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Polymer 40 (1999) 3565–3573

polymer

Molecular weight distribution of graft copolymers prepared from macromonomers

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Received 11 May 1998; received in revised form 1 July 1998; accepted 10 July 1998

Abstract

A fundamental theoretical investigation is conducted for the molecular weight distribution formed in free-radical and living copolymerizations with macromonomers by using the random sampling technique. General analytical expressions for the number- and weight-average molecular weight developments are obtained. The full molecular weight distribution functions are presented for some simpler cases with low mole fractions of macromonomers. The present theoretical analysis provides a great insight into the complex molecular buildup processes, and thus leads to a better control of the graft copolymers. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Macromonomer; Molecular weight distribution; Free-radical copolymerization

1. Introduction

In general, graft copolymers are special polymers and are expensive to produce commercially. However, the introduction of branches onto polymer chains facilitates one to control the processability and rheological properties greatly. In addition, copolymers have advantages in obtaining a better balance of properties for commercial applications.

Copolymerization with a macromonomer is considered an effective method to produce well-defined graft copolymers, and it is usually claimed that this technique offers better control than procedures involving 'grafting onto' and 'grafting from' techniques [1]. There have been numerous publications concerning experimental investigations of copolymerization with macromonomers [1,2]. On the other hand, however, only a small number of theoretical studies that provide basic principles in controlling nonlinear structure formation have been published so far [3–5].

In controlling the properties of graft copolymers, one needs to consider, at least, the chemical composition distribution and the molecular weight distribution (MWD). Stejskal et al. [3,4] derived analytical expressions for the instantaneous chemical composition distribution formed in free-radical copolymerization with a macromonomer, when both backbone and macromonomer chains conform to the Schulz–Zimm distribution (or the branch chains with a uniform distribution). They showed a basic strategy to obtain the MWD functions [3]. However, the distribution functions were not given in a closed form. Quite recently, Zhu et al. [5] obtained the analytical formulae for the instantaneous MWD [more strictly, the distribution in terms of chain length (degree of polymerization)] formed in free-radical copolymerization, on the basis of the integro-differential equation, similar to that developed by Saito [6], under conditions where the backbone chains follow the most probable distribution and the macromonomer chains conform to the most probable distribution or a uniform distribution. Gu et al. [7] considered the cases of the branch chains having uniform and Schulz–Zimm distributions, in a more general context of comb-branched copolymers. Their chain length distribution functions are given, however, by the bivariate distributions of backbone and branch chain lengths separately, not as a function of the total chain length of the comb polymers. Concerning the average chain lengths, the averages have been derived exclusively from the full chain length distribution functions, and therefore, they are given only for several limited cases.

In this work, the random sampling technique [8] is used to investigate the MWD formed in copolymerization with a macromonomer. In this technique, no abstract mathematics are required. Both free-radical and living copolymerizations are considered in the present report. Simple analytical expressions are given for the number- and weight-average molecular weights that can be applied to any distribution of both backbone and macromonomer chains. For the special cases considered by Zhu et al. [5], the present solutions

PII: S0032-3861(98)00543-6

reduce to their equations. As for the full MWD, we restrict ourselves to some simpler cases in which analytical expressions can be obtained in a straightforward manner. (More general cases can be solved by using a Monte Carlo method, as shown elsewhere [9].) The differences in the molecular weight and the chain length distributions are highlighted for the cases where the average molecular weights of monomeric units in backbone and macromonomer chains are significantly different.

2. Average molecular weights

2.1. Average molecular weights of branch chains

Consider the copolymerization of a small monomer (M_1) and macromonomer (M_2). There are two types of linear chains in graft copolymers; backbone chains and branch chains. In this report, the terminal functional unit (double bond) of a macromonomer that has copolymerized is regarded as belonging to the backbone chain (chain A), not the branch chain (chain B), as shown in Fig. 1. This is not a requirement for the present theory to be applied; however, this treatment facilitates the later development significantly. Obviously, when the chain length (degree of polymerization) of the macromonomer is large enough, the average chain length of the branch chain is approximately equal to that of the macromonomer; however, if the macromonomer chains are not long enough, one needs the following modification.

Suppose that the number- and weight-average chain lengths of macromonomers are given by $\bar{P}_{\mathrm{np},2}$ and $\bar{P}_{\mathrm{wp},2}$, respectively. The subscripts 'np' and 'wp' are used to represent the number- and weight-average of primary chains, respectively, and the subscript '2' is used for the macromonomer. Within the macromonomer molecules that are incorporated into graft copolymers, the terminal functional units belong to the backbone polymer chain. Therefore, the number-average chain length of branch chains, $P_{\mathrm{np,B}}$ is simply given by:

$$\bar{P}_{\mathrm{np,B}} = \bar{P}_{\mathrm{np},2} - 1 \tag{1}$$

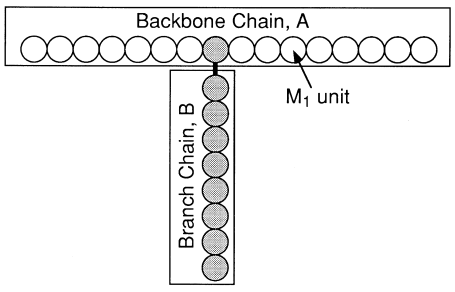

Fig. 1. Schematic drawing for the definition of the backbone and branch chains in the present report. Note that the terminal functional unit of the macromonomer becomes a part of the backbone chain, not the branch chain in the present definition.

As shown in Appendix A, the weight-average chain length of the branch chain, $\bar{P}_{\mathrm{wp,B}}$ is given by:

$$\bar{P}_{\mathrm{wp,B}} = (\bar{P}_{\mathrm{wp},2} - 1)(\bar{P}_{\mathrm{np},2}/\bar{P}_{\mathrm{np,B}}) - 1 \tag{2}$$

Similarly, denoting the number- and weight-average molecular weights of the macromonomers by $\bar{M}_{\mathrm{np},2}$ and $\bar{M}_{\mathrm{wp},2}$, respectively, the number- and weight-average molecular weights of branch chains are given by:

$$\bar{M}_{\mathrm{np,B}} = \bar{M}_{\mathrm{np},2} - m_{2,f} \tag{3}$$

$$\bar{M}_{\mathrm{wp,B}} = (\bar{M}_{\mathrm{wp},2} - m_{2,f})(\bar{M}_{\mathrm{np},2}/\bar{M}_{\mathrm{np,B}}) - m_{2,f} \tag{4}$$

where $m_{2,f}$ is the molecular weight of the terminal functional unit.

2.2. Branching density

The branching density, ρ, is defined as the fraction of the unit that bears a tribranch point within the backbone chain. For free-radical copolymerization with a macromonomer, the branching density of backbone polymer chains formed instantaneously is given by:

$$\rho = F_2 \text{ (free-radical copolymerization)} \tag{5}$$

where F_2 is the instantaneous mole fraction of M_2 incorporated into backbone chains.

