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Average properties of polymer blends formed between two polydisperse reactive polymers

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A general model for calculating the average properties of the copolymer formed between two polydisperse reactive polymers is developed. $\overline{M}_n$, $\overline{M}_w$, $\overline{M}_z$, $\overline{M}_{z+1}$ and other higher average molecular weights can all be described as a function of the reaction conversion and the average properties of two reactive polymers directly without calculation of the complete distribution. The predictive capacity of the model is limited to reaction before gelation and can be used for prediction of the gel point. The model is explicitly formulated and can therefore be readily applied. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Blending two or more existing polymers provides the opportunity to make new materials with improved properties. The study of polymer blends has therefore recently developed rapidly. In some cases, reactive extrusion is used for compatibilizing dissimilar polymers[1-3]. New covalent bonds are formed by grafting reaction between two reactive polymers during the extrusion process. As a knowledge of the molecular weight distribution of polymers is essential for synthesis and application, a quantitative description of average properties of the resulting copolymer formed by two reactive polymers is also of prime importance in its physical characterization.

Despite the large number of studies on the theory of network formation for polymers formed from two types of monomer[4-16], very few studies have been published on the theory of grafting reactions between two reactive polymers. Recently, Nie *et al.*[17,18] proposed a kinetic approach for the grafting system between two reactive polymers. In their model, the kinetic equations describing the rate of change of the concentrations of individual polymer species are listed. With the approximation of two reactive polymers having an infinite number of reactive groups, the concentrations of individual species are solved as a function of the grafting conversion. Then, the average molecular weights ($\overline{M}_n$ and $\overline{M}_w$) are computed from the concentrations of individual polymer species formed or by introducing probability generating functions. For the general case of polymer blends formed from two polydisperse reactive polymers, the mathematics involved in their model becomes very complex.

The objective of this paper is to develop, based on the probability theory originally proposed by Macosko and Miller[13], a systematic approach for calculating all the average molecular weights of the resulting copolymer formed between two polydisperse reactive polymers. Gel point, $\overline{M}_n$, $\overline{M}_w$, $\overline{M}_z$, $\overline{M}_{z+1}$ and other higher average molecular weights can all be described as a function of the reaction conversion and the average properties of two polydisperse reactive polymers directly, without calculation of the complete distribution.

THEORY

In the derivation, we 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; (3) intramolecular reactions are forbidden. In addition, the interacting polymer–polymer system is assumed to be completely mixed in formulating the model.

Consider a copolymerization system consisting of n_A moles of polymer A with reactive sites 'a', reacting with n_B moles of polymer B with reactive sites 'b'. Since polymer A is polydisperse, let $n_{A,i}$ ($i = 1,2,\ldots,f$) represent the number of moles of 'polymer A with i reactive sites' (denoted A_i) and its molecular weight be $M_{A,i}$. Similarly, since polymer B is polydisperse, let $n_{B,i}$ ($i = 1,2,\ldots,g$) represent the number of moles of 'polymer B with i reactive sites' (denoted B_i) and its molecular weight be $M_{B,i}$. By our definition, $\sum_{i=1}^{f} n_{A,i} = n_A$ and $\sum_{i=1}^{g} n_{B,i} = n_B$. Denote $n_{A,i}/n_A = p_i$ and $n_{B,i}/n_B = q_i$, where p_i represents the fraction of 'polymer A with i reactive sites', and q_i represents the fraction of 'polymer B with i reactive sites'.

Let α represent the fraction of 'a' sites that have reacted and β the fraction of 'b' sites that have reacted. In other words, α 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 (or expected) number of 'a' sites consumed for 'polymer A with i reactive sites' at conversion α is:

$$\lambda_{A,i} = i\alpha \quad (1)$$

By the law of total probability for expectation, the average number (or the expected number) of 'a' sites consumed for polymer A at conversion α is given by:

$$\lambda_A = \sum_{i=1}^{f} (p_i \lambda_{A,i}) = \alpha \sum_{i=1}^{f} (ip_i) = \alpha(\overline{M}_{n,A}/M_{A,1}) \quad (2)$$

Similarly, the average (or expected) number of 'b' sites consumed for 'polymer B with i reactive sites' at conversion α is:

$$\lambda_{B,i} = i\beta \quad (3)$$

and the average number (or the expected number) of 'b' sites consumed for polymer B at conversion α is given by:

$$\lambda_B = \sum_{i=1}^{g} (q_i \lambda_{B,i}) = \beta \sum_{i=1}^{g} (iq_i) = \beta(\overline{M}_{n,B}/M_{B,1}) \quad (4)$$

Note that $\sum_{i=1}^{f}(ip_i)$ and $\sum_{i=1}^{g}(iq_i)$ are replaced by $\overline{M}_{n,A}/M_{A,1}$ and $\overline{M}_{n,B}/M_{B,1}$, respectively (see Appendix A). $\overline{M}_{n,A}$ and $\overline{M}_{n,B}$ represent the number-average molecular weights of polymer A and polymer B respectively. $M_{A,1}$ and $M_{B,1}$ are the molecular weights of 'polymer A with one reactive site' and 'polymer B with one reactive site' respectively. It is assumed that the reactive sites are uniformly distributed on the polymer chain for both polymer A and polymer B, i.e. $M_{A,i} = iM_{A,1}$ and $M_{B,i} = iM_{B,1}$. $M_{A,i}$ and $M_{B,i}$ are the molecular weights of 'polymer A with i reactive sites' and 'polymer B with i reactive sites' respectively.

By stoichiometry, we have:

$$n_A \lambda_A = n_B \lambda_B \quad (5)$$

Substituting equations (2) and (4) into equation (5) gives:

$$n_A \alpha(\overline{M}_{n,A}/M_{A,1}) = n_B \beta(\overline{M}_{n,B}/M_{B,1}) \quad (6)$$

or:

$$\beta = n_A \alpha(\overline{M}_{n,A}/M_{A,1})/[n_B(\overline{M}_{n,B}/M_{B,1})] = r\alpha \quad (7)$$

where:

$$r = n_A(\overline{M}_{n,A}/M_{A,1})/[n_B(\overline{M}_{n,B}/M_{B,1})] \quad (8)$$

Number-average molecular weight ($\overline{M}_n$)

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

$$\overline{M}_n = m_{total}/n_{total} \quad (9)$$

where:

$$m_{total} = \sum_{i=1}^{f} (n_{A,i} M_{A,i}) + \sum_{i=1}^{g} (n_{B,i} M_{B,i}) = n_A \overline{M}_{n,A} + n_B \overline{M}_{n,B} \quad (10)$$

$$n_{total} = n_A + n_B - n_A \lambda_A = n_A + n_B - \alpha n_A(\overline{M}_{n,A}/M_{A,1}) \quad (11)$$

or:

$$n_{total} = n_A + n_B - n_B \lambda_B = n_A + n_B - r\alpha n_B(\overline{M}_{n,B}/M_{B,1}) \quad (12)$$

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 equation (11) or equation (12), represents the number of molecules present at conversion α. Therefore, $\overline{M}_n$ of the resulting copolymer is a function of $\overline{M}_{n,A}$, $\overline{M}_{n,B}$ and conversion α.

