Average Degrees of Polymerization and Molar Masses of Branched and Hyperbranched Condensation Polymers: Recursive Probability Approach

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ABSTRACT: This article extends the “in−out” recursive probability method of Macosko and Miller to the polycondensation of mixtures of polyfunctional monomers bearing A- and/or B-groups. Explicit relationships of the theoretical average degrees of polymerization and average molar masses are established in the most general case and can be applied to any linear, hyperbranched, or network polymerizations, leading in the latter case to the value of the conversion at the gel point. These relationships reduce to those of Stockmayer in the case of reactions involving monomers bearing either A- or B-groups. The effect of the elimination of a condensation byproduct is also examined. An approximate explicit expression of the mass-average molar mass is proposed, allowing calculations with an error in the 1−3% range when water is the byproduct. Some examples are treated to illustrate the method, including AA + BB + AB, AB + B_g, AB_f, A_fB_g, $AB_f + B_g$, and more complex polymerizations. The effect of the functionality of the core molecule on the polydispersity of hyperbranched polymers is examined for various systems.

Introduction

A general expression for the chain length distribution (CLD) of AB_f-type hyperbranched condensation polymers was derived by Flory[1] in 1952, by a combinatorial and statistical approach assuming equal reactivity of all A- and B-groups and the absence of intramolecular reactions. Simple analytic expressions of the number- and mass-average degrees of polymerization ($\overline{X_n}$ and $\overline{X_w}$) and of the polydispersity index (PDI) were obtained from the CLD statistical moments. This approach was further extended to AB_f-type systems in which the f reactive B-groups are unequally reactive, hence distinguishable, such as saccharide derivatives.[2,3] The derivation of CLD and its moments by the combinatorial approach becomes quite complex and tedious as soon as mixtures of polyfunctional monomers are involved. Stockmayer[4,5] derived a general expression giving the CLD of condensation polymers obtained by reacting mixtures of A_f monomers with mixtures of B_g monomers. Gordon, later, developed a probabilistic generating function method to directly derive the CLD moments of nonlinear condensation polymers using the theory of stochastic branching processes[6,7] that was applied to the formation of ABB′-type hyperbranched polymers, in which B and B′ have different reactivities with A.[8,9] However, these probabilistic approaches were not further extended to mixtures of monomers bearing both A-groups and B-groups. Consequently, the CLD, average degrees of polymerization and polydispersity index of even relatively simple hyperbranched polymers, such as those obtained by reacting an AB_f-type monomer with a B_g-type core molecule, are not available by these approaches.

Another way to derive the CLD and average degrees of polymerization of condensation polymers is through the kinetic approach.[10,11] In this approach, the concentration of a given *x*-mer is calculated from the rates of all individual reactions in which it is involved.[12] In the case of nonlinear polycondensation, the resulting infinite set of differential equations can be solved in the most general case with the help of a generating function method.[13−16] Relationships giving the CLD, its moments, and other average properties can thus be established as a function of time or conversion for a particular system of interest. First-shell substitution effects can easily be taken into account, e.g., in the case of AB_2-type polymerization by introducing two rate constants, k_T and k_L, for reactions involving the B-groups of terminal and linear units, respectively. This approach was applied to AB_2-[17−19] and to $AB_2 + B_3$-[20,21] type hyperbranched polymers, showing that a positive substitution effect, i.e., a reactivity increase of the second B-group after reaction of the first one, leads to higher degrees of branching and broader CLD than in the case of equal reactivity.[17,19,21] The presence of a polyfunctional core molecule results in CLD narrowing,[20,21] which is enhanced when the AB_2 monomer is slowly introduced into reaction medium.[22,23] Recently the kinetic approach was generalized to AB_f polymers.[24] The Monte Carlo simulation of AB_2 [25−27] and $AB_2 + B_3$ [28] polymerizations gave essentially similar results. It must also be noted that, instead of using a numerical resolution of kinetic equations, explicit expressions of average DP's were proposed for $AB_g + B_f$ polymers assuming equal reactivity of A- and B-groups,[29,30] and, quite recently, for AB_2 polymers in the case of the first shell substitution effect.[31] The application of the kinetic approach to more complex hyperbranched polymers, although possible,[13,14] has not yet been reported. It would obviously lead to complex expressions, difficult to generate and to apply to practical cases.

In 1976, Macosko and Miller introduced the “in−out” recursive probability approach of nonlinear polymerization. This method uses elementary probability laws and the recursive nature of the branching process, and does not require CLD calculations nor complex mathematical formalism.[32−39] It is less powerful than the kinetic or probabilistic approaches, since the CLD cannot be calculated, but average molar masses and other

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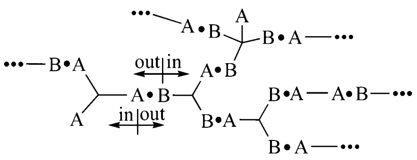
Scheme 1

Scheme 2



pre- and post-gel properties of complex polymer systems can be derived in a quite simple way. However, with the exception of the A_fB_g-type polymerization,[40] the method has not yet been applied to the formation of hyperbranched polymers.

This article extends the "in−out" recursive probability method to the most general case of polymerization of mixtures of polyfunctional monomers bearing A- and/or B-groups. Applications to some branched, hyperbranched, and network polymerization systems are also presented and discussed.

Results and Discussion

1. Initial Relationships. All calculations carried out in this article follow Flory's[1] and Stockmayer's[4,5] simplifying assumptions namely: (i) All A-groups and all B-groups are equally reactive, (ii) no intramolecular reactions take place (i.e., cyclization is neglected), and (iii) no side-reactions take place. 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), where A·B represents a newly formed linking group between monomer units.

The initial medium contains n_1, n_2, ..., n_k mol of monomer #1, #2, ..., #*k*. Each monomer molecule of type *i* ($i = 1, 2, ..., k$) has $f_{A,i}$ reactive A-groups and $f_{B,i}$ reactive B-groups (at least $f_{A,i}$ or $f_{B,i}$ is $\neq 0$). After a certain reaction time, conversions p_A and p_B are reached and a polymer is formed, in which a fraction p_A of A-groups and a fraction p_B of B-groups have reacted and fractions $1 - p_A$ and $1 - p_B$ have not. Under the equal reactivity assumption of Flory and Stockmayer, the probability that a randomly picked A-group (respectively B-group) has reacted is conversion p_A (respectively p_B). Using the formalism of the "in−out" recursive approach, N_A^{out} and N_A^{in} are defined as the number of monomer units (i.e., the degree of polymerization of the branch) seen by a random A-group looking respectively "out" and "into" the monomer unit to which it belongs (Scheme 2). Similar definitions apply for N_B^{out} and N_B^{in}. The corresponding molar masses are noted W_A^{out}, W_A^{in}, W_B^{out}, and W_B^{in}.

Mass-Average Degree of Polymerization $\overline{X_w}$. $\overline{X_w}$ is the expected number $E(N)$ (average number) of monomer units in a molecule chosen by picking a monomer unit randomly in the polymer. The number N_i of monomer units in a molecule picked at random by a *i*-type monomer unit is

$$N_i = 1 + f_{A,i}N_A^{out} + f_{B,i}N_B^{out} \tag{1}$$

Applying the addition law for expectations of sums of random variables:

$$E(N) = \overline{X_w} = \sum_{i=1}^{i=k}\alpha_i E(N_i) = 1 + \sum_{i=1}^{i=k}\alpha_i f_{A,i}E(N_A^{out}) + \sum_{i=1}^{i=k}\alpha_i f_{B,i}E(N_B^{out}) \tag{2}$$

where α_i is the number-fraction of *i*-type monomer units in the polymer. Since the number and nature of monomer units do not change during polycondensations or polyadditions, $\alpha_i = \alpha_i^0$, number-fraction of *i*-type monomer molecules in initial monomer mixture. Therefore, eq 2 can be written:

$$\overline{X_w} = 1 + \overline{f_{n,A}^0}E(N_A^{out}) + \overline{f_{n,B}^0}E(N_B^{out}) \tag{3}$$

where $\overline{f_{n,A}^0}$ and $\overline{f_{n,B}^0}$ are the initial number-average A-group and B-group functionalities, i.e., the ratio of the number of A-groups and B-groups to the number of molecules in starting monomer mixture:

$$\overline{f_{n,A}^0} = \sum_{i=1}^{i=k}\alpha_i^0 f_{A,i} = \sum_{i=1}^{i=k} f_{A,i}\frac{n_i}{\sum_{i=1}^{i=k} n_i} \tag{4}$$

$$\overline{f_{n,B}^0} = \sum_{i=1}^{i=k}\alpha_i^0 f_{B,i} = \sum_{i=1}^{i=k} f_{B,i}\frac{n_i}{\sum_{i=1}^{i=k} n_i} \tag{5}$$

These number-average functionalities are known from starting medium composition. The calculation of $\overline{X_w}$ from eq 3, therefore, only requires $E(N_A^{out})$ and $E(N_B^{out})$.

