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First Shell Substitution Effects in Hyperbranched Polymers: Kinetic−Recursive Probability Analysis

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ABSTRACT: The kinetic−probability approach taking into account first shell substitution effects (FSSE) is applied to hyperbranched condensation polymerizations. Simple explicit relationships giving the mass-average molar mass ($\overline{M}_w$) and mass-average degree of polymerization ($\overline{X}_w$) as a function of conversion, of initial monomer mixture composition and of polymer architecture at a given reaction time are derived using the "in−out" recursive probability approach. Three experimentally available parameters, the A-, B-, and AB-branching factors (δ_A, δ_B, and δ_{AB}) are introduced to describe polymer branching. δ_B generalizes Frey's degree of branching to polymerizations involving any type of monomer mixture and can directly be used to calculate polymer $\overline{M}_w$. δ_{AB} characterizes the substitution effects induced on A-group reactivity by the reaction of B-groups (and vice versa). This effect, generally neglected in hyperbranched polymerization studies, may exert a dramatic influence on hyperbranched polymer dispersity ($\overline{M}_w/\overline{M}_n$). Two systems, AB_f polymerizations and $AB_f + B_g$ polymerizations, are taken as examples and discussed to illustrate the method. The polymerizations of 2,2-bis(hydroxymethyl)propanoic acid (BMPA) (AB_2 polymerization) and of BMPA with Pentaerythritol ($AB_2 + B_4$ polymerization) are more specifically studied. The results are compared to experimental data, showing that negative FSSE involving both OH and COOH groups take place, leading to much lower dispersities and branching factors than expected for ideal (random) polymerizations. The method can be extended to any type of condensation polymerizations.

Introduction

Hyperbranched polymers form a class of polymers characterized by a highly branched macromolecular architecture and a large number of end groups. They exhibit properties notably different from those of linear polymers in terms of, e.g., viscosity profile, solubility, and end group reactivity. These properties can easily be tailored by copolymerization or by end group modification for applications in many fields, e.g., viscosity modifiers, cross-linking agents, compatibilizers, polymers for waterborne compositions, or sophisticated drug delivery systems.[1−3] A number of hyperbranched polymers have been described in the past 15 years, some of which are now commercially available.[4,5] These polymers are most often obtained by polycondensation reactions involving AB_f and $AB_f + B_g$ monomer systems, where A and B denote mutually reactive functional groups. Unlike linear condensation polymers, which always exhibit molar-mass dispersities $D_M = \overline{M}_w/\overline{M}_n$ close to 2, the molecular distribution of hyperbranched polymers may become very broad at high conversion: As shown by Flory,[6] the dispersity of AB_f polymers approaches infinity as conversion approaches 1. We have recently applied the "in−out" recursive probability approach to derive simple analytic expressions giving the dispersities of $AB_f + B_g$ and more complex hyperbranched polymers as a function of conversion and initial medium composition.[7] However, these expressions were established under Flory's simplifying assumption of equal reactivity of functional groups (ideal polycondensations) and cannot be applied when substitution effects take place. In hyperbranched polymers, the deviation from ideality is generally characterized by the degree of branching (DB), a parameter introduced by Frey et al. and defined as the ratio of the number of actual growth directions to the maximum number of possible growth directions.[8−10] In the case of AB_2 ideal (random) hyperbranched polymers DB = $^1/_2$. Negative substitution effects, i.e., decrease of second B-group reactivity after reaction of the first one, lead to DB < $^1/_2$, with DB = 0 in the limiting case of linear polymers. To obtain highly branched polymers (DB > $^1/_2$), positive substitution effects are obviously desirable. It is clear that DB and $\overline{M}_w$ are strongly interdependent: For AB_2 polymers, when DB = 0 (linear polymers) molar-mass dispersity is close to 2, while it approaches infinity at high conversion when DB = $^1/_2$ (random polymers). Therefore, it appears important to understand the relationships between polymerization conditions and the molar mass, molecular distribution and degree of branching of hyberbranched polymers. The aims of this paper are as follows.

(i) The first aim is to derive a simple general expression of the $\overline{M}_w$ and D_M of hyperbranched polymer as functions of conversion, of initial medium composition and of polymer branching "quality". For this purpose, Frey's degree of branching is not adequate, and three parameters, the *branching factors*, must be introduced to characterize the substitution effects induced by the reaction of A- or B-groups on the reactivity of the remaining unreacted A- or B-groups of the same monomer unit. Deriving $\overline{M}_w$ from the branching factors can be done under the simplifying assumptions of the first shell substitution effects (FSSE), where the reactivity of a given reactive group depends only on the status (reacted or unreacted) of the other groups present on the same monomer unit. At a given reaction time, if polymer composition is known in terms of monomer units (e.g., mole fractions of dendritic, terminal, linear, focal, ... units), it is possible to calculate the branching factors, then $\overline{X}_w$ and $\overline{M}_w$.

(ii) The second aim is to study the variations of branching factors (and average molar masses) with time using the FSSE kinetic approach and to examine the dependence of these

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parameters on rate constants in some simple cases taken as examples.

The hyperbranched polymerization modeling presented in this paper consists, therefore, of two conceptual steps: (i) a kinetic step in which the A- and B-groups transform into reacted A- and B-groups with rate constants depending only on the nature of the monomer unit to which they belong and (ii) a probabilistic step where the resulting monomer units are randomly combined by their reacted A- and B-groups to build the hyperbranched architecture. These two steps are obviously simultaneous in reality. This "kinetic-probability", or "kinetic-statistical", approach has frequently been used for polymerization reaction modeling. However, to our best knowledge, it has never been applied to hyperbranched polymerizations.

As pointed out by several authors,[11−15] this approach is only approximate, because there is no information stored on sequence order in the structures generated during the second conceptual step, which involves a random combination of reacted monomer units.[15] The only exact approach is a kinetic modeling where the concentration of each possible molecule is determined from the rates of all individual reactions in which it is involved. The resulting infinite system of differential equations must be solved by truncation or generating function methods.[16−18] This kinetic approach has been extensively studied by Kuchanov et al., who first derived general equations for distributions in branched polycondensations of monomers with kinetically dependent functional groups.[19] They introduced the "extended Flory principle" allowing one to write these general equations in terms of kinetically independent units (monads).[20] On the other hand, Sarmoria et al.[11] refined the approximate kinetic-probability model (the "minimal" model) by using a repeatedly made probabilistic analysis at small time intervals (conversion discretization). They discussed the validity of the minimal model for A_3 homopolymerizations and found that the errors on the gel point become significant only for systems where rate constants differ widely (2 decades and more). Kuchanov et al. analyzed the errors committed by the minimal model on the gel points of A_3 and A_4 polymerizations in more general kinetic situations where the rate constants $k_{i,j}$ of chemical reactions between units of ith and jth kind cannot be written as product $k_i k_j$.[21,22] Regions within the rate constant space were specified where the minimal model gives sufficiently accurate approximations. The errors on the gel point were found to become significant when rate constants differ from 2 decades or more or when their variation exhibit non-monotonicity, e.g., strongly increasing rate constants after the first substitutions and decreasing rate constants after the other ones, a situation rare in practice. As pointed out by other authors,[13,15] the minimal model appears to give good approximations for all systems of practical interest. It is also worth mentioning that Kuchanov et al. introduced an exact kinetic-statistical method,[23,24] that was recently extended to take into account monomer configurational aspects.[25] In this method, reacted functional groups are distinguished by two parameters, "color" i and "label" τ, $\overline{A_i}(\tau)$ denoting a reacted A-group formed at moment τ from a A-group attached to a monomer unit with "i" reacted groups. Given these parameters, it is possible to calculate the statistical characteristics of branched polymers via the theory of general branching processes.[24,25]

Until now, hyperbranched polymerizations have been modeled exclusively by the exact kinetic approach: AB_2 polymerizations, in which the reactivity of B-groups on terminal units (rate constant k_T) is different from the reactivity of B-groups on linear units (rate constant $k_L \neq k_T$),[26−30] $AB_2 + B_3$ polymerizations with 3 rates constants,[31,32] and AB_f polymerization assuming non-equal reactivity of all B-groups (f rate constants).[33,34] The results reported are in agreement with Monte Carlo simulations,[35−37] and show increasing DB and broader molar mass distribution for AB_f systems exhibiting positive substitution effects. The addition of a core molecule narrows the distribution but also limits the maximum achievable molar mass.[31,32] In all these studies, the number of rate constants is quite limited. Possible substitution effects exerted on unreacted A-groups by the reaction of B-groups have never been studied. In this case, the number of rate constants to be taken into account dramatically increases, e.g., to 12 in the simplest AB_2 system. Although it would be possible to apply the exact approach to such systems, the approximate FSSE kinetic-probability minimal model appears simpler and quite suited to deal with systems involving complex mixtures of polyfunctional monomers.

In the first part of this article, we apply the "in−out" recursive probability approach of Macosko and Miller[38−43] to derive a general expression of $\overline{X_w}$ and $\overline{M_w}$ for FSSE polycondensations of monomers containing A and/or B groups. In order to do this, we introduce *branching factors*, which characterize substitution effects and polymer architecture and extend the concept of *degree of branching* to any type of polymers.

In the second part, we analyze the variations of branching factors, molar masses and dispersities in various kinetic situations for two industrially important systems: (i) AB_f polymerizations, comparing more specifically the results obtained on the AB_2 system with kinetic situations reported in the literature by the kinetic approach and (ii) $AB_f + B_g$ polymerizations, taking $AB_2 + B_4$ polymerizations as example, a system which, to our best knowledge, has not yet been modeled in literature.

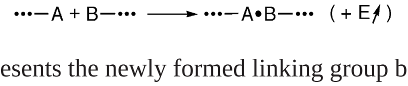
In order to illustrate the simplicity and the usefulness of the method, we also apply it on experimental data obtained on the polymerization of 2,2-bis(hydroxymethyl)propanoic acid (AB_2 polymerization) and of 2,2-bis(hydroxymethyl)propanoic acid with Pentaerythritol ($AB_2 + B_4$ polymerization).

Results and Discussion

Recursive Probability Analysis. 1. General Relationships. All calculations carried out in this article suppose that (i) no intramolecular reactions take place (i.e., cyclization is neglected) and (ii) no side-reactions take place. Under the first shell substitution effect hypotheses, the reactivity of a given functional group on a monomer unit depends on the status (reacted or unreacted) of the remaining functional groups of that unit, but it does not depend on the status of the other functional groups present on the rest of the molecule and it does not depend on the nature of the molecule with which it reacts.

The elementary growth step involves a reaction between reactive A- and B-groups, with (polycondensation) or without (polyaddition) elimination of a condensation byproduct E (Scheme 1).

Scheme 1



A•B represents the newly formed linking group between two monomer units. The initial medium contains n_1, n_2, ..., n_u mol of monomer no. 1, no. 2, ..., no. u. Each monomer molecule of i-type ($i = 1, 2, ..., u$), of molar mass M_i, has a total of $f_{A,i}$ reactive A-groups and $f_{B,i}$ reactive B-groups. After a certain reaction time, a polymer is formed, in which a fraction p_A of A-groups and a fraction p_B of B-groups have mutually reacted. If (i,j_A,j_B) denotes a i-type monomer unit in which exactly j_A A-groups ($j_A = 0,1, ..., f_{A,i}$) and j_B B-groups ($j_B = 0, 1, ...,$

$f_{B,i}$) have reacted and n_{i,j_A,j_B} the number of moles of such units in the polymer sample, the mole fraction of (i,j_A,j_B) units in the polymer sample, p_{i,j_A,j_B}, can be written:

$$p_{i,j_A,j_B} = \frac{n_{i,j_A,j_B}}{\sum_{i,j_A,j_B} n_{i,j_A,j_B}} \tag{1}$$

where $\sum_{i,j_A,j_B}$ represents the triple summation over all types of monomer units ($i = 1, 2, ..., u$; $j_A = 0, 1, ..., f_{A,i}$ and $j_B = 0,1, ..., f_{B,i}$).

At any reaction time, polymer composition can be described by the composition matrix $\boldsymbol{p}$:

$$\boldsymbol{p} = [p_{i,j_A,j_B}] \tag{2}$$

$\boldsymbol{p}$ can in principle be determined experimentally, e.g., by NMR in the case of simple polymerizations, or by a kinetic analysis under the FSSE hypotheses if the relevant rate constants are known (kinetic-probability model).

