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# A theoretical model of hyperbranched polymerization involving an AB$f$ monomer

## Part II. THE AVERAGE POLYMERIZATION DEGREE AND DISPERSITY INDEX[**)]

**Summary** — A generalized theoretical model of hyperbranched polymerization of an AB$_f$ monomer was used to calculate the weight average polymerization degree ($P_w$) and dispersity index ($D_M$) of the resulting hyperbranched polymers. The monomer functionalities were $f = 2$, 4, or 6. The model derived in Part I of the series and based on the Smoluchowski coagulation equation was used. The monomer functional groups B reacted according to the *first shell substitution effect* principle. Both, the weight average polymerization degree and dispersity index were found to grow with conversion the faster, the higher was the monomer functionality and the more positive was the substitution effect.

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

The new methods of polymer syntheses developed in recent years fostered the search for polymer molecules of various, but well defined non-linear structures. Among them there were polymers consisting of highly branched molecules, called the hyperbranched polymers. Certain unique properties and typically one-step polymerization technique made these products more and more desirable in many applications. They could be used mostly as modifiers, multifunctional crosslinking agents, drug or gene carriers, nanofillers *etc.* [1—5]. The present day state-of-the-art in the field have been summarized in recent reviews [6—8].

A statistical model linking the size distribution of hyperbranched polymers with monomer conversion was developed by Flory as early as in 1952 [9]. Since then, and particularly since the beginning of the nineties, over 5000 papers on the synthesis and properties of hyperbranched molecules appeared [7]. Many different me-

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**) Part I — see [19].

thods of modelling the hyperbranched polymerization have also been developed [10—13]. The hyperbranched polymers can conveniently be obtained by polymerization of an $AB_2$ monomer (A and B stand for functional groups or sites reacting with each other). A hyperbranched polymer of somewhat reduced dispersity index, but also of reduced average molecular weight, is obtained when some amount of compound $B_3$ is present beside the $AB_2$ monomer. A kinetic model of these kinds of polymerizations, which took into account the so-called *first shell substitution effect*, was presented in our previous papers [14, 15]. The substitution effect models the change in reactivity of a functional group located in close proximity to another reactive group as this other group reacts (site becomes substituted).

Hyperbranched polymers can also be obtained from monomers having more than two B groups, *i.e.* from monomers $AB_f$ ($f > 2$). Ishida *et al.* [16] have shown that by using monomers $AB_4$ or $AB_8$ one obtains aromatic polyamides of substantially higher degree of branching (*DB*) than those prepared from the $AB_2$ monomer [16]. Monomers $AB_3$ or $AB_4$ were used [17] to prepare polymers of *DB* higher than 0.67. The degree of branching is a measure of branching perfectness; it is zero for linear chains and equals to one for an ideal dendrimer containing only branching and terminal units [18].

In a theoretical analysis presented in our previous paper (Part I) [19] a general kinetic model of polymerization of an $AB_f$ monomer was developed. Of particular interest there were the effect of monomer functionality ($f$ = 2, 4, 6) and magnitude of the first shell substitution effect on the *DB*.

In this paper we extend the model and use it to calculate the average degrees of polymerization (number and weight averages, $P_n$ and $P_w$, respectively) and their ratio, *i.e.* the dispersity index $D_M = P_w/P_n$.

## KINETIC MODEL OF POLYMERIZATION

In our model all molecules present in the system at any conversion degree of functional groups are coded with an $f$-component vector $s = (s_0, s_1, ..., s_{f\text{-}1})$, where $s_i$ stands for the number of units with exactly $i$ groups B reacted. We disregard the possibility of intramolecular reactions within one molecule. Thus, a monomer molecule has the code {1, 0, 0,..., 0}, a dimer has the code {1, 1, 0,..., 0}, *etc.* The concentrations of molecules sharing the same codes are $[s_0, s_1, ..., s_{f\text{-}1}]$. The concentrations are conveniently expressed as the numbers of molecules of a given code divided by the total number of units. At the beginning of a polymerization, when starting from the monomer, one has [1, 0, 0,..., 0] = 1 and the concentrations of any other species are zeros. Note that molecules sharing the same code may differ in the structure, but the reactivities of their corresponding functional groups are necessarily identical.

