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Modelling of Hyperbranched and Network Polymerisation

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SUMMARY: Two basic groups of models of polymerisation, the classical, known as the Flory-Stockmayer models, and the computer based ones which are in fact Monte-Carlo simulation techniques are briefly reviewed. The notion of time correlations is explained. Four versions of kinetic modelling of hyperbranched polymerisation are presented.

Introduction

The term modelling stands in this paper for the attempts of predicting the effects of reactivities of monomers or their functional groups as well as of the reaction paths in polymerisation systems on the size distribution of polymer species formed during polymerisation. In short, we discuss the conversion - size distribution relationships in polymerising systems. We concentrate on the step-growth polymerisation systems leading to either cross-linked or hyperbranched polymers. According to IUPAC recommendations$^{1)}$, the polymerisation leading to cross-linked polymers is termed the *network polymerisation*. By analogy, the polymerisation involving an AB_f monomer (A and B are reactive groups) that leads to hyperbranched polymers should be called the *hyperbranched polymerisation*.

We start with a brief review of the methods of modelling in order to introduce the notion of the time correlations that affect size distribution of polymer species. Then we discuss the kinetic methods of modelling by using the Smoluchowski coagulation equation. Finally, the Smoluchowski-like equations describing the time evolution of size distribution in hyperbranched polymerisation of an AB_2 monomer are presented in several versions that tackle intramolecular reactions (cyclization) and take into account changes in reactivities of functional groups.

The methods of modelling

Two general groups of modelling methods are used to predict the conversion - size distribution relationship in network polymerisation. These are:

- the classical theories, usually termed the Flory-Stockmayer model, and
- the computer based models utilizing Monte-Carlo techniques.

Both are essentially graph-like models. They usually ignore the actual shape or size of reacting molecules as well as disregard any specific interactions between species other than

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chemical affinity that leads to bond formation. A multi-functional monomer with, say three functional groups or reactive sites is represented in the model by a point connected to at most three adjacent units.

The classical theory

The classical theory is based on stochastic arguments$^{2)}$. The models based on the classical theory can be classified into two groups differing in the philosophy, methodology and results. As the background both have the main paradigm of chemistry, the Gulberg and Waage law of mass action$^{3)}$ and belong to the class of mean-field models.

The ***statistical*** methods of modelling are the oldest and best-known classical methods used for predicting the conversion - size distribution relationships. The original Flory$^{4)}$ and Stockmayer$^{5)}$ works were based on statistical arguments. Many authors later applied the same philosophy of modelling. The best knowns are the *cascade theory* introduced by Gordon$^{6)}$, the *rate model* of Stepto's school$^{7)}$, the *recursive method* by Miller and Macosko$^{8)}$, and the direct Markovian modelling$^{9)}$ used recently by Tobita$^{10)}$. A number of authors including Kajiwara$^{11)}$, Burchard$^{12)}$, and particularly Dušek and his coworkers$^{13)}$ used the most comprehensive Gordon's approach to solve many quite sophisticated problems related to polymer network formation.

The independent variable used in the statistical theories of polymer network formation is the set of probabilities at which particular functional groups or reactive sites at units are being reacted. The set is usually related to the conversion degree in the system and, if necessary, to the ratio at which the groups are present in the system at the start of reaction.

The general procedure of a statistical method is:

- at a given extent of reaction calculate the set of probabilities at which ***units*** in the system are at a certain substitution degree, i.e., linked to zero, one, two, three, etc., neighbouring units; since the probabilities can be identified with mole fractions, use rate equations to calculate instantaneous concentrations and rates at which the units are formed from less substituted, and converted into more substituted, ones;
- use an appropriate mathematical tool to convert the calculated set of probabilities (mole fractions of units) into the set of probabilities of finding polymer species of polymerisation degree one, two, three, etc., i.e., into the size distribution;
- from the resulting probability distribution function often available only in an implicit form, extract moments of size distribution, moment related measurable quantities, or an explicit form of size distribution.

The step of converting the probabilities of functional groups being reacted into the probabilities of finding units with a given substitution degree reflects the reaction paths in the system. As mentioned above, because of the graph-like nature of the theories, the "units" may well be polymer chains with some distribution of the number of functional groups or sites$^{14)}$.

In the alternative ***kinetic*** approach to modelling polymerisation systems, exactly the same reaction paths are considered as in statistical methods. The general algorithm is the following.