For free-radical copolymerization, the ρ-value is different, depending on the birth time of the backbone polymer chains. The branching density, ρ of the backbone polymer chains formed at a given time, can be obtained on the basis of the appropriate copolymerization model, such as the terminal and penultimate models. In free-radical polymerization, the backbone chains, once formed, are dead and do not change their structure during polymerization; however, the branching density and the branched structure of the newly formed polymers are, in general, different from those of the previously formed ones. We derive the analytical expressions for the average molecular weights for the instantaneous MWDs, with those for the accumulated copolymers being obtained through the integration of the instantaneous averages.

For living copolymerization, the compositional drift occurs along the growing backbone polymer chain. In this case, the expected branching density (averaged along the chain) is the same for all backbone chains, and the branching density is given by:

$$\rho = \bar{F}_2 \text{ (living copolymerization)} \tag{6}$$

where $\bar{F}_2$ is the accumulated mole fraction of M_2 incorporated into backbone chains.

In living copolymerization, the branching density of the backbone chains changes during polymerization; however, the expected branching density is the same for all backbone chains.

To facilitate the theoretical treatments of the molecular weights, rather than chain lengths, let us define branching

density with respect to the molecular weight of backbone chains as follows:

$$\rho' = \frac{\rho}{(1-\rho)m_1 + \rho m_{2,f}} \tag{7}$$

where m_1 is the molecular weight of M_1.

In this report, we consider the cases where the number of branch points on a backbone polymer chain conforms to the binomial distribution, without any preferential incorporation of branch chains into any backbone chain, i.e. we assume that nonrandom situations, such as that smaller branch chains tend to be connected to smaller backbone chains, do not occur. For free-radical copolymerization, the binomial distribution assumption can be applied strictly for the instantaneously formed polymers when the copolymerization is ideal (in the terminal model, the product of the reactivity ratios, $r_1 r_2 = 1$), and it is a good approximation when the mole fraction of the macromonomer is small enough. Because the molecular weight of the macromonomer is usually much larger than that for the small monomer (M_1), the mole fraction of the macromonomer (M_2) is quite small in most copolymerization cases.

For a batch living copolymerization, the assumption that the number of branch points on a backbone polymer chain follows the binomial distribution was shown to be a reasonable approximation when the branching density is small enough [10]. Note that because only the number of branch chains for a given backbone chain matters in terms of the MWD, the obtained MWD is equivalent to that formed in the random incorporation of branch chains with branching density, $\rho = \bar{F}_2$, when the binomial distribution assumption is valid for the number of branch points.

Therefore, the analytical expressions derived in the following sections can be applied both for free-radical and living copolymerization with usual polymerization conditions.

2.3. Number-average molecular weight

In the present theoretical development of the fundamental equations, the unreacted macromonomers are not considered as polymers, and all polymer molecules are either comb polymers (true copolymer) or ungrafted backbone polymers, as was considered by other researchers [3–5].

The number-average chain length is the expected chain length when a polymer molecule is selected on a number basis. In the present reaction system, the selection on a number basis can be conducted by selecting a chain end of the backbone chain randomly. Suppose that we have selected the chain end of a backbone chain as shown in Fig. 2. Because the selection is made on a number basis, the expected chain length of this backbone chain is the number-average chain length of the backbone chain, $\bar{P}_{\mathrm{np,A}}$. (The subscript A denotes the backbone polymer chains, as was shown in Fig. 1.) The expected number of branch points on this backbone chain is $\bar{P}_{\mathrm{np,A}}\rho$. Because only the terminal

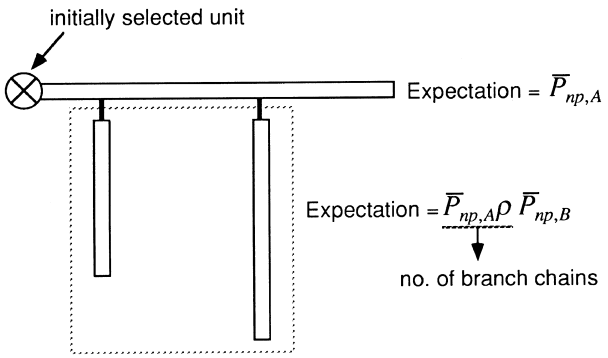

Fig. 2. Schematic drawing for the derivation of the number-average chain length.

functional group of a macromonomer can react, the incorporated branch chains are considered to be chosen on a number basis. The expected chain length of each branch chain is, therefore, $\bar{P}_{\mathrm{np,B}}$. The total expected chain length when a polymer molecule is chosen on a number basis, which is equal to the number-average chain length of the polymers, $\bar{P}_{\mathrm{n}}$ is given by:

$$\bar{P}_{\mathrm{n}} = \bar{P}_{\mathrm{np,A}}(1 + \rho\bar{P}_{\mathrm{np,B}}) \tag{8}$$

Similar reasoning leads to the number-average molecular weight, $\bar{M}_{\mathrm{n}}$ as follows:

$$\bar{M}_{\mathrm{n}} = \bar{M}_{\mathrm{np,A}}(1 + \rho'\bar{M}_{\mathrm{np,B}}) \tag{9}$$

For a batch free-radical copolymerization, the number-average chain length of the accumulated polymers, $\overline{\bar{P}}_{\mathrm{n}}$, when the total monomer conversion on a molar basis is x, is given by:

$$\overline{\bar{P}}_{\mathrm{n}} = \frac{x_{\mathrm{w}}}{\int_0^{x_{\mathrm{w}}} \frac{\mathrm{d}x_{\mathrm{w}}}{\bar{P}_{\mathrm{n}}}} = \frac{x_{\mathrm{w}}(1 + f_2^0\bar{P}_{\mathrm{np,B}})}{\int_0^{x} \left\{ \frac{1 + F_2\bar{P}_{\mathrm{np,B}}}{\bar{P}_{\mathrm{np,A}}(1 + F_2\bar{P}_{\mathrm{np,B}})} \right\} \mathrm{d}x} \tag{10}$$

where f_2^0 is the initial mole fraction of M_2 and x_{w} is the monomeric unit-based conversion defined by:

$$x_{\mathrm{w}} = \frac{x(1 + \bar{F}_2\bar{P}_{\mathrm{np,B}})}{1 + f_2^0\bar{P}_{\mathrm{np,B}}} \tag{11}$$