The size distribution of molecular species can conveniently be described by the polynomial function:

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

The dummy variables $x_0$ to $x_{f\text{-}1}$ have no physical meaning and are used merely to carry out mathematical manipulations. The set of reduced rate constants $\kappa_1$ to $\kappa_{f\text{-}1}$ is defined by the relation:

$$\kappa_i = \frac{(f-i)k_i}{fk_0}; \; i = 1, 2, ..., f\text{-}1 \tag{2}$$

where: $k_i$ — *contribution to the rate constant from a reactive group at the unit with exactly i reacted B groups.*

The actual rate constant of each elementary reaction step is the product $k^* k_A k_i$ where $k^*$ is a constant and $k_A$ is related to the reactivity of A group only. The product form of the rate constant is equivalent to the assumption that the contributions from individual units to the activation energy are additive [20, 21]. Both $k^*$ and $k_A$ are in eq. (3), below, absorbed into time units together with $fk_0$ [22]. In other words, the relative rate constant $\kappa_i$ measures the reactivity of a unit relative to that of the unit with no B group yet reacted. This means that the monomer unit as well as each terminal one linked through its A group reacts *via* one of its B groups at the rate constant equal to 1.

Smoluchowski-like coagulation equation describing the time evolution of the size distribution function $H$ was derived in the previous paper [19]. It reads:

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

where:

$$H_p \equiv H_p(\tau) = \sum_{s_0=1}^{\infty} \sum_{s_1=0}^{\infty} ... \sum_{s_{f-1}=0}^{\infty} [s_0, s_1, ..., s_{f-1}] \tag{4}$$

is obtained by making the substitution:

$$(x_0, x_1, ..., x_{f-1}) = (1, \kappa_1^{-1}, ..., \kappa_{f-1}^{-1}) \tag{5}$$

in equation (1). Equation (5) should be understood as the simultaneous substitutions: $x_0 = 1/\kappa_1$; $x_2 = 1/\kappa_2$; *etc.* The functions $H_{x_0}, H_{x_1}$, …, are defined thus:

$$\begin{aligned} H_{x_0} &= \left. \frac{\partial H}{\partial x_0} \right|_{x_0=1; x_1=1/\kappa_1; ..; x_{f-1}=1/\kappa_{f-1}} \\ H_{x_1} &= \left. \frac{\partial H}{\partial x_1} \right|_{x_0=1; x_1=1/\kappa_1; ..; x_{f-1}=1/\kappa_{f-1}} \quad etc. \end{aligned} \tag{6}$$

In other words, the functions having dummy variables as subscripts are the partial derivatives with respect to the corresponding variable, calculated at the (reference) point defined by eq. (5). It is not difficult to verify that, for example,

$$H_{x_1} = H_{x_1}(\tau) = \kappa_1 \sum\sum\dots\sum s_1[s_0, s_1, \dots, s_{f-1}] \tag{7}$$

is the $\kappa_1$ times the fraction of units in the whole system having exactly one reacted B group.

The substitution eq. (5) makes all the dummy variables from eq. (1) or from derivatives of $H$ vanishing and becoming functions of time only.

The functions with two dummy variables as subscripts are the second derivatives of $H$ with respect to the respective dummies, again calculated at the reference point given by eq. (5).

Smoluchowski-like equation can be used to extract moments of distribution. Since the polymerization degree ($P$) of the molecules sharing the code $\{s_0, s_1, \dots, s_{f-1}\}$ is [19]:

$$P = (f-1)^{-1}\left[(s_0 f + s_1(f-1) + \dots + s_{f-1}) - 1\right] \tag{8}$$

the $r$-th moment of the distribution is

$$M_r = \sum_{s_0=1}\sum_{s_1=0}\dots\sum_{s_{f-1}=0}[s_0, s_1, \dots, s_{f-1}]P^r \tag{9}$$

The number and weight averages of polymerization degree are expressed in terms of the moments, namely [22]:

$$P_n = \frac{M_1}{M_0} \tag{10}$$

$$P_w = \frac{M_2}{M_1} \tag{11}$$

and, as follows from the choice of concentration units: $M_1 = 1$. Thus,

$$P_n = M_0^{-1} = H_p^{-1} \tag{12}$$

and

$$P_w = M_2 \tag{13}$$

To illustrate the procedure of using Smoluchowski-like equation (3), let us develop the moment equation (9) for $r = 2$ and $f = 2$ (monomer $AB_2$). From eq. (8) we get $P = 2s_0 + s_1 - 1$ and $P^2 = 4s_0^2 + s_1^2 + 4s_0s_1 - 4s_0 - 2s_1 + 1 = 4s_0(s_0 - 1) + 4s_0s_1 + s_1(s_1 - 1) - s_1 + 1$. Hence, in terms of $H$ functions, the result is:

$$M_2 = P_w = 4H_{x_0x_0} + 4H_{x_0x_1}/\kappa_1 + H_{x_1x_1}/\kappa_1^2 - H_{x_1}/\kappa_1 + H_p \tag{14}$$

Analogous expressions for the second moment of size distribution in the polymerization of $AB_4$ and $AB_6$ monomers contain more and more terms and require slightly tedious, but otherwise straightforward derivation.