Weight-average molecular weight ($\overline{M}_w$)

Pick a reactive site 'a' at random from a randomly chosen 'polymer A with i reactive sites' (denoted A_i) as sketched in *Figure 1*. The random variable, $W_{A,i}^{out}$, is the weight attached to 'a' looking out from its parent molecule in the direction $\xrightarrow{1}$. Based on assumptions (1) and (2) above, $W_{A,i}^{out}$ is independent of the number of reactive sites of polymer A to which the randomly chosen 'a' belongs; therefore $W_{A,i}^{out}$ can be represented as W_A^{out}. Then:

$$W_A^{out} = \begin{cases} 0, \; P = 1 - \alpha \text{ (if site a does not react)} \\ W_{B,i}^{in}, \; P = \alpha[iq_i / \sum_{i=1}^{g} (iq_i)] \; (i = 1, 2, \ldots, g) \text{ (if site a reacts with site b)} \end{cases}$$

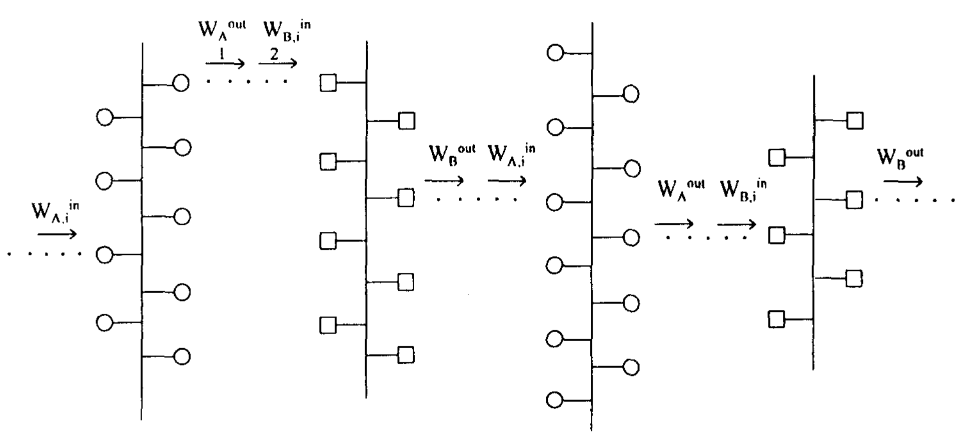

Figure 1 Schematic illustration of polymer formed by grafting reaction between polymer A and polymer B, both polydisperse: ○, site 'a' on polymer A; □, site 'b' on polymer B; ·····, grafting reaction between polymer A and polymer B

where P denotes probability and $W^{in}_{B,i}$ is the weight attached to site 'b' of 'polymer B with i reactive sites' (denoted B_i) looking along $\rightarrow^2$ into its parent molecule. Since the number of reactive sites of polymer B to which $W^{in}_{B,i}$ belongs determines the number of sites on that polymer B available for reaction, the subscript i in $W^{in}_{B,i}$ is needed to specify the number of reactive sites of polymer B to which $W^{in}_{B,i}$ belongs (similarly, $W^{out}_{B,i}$ can be represented as W^{out}_{B} and the subscript i in $W^{in}_{A,i}$ is needed to specify the number of reactive sites of polymer A to which $W^{in}_{A,i}$ belongs). Since the number of reactive sites on all the B_i is $n_B iq_i$ and the total number of reactive sites 'b' in the system is $\sum_{i=1}^{g}(n_B iq_i)$, the probability that a randomly chosen reactive site 'b' belongs to B_i can be denoted $iq_i/\sum_{i=1}^{g}(iq_i)$.

As α represents the fraction of 'a' sites that have reacted (i.e. α represents the probability of a randomly chosen 'a' reacting with 'b'), the probability of a randomly chosen 'a' reacting with B_i is $\alpha[iq_i/\sum_{i=1}^{g}(iq_i)]$. By the law of total probability for expectation, we have:

$$E(W^{out}_{A}) = \sum_{i=1}^{g}\{E(W^{in}_{B,i})\cdot\alpha[iq_i/\sum_{i=1}^{g}(iq_i)]\} + 0\cdot(1-\alpha)$$

$$= \alpha[\sum_{i=1}^{g} iq_i E(W^{in}_{B,i})]/\sum_{i=1}^{g}(iq_i) \qquad (13)$$

$$= \alpha M_{B,1}[\sum_{i=1}^{g} iq_i E(W^{in}_{B,i})]\,\overline{M}_{n,B}$$

where $\sum_{i=1}^{g}(iq_i)$ is replaced by $\overline{M}_{n,B}/M_{B,1}$ (see Appendix A). A similar argument can be applied to W^{out}_{B}. Therefore:

$$E(W^{out}_{B}) = r\alpha M_{A,1}[\sum_{i=1}^{f} ip_i E(W^{in}_{A,i})]\,\overline{M}_{n,A} \qquad (14)$$

Considering the copolymerization between two polydisperse polymers (polymer A and polymer B), we can derive for a randomly chosen 'polymer A with i reactive sites' (denoted A_i):

$$W^{in}_{A,i} = M_{A,i} + \sum_{j=1}^{i-1} W^{out}_{A,j} \; (i = 1, 2, \ldots, f) \qquad (15)$$

where $M_{A,i}$ is the molecular weight of A_i and $W^{out}_{A,j}$ is the weight attached to the jth branch of a randomly chosen A_i. Note that A_i has i reactive sites and $W^{out}_{A,j}$ ($j = 1,2,\ldots,i-1$) are independent random variables with the same distribution: W^{out}_{A}. Similarly, for a randomly chosen 'polymer B with i reactive sites' (denoted B_i):

$$W^{in}_{B,i} = M_{B,i} + \sum_{j=1}^{i-1} W^{out}_{B,j} \; (i = 1, 2, \ldots, g) \qquad (16)$$

where $M_{B,i}$ is the molecular weight of B_i and $W^{out}_{B,j}$ is the weight attached to the jth branch of a randomly chosen B_i. Note that B_i has i reactive sites and $W^{out}_{B,j}$ ($j = 1,2,\ldots,i-1$) are independent random variables with the same distribution: W^{out}_{B}. These two sets of equations (equations (15) and (16)) will recycle due to the recursive nature of the structure. Taking the expectation of equation (15) leads (see Appendix B) to:

$$E(W^{in}_{A,i}) = M_{A,i} + (i-1)E(W^{out}_{A}) \; (i = 1, 2, \ldots, f) \qquad (17)$$