Similarly, the number-average molecular weight of the accumulated polymers, $\overline{\bar{M}}_{\mathrm{n}}$, is given by:

$$\overline{\bar{M}}_{\mathrm{n}} = \frac{x_{\mathrm{w}}'}{\int_0^{x_{\mathrm{w}}'} \frac{\mathrm{d}x_{\mathrm{w}}'}{\bar{M}_{\mathrm{n}}}} = \frac{x_{\mathrm{w}}'(f_1^0 m_1 + f_2^0\bar{M}_{\mathrm{np,2}})}{\int_0^{x} \left(\frac{F_1 m_1 + F_2\bar{M}_{\mathrm{np,2}}}{\bar{M}_{\mathrm{np,A}}(1 + \rho'\bar{M}_{\mathrm{np,B}})} \right) \mathrm{d}x} \tag{12}$$

where f_1^0 is the initial mole fraction of M_1, and x_{w}' is the weight-based conversion defined by:

$$x_{\mathrm{w}}' = \frac{x(\bar{F}_1 m_1 + \bar{F}_2\bar{M}_{\mathrm{np,2}})}{f_1^0 m_1 + f_2^0\bar{M}_{\mathrm{np,2}}} \tag{13}$$

2.4. Weight-average molecular weight

The weight-average chain length is the expected chain

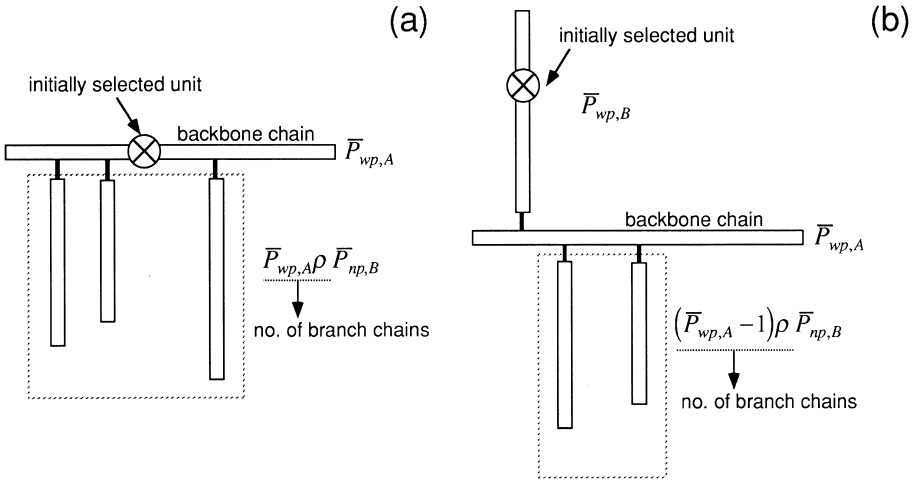

Fig. 3. Schematic drawing for the derivation of the weight-average chain length.

length when a chain is selected on a weight basis. The selection on a weight basis can be conducted by randomly selecting one unit from all of the units bound to polymeric species. When we choose one unit randomly, the chosen unit must belong to either a backbone or a branch chain. The probability of choosing a unit belonging to a backbone chain is given by:

$$w_{\mathrm{A}} = \frac{1}{1+\rho\bar{P}_{\mathrm{np,B}}} \tag{14}$$

Suppose that we have randomly chosen a unit that belongs to a backbone polymer chain, as shown in Fig. 3(a). Because the selection is conducted on a weight basis, the expected chain length of the selected backbone chain is the weight-average chain length of the backbone polymer chains, $\bar{P}_{\mathrm{wp,A}}$. The expected number of the connected branch chain is $\bar{P}_{\mathrm{wp,A}}\rho$. Because only the terminal functional group on the macromonomer reacts, the expected chain length of each branch chain is the number-average chain length of the branch chains, $\bar{P}_{\mathrm{np,B}}$. The total expected number of units (degree of polymerization), given a unit belonging to a backbone chain that has been chosen, $\bar{P}_{\mathrm{w}}^{(\mathrm{A})}$, is given by:

$$\bar{P}_{\mathrm{w}}^{(\mathrm{A})} = \bar{P}_{\mathrm{wp,A}}(1+\rho\bar{P}_{\mathrm{np,B}}) \tag{15}$$

On the other hand, suppose that we have randomly chosen a unit that belongs to a branch chain, as shown in Fig. 3(b). Because the selection is conducted on a weight basis, the expected chain length of the selected branch chain is the weight-average chain length of the branch polymer chains, $\bar{P}_{\mathrm{wp,B}}$. This branch chain must be connected to a backbone polymer chain. Because any unit on the backbone chain can be connected, the connected backbone polymer chain is considered to be selected on a weight basis; therefore, the expected chain length of the backbone chain is $\bar{P}_{\mathrm{wp,A}}$. Then, the expected number of the connected branch chains is $(\bar{P}_{\mathrm{wp,A}}-1)\rho$. Here, $(\bar{P}_{\mathrm{wp,A}}-1)$ is used instead of $\bar{P}_{\mathrm{wp,A}}$, because one unit on the backbone chain is connected to the initially selected branch chain. The expected chain length of each branch chain is the number-average chain length of the branch chains, $\bar{P}_{\mathrm{np,B}}$. Therefore, the expected number of units, given a unit belonging to a backbone chain that has been chosen, $\bar{P}_{\mathrm{w}}^{(\mathrm{B})}$, is given by:

$$\bar{P}_{\mathrm{w}}^{(\mathrm{B})} = \bar{P}_{\mathrm{wp,B}} + \bar{P}_{\mathrm{wp,A}} + (\bar{P}_{\mathrm{wp,A}}-1)\rho\bar{P}_{\mathrm{np,B}} \tag{16}$$

The total expected number of units when one unit is chosen randomly, which is equal to the weight-average chain length, $\bar{P}_{\mathrm{w}}$, is given by:

$$\bar{P}_{\mathrm{w}} = w_{\mathrm{A}}\bar{P}_{\mathrm{w}}^{(\mathrm{A})} + (1-w_{\mathrm{A}})\bar{P}_{\mathrm{w}}^{(\mathrm{B})} = \bar{P}_{\mathrm{wp,A}}(1+\rho\bar{P}_{\mathrm{np,B}}) + \frac{\rho\bar{P}_{\mathrm{np,B}}(\bar{P}_{\mathrm{wp,B}}-\rho\bar{P}_{\mathrm{np,B}})}{1+\rho\bar{P}_{\mathrm{np,B}}} \tag{17}$$

Similar reasoning leads to the weight-average molecular weight, $\bar{M}_{\mathrm{w}}$, as follows:

$$\bar{M}_{\mathrm{w}} = \bar{M}_{\mathrm{wp,A}}(1+\rho'\bar{M}_{\mathrm{np,B}}) + \frac{\rho'\bar{M}_{\mathrm{np,B}}(\bar{M}_{\mathrm{wp,B}}-\rho'\bar{M}_{\mathrm{np,B}})}{1+\rho'\bar{M}_{\mathrm{np,B}}} \tag{18}$$

