

# A Stepwise Scheme for the Calculation of Molecular Weight Distribution in Condensation Polymers. II. Scheme for Bimolecular Condensation Polymers

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## SYNOPSIS

A stepwise scheme, reported recently for the calculation of molecular weight distributions in AB monomolecular condensation polymers under the condition of unequal reactivity, has been applied to the more common AA, BB bimolecular condensation polymers. In the scheme a condensation polymerization is arbitrarily subdivided into a number of steps. The polymer obtained in one step is treated as the monomer for the next step. In each of the steps, Flory's distribution for condensation polymer under equal reactivity is used as the molecular weight distribution for that step. Reactivity variances are incorporated into the calculation through the application of weighing factors on the concentrations of the reacting molecules in each of the steps. In the bimolecular case, three types of monomers, AA, BB, and AB, must be considered for the intermediate polymerization steps. The required distribution of this trimolecular condensation under equal reactivity conditions is not available and has to be derived. As expected, the application of the scheme to bimolecular condensation is more complex but numerical calculations using the scheme should still be manageable on a desktop computer with suitable memory capacity. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Flory's<sup>1</sup> well known molecular weight distribution (MWD) for condensation polymers was derived by assuming equal reactivity for all the functional groups regardless of the length of chains to which they were attached. The equal reactivity condition has been observed in most condensation polymerizations<sup>2</sup> but it is not expected to apply when the rate of polymerization is controlled by diffusion.<sup>3,4</sup>

Unequal reactivity and other special conditions in condensation polymerization have been treated extensively. Both kinetic approaches<sup>5-9</sup> and statistical approaches<sup>10,11</sup> have been used to calculate MWD in these polymers. In some treatments<sup>12-15</sup>

only the average molecular weights were deduced. More recently a stepwise scheme<sup>16</sup> was shown to be useful for the calculation of MWD in condensation polymers prepared under several unusual conditions. The equations for applying the scheme were derived only for the simpler AB monomolecular condensation polymerization. In this paper the application of the same scheme to the more common AA, BB biomolecular condensation polymers is discussed.

In the stepwise scheme, a polymerization reaction is arbitrarily subdivided into a number of steps. The polymer obtained in one step is treated as the monomer for the next step. In each of the steps, Flory's distribution<sup>1</sup> for condensation polymer under equal reactivity is used as the molecular weight distribution for that step. Changes in reactivity are incorporated into the calculation through the application of weighing factors on the concentrations of the reacting molecules in the steps.

In an AB monomolecular condensation, Flory's

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distribution is the simple "most probable" distribution and the resulting polymer chains all have A functionality at one end and B functionality at the other end. The polymer used as monomer for the intermediate steps is therefore also AB in functionality. In an AA, BB bimolecular condensation, three types of polymer chains are formed. The chains with an even number in the degree of polymerization,  $x$ , have A functionality at one end and B functionality at the other end. The distribution of the even  $x$  chains is given by  $Ne(x)$  in eq. (1). The chains with an odd number of  $x$ , can have A functionality at both ends or B functionality at both ends. The distribution of these two odd  $x$  chains is given by  $Noa(x)$  and  $Nob(x)$ , in eqs. (2) and (3).

$$Ne(x) = p^{x-1} r^{x/2} \left[ \frac{2(1-p)(1-rp)}{(1+1/r-2p)r} \right] \quad (1)$$

$$Noa(x) = p^{x-1} r^{x/2} \left[ \frac{(1-p)^2 r^{-1/2}}{1+1/r-2p} \right] \quad (2)$$

$$Nob(x) = p^{x-1} r^{x/2} \left[ \frac{(1-rp)^2 r^{-3/2}}{1+1/r-2p} \right]. \quad (3)$$

In the three distribution equations,  $r$  is the mole ratio of AA to BB, with BB representing the monomer in excess. It follows that  $r$  is always smaller than 1. The variable  $p$  is the fraction of A functionality consumed in the polymerization;  $p$  is 1 if all of A are reacted. The overall number distribution  $N(x)$  is the sum of  $Ne(x)$ ,  $Noa(x)$ , and  $Nob(x)$ . In the stepwise scheme, only in the first step where the polymerization is truly bimolecular and the three Flory's equations can be used to describe the distribution of the resulting polymer. This first step generates three monomers, AA, BB, and AB, and for all the rest of the steps three monomers are at the start of each polymerization step. For these steps, new equations to describe the distribution in this AA, BB, AB trimolecular condensation polymer under equal reactivity have to be derived.

## DERIVATION OF THE DISTRIBUTION FOR TRIMOLECULAR CONDENSATION

Let  $N_{aa}$ ,  $N_{bb}$ , and  $N_{ab}$  represent the starting moles of AA, BB, and AB monomers, respectively. The numbers of moles of A and B functionalities at the start,  $N_a$  and  $N_b$  are

$$N_a = 2N_{aa} + N_{ab} \quad N_b = 2N_{bb} + N_{ab}. \quad (4)$$

Let  $z_a$  be the fraction of A functionality on AA monomer. The fraction of A functionality on AB monomer is therefore  $1 - z_a$ . When A reacts with B, the probability that it is from an AA or from an AB monomer is therefore  $z_a$  or  $1 - z_a$ , respectively. Similarly  $z_b$  and  $1 - z_b$  are used to designate the origin of B functionality.

$$z_a = \frac{2N_{aa}}{2N_{aa} + N_{ab}} \quad 1 - z_a = \frac{N_{ab}}{2N_{aa} + N_{ab}} \quad (5)$$

$$z_b = \frac{2N_{bb}}{2N_{bb} + N_{ab}} \quad 1 - z_b = \frac{N_{ab}}{2N_{bb} + N_{ab}}. \quad (6)$$

For convenience in the derivation, two conversion numbers,  $p_a$ , the fraction of A reacted and  $p_b$ , the fraction of B reacted will be used.