- Write down equations for rates at which ***whole molecules*** appear in the system formed from smaller building blocks and vanish in reactions with other molecules;
- use an appropriate mathematical tool to convert the resulting infinite set of rate equations into a manageable form, usually into a single or a small set of "master" rate equations;
- extract the parameters of the system, such as averages of molecular weight, from the master equation(s).

The kinetic models seem mathematically slightly more demanding than statistical ones. Their main disadvantage, however, is that in all systems, beside the simplest ones, they fail beyond the gel point and hence cannot be used to evaluate the structure and properties of gel molecule.

Substitution effects and time correlations

The basic difference between the two alternative classical methods of modelling is that in the statistical methods, the type of size distribution of polymer species is implicitly imposed on the system by selecting the method of compounding the sets of probabilities. In other words, the links do not carry information on the moment they were formed, just the information on the types of functional groups they connect. Hence the statistical methods generate the size distribution of the systems that behave as if the system were in equilibrium at each conversion degree$^{15)}$.

In kinetic calculations, on the other hand, the track is kept of the sizes of polymer species from the beginning of polymerisation up to the given conversion degree. Kuchanov$^{16)}$ was the first to demonstrate that in the presence of substitution effects, the kinetic modelling yielded results that differed from those calculated for the very same model by using statistical arguments. These differences were due to the so-called time correlations, which the statistical analysis usually fails to take into account. The substitution effect is the change of reactivity of a functional group at a unit due to substitution of the latter. This kind of substitution effect has been termed by Gordon and Scantlebury$^{17)}$ the first shell substitution effect. In polymerisation model involving monomers with functional groups reacting with a strong first shell substitution effect, the kinetic calculations yielded quite different conversion dependence of the weight average degree of polymerisation or the gel point conversion[18] as compared with statistical calculations for exactly the same systems.

The idea of the time correlation effect is illustrated in Fig. 1 where two size distributions are presented, each obtained at 50% conversion of some 20 bi-functional units. If we agree intuitively that distribution *A* is the most probable one, the other one is an example of non-equilibrium size distribution that may be formed in a kinetically controlled reaction. Note that both distributions share the same number average degree of polymerisation. Unlike higher averages, the latter is not affected by time correlations[18].

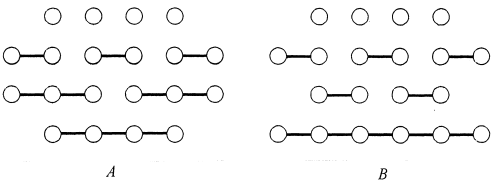

Figure 1. Illustration of the effect of time correlations on size distribution in homopolymerisation of 2-functional monomer. Distribution *B* differs from the most probable one (*A*) if the sequence of bond formation is affected be substitution effects.

Monte-Carlo methods

There are two groups of computer-based methods of modelling network polymerisation involving random number generators. The first one is simply the Monte-Carlo method of solving various equations arising from modelling that cannot be solved otherwise, i.e., neither analytically nor numerically without random number generator. This group of methods of modelling can be termed the pseudo-classical models.

The percolation methods[19] both on- and off-lattice[20] constitute the other group of Monte-Carlo modelling. The percolation-based methods reached a high level of development following the higher and higher efficiency of modern computers.

The Smoluchowski coagulation equation

The equation devised by Smoluchowski in 1916[21] is in fact infinite set of rate equations of the form:

$$\frac{\mathrm{d}[k]}{\mathrm{d}t} = \frac{1}{2}\sum_{i=1}^{k-1} K_{i,k-i}[i][k-i] - [k]\sum_{i=1}^{\infty} K_{k,i}[i] \tag{1}$$

where $[k]$ ($k = 1,2,\ldots$) is the concentration of species (aggregates, polymer molecules, etc.) consisting of k units, t is time, and $K_{i,k}$ is the rate constant for the reaction of i-mers with k-mers. The positive terms in eq. (1) are the rates of k-mer formation from matching smaller molecules and the negative terms are the rates at which k-mers vanish in reactions with other molecules. For some forms of $K_{i,j}$ the Smoluchowski equation can be solved analytically, i.e., the time dependence of the size distribution can be expressed explicitly. For certain monomers the rate constants $K_{i,j}$ can be expressed as products of functions of i and j only, say s_i and s_j. Then the master equations mentioned above can be derived from the Smoluchowski coagulation equation by multiplying each rate equation by x^{s_k} where x is a dummy variable and summing them up for every k.