When the branching density is small enough, Eq. (17) reduces to:

$$\bar{P}_{\mathrm{w}} \cong \bar{P}_{\mathrm{wp,A}}(1+\rho\bar{P}_{\mathrm{np,B}}) + \frac{\rho\bar{P}_{\mathrm{np,B}}\bar{P}_{\mathrm{wp,B}}}{1+\rho\bar{P}_{\mathrm{np,B}}} \ (\text{for } \rho \ll 1) \tag{19}$$

In this case, the polydispersity index ($D \equiv \bar{P}_{\mathrm{w}}/\bar{P}_{\mathrm{n}}$) is given by:

$$D \cong D_{\mathrm{A}} + D_{\mathrm{B}}\left(\frac{\eta}{1+\rho\bar{P}_{\mathrm{np,B}}}\right)^2\rho\bar{P}_{\mathrm{np,A}} \ (\text{for } \rho \ll 1) \tag{20}$$

where $D_{\mathrm{A}} = \bar{P}_{\mathrm{wp,A}}/\bar{P}_{\mathrm{np,A}}$, $D_{\mathrm{B}} = \bar{P}_{\mathrm{wp,B}}/\bar{P}_{\mathrm{np,B}}$, and $\eta = \bar{P}_{\mathrm{np,B}}/\bar{P}_{\mathrm{np,A}}$.

Zhu et al. [5] obtained the polydispersity index on the basis of the full chain-length distribution function under two cases: (i) where both backbone and branch chains follow the most probable distribution ($D_{\mathrm{A}} = D_{\mathrm{B}} = 2$); and (ii) where the backbone chains have the most probable

distribution ($D_A = 2$) and the branch chains have a uniform distribution ($D_B = 1$). Eq. (20) reduces to the equations derived by Zhu et al. [5] under these special conditions.

For batch free-radical copolymerizations, the weight-average chain length of the accumulated polymers, $\overline{\overline{P}}_w$, when the total monomer conversion is x, is given by:

$$\overline{\overline{P}}_w = \frac{1}{x_w}\int_0^x \bar{P}_w\left(\frac{dx_w}{dx}\right)dx$$

$$= \frac{1}{x_w(1+f_2^0\bar{P}_{np,B})}\int_0^x \bar{P}_w(1+F_2\bar{P}_{wp,B})dx \quad (21)$$

For the reactor operations other than a batch reactor, one can obtain $\overline{\overline{P}}_w$ by properly integrating $\bar{P}_w$, taking account of the residence time distribution.

Similarly, the weight-average molecular weight of the accumulated polymers, $\overline{\overline{M}}_w$ is given by:

$$\overline{\overline{M}}_w = \frac{1}{x_w'}\int_0^{x_w'} \bar{M}_w dx_w'$$

$$= \frac{1}{x_w'(f_1^0 m_1 + f_2^0\bar{M}_{np,2})}\int_0^x \bar{M}_w(F_1 m_1 + F_2\bar{M}_{np,2})dx \quad (22)$$

2.5. Illustrative calculations

The first example is a free-radical copolymerization. To illustrate a very fundamental feature of the graft copolymers, let us assume that the MWD of backbone chains do not change during polymerization. The parameters used for the calculation are as follows: $\bar{P}_{np,A} = 200$; $\bar{P}_{wp,A} = 400$; $\bar{P}_{np,B} = 100$; $\bar{P}_{wp,B} = 110$; and the initial mole fraction of the macromonomer, $f_2^0 = 0.01$. We used the terminal model for the copolymerization, and the product of the reactivity ratios ($r_1 r_2$) is set to be unity. (Because the mole fraction of the macromonomer is small enough, the r_2-value has minor effects on the copolymer composition.)

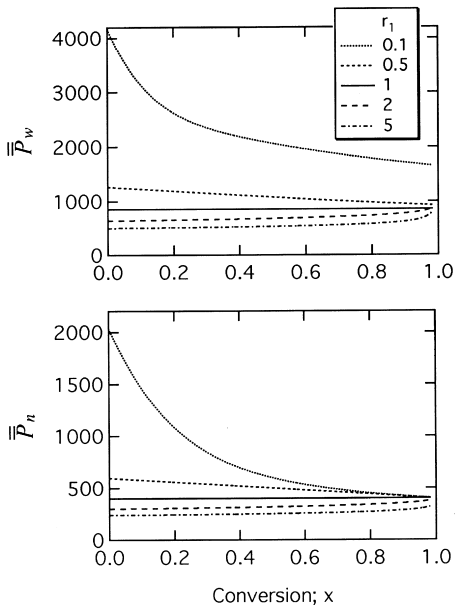

Fig. 4. Calculated number- and weight-average chain length developments of the accumulated polymers during free-radical copolymerizations under conditions: $\bar{P}_{np,A} = 200$; $\bar{P}_{wp,A} = 400$; $\bar{P}_{np,B} = 100$; $\bar{P}_{wp,B} = 110$; and $f_2^0 = 0.01$.

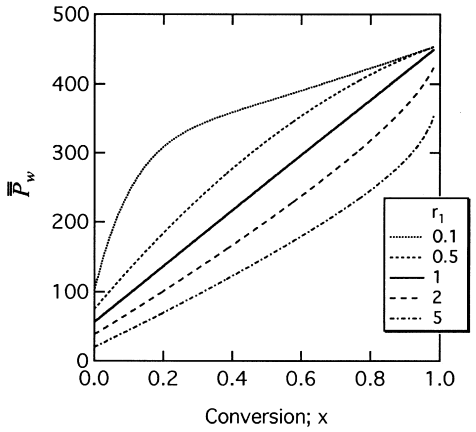

Fig. 5. Calculated weight-average chain length development in living copolymerizations under conditions: $[M]_0/[I]_0 = 200$; $\bar{P}_{np,B} = 100$; $\bar{P}_{wp,B} = 110$; and $f_2^0 = 0.01$.

Fig. 4 shows the number- and weight-average chain length developments of the accumulated polymers during free-radical copolymerization. Eqs. (10) and (21) are used for the calculations. The average chain lengths change significantly during polymerization, especially when the reactivity ratio, r_1, is small, i.e. when the macromonomers are preferentially incorporated into polymer molecules.

The second example is a batch living copolymerization. Strictly, the formulation of the MWD in living copolymerization is not an easy task even for the linear polymer formation [11]. However, at least when the mole fraction of M_2 is much smaller than unity, the backbone chain length distribution would be approximated well by the Poisson distribution in a batch polymerization. Then, the number- and weight-average chain lengths of the backbone chains at conversion x is given by:

$$\bar{P}_{np,A} = ([M]_0/[I]_0)x \quad (23)$$

$$\bar{P}_{wp,A} = \bar{P}_{np,A} + 1 \quad (24)$$

where $[M]_0$ is the initial total monomer concentration, and $[I]_0$ is the initiator concentration. (Note that the initiator units are not included in counting the chain length in the above equations.)