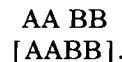
$$p_a = \frac{N'_a}{N_a} \quad p_b = \frac{N'_b}{N_b} \quad (7)$$

where  $N'_a$  is the number of moles of A reacted and  $N'_b$ , the number of moles of B reacted. The two  $p$ 's are not independent of each other as the nature of condensation reaction dictates that  $N'_a$  is always equal to  $N'_b$ . The conversion  $p_a$  is the  $p$  in Flory's eqs. (1)–(3).

The chains starting with A functionality at the end will be considered first. For  $x = 1$ , the chain is the monomer AA and the number of moles of it,  $\bar{N}_{AA}(1)$ , should be the amount of monomer AA multiplied by the probabilities that neither of the A functionality has reacted.

$$\bar{N}_{AA}(1) = N_{aa}(1 - p_a)(1 - p_a). \quad (8)$$

For  $x = 2$ , the chains can originate from two sources. One starts with AA and the other with AB. Since monomer AB is a dimer of AA with BB formed during the earlier condensation step, we use [AABB] for it in the representation below. The two possible chains are



The moles of AA is  $N_{aa}$ . For one end of it unreacted and the other end reacted, the probability is  $(1 - p_a)p_a$ . For the reacting A function to find a BB monomer instead of a BA monomer the probability is  $z_b$  and for the other end of BB unreacted the probability is  $(1 - p_b)$ . The number of moles

for the first chain is the product of all the probabilities times  $N_{aa}$  or

$$N_{aa}(1-p_a)p_az_b(1-p_b).$$

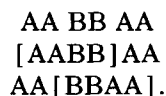
For the second chain, the number of moles of chains starting with an A of an AB monomer is  $(1/2)N_{ab}$  times  $(1-p_a)$ . For the B end of AB remaining unreacted, the probability is  $(1-p_b)$ . The number of moles of the second chain is therefore:

$$\frac{1}{2}N_{ab}(1-p_a)(1-p_b).$$

The total number of moles for  $x = 2$  is

$$\begin{aligned} \bar{N}_{AB}(2) &= N_{aa}(1-p_a)p_az_b(1-p_b) \\ &+ \frac{1}{2}N_{ab}(1-p_a)(1-p_b). \quad (9) \end{aligned}$$

For  $x = 3$ , the possible chains are



For the first two chains, the configuration is the chains for  $x = 2$  reacted with another AA monomer. Equation (9) can be rewritten as

$$\begin{aligned} \bar{N}_{AB}(2) &= [N_{aa}(1-p_a)p_az_b + \frac{1}{2}N_{ab}(1-p_a)] \\ &\times (1-p_b) = C_A(2)(1-p_b) \end{aligned}$$

with  $C_A(2)$  representing the expression in the brackets. The expression  $C_A(2)$  represents also the  $x = 2$  chains with the B functionality at the end uncommitted. The number of moles of these uncommitted chains to react with an A belonging to an AA monomer is

$$C_A(2)p_bz_a.$$

This expression multiplied by the probability for the other end of AA remain unreacted is the total number of moles of the first two chains

$$C_A(2)p_bz_a(1-p_a).$$

Similarly the third chain can be considered as the chain of  $x = 1$  reacted with another AB monomer. If eq. (8) is rewritten as

$$\begin{aligned} \bar{N}_{AA}(1) &= [N_{aa}(1-p_a)](1-p_a) \\ &= C_A(1)(1-p_a) \end{aligned}$$

the number of moles for the third chain is

$$C_A(1)p_a(1-z_b)(1-p_a).$$

The total number of moles for chains with  $x = 3$  starting with A functionality is

$$\begin{aligned} \bar{N}_{AA}(3) &= C_A(2)p_bz_a(1-p_a) \\ &+ C_A(1)p_a(1-z_b)(1-p_a) \quad (10) \end{aligned}$$

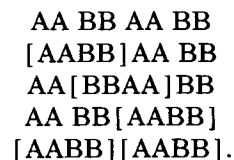
or,

$$\bar{N}_{AA}(3) = C_A(3)(1-p_a)$$

with

$$C_A(3) = C_A(2)p_bz_a + C_A(1)p_a(1-z_b). \quad (11)$$

For  $x = 4$ , five chains are possible



The first three chains are the chains with  $x = 3$  reacted with monomer BB and the last two are the chains with  $x = 2$  reacted with monomer AB. Therefore for  $x = 4$ ,

$$\begin{aligned} \bar{N}_{AB}(4) &= C_A(3)p_az_b(1-p_b) \\ &+ C_A(2)p_b(1-z_a)(1-p_b) \end{aligned}$$

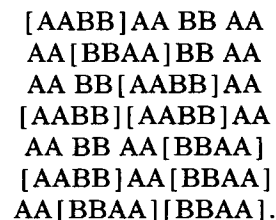
or,

$$\bar{N}_{AB}(4) = C_A(4)(1-p_b)$$

with

$$C_A(4) = C_A(3)p_az_b + C_A(2)p_b(1-z_a).$$

For  $x = 5$ , the number of possible chains is eight, which is the sum of the number of chains for the previous two DP's.