Miller and Macosko[40] derived an expression of $\overline{M_w}$ for $A_f + B_2$ and $A_f + A_2 + B_2$ condensation polymers with FSSE by the "in−out" recursive probability approach. Using the same method, we derived general expressions of $\overline{M_w}$ and $\overline{X_w}$ for condensation polymers obtained from mixtures of monomers bearing A and/or B groups (eqs 3 and 4). The details are given in Appendix A. It should be mentioned that an equivalent expression could also be derived by the stochastic graph theory using propagation expectations.[44−50]

$$\overline{M_w} = \frac{\overline{M_w^0 M_n^0} - p_A \overline{f_{n,A}^0} {M_E}^2}{\overline{M_n^0} - p_A \overline{f_{n,A}^0} M_E} + \frac{p_A \overline{f_{n,A}^0}}{\overline{M_n^0} - p_A \overline{f_{n,A}^0} M_E} \times \left[\frac{2(1-\delta_{AB})(M_a - M_E)(M_b - M_E) + \delta_A (M_b - M_E)^2 + \delta_B (M_a - M_E)^2}{(1-\delta_{AB})^2 - \delta_A \delta_B}\right] \tag{3}$$

The mass-average degree of polymerization is obtained from eq 3 by setting all masses to 1 and M_E to 0:

$$\overline{X_w} = 1 + p_A \overline{f_{n,A}^0} \frac{2(1-\delta_{AB}) + \delta_A + \delta_B}{(1-\delta_{AB})^2 - \delta_A \delta_B} \tag{4}$$

In these equations, $\overline{M_n^0}$ and $\overline{M_w^0}$ are the number-average and the mass-average molar masses of the initial monomer mixture, M_E is the molar mass of condensation byproduct ($M_E = 0$ for polyadditions) and $\overline{f_{n,A}^0}$ is the initial number-average A-group functionality, i.e., the ratio of the number of A-groups to the number of molecules in initial monomer mixture—or the ratio of the total number of A-groups (reacted and unreacted) to the total number of monomer units in the polymer:

$$\overline{f_{n,A}^0} = \frac{\sum_{i=1}^{u} f_{A,i} n_i}{\sum_{i=1}^{u} n_i} = \frac{\sum_{i=1}^{u} f_{A,i} n_i}{\sum_{i,j_A,j_B} n_{i,j_A,j_B}} \tag{5}$$

δ_A, δ_B, δ_{AB}, M_a and M_b are the following summations:

$$\delta_A = \frac{\sum_{i,j_A,j_B} j_A (j_A - 1) p_{i,j_A,j_B}}{\sum_{i,j_A,j_B} j_A p_{i,j_A,j_B}} = \sum_{i,j_A,j_B} j_A \left(\frac{j_A p_{i,j_A,j_B}}{\sum_{i,j_A,j_B} j_A p_{i,j_A,j_B}}\right) - 1 \tag{6}$$

$$\delta_B = \frac{\sum_{i,j,k} j_B (j_B - 1) p_{i,j_A,j_B}}{\sum_{i,j,k} j_B p_{i,j_A,j_B}} = \sum_{i,j_A,j_B} j_B \left(\frac{j_B p_{i,j_A,j_B}}{\sum_{i,j_A,j_B} j_B p_{i,j_A,j_B}}\right) - 1 \tag{7}$$

$$\delta_{AB} = \frac{\sum_{i,j_A,j_B} j_A j_B p_{i,j_A,j_B}}{\sum_{i,j_A,j_B} j_A p_{i,j_A,j_B}} = \sum_{i,j_A,j_B} j_B \left(\frac{j_A p_{i,j_A,j_B}}{\sum_{i,j_A,j_B} j_A p_{i,j_A,j_B}}\right) \tag{8}$$

$$M_a = \frac{\sum_{i,j_A,j_B} M_i j_A p_{i,j_A,j_B}}{\sum_{i,j_A,j_B} j_A p_{i,j_A,j_B}} = \sum_{i,j_A,j_B} M_i \left(\frac{j_A p_{i,j_A,j_B}}{\sum_{i,j_A,j_B} j_A p_{i,j_A,j_B}}\right) \tag{9}$$

$$M_b = \frac{\sum_{i,j_A,j_B} M_i j_B p_{i,j_A,j_B}}{\sum_{i,j_A,j_B} j_B p_{i,j_A,j_B}} = \sum_{i,j_A,j_B} M_i \left(\frac{j_B p_{i,j_A,j_B}}{\sum_{i,j_A,j_B} j_B p_{i,j_A,j_B}}\right) \tag{10}$$

All these summations can easily be calculated if polymer composition matrix $\boldsymbol{p}$ is experimentally known or can be derived by a kinetic treatment.

M_a and M_b are the expected molar mass of a monomer unit chosen by picking a reacted A-group and a reacted B-group at random, respectively (without taking byproduct elimination into account). The δ's are average quantities that characterize the "quality" of polymer branching at any reaction time. They depend on the extent of reaction, on starting monomers functionalities and on substitution effects taking place during the polymerization. Their physical meaning is discussed below.

Since the number-average degree of polymerization and molar mass condensation or addition polymers are always given by eqs 11 and 12

$$\overline{X_n} = \frac{1}{1 - p_A \overline{f_{n,A}^0}} \tag{11}$$

$$\overline{M_n} = \overline{X_n}(\overline{M_n^0} - M_E) + M_E \tag{12}$$

it is easy to obtain the degree-of-polymerization dispersity $D_X = \overline{X_w}/\overline{X_n}$ and the molar-mass dispersity $D_M = \overline{M_w}/\overline{M_n}$ from eqs 3 and 4.

The conversion at the gel point can also be deduced from eq 4, by solving eq 13.

$$(1-\delta_{AB})^2 - \delta_A \delta_B = 0 \tag{13}$$

2. Branching Factors $\boldsymbol{\delta}$. A- and B-Branching Factors, $\boldsymbol{\delta_A}$ and $\boldsymbol{\delta_B}$. Examining the last part of eq 6 shows that δ_A is the expected number of *additional* reacted A-groups on a unit chosen by picking a reacted A-group at random. In other words, δ_A is the average number of A-type "children" (i.e., the number of A-groups connected to other branches of the macromolecule)

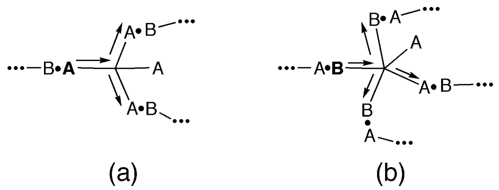


Figure 1. (a) Reacted A-group with two A-type children on a A_4 monomer unit, and (b) reacted B-group with two B-type children and one A-type child on a A_2B_3 monomer unit.

issued from a reacted A-group of the same monomer unit (Figure 1a). By analogy with the terminology used for tree data structures, it can be termed as the “A-average A-branching factor” or simply the “A-branching factor”. Using this terminology, focal and terminal units would, respectively, be root and leaf nodes and dendritic and linear units, inner nodes. A symmetrical definition obviously applies for the B-branching factor δ_B. The definition of δ_B is close to that of the *average number of branches* (*ANB*) introduced by Frey et al. for describing AB_f hyperbranched polymers.[9,10] *ANB* is the expectation of the number of branches issued from a random *monomer unit* containing a reacted B-group. It is slightly different from δ_B, which is the expectation of the number of branches issued from a random *reacted B*. The statistical weight of monomer units having a high number of reacted B-groups is larger in δ_B. We show below that δ_B reduces to Frey’s degree of branching DB for AB_2 polymerizations. The branching factors not only characterize polymer branching for any type of monomer mixtures at any conversion, but can also directly be used to in eqs 3 and 4 to calculate the mass-average molar mass $\overline{M_w}$ and degree of polymerization $\overline{X_w}$ of branched or hyperbranched polymers. Note that the *weight-average real functionalities* of Durand and Bruneau[49,50] are in fact $\delta_A + 1$ and $\delta_B + 1$, respectively.

AB-Branching Factor δ_{AB}. Similarly, δ_{AB} is the expected number of reacted B-groups on a unit chosen by picking a reacted A-group at random (Figure 1b). It must be underlined that δ_{BA}, the expected number of reacted A-groups on a unit chosen by picking a reacted B-group at random is equal to δ_{BA} due to reaction stoichiometry (see eqs 56 and 59 in Appendix A). δ_{AB} reflects the “crossed” influence of the reaction of a group of one type on the reactivity of groups of the other type on the same monomer unit.

Branching Factors in Ideal Polycondensations (Equal Reactivity of Functional Groups). The physical meaning of the branching factors is better understood when examining ideal polymerizations (equal reactivity). In the absence of substitution effects, all functional groups react independently and p_{i,j_A,j_B} is given by the binomial probability:

$$p_{i,j_A,j_B} = \alpha_i \binom{f_{A,i}}{j_A} p_A^{j_A}(1-p_A)^{f_{A,i}-j_A} \binom{f_{B,i}}{j_B} p_B^{j_B}(1-p_B)^{f_{B,i}-j_B} \tag{14}$$

where α_i is the mol fraction of monomer no. i in initial mixture (or the mol fraction of i-type monomer units in the polymer). From eqs 6 and 14:

$$\delta_A = \frac{\sum_{i=1}^{i=u} \alpha_i f_{A,i} p_A{}^2 (f_{A,i}-1)}{\sum_{i=1}^{i=u} \alpha_i f_{A,i} p_A} = p_A \left(\frac{\sum_{i=1}^{i=u} \alpha_i f_{A,i}{}^2}{\sum_{i=1}^{i=u} \alpha_i f_{A,i}} - 1 \right) \tag{15}$$

The fraction involving summations in the last part of eq 15 is the expectation of the number of A-groups attached to a monomer randomly picked by a A-group in the initial medium, i.e., the initial A-average A-group functionality,[7] $\overline{f^{0}_{a,A}}$ (the “effective functionality” of Stockmayer[51]):

$$\overline{f^{0}_{a,A}} = \sum_{i=1}^{i=u} f_{A,i} \frac{f_{A,i} n_i}{\sum_{i=1}^{i=u} f_{A,i} n_i} \tag{16}$$

Therefore

$$\delta_A = p_A(\overline{f^{0}_{a,A}} - 1) \tag{17}$$

Equation 17 is quite logical: In the absence of substitution effects, the *additional* number of A-groups (reacted *and* nonreacted) on a monomer unit chosen by randomly picking a random A-group (reacted *or* nonreacted) in the polymer is obviously $\overline{f^{0}_{a,A}} - 1$ and the additional number of *reacted* A-groups (i.e., $\overline{\delta_A}$) is $p_A(\overline{f^{0}_{a,A}} - 1)$. Since there is no substitution effect $p_A(\overline{f^{0}_{a,A}} - 1)$ is also the additional number of reacted A-groups of a monomer unit chosen by picking a *reacted* A-group at random, i.e., δ_A. Similarly:

$$\delta_B = p_B(\overline{f^{0}_{b,B}} - 1) \tag{18}$$

where $\overline{f^{0}_{b,B}}$ is given by

$$\overline{f^{0}_{b,B}} = \sum_{i=1}^{i=u} f_{B,i} \frac{f_{B,i} n_i}{\sum_{i=1}^{i=u} f_{B,i} n_i} \tag{19}$$

For AB_2 polymerizations $\overline{f^{0}_{a,A}} = 1$ and $\overline{f^{0}_{b,B}} = 2$. Therefore, $\delta_A = 0$ and $\delta_B = p_B = p_A/2$. It is clear that a positive substitution effect on B, i.e., an increase of B reactivity after reaction of the first one, will lead to an increase in the average number of reacted B “seen” by a random reacted B on the same monomer unit and, therefore, to $\delta_B > p_A/2$. Similarly, negative substitution effects obviously lead to $\delta_B < p_A/2$.

Substituting eq 14 into eq 8 and introducing the initial B-average A-group functionality, $\overline{f^{0}_{b,A}}$, and the initial A-average B-group functionality, $\overline{f^{0}_{a,B}}$,[7] leads to

$$\delta_{AB} = p_A \overline{f^{0}_{b,A}} = p_B \overline{f^{0}_{a,B}} \tag{20}$$

with

$$\overline{f^{0}_{b,A}} = \sum_{i=1}^{i=u} f_{A,i} \frac{f_{B,i} n_i}{\sum_{i=1}^{i=u} f_{B,i} n_i} \tag{21}$$

and

$$\overline{f^{0}_{a,B}} = \sum_{i=1}^{i=u} f_{B,i} \frac{f_{A,i} n_i}{\sum_{i=1}^{i=u} f_{A,i} n_i} \tag{22}$$

For AB$_f$ polymerizations in the ideal case, $\overline{f^{\,0}_{\mathrm{b,A}}} = 1$ and $\delta_{\mathrm{AB}} = p_{\mathrm{A}}$. Positive substitution effects result in $\delta_{\mathrm{AB}} > p_{\mathrm{A}}$ and negative ones to $\delta_{\mathrm{AB}} < p_{\mathrm{A}}$. δ_{AB} reaches the limiting value 1 when $p_{\mathrm{A}} = 1$, whatever the substitution effects. Examining eq 4 shows that small deviations of δ_{AB} from ideality would lead to strong increase/decrease of $\overline{X_{\mathrm{w}}}$ (and D_{X}) when positive/negative substitution effects take place.

