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Molecular weight distribution of step-growth comb-branched polymers

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Abstract

A probability model is developed for determining the average properties of the comb-branched polymer formed through random connection of two different types of polymer chains with one type as the backbone and the other as side chains. $\bar{M}_n$, $\bar{M}_w$ and other higher average molecular weights can all be described as a function of the reaction conversion and the average properties of two polydispersed polymer chains directly without the knowledge of the whole distributions. The simulation results indicate that, as the molecular weight of the backbone polymer is usually much larger than that of the side chain polymer, the polydispersity of the resulting comb polymers is mainly determined by the polydispersity of the backbone at the end of the reaction.

Keywords: Molecular weight distribution; Comb-branched polymer; Polydispersity index

1. Introduction

Branched polymers with well-defined chain structures often provide many special properties and can therefore be readily utilized in a wide range of practical applications [1–5]. In particular, synthesis and characterization of polymers with comb branching has recently received much attention. A comb polymer has a backbone with attached side chains. Since the side and backbone chains can have different chemical compositions, such comb copolymers can exhibit special functions in many applications. As many important mechanical and physical properties of polymeric materials depend on and vary considerably with their molecular weight distribution (MWD), a quantitative description of the resulting MWD of comb copolymers has long been an important research subject.

Despite the large number of studies on the theory of network formation for polymers in the literature [6–26], very few studies have been published on the theory of formation of comb-branched polymers. Recently, Zhu et al. [27–30] developed analytical expressions for the MWD of comb-branched copolymer assembled from backbones and side chains having uniform and/or Schulz–Zimm distribution. The MWDs of backbones and side chains are needed only when the MWD of the resulting comb-branched polymer is to be predicted. For the average molecular weights, no specific MWDs are needed. The number-average and weight-average molecular weights of the resulting comb-branched polymer can be calculated provided the number-average and weight-average molecular weights of backbones and side chains, as well as the branching density, are given. In practice, it is often difficult to obtain the whole MWD for polymers. The knowledge of the average properties of polymers, instead of the whole distribution, is often sufficient for many practical applications.

The 'In–out' recursive probability model presented by Macosko and Miller [17–19] has been a useful approach for obtaining the average properties without the need to calculate the MWDs. Recently, Shiau [31–35] has further extended the concept of the in–out analysis to apply to different classes of step-growth polymer systems. The objective of this paper is, based on the in–out recursive analysis, to develop a statistical approach for obtaining the average molecular weights of the comb-branched copolymer formed through random connection of two different types of polymer chains with one type as the backbone and the other as side chains.

2. Theory

Consider the formation of comb polymers through random grafting between two different types of pre-formed polymers—n_A moles of the backbone 'polymer A' and n_B moles of the side chain 'polymer B'. In general, backbone and side chains might have different chemical properties

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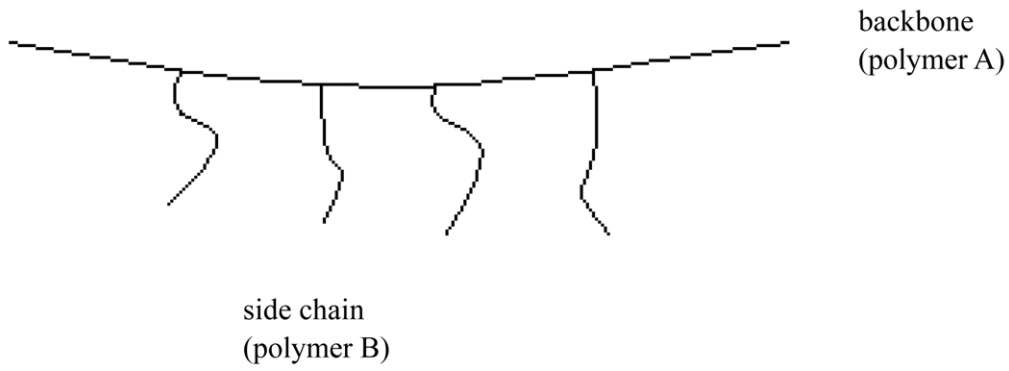

Fig. 1. Schematic representation of the comb-branched polymer.

and thus separate MWDs. It is assumed that every monomeric unit on the backbone polymer A has a reactive site 'a' which can react with the coreactive chain end 'b' on the side chain polymer B. Since there is only one coreactive chain end 'b' on each side chain polymer B, further branching on the side chains is disallowed. Thus comb polymers having a backbone (polymer A) with different numbers of attached side chains (polymer B) are formed (see Fig. 1). In the following derivation, we will retain Flory's simplifying assumptions [8]: (1) all functional groups of the same type are chemically equivalent and hence equally reactive; (2) the reactivity of a given group is independent of the size or structure of the molecule to which it is attached.

Since polymer A is polydispersed, let $n_{A,i}$ $(i = 1, 2, \ldots)$ represent the number of moles of 'polymer A with i monomeric units' (denoted as A_i) and its molecular weight is iM_A. Similarly, since polymer B is polydispersed, let $n_{B,i}$ $(i = 1, 2, \ldots)$ represent the number of moles of 'polymer B with i monomeric units' (denoted as B_i) and its molecular weight is iM_B. Here, M_A and M_B represent the molecular weights of 'polymer A with one monomeric unit' and 'polymer B with one monomeric unit', respectively. By our definition, $\sum_{i=1}^{\infty} n_{A,i} = n_A$ and $\sum_{i=1}^{\infty} n_{B,i} = n_B$. Denote $n_{A,i}/n_A = p_i$ and $n_{B,i}/n_B = q_i$, where p_i represents the number fraction of polymer A with i monomeric units and q_i represents the number fraction of polymer B with i monomeric units.