By the same reasonings, the number of moles for  $x = 5$  is:

$$\bar{N}_{AA}(5) = C_A(4)p_b z_a(1 - p_a) + C_A(3)p_a(1 - z_b)(1 - p_a)$$

or

$$\bar{N}_{AA}(5) = C_A(5)(1 - p_a)$$

with

$$C_A(5) = C_A(4)p_b z_a + C_A(3)p_a(1 - z_b).$$

In general, the recursive equations for odd  $x$  are:

$$\bar{N}_{AA}(x) = C_A(x)(1 - p_a) \quad (12)$$

$$C_A(x) = C_A(x-1)p_b z_a + C_A(x-2)p_a(1 - z_b) \quad (13)$$

and for even  $x$  are:

$$\bar{N}_{AB}(x) = C_A(x)(1 - p_b) \quad (14)$$

$$C_A(x) = C_A(x-1)p_a z_b + C_A(x-2)p_b(1 - z_a). \quad (15)$$

Equations (12) and (14) are valid for all odd  $x$  or even  $x$  whereas eqs. (13) and (15) are valid for  $x > 2$ . The starting equations for the recursive eqs. (13) and (15) are:

$$C_A(1) = N_{aa}(1 - p_a) \quad (16)$$

$$C_A(2) = N_{aa}(1 - p_a)p_a z_b + \frac{1}{2}N_{ab}(1 - p_a). \quad (17)$$

The corresponding set of equations for chains starting with the B functionality can be deduced similarly: for odd  $x$ :

$$\bar{N}_{BB}(x) = C_B(x)(1 - p_b) \quad (18)$$

$$C_B(x) = C_B(x-1)p_a z_b + C_A(x-2)p_b(1 - z_a); \quad (19)$$

for even  $x$ :

$$\bar{N}_{BA}(x) = C_B(x)(1 - p_a) \quad (20)$$

$$C_B(x) = C_B(x-1)p_b z_a + C_B(x-2)p_a(1 - z_b); \quad (21)$$

and for the starting equations:

$$C_B(1) = N_{bb}(1 - p_b) \quad (22)$$

$$C_B(2) = N_{bb}(1 - p_b)p_b z_a + \frac{1}{2}N_{ab}(1 - p_b). \quad (23)$$

The total moles of all chains  $N_t$  at conversion  $p_a$ , is one half of the unreacted A and B.

$$\begin{aligned} N_t &= [2N_{aa}(1 - p_a) + N_{ab}(1 - p_a) \\ &\quad + 2N_{bb}(1 - p_b) + N_{ab}(1 - p_b)]/2 \\ &= N_{aa}(1 - p_a) + N_{bb}(1 - p_b) \\ &\quad + N_{ab} \frac{(1 - p_a) + (1 - p_b)}{2}. \quad (24) \end{aligned}$$

Equation (24) can be transformed to another form by using  $p$  for  $p_a$  and  $r$  as the ratio of  $N_a$  to  $N_b$ . (Earlier  $r$  was defined as the ratio of moles of AA monomer to BB monomer for Flory's distribution eqs. (1)–(3). It is restated here as the ratio of A functionality to B functionality.)

$$N_t = \left( \frac{N_a}{2} \right) (1 + 1/r - 2p). \quad (25)$$

The expression in the parentheses in eq. (25) is identical to the denominators in Flory's distribution eqs. (1)–(3). The normalized distribution equations for trimolecular condensation under equal reactivity are obtained by applying  $N_t$  to eqs. (12), (14), (18), and (20). For even  $x$ :

$$\begin{aligned} Ne(x) &= \frac{1}{N_t} [\bar{N}_{AB}(x) + \bar{N}_{BA}(x)] \\ &= \frac{2}{N_t} \bar{N}_{AB}(x) = \frac{2}{N_t} \bar{N}_{BA}(x); \quad (26) \end{aligned}$$

for odd  $x$ :

$$Noa(x) = \frac{1}{N_t} \bar{N}_{AA}(x) \quad (27)$$

$$Nob(x) = \frac{1}{N_t} \bar{N}_{BB}(x). \quad (28)$$

A feature of the above derivation is that the function  $\bar{N}_{AB}(x)$  should be identical to  $\bar{N}_{BA}(x)$  as they represent the same chain configurations. For even  $x$ , there should be no difference between chains

starting with an A function or a B function. For example when  $x = 2$ ,

$$\begin{aligned}\bar{N}_{AB}(2) &= C_A(2)(1 - p_b) \\ &= [N_{aa}(1 - p_a)p_a z_b \\ &\quad + \frac{1}{2}N_{ab}(1 - p_a)](1 - p_b) \\ &= [N_{aa}p_a z_b + \frac{1}{2}N_{ab}](1 - p_a)(1 - p_b).\end{aligned}$$