It results from the preceding analysis that $\overline{X_{\mathrm{w}}}$ and $\overline{M_{\mathrm{w}}}$, D_{X} and D_{M} and the various degrees of branching can be calculated if polymer composition matrix $\boldsymbol{p}$ is known, in other words if the mole fraction of the various types of monomer units are known. $\boldsymbol{p}$ was experimentally determined for some hyperbranched polymers by NMR analysis.[52,53] In these cases, the recursive probability approach, under the FSSE minimal model discussed above, should provide interesting information on the average molar masses and dispersities of hyperbranched polymers. $\boldsymbol{p}$ can also be calculated from a kinetic analysis if the various reaction rate constants are known. If not all the constants are known, but positive or negative substitution effects are supposed, a kinetic analysis with arbitrary chosen values followed by the application of eq 4 could also provide useful trends. The next section discusses FSSE in AB$_f$, and AB$_f$ + B$_g$ hyperbranched polymerizations using the kinetic-probability minimal model.

Kinetic Treatment. 1. Kinetic Model. Before going into the discussion of substitution effects, it is necessary to comment the kinetic model used to calculate the mole fractions of the various types of monomer units (polymer composition matrix $\boldsymbol{p}$). The reactions between A and B-groups present in reaction medium are assumed to be second-order (Scheme 2):

Scheme 2

$$\cdots\!-\mathrm{A}^{(\alpha)} + {}^{(\beta)}\mathrm{B}-\cdots \xrightarrow{k\alpha\beta} \cdots\!-\mathrm{A{\bullet}B}-\cdots \quad (+\,\mathrm{E}\!\nearrow)$$

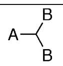
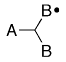
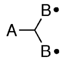
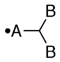
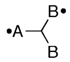
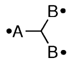
In Scheme 2, α-type and β-type species are monomer units with unreacted A-groups and unreacted B-groups, respectively and $k_{\alpha\beta}$ the corresponding rate constant. According to the FSSE model, the reactivity of given A- or B-groups only depends on the status (reacted or unreacted) of the other groups present on the monomer unit to which they belong. Therefore, the kinetic analysis has to take into account a limited number of species and rate constants only, e.g., $2(f + 1)$ monomer units and $2f(f + 1)$ rate constants for AB$_f$ polymerizations. Since the absolute values of rate constants and concentrations have no interest for comparing the influence of FSSE on polymer composition and average molar masses, the reaction between A-groups and B-groups of AB$_f$ monomer molecules was chosen as a reference and its rate constant was arbitrarily set to $k = 1$. With this convention, positive and negative substitution effects lead to rate constants respectively >1 and <1. Concentrations were normalized with respect to the sum of initial reactant concentrations, so that computations directly yield the mole fractions $p_{i,j_{\mathrm{A}},j_{\mathrm{B}}}$ of the various monomer units to be used in eqs 6−8 and eq 4. The derivation of the differential equation system, straightforward but tedious for mixtures of polyfunctional monomers, was carried out using the matrix notation of Schmaljohann et al.,[54] which also simplifies the discussion of kinetic effects. According to this notation, the matrix $\boldsymbol{k}$ of rate constants is written as given in Table 1 where k_{11} is the rate constant of the reaction between one A-group and one B-group of monomer molecules ($k_{11} = 1$). The resulting set of simultaneous equations was numerically integrated, yielding the variations of the mole fractions of all types of monomer units vs time, from which the variations of the average degrees of polymerization, dispersities and branching factors were calculated vs time or conversion.

Table 1. Matrix $\boldsymbol{k}$ of Reaction Rate Constants[a]

	β-type species
α-type species	$\begin{array}{c\|cccc} & \#1 & \#2 & \cdots & \#n \\ \hline \#1 & k_{11} & k_{12} & \cdots & k_{1n} \\ \#2 & k_{21} & k_{22} & \cdots & k_{2n} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \#m & k_{m1} & k_{m2} & \cdots & k_{mn} \end{array}$

[a] α-type and β-type species are the monomer units containing unreacted A-groups and B-groups, respectively.

Table 2. Monomer Units Present in AB$_2$ Polymerization[a]

Monomer units	Formulas	Notations
Monomer molecule		M
Linear focal		F$_\mathrm{L}$
Dendritic focal		F$_\mathrm{D}$
Terminal		T
Linear		L
Dendritic		D

[a] A• and B• denote reacted A- and B-groups. In the formulas, M, F_{L}, F_{D}, T, L, and D, represent the corresponding mole fractions with respect to all monomer units present in the polymer.

2. First Shell Substitution Effects in Hyperbranched AB$_f$ polymers. A- and B-Branching Factors $\boldsymbol{\delta_{\mathrm{A}}}$ and $\boldsymbol{\delta_{\mathrm{B}}}$. In AB$_f$ hyperbranched polymers, only one type of monomer is reacted ($i = 1$) and this monomer contains only one A-group ($j_{\mathrm{A}} = 0, 1$). Therefore, $\delta_{\mathrm{A}} = 0$ and δ_{B} is given by eq 23:

$$\delta_{\mathrm{B}} = \frac{\displaystyle\sum_{j_{\mathrm{B}}=0}^{j_{\mathrm{B}}=f} j_{\mathrm{B}}(j_{\mathrm{B}} - 1)(p_{1,0,j_{\mathrm{B}}} + p_{1,1,j_{\mathrm{B}}})}{\displaystyle\sum_{j_{\mathrm{B}}=0}^{j_{\mathrm{B}}=f} j_{\mathrm{B}}(p_{1,0,j_{\mathrm{B}}} + p_{1,1,j_{\mathrm{B}}})} \tag{23}$$

When $f = 2$ (AB$_2$ polymers)

$$\delta_{\mathrm{B}} = \frac{(p_{1,0,1} + p_{1,1,1}) + 4(p_{1,0,2} + p_{1,1,2})}{(p_{1,0,1} + p_{1,1,1}) + 2(p_{1,0,2} + p_{1,1,2})} - 1 = \frac{2(p_{1,0,2} + p_{1,1,2})}{2(p_{1,0,2} + p_{1,1,2}) + (p_{1,0,1} + p_{1,1,1})} \tag{24}$$

$p_{1,1,1}$ and $p_{1,1,2}$ are the mole fractions of linear (L) and dendritic (D) units, respectively and $p_{1,0,1}$ and $p_{1,0,2}$ are the mole fractions of linear focal (F_{L}) and dendritic focal (F_{D}) units, respectively (Table 2):

$$\delta_{\mathrm{B}} = \frac{2(D + F_{\mathrm{D}})}{2(D + F_{\mathrm{D}}) + L + F_{\mathrm{L}}} \tag{25}$$

Consequently, in the case of AB$_2$ polymerization, δ_{B} is equal to Frey's degree of branching DB,[9] where the mole fractions of dendritic and linear units also include the corresponding focal units. In the general case of AB$_f$ polymerizations ($f \neq 2$), δ_B (eq 23) is different from DB, which is given by eq 26 using our notations:

$$\mathrm{DB} = \frac{f}{f-1} \frac{\sum_{j_B=1}^{j_B=f} (j_B - 1)(p_{1,0,j_B} + p_{1,1,j_B})}{\sum_{j_B=1}^{j_B=f} j_B (p_{1,0,j_B} + p_{1,1,j_B})} \tag{26}$$

When the polymer contains linear and terminal units only ($p_{1,j_A,j_B} = 0$ for $j_B \neq 0$ or 1), it is easy to show from eq 23 that $\delta_B = 0$. When the polymer contains fully reacted dendritic units, dendritic focal units, terminal units and unreacted monomer molecules only ($p_{i,j_A,j_B} = 0$ for $j_B \neq 0$ or f), δ_B reaches a maximum: $\delta_B = f - 1$. In the absence of substitution effects, eq 18 yields: $\delta_B = (f - 1)p_B$. Therefore, δ_B varies between 0 (linear polymers) and ($f - 1$) (fully dendritic polymers) and takes the value $\delta_B = (f - 1)/f$ at total conversion ($p_A = 1$) for random hyperbranched polymers. It should also be underligned that DB is indeterminate for AB polymerizations ($f = 1$) while $\delta_B = 0$, as expected for a linear polymerization. In the case of AB$_3$ polymerizations, semi-dendritic units (1 reacted A, 2 reacted B, mole fraction: S_D) and semi-dendritic focal units (1 unreacted A, 2 reacted B, mole fraction: F_{SD}) are present. According to eq 23 the B-branching factor is simply defined by eq 27:

$$\delta_B = \frac{6(D + F_D) + 2(S_D + F_{SD})}{3(D + F_D) + 2(S_D + F_{SD}) + L + F_L} \tag{27}$$

When p_A is close to 1, the contribution of focal units becomes negligible and the following relationship may be used:

$$\delta_B \approx \frac{6D + 2S_D}{3D + 2S_D + L} \tag{28}$$

AB-Branching Factor δ_{AB}. δ_{AB} simplifies to

$$\delta_{AB} = \frac{\sum_{j_B=0}^{j_B=f} j_B p_{1,1,j_B}}{\sum_{j_B=0}^{j_B=f} p_{1,1,j_B}} = \frac{\sum_{j_B=0}^{j_B=f} j_B p_{1,1,j_B}}{\sum_{j_A=0}^{j_A=1} \sum_{j_B=0}^{j_B=f} j_B p_{1,j_A,j_B}} \tag{29}$$

For AB$_2$ polymers:

$$\delta_{AB} = \frac{p_{1,1,1} + 2p_{1,1,2}}{(p_{1,0,1} + p_{1,1,1}) + 2(p_{1,0,2} + p_{1,1,2})} = \frac{2D + L}{2(D + F_D) + L + F_L} = \frac{2D + L}{p_A} \tag{30}$$

For AB$_3$ polymers:

$$\delta_{AB} = \frac{p_{1,1,1} + 2p_{1,1,2} + 3p_{1,1,3}}{(p_{1,0,1} + p_{1,1,1}) + 2(p_{1,0,2} + p_{1,1,2}) + 3(p_{1,0,3} + p_{1,1,3})} = \frac{3D + 2S_D + L}{p_A} \tag{31}$$

Table 3. Matrix *k* of Reaction Rate Constants for AB$_2$ Polymerization[a]

	β-type species			
	M	F$_L$	T	L
α-type species M	k_{11}	k_{12}	k_{13}	k_{14}
F$_L$	k_{21}	k_{22}	k_{23}	k_{24}
F$_D$	k_{31}	k_{32}	k_{33}	k_{34}

[a] See Table 2 for monomer unit notations. M and F$_L$ units, which present both unreacted A- and B-groups, appear in both rows and columns.

Mass-Average Degree of Polymerization. According to eq 4, the mass-average degree of polymerization of AB$_f$ polymers is

$$\overline{X_w} = 1 + \frac{2p_A}{1 - \delta_{AB}} + \frac{p_A \delta_B}{(1 - \delta_{AB})^2} \tag{32}$$

The degree-of-polymerization dispersity is simply given by $D_X = (1 - p_A)\overline{X_W}$. Equation 32 reduces to the well-known Flory's equation[6] for AB$_f$ hyperbranched polymers in the ideal case (equal reactivity of functional groups), as $\delta_{AB} = p_A$ and $\delta_B = p_A(f - 1)/f$:

$$\overline{X_w} = \frac{1 - \frac{p_A^{\,2}}{f}}{(1 - p_A)^2} \tag{33}$$

Since positive substitution effects increase both B- and AB-branching factors, it is clear from eq 32 that the resulting polymers would exhibit larger dispersities than those obtained in the ideal case. It is also clear that small deviations of δ_{AB} from ideality ($\delta_{AB} = p_A$) could exert dramatic effects on $\overline{X_w}$ and dispersity.

FSSE in AB$_2$ Polymerizations. Some authors have already discussed the variations of monomer unit fractions during AB$_2$ polymerizations when first shell substitution effects take place.[10,52,53] Here, we complete these studies by examining the variations of $\overline{X_w}$ and dispersity in the three major kinetic situations depicted by Schmaljohann et al.:[54] (1) the reactivity of the second B-group increases/decreases after reaction of the first one, but A-group reactivity remains unchanged, (2) A-group reactivity increases/decreases after reaction of B-groups, but B-group reactivity remains unchanged, and (3) the reactivity of B-groups increases/decreases after A-group has reacted. The general rate constant matrix of AB$_2$ polymerization and the matrices corresponding to situations 1−3 are respectively given in Tables 3 and 4. For numerical integrations, the rate constant k was set to 2^n (positive substitution effect) or 2^{-n} (negative substitution effect) with $n = 0, 1, 2, 3$.