Table 1. The master equations obtained from the Smoluchowski coagulation equation that are suitable for kinetic modelling of homopolymerisation of some monomers. A and B are functional groups and R stands for an organic moiety$^{22)}$.

Monomer	$K_{i,j}(=s_i s_j)$	Master equation
RA_2	1	$\frac{\partial H}{\partial t}=\frac{1}{2}H^2-HH_0$
RA_f	$[(f-2)i+2][(f-2)j+2]$	$\frac{\partial H}{\partial t}=\frac{1}{2}\left(\frac{\partial H}{\partial x}\right)^2-x\left(\frac{\partial H}{\partial x}\right)H_x$
RA_∞	ij	$\frac{\partial H}{\partial t}=\frac{x^2}{2}\left(\frac{\partial H}{\partial x}\right)^2-x\left(\frac{\partial H}{\partial x}\right)H_x$
ARB_2	$i+j+2^*$	$\frac{\partial H}{\partial t}=\left(x\frac{\partial H}{\partial x}+H\right)(H-H_0)-(H_x-H_0)H$
$K_{i,j}=A+B(i+j)+Cij$		Solved by Spouge^{23}
$H(t,x)=\sum_{i=1}^{\infty}[i]x^{s_i}$; $H_0(t)\equiv H(t,1)=\sum_{i=1}^{\infty}[i]$; $H_x(t)\equiv\left(\frac{\partial H}{\partial t}\right)\Big\vert_{x=1}=\sum_{i=1}^{\infty}s_i[i]$		

*Here, the rate constant is not a product and s_i should be replaced by i in the last raw definition of H, see the following chapter.

Kinetic modelling of hyperbranched polymerisation

Below we outline four kinetic models of polymerisation of an AB_2 monomer. The interest in modelling polymerisation of AB_2 monomers has recently revitalized mostly because of the attempts of synthesis of hyperbranched polymer resembling dendrimers$^{24\text{-}26)}$. The models presented here are based on the Smoluchowski coagulation equation. Apart of the simplest first model all the remaining are new ones. The models gradually take into account more and more factors that affect size distribution evolution in hyperbranched polymerisation. The models are limited to AB_2 (or ARB_2) monomers, but can easily be generalized to describe polymerisation of an AB_f one.

The random case

In the random case dealt with many years ago by Flory[27)] and later by Ziff and others[28)], the reactivity of functional groups does not change during the process and only acyclic molecules are formed (intramolecular reactions are excluded). Then the rate constant of the reaction between i-mer with j-mer can be written as

$$K_{i,j} = \kappa(i + j + 2) \tag{2}$$

where κ is the contribution to the rate constant independent of the size of reacting molecules, and the term $i + j + 2$ takes into account all possibilities the molecules can react with each other. (The contribution κ at each $K_{i,j}$ was omitted in Table 1. This quantity does not affect calculations, it just modifies time units.) The single A group of an i-mer may react with any of $j + 1$ B groups of j-mer. And *vice-versa*, the A group of j-mer may react with one of $i + 1$ B groups in i-mer.

It is merely the matter of algebra to show that multiplication of time units by κ (new time variable: $\tau = \kappa t$) and adding up all terms in the Smoluchowski coagulation equation premultiplied by exp(kx) for each k, yields the partial differential (master) equation

$$\frac{\partial G}{\partial \tau} = \left(\frac{\partial G}{\partial x} + G \right)(G - G_0) - (G_x + G_0)G \tag{3}$$

for the counting function

$$G(\tau, x) = \sum_{i=1}^{\infty} [i] e^{ix} \tag{4}$$

where x is a dummy variable of no physical meaning,

$$G_0 = G_0(\tau) = G(\tau, 0) = \sum_{i=1}^{\infty} [i] \tag{5}$$

and

$$G_x = G_x(\tau) \equiv \left. \frac{\partial G}{\partial x} \right|_{x=0} = \sum_{i=1}^{\infty} i[i] \tag{6}$$

The concentration of i-mers, $[i]$ is conveniently expressed as the number of i-mers divided by the total number of units in the system.

Equation (4) can be solved analytically, but for practical purposes it is sufficient to find analytical expressions for averages of polymerisation degree or the explicit distribution. The latter is also available by solving the Smoluchowski equation one be one for each k. Some of these quantities are presented in Table 2.