Similarly

$$\bar{N}_{BA}(2) = [N_{bb}p_b z_a + \frac{1}{2}N_{ab}](1 - p_b)(1 - p_a).$$

The second terms in the two equations are identical. The first term in the brackets of the equation for  $\bar{N}_{AB}(2)$  is

$$N_{aa}p_a z_b = N_{aa} \frac{N'_a}{2N_{aa} + N_{ab}} \frac{2N_{bb}}{2N_{bb} + N_{ab}}.$$

The substitution for  $p_a z_b$  is by virtue of eqs. (4), (6), and (7). Similarly for  $\bar{N}_{BA}(2)$

$$N_{bb}p_b z_a = N_{bb} \frac{N'_b}{2N_{bb} + N_{ab}} \frac{2N_{aa}}{2N_{aa} + N_{ab}}.$$

Because condensation polymerization dictates that the number of moles of A reacted,  $N'_a$ , must be identical to the number of moles of B reacted,  $N'_b$ ,  $\bar{N}_{AB}(2)$  is identical to  $\bar{N}_{BA}(2)$ .

## STEPWISE SCHEME FOR BIOMOLECULAR CONDENSATION

### The Two-Step Scheme

The two-step calculation is the basic element in the stepwise scheme. In the two-step calculation, a polymerization is taken to an intermediate conversion  $p_1$  in the first step and to the final conversion  $p$  ( $p$  is used interchangeably with  $p_a$ ) in the second step. A polymerization can be subdivided into as many steps as needed to accommodate the varying reaction conditions. The multi-step scheme is the repeats of the two-step calculation as shown earlier<sup>16</sup> for the case of AB monomolecular condensation.

In an AA BB bimolecular condensation, the distribution eqs. (1)–(3) describe the polymer of the first step with  $p_1$  as  $p$  in the equations. In the second step, the monomers are the polymers from the first step. Since three types of polymers AA, BB, and AB are produced in the first step and they are the

monomers for the second step, Flory's eqs. (1)–(3), are no longer applicable.

Equations (26)–(28) now describe the distribution of the trimolecular condensation in the second step. The conversion  $p_2$  for the second step is

$$p_2 = \frac{p - p_1}{1 - p_1}.$$

The conversions  $p$ ,  $p_1$ , and  $p_2$  all refer to the fraction of functionality A reacted. The  $r$  ratio for the first step is the same as that for the overall step, that is,

$$r_1 = r.$$

The  $r$  ratio for the second step  $r_2$  is

$$r_2 = \frac{r(1 - p_1)}{1 - rp_1}.$$

Subscript 1 is used to denote variables for step 1; subscript 2 for variables for step 2; and variables without a numerical subscript are for the overall polymerization. This convention will be used for all other variables and functions.

The calculation for the overall distribution  $N(x)$  is the incorporation of the distribution of the first step  $N_1(x)$  into the distribution of the second step  $N_2(x)$ . This is the best illustrated by the example below for the case of overall DP 3 in the AB monomolecular condensation. For the DP 3 member of the overall distribution  $N(3)$ , three members in  $N_2(x)$  are contributing. They are  $N_2(1)$ ,  $N_2(2)$ , and  $N_2(3)$ . For  $N_2(1)$  to become  $N(3)$  the monomer must be a DP 3 chain from step 1. Its concentration is given by  $N_1(3)$ . The portion of  $N_2(1)$  that contributes to  $N(3)$  is therefore the product of  $N_2(1)$  and  $N_1(3)$ . This chain is given by the first line below and the expression to the right is the contribution of this chain to the overall distribution  $N(3)$ . Underline is used to indicate a chain segment from a monomer of DP greater than 1 in the configuration. For  $N_2(2)$  one of the two monomers must be a DP 1 chain and the other a DP 2 chain. Two possible permutations exist as depicted by the group of two chains below. Their contributions to  $N(3)$  are given by the corresponding expressions at the right. For  $N_2(3)$  the three monomers must all be of DP 1 to give a total DP of 3. The last line below is this chain and its contribution to  $N(3)$ . The sum of all four expressions is the distribution  $N(3)$  for the overall polymer.

$$\begin{array}{ll}
 \underline{ABABAB} & N_2(1) N_1(3) \\
 \underline{ABAB} \text{ AB} & N_2(2) N_1(2) N_1(1) \\
 \text{AB } \underline{ABAB} & N_2(2) N_1(1) N_1(2) \\
 \text{AB AB AB} & N_2(3) N_1(1) N_1(1) N_1(1).
 \end{array}$$

The recursive equations for calculating all members of the distribution  $N(x)$  for monomolecular condensation polymers were derived from the above consideration.

For the bimolecular condensation, the logic is the same but the derivation has to deviate some from the above approach. In the second step of a bimolecular condensation, three monomers AA, BB, and AB are involved. The number of moles of AA for step 2 condensation,  $N_{aa2}$ , is the sum of all polymers with A at both ends produced from step 1 polymerization, as given by the first equation below. Similarly the moles of BB and AB monomers in step 2 polymerization are given by the other two equations below.

$$N_{aa2} = \sum_{x=1,3,5,\dots}^{\infty} \bar{N}_{AA1}(x) \quad (29)$$

$$N_{bb2} = \sum_{x=1,3,5,\dots}^{\infty} \bar{N}_{BB1}(x) \quad (30)$$

$$\begin{aligned}
 N_{ab2} &= \sum_{x=2,4,6,\dots}^{\infty} 2\bar{N}_{AB1}(x) \\
 &= \sum_{x=2,4,6,\dots}^{\infty} 2\bar{N}_{BA1}(x). \quad (31)
 \end{aligned}$$

The computation for the number of moles for each monomer is necessary because their relative amounts dictate the distribution of the resulting polymer. In AB monomolecular condensation, there is not such a need because only one monomer is involved.

