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Morphology

Build-up of Polymer Networks by Initiated Polyreactions

1. Comparison of Kinetic and Statistical Approaches to the Living Polymerization Type of Build-up

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Dedicated to Dr. B. Sedláček on the occasion of his 60th birthday

Summary

Theoretical treatment of network formation with participation of initiated reactions is to be based on the kinetic (coagulation) theory, because the application of the statistical network build-up from monomer units (cascade substitution) can be a source of serious deviations. This comparison is demonstrated by the degree-of-polymerization distribution obtained in the linear living polymerization and the gel point conversion in the multifunctional polymerization involving a monomer with two groups of independent reactivity

Introduction

The existing theories of network build-up can be divided into two caterories:

(a) graph-like models not associated with the dimensionality of space,

(b) simulation of network build-up in n-dimensional space.

The embedment into n-dimensional space simulates more or less rigorously spatial correlations manifested particularly by cyclization. However, even in the absence or with neglect of spatial correlations, there may exist long-range stochastic correlations (cf. e.g.(1). In this case, using the statistical theories the branched and crosslinked structures are generated from units at every stage of the crosslinking reaction irrespective of the preceding states of the system with respect to the connectivity pattern between the units. This approach is rigorous for equilibrium controlled reactions but does not describe adequately the build-up by kinetically controlled reactions (2-4).

The kinetically controlled network build-up is adequately described by coagulation equations of the Smoluchowski type (cf. e.g. (5,6)). The reactions controlled by chemical kinetics based on the mass action law are described by a special form of the coagulation equation in which the kernel of the equation is proportional to the number of reactive groups of a given type in both interacting aggregates (molecules) and by the corresponding rate constants characterizing the intensity of bond formation. As has been shown (2,8), both the statistical and kinetic method give the same results for systems without stochastic correlations, e.g. for reactions without substitution effect. In step polyaddition reactions with substitution effect, the deviations arising from the (incorrect) application of the statistical method were found not to be too serious for systems of experimental importance (3,7). Apart from the mathematical complexity of solution for a certain polyfunctional system, the kinetic method has the disadvantage that it regards the gel as one "molecule" and cannot in any way characterize its internal structure.

However, in a number of systems the crosslinking reaction is released by an initiating species which can be present in the system or formed in the course of reaction. In this contribution, it is shown on the example of the living polymerization that application of the statistical approach may lead to serious deviations. The linear polymerization will be treated first to demonstrate the application of the formalism of the generating functions, the use of which is of great advantage in treating polyfunctional systems.

Linear Living Polymerization

The build-up of linear chains by reacting the monomer **M** with initiator **I** and reactive ends of polymers P_i of the degrees of polymerization i is described by the following scheme

$$\begin{array}{l} M + I \xrightarrow{k_I} P_1 \\ M + P_1 \xrightarrow{k_p} P_2 \\ \vdots \\ M + P_k \xrightarrow{k_p} P_{k+1} \\ \vdots \end{array} \qquad (1)$$

and the following set of kinetic equations

$$\begin{array}{l} di/dt = -k_I mi \\ dc_1/dt = k_I mi - k_p mc_1 \\ \vdots \\ dc_k/dt = k_p mc_{k-1} - k_p mc_k \\ \vdots \end{array} \qquad (2)$$

where m, i, c_1, ..., c_k are molar concentrations of M, I, P_1, ... P_k, respectively

This set of differential equations has already been solved (cf. e.g.(8)) to obtain the degree-of-polymerization averages as a function of k_p, k_I and monomer consumption.

Next, the transformation of set (2) to the differential equation (4) for the number fraction generating function (gf) $g(z)$ is performed by multiplying each equation for c_k of set (2) by the k-th power of the variable of the gf z^k. The gf $g(z)$ is defined as

$$g(z) \equiv \sum_i c_i z^i \qquad (3)$$

Transformation of Eq.(2) yields

$$\frac{dg(z)}{d\tau} = mg(z)(z-1) + mg(z)(z-1) + \kappa mzi \qquad (4)$$

where $\kappa = k_I/k_P$ and $\tau = k_P t$.