Let α represent the fraction of sites 'a' which have reacted and β the fraction of sites 'b' which have reacted. In other words, α, also referred to as the branching density, represents the probability of a randomly chosen 'a' reacting with 'b' and β represents the probability of a randomly chosen 'b' reacting with 'a'. Then, the average number of sites 'a' reacted for polymer A with i monomeric units at conversion α is:

$$\lambda_{A,i} = i\alpha. \tag{1}$$

Note that every monomeric unit on the backbone polymer A has a reactive site 'a'. By the law of total probability for expectation, the average number of sites 'a' reacted for polymer A at conversion α, also termed as the average number of branching points per backbone chain, is given by:

$$\lambda_A = \sum_{i=1}^{\infty} (p_i \lambda_{A,i}) = \alpha \sum_{i=1}^{\infty} (ip_i) = \alpha(\bar{M}_{n,A}/M_A) \tag{2}$$

Note that $\sum_{i=1}^{\infty} (ip_i)$ is replaced by $\bar{M}_{n,A}/M_A$ (see Appendix A). $\bar{M}_{n,A}$ represents the number-average molecular weight of polymer A. On the other hand, since there is only one coreactive chain end 'b' on each side chain polymer B, the average number of sites 'b' reacted for polymer B at conversion α, also termed as the average number of branching points per side chain, is given by:

$$\lambda_B = \beta. \tag{3}$$

By stoichiometry, we have:

$$n_A \lambda_A = n_B \lambda_B. \tag{4}$$

Substituting Eqs. (2) and (3) into Eq. (4) gives:

$$n_A \alpha(\bar{M}_{n,A}/M_A) = n_B \beta \tag{5}$$

or

$$\beta = (n_A/n_B)(\bar{M}_{n,A}/M_A)\alpha = r\alpha \tag{6}$$

where $r = (n_A/n_B)(\bar{M}_{n,A}/M_A)$.

2.1. Number-average molecular weight

By definition, $\bar{M}_n$ is just the total mass, m_{total}, divided by the number of molecules present at conversion α, n_{total}. Then:

$$\bar{M}_n = m_{total}/n_{total} \tag{7}$$

where

$$m_{total} = \sum_{i=1}^{\infty} (n_{A,i} iM_A) + \sum_{i=1}^{\infty} (n_{B,i} iM_B) = n_A \bar{M}_{n,A} + n_B \bar{M}_{n,B} \tag{8}$$

$$n_{total} = n_A + n_B - n_A \lambda_A = n_A + n_B - \alpha n_A (\bar{M}_{n,A}/M_A) \tag{9}$$

or

$$n_{total} = n_A + n_B - n_B \lambda_B = n_A + n_B - \beta n_B. \tag{10}$$

Note that $n_A + n_B$ is the total number of moles of polymer A and polymer B initially in the system and $n_A\lambda_A$ (or $n_B\lambda_B$) is the total number of bonds formed at conversion α. Since each bond binds two molecules into one, n_{total}, calculated in Eq. (11) or (12), represents the number of molecules present at conversion α. Therefore, $\bar{M}_n$ of the resulting copolymer is a function of $\bar{M}_{n,A}$, $\bar{M}_{n,B}$ and conversion α.

2.2. Weight-average molecular weight

Pick a reactive site 'a' at random from a randomly chosen backbone polymer A with i monomeric units (denoted as A_i) as shown in Fig. 1. The random variable, $W^{out}_{a,i}$, is the weight attached to 'a' looking out from its parent molecule in the direction $\xrightarrow{1}$. Based on assumptions (1) and (2) described earlier, $W^{out}_{a,i}$ is independent of the number of monomeric units of the backbone polymer A to which the randomly chosen 'a' belongs; therefore, $W^{out}_{a,i}$ can be represented as W^{out}_a. Then:

$$W^{out}_a = \begin{cases} 0, & P = 1-\alpha \quad \text{(if site 'a' does not react)} \\ W_b, j^{in}, & P = \alpha q_j \ (j = 1,2,\ldots) \quad \text{(if site 'a' reacts with site 'b')} \end{cases}$$

where P denotes probability and $W^{in}_{b,j}$ is the weight attached to site 'b' of side chain 'polymer B with j monomeric units' (denoted as B_j) looking along $\xrightarrow{2}$ into its parent molecule. The probability that a randomly chosen reactive site 'b' belongs to B_j is q_j. By the law of total probability for expectation, we have:

$$E(W^{out}_a) = \sum_{j=1}^{\infty}\left[E\left(W^{in}_{b,j}\right)\alpha q_j\right] + 0(1-\alpha) = \alpha\sum_{j=1}^{\infty}\left[q_j E\left(W^{in}_{b,j}\right)\right]. \tag{11}$$

Similarly, pick a reactive site 'b' at random from a randomly chosen side chain polymer B with i monomeric units (denoted as B_i) as shown in Fig. 2. The random variable, $W^{out}_{b,i}$, is the weight attached to 'b' looking out from its parent molecule in the direction $\xrightarrow{3}$. Based on assumptions (1) and (2) described earlier, $W^{out}_{b,i}$ is independent of the number of monomeric units of the side chain polymer B to which the randomly chosen 'b' belongs, therefore, $W^{out}_{b,i}$ can be represented as W^{out}_b. Then:

$$W^{out}_b = \begin{cases} 0, & P = 1-r\alpha \quad \text{(if site 'b' does not react)} \\ W^{in}_{a,k}, & P = r\alpha\left[kp_k/\sum_{k=1}^{\infty}(kp_k)\right] \ (k = 1,2,\ldots) \quad \text{(if site 'b' reacts with site 'a')} \end{cases}$$

where P denotes probability and $W^{in}_{a,k}$ is the weight attached to site 'a' of backbone 'polymer A with k monomeric units' (denoted as A_k) looking along $\xrightarrow{2}$ into its parent molecule. Since the number of reactive sites on all the A_k is $n_A kp_k$ and the total number of reactive sites 'a' in the system is $\sum_{k=1}^{\infty}(n_A kp_k)$, the probability that a randomly chosen reactive site 'a' belongs to A_k can be denoted as $kp_k/\sum_{k=1}^{\infty}(kp_k)$. By the law of total probability for expectation, we have:

$$E(W^{out}_b) = \sum_{k=1}^{\infty}\left\{E\left(W^{in}_{a,k}\right)r\alpha\left[kp_k/\sum_{k=1}^{\infty}(kp_k)\right]\right\} + 0(1-r\alpha)$$

$$= r\alpha(M_A/\bar{M}_{n,A})\sum_{k=1}^{\infty}\left[kp_k E\left(W^{in}_{a,k}\right)\right] \tag{12}$$

where $\sum_{k=1}^{\infty}(kp_k)$ is replaced by $\bar{M}_{n,A}/M_A$ (see Appendix A).