As in the case for the trimolecular condensation, chains starting with A functionality at the end will be treated first. The first member in this family of chains is AA, the AA monomer having survived reactions in both polymerization steps. The DP for the second polymerization step, of course, is 1 and the number of moles of it is given by

$$\bar{N}_{AA2}(1) = N_{aa2}(1 - p_2)(1 - p_2). \quad (32)$$

Equation (32) is eq. (8) cast in the variables for step 2 polymerization. The AA monomer for step 2 consists of a family of polymer chains from step 1.

Only the DP 1 member of these will give the desired final chain. Therefore the moles of AA for the overall two-step scheme,  $\bar{N}_{AA}(1)$  is

$$\bar{N}_{AA}(1) = \bar{N}_{AA2}(1) \frac{\bar{N}_{AA1}(1)}{N_{aa2}}.$$

In the monomolecular condensation the quotient in the above equation would simply be  $N_1(1)$ . In the present case this quotient is not  $N_{oa1}(1)$  that is the distribution of AA normalized with respect to the entire population of the polymer from step 1. The normalization is with respect only to the chains from step 1 with A function at both ends. Let these specially normalized quotients be given by the symbols below

$$N_{AA1}(x) = \frac{\bar{N}_{AA1}(x)}{N_{aa2}}$$

$$N_{BB1}(x) = \frac{\bar{N}_{BB1}(x)}{N_{bb2}}$$

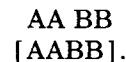
$$N_{AB1}(x) = \frac{2\bar{N}_{AB1}(x)}{N_{ab2}} = \frac{2\bar{N}_{BA1}(x)}{N_{ab2}}.$$

The overall distribution for AA chain with DP 1 can now be written as

$$\begin{aligned}
 \bar{N}_{AA}(1) &= \bar{N}_{AA2}(1) N_{AA1}(1) \\
 &= N_{aa2}(1 - p_2)(1 - p_2) N_{AA1}(1). \quad (33)
 \end{aligned}$$

In the above equations, functions with a bar over the symbols are unnormalized functions. Because functions are not normalized uniformly in the present treatment, it is convenient to keep some unnormalized forms in the equations.

For  $x = 2$ , the chains are the ones starting with A and ending with B. These chains can be formed by the dimerization of AA with BB as depicted by the first chain below or simply the unreacted AB monomer as depicted by the second chain. The brackets are used to indicate an AB monomer.



The number of moles for the above chains  $\bar{N}_{AB2}(2)$  resulting from trimolecular condensation is given by eq. (9). The contribution by the first chain to  $\bar{N}_{AB2}(2)$  is given by the first term in eq. (9)

$$N_{aa2}(1 - p_2)p_2z_b(1 - p_b2).$$

In order to give the overall chain a DP of 2, the monomer AA and BB must both be of DP 1 from step 1. Therefore the contribution of the first chain toward  $\bar{N}_{AB}(2)$  is given by

$$N_{aa2}(1 - p_2)p_2z_b(1 - p_{b2})N_{AA1}(1)N_{BB1}(1).$$

The contribution by the second chain to  $\bar{N}_{AB2}(2)$  is given by the second term in eq. (9)

$$\frac{1}{2}N_{ab2}(1 - p_2)(1 - p_{b2}).$$

For the second chain to have an overall DP of 2, the AB monomer or [AABB] for step 2 must be also of DP2. Therefore its contribution towards  $\bar{N}_{AB}(2)$  is given by

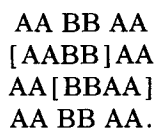
$$\frac{1}{2}N_{ab2}(1 - p_2)(1 - p_{b2})N_{AB1}(2).$$

The expression for  $\bar{N}_{AB}(2)$  is therefore

$$\begin{aligned} \bar{N}_{AB}(2) &= N_{aa2}(1 - p_2)p_2z_b(1 - p_{b2})N_{AA1}(1) \\ &\times N_{BB1}(1) + \frac{1}{2}N_{ab2}(1 - p_2)(1 - p_{b2})N_{AB1}(2). \end{aligned} \quad (34)$$

The function  $\bar{N}_{AB2}(2)$  has been split into parts in the derivation of  $\bar{N}_{AB}(2)$ . The split was not involved in the treatment for the monomolecular condensation.

For  $x = 3$ , there are four ways to form the chains.