Situation 1: The reactivity of terminal units is different from that of linear units ($k_T = 1$; $k_L = k$). The variations of δ_{AB} vs conversion are linear whatever k ($\delta_{AB} = p_A$) (Figure 2a). This is easily understood, as the A-groups of monomer molecules (M), of F$_L$ units and of F$_D$ units have the same reactivity (see the rows of the corresponding ***k*** matrix in Table 4). On the other hand, δ_B is above (increasing effect) or below (decreasing effect) the straight line corresponding to the ideal case ($\delta_B = p_A/2$) (Figure 2b). High δ_B values can be achieved in the case of strong positive substitution effects, e.g., $\delta_B = 0.87$ for $k = 8$, but, as shown in Figure 2c, polymer dispersity strongly increases at increasing δ_B. Several authors studied this situation by the exact

Table 4. Rate Constant Matrices for the Three Major Situations Occurring in AB_2 Polymerizations[a]

Situation (1)	Situation (2)	Situation (3)
$\begin{bmatrix} 1 & k & 1 & k \\ 1 & k & 1 & k \\ 1 & k & 1 & k \end{bmatrix}$	$\begin{bmatrix} 1 & 1 & 1 & 1 \\ k & k & k & k \\ k^2 & k^2 & k^2 & k^2 \end{bmatrix}$	$\begin{bmatrix} 1 & 1 & k & k \\ 1 & 1 & k & k \\ 1 & 1 & k & k \end{bmatrix}$

[a] Situation 1: The reactivity of the second B-group increases ($k > 1$) or decreases ($k < 1$) after reaction of the first one; A-group reactivity remains unchanged. Situation 2: A-group reactivity increases ($k > 1$) or decreases ($k < 1$) after reaction of the B-groups; B-group reactivity remains unchanged. Situation 3: The reactivity of B-groups increases ($k > 1$) or decreases ($k < 1$) after reaction of the A-group.

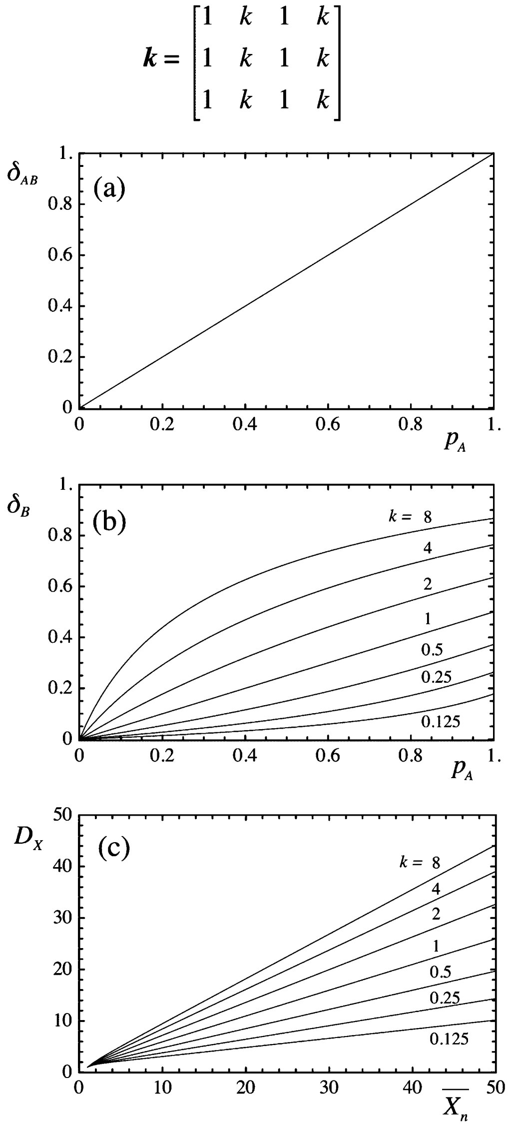


Figure 2. AB_2 polycondensation in the kinetic situation 1 (see Tables 3 and 4): Variations of (a) δ_{AB} vs conversion p_A (same value whatever k), (b) δ_B vs conversion p_A, and (c) degree-of-polymerization dispersity $D_X = \overline{X_w}/\overline{X_n}$ vs $\overline{X_n}$. Positive substitution effects: $k = 2, 4, 8$. Negative substitution effects: $k = 0.5, 0.25, 0.125$. $k = 1$ corresponds to the ideal case (no substitution effect).

kinetic model in order to determine AB_2 hyperbranched polymer distribution functions and their moments.[28−30,34,37] The $\overline{X_w}$ calculated by the exact kinetic model are identical to those determined in the present study, showing that the kinetic-probability minimal model provides accurate and significant information on these hyperbranched polymerizations.

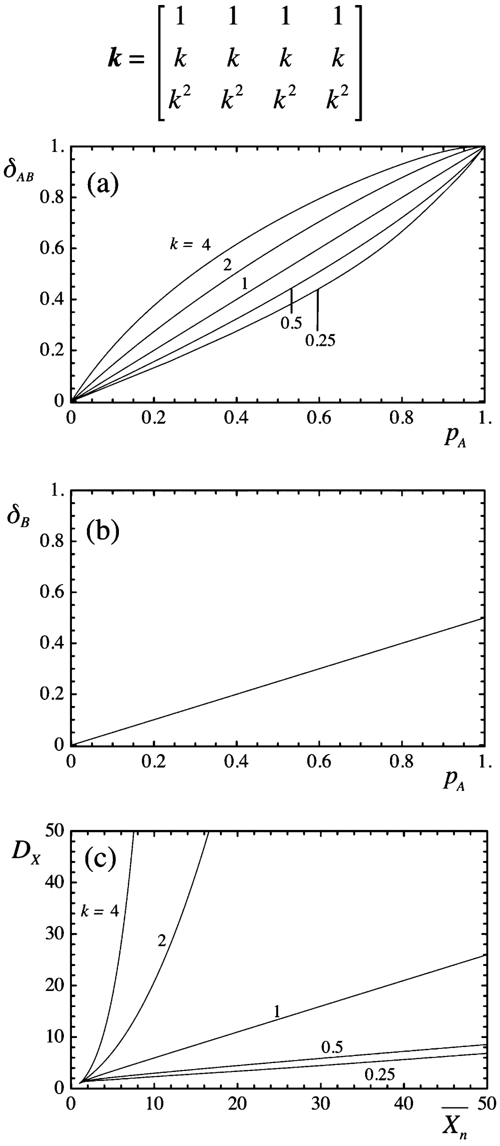


Figure 3. AB_2 polycondensation in the kinetic situation 2 (see Tables 3 and 4): Variations of (a) δ_{AB} vs conversion p_A, (b) δ_B vs conversion p_A (same value whatever k), and (c) degree-of-polymerization dispersity $D_X = \overline{X_w}/\overline{X_n}$ vs $\overline{X_n}$. Positive substitution effects: $k = 2, 4$. Negative substitution effects: $k = 0.5, 0.25$. $k = 1$ corresponds to the ideal case (no substitution effect).

Situation (2): The reaction of B increases/decreases the reactivity of A, but all B-groups remain equally reactive (see the columns of the corresponding ***k*** matrix in Table 4). The linear variation of δ_B whatever k reflects the equal reactivity of all B-groups ($\delta_B = p_A/2$) (Figure 3b). δ_{AB} increases or decreases in the 0.5 conversion region and approaches 1 at high conversion (Figure 3a). As already reported by Schmaljohann et al.,[54] polymer composition changes only moderately with respect to the ideal case. However, Figure 3c shows that dramatic increases or decreases of polymer dispersity take place in this case. When the reactivity of F_L and F_D A-groups is lower than that of the

$$\boldsymbol{k} = \begin{bmatrix} 1 & 1 & k & k \\ 1 & 1 & k & k \\ 1 & 1 & k & k \end{bmatrix}$$

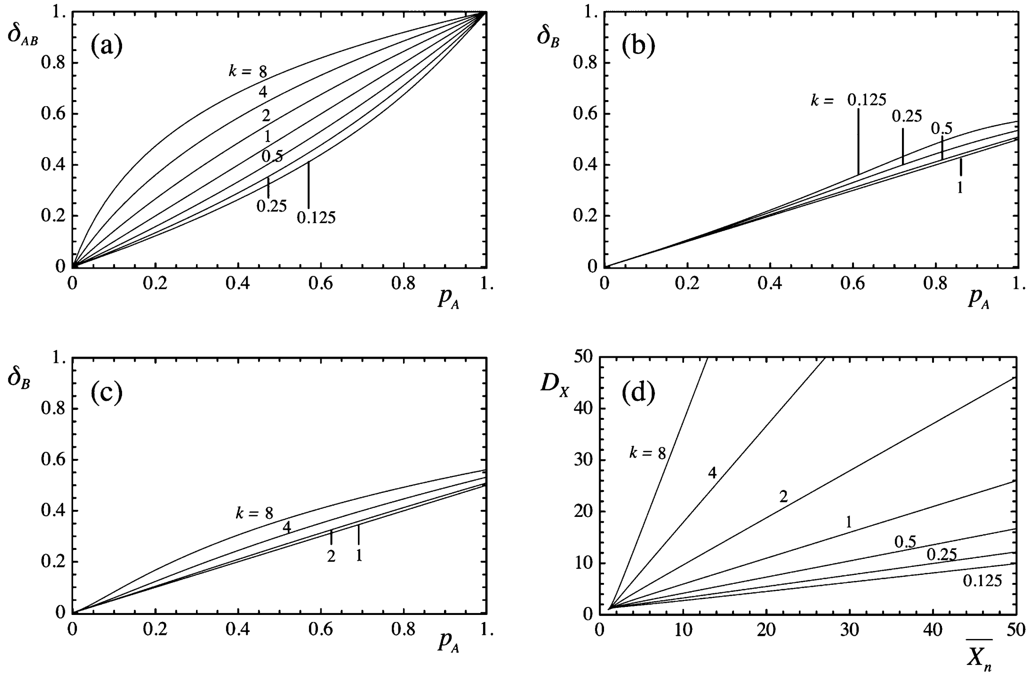


Figure 4. AB$_2$ polycondensation in the kinetic situation 3 (see Tables 3 and 4). Variations of (a) δ_{AB} vs conversion p_A, (b) δ_B vs conversion p_A in the case of negative substitution effects, (c) δ_B vs conversion p_A in the case of positive substitution effects, and (d) degree-of-polymerization dispersity $D_X = \overline{X_w}/\overline{X_n}$ vs $\overline{X_n}$. Positive substitution effects: $k = 2, 4, 8$. Negative substitution effects: $k = 0.5, 0.25, 0.125$. $k = 1$ corresponds to the ideal case (no substitution effect).

monomer, polymers of quite low dispersity are formed ($D_X = 2.32$ when $\overline{X_n} = 10$ for $k = 0.25$) while polymers of very high dispersity are formed in the reverse case ($D_X = 110$ when $\overline{X_n} = 10$ for $k = 4$). This clearly reflects the considerable influence of the "crossed" AB degree of branching on polymer dispersity.

Situation 3: In that case, the reaction of A increases/decreases the reactivity of B-groups: The B-groups of T and L units are more/less reactive than those of M and F$_L$ units (compare columns 1 and 2 to columns 3 and 4 of the corresponding **k** matrix in Table 4). This situation is more complex, as shown by Figure 4. δ_B is close to the ideal value ($\delta_B = p_A/2$), but slightly above, even when B reactivity decreases. The AB-branching factor δ_{AB} is also changed, due to variations in the consumption rate of M and F$_L$ focal units (α-type units) by reactions involving their B-groups. The molecular distribution also depends strongly on reactivity changes, negative and positive substitution effects leading to large D_X decrease and increase, respectively.

To conclude this section, a very favorable situation would be an AB$_2$ monomer exhibiting positive substitution effects on B and negative substitution effects on A, with, e.g.:

$$\boldsymbol{k} = \begin{bmatrix} 1 & 4 & 1 & 4 \\ 0.5 & 2 & 0.5 & 2 \\ 0.25 & 1 & 0.25 & 1 \end{bmatrix}$$

Polymers of high B-branching factor ($\delta_B = DB = 0.76$) and relatively low D_X for AB$_2$ hyperbranched systems ($D_X = 10.4$) would be obtained at $p_A = 0.98$ ($\overline{X_n} = 50$).

We illustrate the usefulness of the method by applying it to a hyperbranched polymer obtained by the bulk reaction of 2,2-bis(hydroxymethyl)propanoic acid at 140 °C for 1 h in the presence of 0.1 mass % *p*-toluenesulfonic acid (see ref[55] for experimental details). The various focal, linear, dendritic, and terminal units can be detected in the ^{13}C NMR spectrum and quantified (Figure 5a). From this spectrum, experimental values of p_A, δ_B and δ_{AB} can easily be determined by peak integrations. The experimental values of δ_B and δ_{AB} (0.30 and 0.69, respectively) are much lower than those calculated from p_A assuming a random polymerization (0.42 and 0.83, respectively), thus reflecting the existence of strongly negative AB- and B-substitution effects during the polymerization (Table 5). $\overline{X_w}$, $\overline{M_w}$ and D_X and D_M dispersities can be very simply calculated by applying the relationships given above to the experimental values of p_A, δ_B and δ_{AB} (Table 5). A detailed discussion of these results is beyond the scope of this article, but it can easily be seen that these substitution effects result in much lower dispersities than expected for a random polymerization and that the corresponding kinetic situation appears to be a combination of situations 2 and 3 or situations 1−3 with $k < 1$. It must last be underlined that the existence of AB substitution effects has not previously been reported in hyperbranched polymers.

