Build-up of polymer networks by initiated polyreactions
3. Analysis of the fragment approach
to the living polymerization type of build-up

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SUMMARY

A fragment approach, consisting of a selection of different fragments from which the network may be built-up, together with a kinetic scheme giving the evolution of such fragments during polymerization and a recursive approach for derivation of statistical averages, is used in the analysis of the build-up of polymer networks by initiated polyreactions. Gelation conditions are predicted for two simple cases: the living polymerization of a (tetrafunctional) monomer with two polymerizable groups and the polyetherification released by polyamine-polyepoxide addition. When the size of the fragments is increased, the solution converges to the exact solution given by the kinetic theory.

INTRODUCTION

For generation of branched and crosslinked structures, two analytical methods are available: (a) the statistical generation from monomer units or larger structural units (fragments) and (b) the kinetic method in which the process of network build-up closely follows the chemical kinetics (1). It was shown (2) that the statistical generation of linear chains always lead to the most probable or pseudo most probable distribution. The term *pseudo most probable* has been reserved for a distribution in which the distribution of the low molecular weight species is deterministic (determined by the kinetics) and the rest of the distribution is of the most probable type. The kinetic generation gives different distributions; for instance, the Poisson distribution for the case of initiated polymerization with fast initiation. The application of the statistical generation to kinetically controlled polyfunctional reactions may lead to significant deviations in structural parameters.

However, for a number of complex reactions the infinite set of kinetic differential equations may be difficult or impossible to solve. Then, the method of moments is still feasible for getting information on the degree -of-polymerization averages and the gel point (3) and the procedure can be generalized by using computer algoritms for synthesis of the reactions schemes governing the process, formulation of the kinetic differential equations and formulation and solution of the set of differential equations for the moments (4). This method cannot be at present applied beyond the gel point, however.

Therefore, the fragment method based on statistical generation from structural fragments larger than the monomer unit is of importance. This method has been successfully used in the formation of phenolic resins (5,6) and polyetherification accompanying the polyepoxy-polyamine reaction (7).

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The distribution of fragments used in the generation is obtained by solution of a limited number of kinetic differential equations. It is expected that, by increasing the size of the fragment, one should approach the exact solution given by the kinetic theory.

This contribution analyzes the effect of increasing fragment size on the gel point conversion in the initiated polymerization of a monomer with two polymerizable groups of independent reactivity and in the polyetherification released by the polyepoxy-polyamine addition. The results are compared with those obtained by the exact solution using the kinetic method (2,8).

FRAGMENT APPROACH TO INITIATED POLYREACTION OF A MONOMER WITH TWO FUNCTIONAL GROUPS

A rigorous calculation of the gel point conversion in the living polymerization of a monomer with two polymerizable groups of independent and equal reactivity was reported by Dušek and Šomvársky (2). The gel point depends on the ratio of initiation and propagation rate constants, $K = k_I/k_p$, and on the ratio of initial concentrations of initiator and monomer, $R = i_0/m_0$.

Let us apply the fragment approach to this system using different levels of initial information (size of fragments)

(a) First fragment level

The following fragments are considered:

F1 = □ (unreacted initiator)   F4 = (+)●(−) (middle fragment)
F2 = ○ (half of an unreacted monomer)   F5 = (+)● (end fragment)
F3 = ■− (−)(reacted initiator)

In order to build up the network, (−) groups are to be joined with (+) groups, and segments (issuing from the half monomer) among themselves.