Considering the polymerization between the polydispersed backbone chains polymer A and the polydispersed side chains polymer B, we can derive, for a randomly chosen backbone polymer A with k monomeric units (denoted as A_k):

$$W^{in}_{a,k} = kM_A + \sum_{i=1}^{k-1} W^{out}_{a,i} \qquad (k = 1,2,\ldots) \tag{13}$$

where kM_A is the molecular weight of A_k and $W^{out}_{a,i}$ is the weight attached to the ith branch of a randomly chosen A_k. Note that A_k has k reactive sites and $W^{out}_{a,i}$ $(i = 1,2,\ldots,k-1)$ are independent random variables with the same distribution, W^{out}_a. Taking the expectation of Eq. (13) leads to (see Appendix B):

$$E\left(W^{in}_{a,k}\right) = kM_A + (k-1)E(W^{out}_a) \qquad (k = 1,2,\ldots). \tag{14}$$

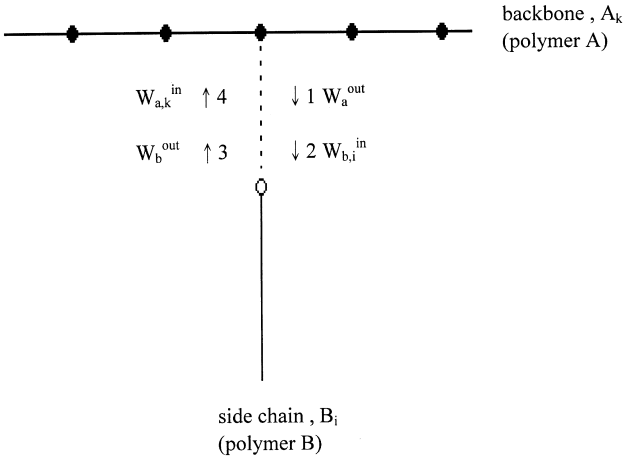

Fig. 2. Schematic illustration of the comb-branched polymer formed through random connection of the backbone and the side chain (Here, '●'represents the reactive site on the backbone and '○' represents the reactive site on the side chain).

Multiplying both sides of Eq. (11) by kp_k and taking the summation from $k = 1$ to ∞, we have

$$\sum_{k=1}^{\infty}\left[kp_kE\left(W_{a,k}^{in}\right)\right] = M_A\sum_{k=1}^{\infty}(k^2p_k) + E\left(W_a^{out}\right)\sum_{k=1}^{\infty}[k(k-1)p_k]$$
$$= \bar{M}_{n,A}\bar{M}_{w,A}/M_A + E\left(W_a^{out}\right)(\bar{M}_{n,A}/M_A)(\bar{M}_{w,A}/M_A - 1). \quad (15)$$

Similarly, for a randomly chosen side chain polymer B with i monomeric units (denoted as B_j), we have:

$$W_{b,j}^{in} = jM_B \qquad (j = 1, 2, \ldots) \quad (16)$$

where jM_B is the molecular weight of B_i. Taking the expectation of Eq. (16) leads to:

$$E\left(W_{b,j}^{in}\right) = jM_B \qquad (j = 1, 2, \ldots). \quad (17)$$

Multiplying both sides of Eq. (17) by q_i and taking the summation from $i = 1$ to ∞, we have:

$$\sum_{j=1}^{\infty}\left[q_iE\left(W_{b,j}^{in}\right)\right] = M_B\sum_{j=1}^{\infty}(jq_j) = \bar{M}_{n,B}. \quad (18)$$

Substituting Eqs. (15) and (18) into Eqs. (11) and (12), $E(W_a^{out})$ and $E(W_b^{out})$ can be solved as:

$$E\left(W_a^{out}\right) = \alpha\bar{M}_{n,B} \quad (19)$$

$$E\left(W_b^{out}\right) = r\alpha[\bar{M}_{w,A} + \alpha\bar{M}_{n,B}(\bar{M}_{w,A}/M_A - 1)]. \quad (20)$$

The molecular weight, $W_{A,i}$, of the entire molecule to which a randomly chosen backbone A_i belongs, will just be the molecular weight of A_i plus the weights attached to i reactive sites looking out from each site. Therefore:

$$W_{A,i} = iM_A + \sum_{j=1}^{i}W_{a,j}^{out} \qquad (i = 1, 2, \ldots). \quad (21)$$

Taking the expectation of this equation leads to (see Appendix B):

$$E(W_{A,i}) = iM_A + iE\left(W_a^{out}\right) \qquad (i = 1, 2, \ldots). \quad (22)$$

Similarly, $W_{B,i}^{out}$, the molecular weight of the entire molecule to which a randomly chosen side chain B_i belongs, will just be the molecular weight of B_i plus the weight attached to its chain end. Then:

$$W_{B,i} = iM_B + W_b^{out} \qquad (i = 1, 2, \ldots). \quad (23)$$

Taking the expectation of this equation leads to:

$$E(W_{B,i}) = iM_B + E\left(W_b^{out}\right) \qquad (i = 1, 2, \ldots). \quad (24)$$

Let $y_{A,i}$ and $y_{B,i}$ denote the weight fraction of backbone A_i and the weight fraction of side chain B_i in the system, respectively:

$$y_{A,i} = n_{A,i}iM_A/\left[\sum_{i=1}^{\infty}(n_{A,i}iM_A) + \sum_{i=1}^{\infty}(n_{B,i}iM_B)\right]$$
$$= n_{A,i}iM_A/(n_A\bar{M}_{n,A} + n_B\bar{M}_{n,B}) \quad (25)$$

$$y_{B,i} = n_{B,i}iM_B/\left[\sum_{i=1}^{\infty}(n_{A,i}iM_A) + \sum_{i=1}^{\infty}(n_{B,i}iM_B)\right]$$
$$= n_{B,i}iM_B/(n_A\bar{M}_{n,A} + n_B\bar{M}_{n,B}). \quad (26)$$