Fig. 5 shows the calculated weight-average chain length developments under conditions: $[M]_0/[I]_0 = 200$; $\bar{P}_{np,B} = 100$; $\bar{P}_{wp,B} = 110$; and $f_2^0 = 0.01$. We used the terminal model to describe the copolymer composition development. Because the chain lengths of backbone chains increase with polymerization, the average chain length becomes larger as polymerization proceeds.

3. Molecular weight distribution

The random sampling technique can be used to obtain the full MWD functions. Both the number- and weight-based MWD can be obtained directly through the random sampling technique [8]. In the present reaction system, it is easier to derive number-based MWD, because we can sample polymer molecules on a number basis by selecting a chain end of the backbone chain randomly. Fig. 6 shows some examples of the polymers with k branch chains. In the present theoretical derivation, we consider only the cases where the branching density is much smaller than unity, i.e. $\rho \ll 1$.

The MWD of a graft copolymer system is the sum of the fractional MWDs containing 0,1,2,$\cdots$ branches, and the number fraction distribution $N(r)$, where r is the chain length, is given by:

$$N(r) = \sum_{k=0}^{\infty} N_k(r) \tag{25}$$

where $N_k(r)$ is the fractional number-based chain length distribution containing k branch points.

To obtain a polymer molecule without a branch point ($k = 0$) by randomly sampling one chain end of the backbone chain, the selected backbone chain must not possess any branch points. The fractional number-based chain length distribution, $N_0(r)$ is given by:

$$N_0(r) = (1-\rho)^r N_{\mathrm{p,A}}(r) \tag{26}$$

where $N_{\mathrm{p,A}}(r)$ is the number-based chain length distribution of backbone chains.

Next we consider the cases with $k = 1$. When we select one chain end randomly, as shown in Fig. 6, the backbone chain length that involves this particular chain end follows $N_{\mathrm{p,A}}(r)$. A branched polymer molecule with chain length r can be formed when a backbone with chain length s is connected with a branch chain with chain length $r - s$. Under condition, $\rho \ll 1$, the number of branch points on a backbone chain follows the binomial distribution both for free-radical and living [10] copolymerization. Therefore, the fractional number-based chain length distribution with $k = 1$, $N_1(r)$ is given by:

$$N_1(r) = \sum_{s=1}^{r-1} N_{\mathrm{p,A}}(s) \binom{s}{1} \rho(1-\rho)^{s-1} N_{\mathrm{p,B}}(r-s)$$

$$\cong \rho \int_0^r s \exp(-\rho s) N_{\mathrm{p,A}}(s) N_{\mathrm{p,B}}(r-s)\mathrm{d}s \tag{27}$$

When the sampling is conducted on a number basis, the apparent formulation is essentially the same as the conventional methods in which the concentration of each type of polymeric species is considered [7].

Similarly, $N_2(r)$ is given by:

$$N_2(r) = \sum_{s_1=1}^{r-1} N_{\mathrm{p,A}}(s_1) \binom{s_1}{2} \rho^2 (1-\rho)^{s_1-2} \times \sum_{s_2=1}^{r-s_1-1} N_{\mathrm{p,B}}(s_2) N_{\mathrm{p,B}}(r-s_1-s_2)$$

$$\cong \frac{\rho}{2!} \int_0^r s_1^2 \exp(-\rho s_1) N_{\mathrm{p,A}}(s_1) \times \int_0^{r-s_1} N_{\mathrm{p,B}}(s_2) N_{\mathrm{p,B}}(r-s_1-s_2)\mathrm{d}s_2\mathrm{d}s_1 \tag{28}$$

In general, $N_k(r)$ is given by:

$$N_k(r) \cong \frac{\rho^k}{k!} \int_0^r s_1^k \exp(-\rho s_1) N_{\mathrm{p,A}}(s_1) \int_0^{r-s_1} N_{\mathrm{p,B}}(s_2) \cdots \int_0^r - \sum_{i=1}^{k-1} s_i N_{\mathrm{p,B}}(s_k) N_{\mathrm{p,B}}(r - \sum_{i=1}^{k} s_i) \times \mathrm{d}s_k \mathrm{d}s_{k-1} \cdots \mathrm{d}s_2 \mathrm{d}s_1 \tag{29}$$

Denoting the number-based molecular weight distribution of the backbone and branch chains by $N'_{\mathrm{p,A}}(M)$ and $N'_{\mathrm{p,B}}(M)$, respectively, the fractional number-based molecular weight distribution containing k branch points, $N'_k(M)$ is given by:

$$N'_k(M) \cong \frac{(\rho')^k}{k!} \int_0^M S_1^k \exp(-\rho' S_1) N'_{\mathrm{p,A}}(S_1) \int_0^{M-S_1} N'_{\mathrm{p,B}}(S_2) \cdots \int_0^M - \sum_{i=1}^{k-1} S_i N'_{\mathrm{p,B}}(S_k) N'_{\mathrm{p,B}} \times (M - \sum_{i=1}^{k} S_i) \mathrm{d}S_k \mathrm{d}S_{k-1} \cdots \mathrm{d}S_2 \mathrm{d}S_1 \tag{30}$$

The analytical solutions for two simplified cases are shown below.

3.1. Case 1: both backbone and branch chains conform to the most probable distribution

We first consider the case where the number fraction

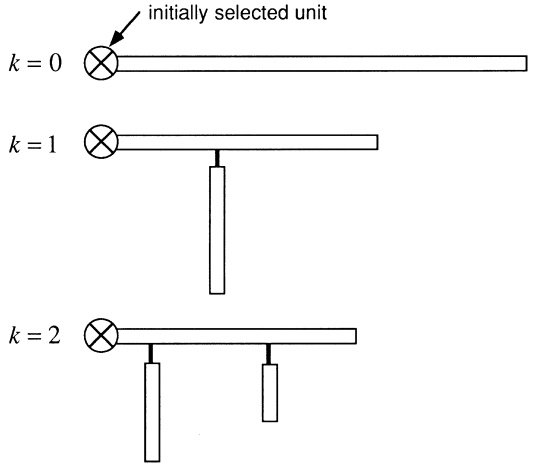

Fig. 6. Schematic representation of the comb structure with k branch chains.

distributions of the backbone and branch chains are given by the following equations:

$$N_{\mathrm{p,A}}(r) = \frac{1}{\bar{P}_{\mathrm{np,A}}}\exp\left(-\frac{r}{\bar{P}_{\mathrm{np,A}}}\right) \tag{31}$$

$$N_{\mathrm{p,B}}(r) = \frac{1}{\bar{P}_{\mathrm{np,B}}}\exp\left(-\frac{r}{\bar{P}_{\mathrm{np,B}}}\right) \tag{32}$$

In free-radical polymerization, the instantaneous chain length distribution of backbone chains conforms to the most probable distribution without contribution of bimolecular termination by combination. (The chainlength-dependent kinetics are not considered in the present report.)

