

A Stepwise Scheme for the Calculation of Molecular Weight Distribution in Condensation Polymers. I. Scheme for Monomolecular Condensation Polymers

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SYNOPSIS

A stepwise scheme has been devised for the calculation of molecular weight distribution in condensation polymers prepared under the condition of unequal reactivity. 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 the 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. The distributions of polymers prepared under other unusual conditions, such as monomers with only limited solubility or endcapping at late stages of the condensation reaction, can also be conveniently calculated by this scheme. The treatment presented in this paper is devoted only to polymers prepared by monomolecular condensation. Extension to bimolecular condensation will not be trivial and will be the subject of another paper. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In monomolecular condensation of the A–B monomer, Flory¹ showed that under the condition of equal reactivity the molecular weight distribution (MWD) of the polymer followed a simple function known as the most probable distribution. Later polymerization under more general conditions has been treated by others. The approach used was through the solution of a large set of kinetic equations, one for each molecular species. An example was the treatment described by Nanda and Jain.² Their rate equations were

$$\begin{aligned} dN_1/dt &= -N_1 \sum_r k_{1r} N_r, \\ dN_x/dt &= \frac{1}{2} \sum_{s=1}^{x-1} k_{x-s,s} N_s N_{x-s} \\ &\quad - N_x \sum_r k_{xr} N_r, \quad x > 1 \quad (1) \end{aligned}$$

where N_x is the mole of x -mer and k_{xr} is the rate constant for the condensation reaction involving the specific x and r mers. They succeeded to deduce the molecular weight averages for the case where the rate constant varied linearly with chain length. The same kinetic approach was used by Gupta et al.³ to treat the polymerization of monomers having reactivity different from their homologs. Equations in (1) are similar in form to the kinetic equations for free-radical vinyl polymerization and should be amenable to numerical solutions. Nonetheless, they are much more complex than are the free-radical situations because a two-dimensional array of rate constants is involved. In free-radical polymerization, chain growths are the result of the addition of monomer to polymeric molecules. No polymer–polymer reactions are involved and only a one-dimensional array of rate constants is in the rate equations. The situation becomes even more complex for A–A, B–B bimolecular condensation because three type of chains, chains with A functionality on both ends, with B functionality on both ends, and with A and B at each ends, are involved in the growing process. The crossover reactions among the different types of chains may need to be added to the

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collection of differential equations. Clearly, a different approach is desired. The scheme of calculation to be presented in this paper is an attempt to meet this need. For the purpose of demonstrating the validity of the scheme, the simpler monomolecular condensation is treated first. Treatment of the more complex A-A B-B bimolecular condensation will be the subject of a future paper.

OUTLINE OF THE SCHEME

According to Flory, when equal reactivity applies, $N(x)$, the mole fraction of x -mer, for A-B condensation is given by

$$N(x) = p^{x-1}(1-p) \quad (2)$$

where p is the probability for A functionality to become reacted and $(1-p)$ is the probability for A to remain unreacted. A chain of length x will have $(x-1)$ monomer units with A reacted and one monomer unit at the end with A unreacted. The fraction of such a chain in the polymerization mixture is therefore given by the expression on the right-hand side of eq. (2). $N(x)$ is also the number distribution of the degree of polymerization (DP).

In our scheme, a condensation reaction is subdivided into an arbitrary number of steps. Flory's distribution is applied to each of the steps. The probability functions for each step can be altered to suit the polymerization condition. We will present a two-step scheme first. The two-step scheme is the basic formulation for further subdivision of the polymerization.

THE TWO-STEP SCHEME

In the two-step scheme, a polymerization is taken to an intermediate conversion p_1 in the first step and then to the final conversion p in the second step. The distribution $N_1(x)$ at the end of the first step, i.e., at conversion p_1 , is

$$N_1(x) = p_1^{x-1}(1-p_1) \quad (3)$$

The additional conversion p_2 needed for the second step to reach the final conversion p is

$$p_2 = (p - p_1)/(1 - p_1) \quad (4)$$

The numerator in (4) is the conversion required to go from p_1 to p and the denominator is the remaining unreacted functional group at p_1 .