The DP in step 2 polymerization is 3 for the first three chains. For the fourth chain, the DP in step 2 polymerization is 1 and the monomer AA itself has a DP of 3. By following the same reasoning, we have

$$\begin{aligned} \bar{N}_{AA}(3) &= N_{aa2}(1 - p_2)p_2z_b p_{b2}z_a(1 - p_2)N_{AA1}(1) \\ &\times N_{BB1}(1)N_{AA1}(1) + \frac{1}{2}N_{ab2}(1 - p_2) \\ &\times p_{b2}z_a(1 - p_2)N_{AB1}(2)N_{AA1}(1) + N_{aa2}(1 - p_2) \\ &\times p_2(1 - z_b)(1 - p_2)N_{AA1}(1)N_{BA1}(2) \\ &+ N_{aa2}(1 - p_2)(1 - p_2)N_{AA1}(3). \end{aligned} \quad (35)$$

If eq. (34) is rewritten as:

$$\bar{N}_{AB}(2) = A(2, 2)(1 - p_{b2})$$

with

$$\begin{aligned} A(2, 2) &= N_{aa2}(1 - p_2)p_2z_bN_{AA1}(1)N_{BB1}(1) \\ &+ \frac{1}{2}N_{ab2}(1 - p_2)N_{AB1}(2) \end{aligned}$$

then the first two terms in eq. (35) can be written as

$$A(2, 2)p_{b2}z_aN_{AA1}(1)(1 - p_2).$$

Similarly eq. (33) can be converted to:

$$\bar{N}_{AA}(1) = A(1, 1)(1 - p_2)$$

with

$$A(1, 1) = N_{aa2}(1 - p_2)N_{AA1}(1).$$

The third term in eq. (35) can now be written as

$$A(1, 1)p_2(1 - z_b)N_{BA1}(2)(1 - p_2).$$

Substituting these expressions into eq. (35), we have

$$\begin{aligned} \bar{N}_{AA}(3) &= A(2, 2)p_{b2}z_aN_{AA1}(1)(1 - p_2) \\ &+ A(1, 1)p_2(1 - z_b)N_{BA1}(2)(1 - p_2) \\ &+ N_{aa2}(1 - p_2)(1 - p_2)N_{AA1}(3). \end{aligned}$$

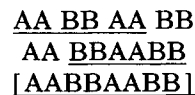
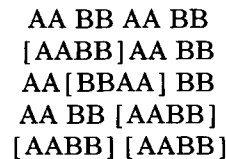
In coefficient  $A(x, x')$ ,  $x$  is the DP for the overall polymerization;  $x'$  is the DP for step 2 polymerization. Using this convention, we rewrite eq. (35) as:

$$\bar{N}_{AA}(3) = [A(3, 3) + A(3, 1)](1 - p_2)$$

with

$$\begin{aligned} A(3, 3) &= A(2, 2)p_{b2}z_aN_{AA1}(1) \\ &+ A(1, 1)p_2(1 - z_b)N_{BA1}(2) \\ A(3, 1) &= N_{aa2}(1 - p_2)N_{AA1}(3). \end{aligned}$$

For  $x = 4$  the chains to be considered are:



The first group of five chains are from a DP of 4 in step 2 polymerization and the second group of 3 chains are from a DP of 2 in step 2 polymerization. The number of moles for DP 4 chains starting with A is

$$\bar{N}_{AB}(4) = [A(4, 4) + A(4, 2)](1 - p_{b2}).$$

In the first three chains in the first group of five are the A(3, 3) chains with BB attached and the last two are A(2, 2) chains with [AABB] attached. Therefore

$$A(4, 4) = A(3, 3)p_2z_bN_{BB1}(1) + A(2, 2)p_{b2}(1 - z_a)N_{AB1}(2).$$

For the second group of chains

$$A(4, 2) = [A(3, 1)N_{BB1}(1) + A(1, 1)N_{BB1}(3)]p_2z_b + \frac{1}{2}N_{ab2}(1 - p_2)N_{AB1}(4).$$

For  $x = 5$

AA BB AA BB AA  
[AABB]AA BB AA  
AA[BBAA] BB AA  
AA BB [AABB] AA  
[AABB] [AABB] AA  
AA BB AA [BBAA]  
[AABB]AA [BBAA]  
AA [BBAA] [BBAA]

AA BB AA BB AA  
AA BBAABB AA  
[AABBAABB] AA  
AA BB AA BB AA  
[AABB] AA BB AA  
AA BB AA [BBAA]  
AA [BBAABBAA]

AABBAABBAA

The chains are from DP of 5, 3, and 1 in step 2 polymerization. The DP 5 group is formed from adding AA to A(4, 4), and [AABB] to A(3, 3). The DP 3 group are formed from adding AA to A(4, 2), A(2, 2), and [AABB] to A(3, 1) and A(1, 1). The chain for DP 1 is the chain formed from the monomer AA of DP 5 in step 1 polymerization. The number of moles for DP 5 chains starting with A is therefore

$$\bar{N}_{AA}(5) = [A(5, 5) + A(5, 3) + A(5, 1)](1 - p_2)$$

with

$$A(5, 5) = A(4, 4)N_{AA1}(1)p_{b2}z_a + A(3, 3)N_{BA1}(2)p_2(1 - z_b)$$

$$A(5, 3) = [A(4, 2)N_{AA1}(1) + A(2, 2)N_{AA1}(3)]p_{b2}z_a + [A(3, 1)N_{BA1}(2) + A(1, 1)N_{BA1}(4)]p_2(1 - z_b)$$