The kinetic scheme may be written as

$$F1 + F2 \xrightarrow{k_I} F3 + F5 \tag{1}$$

$$F5 + F2 \xrightarrow{k_p} F4 + F5 \tag{2}$$

from which we get

$$F2 = m_0 - (1 - 1/K)(i_0 - F1) - (i_0/K)\ln(i_0/F1) \tag{3}$$

$$F3 = F5 = i_0 - F1 \tag{4}$$

$$F4 = m_0 - F2 + F1 - i_0 \tag{5}$$

By defining the conversion

$$\alpha_M = (m_0 - F2)/m_0 \tag{6}$$

and

$$\phi_M = 1 - (i_0 - F1)/(m_0 - F2) = 1 - [R - (F1/m_0)]/\alpha_M \tag{7}$$

Eqs.(3) to (5) may be written as

$$\alpha_M = (1 - 1/K)\alpha_M(1 - \phi_M) + (R/K)\ln(R/K - \alpha_M(1 - \phi_M)) \tag{8}$$

$$F3/m_0 = F5/m_0 = \alpha_M(1 - \phi_M) \tag{9}$$

$$F4/m_0 = \alpha_M\phi_M \tag{10}$$

Once the evolution of the fragments in the course of the polymerization is known, the statistical averages may be calculated. One defines:

$Y(+)$ = average weight hanging from a $-$ (+)
$Y(-)$ = average weight hanging from a $-$ (-)
W = average weight hanging from a $-$

$$Y(+) = \{F3\ M_I + F4[M_M + Y(+) + W]\}/(F3 + F4) \tag{11}$$

M_I and M_M are, respectively, the molecular masses of the initiator and the monomer. It must be noticed that, as the probability of joining an F3 is taken as F3/(F3 + F4) while that of joining an F4 is F4(F3 + F4), the most probable distribution of fragments in the network is implicitly assumed. Similarly,

$$Y(-) = \{F4[M_M + Y(-) + W] + F5(M_M + W)\}/(F4 + F5) \tag{12}$$

$$W = \{F2\ M_M + F4[M_M + Y(+) + Y(-)] + F5[M_M + Y(+)]\}/(F2 + F4 + F5) \tag{13}$$

By getting $Y(+)$ from Eq.(11), $Y(-)$ from Eq.(12), replacing them in Eq.(13) with the aid of Eqs.(6), (9) and (10), and stating the condition that W (and consequently $Y(+)$ and $Y(-)$) go to infinity, the following gelation condition results

$$1 = \phi_M(1 + 2\alpha_M) \tag{14}$$

This is exactly the same condition as that obtained in Ref. 2 using cascade generation.

Once R and K are fixed, the gelation conversion α_M(gel) is obtained from the simultaneous solution of Eqs.(8) and (14).

It may be of interest to show the generation of this result using the theory of branching processes and the same fragment distribution. This distribution with respect to the number and type of bonds can be written down in the form of probability generating functions (pgf) F_{OI} and F_{OM} for the initiator and the (tetrafunctional) monomer, respectively,

$$F_{OI}(z) = F1 + F3\ z_+ \tag{15}$$

$$F_{OM}(z) = [f_{OM}(z)]^2 = [F2 + F4(\phi_I z_+ z_I + \phi_M z_+ z_-) + F5(\phi_I z_I + \phi_M z_-)]^2 \tag{16}$$

where z is the pgf variable and the subscript denotes the type of group to which the bond extends. For example, z_+ at F3 in F_{OI} means that the bond extends from the (-) group of I to the (+) group of a monomer unit. The factors ϕ_M and $\phi_I = 1 - \phi_M$ are probabilities that an (+) group is coupled with a monomer unit and I, respectively; $\phi_M = F4/(F4 + F5)$, F3 = F5. Since we are interested only in the gel point, the quantity F_{OI} for the monofunctional initiator is irrelevant and $z_I = 1$ in F_{OM}.

