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## A theoretical model of hyperbranched polymerization involving an $AB_f$ monomer

### Part I. DEGREE OF BRANCHING

*Affectionately dedicated to my tutor, Professor Bożena Kolarz on Her Jubilee.*

**Summary** — A generalized theoretical model of hyperbranched polymerization of an  $AB_f$  monomer is derived. The model is a classical mean-field one based on the Smoluchowski coagulation equation. The monomer functional groups B react according to the *first shell substitution effect* principle. It is shown that irrespectively of the monomer functionality ( $f$ ), the number average molecular weight of hyperbranched polymers depend on conversion of A groups in exactly the same way. Also the *degree of branching*, a parameter describing perfectness of polymer structure changes very slightly with increasing functionality of the monomer.

**Key words:** hyperbranched polymerization, kinetic model, Smoluchowski coagulation equation, substitution effect, functionality of the monomers, degree of branching.

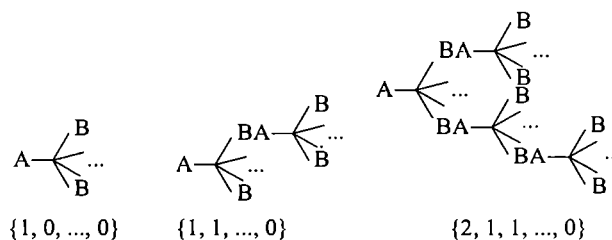
An interest in hyperbranched polymers has recently rapidly grown mostly because of the expected similarity of the behaviour of hyperbranched polymers to dendrimers and also due to potential applications of the hyperbranched polymers as polymer modifiers and multifunctional cross-linking agents [1–7].

In fact the idea of using multifunctional monomers in polymerization that produce highly branched, but not cross-linked material is known since the fundamental works by Flory [8, 9] who derived an explicit function for the size distribution in polymerization of an  $AB_2$  monomer. More recently, the same problem was tackled by several authors, including the present one [10–12]. This paper deals with the kinetic model of polymerization of an  $AB_f$  monomer with arbitrary  $f$ . In particular, the degree of branching in model hyperbranched polymers is analyzed.

#### CODING OF MOLECULES

In order to follow the changes in the content of molecules of different reactivity (rather than different size or structure) it is necessary to use a proper coding system. Since the monomer considered reacts with the “*first shell*

*substitution effect*” (cf. ref. [13]), a method of coding molecules has to be applied, similar to that used in previous papers [15, 14]. Thus, each molecule has a code in the form of an  $f$ -component vector:  $s = (s_0, s_1, \dots, s_{f-1})$ , the entry  $s_i$  of which is the numbers of units with exactly  $i$  B groups already reacted. Note that the units with all  $f$  groups B reacted are not counted and that there is no one-to-one correspondence between a single vector and the structure of its corresponding molecule. One vector may describe the structure of many isomeric molecules, but they all share the same reactivity of their B groups. Examples of small molecules that are present in the sys-



*Scheme A. Examples of hyperbranched molecules and their corresponding codes*

tem and their corresponding composition vectors are shown in Scheme A. Only acyclic molecules are considered in this paper.

### THE SMOLUCHOWSKI-LIKE COAGULATION EQUATION

The original Smoluchowski equation [16] is in fact an infinite set of differential equations describing the rates at which a molecule consisting of a certain number of identical units (an  $i$ -mer) is formed out of two matching smaller components and the rate at which this molecule vanishes from the system in reactions with other molecules. All reactions are considered to be the second order reactions and the rate constant for all reactions between the same reactive groups are the same [13]. Analogous rate reactions, but with different reaction constants for each type of unit can be written for polymerization of an  $AB_f$  monomer. From the sum of rates of all possible reactions, at which an  $s$  molecule is formed, the rates of reactions are subtracted, at which this molecule is eliminated from the system. All the rates are products of appropriate rate constants and concentrations. To write down all these rates is quite tedious an operation, but otherwise it is straightforward. Then, the product of dummy variables multiplies the resulting rate equation:

$$x_0^{s_0} (\kappa_1 x_1)^{s_1} \dots (\kappa_{f-1} x_{f-1})^{s_{f-1}} \quad (1)$$

where:

$$\kappa_i = \frac{(f-i)k_i}{fk_0}; \quad i = 1, 2, \dots, f-1 \quad (2)$$

is the relative rate constant describing the ratio of the reactivity of B groups in the unit with  $i$  groups already reacted ( $k_i$ ) and the reactivity of B groups in a terminal unit (or monomer) ( $k_0$ ).