By definition, $\bar{M}_w$, the first moment of the MWD, can be expressed as:

$$\bar{M}_w = E(W) = \sum_{i=1}^{\infty}[y_{A,i}E(W_{A,i})] + \sum_{i=1}^{\infty}[y_{B,i}E(W_{B,i})]$$
$$= \left\{\sum_{i=1}^{\infty}[n_{A,i}iM_AE(W_{A,i})] + \sum_{i=1}^{\infty}[n_{B,i}iM_BE(W_{B,i})]\right\}/(n_A\bar{M}_{n,A} + n_B\bar{M}_{n,B}) \quad (27)$$

where

$$\sum_{i=1}^{\infty}[n_{A,i}iM_AE(W_{A,i})] = n_A\sum_{i=1}^{\infty}\{p_iiM_A[iM_A + iE(W_a^{out})]\}$$
$$= n_AM_A[M_A + E(W_a^{out})]\sum_{i=1}^{\infty}(i^2p_i)$$
$$= n_A\bar{M}_{n,A}[\bar{M}_{w,A} + E(W_a^{out})\bar{M}_{w,A}/M_A]. \quad (28)$$

Note that $\sum_{i=1}^{\infty}(i^2p_i)$ is replaced by $\bar{M}_{n,A}\ \bar{M}_{w,A}/M_A^2$ (see Appendix A). Similarly:

$$\sum_{i=1}^{\infty}[n_{B,i}iM_BE(W_{B,i})] = n_B\sum_{i=1}^{\infty}\{q_iiM_B[iM_B + E(W_b^{out})]\}$$
$$= n_B\left[M_B^2\sum_{i=1}^{\infty}(i^2q_i) + M_BE(W_b^{out})\sum_{i=1}^{\infty}(iq_i)\right]$$
$$= n_B\bar{M}_{n,B}[\bar{M}_{w,B} + E(W_b^{out})]. \quad (29)$$

Since $E(W_a^{out})$ and $E(W_b^{out})$ are given in Eqs. (21) and (22), substituting Eqs. (29) and (30) into Eq. (28) gives:

$$\bar{M}_w = y_A(\bar{M}_{w,A} + \alpha\bar{M}_{n,B}\bar{M}_{w,A}/M_A) + y_B\{\bar{M}_{w,B} + r\alpha[\bar{M}_{w,A} + \alpha\bar{M}_{n,B}(\bar{M}_{w,A}/M_A - 1)]\} \quad (30)$$

where y_A and y_B represent the initial weight fraction of backbone polymer A and the initial weight fraction of side chain

polymer B in the system, respectively:

$$y_A = \sum_{i=1}^{\infty}(n_{A,i}iM_A)/\left[\sum_{i=1}^{\infty}(n_{A,i}iM_A) + \sum_{i=1}^{\infty}(n_{B,i}iM_B)\right] = n_A\bar{M}_{n,A}/(n_A\bar{M}_{n,A} + n_B\bar{M}_{n,B}) \quad (31)$$

$$y_B = \sum_{i=1}^{\infty}(n_{B,i}iM_B)/\left[\sum_{i=1}^{\infty}(n_{A,i}iM_A) + \sum_{i=1}^{\infty}(n_{B,i}iM_B)\right] = n_B\bar{M}_{n,B}/(n_A\bar{M}_{n,A} + n_B\bar{M}_{n,B}). \quad (32)$$

Therefore, $\bar{M}_w$ of the resulting comb polymer, given in Eq. (30), is a function of $\bar{M}_{n,A}$, $\bar{M}_{n,B}$, $\bar{M}_{w,A}$, $\bar{M}_{w,B}$ and conversion α. Gelation occurs when $\bar{M}_w$ diverges (becomes infinite). As shown in Eq. (30), $\bar{M}_w$ will never diverge for $0 \le \alpha \le 1$.

2.3. Other higher average molecular weights

In this section, a general formula will be developed for any other higher average molecular weights. For instance, $\bar{M}_z$ is defined as $E(W^2)/E(W)$. Since the formula for $E(W)$ is given in Eq. (27), the remaining work is to derive $E(W^2)$. To find a general formula, $E(W^n)$ will be developed instead of $E(W^2)$. In general, $E(W^n)$ can be developed by taking the nth power on both sides of Eqs. (13) and (16) and repeating the calculations as described earlier. Then:

$$\left(W_{a,k}^{in}\right)^n = k^nM_A^n + nk^{n-1}M_A^{n-1}\left(\sum_{i=1}^{k-1}W_{a,i}^{out}\right) + \frac{n(n-1)}{2!}k^{n-2}M_A^{n-2}\left(\sum_{i=1}^{k-1}W_{a,i}^{out}\right)^2 + \frac{n(n-1)(n-2)}{3!}k^{n-3}M_A^{n-3}\left(\sum_{i=1}^{k-1}W_{a,i}^{out}\right)^3 + \cdots + \left(\sum_{i=1}^{k-1}W_{a,i}^{out}\right)^n \qquad (i = 1, 2, \ldots) \quad (33)$$

$$\left(W_{b,j}^{in}\right)^n = j^nM_B^n \qquad (i = 1, 2, \ldots). \quad (34)$$

As described before, $E[(W_{a,k}^{in})^n]$ and $E[(W_{b,j}^{in})^n]$ can be obtained by taking the expectation of the above equations (see Appendix B). Then, $\sum_{k=1}^{\infty}\{kp_kE[(W_{a,k}^{in})^n]\}$ and $\sum_{j=1}^{\infty}\{q_jE[(W_{b,j}^{in})^n]\}$ can be derived. Similar to the development of Eqs. (11) and (12), if the random variables $(W_a^{out})^n$ and $(W_b^{out})^n$ are used instead of W_a^{out} and W_b^{out}, respectively, we have:

$$E\left[(W_a^{out})^n\right] = \alpha\sum_{j=1}^{\infty}\left\{q_iE\left[\left(W_{b,j}^{in}\right)^n\right]\right\} \quad (35)$$

$$E\left[(W_b^{out})^n\right] = r\alpha(M_A/\bar{M}_{n,A})\sum_{k=1}^{\infty}\left\{kp_kE\left[\left(W_{a,k}^{in}\right)^n\right]\right\}. \quad (36)$$

Thus, $E[(W_a^{out})^n]$ and $E[(W_{b,}^{out})^n]$ can be determined.