The pgf's for units in generation g>0 are obtained by differentiation. F_+ and F_- are pgfs for units rooted (on the preceding generation) by their (+) or (-) group, respectively. Thus,

$$F_+(z) = (\partial F_{OM}/\partial z_+)N = f_{OM}(z) \tag{17}$$

$$F_-(z) = (\partial F_{OM}/\partial z_-)N = f_{OM}(z)(F4z_+ + F5)/(F4 + F5) \tag{18}$$

(N is a normalizer), and the gel point conversion is determined by the relation

$$\det \begin{vmatrix} 1 - F_+^+ & -F_-^+ \\ -F_+^- & 1 - F_-^- \end{vmatrix} = 0 \qquad (19)$$

where $F_+^+ = (\partial F_+(z)/\partial z_+)_{z_+=z_-=1}$ and the other symbols have an analogous meaning. After substituting the values of derivatives obtained from Eqs. (17) and (18) one gets condition (14).

(b) Second fragment level

At this level, we do not allow the middle unit to be joined directly to a reacted initiator or to the end fragment of the living chain. So, the following fragments are used

F1 = □   F5 = (+)-●-(-)
F2 = ○   F6 = (+)-●-●
F3 = ■-●   F7 = ■-●-(-)
F4 = ■-●-●

In this case, the concentrations up to the dimer are calculated rigorously.
The kinetic scheme may be then written as

$$F1 + F2 \xrightarrow{k_I} F3 \qquad\qquad F4 + F2 \xrightarrow{k_p} F6 + F7$$

$$F3 + F2 \xrightarrow{k_p} F4 \qquad\qquad F6 + F2 \xrightarrow{k_p} F5 + F6$$

By formulating the corresponding kinetic equations and using the Runge-
-Kutta 4th order method, the concentrations of different fragments in the course of polymerization are established.
The average weight hanging from different linkages are given by:

$$Y(+) = \{F5[M_M + Y(+) + W] + F7[M_M + M_I + W]\}/(F5 + F7) \qquad (20)$$

$$Y(-) = \{F5[M_M + Y(-) + W] + F6[2(M_M + W)]\}/(F5 + F6) \qquad (21)$$

$$W = (1/m_0)\{F2\,M_M + F3(M_M + M_I) + 2F4(2M_M + M_I + W) +$$

$$F5[M_M + Y(+) + Y(-)] + 2F6[2M_M + W + Y(+)] + F7[M_M + M_I + Y(-)]\} \qquad (22)$$

where $m_0 = F2 + F3 + 2F4 + F5 + 2F6 + F7$.
By substituting $Y(+)$ and $Y(-)$ into W and taking into account that
$F6 = F7$, the following gelation condition (leading to W, $Y(+)$, $Y(-) \to \infty$)
results

$$F2 + F3 - 5F5 - 3F6 - 2(F5)^2/F6 = 0 \qquad (23)$$
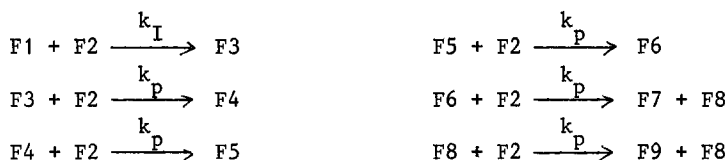
Provided that R and K are fixed, Eq.(23) is satisfied for a certain
$\alpha_M = (F3 + 2F4 + F5 + 3F6)/m_0$. The condition is easily calculated from the
knowledge of the fragments concentration as a function of conversion.

(c) Third fragment level

Each new fragment level requires the introduction of two new species.
In this case, we get

F1 to F4 as in the previous case   F7 = ■-●-●- (-)
F5 = ■-●-●-●   F8 = (+)-●-●-●
F6 = ■-●-●-●-●   F9 = (+)-●-(-)
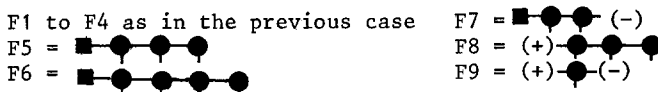
Now, the concentrations up to the tetramer are rigorously calculated
using the scheme

$$F1 + F2 \xrightarrow{k_I} F3 \qquad\qquad F5 + F2 \xrightarrow{k_p} F6$$

$$F3 + F2 \xrightarrow{k_p} F4 \qquad\qquad F6 + F2 \xrightarrow{k_p} F7 + F8$$

$$F4 + F2 \xrightarrow{k_p} F5 \qquad\qquad F8 + F2 \xrightarrow{k_p} F9 + F8$$

The concentrations of the different fragments were obtained by solving numerically the kinetic equations.