Finally, the rate equations for every  $s_i$  are summed up. After some elementary algebraic operations one obtains the following Smoluchowski-like equation:

$$\begin{aligned} \frac{\partial H}{\partial \tau} = & H \left[ (\kappa_1 x_1) \frac{\partial H}{\partial x_0} + (\kappa_2 x_2) \frac{\partial H}{\partial x_1} + \dots + (\kappa_{f-1} x_{f-1}) \frac{\partial H}{\partial x_{f-2}} + \frac{\partial H}{\partial x_{f-1}} \right] + \\ & - H_p \left[ x_0 \frac{\partial H}{\partial x_0} + (\kappa_1 x_1) \frac{\partial H}{\partial x_1} + \dots + (\kappa_{f-1} x_{f-1}) \frac{\partial H}{\partial x_{f-1}} \right] + \\ & - H (H_{x_0} + H_{x_1} + \dots + H_{x_{f-1}}) \end{aligned} \quad (3)$$

where the counting (generating) function  $H$ , containing all information about the distribution of concentrations of all molecules, is defined thus:

$$H(x_0, x_1, \dots, x_{f-1}, \tau) = \sum_{s_0=1}^{\infty} \sum_{s_1=0}^{\infty} \dots \sum_{s_{f-1}=0}^{\infty} [s_0, s_1, \dots, s_{f-1}] x_0^{s_0} (\kappa_1 x_1)^{s_1} \dots (\kappa_{f-1} x_{f-1})^{s_{f-1}} \quad (4)$$

and the brackets are used to denote the concentration of the molecules sharing the same code. The concentration

is conveniently expressed in terms of the number of molecules sharing the same code divided by the total number of units in the system. The reduced time  $\tau$  is the actual time multiplied by  $fk_0$ . The other symbols used in equation (3) are:  $H_p$  is the function  $H$  in the special reference point:  $\{x_0, x_1, \dots, x_{f-1}\} = \{1, \kappa_1^{-1}, \dots, \kappa_{f-1}^{-1}\}$  where the product involving dummy variables ( $x_i$ ) vanishes from eq. (4) and

$$H_p \equiv H_p(\tau) = \sum_{s_0=1}^{\infty} \sum_{s_1=0}^{\infty} \dots \sum_{s_{f-1}=0}^{\infty} [s_0, s_1, \dots, s_{f-1}] \quad (5)$$

Note that, with the concentration units adopted,  $H_p(0) = 1$  and  $1/H_p$  is the number average polymerization degree in the system. The functions  $H_{x_i}$  are the partial derivatives of  $H$  with respect to  $x_i$  ( $i = 0, 1, \dots, f-1$ ), also calculated at the reference point (they are functions of time, only).

### CONVERSION DEGREE

As already mentioned, the Smoluchowski-like equation (3) describes the time evolution of the entire molecular size distribution in the polymerization system. All molecular parameters become available by solving ordinary differential equations that are derived from eq. (3). Here we demonstrate the methods of extracting the conversion degree, number average polymerization degrees, and the modified degree of branching.

The conversion degree ( $p$ ) is defined differently than in the original works of Flory [9] or Ziff [17]. It is the fraction of all A groups that have reacted. Thus,  $p$  varies from 0 to 1, not from 0 to  $1/f$  as in the original definition by Flory.

The conversion degree can be calculated by making use of the definition of concentration units. Since, as follows from eq. (5),  $H_p$  is the number of molecules per unit, and one reacted B group reduces the number of molecules by one, the conversion degree is simply

$$p = 1 - H_p \quad (6)$$

$H_p$  is obtained directly from eq. (3) by converting the latter into the ordinary differential equation. This is done by substituting  $\{x_0, x_1, \dots, x_{f-1}\}$  by  $\{1, \kappa_1^{-1}, \dots, \kappa_{f-1}^{-1}\}$  in all functions. Then eq. (3) becomes:

$$\dot{H}_p = -H_p (H_{x_0} + H_{x_1} + \dots + H_{x_{f-1}}) \quad (7)$$

Similarly, the functions on the right-hand-side of eq. (7) are available by solving the system of differential equations obtained by differentiating eq. (3) with respect to every dummy variable followed by substituting  $\{x_0, x_1, \dots, x_{f-1}\}$  by  $\{1, \kappa_1^{-1}, \dots, \kappa_{f-1}^{-1}\}$ .