The distribution $N_2(x)$ for the polymerization in the second step is

$$N_2(x) = p_2^{x-1}(1-p_2) \quad (5)$$

The monomer for the second step is not the primary monomer but the polymer at the end of the first step with a distribution $N_1(x)$.

For $x = 1$ in the overall $N(x)$ at the end of the second step, the DP must be 1 for N_2 and also must be 1 for N_1 ; thus

$$N(1) = N_2(1)N_1(1) \quad (6)$$

$N_2(1)$ is the probability of any chain having only one mer in the second step of condensation and $N_1(1)$ is the probability for that mer being an A-B monomer.

For $N(2)$, x can be 1 or 2 for N_2 . When x is 1 for N_2 , x must be 2 for N_1 . When x is 2 for N_2 , there are two mers involved in the second step and they both must have $x = 1$:

$$N(2) = N_2(1)N_1(2) + N_2(2)N_1(1)N_1(1) \quad (7)$$

Similarly for $N(3)$ and $N(4)$, we have

$$\begin{aligned} N(3) &= N_2(1)N_1(3) + N_2(2)N_1(1)N_1(2) \\ &\quad + N_2(2)N_1(2)N_1(1) \\ &\quad\quad\quad + N_2(3)N_1(1)N_1(1)N_1(1) \\ N(4) &= N_2(1)N_1(4) + N_2(2)N_1(1)N_1(3) \\ &\quad + N_2(2)N_1(2)N_1(2) \\ &\quad + N_2(2)N_1(3)N_1(1) \\ &\quad + N_2(3)N_1(1)N_1(1)N_1(2) \\ &\quad + N_2(3)N_1(1)N_1(2)N_1(1) \\ &\quad + N_2(3)N_1(2)N_1(1)N_1(1) \\ &\quad + N_2(4)N_1(1)N_1(1)N_1(1)N_1(1) \quad (8) \end{aligned}$$

The product of N_1 functions associated with each N_2 follows a permutation order. The number of N_1 's in each of the products is the DP in N_2 . The sum of the DP in all the N_1 's in the product is the overall DP in $N(x)$ function. In general, $N(x)$ can be written as

$$N(x) = \sum_{i=1}^x N_2(i)B(x, i) \quad (9)$$

where $B(x, i)$ represents the permutation array of N_1 's. In $B(x, i)$, x is the DP in the overall N function

and i is the DP in N_2 . The permutation array $B(x, i)$ can be written as a recurring function given by eq. (10):

$$B(x, 1) = N_1(x)$$

$$B(x, i) = \sum_{j=1}^{x+1-i} N_1(j)B(x-j, i-1), \quad \text{for } i > 1 \quad (10)$$

Equations (9) and (10) can be programmed easily in simple computer languages.

VALIDITY OF THE SCHEME

Since $N_1(x)$ and $N_2(x)$ are normalized functions. For the expression derived for $N(x)$ to be valid, $N(x)$ should also be a normalized function. By inspection of eqs. (6)–(8), one may see that the sum of the terms associated with $N_2(1)$ in the entire set of $N(x)$ is

$$N_2(1) \sum_{j=1}^{\infty} N_1(j) \equiv N_2(1) \quad (11)$$

Since N_1 is normalized, the above expression reduces to $N_2(1)$ itself.

The sum of the terms associated with $N_2(2)$ is

$$N_2(2) \sum_{j=1}^{\infty} N_1(j) \sum_{j=1}^{\infty} N_1(j) \equiv N_2(2) \quad (12)$$

For the same reason, this reduces also to $N_2(2)$. It follows that

$$\sum_{x=1}^{\infty} N(x) = \sum_{i=1}^{\infty} N_2(i) \quad (13)$$

Since N_2 is normalized, $N(x)$ in eq. (9) is also normalized. The normalization requirement for eqs. (9) and (10) to be valid is therefore satisfied.