Multiplying both sides of the above equation by ip_i and summing from $i = 1$ to f, we have:

$$\sum_{i=1}^{f}[ip_i E(W^{in}_{A,i})]$$

$$= \sum_{i=1}^{f}(ip_i M_{A,i}) + E(W^{out}_{A})\sum_{i=1}^{f}[i(i-1)p_i] \qquad (18)$$

$$= (\overline{M}_{n,A}\overline{M}_{w,A})/M_{A,1} + E(W^{out}_{A})[(\overline{M}_{n,A}\overline{M}_{w,A})/M^2_{A,1} - \overline{M}_{n,A}/M_{A,1}]$$

where $\sum_{i=1}^{f}(ip_i M_{A,i})$, $\sum_{i=1}^{f}(ip_i)$ and $\sum_{i=1}^{f}(i^2 p_i)$ are replaced by $(\overline{M}_{n,A}\overline{M}_{w,A})/M_{A,1}$, $\overline{M}_{n,A}/M_{A,1}$ and $(\overline{M}_{n,A}\overline{M}_{w,A})/M^2_{A,1}$ respectively (see Appendix A). $\overline{M}_{w,A}$ represents the weight-average molecular weight of polymer A. A similar argument can be applied to $W^{in}_{B,i}$. Therefore:

$$E(W^{in}_{B,i}) = M_{B,i} + (i-1)E(W^{out}_{B}) \; (i = 1, 2, \ldots, g) \qquad (19)$$

and

$$\sum_{i=1}^{g}[iq_i E(W^{in}_{B,i})] = (\overline{M}_{n,B}\overline{M}_{w,B})/M_{B,1} + E(W^{out}_{B}) \times [(\overline{M}_{n,B}\overline{M}_{w,B})/M^2_{B,1} - \overline{M}_{n,B}/M_{B,1}] \qquad (20)$$

Substituting equations (18) and (20) into equations (13) and (14), $E(W^{out}_{A})$ and $E(W^{out}_{B})$ can be solved simultaneously as:

$$E(W^{out}_{A}) = \alpha[\overline{M}_{w,B} + r\alpha\overline{M}_{w,A}(\overline{M}_{w,B}/M_{B,1} - 1)]/[1 - r\alpha^2(\overline{M}_{w,A}/M_{A,1} - 1)(\overline{M}_{w,B}/M_{B,1} - 1)] \qquad (21)$$

$$E(W^{out}_{B}) = r\alpha[\overline{M}_{w,A} + \alpha\overline{M}_{w,B}(\overline{M}_{w,A}/M_{A,1} - 1)]/[1 - r\alpha^2(\overline{M}_{w,A}/M_{A,1} - 1)(\overline{M}_{w,B}/M_{B,1} - 1)] \qquad (22)$$

The molecular weight, $W_{A,i}$, of the entire molecule to which a randomly chosen 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:

$$W_{A,i} = M_{A,i} + \sum_{j=1}^{i} W^{out}_{A,j} \; (i = 1, 2, \ldots, f) \qquad (23)$$

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

$$E(W_{A,i}) = M_{A,i} + iE(W^{out}_{A}) \; (i = 1, 2, \ldots, f) \qquad (24)$$

A similar argument can be applied to $W_{B,i}$, the molecular weight of the entire molecule to which a randomly chosen B_i belongs. Then:

$$E(W_{B,i}) = M_{B,i} + iE(W^{out}_{B}) \; (i = 1, 2, \ldots, g) \qquad (25)$$

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

$$y_{A,i} = n_{A,i}M_{A,i}/[\sum_{i=1}^{f}(n_{A,i}M_{A,i}) + \sum_{i=1}^{g}(n_{B,i}M_{B,i})] \qquad (26)$$

$$= n_{A,i}M_{A,i}/(n_A\overline{M}_{n,A} + n_B\overline{M}_{n,B})$$

$$y_{B,i} = n_{B,i}M_{B,i}/[\sum_{i=1}^{f}(n_{A,i}M_{A,i}) + \sum_{i=1}^{g}(n_{B,i}M_{B,i})] \quad (27)$$
$$= n_{B,i}M_{B,i}/(n_A\overline{M}_{n,A} + n_B\overline{M}_{n,B})$$

By definition, $\overline{M}_w$, the first moment of the molecular weight distribution, can be expressed as:

$$\overline{M}_w = E(W) = \sum_{i=1}^{f}[y_{A,i}E(W_{A,i})] + \sum_{i=1}^{g}[y_{B,i}E(W_{B,i})]$$
$$= \{\sum_{i=1}^{f}[n_{A,i}M_{A,i}E(W_{A,i})] + \sum_{i=1}^{g}[n_{B,i}M_{B,i}E(W_{B,i})]\}/ (n_A\overline{M}_{n,A} + n_B\overline{M}_{n,B}) \quad (28)$$

where:

$$\sum_{i=1}^{f}[n_{A,i}M_{A,i}E(W_{A,i})] = n_A\sum_{i=1}^{f}\{p_iM_{A,i}[M_{A,i} + iE(W_A^{out})]\}$$
$$= n_A[\sum_{i=1}^{f}(p_iM_{A,i}^2) + E(W_A^{out})\sum_{i=1}^{f}(ip_iM_{A,i})] \quad (29)$$
$$= n_A[\overline{M}_{n,A}\overline{M}_{w,A} + E(W_A^{out})(\overline{M}_{n,A}M_{w,A})/M_{A,1}]$$

Note that $\sum_{i=1}^{f}(p_iM_{A,i}^2)$ and $\sum_{i=1}^{f}(ip_iM_{A,i})$ are replaced by $\overline{M}_{n,A}\overline{M}_{w,A}$ and $(\overline{M}_{n,A}\overline{M}_{w,A})/M_{A,1}$ respectively (see Appendix A). Similarly:

$$\sum_{i=1}^{g}n_{B,i}M_{B,i}E(W_{B,i}) = n_B[\overline{M}_{n,B}\overline{M}_{w,B} + E(W_B^{out}) \times (\overline{M}_{n,B}\overline{M}_{w,B})/M_{B,1}] \quad (30)$$

Since $E(W_A^{out})$ and $E(W_B^{out})$ are given in equations (21) and (22), substituting equations (29) and (30) into equation (28) gives:

$$\overline{M}_w = y_A\frac{\overline{M}_{w,A} + \alpha(\overline{M}_{w,A}/M_{A,1})[\overline{M}_{w,B} + r\alpha\overline{M}_{w,A}(\overline{M}_{w,B}/M_{B,1} - 1)]}{1 - r\alpha^2(\overline{M}_{w,A}/M_{A,1} - 1)(\overline{M}_{w,B}/M_{B,1} - 1)} + y_B\frac{\overline{M}_{w,B} + r\alpha(\overline{M}_{w,B}/M_{B,1})[\overline{M}_{w,A} + \alpha\overline{M}_{w,B}(\overline{M}_{w,A}/M_{A,1} - 1)]}{1 - r\alpha^2(\overline{M}_{w,A}/M_{A,1} - 1)(\overline{M}_{w,B}/M_{B,1} - 1)} \quad (31)$$

where y_A and y_B represent the initial weight fractions of polymer A and polymer B in the system, respectively:

$$y_A = \sum_{i=1}^{f}(n_{A,i}M_{A,i})/[\sum_{i=1}^{f}(n_{A,i}M_{A,i}) + \sum_{i=1}^{g}(n_{B,i}M_{B,i})]$$
$$= n_A\overline{M}_{n,A}/(n_A\overline{M}_{n,A} + n_B\overline{M}_{n,B}) \quad (32)$$

$$y_B = \sum_{i=1}^{g}(n_{B,i}M_{B,i})/[\sum_{i=1}^{f}(n_{A,i}M_{A,i}) + \sum_{i=1}^{g}(n_{B,i}M_{B,i})]$$
$$= n_B\overline{M}_{n,B}/(n_A\overline{M}_{n,A} + n_B\overline{M}_{n,B}) \quad (33)$$