Since

$$di/d\tau = -\kappa mi \quad \text{or} \quad \int m d\tau = -(\ln i)/\kappa, \qquad (5)$$

the solution for $g(z)$ is obtained in the following form

$$g(z) = \frac{\kappa z i_0}{z - 1 + \kappa} \left[(i/i_0)^{-(z-1)/\kappa} - (i/i_0) \right], \qquad (6)$$

where i_0 is the concentration of I at t=0. The $g(z)$ is not normalized to unity, $g(1) = i_0 - i$, since according to the definition (3), c_i is time dependent and equals $i_0 - i$. The dependence of $g(z)$ on i can be transformed to the dependence on m considering Eq.(5), together with the time dependence of monomer consumption

$$dm/d\tau = - \kappa mi - m(i_0 - i) \qquad (7)$$

which yields

$$m_0 - m = ((\kappa - 1)/\kappa)(i_0 - i) + (i_0/\kappa)\ln(i_0/i) \qquad (8)$$

For $\kappa \gg 1$, at t=0 $c_1 = c_{10} = i_0$ and

$$g(z) = i_0 z e^{(z-1)[(m_0-m)/i_0 - 1]}$$

and the normalized gf

$$g(z) = ze^{(z-1)(\bar{P}_n-1)} = \sum_x \frac{x(\bar{P}_n-1)^{x-1} e^{-(\bar{P}_n-1)} z^x}{x!} \qquad (9)$$

is the gf for the Poisson distribution.

The degree-of-polymerization averages can be directly obtained from the moments of $g(z)$. The number average $\bar{P}_n$ follows also from stoichiometric considerations

$$\bar{P}_n = g'(1)/g(1) = (m_0 - m)/(i_0 - i) \qquad (10)$$

The weight average $\bar{P}_w$ is derived from the weight fraction gf $W(z)$

$$W(z) = zg'(z)/g'(1) \qquad (11)$$

$$\bar{P}_w = W'(1) = g''(1)/g'(1) + 1 \qquad (12)$$

$$= (i_0/\kappa^2)\{\ln^2(i/i_0) - 2(\kappa - 1)[\ln(i/i_0) + 1 - i/i_0]\}$$

The derivation of higher averages is straightforward; e.g. P_z is derived from $Z(z) = zW'(z)/W'(1)$, $\bar{P}_z = Z'(1)$. In these expressions, $X'(z) = \partial X(z)/\partial z$ and $X''(z) = \partial^2 X(z)/\partial z^2$.

Examples of variations of $\bar{P}_w/\bar{P}_n$ as a function of κ, the initial ratio i_0/m_0 and monomer conversion $\alpha_M = (m_0 - m)/m_0$ are given in Table 1 which shows that the polydispersity is determined mainly by κ and i_0/m_0.

Table 1 Variation of polydispersity $\bar{P}_w/\bar{P}_n$

	$\alpha_M = 0.1$				$\alpha_M = 1.0$			
i_0/m_0 \ κ	0.01	0.1	1.0	10	0.01	0.1	1.0	10
0.001	1.18	1.02	1.01	1.01	1.01	1.00	1.00	1.00
0.01	1.30	1.22	1.10	1.09	1.18	1.02	1.01	1.01
0.1	1.35	1.35	1.26	1.11	1.30	1.22	1.10	1.09
0.5	1.37	1.29	1.09	1.01	1.34	1.34	1.29	1.25

Generation of Chains from Polyads

Statistical generation of chains from monomer units, dyads, triads, ... etc. is an alternative way which corresponds to the first, second, third,... etc., order of Markovian statistics. There is no reason for the use of this approach in generating linear chains, but the method would be of interest for non-linear polyfunctional systems, because it could be used also for the description of the gel. The purpose of this section is to compare the exact kinetic solution with the approximate generation from polyads. In this approach, the DP distribution is generated from polyads composed of k monomer units and from j-mers ($j \leq k$) the concentrations of which are determined by k + 2 kinetic differential equations. For example, if the build-up is executed from triads, the concentrations c of the following species are calculated