Mass-Average Molar Mass (Weight-Average Molecular Weight) $\overline{M_w}$. $\overline{M_w}$ is the expected molar mass of a molecule chosen by randomly picking a mass unit in the polymer, i.e., by randomly picking a monomer unit by mass. Using a similar treatment as above, but with masses W_A^{out}, W_A^{in}, W_B^{out}, and W_B^{in}:

$$\overline{M_w} = \sum_{i=1}^{i=k}\omega_i E(W_i) = \sum_{i=1}^{i=k}\omega_i (M_i + f_{A,i}E(W_A^{out}) + f_{B,i}E(W_B^{out})) \tag{6}$$

where ω_i is the mass fraction of *i*-type monomer units in the polymer. Introducing mass-average functionalities

$$\overline{f_{w,A}} = \sum_{i=1}^{i=k}\omega_i f_{A,i} \tag{7}$$

$$\overline{f_{w,B}} = \sum_{i=1}^{i=k}\omega_i f_{B,i} \tag{8}$$

Equations 6−8 lead to

$$\overline{M_w} = \sum_{i=1}^{i=k}\omega_i M_i + \overline{f_{w,A}}E(W_A^{out}) + \overline{f_{w,B}}E(W_B^{out}) \tag{9}$$

When no reaction byproduct is eliminated, ω_i does not change during the reaction. Thus, for polyadditions

$$\overline{M_w} = \overline{M_w^0} + \overline{f_{w,A}^0}E(W_A^{out}) + \overline{f_{w,B}^0}E(W_B^{out}) \tag{10}$$

where $\overline{M_w^0}$ is the mass-average molar mass of initial monomer mixture, ω_i^0 the mass-fraction of *i*-type monomer in initial medium and $\overline{f_{\mathrm{w,A}}^{0}}$ and $\overline{f_{\mathrm{w,B}}^{0}}$ the initial mass-average A-group and B-group functionalities:

$$\overline{f_{\mathrm{w,A}}^{0}} = \sum_{i=1}^{i=k} \omega_i^0 f_{\mathrm{A},i} = \sum_{i=1}^{i=k} f_{\mathrm{A},i} \frac{n_i M_i}{\sum_{i=1}^{i=k} n_i M_i} \qquad (11)$$

$$\overline{f_{\mathrm{w,B}}^{0}} = \sum_{i=1}^{i=k} \omega_i^0 f_{\mathrm{B},i} = \sum_{i=1}^{i=k} f_{\mathrm{B},i} \frac{n_i M_i}{\sum_{i=1}^{i=k} n_i M_i} \qquad (12)$$

In the case of polycondensation reactions, ω_i slightly changes with conversion due to the elimination of the condensation byproduct and eq 10 cannot be applied. The treatment of this case is discussed in Appendix A.

Number-Average Degree of Polymerization $\overline{X_{\mathbf{n}}}$. Using the initial number-average functionalities defined above, $\overline{X_{\mathrm{n}}}$ can always be calculated by eq 13:

$$\overline{X_{\mathrm{n}}} = \frac{1}{1 - p_{\mathrm{A}}\overline{f_{\mathrm{n,A}}^{0}}} = \frac{1}{1 - p_{\mathrm{B}}\overline{f_{\mathrm{n,B}}^{0}}} \qquad (13)$$

The polydispersity index can, in turn, be derived from eqs 3 and 13.

Number-Average Molar Mass $\overline{M_{\mathbf{n}}}$. In polycondensation reactions, a byproduct E of molar mass M_{E} is eliminated from reaction medium and must be taken into account in the calculation of average molar masses. Since the number-average molar mass is the ratio of polymer mass to the number of molecules, the derivation of eq 14 is immediate:[41]

$$\overline{M_{\mathrm{n}}} = \frac{\sum_{i=1}^{i=k} M_i n_i - M_{\mathrm{E}} p_{\mathrm{A}} \sum_{i=1}^{i=k} f_{\mathrm{A},i} n_i}{\sum_{i=1}^{i=k} n_i - p_{\mathrm{A}} \sum_{i=1}^{i=k} f_{\mathrm{A},i} n_i} = \overline{X_{\mathrm{n}}}(\overline{M_{\mathrm{n}}^{0}} - M_{\mathrm{E}}) + M_{\mathrm{E}} \qquad (14)$$

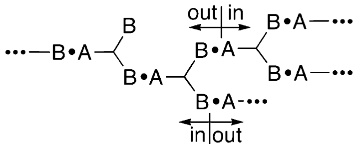
where $\overline{M_{\mathrm{n}}^{0}}$ is the number-average molar mass of starting monomer mixture. For polyaddition reactions, $M_{\mathrm{E}} = 0$ and eq 14 becomes

$$\overline{M_{\mathrm{n}}} = \overline{X_{\mathrm{n}}}\,\overline{M_{\mathrm{n}}^{0}} \qquad (15)$$

Thus, explicit expressions of $\overline{X_{\mathrm{n}}}$ and $\overline{M_{\mathrm{n}}}$ (eqs 13 and 14) can always be obtained. To obtain explicit expressions of $\overline{X_{\mathrm{w}}}$ and $\overline{M_{\mathrm{w}}}$ from eqs 3 and 10, it is necessary to determine $E(N_{\mathrm{A}}^{\mathrm{out}})$, $E(N_{\mathrm{B}}^{\mathrm{out}})$, $E(W_{\mathrm{A}}^{\mathrm{out}})$, and $E(W_{\mathrm{B}}^{\mathrm{out}})$. This can be done by examining the recursive statistical structure of polymer branches emanating from random A- and B-groups. The resulting expressions will hold for any type of monomer mixture and for any type of resulting polyaddition polymer structure or architecture, including linear, branched, and hyperbranched ones. Before examining the most general case and in order to illustrate the method, we will first consider a very simple case: AB_f monomer polymerization.

2. $\mathbf{AB}_f$ Monomer Polymerization. In this case, the derivation of $\overline{X_{\mathrm{w}}}$ by the "in−out" recursive approach is straightforward (Scheme 3).

Scheme 3. $\mathbf{AB_2}$ Hyperbranched Polymer



Only one type of monomer unit is present in the polymer. Since A reacts only with B and vice versa, the random variables $N_{\mathrm{A}}^{\mathrm{out}}$, $N_{\mathrm{B}}^{\mathrm{out}}$, $N_{\mathrm{A}}^{\mathrm{in}}$, and $N_{\mathrm{B}}^{\mathrm{in}}$ satisfy the following relationships:

$$N_{\mathrm{A}}^{\mathrm{out}} = \left\{ \begin{matrix} N_{\mathrm{B}}^{\mathrm{in}} & \text{if A has reacted (probability } p_{\mathrm{A}}) \\ 0 & \text{if A has not reacted (probability } 1 - p_{\mathrm{A}}) \end{matrix} \right\} \qquad (16)$$

$$N_{\mathrm{B}}^{\mathrm{in}} = 1 + (f - 1)N_{\mathrm{B}}^{\mathrm{out}} + N_{\mathrm{A}}^{\mathrm{out}} \qquad (17)$$

$$N_{\mathrm{B}}^{\mathrm{out}} = \left\{ \begin{matrix} N_{\mathrm{A}}^{\mathrm{in}} & \text{if B has reacted (probability } p_{\mathrm{B}}) \\ 0 & \text{if B has not reacted (probability 1 - } p_{\mathrm{B}}) \end{matrix} \right\} \qquad (18)$$

$$N_{\mathrm{A}}^{\mathrm{in}} = 1 + f\,N_{\mathrm{B}}^{\mathrm{out}} \qquad (19)$$

The application of the theorem of total probabilities for expectations to eqs 16 and 18 and of the theorem of the addition law for expectations of sums of random variables to eqs 17 and 19 lead to

$$E(N_{\mathrm{A}}^{\mathrm{out}}) = p_{\mathrm{A}}E(N_{\mathrm{B}}^{\mathrm{in}}) + 0(1 - p_{\mathrm{A}}) = p_{\mathrm{A}}E(N_{\mathrm{B}}^{\mathrm{in}}) \qquad (20)$$

$$E(N_{\mathrm{B}}^{\mathrm{in}}) = 1 + (f - 1)E(N_{\mathrm{B}}^{\mathrm{out}}) + E(N_{\mathrm{A}}^{\mathrm{out}}) \qquad (21)$$

$$E(N_{\mathrm{B}}^{\mathrm{out}}) = p_{\mathrm{B}}E(N_{\mathrm{A}}^{\mathrm{in}}) \qquad (22)$$

$$E(N_{\mathrm{A}}^{\mathrm{in}}) = 1 + fE(N_{\mathrm{B}}^{\mathrm{out}}) \qquad (23)$$