3. First Shell Substitution Effects in Hyperbranched AB$_f$ + B$_g$ Polymers. In AB$_f$ + B$_g$ polymers, the B$_g$ comonomer ("core molecule") acts as a chain limiter and, as shown on AB$_2$ + B$_3$ polymerizations by the exact kinetic model, also narrows molar mass distributions.[31,32] The Boltorn polyester series, prepared by polyesterification of 2,2-bis(hydroxymethyl)propanoic acid (AB$_2$ monomer) and ethoxylated Pentaerythritol (B$_4$ core molecule), is a commercial example of such polymers.

A- and B-Branching Factors δ_A and δ_B. Frey's degree of branching is not defined in this case, but A- and B-branching factors can be easily calculated from their definitions (eqs 6 and 7). Since the B$_g$ core molecule does not contain any A-group

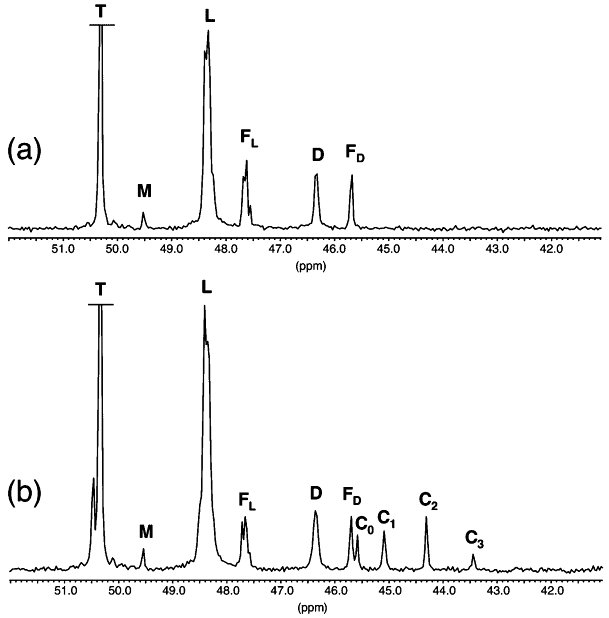


Figure 5. ^{13}C NMR spectra (75 MHz, DMSO-d_6, ref δ(DMSO) = 39.43 ppm) of (a) 2,2-bis(hydroxymethyl)propanoic acid (BMPA) polymer and (b) BMPA−Pentaerythritol (PE) polymer ([PE]/[BMPA] = 1/12 mol/mol, 140 °C, 1 h, 0.1 mass % *p*-toluenesulfonic acid. See ref 55 for experimental details). M, F_L, and F_D are unreacted monomer molecules, linear focal units and dendritic focal units, respectively. T, L, and D are terminal, linear, and dendritic units, respectively. C0−C4 are PE units with 0 to 4 reacted B-groups. C4 is not detected in the spectrum. See Table 2 for the notations of the other monomer units.

Table 5. Bulk Polymerization of 2,2-Bis(hydroxymethyl)propanoic Acid (BMPA) and of BMPA with Pentaerythritol (PE) (140 °C, 1 h, 0.1% Mass % *p*-Toluenesulfonic Acid)[b]

	BMPA polymer		BMPA:PE polymer (12:1 mol:mol)	
	random	FSSE	random	FSSE
p_A	0.831[a]	0.831[a]	0.896[a]	0.896[a]
δ_B	0.416	0.303[a]	0.494	0.389[a]
δ_{AB}	0.831	0.695[a]	0.768	0.672[a]
$\overline{X_n}$	5.93	5.93	5.00	5.00
$\overline{X_w}$	23.0	9.17	15.74	8.76
$\overline{M_n}$	707	707	599	599
$\overline{M_w}$	2641	1028	1815	1018
D_X	3.88	1.54	2.72	1.75
D_M	3.74	1.45	2.63	1.70

[a] Measured by ^{13}C NMR. [b] A-group conversion (p_A), B- and AB-branching factors (δ_B and δ_{AB}), number- and mass-average degrees of polymerization ($\overline{X_n}$ and $\overline{X_w}$), number- and mass-average molar masses ($\overline{M_n}$ and $\overline{M_w}$) and degree-of-polymerization- and molar-mass dispersities (D_X = {$\overline{X_w}/\overline{X_n}$ and $D_M = \overline{M_w}/\overline{M_n}$) from ^{13}C NMR data are given. Random: Calculated from experimental values of p_A assuming a random polymerization. FSSE: Calculated from experimental values of p_A, δ_B and δ_{AB}.

and the AB$_f$ monomer contains only one, $\delta_A = 0$ and δ_B is given by

$$\delta_B = \frac{\sum_{j_B=0}^{f} j_B(j_B - 1)(p_{1,0,j_B} + p_{1,1,j_B}) + \sum_{j_B=0}^{g} j_B(j_B - 1)(p_{2,0,j_B})}{\sum_{j_B=0}^{f} j_B(p_{1,0,j_B} + p_{1,1,j_B}) + \sum_{j_B=0}^{g} j_B(p_{2,0,j_B})} \tag{34}$$

When $f = 2$ and $g = 4$ (AB$_2$ + B$_4$ polymers):

$$\delta_B = \frac{2(p_{1,0,2} + p_{1,1,2}) + 2p_{2,0,2} + 6p_{2,0,3} + 12p_{2,0,4}}{2(p_{1,0,2} + p_{1,1,2}) + p_{1,0,1} + p_{1,1,1} + p_{2,0,1} + 2p_{2,0,2} + 3p_{2,0,3} + 4p_{2,0,4}} \tag{35}$$

(2,0,1) through (2,0,4) units are core units with 1 to 4 reacted B groups. Noting *C*1-*C*4 the mole fractions of these units and using the notation of eq 25 for the mole fractions of AB$_2$ monomer units, eq 35 can be written in a more conventional way:

$$\delta_B = \frac{2(D + F_D) + 2C_2 + 6C_3 + 12C_4}{2(D + F_D) + L + F_L + C_1 + 2C_2 + 3C_3 + 4C_4} \tag{36}$$

In the case of the ideal polymerization of 1 mol AB$_f$ and x mol B$_g$ (absence of substitution effects), δ_B can be calculated from eqs 18 and 19:

$$(\delta_B)_{\text{random}} = p_B(\overline{f^{\,0}_{b,B}} - 1) = p_A \frac{f(f - 1)}{(f + gx)^2} \tag{37}$$

The largest δ_B value would be obtained at complete conversion for a polymer containing only dendritic and terminal AB$_f$ units and fully reacted B$_g$ units, respectively noted (1,1,f) and (1,1,0) and (2,0,g). Hence:

$$(\delta_B)_{\max} = \frac{f(f - 1)\frac{1 - gx}{f(1 + x)} + g(g - 1)\frac{x}{1 + x}}{f\frac{1 - gx}{f(1 + x)} + g\frac{x}{1 + x}} =$$
$$(f - 1)(1 - gx) + g(g - 1)x \tag{38}$$

The lowest value ($\delta_B = 0$) corresponds to a polymer without any (1,0,$j_B > 1$) nor (2,0,$j_B > 1$) units, i.e., a linear polymer.

The δ_B branching factor depends on conversion, on core molecule content and on the amount of branched units in the polymer. For instance, the branching factor of a polymer obtained by reacting 1 mol AB$_2$ and 0.05 mol B$_4$ varies between 0 (linear polymer) and 1.4 (fully dendritic polymer) and takes the value 0.413 in the absence of substitution effects (random polymer).

AB-Branching Factor δ_{AB}. Since only the AB$_f$ monomer contains A-groups, eq 8 giving δ_{AB} simplifies to eq 29 and in the case of AB$_2$ + B$_g$ polymerizations, to eq 30.

Mass-Average Degree of Polymerization. According to eq 4, the mass-average degree of polymerization of a polymer obtained by reacting 1 mol of AB$_f$ monomer and x mol of B$_g$ core molecule is given by

$$\overline{X_w} = 1 + \frac{2p_A}{(1 + x)(1 - \delta_{AB})} + \frac{p_A\delta_B}{(1 + x)(1 - \delta_{AB})^2} \tag{39}$$

This equation reduces to eq 76 of ref 7 in the ideal case.

FSSE in AB$_2$ + B$_4$ Hyperbranched Polymers. First shell substitution effects in AB$_2$ + B$_4$ hyperbranched polymers have never been studied. Since the rate constant matrix (Table 6) contains 24 elements, the number of kinetic situations to be examined increases considerably with respect to AB$_2$ polymerizations. The method can obviously be applied to any type of kinetic situation, but, in the following, we consider four chemically reasonable kinetic situations only (kinetic situations 4−7).

Situation 4: The A-groups and the B-groups of each type of monomer units are equally reactive, but the reactivity of the

Table 6. Matrix *k* of Reaction Rate Constants for $AB_2 + B_4$ Polymerization[a]

		β-type species							
		M	F_L	T	L	C0	C1	C2	C3
α-type species	M	k_{11}	k_{12}	k_{13}	k_{14}	k_{15}	k_{16}	k_{17}	k_{18}
	F_L	k_{21}	k_{22}	k_{23}	k_{24}	k_{25}	k_{26}	k_{27}	k_{28}
	F_D	k_{31}	k_{32}	k_{33}	k_{34}	k_{35}	k_{36}	k_{37}	k_{38}

[a] C0−C3 represent B_4 monomer units with 0−3 reacted B-groups (see Table 2 for notations of AB_2 monomer units). M and F_L, which present both unreacted A- and B-groups, appear in both rows and columns.

Table 7. Rate Constant Matrices for Four Major Situations Occurring in $AB_2 + B_4$ Polymerizations[a]

Situation (4)	Situation (5)
$\begin{bmatrix} 1 & 1 & 1 & 1 & k' & k' & k' & k' \\ 1 & 1 & 1 & 1 & k' & k' & k' & k' \\ 1 & 1 & 1 & 1 & k' & k' & k' & k' \end{bmatrix}$	$\begin{bmatrix} 1 & k & 1 & k & 1 & k' & k'^2 & k'^3 \\ 1 & k & 1 & k & 1 & k' & k'^2 & k'^3 \\ 1 & k & 1 & k & 1 & k' & k'^2 & k'^3 \end{bmatrix}$
Situation (6)	**Situation (7)**
$\begin{bmatrix} 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ k & k & k & k & k' & k' & k' & k' \\ k^2 & k^2 & k^2 & k^2 & k'^2 & k'^2 & k'^2 & k'^2 \end{bmatrix}$	$\begin{bmatrix} 1 & 1 & k & k & k' & k' & k' & k' \\ 1 & 1 & k & k & k' & k' & k' & k' \\ 1 & 1 & k & k & k' & k' & k' & k' \end{bmatrix}$

[a] Situation 4: Equal reactivity of the B-groups of AB_2 and of the B-groups of B_4, with $k \neq k'$. Situation 5: The reactivity of the second B-group of AB_2 increases ($k > 1$) or decreases ($k < 1$) after reaction of the first one; A-group reactivity remains unchanged and the reactivity of the B-groups of B_4 increase ($k' > 1$) or decrease ($k' < 1$) after reaction of the preceding one. Situation 6: A-group reactivity increases ($k > 1$; $k' > 1$) or decreases ($k < 1$; $k' < 1$) after reaction of the B-groups of AB_2 units; B-group reactivity remains unchanged. Situation 7: The reactivity of the B-groups of AB_2 increases ($k > 1$) or decreases ($k < 1$) after reaction of the A-group; the reactivity of B_4 remains unchanged.

B-groups of B_4 units (rate constant = k') can be different from the reactivity of the B-groups of AB_2 units (rate constant = 1) (Table 7).

Figure 6b shows that the variations of the B-branching factor δ_B strongly depend on the reactivity of the core molecule. High δ_B values (0.9) are reached when $k' = 8$. On the other hand, only small differences on δ_B occur when the reactivity of B_4 is lower than that of AB_2. The AB-branching factor δ_{AB} is indirectly affected by the reactivity of B_4: When A reacts preferentially with B_4 (high B_4 reactivity), the number of reacted B-groups "seen" by a random reacted A-group on the same AB_2 monomer unit decreases, leading to a decrease of δ_{AB} (Figure 6a). High k' values also lead to much lower dispersities for final polymer (compare curves 1, 5, and 9 ($k' = 0.25$, 1 and 4) in Figure 6c, for instance), a result already reported for $AB_2 + B_3$ hyperbranched polymerizations in this kinetic situation.[31] As expected, increasing the core molecule content decreases both final $\overline{X}_n$ and D_X. However, at a given $\overline{X}_n$, increasing the core molecule content leads to increasing D_X when $k' < 1$ and to decreasing D_X when $k' \geq 1$ (compare curves 1, 2, 3, and 4 ($k' = 0.25$; $x = 0.01$ to 0.1) and curves 9, 10, 11, and 12 ($k' = 4$; $x = 0.01$ to 0.1) in Figure 6c). It results from the analysis of this situation that hyperbranched polymers with high B-branching factors and low dispersities are obtained when using highly reactive core molecules. The limiting situation $k' \rightarrow \infty$ would obviously be like reacting a B_8 core molecule in the ideal case.