$$A(5, 1) = N_{aa2}(1 - p_2)N_{AA1}(5).$$

Similarly for  $x = 6$ , we have

$$\bar{N}_{AB}(6) = [A(6, 6) + A(6, 4) + A(6, 2)](1 - p_{b2})$$

with

$$A(6, 6) = A(5, 5)N_{BB1}(1)p_2z_b + A(4, 4)N_{AB1}(2)p_{b2}(1 - z_a)$$

$$A(6, 4) = [A(5, 3)N_{BB1}(1) + A(3, 3)N_{BB1}(3)]p_2z_b + [A(4, 2)N_{AB1}(2) + A(2, 2)N_{AB1}(4)]p_{b2}(1 - z_a)$$

$$A(6, 2) = [A(5, 1)N_{BB1}(1) + A(3, 1)N_{BB1}(3) + A(1, 1)N_{BB1}(5)]p_2z_b + \frac{1}{2}N_{ab2}(1 - p_2)N_{AB1}(6).$$

The pattern for the recursive equations that emerges from the above is: for odd  $x$ 's

$$\bar{N}_{AA}(x) = (1 - p_2) \sum_{i=1,3,\dots}^x A(x, i) \quad (36)$$

with

$$A(x, 1) = N_{aa2}(1 - p_2)N_{AA1}(x) \quad (37)$$

$$A(x, i) = \left[ \sum_{j=1,3,\dots}^{x-i+1} A(x-j, i-1)N_{AA1}(j) \right] p_{b2}z_a + \left[ \sum_{j=2,4,\dots}^{x-i+2} A(x-j, i-2)N_{BA1}(j) \right] p_2(1 - z_b); \quad (38)$$

for even  $x$ 's

$$\bar{N}_{AB}(x) = (1 - p_{b2}) \sum_{i=2,4,\dots}^x A(x, i) \quad (39)$$



$$A(x, 2) = \left[ \sum_{j=1,3,\dots}^{x-1} A(x-j, 1)N_{BB1}(j) \right] p_2 z_b + \frac{1}{2} N_{ab2}(1-p_2)N_{AB1}(x) \quad (40)$$

$$A(x, i) = \left[ \sum_{j=1,3,\dots}^{x-i+1} A(x-j, i-1)N_{BB1}(j) \right] p_1 z_b + \left[ \sum_{j=2,4,\dots}^{x-i+2} A(x-j, i-2)N_{AB1}(j) \right] p_{b2}(1-z_a). \quad (41)$$

Similarly equations for chains starting with B functionality, are as follows: for odd  $x$ 's:

$$\bar{N}_{BB}(x) = (1-p_{b2}) \sum_{i=1,3,\dots}^x B(x, i) \quad (41)$$

with

$$B(x, 1) = N_{bb2}(1-p_{b2})N_{BB1}(x) \quad (42)$$

$$B(x, i) = \left[ \sum_{j=1,3,\dots}^{x-i+1} B(x-j, i-1)N_{BB1}(j) \right] p_2 z_b + \left[ \sum_{j=2,4,\dots}^{x-i+2} B(x-j, i-2)N_{AB1}(j) \right] p_{2b}(1-z_a); \quad (43)$$

and for even  $x$ 's

$$\bar{N}_{BA}(x) = (1-p_2) \sum_{i=2,4,\dots}^x B(x, i) \quad (44)$$

with

$$B(x, 2) = \left[ \sum_{j=1,3,\dots}^{x-1} B(x-j, 1)N_{AA1}(j) \right] p_{b2} z_a + \frac{1}{2} N_{ba2}(1-p_{b2})N_{BA1}(x) \quad (45)$$

$$B(x, i) = \left[ \sum_{j=1,3,\dots}^{x-i+1} B(x-j, i-1)N_{AA1}(j) \right] p_{b2} z_a + \left[ \sum_{j=2,4,\dots}^{x-i+2} B(x-j, i-2)N_{BA1}(j) \right] p_2(1-z_b). \quad (46)$$

The total number of chains for step 2 calculation is the same as that in eq. (24) for trimolecular con-

densation. With the proper subscripted symbols, eq. (24) is now

$$N_{t2} = N_{aa2}(1-p_2) + N_{bb2}(1-p_{b2}) + N_{ab2} \frac{(1-p_2) + (1-p_{b2})}{2}$$

or in another form

$$N_{t2} = \left( \frac{N_{a2}}{2} \right) (1 + 1/r_2 - 2p_2).$$

The symbol  $N_{a2}$  is the total number of A functionalities before step 2 polymerization or

$$N_{a2} = 2N_{aa2} + N_{ab2}.$$

The final distribution functions for the overall polymerization are

$$Ne(x) = \frac{1}{N_{t2}} [ \bar{N}_{AB}(x) + \bar{N}_{BA}(x) ] = \frac{2}{N_{t2}} \bar{N}_{AB}(x) = \frac{2}{N_{t2}} \bar{N}_{BA}(x) \quad (47)$$

$$Noa(x) = \frac{1}{N_{t2}} \bar{N}_{AA}(x) \quad (48)$$

$$Nob(x) = \frac{1}{N_{t2}} \bar{N}_{BB}(x). \quad (49)$$

### Verification of the Derivation

As in the case for monomolecular condensation,<sup>16</sup> the equations derived for the stepwise scheme can be tested for their validity by comparing the first 10 members of the distribution calculated directly to those calculated by the two-step scheme. In Table I, the numbers in the columns marked "Direct" were calculated from the Flory distribution eqs. (1)–(3). For the 2-step calculations, eqs. (1)–(3) were used for the first step and eqs. (47)–(49) were used for the second step. There is total agreement between the numbers calculated by the two methods at  $p = 0.9$ ,  $r = 0.9$  and  $p_1 = 0.45$ . For this case  $r_2$  is 0.83193,  $p_2$  is 0.81818 for the second step.