For example, $N_3(r)$ can be obtained as follows:

$$\begin{aligned} N_3(r) \cong & \frac{\rho^3}{3!}\int_0^r s_1^3 \exp(-\rho s_1) N_{\mathrm{p,A}}(s_1) \int_0^{r-s_1} N_{\mathrm{p,B}}(s_2) \\ & \times \int_0^{r-s_1-s_2} N_{\mathrm{p,B}}(s_3) N_{\mathrm{p,B}}(r-s_1-s_2-s_3)\mathrm{d}s_3\mathrm{d}s_2\mathrm{d}s_1 \\ = & \frac{\rho^3 \exp(-r/\bar{P}_{\mathrm{np,B}})}{3!2!\bar{P}_{\mathrm{np,A}}(\bar{P}_{\mathrm{np,B}})^3}\int_0^r s^3(r-s)^2 \\ & \exp\left(-\frac{\xi}{\bar{P}_{\mathrm{np,A}}\bar{P}_{\mathrm{np,B}}}s\right)\mathrm{d}s \end{aligned} \tag{33}$$

where:

$$\xi = \rho\bar{P}_{\mathrm{np,A}}\bar{P}_{\mathrm{np,B}} + \bar{P}_{\mathrm{np,B}} - \bar{P}_{\mathrm{np,A}} \tag{34}$$

In general, one obtains:

$$\begin{aligned} N_k(r) = & \frac{\rho^k \exp(-r/\bar{P}_{\mathrm{np,B}})}{k!(k-1)!\bar{P}_{\mathrm{np,A}}(\bar{P}_{\mathrm{np,B}})^k}\int_0^r s^k(r-s)^{k-1} \\ & \exp\left(-\frac{\xi}{\bar{P}_{\mathrm{np,A}}\bar{P}_{\mathrm{np,B}}}s\right)\mathrm{d}s \end{aligned} \tag{35}$$

Eq. (35) can be solved to give:

$$\begin{aligned} N_k(r) = & \frac{\pi^{1/2} r^{1/2+k}}{2\bar{P}_{\mathrm{np,A}}k!}\left(\frac{\rho}{\bar{P}_{\mathrm{np,B}}}\right)^k\left(\frac{\xi}{\bar{P}_{\mathrm{np,A}}\bar{P}_{\mathrm{np,B}}}\right)^{1/2-k} \\ & \exp\left(-\frac{\xi+2\bar{P}_{\mathrm{np,A}}}{2\bar{P}_{\mathrm{np,A}}\bar{P}_{\mathrm{np,B}}}r\right) \\ & \times\left\{I_{-1/2+k}\left(\frac{r\xi}{2\bar{P}_{\mathrm{np,A}}\bar{P}_{\mathrm{np,B}}}\right)\right. \\ & \left.-I_{1/2+k}\left(\frac{r\xi}{2\bar{P}_{\mathrm{np,A}}\bar{P}_{\mathrm{np,B}}}\right)\right\} \\ = & \frac{r^{2k}}{\bar{P}_{\mathrm{np,A}}(2k)!}\left(\frac{\rho}{\bar{P}_{\mathrm{np,B}}}\right)^k \exp\left\{-\left(\frac{1}{\bar{P}_{\mathrm{np,A}}}+\rho\right)r\right\} \\ & \times {}_1F_1\left[k;2k+1;r\xi/(\bar{P}_{\mathrm{np,A}}\bar{P}_{\mathrm{np,B}})\right] \end{aligned} \tag{36}$$

where $I_n(z)$ is the modified Bessel function of the first kind, and ${}_1F_1[a;b;z]$ is the Kummer confluent hypergeometric function. The whole chain length distribution can be obtained by summing up $N_k(r)$ for all k-values, as described by Eq. (25).

The number- and weight-average chain lengths within the polymeric species containing k branches are given by:

$$\bar{P}_{\mathrm{n},k} = \frac{\int_0^\infty rN_k(r)\mathrm{d}r}{\int_0^\infty N_k(r)\mathrm{d}r} = \frac{\bar{P}_{\mathrm{np,A}} + k\zeta}{1+\rho\bar{P}_{\mathrm{np,A}}} \tag{37}$$

$$\bar{P}_{\mathrm{w},k} = \frac{\int_0^\infty r^2N_k(r)\mathrm{d}r}{\int_0^\infty rN_k(r)\mathrm{d}r} = \frac{(1+k)\{2(\bar{P}_{\mathrm{np,A}})^2 + k\zeta^2\}}{(1+\rho\bar{P}_{\mathrm{np,A}})(\bar{P}_{\mathrm{np,A}}+k\zeta)} \tag{38}$$

where $\zeta = \xi + 2\bar{P}_{\mathrm{np,A}} = \rho\bar{P}_{\mathrm{np,A}}\bar{P}_{\mathrm{np,B}} + \bar{P}_{\mathrm{np,A}} + \bar{P}_{\mathrm{np,B}}$.

Eqs. (36)–(38) agree with those obtained on the basis of the integro-differential equation by Zhu et al. [5].

In terms of the molecular weight rather than chain length, the following equations can be derived:

$$\begin{aligned} N_k'(M) = & \frac{M^{2k}}{\bar{M}_{\mathrm{np,A}}(2k)!}\left(\frac{\rho'}{\bar{M}_{\mathrm{np,B}}}\right)^k \exp\left\{-\left(\frac{1}{\bar{M}_{\mathrm{np,A}}}+\rho'\right)M\right\} \\ & \times {}_1F_1\left[k;2k+1;M\xi'/(\bar{M}_{\mathrm{np,A}}\bar{M}_{\mathrm{np,B}})\right] \end{aligned} \tag{39}$$

$$\bar{M}_{\mathrm{n},k} = \frac{\bar{M}_{\mathrm{np,A}} + k\zeta'}{1+\rho'\bar{M}_{\mathrm{np,A}}} \tag{40}$$

$$\bar{M}_{\mathrm{w},k} = \frac{(1+k)\{2(\bar{M}_{\mathrm{np,A}})^2 + k(\zeta')^2\}}{(1+\rho'\bar{M}_{\mathrm{np,A}})(\bar{M}_{\mathrm{np,A}}+k\zeta')} \tag{41}$$

where $\xi' = \rho'\bar{M}_{\mathrm{np,A}}\bar{M}_{\mathrm{np,B}} + \bar{M}_{\mathrm{np,B}} - \bar{M}_{\mathrm{np,A}}$ and $\zeta' = \rho'\bar{M}_{\mathrm{np,A}}\bar{M}_{\mathrm{np,B}} + \bar{M}_{\mathrm{np,A}} + \bar{M}_{\mathrm{np,B}}$.

