the number of bonds with infinite continuation issuing from a cluster. The pgf T_C is obtained from F_{0C} by making the substitution $z_{xY} = v_{xY} + (1 - v_{xY})z$. Thus,

$$T_C(z) = v_{aC} + (1 - v_{aC})z\, \theta_E^2 \exp(\theta_E - 1)\, \rho\alpha_{ETH} = \sum_i t_i z^i \tag{19}$$

and

$$\theta_E = \phi_1 [v_{eC} + (1 - v_{eC})z] + \phi_2$$

In counting EANC's, the following schemes are possible (Fig.1):
(1) All active branch points are counted (scheme A). Each active branch point (a branch point from which at least three bonds have infinite continuation) contributes by 3/2 to the number of EANC's, N_e. It can be seen that in structure A there are $i - 2$ such branch points. Therefore,

$$N_{e1} = (3/2) n_C \sum_{i=3} (i - 2) t_i \tag{20}$$

The sum on the right-hand-side of Eq.(20) can be expressed in terms of values of T_C and its derivatives. Using the following abbreviations

$$T_C(N) = T_C(z{=}N) \ , \quad T'_C(N) = (\partial T_C(z)/\partial z)_{z=N} \quad \text{and}$$

$$T''(N) = (\partial^2 T_C(z)/\partial z^2)_{z=N}$$

one can write

$$\sum_{i=3} i t_i = T'_C(1) - T'_C(0) - T''_C(0), \quad 2 \sum_{i=3} t_i = 2 - 2T_C(0) - 2T'_C(0) - T''_C(0)$$

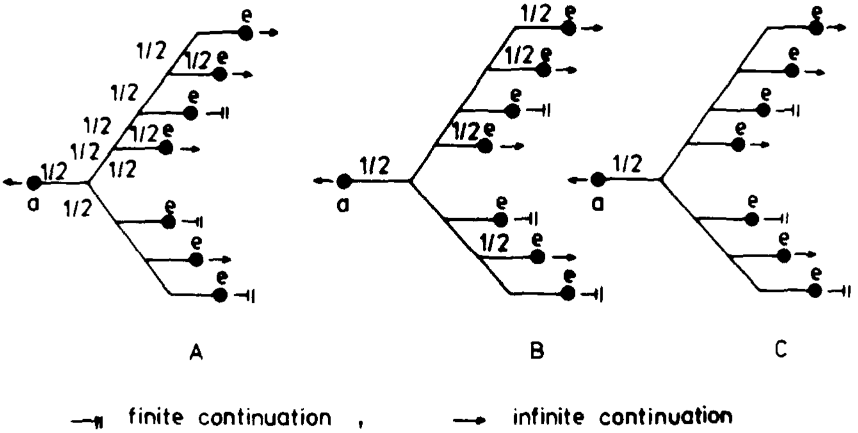

Figure 1. Various schemes of counting of elastically active network chains

Thus,

$$N_{e1} = 3/2\ n_C\ [T_C'(1) + T_C'(0) + 2\,T_C(0) - 2] \qquad (21)$$

(2) The ether bridges $-CH-CH_2-O-$ are not counted, the bridges in diamine and diepoxide are counted (scheme B)

$$N_{e2} = (1/2)n_C \sum_{i=3} it_i = (1/2)n_C[T_C'(1) - T_C'(0) - T_C''(0)] \qquad (22)$$

(3) Only the bridge in diamine is counted (scheme C). Such situation may arise if this bridge is long and flexible compared to diepoxide and ether bridges, e.g., if a polyether diamine is used. In that case, the Ca bond must have an infinite continuation and at least two other bonds (Ce) must have an infinite continuation: therefore, the pgf T_C is transformed as follows

$$T_C(z) = [v_{aC} + (1 - v_{aC})z]\ T_{Ce}(z) \qquad (23)$$

$$T_{Ce}(z) \equiv \sum_i t_{ei} z^i = \theta_E^2 \exp[(\theta_E - 1)\rho\,\alpha_{ETH}] \qquad (24)$$

$$N_{e3} = (1/2)\, n_C\, (1 - v_{aC}) \sum_{i=2} t_{ei} = (1/2)\, n_C(1 - v_{aC})\ [1 - T_{Ce}(0) - T_{Ce}'(0)] \qquad (25)$$

where the meaning of the value of pgf's and their derivatives is the same as before except that they are derived from the pgf (24).