Therefore, $\overline{M}_w$ of the resulting copolymer, given in equation (31), is a function of $\overline{M}_{n,A}$, $\overline{M}_{n,B}$, $\overline{M}_{w,A}$, $\overline{M}_{w,B}$ and conversion α. The value of α at which $\overline{M}_w$ diverges is called the gel point (α_{gel}). As shown in equation (31), $\overline{M}_w$ becomes infinite when:

$$\alpha_{gel}^2 = 1/[r(\overline{M}_{w,A}/M_{A,1} - 1)(\overline{M}_{w,B}/M_{B,1} - 1)] \quad (34)$$

For the monodisperse polymer A and polymer B, we have $\overline{M}_{n,A} = \overline{M}_{w,A}$ and $\overline{M}_{n,B} = \overline{M}_{w,B}$. Then the number of reactive sites 'a' on polymer A is:

$$f = \overline{M}_{w,A}/M_{A,1} \quad (35)$$

Similarly, the number of reactive sites 'b' on polymer B is:

$$g = \overline{M}_{w,B}/M_{B,1} \quad (36)$$

Substituting equations (35) and (36) into equation (31), $\overline{M}_w$ reduces to the result derived by Macosko and Miller[13] and Shiau[16] for a copolymerization system between n_A moles of f-functional A-type monomers and n_B moles of g-functional B-type monomers.

Z-average molecular weight ($\overline{M}_z$)

$\overline{M}_z$ is defined as the ratio of the second moment of the molecular weight distribution, $E(W^2)$, to the first moment, $E(W)$. Note that $\overline{M}_w$ represents $E(W)$. Thus:

$$\overline{M}_z = E(W^2)/E(W) \quad (37)$$

Taking the square of both sides of equation (15) yields:

$$(W_{A,i}^{in})^2 = M_{A,i}^2 + 2M_{A,i}(\sum_{j=1}^{i-1}W_{A,j}^{out}) + (\sum_{j=1}^{i-1}W_{A,j}^{out})^2 \quad (i = 1, 2, \ldots, f) \quad (38)$$

Taking the expectation of the above equation (see Appendix B) gives:

$$E[(W_{A,i}^{in})^2] = M_{A,i}^2 + 2(i-1)M_{A,i}E(W_A^{out}) + (i-1)E[(W_A^{out})^2] + (i-1)(i-2)[E(W_A^{out})]^2 \quad (i = 1, 2, \ldots, f) \quad (39)$$

Multiplying both sides of the above equation by ip_i and summing from $i = 1$ to f, we have:

$$\sum_{i=1}^{f}\{ip_iE[(W_{A,i}^{in})^2]\} = \sum_{i=1}^{f}(ip_iM_{A,i}^2) + 2E(W_A^{out})\sum_{i=1}^{f}[i(i-1)p_iM_{A,i}] + E[(W_A^{out})^2]\sum_{i=1}^{f}[i(i-1)p_i] + [E(W_A^{out})]^2\sum_{i=1}^{f}[i(i-1)(i-2)p_i] \quad (40)$$

where the terms $\sum_{i=1}^{f}(ip_iM_{A,i}^2)$, $\sum_{i=1}^{f}(ip_iM_{A,i})$, $\sum_{i=1}^{f}(i^2p_iM_{A,i})$, $\sum_{i=1}^{f}(ip_i)$, $\sum_{i=1}^{f}(i^2p_i)$ and $\sum_{i=1}^{f}(i^3p_i)$ can be replaced by the average properties of polymer A (see Appendix A). Similarly, we can derive:

$$\sum_{i=1}^{g} \{iq_i E[(W_{B,i}^{in})^2]\} = \sum_{i=1}^{g} (iq_i M_{B,i}^2) + 2E(W_B^{out}) \sum_{i=1}^{g} [i(i-1)q_i M_{B,i}] + E[(W_B^{out})^2] \sum_{i=1}^{g} [i(i-1)q_i] + [E(W_B^{out})]^2 \sum_{i=1}^{g} [i(i-1)(i-2)q_i] \quad (41)$$

Then, similar to the development of equations (13) and (14), if the random variables $(W_A^{out})^2$ and $(W_B^{out})^2$ are used instead of W_A^{out} and W_B^{out} respectively, we have:

$$E[(W_A^{out})^2] = \alpha M_{B,1} \{ \sum_{i=1}^{g} iq_i E[(W_{B,i}^{in})^2] \} / \overline{M}_{n,B} \quad (42)$$

$$E[(W_B^{out})^2] = r\alpha M_{A,1} \{ \sum_{i=1}^{f} ip_i E[(W_{A,i}^{in})^2] \} / \overline{M}_{n,A} \quad (43)$$

Thus, by substitution of equations (40) and (41) into equations (42) and (43), $E[(W_A^{out})^2]$ and $E[(W_B^{out})^2]$ can be solved simultaneously, since $E(W_A^{out})$ and $E(W_B^{out})$ have been given in equations (21) and (22).

Taking the square on both sides of equation (23) yields:

$$W_{A,i}^2 = M_{A,i}^2 + 2M_{A,i}(\sum_{j=1}^{i} W_{A,j}^{out}) + (\sum_{j=1}^{i} W_{A,j}^{out})^2 \quad (i = 1, 2, \ldots, f) \quad (44)$$

Taking the expectation of the above equation (see Appendix B) gives:

$$E(W_{A,i}^2) = M_{A,i}^2 + 2iM_{A,i}E(W_A^{out}) + iE[(W_A^{out})^2] + i(i-1)[E(W_A^{out})]^2 \quad (i = 1, 2, \ldots, f) \quad (45)$$

Similarly, we can derive:

$$E(W_{B,i}^2) = M_{B,i}^2 + 2iM_{B,i}E(W_B^{out}) + iE[(W_B^{out})^2] + i(i-1)[E(W_B^{out})]^2 \quad (i = 1, 2, \ldots, g) \quad (46)$$

Then $E(W^2)$, by definition, can be expressed as:

$$E(W^2) = \sum_{i=1}^{f} [y_{A,i}E(W_{A,i}^2)] + \sum_{i=1}^{g} [y_{B,i}E(W_{B,i}^2)] = \{ \sum_{i=1}^{f} [n_{A,i}M_{A,i}E(W_{A,i}^2)] + \sum_{i=1}^{g} [n_{B,i}M_{B,i}E(W_{B,i}^2)] \} / (n_A\overline{M}_{n,A} + n_B\overline{M}_{n,B}) \quad (47)$$

where:

$$\sum_{i=1}^{f} [n_{A,i}M_{A,i}E(W_{A,i}^2)] = n_A \sum_{i=1}^{f} [p_i M_{A,i} E(W_{A,i}^2)] = n_A \{ \sum_{i=1}^{f} (p_i M_{A,i}^3) + 2E(W_A^{out}) \sum_{i=1}^{f} (ip_i M_{A,i}^2) + E[(W_A^{out})^2] \times \sum_{i=1}^{f} (ip_i M_{A,i}) + [E(W_A^{out})]^2 \sum_{i=1}^{f} [i(i-1)p_i M_{A,i}] \} \quad (48)$$

$$\sum_{i=1}^{g} [n_{B,i}M_{B,i}E(W_{B,i}^2)] = n_B \sum_{i=1}^{g} [q_i M_{B,i} E(W_{B,i}^2)] = n_B \{ \sum_{i=1}^{g} (q_i M_{B,i}^3) + 2E(W_B^{out}) \sum_{i=1}^{g} (iq_i M_{B,i}^2) + E[(W_B^{out})^2] \times \sum_{i=1}^{g} (iq_i M_{B,i}) + [E(W_B^{out})]^2 \sum_{i=1}^{g} [i(i-1)q_i M_{B,i}] \} \quad (49)$$

Note that the terms such as $\sum_{i=1}^{f}(p_i M_{A,i}^3)$, $\sum_{i=1}^{f}(ip_i M_{A,i}^2)$, $\sum_{i=1}^{g}(q_i M_{B,i}^3)$, $\sum_{i=1}^{g}(iq_i M_{B,i}^2)$, etc., can be replaced by the average properties of polymer A and polymer B, respectively (see Appendix A).