The reader might wish to verify that:

$$\dot{H}_{x_0} = -H_p H_{x_0} \quad (8)$$

$$\text{and} \quad \dot{H}_{x_i} = -\kappa_i H_p (H_{x_i} - H_{x_{i-1}}) \quad (9)$$

for:  $i = 1, 2, \dots, f-1$ .

Further differentiation of partial derivatives  $\frac{\partial^2 H}{\partial \tau \partial x_i}$  with respect to dummy variables  $x_i$  followed by evaluating their functional forms in the reference point  $\{1, \kappa_1^{-1}, \dots, \kappa_{f-1}^{-1}\}$  yield more ordinary differential equations with respect to time for the functions such as, e.g.  $H_{x_0, x_2}$ , that are needed for calculating weight-average polymerization degree *via* moments of size distribution and will not be considered in this paper.

### MOMENTS OF SIZE DISTRIBUTION

Let the molecule  $s = (s_0, s_1, \dots, s_{f-1})$  has polymerization degree  $P$ . The relation between the code numbers and the size  $P$  is straightforward. As one can easily verify, any hyperbranched molecule of size  $P$  prepared from  $AB_f$  monomer has  $P(f-1)+1$  unreacted B groups. On the other hand, the number of free B groups is  $s_0 f + s_1(f-1) + \dots + s_{f-1}$ . Hence,

$$P = (f-1)^{-1} (s_0 f + s_1(f-1) + \dots + s_{f-1}) - 1 \quad (10)$$

The  $k$ -th moment of size distribution is defined thus:

$$M_k = \sum_{s_0=1} \sum_{s_1=0} \dots \sum_{s_{f-1}=0} [s_0, s_1, \dots, s_{f-1}] P^k \quad (11)$$

where  $P$  is given by eq. (10) and the square brackets denote the concentration of the molecules sharing the same set of code numbers.

Note that the zero-th moment is just  $H_p = 1/P_n$ . The first moment is the sum of all units in the molecules divided by the total number of units (*cf.* the definition of concentration units), hence,  $M_1 = 1$ , and the second moment  $M_2$  is the weight average polymerization degree in the system,  $P_w$ . It is not difficult to see that components of the sum in eq. (11) for  $k = 1$  and 2 have the form  $s_i [s_0, s_1, \dots, s_{f-1}]$  and  $s_i s_j [s_0, s_1, \dots, s_{f-1}]$ , respectively ( $i, j = 1, 2, \dots, f-1$ ). These products are expressed by  $\kappa_i^{-1} H_{x_i}$  and  $\kappa_i^{-1} \kappa_j^{-1} H_{x_i, x_j}$ , respectively.

The striking conclusion is that the number average degree of polymerization is given by the familiar equation [9, 14, 15]:

$$P_n = \frac{1}{1-p} \quad (12)$$

in spite of the number of B groups in  $AB_f$  monomer ( $f$ ), provided the conversion is expressed as the fraction of A groups that have reacted [*cf.* eq. (6)].

The time or conversion evolution of the weight average polymerization degree does depend on  $f$ , but this analysis will be dealt with in a forthcoming paper.

### DEGREE OF BRANCHING

The degree of branching ( $DB$ ) in hyperbranched polymer molecules was introduced (*cf.*, e.g. ref. [18]) as a measure of their branching perfectness. For the most common  $AB_2$ -type polymers it was defined as twice the