$$\begin{array}{lll} \boxed{0} & c_1 & \\ \boxed{1}\boxed{1} & c_2 & \text{oligomers} \\ \boxed{1}\boxed{2}\boxed{1} & c_3 & \end{array} \qquad \begin{array}{lll} \boxed{1}\boxed{2}\boxed{2} & c_{122} & \\ \boxed{2}\boxed{2}\boxed{2} & c_{222} & \text{triads ,} \\ \boxed{2}\boxed{2}\boxed{1} & c_{221} & \end{array}$$

where $\boxed{0}$ means the polymer of DP 1, $\boxed{1}$ and $\boxed{2}$ the terminal and inner units of the chain, respectively. The probability of finding, e.g., a pentamer is proportional to the product $c_{122} \times c_{222} c_{221}$, where $c_{122} = c_{221}$. If one cuts off from the distribution the oligomers (c_1–c_3 of which has been obtained by the exact solution), the renormalized distribution of r-mers ($r > k$) is a function of a single parameter $p = c_{222}/(c_{222} + c_{122})$, and the distribution function is a truncated most probable distribution described, e.g., by the number fraction gf

$$N(z) = \sum_x p^{x-1}(1-p)z^{x+k} = \frac{(1-p)z^{k+1}}{(1-pz)} \qquad (13)$$

The whole DP distribution includes also the r-mers, r=1-3, and it is easy to show that the resulting $\bar{P}_w/\bar{P}_n$ converges to 2 for $p \longrightarrow 1$, which is characteristic of the most probable distribution irrespective of k.

These results shows that the application of the higher-order Markovian statistics in the generation of initiated polymer structures is expected to have only a limited success, particularly at high $\bar{P}_n$. Moreover, the application of higher order Markovian statistics to polyfunctional systems, i.e., a build-up from tree-like clusters, meets with difficulties, because the formation of one bond in an f-functional system affects the state of up to 2f clusters in the case of the first-neighbour effect, 2f(f-1) in the case of the second-nearest neghbour effect, etc. The direct kinetic generation is therefore preferred wherever possible.

Non-linear Polymerization

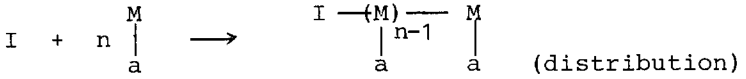
The network build-up from monomers having more than one polymerizable group can be described by solving the corresponding kinetic scheme. However, the inapplicability of the kinetic approach to the characterization of the gel structure has already been mentioned.

A considerable simplification can be achieved if the reactivity of functional groups is independent which is often the case. It has been suggested (1,9), that in the case of an independent reactivity of groups in the polyfunctional monomer there does not exist any stochastic correlation between them. In this case, the polyfunctional living polymerization can be treated as follows (the example is given for a monomer with two functional groups)

(a) the connections between the independent groups are cut and points of cuts are labelled by label a

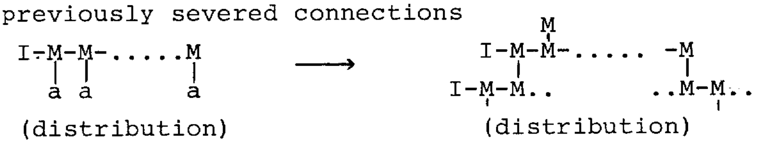
$$\underset{M}{\overset{M}{|}} \longrightarrow 2\,\underset{a}{\overset{M}{|}}$$

(b) the initiated polymerization is carried out using the kinetic method



$$I + n\,\underset{a}{\overset{M}{|}} \longrightarrow I-\underset{a}{\underset{|}{(M)}}_{n-1}-\underset{a}{\underset{|}{M}} \quad \text{(distribution)}$$

(c) the labelled points are combined at random to reform the previously severed connections