The functions $H$ with two subscripts that are needed in the second moment expressions as well as those with one subscript become available in the form of a set of ordinary differential equations with respect to time as the only variable. The set is obtained from (3) by its differentiation twice with respect to dummy variables followed by setting $(x_0, x_1, \dots, x_{f-1}) = (1, \kappa_1^{-1}, \dots, \kappa^{-1}_{f-1})$. The differential equation describing the function $H_p$ is obtained by simply setting $(x_0, x_1, \dots, x_{f-1}) = (1, \kappa_1^{-1}, \dots, \kappa^{-1}_{f-1})$ directly in eq. (3). The set of all differential equations obtained by differentiation eq. (3) with respect to each dummy variable plus that for $H_p$ can be solved numerically for any set of $\kappa$ values by using any commercial software.

To express the results in terms of the conversion degree we make use of the definition of concentration units. Since, as follows from eq. (4), $H_p$ is the number of molecules per monomer unit, and each reacted B group reduces the number of molecules by one, the conversion degree, $p$ is simply:

$$p = 1 - H_p \tag{15}$$

Eventually, from eqs. (12) and (15) we get the familiar [23]:

$$P_n = \frac{1}{H_p} = \frac{1}{1-p} \tag{16}$$

Finally, the dispersity index reads:

$$D_M = \frac{P_w}{P_n} = H_p M_2 \tag{17}$$

## RESULTS AND DISCUSSION

We solved the sets of differential equations for functions $H$ with up to two subscripts. The sets were derived for $f = 2$, 4, and 6. They consisted of 6, 15, and 28 ordinary differential equations, respectively. The method of deriving the equation was outlined in Part I [19]. The equations were solved numerically as described in [10]. The calculations were carried out for 5 sets of reduced rate constants $\kappa_i$ ($i = 1, 2, \dots, f$-1). The constants are the measures of the first shell substitution effect. The $\kappa$ values were calculated using eq. (2) by taking: $k_i = 3k_{i-1}$, $k_i = 2k_{i-1}$, $k_i = k_{i-1}$, (random case), $k_i = 3k_{i-1}/2$, or $k_i = k_{i-1}/3$. In all cases $k_0 = 1$. The first two cases corresponded to the so-called positive substitution effect, while the last two, to the negative substitution effect. The physical meaning of the first shell substitution effect modeled in this way was the following. In the first case ($k_i = 3k_{i-1}$) the group B in a unit with $i$ reacted B groups was 3 times more reactive than the same group in a unit with $i$-1 reacted B groups. On the other hand, in the case $k_i = k_{i-1}/3$, each next B group in a unit reacted 3 times slower than the previous one. In the random case the reactivity of B groups did not depend on the substitution degree of a unit.

The results of calculations are presented in graphical form in plots illustrating the change of weight average degree of polymerization of hyperbranched molecules (Fig. 1) and their dispersity index (Fig. 2). In all plots there are 5 curves corresponding to different substitution effects. The most top curve corresponds to the strongest positive substitution effect ($k_i = 3k_{i-1}$) whereas the lowest to the strongest negative substitution effect ($k_i = k_{i-1}/3$). As can be seen, the character of relationships of $P_w$ or $D_M$ on conversion does not change qualitatively