The solutions of the set of eqs 20−23 are

$$E(N_{\mathrm{B}}^{\mathrm{out}}) = \frac{p_{\mathrm{B}}}{1 - fp_{\mathrm{B}}} \qquad (24)$$

$$E(N_{\mathrm{A}}^{\mathrm{out}}) = \frac{p_{\mathrm{A}}(1 - p_{\mathrm{B}})}{(1 - p_{\mathrm{A}})(1 - fp_{\mathrm{B}})} \qquad (25)$$

Substituting eqs 24 and 25 into eq 3 with $\overline{f_{\mathrm{n,A}}^{0}} = 1$ and $\overline{f_{\mathrm{n,B}}^{0}} = f$ gives

$$\overline{X_{\mathrm{w}}} = 1 + \frac{p_{\mathrm{A}}(1 - p_{\mathrm{B}})}{(1 - p_{\mathrm{A}})(1 - fp_{\mathrm{B}})} + f\frac{p_{\mathrm{B}}}{1 - fp_{\mathrm{B}}} \qquad (26)$$

Since $p_{\mathrm{A}} = fp_{\mathrm{B}}$:

$$\overline{X_{\mathrm{w}}} = \frac{1 - \frac{{p_{\mathrm{A}}}^2}{f}}{(1 - p_{\mathrm{A}})^2} \qquad (27)$$

and

$$\mathrm{PDI} = \frac{\overline{X_{\mathrm{w}}}}{\overline{X_{\mathrm{n}}}} = \frac{1 - \frac{{p_{\mathrm{A}}}^2}{f}}{1 - p_{\mathrm{A}}} \qquad (28)$$

The result found by Flory[1] is obtained in a quite simple way.

$\overline{M_w}$ can be obtained by a similar treatment from expected masses instead of expected numbers of monomer units. However, since there is only one type of monomer unit (AB_f, molar mass M_0), it is obviously given by eq 29 for polyaddition reactions:

$$\overline{M_w} = M_0 \overline{X_w} \tag{29}$$

The case of polycondensation reactions is more complex, since a condensate E (molar mass M_E) is eliminated from reaction medium. The mass of a given monomer unit depends on the number of reacted A-groups and B-groups present on that monomer unit. If (j_A, j_B) denotes a monomer unit with j_A and j_B reacted A- and B-groups, ω_{j_A,j_B}, the mass fraction of such units, and W_{j_A,j_B}, the mass of a molecule to which a random (j_A, j_B) belongs, eq 6 becomes

$$\overline{M_w} = \sum_{j_A=0}^{j_A=1} \sum_{j_B=0}^{j_B=f} \omega_{j_A,j_B} E(W_{j_A,j_B}) \tag{30}$$

where $E(W_{j_A,j_B})$ is the expected mass of a molecule picked randomly by a (j_A, j_B) unit:

$$E(W_{j_A,j_B}) = M_0 + j_A E(W_{A,r}^{out}) + j_B E(W_{B,r}^{out}) \tag{31}$$

In eq 31, $E(W_{A,r}^{out})$ and $E(W_{B,r}^{out})$ are the expected masses seen by *reacted* A- and B-groups looking “out” from their monomer unit. If the loss of condensate is taken into account in the “out” expectations:

$$E(W_{A,r}^{out}) = E(W_B^{in}) - M_E \tag{32}$$

$$E(W_{B,r}^{out}) = E(W_A^{in}) - M_E \tag{33}$$

Hence, from eq 31:

$$E(W_{j_A j_B}) = M_0 + j_A(E(W_B^{in}) - M_E) + j_B(E(W_A^{in}) - M_E) \tag{34}$$

The set of eqs 20−23 can be transposed to mass expectations, taking into account the loss of E:

$$E(W_A^{out}) = p_A E(W_{B,r}^{out}) = p_A(E(W_B^{in}) - M_E) \tag{35}$$

$$E(W_B^{in}) = M_0 + (f-1)E(W_B^{out}) + E(W_A^{out}) \tag{36}$$

$$E(W_B^{out}) = p_B E(W_{A,r}^{out}) = p_B(E(W_A^{in}) - M_E) \tag{37}$$

$$E(W_A^{in}) = M_0 + f\,E(W_B^{out}) \tag{38}$$

Solving eqs 35−38 leads to

$$E(W_A^{in}) = \frac{M_0 - p_A M_E}{1 - p_A} \tag{39}$$

$$E(W_B^{in}) = \frac{M_0 - p_B(M_0 - M_E) - p_A M_E(2 - p_A)}{(1-p_A)^2} \tag{40}$$

The substitution of eqs 39 and 40 in eq 34 yields $E(W_{j_A,j_B})$:

$$E(W_{j_A,j_B}) = M_0 + j_A(M_0 - M_E)\frac{1-p_B}{(1-p_A)^2} + j_B(M_0 - M_E)\frac{1}{1-p_A} \tag{41}$$

We have now to calculate the mass fraction ω_{j_A,j_B} of (j_A, j_B) units. If all A-groups and all B-groups are equally reactive (i.e., if there is no substitution effect), the number of reacted A- and B-groups of a random monomer unit are independent binomial random variables. Therefore, the number n_{j_A,j_B} of (j_A, j_B) units is

$$n_{j_A,j_B} = n_0(p_A^{\,j_A}(1-p_A)^{1-j_A})\left(\frac{f!}{j_B!(f-j_B)!}p_B^{\,j_B}(1-p_B)^{1-j_B}\right) \tag{42}$$

where n_0 is the total number of AB_f units. Supposing that a reacted A-group contributes M_{EA} to the condensate and a B-group M_{EB} (with $M_{EA} + M_{EB} = M_E$),[32] the mass of a (j_A, j_B) unit is $M_0 - j_A M_{EA} - j_B M_{EB}$. Since polymer mass is obviously $n_0(M_0 - p_A M_E)$:

$$\omega_{j_A,j_B} = \frac{n_{j_A,j_B}(M_0 - j_A M_{EA} - j_B M_{EB})}{n_0(M_0 - p_A M_E)} \tag{43}$$

Therefore, the mass-average molar mass is given by

$$\overline{M_w} = \sum_{j_A=0}^{j_A=1}\sum_{j_B=0}^{j_B=f} \frac{n_{j_A,j_B}(M_0 - j_A M_{EA} - j_B M_{EB})}{n_0(M_0 - p_A M_E)}\left(M_0 + j_A(M_0 - M_E)\frac{1-p_B}{(1-p_A)^2} + j_B(M_0 - M_E)\frac{1}{1-p_A}\right) \tag{44}$$

After development and simplification, eq 44 yields

$$\overline{M_w} = (M_0 - M_E)\left(\frac{1}{1-p_A} + \frac{M_0 - M_E}{M_0 - p_A M_E}\,\frac{p_A - \frac{p_A^{\,2}}{f}}{(1-p_A)^2}\right) + M_E \tag{45}$$

As expected, since the number of reacted A-groups is always equal to the number of reacted B-groups, M_{EA} and M_{EB} vanish from the final relationship. Equation 45 is equivalent to eq 29 when $M_E = 0$ (polyaddition). It can be simplified into approximate eq 46 when p_A is close to 1:

$$\overline{M_w} \approx (M_0 - M_E)\overline{X_w} + M_E \tag{46}$$

It is worth mentioning that the relative error committed on $\overline{M_w}$ when using eq 46 instead of eq 45 is relatively low even at low conversions. For instance, the maximum error committed on poly(2,2′-bis(hydroxymethyl)propanoic acid) $\overline{M_w}$ is 3.05% for $p_A = 0.527$. For AB_f polycondensations, the maximum error is $32(M_E/M_0)$%, when $M_E/M_0 < 0.4$ and $f \leq 20$. This accuracy may be sufficient for practical purposes.