For this type of generation, the gf g(z) is directly applicable with a small modification. Some of the groups in the polymer also include unreacted groups, so that M—a units (fraction m) should also be included. Instead of g(z), one has to consider the gf G(z)

$$G(z) = g(z) + mz \tag{14}$$

The variable z is now related not to counting monomer units in the polymer, but to bonds issuing to the next generation. Therefore, G(z) becomes a gf for the number of bonds issuing from a (kinetically generated) chain in the root to the first generation per chain in the root. Thus, by replacing formally z for z_a, one obtains the gf $G_1(z_a)$ for the number of bonds issuing from a unit in generation $g > 0$

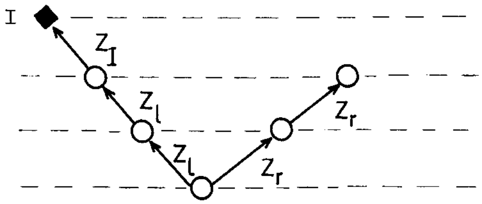
$$G_1(z_a) = G'(z_a)/G'(1) = (g'(z_a) + m)/(g'(1) + m) \tag{15}$$

and the gel point condition

$$G_1'(1) = g''(1)/(g'(1)+m) = 1 \qquad (16)$$

from which the critical conversion can be calculated as a function of κ and i_0/m_0 (Table 2)

For the sake of comparison, the same system is treated statistically using the cascade generation. Because the two polymerizable groups are independent in their reactivity, the reacted and unreacted groups are placed in generation zero, and their distribution with respect to the number and type of issuing bonds is described by the pgf $f_0(z)$; the pgf corresponding to the monomer with two groups $F_0(z)$ is obtained by convolution $F_0(z) = f_0^2(z)$. One has to distinguish between directions of bonds leading to the bound initiating species (e.g. left direction) and to the living chain end (right direction). This situation is illustrated by the following scheme



Thus,

$$F_0(\mathbf{z}) = f_0^2(z) = [(1-\alpha_M)+\alpha_M(\phi_I z_I + \phi_M z_\ell)(\phi_I+\phi_M z_r)]^2 \qquad (17)$$

where z_ℓ and z_r are the pgf variables referring to the left branch (terminated by initiator) and right branch (terminated by the living end), respectively, and z_I refers to the initiating species; ϕ_I and $\phi_M = 1-\phi_I$ are probabilities that a bond from a monomer unit leads to the initiator species in the left branch (living end in the right branch) and another monomer unit, respectively,

$$\phi_I = (i_0 - i)/(m_0 - m)$$

It can be shown that, since the initiating species is monofunctional, z_I can be dropped ($z_I = 1$), and $z_\ell = z_r$, which yields

$$F_0(z) = [1 - \alpha_M + \alpha_M(\phi_I + \phi_M z)^2]^2 \qquad (18)$$

The pgf F_1 for the number of bonds issuing from a unit on generation $g > 0$ is obtained form F_0 by differentiation

$$F_1(z) = (\phi_I + \phi_M z)[1 - \alpha_M + \alpha_M(\phi_I + \phi_M z)^2] , \qquad (19)$$

and the gel point condition is given by

$$F_1'(1) = \phi_M(1 + 2\alpha_M) = 1 . \qquad (20)$$

The critical conversions calculated by the rigorous kinetic method (Eq.(16) and approximate statistical method Eq.(20)) are compared in Table 2.

Table 2 Gel point conversion in the living polymerization of a monomer with two polymerizable groups of independent and equal reactivity

κ	0.01		0.1		1.0		10	
i_0/m_0	K	S	K	S	K	S	K	S
0.001	0.020	0.015	0.030	0.022	0.032	0.023	0.032	0.023
0.01	0.046	0.036	0.083	0.063	0.100	0.076	0.105	0.076
0.1	0.102	0.081	0.204	0.168	0.316	0.257	0.332	0.279
0.5	0.177	0.146	0.375	0.324	0.707	0.643	0.864	0.809

K - kinetic method, S - statistical (cascade) method

As expected, the gel point conversion calculated rigorously is higher by 20-25% compared to that calculated statistically due to a narrower degree-of-polymerization distribution. Such difference is rather serious and may completely distort the effect of unequal or dependent reactivities, if it is operative. The application of a combination of the kinetic and statistical method is, therefore, necessary.

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