The concentration of EANC's per unit volume of the gel, ν_{ei}, is given by

$$\nu_{ei} = d\,N_{ei}/(\bar{M}(1 - w_s)) \qquad (26)$$

where d is density of the system and $\bar{M}$ is the number average molecular weight of the system prior to coupling of labels

$$\bar{M} = n_C[M_A + M_E(2 + \rho\alpha_{ETH})] + (1 - n_C)\, M_E \qquad (27)$$

DISCUSSION

The derivation presented here shows that the extension of the rigorous treatment to postgel parameters is relatively simple and is of the same degree of complexity or even simpler than approximate treatment based on build-up from units or larger fragments.

In Fig. 2 examples are given of the variation of the sol fraction w_s and concentration of EANC's ν_{el} (variant 1) with etherification conversion α_{ETH} for a diepoxide-diamine system with $M_A = 200$, $M_E = 175$ and $d = 1.15\ g\ cm^{-3}$. For $\alpha_{ETH} = 0$ the values of $w_s = 1$ and $\nu_{el} = 0$ correspond to the critical ratio $r_E = 6$ for gelation. As expected, with increasing α_{ETH} the sol fraction w_s decreases and the value of ν_{el} increases.

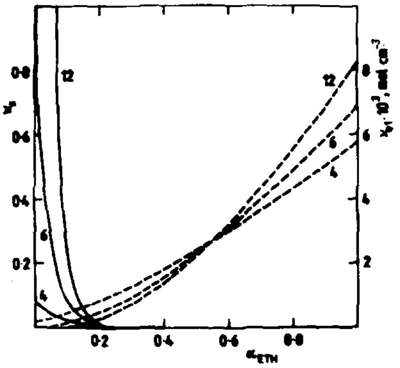

Figure 2. Dependence of the sol w_s and of the number of elastically active network chains per unit volume of the gel, ν_{e1}, (scheme A) on the etherification conversion of epoxy groups α_{ETH} for different molar ratios $r_E = [E]_0/[A]_0$ indicated

In Fig. 3 the dependences of ν_{ei} of all possible variants on α_{ETH} are given for constant value of $r_E = 4$. For low crosslinking densities (very few bonds with infinite continuation) counting of EANC's by variant (1) corresponds to the reality, but at high crosslinking densities one should make the choice of the particular procedure according to the structure and properties of the monomers and purpose of application of the result. It can be seen that $\nu_{e1} = \nu_{e2}$ for $\alpha_{ETH} = 0$, because in this case there is no branching by polyetherification.

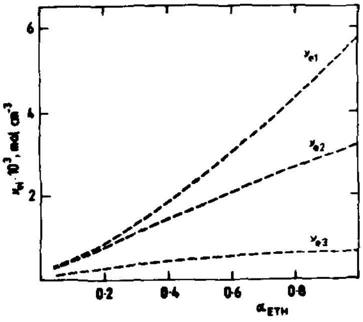

Figure 3. Dependence of ν_e on α_{ETH} for the variants of calculation ν_e indicated and for $r_E = [E]_0/[A]_0 = 4$

As has been stated in Ref. 3, the real mechanism of polyetherification may deviate from the initiated step reaction of the living polymerization type in that probably chain transfer interferes (5). Moreover, in curing of N,N-diglycidylamines and their polyfunctional derivatives, etherification is complicated by cyclization and dependence of reactivity of epoxy groups (6).

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