Situation 5: The A-groups of M, F_L, and F_D units have the same reactivity (see the rows of the corresponding ***k*** matrix in Table 7) but the reaction of a B-group increases/decreases the reactivity of the other B-group(s) present on the same monomer unit. The substitution effects taking place on the B-groups of AB_2 units can be different from those involving B_4 units ($k \neq k'$), but, in order to focus on substitution effects, the rate constants involving the B-groups of AB_2 and B_4 monomer molecules are set to 1. The results are summarized in Figure 7. The comparison of curves 1, 2, and 3 ($k' = 0.5$, negative FSSE on B_4 units), 4, 5, and 6 ($k' = 1$, equal reactivity of B_4 units) and 7, 8, and 9 ($k' = 2$, positive FSSE on B_4 units) shows that increasing k increases δ_B, δ_{AB} and D_X, whatever the substitution effect on B_4. Similarly, the comparison of curves 1, 4, and 7 ($k = 0.5$, negative FSSE on the B-groups of AB_2 units), 2, 5, and 8 (equal reactivity of the B-groups of AB_2 units), and 3, 6, and 9 ($k = 2$, positive FSSE on the B-groups of AB_2 units) shows that increasing k' increases δ_B but decreases both δ_{AB} and D_X. Examining δ_B and D_X values at $p_A = 1$ for all curves indicates that positive FSSE on B_4 ($k' = 2$) always results in higher B-branching factors and lower dispersities. The existence of positive or negative FSSE on AB_2 is less important and the

$$\boldsymbol{k} = \begin{bmatrix} 1 & 1 & 1 & 1 & k' & k' & k' & k' \\ 1 & 1 & 1 & 1 & k' & k' & k' & k' \\ 1 & 1 & 1 & 1 & k' & k' & k' & k' \end{bmatrix}$$

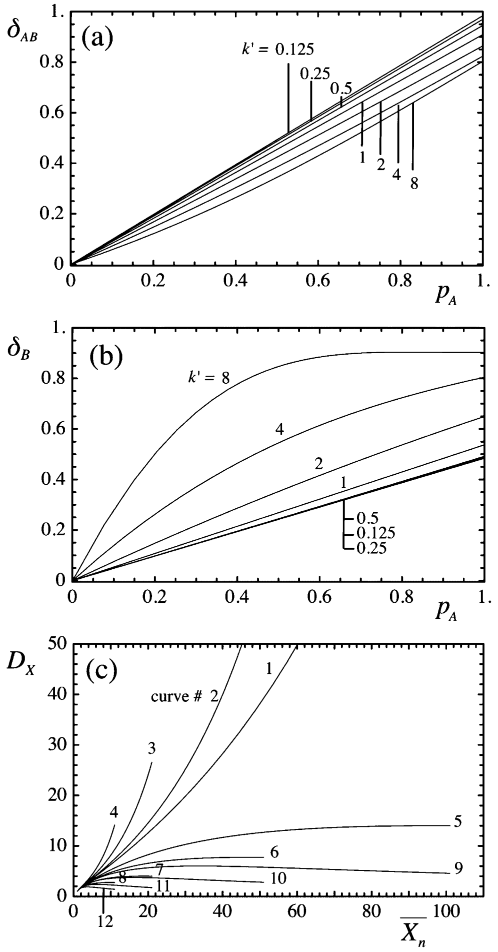


Figure 6. $AB_2 + B_4$ polycondensation ($[B_4]/[AB_2] = x$) in the kinetic situation 4 (see Tables 6 and 7): Variations of (a) δ_{AB} and (b) δ_B vs conversion p_A ($k' = 0.125$, 0.25, 0.5, 1, 2, 4, 8, $x = 0.05$). (c) Variations of degree-of-polymerization dispersity $D_X = \overline{X}_w/\overline{X}_n$ vs $\overline{X}_n$. Curves 1, 2, 3, 4: $k' = 0.25$, $x = 0.01$, 0.02, 0.05, 0.1. Curves 5, 6, 7, 8: $k' = 1$, $x = 0.01$, 0.02, 0.05, 0.1. Curves 9, 10, 11, 12: $k' = 4$, $x = 0.01$, 0.02, 0.05, 0.1.

$$\boldsymbol{k} = \begin{bmatrix} 1 & k & 1 & k & 1 & k' & k'^2 & k'^3 \\ 1 & k & 1 & k & 1 & k' & k'^2 & k'^3 \\ 1 & k & 1 & k & 1 & k' & k'^2 & k'^3 \end{bmatrix}$$

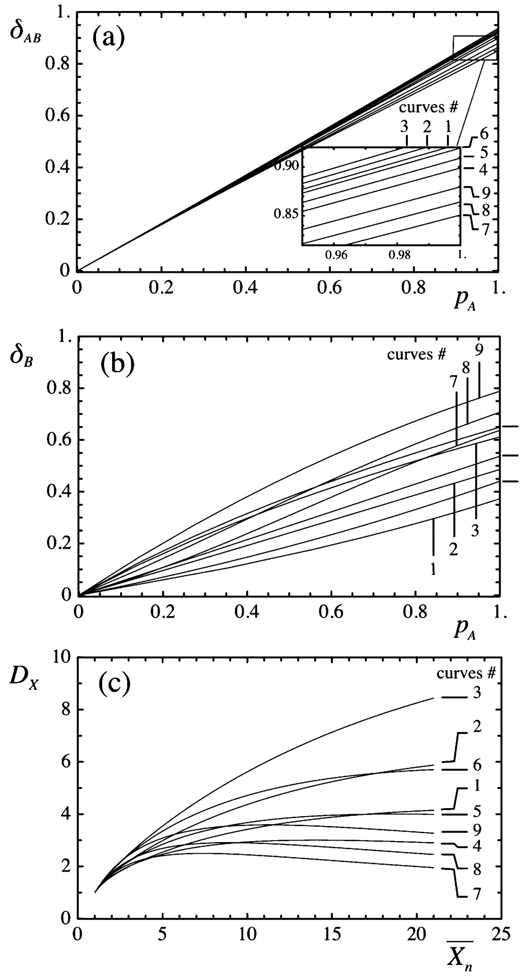


Figure 7. $AB_2 + B_4$ polycondensation ($[B_4]/[AB_2] = 0.05$) in the kinetic situation 5 (see Tables 6 and 7). Variations of (a) δ_{AB} vs conversion p_A, (b) δ_B vs conversion p_A and (c) degree-of-polymerization dispersity $D_X = \overline{X_w}/\overline{X_n}$ vs $\overline{X_n}$. Curves 1, 2, 3: $k' = 0.5$, $k = 0.5$, 1, 2. Curves 4, 5, 6: $k' = 1$, $k = 0.5$, 1, 2. Curves 7, 8, 9: $k' = 2$, $k = 0.5$, 1, 2.

case $k = 1$ and $k' = 2$ would be the best compromise to obtain a polymer with high branching factor and low dispersity.

Situation 6: The reactivity of A-groups increases ($k > 1$; $k' > 1$) or decreases ($k < 1$; $k' < 1$) after reaction of the B-groups of the same AB_2 unit, but the reactivity of B-groups remains unchanged. The comparison of curves 1, 4, and 7, of curves 2, 5, and 8, and of curves 3, 6, and 9 in Figure 8 shows that, for a given k, the highest k' values always lead to the best results (high branching factor δ_B and low dispersity D_X). At a given k/k' ratio, the same final branching factors and dispersity are obtained whatever the substitution effect, positive or negative (compare curves 6 and 2, curves 1, 5, and 9, curves and 4 and 8). The highest B-branching factor and the lowest dispersity are obtained for $k = 0.5$ and $k' = 2$, i.e., when the reactivity of the A-groups decreases from M to F_L and to F_D when they react with AB_2 units but increases when they react with B_4 units, a chemically improbable situation.

$$\boldsymbol{k} = \begin{bmatrix} 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ k & k & k & k & k' & k' & k' & k' \\ k^2 & k^2 & k^2 & k^2 & k'^2 & k'^2 & k'^2 & k'^2 \end{bmatrix}$$

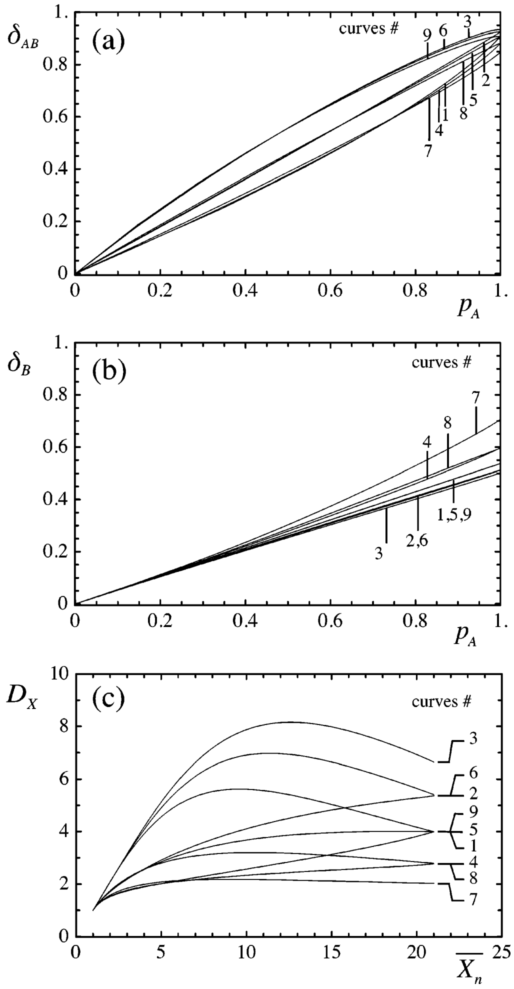


Figure 8. $AB_2 + B_4$ polycondensation ($[B_4]/[AB_2] = 0.05$) in the kinetic situation 6 (see Tables 6 and 7). Variations of (a) δ_{AB} vs conversion p_A, (b) δ_B vs conversion p_A and (c) degree-of-polymerization dispersity $D_X = \overline{X_w}/\overline{X_n}$ vs $\overline{X_n}$. Curves 1, 2, 3: $k' = 0.5$, $k = 0.5$, 1, 2. Curves 4, 5, 6: $k' = 1$, $k = 0.5$, 1, 2. Curves 7, 8, 9: $k' = 2$, $k = 0.5$, 1, 2.

Situation 7: The reactivity of the B-groups of AB_2 increases ($k > 1$) or decreases ($k < 1$) after reaction of the A-group, but the reactivity of B_4 remains unchanged (Figure 9). In this situation, negative substitution effects ($k < 1$) lead to low dispersities D_X whatever the reactivity of B_4 (compare curves 1, 2, and 3, curves 4, 5, and 6, and curves 7, 8, and 9). Meanwhile, high B_4 reactivity ($k' = 2$) leads to the best results in terms of B-branching factor (high δ_B) and dispersity (low D_X) (see curves 7, 8, and 9). In order to obtain hyperbranched polymers with a structure close to that of dendrimers in this kinetic situation, a highly reactive core molecule ($k' > 1$) and negative AB FSSE, ($k < 1$, i.e., higher reactivity of the B-groups of M and F_L units of with respect to L and T units) would be required.

General trends can be drawn from the kinetic situations studied above. In order to obtain a dendrimer-like structure, (i) the core molecule should present the highest reactivity and (ii) the A- and B-groups of monomer molecules should be more reactive than those of linear focal units (F_L), which in turn should be more reactive than the other reactive groups present on growing chains.

The method was applied to a hyperbranched polymer obtained by reacting BMPA and Pentaerythritol (PE) ([PE]/[BMPA] =

$$\boldsymbol{k} = \begin{bmatrix} 1 & 1 & k & k & k' & k' & k' & k' \\ 1 & 1 & k & k & k' & k' & k' & k' \\ 1 & 1 & k & k & k' & k' & k' & k' \end{bmatrix}$$

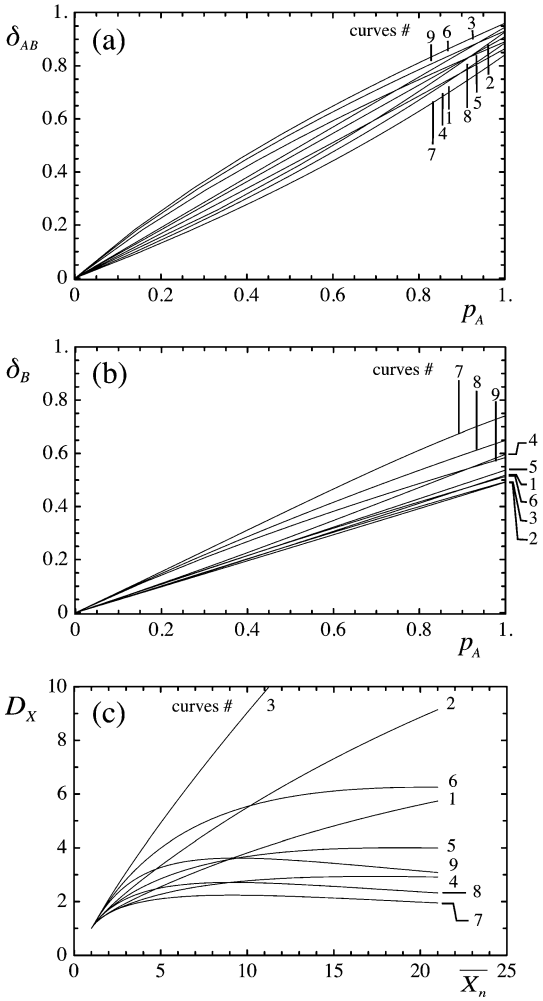


Figure 9. AB$_2$ + B$_4$ polycondensation ([B$_4$]/[AB$_2$] = 0.05) in the kinetic situation (7) (see Tables 6 and 7). Variations of (a) δ_{AB} vs conversion p_A, (b) δ_B vs conversion p_A and (c) degree-of-polymerization dispersity $D_X = \overline{X}_w/\overline{X}_n$ vs $\overline{X}_n$. Curves 1, 2, 3: $k' = 0.5$, $k = 0.5$, 1, 2. Curves 4, 5, 6: $k' = 1$, $k = 0.5$, 1, 2. Curves 7, 8, 9: $k' = 2$, $k = 0.5$, 1, 2.