Following the same procedure as in the previous cases (i.e. calculating $Y(+)$, $Y(-)$ and W and noting that $F7=F8$), the gelation equation is obtained in the form

$$F2 + F3 - 3F5 - 8F6 - 15F9 - 2(F9)^2/F7 = 0 \qquad (24)$$

with $\alpha_M = (F3 + 2F4 + 2F5 + 4F6 + 5F7 + F9)/m_0$,
$m_0 = F2 + F3 + 2F4 + 3F5 + 4F6 + 2F7 + 3F8 + F9$.

The gel point conversions calculated using the fragment approach with increasing fragment level and the exact kinetic solution are given in Table 1.

Table 1

Gel point conversion in living polymerization of a monomer with two polymerizable groups of independent and equal reactivity. RS rigorous solution (1); FA(i) i-th fragment level approach. $\varepsilon\%$ percent error of the FA(3) approximation

$R = i_0/m_0$	RS	FA(1)	FA(2)	FA(3)	$\varepsilon\%$
$K = k_I/k_p = 0.01$
0.001	0.020	0.015	0.016	0.016	20.0
0.01	0.046	0.036	0.037	0.039	15.2
0.1	0.102	0.081	0.088	0.093	8.8
0.5	0.177	0.146	0.162	0.172	2.8
$K = 0.1$
0.001	0.030	0.022	0.023	0.024	20.0
0.01	0.083	0.063	0.069	0.074	10.8
0.1	0.204	0.168	0.189	0.200	2.0
0.5	0.375	0.324	0.366	0.375	0
$K = 1$
0.001	0.032	0.023	0.024	0.025	21.9
0.01	0.100	0.076	0.085	0.092	8.0
0.1	0.316	0.257	0.302	0.315	0.3
0.5	0.707	0.643	0.704	0.707	0
$K = 10$
0.001	0.032	0.023	0.024	0.025	21.9
0.01	0.105	0.076	0.085	0.092	12.4
0.1	0.332	0.279	0.324	0.331	0.3
0.5	0.864	0.809	0.863	0.864	0

POLYETHERIFICATION INDUCED BY POLYAMINE-POLYEPOXIDE ADDITION

In the reaction of an amino group with epoxy group, aminoalcohols containing one or two OH groups are formed. The OH group can further react with epoxy groups. In this reaction, OH group is recovered, an ether bond is formed. The epoxy-amine reaction is usually much faster than the etherification reaction. Thus, polyetherification is initiated by the OH groups of the amino alcohol. This reaction has been treated using the fragment (7) as well as the exact kinetic (8) methods. The amine-diepoxide adducts having 2, 1 or 0 OH groups (0, 1, 2 ether groups), respectively, the middle and end epoxy units in polyether chains were used as fragments. The details of calculation using both types of approach have already been published (Refs. 7 and 8)*. The results are compared in Fig.1 which also shows the case when the network is built-up from monomer units only.
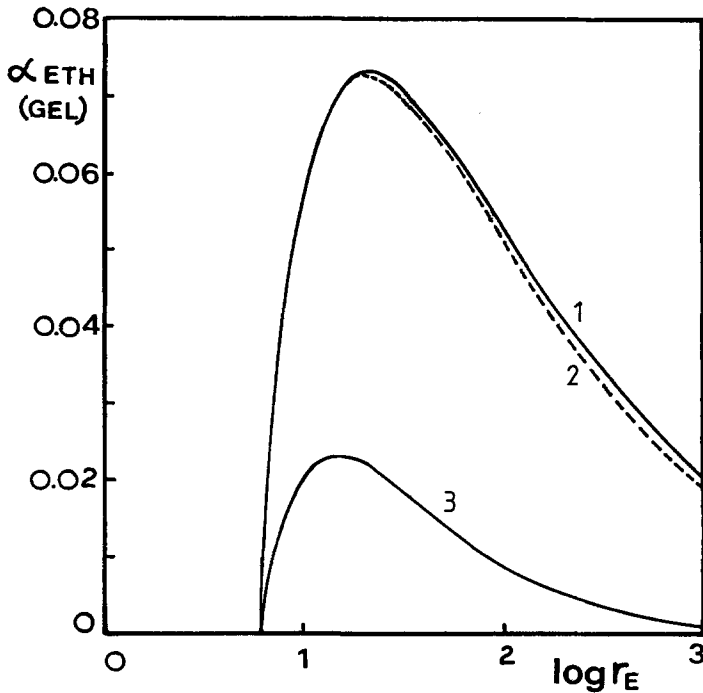