Taking the nth power on both sides of Eqs. (21) and (23) yields:

$$W_{A,i}^n = i^nM_A^n + ni^{n-1}M_A^{n-1}\left(\sum_{j=1}^{i}W_{A,j}^{out}\right) + \frac{n(n-1)}{2!}i^{n-2}M_A^{n-2}\left(\sum_{j=1}^{i}W_{A,j}^{out}\right)^2 + \frac{n(n-1)(n-2)}{3!}i^{n-3}M_A^{n-3}\left(\sum_{j=1}^{i}W_{A,j}^{out}\right)^3 + \cdots + \left(\sum_{j=1}^{i}W_{A,j}^{out}\right)^n \qquad (i = 1, 2, \ldots) \quad (37)$$

$$W_{B,i}^n = i^nM_B^n + ni^{n-1}M_B^{n-1}W_b^{out} + \frac{n(n-1)}{2!}i^{n-2}M_A^{n-2}\left(W_b^{out}\right)^2 + \frac{n(n-1)(n-2)}{3!}i^{n-3}M_B^{n-3}\left(W_b^{out}\right)^3 + \cdots + \left(W_b^{out}\right)^n \quad (i = 1, 2, \ldots) \quad (38)$$

Thus, $E(W_{A,i}^n)$ and $E(W_{B,i}^n)$ can be obtained by taking the expectation of the above equation (see Appendix B). Then, $E(W^n)$, by definition, can be expressed as:

$$E(W^n) = \sum_{i=1}^{\infty}\left[y_{A,i}E\left(W_{A,i}^n\right)\right] + \sum_{i=1}^{\infty}\left[y_{B,i}E\left(W_{B,i}^n\right)\right] = \frac{\sum_{i=1}^{\infty}\left[n_{A,i}M_{A,i}E\left(W_{A,i}^n\right)\right] + \sum_{i=1}^{\infty}\left[n_{B,i}M_{B,i}E\left(W_{B,i}^n\right)\right]}{n_A\bar{M}_{n,A} + n_B\bar{M}_{n,B}} \quad (39)$$

where $\sum_{i=1}^{\infty}[n_{A,i}M_{A,i}E(W_{A,i}^n)]$ and $\sum_{i=1}^{\infty}[n_{B,i}M_{B,i}E(W_{B,i}^n)]$ can be derived in a similar way as before.

3. Results and discussion

In the application of the above-developed model, only the knowledge of the average properties of backbone and side chains polymers, instead of their complete molecular weigh distributions, is needed. An example is illustrated below for the system in which comb-branched polymers are formed through random connection of two different types of polymers chains with one type as the backbone (polymer A) and the other as side chains (polymer B).

The ratio of the two average molecular weights $\bar{M}_w/\bar{M}_n$, referred to as the polydispersity index (PI), depends on the

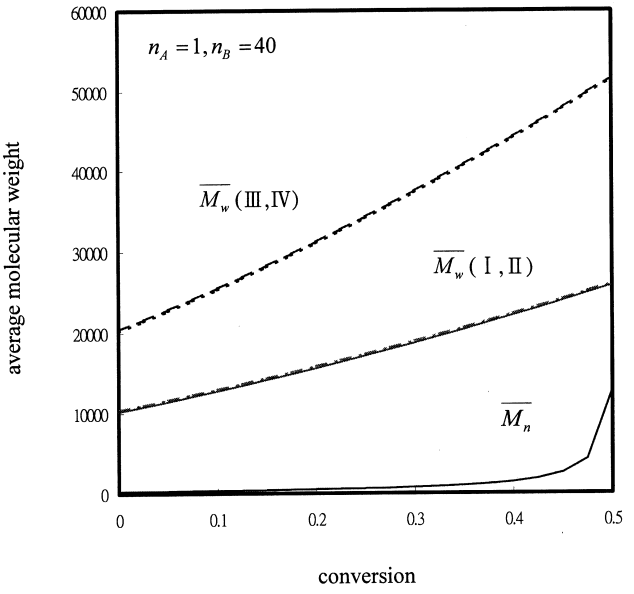

Fig. 3. $\bar{M}_n$ and $\bar{M}_w$ versus conversion α for the resulting comb-branched polymer, — for case I, ----- for case II, ⋯ for case III, - - - for case IV ($n_A = 1$ and $n_B = 40$, which belongs to the first category).

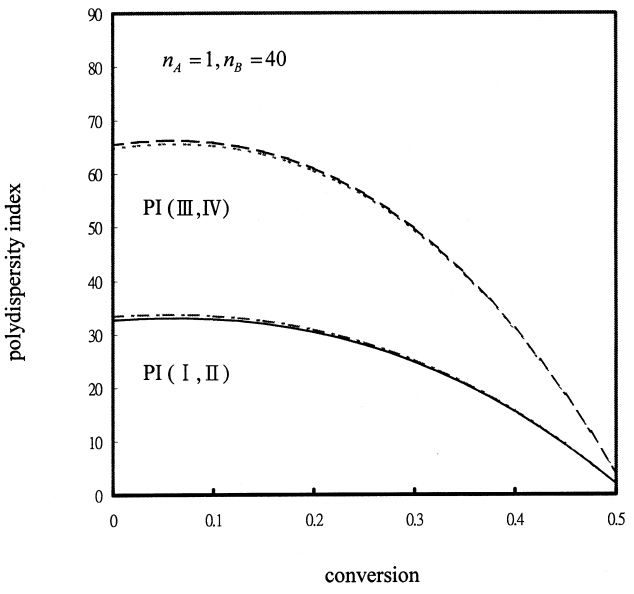

Fig. 4. PI versus conversion α for the resulting comb-branched polymer, — for case I, ----- for case II, ⋯ for case III, - - - for case IV ($n_A = 1$ and $n_B = 40$, which belongs to the first category).