3. General Case. Mass-Average Molar Mass of Polyaddition Polymers. The “in−out” recursive method is now applied to apolymer obtained by the polyaddition (no byproduct elimination) of k different types of monomers, each having a number of A-groups and/or B-groups (see Scheme 2). A random A-group picked in the polymer may have reacted with a B-group present on a monomer unit of any of the different types present in starting reaction medium, or may still be unreacted. Hence:

$$W_{\mathrm{A}}^{\mathrm{out}} = \begin{cases} W_{\mathrm{B},1}^{\mathrm{in}} & \text{if A has reacted with a B-group} \in \\ & \quad \text{monomer unit of type 1} \\ & \quad \vdots \\ W_{\mathrm{B},i}^{\mathrm{in}} & \text{if A has reacted with a B-group} \in \\ & \quad \text{monomer unit of type } i \\ & \quad \vdots \\ W_{\mathrm{B},k}^{\mathrm{in}} & \text{if A has reacted with a B-group} \in \\ & \quad \text{monomer unit of type } k \\ 0 & \text{if A has not reacted} \end{cases} \tag{47}$$

with

$$W_{\mathrm{B},i}^{\mathrm{in}} = M_i + f_{\mathrm{A},i} W_{\mathrm{A}}^{\mathrm{out}} + (f_{\mathrm{B},i} - 1) W_{\mathrm{B}}^{\mathrm{out}} \tag{48}$$

The probability that a random B-group belongs to a i-type monomer unit is

$$P(\mathrm{B} \in i) = \frac{f_{\mathrm{B},i} n_i}{\sum_{i=1}^{k} f_{\mathrm{B},i} n_i} \tag{49}$$

and the probability $P(\mathrm{A{\cdot}B} \in i)$ that a random A-group has reacted with a B-group present on a i-type monomer unit is

$$P(\mathrm{A{\bullet}B} \in i) = p_{\mathrm{A}}\, P(\mathrm{B} \in i) = p_{\mathrm{A}} \frac{f_{\mathrm{B},i} n_i}{\sum_{i=1}^{k} f_{\mathrm{B},i} n_i} \tag{50}$$

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 results in

$$E(W_{\mathrm{A}}^{\mathrm{out}}) = \sum_{i=1}^{i=k} E(W_{\mathrm{B},i}^{\mathrm{in}}) p_{\mathrm{A}} \frac{f_{\mathrm{B},i} n_i}{\sum_{i=1}^{i=k} f_{\mathrm{B},i} n_i} \tag{51}$$

$$E(W_{\mathrm{B},i}^{\mathrm{in}}) = M_i + f_{\mathrm{A},i} E(W_{\mathrm{A}}^{\mathrm{out}}) + (f_{\mathrm{B},i} - 1) E(W_{\mathrm{B}}^{\mathrm{out}}) \tag{52}$$

Symmetrical relationships hold for $E(W_{\mathrm{B}}^{\mathrm{out}})$ and $E(W_{\mathrm{A},i}^{\mathrm{in}})$:

$$E(W_{\mathrm{B}}^{\mathrm{out}}) = \sum_{i=1}^{i=k} E(W_{\mathrm{A},i}^{\mathrm{in}}) p_{\mathrm{B}} \frac{f_{\mathrm{A},i} n_i}{\sum_{i=1}^{i=k} f_{\mathrm{A},i} n_i} \tag{53}$$

$$E(W_{\mathrm{A},i}^{\mathrm{in}}) = M_i + (f_{\mathrm{A},i} - 1) E(W_{\mathrm{A}}^{\mathrm{out}}) + (f_{\mathrm{B},i}) E(W_{\mathrm{B}}^{\mathrm{out}}) \tag{54}$$

The substitution of eqs 52 into 51 leads to

$$E(W_{\mathrm{A}}^{\mathrm{out}}) = p_{\mathrm{A}} \sum_{i=1}^{i=k} M_i \frac{f_{\mathrm{B},i} n_i}{\sum_{i=1}^{i=k} f_{\mathrm{B},i} n_i} + p_{\mathrm{A}} E(W_{\mathrm{A}}^{\mathrm{out}}) \sum_{i=1}^{i=k} f_{\mathrm{A},i} \frac{f_{\mathrm{B},i} n_i}{\sum_{i=1}^{i=k} f_{\mathrm{B},i} n_i} + p_{\mathrm{A}} E(W_{\mathrm{B}}^{\mathrm{out}}) \sum_{i=1}^{i=k} (f_{\mathrm{B},i} - 1) \frac{f_{\mathrm{B},i} n_i}{\sum_{i=1}^{i=k} f_{\mathrm{B},i} n_i} \tag{55}$$

At this point, it is convenient to introduce new average quantities relative to the initial monomer mixture.

- The initial B-average molar mass $\overline{M_b^0}$, i.e., the expectation of the molar mass of a monomer randomly picked by a B-group in initial medium:

$$\overline{M_{\mathrm{b}}^{0}} = \sum_{i=1}^{i=k} M_i \frac{f_{\mathrm{B},i} n_i}{\sum_{i=1}^{i=k} f_{\mathrm{B},i} n_i} \tag{56}$$

- The initial B-average B-group functionality $\overline{f_{\mathrm{b,B}}^{0}}$, i.e., the expectation of the number of B-groups attached to a monomer randomly picked by a B-group in initial medium (the "effective" functionality g_{e} of Stockmayer):

$$\overline{f_{\mathrm{b,B}}^{0}} = \sum_{i=1}^{i=k} f_{\mathrm{B},i} \frac{f_{\mathrm{B},i} n_i}{\sum_{i=1}^{i=k} f_{\mathrm{B},i} n_i} \tag{57}$$

- The initial B-average A-group functionality $\overline{f_{\mathrm{b,A}}^{0}}$, i.e., the expectation of the number of A-groups attached to a monomer randomly picked by a B-group in initial medium:

$$\overline{f_{\mathrm{b,A}}^{0}} = \sum_{i=1}^{i=k} f_{\mathrm{A},i} \frac{f_{\mathrm{B},i} n_i}{\sum_{i=1}^{i=k} f_{\mathrm{B},i} n_i} \tag{58}$$

Equation 55 becomes quite simple:

$$E(W_{\mathrm{A}}^{\mathrm{out}}) = p_{\mathrm{A}} \overline{M_{\mathrm{b}}^{0}} + p_{\mathrm{A}} \overline{f_{\mathrm{b,A}}^{0}} E(W_{\mathrm{A}}^{\mathrm{out}}) + p_{\mathrm{A}} (\overline{f_{\mathrm{b,B}}^{0}} - 1) E(W_{\mathrm{B}}^{\mathrm{out}}) \tag{59}$$

With symmetrical definitions of $\overline{M_{\mathrm{a}}^{0}}$, $\overline{f_{\mathrm{a,B}}^{0}}$ and $\overline{f_{\mathrm{a,A}}^{0}}$, eqs 53 and 54 give

$$E(W_{\mathrm{B}}^{\mathrm{out}}) = p_{\mathrm{B}} \overline{M_{\mathrm{a}}^{0}} + p_{\mathrm{B}} (\overline{f_{\mathrm{a,A}}^{0}} - 1) E(W_{\mathrm{A}}^{\mathrm{out}}) + p_{\mathrm{B}} \overline{f_{\mathrm{a,B}}^{0}} E(W_{\mathrm{B}}^{\mathrm{out}}) \tag{60}$$

Solving eqs 59 and 60 for $E(W_{\mathrm{A}}^{\mathrm{out}})$ and $E(W_{\mathrm{B}}^{\mathrm{out}})$ yields:

$$E(W_{\mathrm{A}}^{\mathrm{out}}) = \frac{p_{\mathrm{A}}\overline{M_{\mathrm{b}}^{0}}(1 - p_{\mathrm{B}}\overline{f_{\mathrm{a,B}}^{0}}) + p_{\mathrm{A}}p_{\mathrm{B}}\overline{M_{\mathrm{a}}^{0}}(\overline{f_{\mathrm{b,B}}^{0}} - 1)}{(1 - p_{\mathrm{A}}\overline{f_{\mathrm{b,A}}^{0}})(1 - p_{\mathrm{B}}\overline{f_{\mathrm{a,B}}^{0}}) - p_{\mathrm{A}}p_{\mathrm{B}}(\overline{f_{\mathrm{a,A}}^{0}} - 1)(\overline{f_{\mathrm{b,B}}^{0}} - 1)} \quad (61)$$

$$E(W_{\mathrm{B}}^{\mathrm{out}}) = \frac{p_{\mathrm{B}}\overline{M_{\mathrm{a}}^{0}}(1 - p_{\mathrm{A}}\overline{f_{\mathrm{b,A}}^{0}}) + p_{\mathrm{A}}p_{\mathrm{B}}\overline{M_{\mathrm{b}}^{0}}(\overline{f_{\mathrm{a,A}}^{0}} - 1)}{(1 - p_{\mathrm{A}}\overline{f_{\mathrm{b,A}}^{0}})(1 - p_{\mathrm{B}}\overline{f_{\mathrm{a,B}}^{0}}) - p_{\mathrm{A}}p_{\mathrm{B}}(\overline{f_{\mathrm{a,A}}^{0}} - 1)(\overline{f_{\mathrm{b,B}}^{0}} - 1)} \quad (62)$$