Figure 1. Dependence of the conversion of excess epoxy groups, α_{ETH}, at the gel point on the initial molar ratio epoxy/amine, r_E, for postetherification following the addition of a diepoxide to a diamine. 1 exact solution, 2 approximation using fragments composed of one amine and two epoxy units, 2 approximation using only amine and epoxy units.

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*There is a misprint in Eq.(28) of Ref.8 which should read

$$1 - [(2 + \rho\alpha_{ETH})(3 + 2\rho\alpha_{ETH}) + \rho\alpha_{ETH}]/r_E = 0 \text{ (see Ref.9)}$$

DISCUSSION

Comparing the gel point conversions calculated for the initiated poly-reaction of a monomer with two functional groups, one can see that the value obtained by using the fragment method is higher than the exact solution. It is so because the fragment method yields a wider distribution of chain lengths. However, using the third level of fragmentation, and particularly if the average chain length is low ($i_0 m_0 \geqq 0.1$), the difference becomes small. The difference becomes larger with increasing chain length. By further increasing the fragment level, a reasonable approximation can be expected for $i_0/m_0 \geqq 0.01$, but only a slow convergence when the i_0/m_0 ratio is smaller.

The case of polyetherification following diamine-diepoxide curing Fig. 1 demonstrates a very close approach to the exact solution by passing from monomer units to larger fragments.

The examples given above show that the results obtained by statistical generation of branched and crosslinked structures from fragments always converge to the exact solution when the fragment size is increased. However, the closeness of approximation depends on the properties of the given system, particularly on the reaction mechanism and kinetics. The fragment approach utilizes elements of higher-order Markovian statistics and the fragment level is in a relation with the order of Markovian statistics. While the application of higher order Markovian statistics is relatively easy for linear systems, it becomes much more difficult for branched systems. The fragment method is less rigorous but easier to apply.

REFERENCES

1. Dušek K., Brit. Polym. J. 17, 185 (1985)
2. Dušek K., Šomvársky J., Polym. Bull. 13, 321 (1985)
3. Kuchanov S.I., Povolotskaya E.S., Vysokomol. Soed. A24, 2190 (1982)
4. Dušek K., Šomvársky J., Paper to be presented at the 5th International Seminar on Polymer Physics, High Tatra Czechoslovakia, April 1987
5. Aranguren M.I., Borrajo J., Williams R.J.J., Ind. Eng. Chem., Prod. Res. Dev. 23, 370 (1984)
6. Vásquez A., Addabo H.E., Williams R.J.J., Ind. Eng. Chem. Prod. Res. Dev. 23, 375 (1984)
7. Riccardi C.C., Williams R.J.J., Polymer 27, 913 (1986)
8. Dušek K., Polym. Bull. 13, 321 (1985)
9. Dušek K., Adv. Polym. Sci. 78, 1 (1986)