Substituting equations (48) and (49) into equation (47), we can obtain a complete formula for $E(W^2)$. Thus, $\overline{M}_z$ can be calculated by equation (37) as a function of the average properties of polymer A and polymer B, and conversion α. For the monodisperse case, $\overline{M}_z$ reduces to the result derived by Macosko and Miller[13] and Shiau[16].

Z + 1-average molecular weight ($\overline{M}_{z+1}$) and other higher average molecular weights

$\overline{M}_{z+1}$ is defined as the ratio of the third moment of the molecular weight distribution, $E(W^3)$, to the second moment, $E(W^2)$. Thus:

$$\overline{M}_{z+1} = E(W^3)/E(W^2) \quad (50)$$

The expression for $E(W^3)$ is derived as follows. Taking the third power on both sides of equation (15) yields:

$$(W_{A,i}^{in})^3 = M_{A,i}^3 + 3M_{A,i}^2(\sum_{j=1}^{i-1} W_{A,j}^{out}) + 3M_{A,i}(\sum_{j=1}^{i-1} W_{A,j}^{out})^2 + (\sum_{j=1}^{i-1} W_{A,j}^{out})^3 \quad (i = 1, 2, \ldots, f) \quad (51)$$

Taking the expectation of the above equation (see Appendix B) gives:

$$E[(W_{A,i}^{in})^3] = M_{A,i}^3 + 3(i-1)M_{A,i}^2 E(W_A^{out}) + 3(i-1)M_{A,i}E[(W_A^{out})^2] + 3(i-1)(i-2)M_{A,i}[E(W_A^{out})]^2 + (i-1)E[(W_A^{out})^3] + 3(i-1)(i-2)E[(W_A^{out})^2]E(W_A^{out}) + (i-1)(i-2)(i-3)[E(W_A^{out})]^3 \quad (i = 1, 2, \ldots f) \quad (52)$$

Multiplying both sides of the above equation by ip_i and summing from $i = 1$ to f, we have:

$$\sum_{i=1}^{f}\{ip_iE[(W_{A,i}^{in})^3]\}$$
$$= \sum_{i=1}^{f}(ip_iM_{A,i}^3) + 3E(W_A^{out})\sum_{i=1}^{f}[i(i-1)p_iM_{A,i}^2]$$
$$+ 3E[(W_A^{out})]^2\sum_{i=1}^{f}[i(i-1)p_iM_{A,i}]$$
$$+ 3[E(W_A^{out})]^2\sum_{i=1}^{f}[i(i-1)(i-2)p_iM_{A,i}] \quad (53)$$
$$+ E[(W_A^{out})^3]\sum_{i=1}^{f}[i(i-1)p_i]$$
$$+ 3E[(W_A^{out})^2]E(W_A^{out})\sum_{i=1}^{f}[i(i-1)(i-2)p_i]$$
$$+ [E(W_A^{out})]^3\sum_{i=1}^{f}[i(i-1)(i-2)(i-3)p_i]$$

Similarly, we can derive:

$$\sum_{i=1}^{g}\{iq_iE[(W_{B,i}^{in})^3]\}$$
$$= \sum_{i=1}^{g}(iq_iM_{B,i}^3) + 3E(W_B^{out})\sum_{i=1}^{g}[i(i-1)q_iM_{B,i}^2]$$
$$+ 3E[(W_B^{out})^2]\sum_{i=1}^{g}[i(i-1)q_iM_{B,i}]$$
$$+ 3[(E(W_B^{out})]^2\sum_{i=1}^{g}[i(i-1)(i-2)q_iM_{B,i}]$$
$$+ E[(W_B^{out})^3]\sum_{i=1}^{g}[i(i-1)q_i]$$
$$+ 3E[(W_B^{out})^2]E(W_B^{out})\sum_{i=1}^{g}[i(i-1)(i-2)q_i]$$
$$+ [E(W_B^{out})]^3\sum_{i=1}^{g}[i(i-1)(i-2)(i-3)q_i] \quad (54)$$

Then, similar to the development of equations (13) and (14), the random variables $(W_A^{out})^3$ and $(W_B^{out})^3$ are used instead of W_A^{out} and W_B^{out} respectively, and we have:

$$E[(W_A^{out})^3] = \alpha M_{B,1}\{\sum_{i=1}^{g} iq_iE[(W_{B,i}^{in})^3]\}/\overline{M}_{n,B} \quad (55)$$

$$E[(W_B^{out})^3] = r\alpha M_{A,1}\{\sum_{i=1}^{f} ip_iE[(W_{A,i}^{in})^3]\}/\overline{M}_{n,A} \quad (56)$$

Thus, by substitution of equations (53) and (54) into equations (55) and (56), $E[(W_A^{out})^3]$ and $E[(W_B^{out})^3]$ can be solved simultaneously, since $E(W_A^{out})$, $E(W_B^{out})$, $E[(W_A^{out})^2]$ and $E[(W_B^{out})^2]$ have been solved previously.

Taking the third power on both sides of equation (23) yields:

$$W_{A,i}^3 = M_{A,i}^3 + 3M_{A,i}^2(\sum_{j=1}^{i} W_{A,j}^{out}) + 3M_{A,i}(\sum_{j=1}^{i} W_{A,j}^{out})^2$$
$$+ (\sum_{j=1}^{i} W_{A,j}^{out})^3 \quad (i = 1, 2, \ldots, f) \quad (57)$$

Taking the expectation of the above equation (see Appendix B) gives:

$$E(W_{A,i}^3) = M_{A,i}^3 + 3iM_{A,i}^2E(W_A^{out}) + 3iM_{A,i}E[(W_A^{out})^2]$$
$$+ 3i(i-1)M_{A,i}[E(W_A^{out})]^2 + iE[(W_A^{out})^3]$$
$$+ 3i(i-1)E[(W_A^{out})^2]E(W_A^{out}) + i(i-1)(i-2)$$
$$\times [E(W_A^{out})]^3 \quad (i = 1, 2, \ldots, f) \quad (58)$$

Similarly, we can derive:

$$E(W_{B,i}^3) = M_{B,i}^3 + 3iM_{B,i}^2E(W_B^{out}) + 3iM_{B,i}E[(W_B^{out})^2]$$
$$+ 3i(i-1)M_{B,i}[E(W_B^{out})]^2 + iE[(W_B^{out})^3]$$
$$+ 3i(i-1)E[(W_B^{out})^2]E(W_B^{out}) + i(i-1)(i-2)$$
$$\times [E(W_B^{out})]^3 \quad (i = 1, 2, \ldots, g) \quad (59)$$