Substituting these equations into eq 10 gives the general relationship between the mass-average molar mass of polyaddition polymers, the composition of starting reaction medium (superscript "0") and conversions p_{A} and p_{B}:

$$\overline{M_{\mathrm{w}}} = \overline{M_{\mathrm{w}}^{0}} + \overline{f_{\mathrm{w,A}}^{0}}\frac{p_{\mathrm{A}}\overline{M_{\mathrm{b}}^{0}}(1 - p_{\mathrm{B}}\overline{f_{\mathrm{a,B}}^{0}}) + p_{\mathrm{A}}p_{\mathrm{B}}\overline{M_{\mathrm{a}}^{0}}(\overline{f_{\mathrm{b,B}}^{0}} - 1)}{(1 - p_{\mathrm{A}}\overline{f_{\mathrm{b,A}}^{0}})(1 - p_{\mathrm{B}}\overline{f_{\mathrm{a,B}}^{0}}) - p_{\mathrm{A}}p_{\mathrm{B}}(\overline{f_{\mathrm{a,A}}^{0}} - 1)(\overline{f_{\mathrm{b,B}}^{0}} - 1)} + \overline{f_{\mathrm{w,B}}^{0}}\frac{p_{\mathrm{B}}\overline{M_{\mathrm{a}}^{0}}(1 - p_{\mathrm{A}}\overline{f_{\mathrm{b,A}}^{0}}) + p_{\mathrm{A}}p_{\mathrm{B}}\overline{M_{\mathrm{b}}^{0}}(\overline{f_{\mathrm{a,A}}^{0}} - 1)}{(1 - p_{\mathrm{A}}\overline{f_{\mathrm{b,A}}^{0}})(1 - p_{\mathrm{B}}\overline{f_{\mathrm{a,B}}^{0}}) - p_{\mathrm{A}}p_{\mathrm{B}}(\overline{f_{\mathrm{a,A}}^{0}} - 1)(\overline{f_{\mathrm{b,B}}^{0}} - 1)} \quad (63)$$

Equation 63 may be applied to any type of monomer mixture and to any type of resulting polyaddition polymer structure or architecture, including linear, branched and hyperbranched ones. It reduces to Stockmayer's general equation[5] when the reaction involves monomers bearing only A-groups and monomers bearing only B-groups ($\overline{f_{\mathrm{b,A}}^{0}} = \overline{f_{\mathrm{a,B}}^{0}} = 0$). This equation can also be applied to mixtures of polydisperse "monomers", such as reactive oligomers. In this case, summations involving $M_i n_i$ and $M_i^2 n_i$ must be replaced by summations involving $\overline{M_{\mathrm{n},i}}n_i$ and $\overline{M_{\mathrm{n},i}}\,\overline{M_{\mathrm{w},i}}n_i$, respectively, where $\overline{M_{\mathrm{n},i}}$ and $\overline{M_{\mathrm{w},i}}$ are the number- and mass-average molar masses of the i-type "monomer".[42] Summations involving only functionalities remain obviously unchanged.

Mass-Average Molar Mass of Polycondensation Polymers. The derivation of $\overline{M_{\mathrm{w}}}$ to include the elimination of a condensation byproduct is similar to that used above for the polycondensation of AB$_f$ polymers and is discussed in detail in Appendix A. The final expression is complex and calculations are preferably carried out numerically. However, approximate values calculated from simplified eq 64 become close to the exact ones as soon as oligomers are formed.

$$\overline{M_{\mathrm{w}}} \approx \overline{M_{\mathrm{w}}^{0}} + \overline{f_{\mathrm{w,A}}^{0}}\frac{p_{\mathrm{A}}(\overline{M_{\mathrm{b}}^{0}} - M_{\mathrm{E}})(1 - p_{\mathrm{B}}\overline{f_{\mathrm{a,B}}^{0}}) + p_{\mathrm{A}}p_{\mathrm{B}}(\overline{M_{\mathrm{a}}^{0}} - M_{\mathrm{E}})(\overline{f_{\mathrm{b,B}}^{0}} - 1)}{(1 - p_{\mathrm{A}}\overline{f_{\mathrm{b,A}}^{0}})(1 - p_{\mathrm{B}}\overline{f_{\mathrm{a,B}}^{0}}) - p_{\mathrm{A}}p_{\mathrm{B}}(\overline{f_{\mathrm{a,A}}^{0}} - 1)(\overline{f_{\mathrm{b,B}}^{0}} - 1)} + \overline{f_{\mathrm{w,B}}^{0}}\frac{p_{\mathrm{B}}(\overline{M_{\mathrm{a}}^{0}} - M_{\mathrm{E}})(1 - p_{\mathrm{A}}\overline{f_{\mathrm{b,A}}^{0}}) + p_{\mathrm{A}}p_{\mathrm{B}}(\overline{M_{\mathrm{b}}^{0}} - M_{\mathrm{E}})(\overline{f_{\mathrm{a,A}}^{0}} - 1)}{(1 - p_{\mathrm{A}}\overline{f_{\mathrm{b,A}}^{0}})(1 - p_{\mathrm{B}}\overline{f_{\mathrm{a,B}}^{0}}) - p_{\mathrm{A}}p_{\mathrm{B}}(\overline{f_{\mathrm{a,A}}^{0}} - 1)(\overline{f_{\mathrm{b,B}}^{0}} - 1)} \quad (64)$$

This equation reduces to approximate eq 46 when applied to AB$_f$ polymerizations.

Figure 1 illustrates the relative error committed on $\overline{M_{\mathrm{w}}}$ for some model polyesterifications when eq 64 is used instead of the exact expression. The relative error is below 1%, 2%, and 3% for the linear, hyperbranched, and network polyesterifications, respectively, when $\overline{M_{\mathrm{w}}} > 2000$. This accuracy may be sufficient for the evaluation of $\overline{M_{\mathrm{w}}}$ in practical cases.

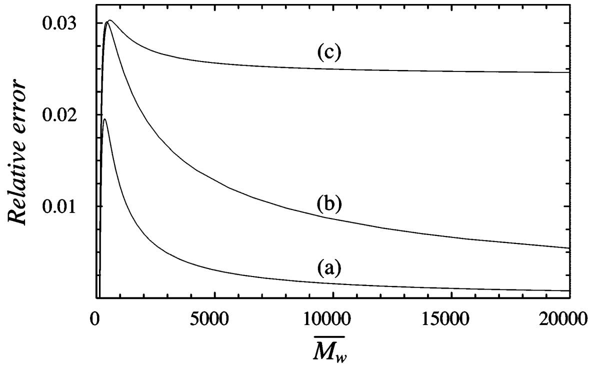


Figure 1. Relative error ($\overline{M_{\mathrm{w}}}$ (eq A5) − $\overline{M_{\mathrm{w}}}$ (eq 64))/$\overline{M_{\mathrm{w}}}$ (eq A5) committed on $\overline{M_{\mathrm{w}}}$ when using eq 64 instead of the numerical resolution of eq A5. Polycondensations of (a) adipic acid, ethane-1,2-diol, and 10-hydroxydecanoic acid (1:1:1 mol); (b) 2,2′-bis(hydroxymethyl)propanoic acid (1 mol) and tetra(hydroxymethyl)methane (0.02 mol); and (c) glycerol (2 mol) and phthalic acid (3 mol).

Mass-Average Degree of polymerization, $\overline{X_{\mathrm{w}}}$. The relationship between $\overline{X_{\mathrm{w}}}$, conversion, and the composition of initial medium can be obtained by following a treatment similar to that used for $\overline{M_{\mathrm{w}}}$, starting from $E(N)$ expectations instead of $E(W)$ expectations. More simply, it is possible to set the molar masses of starting monomers to 1 in eq 63:

$$\overline{X_{\mathrm{w}}} = 1 + \overline{f_{\mathrm{n,A}}^{0}}\frac{p_{\mathrm{A}}(1 - p_{\mathrm{B}}\overline{f_{\mathrm{a,B}}^{0}}) + p_{\mathrm{A}}p_{\mathrm{B}}(\overline{f_{\mathrm{b,B}}^{0}} - 1)}{(1 - p_{\mathrm{A}}\overline{f_{\mathrm{b,A}}^{0}})(1 - p_{\mathrm{B}}\overline{f_{\mathrm{a,B}}^{0}}) - p_{\mathrm{A}}p_{\mathrm{B}}(\overline{f_{\mathrm{a,A}}^{0}} - 1)(\overline{f_{\mathrm{b,B}}^{0}} - 1)} + \overline{f_{\mathrm{n,B}}^{0}}\frac{p_{\mathrm{B}}(1 - p_{\mathrm{A}}\overline{f_{\mathrm{b,A}}^{0}}) + p_{\mathrm{A}}p_{\mathrm{B}}(\overline{f_{\mathrm{a,A}}^{0}} - 1)}{(1 - p_{\mathrm{A}}\overline{f_{\mathrm{b,A}}^{0}})(1 - p_{\mathrm{B}}\overline{f_{\mathrm{a,B}}^{0}}) - p_{\mathrm{A}}p_{\mathrm{B}}(\overline{f_{\mathrm{a,A}}^{0}} - 1)(\overline{f_{\mathrm{b,B}}^{0}} - 1)} \quad (65)$$

Equation 65 can obviously be applied to both polyadditions and polycondensations.