1/12) for 1 h at 140 °C in the presence of 0.1 mass % *p*-toluenesulfonic acid (see ref 55 for experimental details). Each type of monomer units, including residual BMPA and PE, can be quantified in the ^{13}C NMR spectrum given in Figure 5b. The results obtained by applying the relationships given above are reported in Table 5. Like in the case of BMPA homopolymerization, it is easy to see that strong negative AB- and B-substitution effects take place during the synthesis, leading to much lower δ_B and δ_{AB} branching factors and lower D_X and D_M dispersities than expected for a random polymerization. The kinetic situation in this case appears more complex than the elementary situations described above. A detailed discussion of these experimental results is beyond the scope of this article, but, as discussed above for BMPA homopolymerization, a situation with combined negative AB FSSE in AB$_2$ units and negative B FSSE both in AB$_2$ and B$_4$ units is involved in this polymerization: The reactivity of the OH groups of a given monomer unit decreases after reaction of the other OH group(s) and after reaction of the COOH group, while the reactivity of the COOH group also decreases after reaction of the OH groups. This generalized negative FSSE explains why the experimental dispersities reported for BMPA hyperbranched polymers[56] are much lower than expected for random polymers.

Conclusion

The kinetic-probability minimal model was applied to hyperbranched polymerizations to study the influence of first shell substitution effects (FSSE) on the dispersity and the architecture of hyperbranched polymers.

Simple explicit relationships giving the mass-average degree of polymerization, mass-average molar mass and dispersities as a function of conversions, of initial monomer mixture composition and of polymer architecture at a given reaction time are derived using the "in−out" recursive probability approach. Three parameters, the A-, B-, and AB-branching factors (δ_A, δ_B, and δ_{AB}) are introduced to describe polymer branching and kinetic deviations from ideality. These parameters can easily be obtained experimentally, e.g., by NMR spectroscopy.

The B-branching factor, δ_B, generalizes the concept of "degree of branching" to any type of polymerization. It is defined as the expectation of the number of reacted B-groups "seen" by a random reacted B-group looking into the monomer unit to which it belongs, i.e., the number of branches connected to the other B-groups of that monomer unit. This definition is quite simple and the corresponding equation (eq 7) can readily be applied to any type of monomer mixture, such as AB$_f$ + B$_g$ systems or more complex ones. For AB$_2$ polymerizations δ_B reduces to Frey's degree of branching (DB).

The A-branching factor, δ_A, has a symmetrical definition. It is obviously 0 for AB$_f$ hyperbranched polymerizations, but must be taken into account when the initial monomer mixture contains A$_f$-type or A$_f$B$_g$-type monomers.

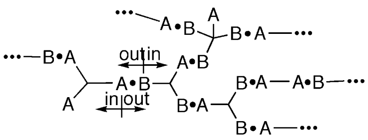
The AB-branching factor, δ_{AB}, characterizes the substitution effects induced on A-group reactivity by the reaction of B-groups and, conversely, the effects induced on B-group reactivity by the reaction of A-groups. Although this effect has always been neglected in hyperbranched polymerization studies, the results presented here show that it could exert a considerable influence on final polymer dispersity.

Using these definitions and the related relationships, the FSSE kinetic-probability minimal model was applied to AB$_f$ and AB$_f$ + B$_g$ hyperbranched polymerizations, taken as examples. The influence of various substitution effects on molar masses and dispersities was more specifically studied on AB$_2$ and AB$_2$ + B$_4$ polymerizations. The results obtained on the specific case of AB$_2$ polymerizations with equal reactivity of A-groups and $k_L \neq k_T$ are identical to literature results obtained by the exact kinetic approach on the same system, showing that the minimal model provides significant information on hyperbranched polymerizations.

The case of AB$_2$ + B$_4$ polymerizations had not yet been studied. The results obtained by the kinetic-recursive probability approach show that high branching factor and low dispersities could be obtained when the core molecule is highly reactive, when the A- and B-groups of monomer molecules are more reactive than those of linear focal units and when the A- and B-groups of linear focal units are more reactive than the other reactive groups present on growing chains.

The method was applied to the polymerization of 2,2-bis(hydroxymethyl)propanoic acid (BMPA) and to the polymerization of BMPA with Pentaerythritol. The mass-average degree of polymerization, mass-average molar mass, dispersities and the branching factors of these polymers were straightforwardly calculated from ^{13}C NMR spectra. From these experimental

Scheme 3



results, it is quite easy to see that a negative FSSE take place, including AB substitution effects between OH and COOH groups of BMPA units. Such substitution effects had never been reported in hyperbranched polymerizations.

It must last be underlined that the method and the general relationships presented in this article are not limited to hyperbranched polymers, but can obviously be applied to any type of polymerizations.

Appendix

Appendix A: Average Degrees of Polymerization and Molar Masses of Polycondensation Polymers by the Recursive Probability Approach under the Hypothesis of First Shell Substitution Effects. According to the notations defined in the main text, the total number of A-groups, n_A, and the number of reacted A-groups, $n_{A,r}$ can be written:

$$n_A = \sum_{i=1}^{i=u} f_{A,i} n_i \tag{40}$$

$$n_{A,r} = \sum_{i,j_A,j_B} j_A n_{i,j_A,j_B} \tag{41}$$

The conversion of A-groups, p_A, is

$$p_A = \frac{n_{A,r}}{n_A} = \frac{\sum_{i,j_A,j_B} j_A n_{i,j_A,j_B}}{\sum_{i=1}^{u} f_{A,i} n_i} = \frac{\sum_{i,j_A,j_B} j_A p_{i,j_A,j_B}}{\overline{f^0_{n,A}}} \tag{42}$$

Since the number of reacted A-groups is always equal to the number of reacted B-groups, eq 42 leads to a relationship between p_A and B-group conversion, p_B:

$$p_A \overline{f^0_{n,A}} = \sum_{i,j_A,j_B} j_A p_{i,j_A,j_B} = p_B \overline{f^0_{n,B}} = \sum_{i,j_A,j_B} j_B p_{i,j_A,j_B} \tag{43}$$

Using the formalism of the "in−out" recursive approach,[38,43] $W^{out}_{A,r}(i,j_A,j_B)$ and $W^{in}_{A,r}(i,j_A,j_B)$ are defined as the molar mass of the branch seen by a *reacted* A-group (A_r) looking "out" and "into" the (i,j_A,j_B) monomer unit to which it belongs (Scheme 3). Similar definitions apply to $W^{out}_{B,r}(i,j_A,j_B)$ and $W^{in}_{B,r}(i,j_A,j_B)$.

The mass-average molar mass, $\overline{M_w}$, is the expected molar mass $E(W)$ of a polymer molecule chosen by picking a unit of mass randomly in the polymer sample. The molar mass W_{i,j_A,j_B} of a polymer molecule picked at random by a (i,j_A,j_B)-type monomer unit is given by eq 44:

$$W_{i,j_A,j_B} = M_i + j_A W^{out}_{A,r}(i,j_A,j_B) + j_B W^{out}_{B,r}(i,j_A,j_B) \tag{44}$$

The probability of picking a (i,j_A,j_B)-type monomer unit by mass is the mass fraction ω_{i,j_A,j_B} of such units. Hence, applying the addition law for expectations of sums of random variables:

$$\overline{M_w} = \sum_{i,j_A,j_B} \omega_{i,j_A,j_B} E(W_{i,j_A,j_B}) \tag{45}$$

When a condensation byproduct E of molar mass M_E is eliminated from reaction medium, the corresponding mass loss must be taken into account in the mass fraction of (i,j_A,j_B)-type units:

$$\omega_{i,j_A,j_B} = \frac{n_{i,j_A,j_B}(M_i - j_A M_{E,A} - j_B M_{E,B})}{\sum_i M_i n_i - M_E p_A \sum_i f_{A,i} n_i} = \frac{p_{i,j_A,j_B}(M_i - j_A M_{E,A} - j_B M_{E,B})}{\overline{M^0_n} - M_E p_A \overline{f^0_{n,A}}} \tag{46}$$

where $M_{E,A}$ and $M_{E,B}$ are respectively the contribution of a reacted A-group and a reacted B group to M_E. The choice of $M_{E,A}$ and $M_{E,B}$ is arbitrary, provided that $M_{E,A} + M_{E,B} = M_E$.

Taking into account the mass loss in the "out" expectations, the molar mass of the branch "seen" by a random reacted B-group (B_r) looking "out" its parent monomer unit is

$$W^{out}_{B,r} = \begin{cases} W^{in}_{A,r}(1,1,0) - M_E \text{ if } A_r \text{ belongs to a } (1,1,0) \text{ unit} \\ W^{in}_{A,r}(1,1,1) - M_E \text{ if } A_r \text{ belongs to a } (1,1,1) \text{ unit} \\ \vdots \\ W^{in}_{A,r}(i,j_A,j_B) - M_E \text{ if } A_r \text{ belongs to a } (i,j_A,j_B) \text{ unit} \\ \vdots \\ W^{in}_{A,r}(u,f_{A,u},f_{B,u}) - M_E \text{ if } A_r \text{ belongs to a } (u,f_{A,u},f_{B,u}) \text{ unit} \end{cases} \tag{47}$$

Since we are dealing with the FSSE kinetic-probability model, the various types of (i,j_A,j_B) monomer units obtained after the kinetic step are randomly combined in the probabilistic step. Therefore, the "out" expectations $W^{out}_{A,r}$ and $W^{out}_{B,r}$ do not depend on the nature of the monomer unit to which A_r and B_r belong and $W^{in}_{A,r}(i,j_A,j_B)$ can be written as

$$W^{in}_{A,r}(i,j_A,j_B) = M_i + (j_A - 1)W^{out}_{A,r} + j_B W^{out}_{B,r} \tag{48}$$

The probability that a random reacted A-group belongs to a (i, j_A, j_B) unit is $j_A p_{i,j_A,j_B}/\sum_{i,j_A,j_B} j_A p_{i,j_A,j_B}$. Applying the theorem of total probability for expectations to eq 47 and the addition theorem for expectations of sum of random variables to eq 48 leads to

$$E(W^{out}_{B,r}) = \sum_{i,j_A,j_B} [E(W^{in}_{A,r}(i,j_A,j_B)) - M_E] \frac{j_A p_{i,j_A,j_B}}{\sum_{i,j_A,j_B} j_A p_{i,j_A,j_B}} \tag{49}$$

$$E(W^{in}_{A,r}(i,j_A,j_B)) = M_i + (j_A - 1)E(W^{out}_{A,r}) + j_B E(W^{out}_{B,r}) \tag{50}$$

Substituting eq 50 into eq 49 and introducing M_a, M_b, δ_A, δ_B, and $\delta_{AB} = \delta_{BA}$, as defined in the main text, leads to

$$E(W^{out}_{B,r}) = \frac{(1 - \delta_{AB})(M_a - M_E) + \delta_A(M_b - M_E)}{(1 - \delta_{AB})(1 - \delta_{BA}) - \delta_A\delta_B} \tag{51}$$

$$E(W^{out}_{A,r}) = \frac{(1 - \delta_{BA})(M_b - M_E) + \delta_B(M_a - M_E)}{(1 - \delta_{AB})(1 - \delta_{BA}) - \delta_A\delta_B} \tag{52}$$