Then $E(W^3)$, by definition, can be expressed as:

$$E(W^3) = \sum_{i=1}^{f}[y_{A,i}E(W_{A,i}^3)] + \sum_{i=1}^{g}[y_{B,i}E(W_{B,i}^3)]$$
$$= \{\sum_{i=1}^{f}[n_{A,i}M_{A,i}E(W_{A,i}^3)] + \sum_{i=1}^{g}[n_{B,i}M_{B,i}E(W_{B,i}^3)]\}/$$
$$\times (n_A\overline{M}_{n,A} + n_B\overline{M}_{n,B}) \quad (60)$$

where:

$$\sum_{i=1}^{f}[n_{A,i}M_{A,i}E(W_{A,i}^3)]$$
$$= n_A\sum_{i=1}^{f}[p_iM_{A,i}E(W_{A,i}^3)]$$
$$= n_A\{\sum_{i=1}^{f}(p_iM_{A,i}^4) + 3E(W_A^{out})\sum_{i=1}^{f}(ip_iM_{A,i}^3)$$
$$+ 3E[(W_A^{out})^2]\sum_{i=1}^{f}(ip_iM_{A,i}^2)$$
$$+ 3[E(W_A^{out})]^2\sum_{i=1}^{f}[i(i-1)p_iM_{A,i}^2] \quad (61)$$
$$+ E[(W_A^{out})^3]\sum_{i=1}^{f}(ip_iM_{A,i})$$
$$+ 3E[(W_A^{out})^2]E(W_A^{out})\sum_{i=1}^{f}[i(i-1)p_iM_{A,i}]$$
$$+ [(E(W_A^{out})]^3\sum_{i=1}^{f}[i(i-1)(i-2)p_iM_{A,i}]\}$$

$$\sum_{i=1}^{g}[n_{B,i}M_{B,i}E(W_{B,i}^3)]$$
$$=n_B\sum_{i=1}^{g}[q_iM_{B,i}E(W_{B,i}^3)]$$
$$=n_B\{\sum_{i=1}^{g}(q_iM_{B,i}^4)+3E(W_B^{out})\sum_{i=1}^{g}(iq_iM_{B,i}^3)$$
$$+3E[(W_B^{out})^2]\sum_{i=1}^{g}(iq_iM_{B,i}^2)$$
$$+3[E(W_B^{out})]^2\sum_{i=1}^{g}[i(i-1)q_iM_{B,i}^2] \quad (62)$$
$$+E[(W_B^{out})^3]\sum_{i=1}^{g}(iq_iM_{B,i})$$
$$+3E[(W_B^{out})^2]E(W_B^{out})\sum_{i=1}^{g}[i(i-1)q_iM_{B,i}]$$
$$+[(E(W_B^{out})]^3\sum_{i=1}^{g}[i(i-1)(i-2)q_iM_{B,i}]\}$$

Substituting equations (61) and (62) into equation (60), we can obtain a complete formula for $E(W^3)$. Thus $\overline{M}_{z+1}$ can be calculated by equation (50) as a function of the average properties of polymer A and polymer B, and conversion α. For the monodisperse case, $\overline{M}_{z+1}$ reduces to the result derived by Shiau[16].

Higher moments of the molecular weight distribution can be derived by a similar approach. In general, $E(W^n)$ is developed as follows. Taking the nth power on both sides of equations (15) and (16) yields:

$$(W_{A,i}^{in})^n=M_{A,i}^n+nM_{A,i}^{n-1}(\sum_{j=1}^{i-1}W_{A,j}^{out})$$
$$+\frac{n(n-1)}{2!}M_{A,i}^{n-2}(\sum_{j=1}^{i-1}W_{A,j}^{out})^2$$
$$+\frac{n(n-1)(n-2)}{3!}M_{A,i}^{n-3}(\sum_{j=1}^{i-1}W_{A,j}^{out})^3+\dots$$
$$+(\sum_{j=1}^{i-1}W_{A,j}^{out})^n \quad (i=1,2,\dots,f) \quad (63)$$

$$(W_{B,i}^{in})^n=M_{B,i}^n+nM_{B,i}^{n-1}(\sum_{j=1}^{i-1}W_{B,j}^{out})$$
$$+\frac{n(n-1)}{2!}M_{B,i}^{n-2}(\sum_{j=1}^{i-1}W_{B,j}^{out})^2$$
$$+\frac{n(n-1)(n-2)}{3!}M_{B,i}^{n-3}(\sum_{j=1}^{i-1}W_{B,j}^{out})^3+\dots$$
$$+(\sum_{j=1}^{i-1}W_{B,j}^{out})^n \quad (i=1,2,\dots,g) \quad (64)$$

As described previously, $E[(W_{A,i}^{in})^n]$ and $E[(W_{B,i}^{in})^n]$ can be obtained by taking the expectation of the above equations (see Appendix B). Then, $\sum_{i=1}^{f}\{ip_iE[(W_A^{in})^n]\}$ and $\sum_{i=1}^{g}\{iq_iE[(W_B^{in})^n]\}$ can be derived. Similar to the development of equations (13) and (14), the random variables $(W_A^{out})^n$ and $(W_B^{out})^n$ are used instead of W_A^{out} and W_B^{out} respectively, and we have:

$$E[(W_A^{out})^n]=\alpha M_{B,1}\{\sum_{i=1}^{g}iq_iE[(W_{B,i}^{in})^n]\}/\overline{M}_{n,B} \quad (65)$$

$$E[(W_B^{out})^n]=r\alpha M_{A,1}\{\sum_{i=1}^{f}ip_iE[(W_{A,i}^{in})^n]\}/\overline{M}_{n,A} \quad (66)$$

Thus $E[(W_A^{out})^n]$ and $E[(W_B^{out})^n]$ can be determined simultaneously.

Taking the nth power on both sides of equation (23) yields:

$$W_{A,i}^n=M_{A,i}^n+nM_{A,i}^{n-1}(\sum_{j=1}^{i}W_{A,j}^{out})$$
$$+\frac{n(n-1)}{2!}M_{A,i}^{n-2}(\sum_{j=1}^{i}W_{A,j}^{out})^2$$
$$+\frac{n(n-1)(n-2)}{3!}M_{A,i}^{n-3}(\sum_{j=1}^{i}W_{A,j}^{out})^3+\dots$$
$$+(\sum_{j=1}^{i}W_{A,j}^{out})^n \quad (i=1,2,\dots,f) \quad (67)$$

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

$$E(W^n)=\sum_{i=1}^{f}[y_{A,i}E(W_{A,i}^n)]+\sum_{i=1}^{g}[y_{B,i}E(W_{B,i}^n)]$$
$$=\{\sum_{i=1}^{f}[n_{A,i}M_{A,i}E(W_{A,i}^n)]+\sum_{i=1}^{g}[n_{B,i}M_{B,i}E(W_{B,i}^n)]\}/$$
$$(n_A\overline{M}_{n,A}+n_B\overline{M}_{n,B}) \quad (68)$$

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

RESULTS AND DISCUSSION

A model is presented in this paper for determining, without calculation of the complete distribution, the gel point, $\overline{M}_n$, $\overline{M}_w$, $\overline{M}_z$, $\overline{M}_{z+1}$ and other higher average molecular weights of the resulting copolymer as a function of the reaction conversion and the average properties of two polydisperse reactive polymers.