breadth of the MWD and is a measure of the polydispersity of a polymer. The value of PI would be unity for a perfectly monodisperse polymer. PI is greater than unity for all actual polymers and increases with increasing polydispersity. Thus, we define:

$$PI_A = \bar{M}_{w,A}/\bar{M}_{n,A} \tag{40}$$

$$PI_B = \bar{M}_{w,B}/\bar{M}_{n,B} \tag{41}$$

$$PI = \bar{M}_w/\bar{M}_n. \tag{42}$$

Since only the backbone polymer A can react with the side chain polymer B and polymers of the same type cannot react with each other, this system can be divided into three categories: (i) when $n_A(\bar{M}_{n,A}/M_A) > n_B$, the side chain polymer B will be all exhausted at the end of the reaction (i.e. $\beta = 1$). Subsequently only the resulting comb polymers and the unreacted backbone polymer A exist in the system. Thus, one obtains that at the end of the reaction $\beta = 1$ and $\alpha = (n_B/n_A)(M_A/\bar{M}_{n,A})$. Note that $n_A\alpha(\bar{M}_{n,A}/M_A) = n_B\beta$ in Eq. (5); (ii) when $n_A(\bar{M}_{n,A}/M_A) < n_B$, the backbone polymer A will be all exhausted at the end of the reaction (i.e. $\alpha = 1$). Subsequently only the resulting comb polymers and the unreacted side chain polymer B exist in the system. Thus, one obtains that at the end of the reaction $\alpha = 1$ and $\beta = (n_A/n_B)(\bar{M}_{n,A}/M_A)$; (iii) when $n_A(\bar{M}_{n,A}/M_A) = n_B$, the backbone polymer A and the side chain polymer B will be all exhausted at the end of the reaction (i.e. $\alpha = \beta = 1$). Subsequently only the resulting comb polymers exist in the system.

In the following calculation, It is assumed that $M_A = 100$, $\bar{M}_{n,A} = 8000$ and $\bar{M}_{n,B} = 120$. To investigate the effects of PI_A and PI_B on PI, four cases will be discussed. Case I represents the case of $PI_A = 2$ and $PI_B = 5$. Case II represents the case of $PI_A = 2$ and $PI_B = 10$. Case III represents the case of $PI_A = 4$ and $PI_B = 5$. Case IV represents the case of $PI_A = 4$ and $PI_B = 10$.

Figs. 3 and 4 are displayed for the example of $n_A = 1$ and $n_B = 40$. Since $n_A(\bar{M}_{n,A}/M_A) > n_B$, this belongs to the first category described before, i.e. at the end of the reaction $\beta = 1$ and $\alpha = (n_B/n_A)(M_A/\bar{M}_{n,A}) = 0.5$. Fig. 3 shows that all four cases lead to the same plot of $\bar{M}_n$, which is consistent with the concept that the polydispersity of the backbone and the side chain does not affect $\bar{M}_n$ of the resulting comb-branched polymers. Note that $\bar{M}_n$ increases slowly for $0 \le \alpha \le 0.45$ and then increases rapidly for $0.45 \le \alpha \le 0.5$. However, $\bar{M}_w$ for the four cases increases nearly linearly within the whole range of α. Cases I and II have similar plots of $\bar{M}_w$ because $PI_A = 2$ for both. Since $\bar{M}_{n,A}$ is much larger than $\bar{M}_{n,B}$, PI of the resulting comb polymers is mainly determined by PI_A while PI_B only slightly affects PI of the resulting comb polymers. Similarly, cases III and IV have similar plots of $\bar{M}_w$ because $PI_A = 4$ for both. However, $\bar{M}_w$ for cases III and IV is about twice that for cases I and II within the whole conversion range. Fig. 4 shows that PI for case III and case IV is about two times of that for case I and case II within the early conversion range. It also indicates that all PI decrease with an increase of the conversion. That is, the breadth of MWD of the resulting comb polymer becomes smaller with an increase of the conversion for all four cases. In addition, PI for cases I and II approaches two and PI for cases III and IV approaches four at $\alpha = 0.5$. Note that at the end of the reaction (i.e. $\alpha = 0.5$.) the side chain polymer B will be all exhausted and subsequently only the resulting comb polymers and the unreacted backbone polymer A exist in

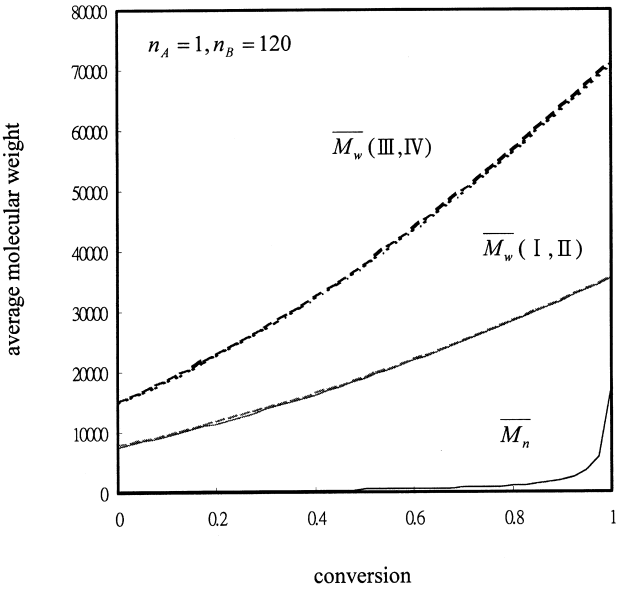

Fig. 5. $\bar{M}_n$ and $\bar{M}_w$ versus conversion α for the resulting comb-branched polymer, — for case I, -·-·- for case II, ··· for case III, - - - for case IV ($n_A = 1$ and $n_B = 120$, which belongs to the second category).

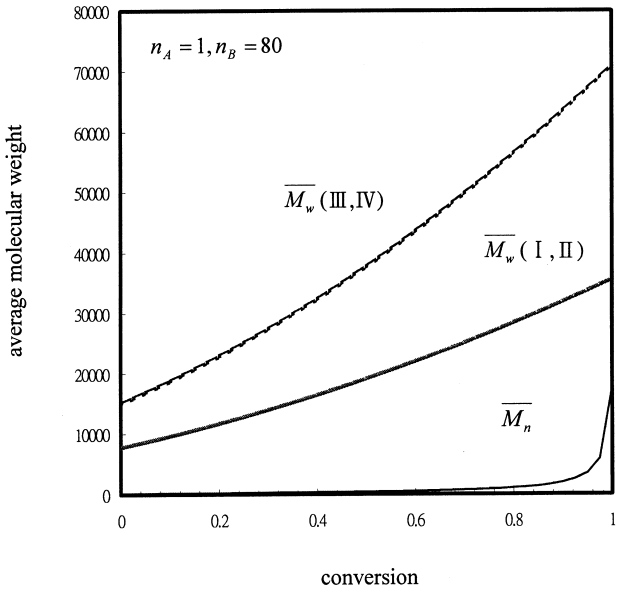

Fig. 7. $\bar{M}_n$ and $\bar{M}_w$ versus conversion α for the resulting comb-branched polymer, — for case I, -·-·- for case II, ··· for case III, - - - for case IV ($n_A = 1$ and $n_B = 80$, which belongs to the third category).

the system. Therefore, the polydispersity of the resulting comb polymers is mainly determined by the polydispersity of the backbone at the end of the reaction.