Table 2. Some explicit expressions obtained from equation (3). They describe the time evolution of number and weight average polymerisation degree, P_n and P_w, respectively, as well as the conversion of A groups in the polymerisation of an AB_2 monomer, p ($z \equiv \exp(\tau)$ where τ is the reduced time)[29].

$P_n = 2z - 1$	$p = 1 - G_0 = 2\frac{z-1}{2z-1}$
$P_w = 2z^2 - 1$	$\frac{P_w}{P_n} = \frac{2z^2-1}{2z-1} = \frac{1-p^2/2}{1-p}$

The random polymerisation with cyclization

The simplest model of AB_2 hyperbranched polymerisation described in previous section can be extended to deal with cyclization. The cyclization introduces long-range correlation into the system and cannot be dealt with rigorously within the frames of the classical theory. We have modified the Smoluchowski equation to encompass cyclization at least approximately. We assumed the intramolecular reactions to proceed with the rate constant proportional to the number of B groups in the molecule with adjusted proportionality constant λ. The Smoluchowski-like master equation derived for this case had the form of two partial differential equations for the acyclic (G) and cyclic molecules (g)[29]

$$\frac{\partial G}{\partial \tau} = \left(\frac{\partial G}{\partial x} + G\right)(G - G_0 - \lambda) - (G_x + G_0 + g_x)G \tag{7}$$

$$\frac{\partial g}{\partial \tau} = \left(\frac{\partial G}{\partial x} + G\right)\lambda + \frac{\partial g}{\partial x}(G - G_0) \tag{8}$$

for the counting functions now defined as

$$G(\tau, x) = \sum_{i=1}^{\infty} [i]_b e^{ix} \tag{9}$$

and

$$g(\tau, x) = \sum_{i=1}^{\infty} [i]_c e^{ix} \tag{10}$$

with superscripts 'b' and 'c' referring the concentrations to branched and cycle containing molecules, respectively

The model described by the set of equations (7) and (8) is a new one and the result may be compared with Monte Carlo model devised recently by Dušek et al.[25]

To illustrate how the model works, in Fig. 2 we present the calculated changes of molecular parameters of the system for just one value of cyclization parameter, $\lambda = 0.05$. More results and details of calculations can be found in ref[29].

The system with substitution effect

A set of equations alternative to (7) and (8) can be obtained for counting functions defined slightly differently, namely for the polynomial functions: $H(\tau,x)=\sum_i [i]_b x^i$ and $h(\tau,x)=\sum_i [i]_c x^i$ (cf. Table 1). Obviously, the form of counting function does not affect the results of modelling. The polynomial functions are preferred when the system reacts with the substitution effect. We limit ourselves to the case where B groups react with the first shell substituting effect$^{17)}$. Hence we need to keep track of the numbers of units in a molecule that posses B groups of the 'first' kind (like in a monomer or in dangling units), and the groups of the 'second' kind (like in units forming linear parts of molecules). The molecules are therefore coded as [*i*,*j*]-mers. The principle of coding is shown in Fig. 3. The coding is not unique for all isomers, but the molecules sharing their codes share also the reactivity. The polymerisation degree of an acyclic [*i*,*j*]-mer is $2i+j-1$ (or $2i+j$ for the molecule containing a cycle). Suppose the ratio of reactivity of the 'first' B group in an AB_2 unit (either in monomer or in dangling units) to that of the 'second' B group is $2\alpha = k_2/k_1$. It can be shown that for the polymerisation system defined in this way, the Smoluchowski-like master equation describing the time evolution of the size distribution has the remarkably compact form:

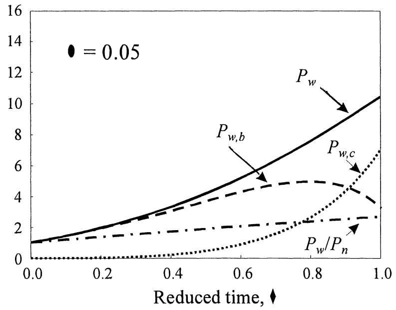

Figure 2. Weight-average polymerization degree of the whole system as well as that of branched and cycle-containing molecules calculated from the set of equations (7) and (8). For details see ref.^{29}

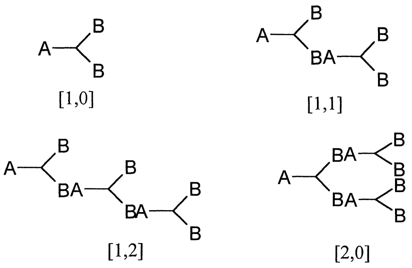

Figure 3. The monomer, dimer, and two isomeric trimers along with their codes.