Numerical results of the model are illustrated in *Figure 2* for the grafting system studied by Nie *et al.*[18]: the hydroxyl groups on cellulose acetate (CA) react with the anhydride groups on styrene–maleic anhydride random copolymer (SMA) to form graft copolymers. There are 85 hydroxyl groups of CA for a number-average molecular weight of 46 000 (polymer A) and 90 anhydrides of SMA for a number-average molecular weight of 120 000 (polymer B). Therefore, $\overline{M}_{n,A}=46\,000$, $\overline{M}_{n,B}=120\,000$, $M_{A,1}=\overline{M}_{n,A}/85$ and $M_{B,1}=\overline{M}_{n,B}/90$. In the calculation, it is assumed for simlicity that $n_A=1$, $n_B=4$, $\overline{M}_{w,A}/\overline{M}_{n,A}=\overline{M}_{z,A}/\overline{M}_{w,A}=\overline{M}_{z+1,A}/\overline{M}_{z,A}=1.5$ and $\overline{M}_{w,B}/\overline{M}_{n,B}=\overline{M}_{z,B}/\overline{M}_{w,B}=\overline{M}_{z+1,B}/\overline{M}_{z,B}=1.5$.

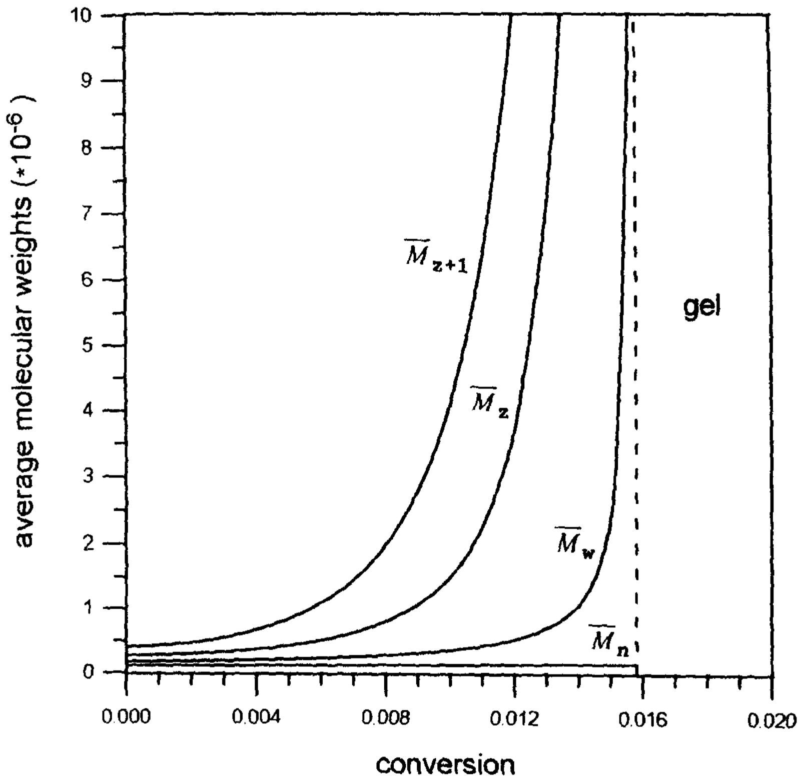

Figure 2 $\overline{M}_n$, $\overline{M}_w$, $\overline{M}_z$ and $\overline{M}_{z+1}$ *versus* conversion α for the polymer formed by grafting reaction between polydisperse polymer A and polymer B

$\overline{M}_n$, $\overline{M}_w$, $\overline{M}_z$, $\overline{M}_{z+1}$ of the resulting copolymer versus reaction conversion (α) are plotted in *Figure 2*. It is observed that $\overline{M}_n < \overline{M}_w < \overline{M}_z < \overline{M}_{z+1}$, which agrees with the definition of the average properties. *Figure 2* also shows that gel point occurs at $\alpha = 0.0158$ as calculated in equation (34), which shows that at the gel point, the average number of hydroxyl groups of CA consumed (λ_A) is 1.34 and the average number of anhydride groups of SMA consumed (λ_B) is 0.336 [as derived in equation (2) and equation (4), $\lambda_A = \alpha(\overline{M}_{n,A}/M_{A,1})$ and $\lambda_B = \beta(\overline{M}_{n,B}/M_{B,1})$]. Therefore it can be concluded that the percentage conversions of the two reactive groups are quite small in the pre-gel region. Besides, it seems probable that one would start with a bimodal distribution in the early stages of reaction if the two reacting polymers have a different initial average molecular weight, which would tend to narrow to a monomodal distribution of much higher average molecular weight prior to gelation.

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 the nth power on both sides of these equations and then taking the expectation of the equations thus obtained. The model developed in this paper provides a general algorithm for solving for these average properties by computer.

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APPENDIX A:

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

$$\overline{M}_{n,A} = [\sum_{i=1}^{f} (n_{A,i}M_{A,i})]/n_A \qquad (A1)$$

$$\overline{M}_{w,A} = [\sum_{i=1}^{f} (n_{A,i}M_{A,i}^2)]/[\sum_{i=1}^{f} (n_{A,i}M_{A,i})] \qquad (A2)$$

$$\overline{M}_{z,A} = [\sum_{i=1}^{f} (n_{A,i}M_{A,i}^3)]/[\sum_{i=1}^{f} (n_{A,i}M_{A,i}^2)] \qquad (A3)$$

$$M_{z+1,A} = [\sum_{i=1}^{f} (n_{A,i}M_{A,i}^4)]/[\sum_{i=1}^{f} (n_{A,i}M_{A,i}^3)] \qquad (A4)$$

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

$$\sum_{i=1}^{f} (ip_i) = \sum_{i=1}^{f} (iM_{A,1}n_{A,i}/M_{A,1}n_A) = [\sum_{i=1}^{f} (n_{A,i}M_{A,i})]/(n_A M_{A,1}) = \overline{M}_{n,A}/M_{A,1} \qquad (A5)$$

Note that $n_A = \sum_{i=1}^{f} n_{A,i}$ and $p_i = n_{A,i}/n_A$. $M_{A,1}$ is the molecular weight of 'polymer A with one reactive site'. The reactive sites 'a' are assumed uniformly distributed on the polymer chain, i.e. $M_{A,i} = iM_{A,1}$. Similarly:

$$\sum_{i=1}^{f} (i^2 p_i) = \sum_{i=1}^{f} (i^2 M_{A,1}^2 n_{A,i}/M_{A,1}^2 n_A) = [\sum_{i=1}^{f} (n_{A,i}M_{A,i}^2)]/(n_A M_{A,1}^2) = (\overline{M}_{n,A}\overline{M}_{w,A})/M_{A,1}^2 \qquad (A6)$$

$$\sum_{i=1}^{f}(i^3p_i)=\sum_{i=1}^{f}(i^3M_{A,1}^3n_{A,i}/M_{A,1}^3n_A)$$
$$=[\sum_{i=1}^{f}(n_{A,i}M_{A,i}^3)]/(n_AM_{A,1}^3) \quad \text{(A7)}$$
$$=(\overline{M}_{n,A}\overline{M}_{w,A}\overline{M}_{z,A})/M_{A,1}^3$$

$$\sum_{i=1}^{f}(i^4p_i)=\sum_{i=1}^{f}(i^4M_{A,1}^4n_{A,i}/M_{A,1}^4n_A)$$
$$=[\sum_{i=1}^{f}(n_{A,i}M_{A,i}^4)]/(n_AM_{A,1}^4) \quad \text{(A8)}$$
$$=(\overline{M}_{n,A}\overline{M}_{w,A}\overline{M}_{z,A}\overline{M}_{z+1,A})/M_{A,1}^4$$