Polydispersity Index, PDI. The derivation of PDI from eqs 13 and 65 is straightforward:

$$\mathrm{PDI} = \frac{\overline{X_{\mathrm{w}}}}{\overline{X_{\mathrm{n}}}} = (1 - \overline{f_{\mathrm{n,A}}^{0}})\overline{\mathrm{DP}_{\mathrm{w}}} \quad (66)$$

Gel Point. The conversion at the gel point for network polymerizations is easy to derive from eqs 63 or 65, since $\overline{M_{\mathrm{w}}}$ or $\overline{X_{\mathrm{w}}} \rightarrow \infty$ when

$$(1 - p_{\mathrm{A}}\overline{f_{\mathrm{b,A}}^{0}})(1 - p_{\mathrm{B}}\overline{f_{\mathrm{a,B}}^{0}}) - p_{\mathrm{A}}p_{\mathrm{B}}(\overline{f_{\mathrm{a,A}}^{0}} - 1)(\overline{f_{\mathrm{b,B}}^{0}} - 1) = 0 \quad (67)$$

Introducing the initial stoichiometric ratio r

$$r = \frac{\sum_{i=1}^{k} f_{\mathrm{A},i}n_i}{\sum_{i=1}^{k} f_{\mathrm{B},i}n_i} \quad (68)$$

and remarking that

$$p_{\mathrm{A}}\overline{f_{\mathrm{b,A}}^{0}} = p_{\mathrm{B}}\overline{f_{\mathrm{a,B}}^{0}} \quad (69)$$

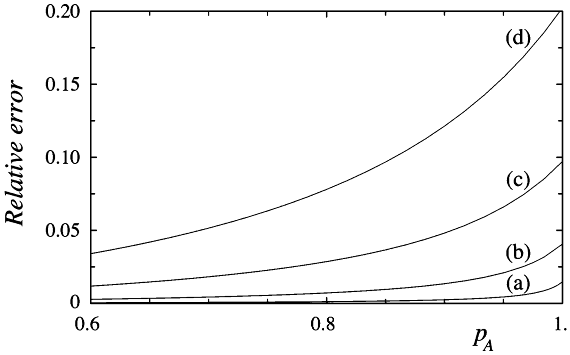


Figure 2. Relative error ($\overline{X_w}$ (eq 72) − $\overline{X_w}$ (eq 65))/$\overline{X_w}$ (eq 65) committed when applying AA+BB relationship (eq 72) instead of general equation (eq 65) to the polycondensation of AB (5 mol) and BB (1 mol) with (a) 1.8 mol, (b) 1.5 mol, (c) 1 mol, and (d) 0.4 mol AA.

the solution of eq 67 in the [0,1] interval gives the conversion at the gel point:

$$(p_A)_{gel} = \frac{\sqrt{r(\overline{f^0_{a,A}} - 1)(\overline{f^0_{b,B}} - 1)} - \overline{f^0_{b,A}}}{r(\overline{f^0_{a,A}} - 1)(\overline{f^0_{b,B}} - 1) - (\overline{f^0_{b,A}})^2} \qquad (70)$$

Equation 70 reduces to Stockmayer's gel point equation[4] for reactions involving only A_f-type and B_g-type monomers ($\overline{f^0_{a,B}} = \overline{f^0_{b,A}} = 0$). In the case of hyperbranched polymers, i.e., for the polymerization of mixtures of AB_f-type and B_g-type monomers, no cross-linking obviously takes place. Since $\overline{f^0_{a,A}} = 1$ and $\overline{f^0_{b,A}} \leq 1$, this would lead to $(p_A)_{gel} \geq 1$. It is also worth remarking that the conversion at the gel point according to the theory of Carothers ($\overline{X_n} \to \infty$) can always be calculated from eq 13 by

$$(p_A)_{gel,Carothers} = \frac{1}{\overline{f^0_{n,A}}} \qquad (71)$$

4. Application to Some Simple Cases. AA + BB + AB Polymerization. In the case of stoichiometric balance of reactive groups (stoichiometric ratio $r = 1$), $\overline{X_w}$ is given by the well-known expression $(1 + p)/(1 - p)$ with $p = p_A = p_B$. However, in the case of stoichiometric imbalance, the AA + BB general formula[41] (eq 72) cannot be applied.

$$\overline{X_w} = \frac{1 + rp_A{}^2 + \dfrac{4r}{r+1}p_A}{1 - rp_A{}^2} \qquad (72)$$

Such reactions are widely used, e.g., in the preparation of reactive oligomers from hydroxyacids or amino acids. The differences between the values obtained from eqs 65 and 72 may be as high as 20% (Figure 2).

AB_f Polymerization. It is easy to check that eq 65 reduces to eq 27 when applied to AB_f polymerizations ($\overline{f^0_{n,A}} = 1$, $\overline{f^0_{n,B}} = f$, $\overline{f^0_{a,A}} = 1$, $\overline{f^0_{b,B}} = f$, $\overline{f^0_{a,B}} = f$, $\overline{f^0_{b,A}} = 1$, $p_A = fp_B$).

A_fB_g Polymerization. The values of average functionalities in this case are $\overline{f^0_{n,A}} = f$, $\overline{f^0_{n,B}} = g$, $\overline{f^0_{a,A}} = f$, $\overline{f^0_{b,B}} = g$, $\overline{f^0_{b,A}} = f$, $\overline{f^0_{a,B}} = g$, and $fp_A = gp_B$. Substitution into eq 65 results in

$$\overline{X_w} = \frac{1 - p_Ap_B}{1 - fp_A(1 - p_B) - gp_B(1 - p_A) - p_Ap_B} \qquad (73)$$

$$\overline{X_w} = \frac{g - fp_A{}^2}{g - 2fgp_A + p_A{}^2(f^2 + fg - f)} \qquad (74)$$

A formula identical to that obtained by Miller et al.[40] on the same system.

$AB_f + B_g$ Polymerization. This case in important in practice as most commercial hyperbranched polymers are synthesized by polymerizing AB_f monomers (e.g., 2,2′-bis(hydroxymethyl)-propanoic acid, AB_2) in the presence of a small amount of a multifunctional core molecule B_g (e.g., Pentaerythritol, B_4). Equation 65 immediately yields $\overline{X_w}$, from which the polydispersity index can be calculated. If starting monomer mixture consists of 1 mol of AB_f and x mol of B_g, the average functionalities are

$$\overline{f^0_{n,A}} = \frac{1}{1+x}; \quad \overline{f^0_{a,A}} = 1; \quad \overline{f^0_{b,A}} = \frac{f}{f+xg};$$
$$\overline{f^0_{n,B}} = \frac{f+xg}{1+x}; \quad \overline{f^0_{b,B}} = \frac{f^2+xg^2}{f+xg}; \quad \overline{f^0_{a,B}} = f$$

Substitution into eqs 13 and 65 leads to

$$\overline{X_n} = \frac{1+x}{1+x-p_A} \qquad (75)$$

$$\overline{X_w} = 1 + \frac{2p_A(f+gx)[f(1-p_A)+gx] + p_A{}^2[f(f-1)+gx(g-1)]}{(1+x)[f(1-p_A)+gx]^2} \qquad (76)$$

Both expressions are different from those previously derived by a kinetic approach for the same system by Yan and Zhou.[30] These authors have chosen not to include the B_g moieties in the count of monomer units and, therefore, the chain lengths they calculated are not degrees of polymerization in the strict sense. The numerical values slightly differ from those obtained through eqs 75 and 76. However, it must be underlined that their method allowed the calculation of the CLD for this system. This cannot be done by the recursive approach.