Fig. 7(a) shows the calculated weight-based chain length distribution as well as the fractional weight-based chain length distribution containing k branches, under conditions: $\bar{P}_{\mathrm{np,A}} = 100$; $\bar{P}_{\mathrm{np,B}} = 200$; and $\rho = 0.005$. Suppose that the

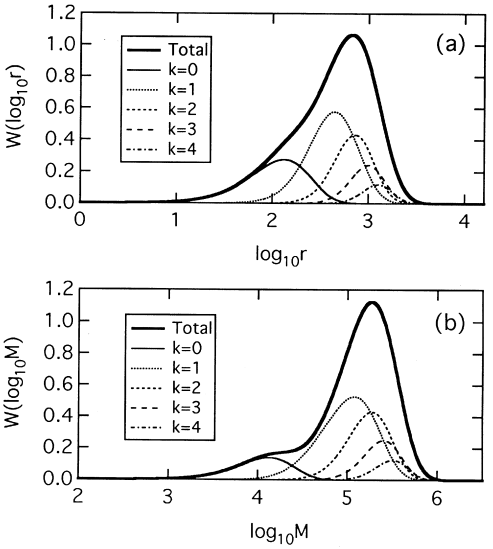

Fig. 7. Weight-based chain length and molecular weight distributions when both backbone and branch chains conform to the most probable distribution, under conditions: $\bar{P}_{\mathrm{np,A}} = 100$; $\bar{P}_{\mathrm{np,B}} = 200$; $\rho = 0.005$; $m_A = 100$; and $m_B = 300$.

average molecular weights of the monomeric unit in the backbone and branch chains are $m_A = 100$ and $m_B = 300$, respectively. In this case, the weight-based molecular weight distribution is shown in Fig. 7(b). When the difference in the molecular weights of the monomeric units in the backbone and branch chains are significantly different, the molecular weight distribution looks different substantially, contrary to the copolymerization of a small monomer pair. One may need to pay careful attention to interpret the experimentally obtained MWDs.

3.2. Case 2: backbone chains with the Schulz–Zimm distribution and branch chains with a uniform distribution

When the branch chains conform to a uniform distribution, a general expression for $N_k(r)$ reduces to:

$$N_k(r) = \rho^k (1-\rho)^{r-k\bar{P}_{\mathrm{np,B}}} - k\binom{r-k\bar{P}_{\mathrm{np,B}}}{k} N_{\mathrm{p,A}}(r-k\bar{P}_{\mathrm{np,B}})$$

$$\cong \rho^k \exp\{-\rho(r-k\bar{P}_{\mathrm{np,B}})\} \times \frac{(r-k\bar{P}_{\mathrm{np,B}})^k}{k!} N_{\mathrm{p,A}}(r-k\bar{P}_{\mathrm{np,B}}) \quad (42)$$

We consider the cases where the backbone chains conform to the Schulz–Zimm distribution, as shown below:

$$N_{\mathrm{p,A}}(r) = \frac{\sigma^\sigma}{\bar{P}_{\mathrm{np,A}}\Gamma(\sigma)} \left(\frac{r}{\bar{P}_{\mathrm{np,A}}}\right)^{\sigma-1} \exp\left(-\frac{\sigma r}{\bar{P}_{\mathrm{np,A}}}\right) \quad (43)$$

where σ is a parameter indicating the narrowness of the distribution breadth, i.e. $\sigma = \bar{P}_{\mathrm{np,A}}/(\bar{P}_{\mathrm{wp,A}} - \bar{P}_{\mathrm{np,A}})$.

With $\sigma = 1$, the Schulz–Zimm distribution reduces to the most probable distribution. In free-radical polymerization, if bimolecular termination by combination is the dominant chain stoppage mechanism, the instantaneous chain length distribution of backbone chains are given by the Schulz–Zimm distribution with $\sigma = 2$. In addition, when the number-average chain length, $\bar{P}_{\mathrm{np,A}}$ is large enough, the Poisson distribution agrees well with the Schulz–Zimm distribution with $\sigma = \bar{P}_{\mathrm{np,A}}$.

By substituting Eq. (43) into Eq. (42), one obtains:

$$N_k(r) = \frac{\rho^k (r-k\bar{P}_{\mathrm{np,B}})^{k+\sigma-1}}{k!\Gamma(\sigma)} \left(\frac{\sigma}{\bar{P}_{\mathrm{np,A}}}\right)^\sigma \exp\left\{-\left(\rho + \frac{\sigma}{\bar{P}_{\mathrm{np,A}}}\right)(r-k\bar{P}_{\mathrm{np,B}})\right\} \quad (44)$$

Fig. 8 shows the calculated weight-based distributions of chain lengths and molecular weights under conditions: $\sigma = 2$; $\bar{P}_{\mathrm{np,A}} = 100$; $\bar{P}_{\mathrm{np,B}} = 200$; $\rho = 0.005$; $m_A = 100$; and $m_B = 300$. The chain length distribution profile is very different from the molecular weight distribution. Note that the condition $\sigma = 2$ corresponds to the cases with free-radical copolymerization when the combination termination is the dominant chain stoppage mechanism. The present distribution profile is for the instantaneous MWD, and the accumulated MWD must be calculated by integrating the instantaneous MWD numerically up to the given conversion level. In addition, the unreacted macromonomers coexist in the reaction mixture. (The accumulated MWD profiles including unreacted macromonomers are shown in Ref. [9].)

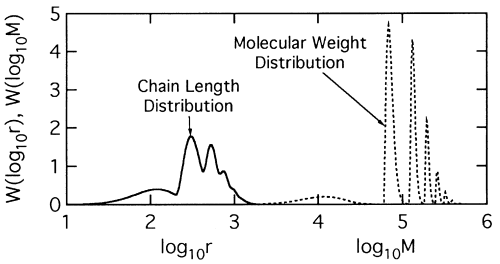

Fig. 8. Weight-based chain length and molecular weight distributions when the backbone chains follow the Schulz–Zimm distribution with $\sigma = 2$ and the branch chains are uniform, under conditions: $\bar{P}_{\mathrm{np,A}} = 100$; $\bar{P}_{\mathrm{np,B}} = 200$; $\rho = 0.005$; $m_A = 100$; and $m_B = 300$.

For living copolymerization, one obtains the accumulated MWD directly through Eq. (44). Fig. 9 shows the calculated MWD development under conditions: $[M]_0/[I]_0 = 200$; $\bar{P}_{\mathrm{np,B}} = 100$; $r_1 = 1$; and $f_2^0 = 0.01$. (The present conditions roughly correspond to the case whose, weight-average chain length development is given by the solid line in Fig. 5.) In the present calculation condition, the branching density is kept constant while the backbone chain length increases during polymerization. The whole chain length distribution shifts to the larger chain length and, at the same time, the peaks for the larger chain lengths (polymer molecules with larger k-values) become larger with the progress of polymerization.