Since $M_{A,i} = iM_{A,1}$, we can also derive the following expressions:

$$\sum_{i=1}^{f}(ip_iM_{A,i})=M_{A,1}\sum_{i=1}^{f}(i^2p_i)=(\overline{M}_{n,A}\overline{M}_{w,A})/M_{A,1} \quad \text{(A9)}$$

$$\sum_{i=1}^{f}(i^2p_iM_{A,i})=M_{A,1}\sum_{i=1}^{f}(i^3p_i)=(\overline{M}_{n,A}\overline{M}_{w,A}\overline{M}_{z,A})/M_{A,1}^2 \quad \text{(A10)}$$

$$\sum_{i=1}^{f}(i^3p_iM_{A,i})=M_{A,1}\sum_{i=1}^{f}(i^4p_i) \quad \text{(A11)}$$
$$=(\overline{M}_{n,A}\overline{M}_{w,A}\overline{M}_{z,A}\overline{M}_{z+1,A})/M_{A,1}^3$$

$$\sum_{i=1}^{f}(ip_iM_{A,i}^2)=M_{A,1}^2\sum_{i=1}^{f}(i^3p_i)=(\overline{M}_{n,A}\overline{M}_{w,A}\overline{M}_{z,A})/M_{A,1} \quad \text{(A12)}$$

$$\sum_{i=1}^{f}(i^2p_iM_{A,i}^2)=M_{A,1}^2\sum_{i=1}^{f}(i^4p_i) \quad \text{(A13)}$$
$$=(\overline{M}_{n,A}\overline{M}_{w,A}\overline{M}_{z,A}\overline{M}_{z+1,A})/M_{A,1}^2$$

$$\sum_{i=1}^{f}(ip_iM_{A,i}^3)=M_{A,1}^3\sum_{i=1}^{f}(i^4p_i) \quad \text{(A14)}$$
$$=(\overline{M}_{n,A}\overline{M}_{w,A}\overline{M}_{z,A}\overline{M}_{z+1,A})/M_{A,1}$$

$$\sum_{i=1}^{f}(p_iM_{A,i})=M_{A,i}\sum_{i=1}^{f}(ip_i)=\overline{M}_{n,A} \quad \text{(A15)}$$

$$\sum_{i=1}^{f}(p_iM_{A,i}^2)=M_{A,1}^2\sum_{i=1}^{f}(i^2p_i)=\overline{M}_{n,A}\overline{M}_{w,A} \quad \text{(A16)}$$

$$\sum_{i=1}^{f}(p_iM_{A,i}^3)=M_{A,1}^3\sum_{i=1}^{f}(i^3p_i)=\overline{M}_{n,A}\overline{M}_{w,A}\overline{M}_{z,A} \quad \text{(A17)}$$

$$\sum_{i=1}^{f}(p_iM_{A,i}^4)=M_{A,1}^4\sum_{i=1}^{f}(i^4p_i)=\overline{M}_{n,A}\overline{M}_{w,A}\overline{M}_{z,A}\overline{M}_{z+1,A} \quad \text{(A18)}$$

Likewise, similar expressions can be derived for polymer B.

APPENDIX B:

Based on probability theory[19], if $X_1, X_2,\ldots,X_f$ are independent random variables with the same distribution X, then:

$$E(\sum_{i=1}^{f}X_i)=\sum_{i=1}^{f}E(X_i)=fE(X) \quad \text{(B1)}$$

$$E(\sum_{i=1}^{f}X_i)^2=E(\sum_{i=1}^{f}X_i^2+\sum_{i=1}^{f}\sum_{j=1,j\neq i}^{f}X_iX_j)$$
$$=E(\sum_{i=1}^{f}X_i^2)+E(\sum_{i=1}^{f}\sum_{j=1,j\neq i}^{f}X_iX_j) \quad \text{(B2)}$$
$$=\sum_{i=1}^{f}E(X_i^2)+\sum_{i=1}^{f}\sum_{j=1,j\neq i}^{f}E(X_i)E(X_j)$$
$$=fE(X^2)+f(f-1)[E(X)]^2$$

$$E(\sum_{i=1}^{f}X_i)^3=E(\sum_{i=1}^{f}X_i^3+3\sum_{i=1}^{f}\sum_{j=1,j\neq i}^{f}X_i^2X_j$$
$$+\sum_{i=1}^{f}\sum_{j=1,j\neq i}^{f}\sum_{k=1,k\neq i\neq j}^{f}X_iX_jX_k)$$
$$=E(\sum_{i=1}^{f}X_i^3)+3E(\sum_{i=1}^{f}\sum_{j=1,j\neq i}^{f}X_i^2X_j)$$
$$+E(\sum_{i=1}^{f}\sum_{j=1,j\neq i}^{f}\sum_{k=1,k\neq i\neq j}^{f}X_iX_jX_k)$$
$$=\sum_{i=1}^{f}E(X_i^3)+3\sum_{i=1}^{f}\sum_{j=1,j\neq i}^{f}E(X_i^2)E(X_j)$$
$$+\sum_{i=1}^{f}\sum_{j=1,j\neq i}^{f}\sum_{k=1,k\neq i\neq j}^{f}E(X_i)E(X_j)E(X_k)$$
$$=fE(X^3)+3f(f-1)E(X^2)E(X)$$
$$+f(f-1)(f-2)[E(X)]^3 \quad \text{(B3)}$$

$$E(\sum_{i=1}^{f}X_i)^n$$
$$=E(\sum_{\substack{n_1,n_2,\ldots,n_f\geq 0\\(n_1+n_2+\ldots+n_f=n)}}^{n}\frac{n!}{n_1!n_2!\ldots n_f!}X_1^{n_1}X_2^{n_2}\ldots X_n^{n_f})$$
$$=\sum_{\substack{n_1,n_2,\ldots,n_f\geq 0\\(n_1+n_2+\ldots+n_f=n)}}^{n}\frac{n!}{n_1!n_2!\ldots n_f!}E(X_1^{n_1}X_2^{n_2}\ldots X_n^{n_f})$$
$$=\sum_{\substack{n_1,n_2,\ldots,n_f\geq 0\\(n_1+n_2+\ldots+n_f=n)}}^{n}\frac{n!}{n_1!n_2!\ldots n_f!}E(X_1^{n_1})E(X_2^{n_2})\ldots E(X_n^{n_f})$$
$$=\sum_{\substack{n_1,n_2,\ldots,n_f\geq 0\\(n_1+n_2+\ldots+n_f=n)}}^{n}\frac{n!}{n_1!n_2!\ldots n_f!}E(X^{n_1})E(X^{n_2})\ldots E(X^{n_f}) \quad \text{(B4)}$$

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