Figs. 5 and 6 are displayed for the example of $n_A = 1$ and $n_B = 120$. Since $n_A(\bar{M}_{n,A}/M_A) < n_B$, this belongs to the second category described before, i.e. at the end of the reaction $\alpha = 1$ and $\beta = (n_A/n_B)(\bar{M}_{n,A}/M_A) = 2/3$. Fig. 5 shows that all four cases lead to the same plot of $\bar{M}_n$. Note that $\bar{M}_n$ increases slowly within the whole conversion range. On the other hand, $\bar{M}_w$ for four cases increases nearly linearly within the whole range of α. Cases I and II have similar plots of $\bar{M}_w$ because $PI_A = 2$ for both. Similarly, cases III and IV have similar plots of $\bar{M}_w$ because $PI_A = 4$ for both. However, $\bar{M}_w$ for cases III and IV is about twice that for cases I and II within the whole reaction range. Fig. 6 shows that all PI first increase and then drop slightly during the reaction. It also indicates that PI for cases III and IV is about twice that for cases I and II within the whole conversion range. Note that at the end of the reaction (i.e. $\alpha = 1$) the backbone polymer A will be all exhausted and subsequently only the resulting comb polymers and the unreacted side chain polymer B exist in the system. Therefore, the breadth of MWD of the resulting comb polymer becomes very large at the end of the reaction.

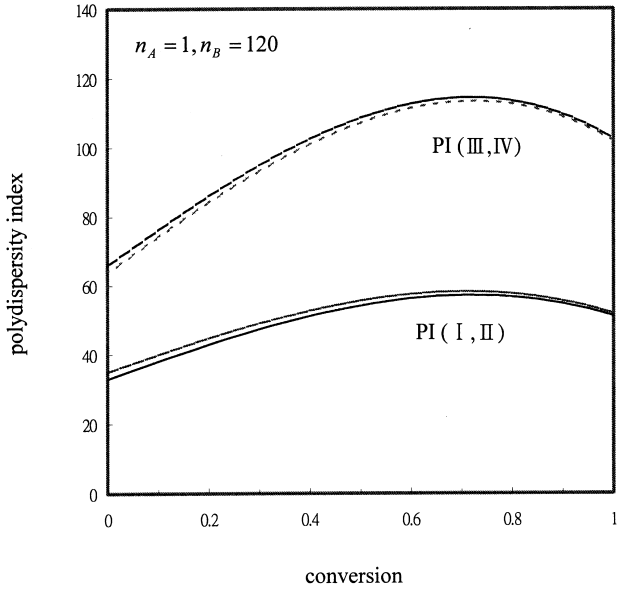

Fig. 6. PI versus conversion α for the resulting comb-branched polymer, — for case I, -·-·- for case II, ··· for case III, - - - for case IV ($n_A = 1$ and $n_B = 120$, which belongs to the second category).

Figs. 7 and 8 are displayed for the example of $n_A = 1$ and $n_B = 80$. Since $n_A(\bar{M}_{n,A}/M_A) = n_B$, this belongs to the third category described before, i.e. at the end of the reaction $\alpha = \beta = 1$. Fig. 7 shows that all four cases lead to the same plot of $\bar{M}_n$. Note that $\bar{M}_n$ increases slowly for $0 \le \alpha \le 0.9$ and then increases rapidly for $0.9 \le \alpha \le 1$. However, $\bar{M}_w$ for the four cases increases nearly linearly within the whole range of α. Cases I and II have similar plots of $\bar{M}_w$ because $PI_A = 2$ for both. Similarly, cases III and IV have similar plots of $\bar{M}_w$ because $PI_A = 4$ for both. However, $\bar{M}_w$ for cases III and IV is about twice that for cases I and II within the early conversion range. Fig. 8 shows that all PI first increase slightly and then drop rapidly during the reaction. In addition, PI for cases I and II approaches two and PI for cases III and IV approaches four at the end of the reaction. Therefore, Fig. 8 exhibits the characteristics of both Figs. 4 and 6. Note that at the end of the reaction the backbone polymer A and the side chain polymer B will be all

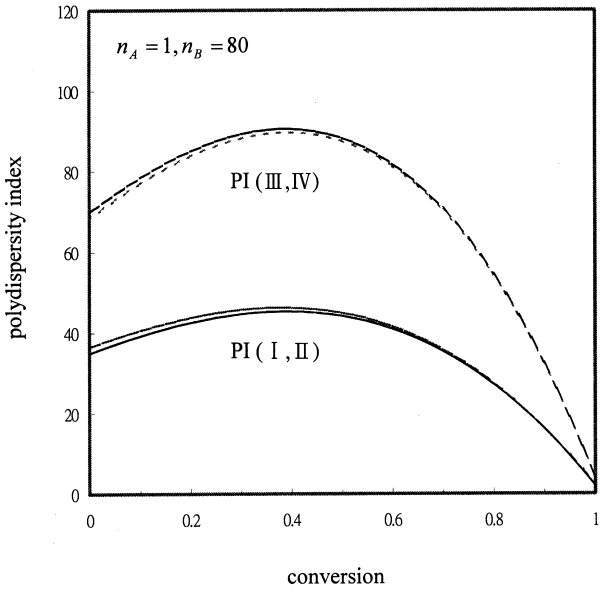

Fig. 8. PI versus conversion α for the resulting comb-branched polymer, — for case I, -·-·- for case II, ··· for case III, - - - for case IV ($n_A = 1$ and $n_B = 80$, which belongs to the third category).

exhausted and subsequently only the resulting comb olymers exist in the system.

4. Conclusions

A model is presented in this paper, without the calculation of the whole distribution, to determine $\bar{M}_n$, $\bar{M}_w$ and PI of the resulting comb polymer, based on the random connection of two different types of polymer chains with one type as the backbone and the other as side chains, as a function of the reaction conversion and the average properties of two polydispersed reactive polymers.