The same agreement can be demonstrated for other values of  $p$ ,  $r$ , and  $p_1$ . An example for low  $p$  and low  $r$  is given in Table II. In this latter case  $r_2$  is 0.48718,  $p_2$  is 0.05263 for the second step.

**Table I Comparison of the First 10 Members of a Bimolecular Condensation Distribution Calculated Directly to That Calculated by the Two-Step Scheme**

DP <i>x</i>	<i>Noa(x)</i>		<i>Nob(x)</i>		<i>Ne(x)</i>	
	Direct	2-Step	Direct	2-Step	Direct	2-Step
1	0.032143	0.032143	0.128929	0.128929		
2					0.109929	0.109929
3	0.023432	0.023432	0.093989	0.093989		
4					0.080138	0.080138
5	0.017082	0.017082	0.068518	0.068518		
6					0.058421	0.058421
7	0.012453	0.012453	0.049950	0.049950		
8					0.042589	0.042589
9	0.009078	0.009078	0.036413	0.036413		
10					0.031047	0.031047

$p = 0.9$ ,  $r = 0.9$ , and  $p_1 = 0.45$ .

## DISCUSSION

As suggested earlier,<sup>16</sup> the stepwise scheme for the calculation of MWD in bimolecular condensation polymers is more complex than that for the monomolecular condensation polymers. There are four equations to define the recursive relations versus only one in the case of monomolecular condensation. The complexity fortunately increased only by two-fold. In monomolecular condensation, the  $B(x, i)$  array, with  $i$  varied from 1 to  $x$ , has the size of one half of a two-dimensional array. In bimolecular condensation two such arrays,  $A(x, i)$  and  $B(x, i)$ , are used in the calculation. If the calculation is carried out to a DP of 1000, each array will have 500,000 members. Based on 8 bytes per number, the two

arrays will occupy 8 MB memory. This still allows the calculation to be carried out on most desktop computers.

Approaches for using the stepwise scheme to calculate the MWD in monomolecular condensation polymers prepared under three unusual conditions, unequal reactivity, limited monomer solubility, and endcapping at late stages of the reaction were discussed<sup>16</sup> before. The same approaches should be usable to treat these cases in bimolecular condensation. However, some specifics in the calculation will be different. For example in monomolecular condensation nearly all functions are self normalized. One can calculate the early part of a distribution and still obtain the correct normalized members of the distribution. In the bimolecular cases,

**Table II Comparison of the First 10 Members of a Bimolecular Condensation Distribution Calculated Directly to That Calculated by the Two-Step Scheme**

DP <i>x</i>	<i>Noa(x)</i>		<i>Nob(x)</i>		<i>Ne(x)</i>	
	Direct	2-Step	Direct	2-Step	Direct	2-Step
1	0.289286	0.289286	0.644643	0.644643		
2					0.061071	0.061071
3	0.001446	0.001446	0.003223	0.003223		
4					0.000305	0.000305
5	7.23E-06	7.23E-06	1.61E-05	1.61E-05		
6					1.53E-06	1.53E-06
7	3.62E-08	3.62E-08	8.06E-08	8.06E-08		
8					7.63E-09	7.63E-09
9	1.81E-10	1.81E-10	4.03E-10	4.03E-10		
10					3.82E-11	3.82E-11

$p = 0.1$ ,  $r = 0.5$ , and  $p_1 = 0.05$ .

the functions are mostly not self normalized. Calculations must be carried out for the entire distribution before the normalization factor can be computed. The purpose of using an endcapping agent will also be different. In monomolecular condensation endcapping is a convenient way to control the molecular weight. Without an endcapping agent, the reaction must be interrupted at a precise degree of conversion to ensure the proper molecular weight for the product, a feat which is difficult to be carried out experimentally. In bimolecular condensation, molecular weight can be controlled by adjusting the relative concentrations of the two monomers. Endcapping may have the desired purpose of masking the functional group on the ends of the chains but may not necessarily be a part of the polymerization scheme.

## CONCLUSIONS

The equations for applying the stepwise scheme to the more common AA, BB bimolecular condensation polymers have been derived. This stepwise scheme is the same as that demonstrated earlier<sup>16</sup> for the calculation of MWD in the AB monomolecular condensation polymers. These equations are expected to be useful in calculating the MWD in polymers prepared under unusual conditions including those prepared under the condition of unequal reactivity.

Required in the derivation were the equations for the distribution of AA, BB, AB trimolecular condensation polymers prepared under equal reactivity. These equations have also been derived.

Proof of validity for the equations of the stepwise scheme was provided by comparing the first 10 members of a distribution calculated by the stepwise scheme to those calculated directly by the Flory equations.<sup>1</sup>

As expected the scheme for bimolecular condensation is more complex than that for monomolecular condensation but numerical calculations using the scheme should still be manageable on desktop computers with suitable memory capacities.

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