The variations of polydispersity index vs conversion for the reaction between AB_f-type monomers ($f = 1-8$) and a B_4-type core-molecule present a steep increase at high conversion when monomer functionality increases (Figure 3). A core functionality $g \geq 4$ is required to obtain a narrow CLD at high conversion

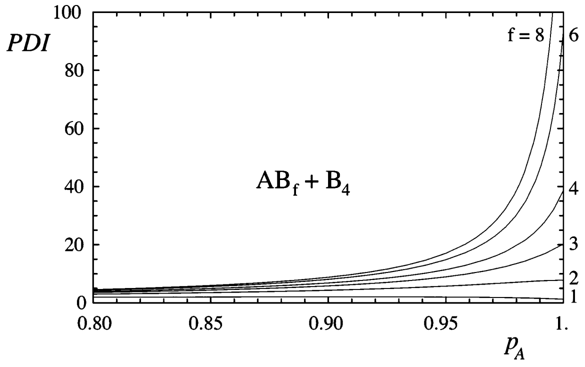


Figure 3. Variation of polydispersity index PDI vs conversion p_A during the polymerization of 1 mol AB_f with 0.02 mol B_4. $f = 1, 2, 3, 4, 6$, and 8.

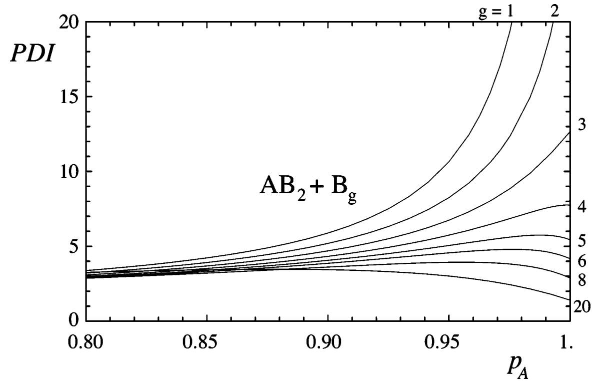


Figure 4. Variation of polydispersity index PDI vs conversion p_A during the polymerization of 1 mol AB_2 with 0.02 mol B_g. $g = 1, 2, 3, 4, 5, 6, 20$.

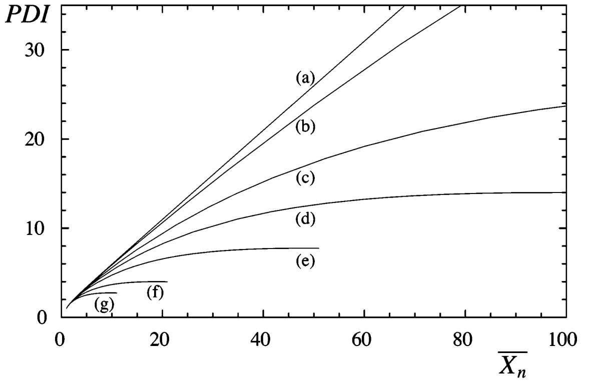


Figure 5. Variation of polydispersity index PDI vs $\overline{X_n}$ during the polymerization of 1 mol AB_2 with (a) 0, (b) 10^{-3}, (c) 5×10^{-3}, (d) 10^{-2}, (e) 2×10^{-2}, (f) 5×10^{-2}, and (g) 10^{-1} mol B_4.

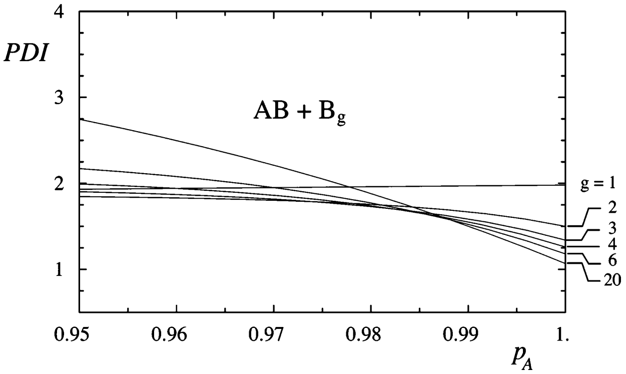


Figure 6. Variation of polydispersity index PDI vs conversion p_A during the polymerization of 1 mol AB with 0.02 mol B_g; $g = 1, 2, 3, 4, 6, 20$.

for the $AB_2 + B_g$ polymerization (Figure 4). More generally it can be shown that a B_{2f} core is required for AB_f monomers in order to limit CLD broadening. Figure 5 illustrates the influence of the core/monomer ratio on polydispersity index and $\overline{X_n}$ in $AB_2 + B_4$ polymerizations. Both dramatically decrease when core concentration increases.

As shown by Flory,[43] the PDI of the 4-branch molecule fraction of AB + B_g polymers is close to $1 + 1/g$, when the amount of B_g is small with respect to that of AB. Since at high conversion the amount of linear species becomes negligible, this property may be used in practice to narrow the CLD of AB-type linear condensation polymers. Figure 6 presents the application of eqs 75 and 76 to this case ($f = 1$) showing that the narrowing occurs only for $p_A > 0.98$.

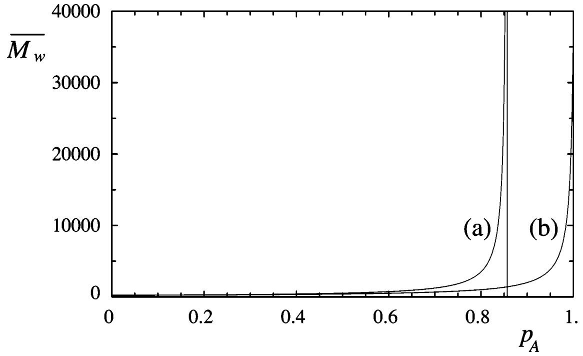


Figure 7. Variation of mass-average molar mass $\overline{M_w}$ versus conversion p_A during the polymerization of 2,2′-bis(hydroxymethyl)propanoic acid (1 mol), adipic acid (1 mol), lactic acid (1 mol), stearic acid (2 mol) and Pentaerythritol: (a) 0.5 mol (conversion at gel point: $p_A = 0.857$) (b) 0.2 mol, no gel point.

Complex Polymerizations. The application of eq 63 to complex monomer mixtures is straightforward. Figure 7 presents the variation of $\overline{M_w}$ for the reaction between 2,2′-bis(hydroxymethyl)propanoic acid (1 mol), adipic acid (1 mol), lactic acid (1 mol), stearic acid (2 mol), and Pentaerythritol (0.5 or 0.2 mol) ($AB_2 + AA + AB + A + B_4$ system). The resulting polymers may find applications in cosmetics. For a given stoichiometric composition, it is important to check that $(p_A)_{gel} > 1$, i.e., cross-linking does not take place during the synthesis. This is the case when 0.2 mol Pentaerythritol is reacted (Figure 7).

Conclusion

The "in−out" recursive probability approach of Macosko and Miller was applied to hyperbranched polycondensations and used to derive expressions of the theoretical mass-average degree of polymerization and mass-average molar mass of polymers obtained by reacting complex mixtures of monomers bearing reactive A-groups and/or B-groups. These expressions reduce to those obtained by Flory[1] and Stockmayer[4,5] by the combinatorial approach for reactions between monomers bearing reactive A-groups and monomers bearing reactive B-groups. These expressions were obtained under the simplifying assumptions of Flory and Stockmayer, which are not fully verified for highly branched or hyperbranched polymers, where substitution effects[44] or cyclizations[45−52] may take place to a large extent. However, the "theoretical" molar masses, degrees of polymerization, and conversion at the gel point that can be calculated from our relationships are of first importance for any hyperbranched or network polymerization study, when monomers bearing both A- and B-groups are involved. The application of this approach to some linear, hyperbranched and network polymerizations discussed in the last part of the article can obviously be extended to virtually any type of monomer mixtures. In the case of polycondensation reactions, the effect of the elimination of a condensation byproduct on average molar masses is examined in detail in Appendix A. The general relationship is complex and the calculations of exact molar masses are preferably carried out numerically. However, approximate $\overline{M_w}$ values can be calculated using a simplified explicit equation with accuracy sufficient for practical purposes.