Up to the present, the analytical solutions of the MWDs have been derived only for the limited cases. For more realistic polymerization conditions, it is straightforward to combine the concept of the random sampling technique with the Monte Carlo simulation method, as shown elsewhere [9].

4. Conclusions

The molecular weight distribution formed in free-radical and living copolymerization with macromonomers is

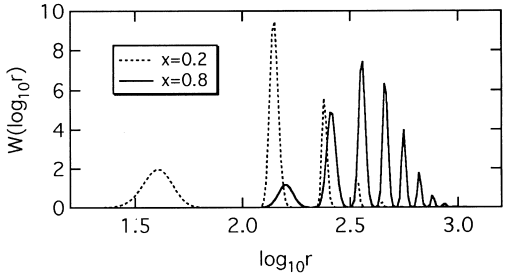

Fig. 9. Weight-based chain length distribution development during living copolymerization with macromonomers having a uniform distribution under conditions: $[M]_0/[I]_0 = 200$; $\bar{P}_{\mathrm{np,B}} = 100$; $r_1 = 1$; and $f_2^0 = 0.01$.

investigated theoretically using the random sampling technique. General analytical solutions for the number- and weight-average molecular weight developments are obtained. These expressions can be used irrespective of the MWD of both the backbone and branch polymer chains.

The analytical solutions of the full molecular weight distribution functions are presented for some simpler distributions of the backbone and branch chains. The differences in the molecular weight and the chain length distributions are highlighted in the illustrative calculations.

For free-radical copolymerization, the present analytical solutions give the instantaneous MWDs, and the accumulated MWDs that are obtained in experiments can be calculated by properly integrating the instantaneous MWDs. For living polymerization, the present analytical expressions directly provide the MWD of the whole formed polymers. The present analytical solutions would provide a great insight in designing the comb-branched graft polymers formed in the copolymerization with macromonomers.

Acknowledgements

I acknowledge Prof. S. Kawaguchi, Toyohashi Institute of Technology, Japan, for useful discussion, and Prof. S. Zhu, McMaster University, Canada, for helpful suggestions.

Appendix A Average chain lengths of branch chains

It is straightforward to derive the number- and weight-average chain lengths of branch chains, $\bar{P}_{\mathrm{np,B}}$ and $\bar{P}_{\mathrm{wp,B}}$, on the basis of the number-based chain length distribution of macromonomer chains $N_{\mathrm{p},2}(r)$, as follows:

$$\bar{P}_{\mathrm{np,B}} = \sum_{r=1}^{\infty} (r-1)N_{\mathrm{p},2}(r) = \bar{P}_{\mathrm{np},2} - 1 \tag{A1}$$

$$\bar{P}_{\mathrm{wp,B}} = \frac{\sum_{r=1}^{\infty} (r-1)^2 N_{\mathrm{p},2}(r)}{\sum_{r=1}^{\infty} (r-1)N_{\mathrm{p},2}(r)} = \frac{\bar{P}_{\mathrm{np},2}\bar{P}_{\mathrm{wp},2} - 2\bar{P}_{\mathrm{np},2} + 1}{\bar{P}_{\mathrm{np,B}}}$$

$$= (\bar{P}_{\mathrm{wp},2} - 1)(\bar{P}_{\mathrm{np},2}/\bar{P}_{\mathrm{np,B}}) - 1 \tag{A2}$$

To show the versatility of the random sampling technique, we derive $\bar{P}_{\mathrm{wp,B}}$ from the point of view of the sampling technique. Suppose that Fig. 10 shows all of the reacted macromonomers. If one randomly chooses one unit from all of the units shown in Fig. 10, the expected chain length is the weight-average chain length of the macromonorners, $\bar{P}_{\mathrm{wp},2}$. When such a selection is conducted, one must choose either a unit belonging to: (a) a terminal unit group; or (b) a group with a unit that becomes a branch chain in graft copolymers. One would choose the terminal unit [belonging to group (a)] with probability $1/\bar{P}_{\mathrm{np},2}$. Given that this event has happened, the expected chain length of the chosen macromonomer is the number-average chain length of the macromonomers $\bar{P}_{\mathrm{np},2}$, because this particular selection process is equivalent to choosing a terminal unit randomly. On the other hand, one would choose a unit other than the terminal unit [belonging to group (b)] with probability $1 - 1/\bar{P}_{\mathrm{np},2}$. In this case, this unit is selected on a weight basis from the units belonging to group (b), and the expected chain length of the macromonomer is the weight-average chain length of the branch chains, $\bar{P}_{\mathrm{wp,B}}$ plus one (terminal unit). Therefore, the weight-average chain length of the macromonomers $\bar{P}_{\mathrm{wp},2}$ can be expressed by:

$$\bar{P}_{\mathrm{wp},2} = (1/\bar{P}_{\mathrm{np},2}) \times \bar{P}_{\mathrm{np},2} + (1 - 1/\bar{P}_{\mathrm{np},2})(\bar{P}_{\mathrm{wp,B}} + 1) \tag{A3}$$

From Eqs. (1) and (A3), one obtains:

$$\bar{P}_{\mathrm{wp,B}} = (\bar{P}_{\mathrm{wp},2} - 1)(\bar{P}_{\mathrm{np},2}/\bar{P}_{\mathrm{np,B}}) - 1 \tag{A4}$$

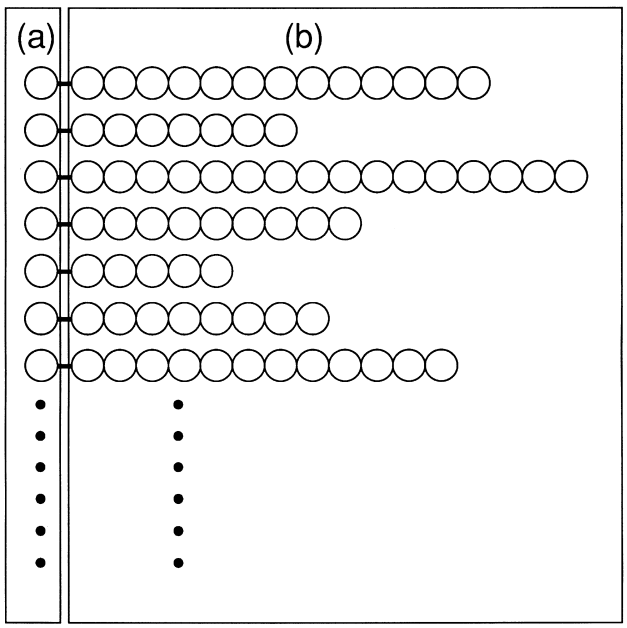

Fig. 10. Schematic representation of macromonomers. The terminal functional groups (a) are incorporated into the backbone chain, while the rest of the monomeric units (b) belong to branch chains.

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