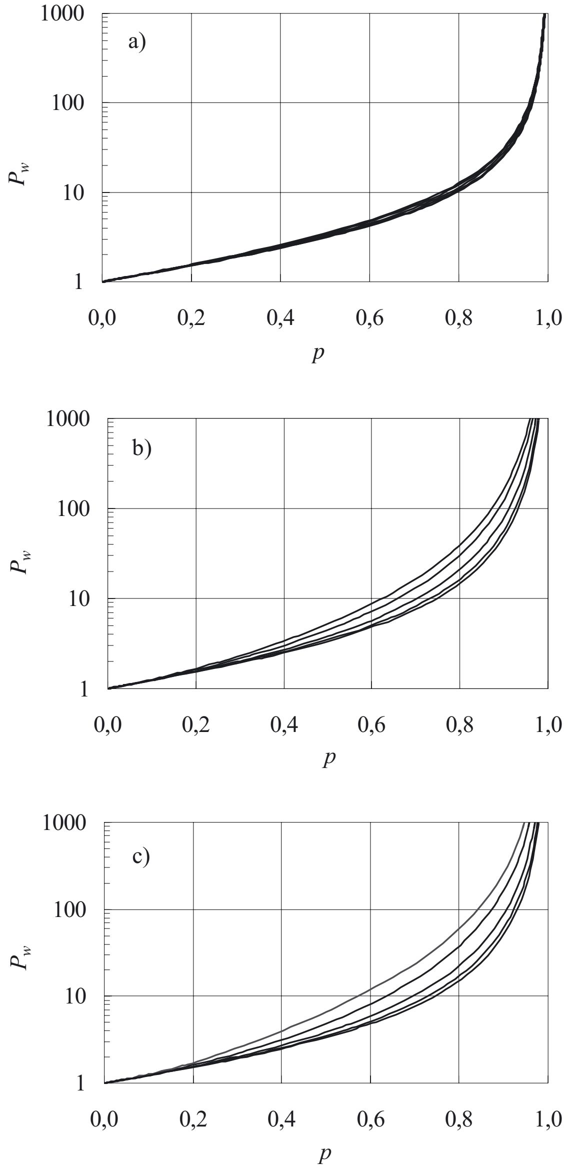

*Fig. 1. Weight average polymerization degree ($P_w$) of hyperbranched polymers versus conversion degree (P) of A groups in polymerization of $AB_f$ monomers reacting with the substitution effects for: a) f = 2, b) f = 4, c) f = 6. In all cases the rate constant of reaction between group A and the first 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 $k_i = k_{i-1}/3$*

neither with increasing functionality nor with the magnitude of substitution effect.

In general, the higher functionality of monomer and the more positive substitution effect, both the weight average polymerization degree and dispersity index grow slightly faster with conversion.

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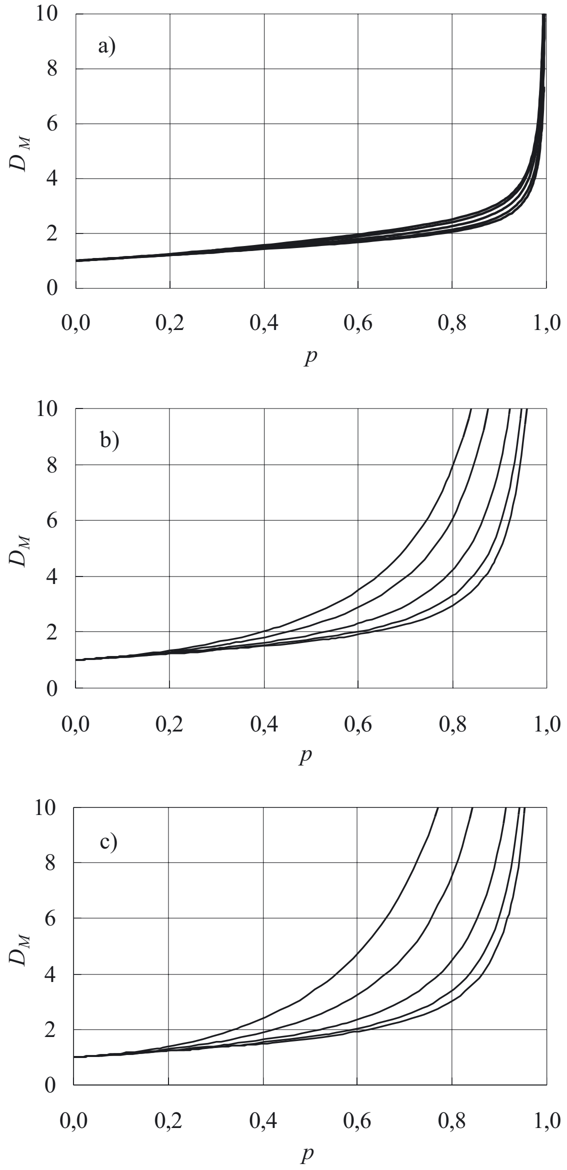

*Fig. 2. Dispersity index ($D_M$) of hyperbranched polymers versus conversion degree (P) of A groups in polymerization of $AB_f$ monomers reacting with the substitution effects for: a) f = 2, b) f = 4, c) f = 6. The curves are in the same order as in Fig. 1*

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