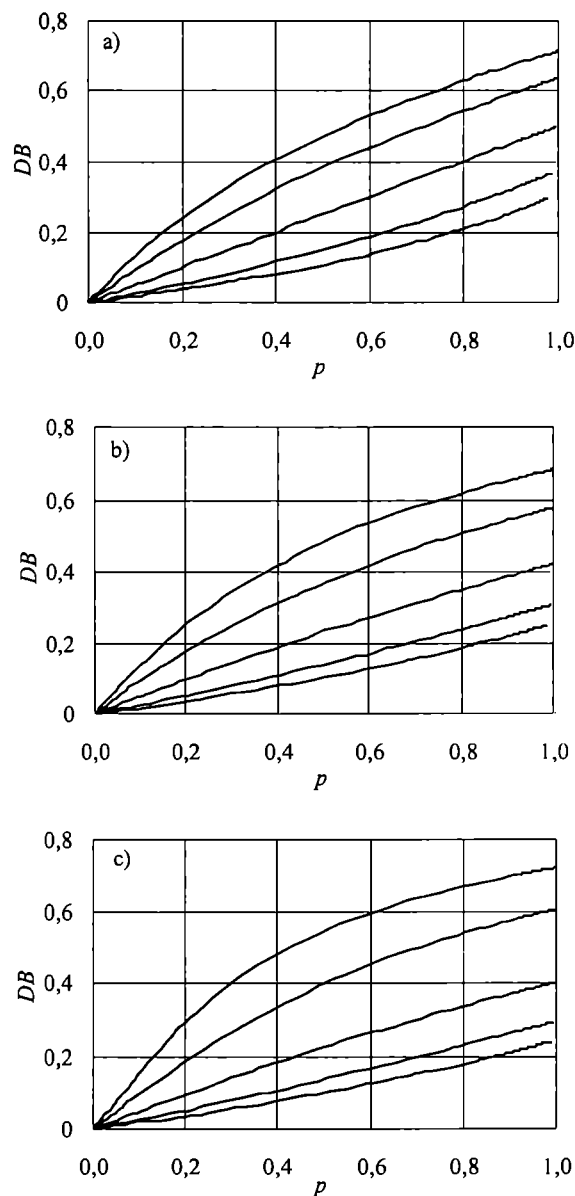


Fig. 1. Degree of branching ( $DB$ ) vs. conversion ( $p$ ) of A groups in polymerization of  $AB_f$  monomers for  $f = 2$  (a), 4 (b) and 6 (c). In all cases the rate constant of reaction between group A and the first B group in a unit,  $k_0 = 1$ . For the curves from top to bottom the rate constant of the reaction of each next B groups was taken to be  $k_i = 3k_{i-1}$ ,  $k_i = 2k_{i-1}$ ,  $k_i = k_{i-1}$  (random case),  $k_i = k_{i-1}/2$ , and  $k_i = k_{i-1}/3$

number of branching (dendritic) units, divided by the total number of units in the system. The degree of branching should be zero for linear polymers and equal to one for a perfect dendrimer. The  $DB$  is the quantity that can be relatively easily evaluated by NMR spectroscopy.

In the random polymerization of an  $AB_2$  monomer (*i.e.*, in the system where monomer reacts with no substitution effect) the branching index grows linearly with conversion of A groups and reaches  $1/2$  at  $p$  approaching 1. The  $DB$  of  $AB_2$  polymer molecules can be in-

creased by using a monomer reacting with positive substitution effect, *i.e.*, the monomer where the second B group reacts faster than the first [10].

For  $f$  higher than 2 the definition of the  $DB$  was provided by Hölter *et al.* [18]. In terms of the symbols used in this paper, the degree of branching is simply expressed as

$$DB = \frac{f(1-H_{x_0}) - \frac{f}{f-1} \sum_{i=1}^{f-1} (f-i)H_{x_i} / \kappa_i}{f(1-H_{x_0}) - \sum_{i=1}^{f-1} (f-i)H_{x_i} / \kappa_i} \quad (13)$$

The results of calculation of the  $DB$  for monomers  $AB_2$ ,  $AB_4$ , and  $AB_6$  are presented in Fig. 1. The curves representing the change of the degree of branching with conversion of A groups were obtained assuming all B groups to react at the same rate (middle curve in each plot, random reaction). The curves just above the middle one, and the highest, were obtained by taking every next B group to react twice or three times faster than the "previous" group, respectively (positive substitution effect). The curve just below the middle one and the lowest were obtained taking the negative substitution effect, where each next B group in the unit reacts two or three times slower than the previous one, respectively. As one can see, in all plots, the degree of branching linearly depends on conversion and the limiting degree of branching at full conversion slightly decreases with functionality  $f$ . This last conclusion agrees with published data [18].

It seems worth pointing out that with the present model it is not necessary anymore to calculate the degree of branching to assess perfectness of branching. With concentrations of units of different substitution degree that are available from the present model at each stage of

reaction, one can easily verify the course of any real polymerization process involving  $AB_f$  monomer.

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