The expression giving the mass-average molar mass of condensation polymers (eq 3) is derived by substituting eqs 46, 50, 51, and 52 into eq 45 and using the following relationships:

$$\sum_{i,\,j_\mathrm{A},\,j_\mathrm{B}} M_i^{\,2} p_{i,\,j_\mathrm{A},\,j_\mathrm{B}} = \overline{M_\mathrm{w}^0}\,\overline{M_\mathrm{n}^0} \tag{53}$$

$$\sum_{i,\,j_\mathrm{A},\,j_\mathrm{B}} M_i j_\mathrm{A} p_{i,\,j_\mathrm{A},\,j_\mathrm{B}} = M_\mathrm{a} p_\mathrm{A}\overline{f^{\,0}_{\mathrm{n,A}}} \tag{54}$$

$$\sum_{i,\,j_\mathrm{A},\,j_\mathrm{B}} M_i j_\mathrm{B} p_{i,\,j_\mathrm{A},\,j_\mathrm{B}} = M_\mathrm{b} p_\mathrm{B}\overline{f^{\,0}_{\mathrm{n,B}}} \tag{55}$$

$$\sum_{i,\,j_\mathrm{A},\,j_\mathrm{B}} j_\mathrm{A} p_{i,\,j_\mathrm{A},\,j_\mathrm{B}} = p_\mathrm{A}\overline{f^{\,0}_{\mathrm{n,A}}} = \sum_{i,\,j_\mathrm{A},\,j_\mathrm{B}} j_\mathrm{B} p_{i,\,j_\mathrm{A},\,j_\mathrm{B}} = p_\mathrm{B}\overline{f^{\,0}_{\mathrm{n,B}}} \tag{56}$$

$$\sum_{i,\,j_\mathrm{A},\,j_\mathrm{B}} j_\mathrm{A}^{\,2} p_{i,\,j_\mathrm{A},\,j_\mathrm{B}} = p_\mathrm{A}\overline{f^{\,0}_{\mathrm{n,A}}}(\delta_\mathrm{A}+1) \tag{57}$$

$$\sum_{i,\,j_\mathrm{A},\,j_\mathrm{B}} j_\mathrm{B}^{\,2} p_{i,\,j_\mathrm{A},\,j_\mathrm{B}} = p_\mathrm{B}\overline{f^{\,0}_{\mathrm{n,B}}}(\delta_\mathrm{B}+1) \tag{58}$$

$$\sum_{i,\,j_\mathrm{A},\,j_\mathrm{B}} j_\mathrm{A} j_\mathrm{B} p_{i,\,j_\mathrm{A},\,j_\mathrm{B}} = p_\mathrm{A}\overline{f^{\,0}_{\mathrm{n,A}}}\delta_\mathrm{AB} = p_\mathrm{B}\overline{f^{\,0}_{\mathrm{n,B}}}\delta_\mathrm{BA} \tag{59}$$

From eqs 56 and 59, it is clear that $\delta_\mathrm{AB} = \delta_\mathrm{BA}$.

Equal Reactivity of Functional Groups. Under Flory's assumptions, $p_{i,j_\mathrm{A},j_\mathrm{B}}$ is given by the binomial probability:

$$p_{i,\,j_\mathrm{A},\,j_\mathrm{B}} = \alpha_i \binom{f_{\mathrm{A},i}}{j_\mathrm{A}} p_\mathrm{A}^{j_\mathrm{A}}(1-p_\mathrm{A})^{f_{\mathrm{A},i}-j_\mathrm{A}} \binom{f_{\mathrm{B},i}}{j_\mathrm{B}} p_\mathrm{B}^{j_\mathrm{B}}(1-p_\mathrm{B})^{f_{\mathrm{B},i}-j_\mathrm{B}} \tag{60}$$

where α_i is the mol fraction of monomer no. i in initial mixture (or the mol fraction of i-type monomer units in the polymer). From eqs 6 and 14:

$$\delta_\mathrm{A} = \frac{\sum_{i=1}^{i=u} \alpha_i f_{\mathrm{A},i} p_\mathrm{A}^{\,2}(f_{\mathrm{A},i}-1)}{\sum_{i=1}^{i=u} \alpha_i f_{\mathrm{A},i} p_\mathrm{A}} = p_\mathrm{A}\left(\frac{\sum_{i=1}^{i=u} \alpha_i f_{\mathrm{A},i}^{\,2}}{\sum_{i=1}^{i=u} \alpha_i f_{\mathrm{A},i}} - 1\right) = p_\mathrm{A}(\overline{f^{\,0}_{\mathrm{a,A}}} - 1) \tag{61}$$

Similarly:

$$\delta_\mathrm{B} = p_\mathrm{B}(\overline{f^{\,0}_{\mathrm{b,B}}} - 1) \tag{62}$$

and

$$\delta_\mathrm{AB} = p_\mathrm{A}\overline{f^{\,0}_{\mathrm{b,A}}} = \delta_\mathrm{BA} = p_\mathrm{B}\overline{f^{\,0}_{\mathrm{a,B}}} \tag{63}$$

M_a and M_b become the initial A- and B-average molar masses become $\overline{M_\mathrm{a}^0}$ and $\overline{M_\mathrm{b}^0}$:[7]

$$\overline{M_\mathrm{a}^0} = \frac{\sum_{i=1}^{i=u} M_i f_{\mathrm{A},i} n_i}{\sum_{i=1}^{i=u} f_{\mathrm{A},i} n_i} \qquad \overline{M_\mathrm{b}^0} = \frac{\sum_{i=1}^{i=u} M_i f_{\mathrm{B},i} n_i}{\sum_{i=1}^{i=u} f_{\mathrm{B},i} n_i}$$

Hence:

$$\begin{aligned}\overline{M_\mathrm{w}} = {} & \frac{\overline{M_\mathrm{w}^0}\,\overline{M_\mathrm{n}^0} - p_\mathrm{A}\overline{f^{\,0}_{\mathrm{n,A}}}M_\mathrm{E}^{\,2}}{\overline{M_\mathrm{n}^0} - p_\mathrm{A}\overline{f^{\,0}_{\mathrm{n,A}}}M_\mathrm{E}} + \frac{p_\mathrm{A}\overline{f^{\,0}_{\mathrm{n,A}}}(M_\mathrm{a}-M_\mathrm{E})}{\overline{M_\mathrm{n}^0} - p_\mathrm{A}\overline{f^{\,0}_{\mathrm{n,A}}}M_\mathrm{E}} \times \\ & \left[\frac{(1-p_\mathrm{B}\overline{f^{\,0}_{\mathrm{a,B}}})(M_\mathrm{b}-M_\mathrm{E}) + p_\mathrm{B}(\overline{f^{\,0}_{\mathrm{b,B}}}-1)(M_\mathrm{a}-M_\mathrm{E})}{(1-p_\mathrm{B}\overline{f^{\,0}_{\mathrm{a,B}}})(1-p_\mathrm{A}\overline{f^{\,0}_{\mathrm{b,A}}}) - p_\mathrm{A}p_\mathrm{B}(\overline{f^{\,0}_{\mathrm{a,A}}}-1)(\overline{f^{\,0}_{\mathrm{b,B}}}-1)}\right] + \\ & \frac{p_\mathrm{B}\overline{f^{\,0}_{\mathrm{n,A}}}(M_\mathrm{b}-M_\mathrm{E})}{\overline{M_\mathrm{n}^0} - p_\mathrm{B}\overline{f^{\,0}_{\mathrm{n,B}}}M_\mathrm{E}} \times \\ & \left[\frac{(1-p_\mathrm{A}\overline{f^{\,0}_{\mathrm{b,A}}})(M_\mathrm{a}-M_\mathrm{E}) + p_\mathrm{A}(\overline{f^{\,0}_{\mathrm{a,A}}}-1)(M_\mathrm{b}-M_\mathrm{E})}{(1-p_\mathrm{B}\overline{f^{\,0}_{\mathrm{a,B}}})(1-p_\mathrm{A}\overline{f^{\,0}_{\mathrm{b,A}}}) - p_\mathrm{A}p_\mathrm{B}(\overline{f^{\,0}_{\mathrm{a,A}}}-1)(\overline{f^{\,0}_{\mathrm{b,B}}}-1)}\right]\end{aligned} \tag{64}$$

This relationship could be drawn from our previous work on the recursive approach in the ideal case.[7] It can also be written under the more compact form:

$$\begin{aligned}\overline{M_\mathrm{w}} = {} & [\overline{M_\mathrm{w}^0}\,\overline{M_\mathrm{n}^0} - p_\mathrm{A}\overline{f^{\,0}_{\mathrm{n,A}}}M_\mathrm{E}^{\,2}]/[\overline{M_\mathrm{n}^0} - p_\mathrm{A}\overline{f^{\,0}_{\mathrm{n,A}}}M_\mathrm{E}] + \\ & \{p_\mathrm{A}\overline{f^{\,0}_{\mathrm{a,A}}}[2(1-p_\mathrm{A}\overline{f^{\,0}_{\mathrm{b,A}}})(M_\mathrm{b}-M_\mathrm{E})(M_\mathrm{a}-M_\mathrm{E}) + \\ & p_\mathrm{B}(\overline{f^{\,0}_{\mathrm{b,B}}}-1)(M_\mathrm{a}-M_\mathrm{E})^2 + p_\mathrm{A}(\overline{f^{\,0}_{\mathrm{a,A}}}-1)(M_\mathrm{b}-M_\mathrm{E})^2]/ \\ & (\overline{M_\mathrm{n}^0} - p_\mathrm{A}\overline{f^{\,0}_{\mathrm{n,A}}}M_\mathrm{E})[(1-p_\mathrm{A}\overline{f^{\,0}_{\mathrm{b,A}}})^2 - p_\mathrm{A}p_\mathrm{B}(\overline{f^{\,0}_{\mathrm{a,A}}} - 1)(\overline{f^{\,0}_{\mathrm{b,B}}} - 1)]\}\end{aligned} \tag{65}$$

Appendix B: Glossary of Symbols

$\overline{X_\mathrm{n}}$	number-average degree of polymerization
$\overline{M_\mathrm{n}}$	number-average molar mass
$\overline{X_\mathrm{w}}$	mass-average degree of polymerization
$\overline{M_\mathrm{w}}$	mass-average molar mass
$D_\mathrm{X} = \overline{X_\mathrm{w}}/\overline{X_\mathrm{n}}$	degree-of-polymerization dispersity
$D_\mathrm{M} = \overline{M_\mathrm{w}}/\overline{M_\mathrm{n}}$	molar-mass dispersity
A and B	mutually reactive chemical groups (either reacted or unreacted)
p_A and p_B	fractions of A and B groups that have reacted
n_i	number of moles of monomer unit i
α_i	number-fraction of i-type monomer units in the polymer
ω_i	mass fraction of i-type monomer units in the polymer
$f_{\mathrm{A},i}$	number of A groups (reacted and unreacted) on i-type monomer units
$f_{\mathrm{B},i}$	number of B groups (reacted and unreacted) on i-type monomer units
$(i,j_\mathrm{A},j_\mathrm{B})$	i-type monomer unit with j_A reacted A-groups and j_B reacted B-groups
$n_{i,j_\mathrm{A},j_\mathrm{B}}$	number of moles of $(i,j_\mathrm{A},j_\mathrm{B})$ monomer units
$p_{i,j_\mathrm{A},j_\mathrm{B}}$	mole fraction of $(i,j_\mathrm{A},j_\mathrm{B})$ monomer units
$\omega_{i,j_\mathrm{A},j_\mathrm{B}}$	mass fraction of $(i,j_\mathrm{A},j_\mathrm{B})$ monomer units
$\overline{f^{\,0}_{\mathrm{n,A}}}$ and $\overline{f^{\,0}_{\mathrm{n,B}}}$	number-average A-group and B-group functionalities of initial monomer mixture
$\overline{f^{\,0}_{\mathrm{a,A}}}$	A-average A-group functionality of initial monomer mixture
$\overline{f^{\,0}_{\mathrm{b,B}}}$	B-average B-group functionality of initial monomer mixture
$\overline{f^{\,0}_{\mathrm{b,A}}}$	B-average A-group functionality of initial monomer mixture
$\overline{f^{\,0}_{\mathrm{a,B}}}$	A-average B-group functionality of initial monomer mixture
$\overline{M_\mathrm{w}}^{0}$	mass-average molar mass of initial monomer mixture
$\overline{M_\mathrm{a}^0}$	A-average molar mass of initial monomer mixture
$\overline{M_\mathrm{b}^0}$	B-average molar mass of initial monomer mixture

W_A^{out} and W_A^{in}	molar masses seen by a random A-group (either reacted or nonreacted) looking respectively "out" and "into" the monomer unit to which it belongs
W_B^{out} and W_B^{in}	molar masses seen by a random B-group (either reacted or nonreacted) looking respectively "out" and "into" the monomer unit to which it belongs
W_{i,j_A,j_B}	molar mass of a molecule picked at random by a (i,j_A,j_B) monomer unit
$E(Y)$	expectation of random variable Y
M_E	molar mass of condensation byproduct E
M_{EA}, M_{EB}	contribution of a reacted A-group (or B-group, respectively) to the molar mass of the condensation byproduct E; $M_{EA} + M_{EB} = M_E$
δ_A and δ_A	A- and B-branching factors
$\delta_{AB} = \delta_{BA}$	AB-branching factor
M_a and M_b	average molar mass of monomer units chosen by picking reacted A-groups and reacted B-groups at random, respectively (without taking byproduct elimination into account)

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