The major advantage of this systematic approach is that, once the basic equations are set up, various average molecular weights can be directly derived by taking *n*th power on both sides of these equations and, then, taking the expectation of thus-obtained equations. The developed model in this paper provides a general algorithm to solve for these average properties by computers.

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Appendix A

For the polydispersed polymer A, various average molecular weights are defined as:

$$\bar{M}_{n,A} = \sum_{i=1}^{\infty} (n_{A,i} i M_A)/n_A \tag{A1}$$

$$\bar{M}_{w,A} = \frac{\sum_{i=1}^{\infty} \left(n_{A,i} i^2 M_A^2\right)}{\sum_{i=1}^{\infty} \left(n_{A,i} i M_A\right)} \tag{A2}$$

$$\bar{M}_{z,A} = \frac{\sum_{i=1}^{\infty} \left(n_{A,i} i^3 M_A^3\right)}{\sum_{i=1}^{\infty} \left(n_{A,i} i^2 M_A^2\right)}. \tag{A3}$$

Then, the following equations can be derived based on the average properties of polymer A:

$$\sum_{i=1}^{\infty} (i p_i) = \sum_{i=1}^{\infty} (i M_A n_{A,i}/M_A n_A) = \bar{M}_{n,A}/M_A \tag{A4}$$

$$\sum_{i=1}^{\infty} (i^2 p_i) = \sum_{i=1}^{\infty} \left(i^2 M_A^2 n_{A,i}/M_A^2 n_A\right) = \bar{M}_{n,A}\bar{M}_{w,A}/M_A^2 \tag{A5}$$

$$\sum_{i=1}^{\infty} (i^3 p_i) = \sum_{i=1}^{\infty} \left(i^3 M_A^3 n_{A,i}/M_A^3 n_A\right) = \bar{M}_{n,A}\bar{M}_{w,A}\bar{M}_{z,A}/M_A^3. \tag{A6}$$

Similar expressions can be derived for polymer B. Thus:

$$\sum_{i=1}^{\infty} (i q_i) = \bar{M}_{n,B}/M_B \tag{A7}$$

$$\sum_{i=1}^{\infty} (i^2 q_i) = \bar{M}_{n,B}\bar{M}_{w,B}/M_B^2 \tag{A8}$$

$$\sum_{i=1}^{\infty} (i^3 q_i) = \bar{M}_{n,B}\bar{M}_{w,B}\bar{M}_{z,B}/M_B^3. \tag{A9}$$

Appendix B

Based on probability theory [36], if $X_1, X_2, \ldots, X_f$ are independent random variables with the same distribution—X, then:

$$E\left(\sum_{i=1}^{f} X_i\right) = \sum_{i=1}^{f} E(X_i) = fE(X) \tag{B1}$$

$$E\left(\sum_{i=1}^{f} X_i\right)^2 = E\left(\sum_{i=1}^{f} X_i^2 + \sum_{i=1}^{f}\sum_{j=1,j\neq i}^{f} X_iX_j\right) = E\left(\sum_{i=1}^{f} X_i^2\right) + E\left(\sum_{i=1}^{f}\sum_{j=1,j\neq i}^{f} X_iX_j\right) = \sum_{i=1}^{f} E\left(X_i^2\right) + \sum_{i=1}^{f}\sum_{j=1,j\neq i}^{f} E(X_i)E(X_j)$$

$$= fE(X^2) + f(f-1)(E(X))^2 \tag{B2}$$

$$E\left(\sum_{i=1}^{f} X_i\right)^3 = E\left(\sum_{i=1}^{f} X_i^3 + 3\sum_{i=1}^{f}\sum_{j=1,j\neq i}^{f} X_i^2X_j + \sum_{i=1}^{f}\sum_{j=1,j\neq i}^{f}\sum_{k=1,k\neq i\neq j}^{f} X_iX_jX_k\right)$$

$$= E\left(\sum_{i=1}^{f} X_i^3\right) + 3E\left(\sum_{i=1}^{f}\sum_{j=1,j\neq i}^{f} X_i^2X_j\right) + E\left(\sum_{i=1}^{f}\sum_{j=1,j\neq i}^{f}\sum_{k=1,k\neq i\neq j}^{f} X_iX_jX_k\right)$$

$$= \sum_{i=1}^{f} E\left(X_i^3\right) + 3\sum_{i=1}^{f}\sum_{j=1,j\neq i}^{f} E\left(X_i^2\right)E(X_j) + \sum_{i=1}^{f}\sum_{j=1,j\neq i}^{f}\sum_{k=1,k\neq i\neq j}^{f} E(X_i)E(X_j)E(X_k)$$

$$= fE(X^3) + 3f(f-1)E(X^2)E(X) + f(f-1)(f-2)(E(X))^3 \tag{B3}$$

$$E\left(\sum_{i=1}^{f} X_i\right)^n = E\left(\sum_{\substack{n_1,n_2,\ldots,n_f\geq 0\\(n_1+n_2+\cdots+n_f=n)}}^{n} \frac{n!}{n_1!n_2!\cdots n_f!}X_1^{n_1}X_2^{n_2}\cdots X_n^{n_f}\right) = \sum_{\substack{n_1,n_2,\ldots,n_f\geq 0\\(n_1+n_2+\cdots+n_f=n)}}^{n} \frac{n!}{n_1!n_2!\cdots n_f!}E\left(X_1^{n_1}X_2^{n_2}\cdots X_n^{n_f}\right)$$

$$= \sum_{\substack{n_1,n_2,\ldots,n_f\geq 0\\(n_1+n_2+\cdots+n_f=n)}}^{n} \frac{n!}{n_1!n_2!\cdots n_f!}E\left(X_1^{n_1}\right)E\left(X_2^{n_2}\right)\cdots E\left(X_n^{n_f}\right) = \sum_{\substack{n_1,n_2,\ldots,n_f\geq 0\\(n_1+n_2+\cdots+n_f=n)}}^{n} \frac{n!}{n_1!n_2!\cdots n_f!}E(X^{n_1})E(X^{n_2})\cdots E(X^{n_f}). \tag{B4}$$

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