$$\frac{\partial H}{\partial \tau}=H\left[(\alpha y)\frac{\partial H}{\partial x}+\frac{\partial H}{\partial y}\right]-H_1\left[x\frac{\partial H}{\partial x}+(\alpha y)\frac{\partial H}{\partial y}\right]-H(H_x+H_y) \tag{11}$$

for the counting function defined thus:

$$H(\tau,x,y)=\sum_{i=1}^{\infty}\sum_{j=0}^{\infty}[i,j]_b x^i(\alpha y)^j \tag{12}$$

Equation (11) carries out all information on the size distribution in the polymerising system as it evolves in polymerisation time τ expressed in reduced units. The related functions of time only are:

$$H_1(\tau) \equiv H[\tau, 1, (1/\alpha)] \text{ and } H_\xi(\tau) \equiv \left.\frac{\partial H}{\partial \xi}\right|_{x=1, y=1/\alpha} \quad ; \xi = x, y \tag{13}$$

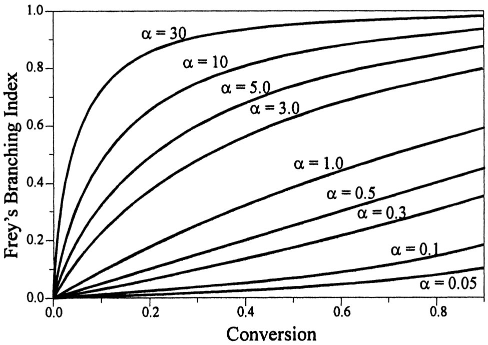

Figure 4. Frey's branching index in the systems where B groups react with substitution effect. The parameter a is twice the ratio of reactivity of 'second' group relative to that of the 'first one in an AB_2 monomer.

Detailed description of derivation of eq. (11) will be published separately. Here we limit ourselves to pointing out that the time dependence of the averages of polymerisation degree derived from eq. (11) for the random case ($k_1 = k_2$) is the same as that in Table 2. It seems also worth noticing that the method of coding the molecules enables expressing analytically the Frey branching index[30)] in the polymerisation system. The results of calculations to be described elsewhere in detail are presented in Fig. 4. Note that the dependence of this index on the A group conversion for the random system ($\alpha = ½$) is linear. It becomes non-linear for the system with groups reacting with substitution effect.

As can be seen in Fig. 4, quite naturally the systems becomes more highly branched at the early stages of polymerisation when the second B group in a unit reacts more readily than the first one ($k_1 < k_2$).

The system with substitution effect and cyclization

Without going into details we will present the so far final version of the Smoluchowski equation based kinetic model of step-wise polymerisation. It takes into account both the substitution effect and cyclization. The latter is again treated in a simplified way with a single parameter λ modifying the chance of intramolecular reaction. The counting function H and its related functions, H_1, H_x, and H_y are defined as in the acyclic case. The functions denoted with symbol h are defined for cycle containing $[i, j]$-mers analogously as those denoted with H for acyclic molecules.

$$\begin{aligned}\frac{\partial H}{\partial \tau} &= \left[(\alpha y)\frac{\partial H}{\partial x}+\frac{\partial H}{\partial y}\right](H-\lambda)-\left[x\frac{\partial H}{\partial x}+(\alpha y)\frac{\partial H}{\partial y}\right]H_1 - H(H_x+H_y+h_x+h_y)\\ \frac{\partial h}{\partial \tau} &= \left[(\alpha y)\frac{\partial H}{\partial x}+\frac{\partial H}{\partial y}\right]\lambda+\left[(\alpha y)\frac{\partial h}{\partial x}+\frac{\partial h}{\partial y}\right]H-\left[x\frac{\partial h}{\partial x}+(\alpha y)\frac{\partial h}{\partial y}\right]H_1\end{aligned} \qquad (14)$$

The molecular parameters of the system described by equations (11) and (14) can be calculated by solving the sets of differential equations obtained from them by successive differentiation, followed by setting the dummy variable to values at which they vanish ($x = 1$, $y = 1/\alpha$). The resulting ordinary differential equations are numerically easily solvable. In the cases where cyclization is taken into account, however, additional self-consisting calculations are required, as the sets of ordinary differential equations do not close up. For details the readers are referred to a forthcoming paper.

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