Appendix A: Mass-Average Molar Mass of Polycondensation Polymers

The derivation of $\overline{M_w}$ in the case of general polycondensation reactions is similar to that described above for AB_f polycondensations. Since k different types of monomers are reacted, each monomer of type i bearing $f_{A,i}$ reactive A-groups and $f_{B,i}$ reactive B-groups, eqs 35−38 are changed to

$$E(W_A^{out}) = p_A\left(\sum_{i=1}^{i=k} E(W_{B,i}^{in})\ \frac{f_{B,i}n_i}{\sum_{i=1}^{i=k} f_{B,i}n_i} - M_E\right) \tag{A1}$$

$$E(W_{B,i}^{in}) = M_i + f_{A,i}E(W_A^{out}) + (f_{B,i} - 1)E(W_B^{out}) \tag{A2}$$

$$E(W_B^{out}) = p_B\left(\sum_{i=1}^{i=k} E(W_{A,i}^{in})\ \frac{f_{A,i}n_i}{\sum_{i=1}^{i=k} f_{A,i}n_i} - M_E\right) \tag{A3}$$

$$E(W_{A,i}^{in}) = M_i + f_{B,i}E(W_B^{out}) + (f_{A,i} - 1)E(W_A^{out}) \tag{A4}$$

If (i,j_A,j_B) denotes a i-type monomer unit with j_A and j_B reacted A- and B-groups, W_{i,j_A,j_B}, the molar mass of a molecule to which a random (i,j_A,j_B) unit belongs, and ω_{i,j_A,j_B}, the mass fraction of such units in the polymer, eq 30 becomes

$$\overline{M_w} = \sum_{i=1}^{i=k} \sum_{j_A=0}^{j_A=f_{A,i}} \sum_{j_A=0}^{j_B=f_{B,i}} \omega_{i,j_A,j_B} E(W_{i,j_A,j_B}) \tag{A5}$$

where $E(W_{i,j_A,j_B})$ is the expected molar mass of a molecule picked randomly by a (i,j_A,j_B) unit:

$$E(W_{i,j_A,j_B}) = M_i + j_A\left(\sum_{i=1}^{i=k} \frac{f_{B,i}n_i}{\sum_{i=1}^{i=k} f_{B,i}n_i} E(W_{B,i}^{in}) - M_E\right) + j_B\left(\sum_{i=1}^{i=k} \frac{f_{A,i}n_i}{\sum_{i=1}^{i=k} f_{A,i}n_i} E(W_{A,i}^{in}) - M_E\right) \tag{A6}$$

Solving eqs A1−A4 gives

$$\sum_{i=1}^{i=k} E(W_{A,i}^{in})\ \frac{f_{A,i}n_i}{\sum_{i=1}^{i=k} f_{A,i}n_i} - M_E = \frac{(\overline{M_a^0} - M_E)(1 - p_A\overline{f_{b,A}^0}) + p_A(\overline{M_b^0} - M_E)(\overline{f_{a,A}^0} - 1)}{(1 - p_A\overline{f_{b,A}^0})(1 - p_B\overline{f_{a,B}^0}) - p_Ap_B(\overline{f_{a,A}^0} - 1)(\overline{f_{b,B}^0} - 1)} \tag{A7}$$

$$\sum_{i=1}^{i=k} E(W_{B,i}^{in})\ \frac{f_{B,i}n_i}{\sum_{i=1}^{i=k} f_{B,i}n_i} - M_E = \frac{(\overline{M_b^0} - M_E)(1 - p_B\overline{f_{a,B}^0}) + p_B(\overline{M_a^0} - M_E)(\overline{f_{b,B}^0} - 1)}{(1 - p_A\overline{f_{b,A}^0})(1 - p_B\overline{f_{a,B}^0}) - p_Ap_B(\overline{f_{a,A}^0} - 1)(\overline{f_{b,B}^0} - 1)} \tag{A8}$$

Substituting eqs A7 and A8 into eq A6 results in

$$E(W_{i,j_A,j_B}) = M_i + j_A\left(\frac{(\overline{M_b^0} - M_E)(1 - p_B\overline{f_{a,B}^0}) + p_B(\overline{M_a^0} - M_E)(\overline{f_{b,B}^0} - 1)}{(1 - p_A\overline{f_{b,A}^0})(1 - p_B\overline{f_{a,B}^0}) - p_Ap_B(\overline{f_{a,A}^0} - 1)(\overline{f_{b,B}^0} - 1)}\right) + j_B\left(\frac{(\overline{M_a^0} - M_E)(1 - p_A\overline{f_{b,A}^0}) + p_A(\overline{M_b^0} - M_E)(\overline{f_{a,A}^0} - 1)}{(1 - p_A\overline{f_{b,A}^0})(1 - p_B\overline{f_{a,B}^0}) - p_Ap_B(\overline{f_{a,A}^0} - 1)(\overline{f_{b,B}^0} - 1)}\right) \tag{A9}$$

If all A-groups and all B-groups are equally reactive, the numbers of reacted A- and B-groups on a i-type monomer unit are independent binomial random variables with parameters j_A, $f_{A,i}$ and j_B, $f_{B,i}$, respectively. Therefore, the number of (i,j_A,j_B) monomer units is

$$n_{i,j_A,j_B} = n_i\binom{f_{A,i}}{j_A}p_A^{\,j_A}(1 - p_A)^{f_{A,i}-j_A}\binom{f_{B,i}}{j_B}p_B^{\,j_B}(1 - p_B)^{f_{B,i}-j_B} \tag{A10}$$

where n_i is the number of i-type monomer units. Equation 43 giving the mass fraction of monomer units becomes

$$\omega_{i,j_A,j_B} = \frac{m_{i,j_A,j_B}}{m_t} = \frac{n_{i,j_A,j_B}(M_i - j_AM_{E,A} - j_BM_{E,B})}{\sum_{i=1}^{i=k} M_in_i - M_Ep_A\sum_{i=1}^{i=k} f_{A,i}n_i} \tag{A11}$$

Programming eqs A5, A9, A10, and A11 leads to the mass-average molar mass of any type of polymer as a function of starting monomer mixture composition and conversion. It must be underlined that the choice of $M_{E,A}$ and $M_{E,B}$ can be arbitrary, provided that $M_{E,A} + M_{E,B} = M_E$.

Appendix B: Glossary of Symbols

$\overline{X_n}$: number-average degree of polymerization
$\overline{M_n}$: number-average molar mass
$\overline{X_w}$: mass-average degree of polymerization
$\overline{M_w}$: mass-average molar mass
PDI: polydispersity index (PDI = $\overline{X_w}/\overline{X_n}$)
A and B: mutually reactive chemical groups (either reacted or unreacted)
p_A and p_B: fractions of initial A and B groups that have reacted
n_i: number of moles of monomer i in initial monomer mixture
$f_{A,i}$: number of B groups on monomer units (or monomer molecules) of type i
$f_{B,i}$: number of B groups on monomer units (or monomer molecules) of type i
α_i^0: number-fraction of i-type monomer units in the initial monomer mixture
α_i: number-fraction of i-type monomer units in the polymer ($\alpha_i = \alpha_i^0$)
ω_i^0: mass-fraction of i-type monomer molecules in the initial monomer mixture
ω_i: mass fraction of i-type monomer units in the polymer ($\omega_i = \omega_i^0$ for polyadditions)
$\overline{f_{n,A}^0}$ and $\overline{f_{n,B}^0}$: number-average A-group and B-group functionalities of initial monomer mixture
$\overline{f_{w,A}^0}$ and $\overline{f_{w,B}^0}$: mass-average A-group and B-group functionalities of initial monomer mixture
$\overline{f_{a,A}^0}$: A-average A-group functionality of initial monomer mixture
$\overline{f_{b,B}^0}$: B-average B-group functionality of initial monomer mixture
$\overline{f_{b,A}^0}$: B-average A-group functionality of initial monomer mixture

$\overline{f^0_{a,B}}$: A-average B-group functionality of initial monomer mixture

$\overline{M}^0_w$: mass-average molar mass of initial monomer mixture

$\overline{M}^0_a$: A-average molar mass of initial monomer mixture

$\overline{M}^0_b$: B-average molar mass of initial monomer mixture

r: stoichiometric ratio (initial number of A groups over the initial number of B groups)

N_A^{out} and N_A^{in}: number of monomer units seen by a random A-group (either reacted or nonreacted) looking respectively "out" and "into" the monomer unit to which it belongs

N_B^{out} and N_B^{in}: number of monomer units seen by a random B-group (either reacted or nonreacted) looking respectively "out" and "into" the monomer unit to which it belongs

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

N_i: number of monomer units in a molecule picked at random by a i-type monomer unit

(i,j_A,j_B): i-type monomer unit with j_A and j_B reacted A- and B-groups

ω_{i,j_A,j_B}: mass fraction of a (i,j_A,j_B) monomer unit

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 the 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 ($M_{EA} + M_{EB} = M_E$)

$(p_A)_{gel}$: conversion of A groups at gel point according to Flory−Stockmayer ($\overline{DP}_w \rightarrow \infty$)

$(p_A)_{gel,Carothers}$: conversion of A groups at gel point according to Carothers ($\overline{DP}_n \rightarrow \infty$)

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