The final proof of validity should be provided by a comparison of the $N(x)$ calculated from the two-step scheme with the $N(x)$ calculated directly from eq. (2). Microsoft®'s Quick BASIC® on a Macintosh® desk-top computer was used to make the calculation. The $N(x)$ for the first 10 DPs calculated for $p = 0.5$ using the two-step scheme and directly using eq. (2) are shown in Table I. In the two-step calculation, the first conversion p_1 was 0.25 and the conversion p_2 for the second step as calculated from eq. (4) was 0.3333333. The two-step and one-step results are shown to be identical. To ensure that the above agreement was not fortuitous, a second calculation was made with steps of much smaller increment of conversion. The results are given in Table II. The agreement was again perfect. The conversions in the second example were $p = 0.05$, $p_1 = 0.025$, and $p_2 = 2.564103\text{E-}02$.

These results assured the validity of the stepwise calculation scheme for any conversion intervals. It follows that the scheme will allow a polymerization to be subdivided into any number of steps in equal or unequal intervals of conversion. The change of polymerization conditions during a polymerization can be incorporated into the calculation by varying the N_1 functions artificially in each of the steps. A few examples are given next.

UNEQUAL REACTIVITY

The unequal rates for different-sized chains can be incorporated in the stepwise calculation scheme by altering the N_1 function. The more reactive shorter chain should be given a higher probability for it to

Table I Comparison of the Distribution Function $N(x)$ for the First 10 DPs Calculated by the Two-step Scheme and Those Calculated Directly by Flory's Most Probable Distribution: Conversion p Was 0.5 and the Intermediate Conversion p_1 Was 0.25

x	$N_1(x)$	$N_2(x)$	$N(x)$ Two-step	$N(x)$ One-step
1	.75	.6666666	.5	.5
2	.1875	.2222222	.25	.25
3	.046875	7.407407E-02	.125	.125
4	1.171875E-02	2.469136E-02	.0625	.0625
5	2.929688E-03	8.230453E-03	.03125	.03125
6	7.324219E-04	2.743485E-03	.015625	.015625
7	1.831055E-04	9.144949E-04	.0078125	.0078125
8	4.577637E-05	3.048316E-04	3.90625E-03	3.90625E-03
9	1.144409E-05	1.016105E-04	1.953125E-03	1.953125E-03
10	2.861023E-06	3.387018E-05	9.765626E-04	9.765625E-04

Table II Comparison of the Distribution Function $N(x)$ for the First 10 DPs Calculated by the Two-step Scheme and Those Calculated Directly by Flory's Most Probable Distribution: Conversion p Was 0.05 and the Intermediate Conversion p_1 Was 0.025

x	$N_1(x)$	$N_2(x)$	$N(x)$ Two-step	$N(x)$ One-step
1	.975	.974359	.95	.95
2	.024375	2.498356E-02	.0475	.0475
3	6.09375E-04	6.406042E-04	.002375	.002375
4	1.523438E-05	1.642575E-05	1.1875E-04	1.1875E-04
5	3.808594E-07	4.211731E-07	5.937501E-06	5.9375E-06
6	9.521485E-09	1.079931E-08	2.96875E-07	2.96875E-07
7	2.380371E-10	2.769054E-10	1.484375E-08	1.484375E-08
8	5.950929E-12	7.100138E-12	7.421876E-10	7.421875E-10
9	1.487732E-13	1.820548E-13	3.710939E-11	3.710938E-11
10	3.71933E-15	4.668073E-15	1.855469E-12	1.855469E-12

react. The $B(x, 1)$ array represents unreacted chains in the second polymerization step. Large weighing factors should be assigned to the N_1 function for the slower reacting chains in the calculation of $B(x, 1)$. The N_1 functions for $B(x, i)$ $i > 1$ should be weighed in a reverse order as they represent the probabilities of reacting chains.

This treatment is exact for $x = 2$ in the second step when only one reaction is involved. For x greater than 2, more than one reaction is involved to form the chain and the unequal reactivity correction will not be fully implemented by applying the same weighing factors for all N_1 functions. One may choose to modify the weighing factors for each of the higher x values to make the formulation exact. Such an approach, of course, greatly complicates the calculation. For a first approximation, it should be justified to ignore the distinction and use the same weighted N_1 functions in $B(x, i)$ calculations for all i 's. The error introduced is small if smaller intervals of conversion are taken for the steps. This is evident because a far greater number of chains will remain as monomer and dimer in smaller increments of conversion, as shown in Table II, in comparison with the results in larger increments, as shown in Table I. By using calculations at progressively smaller intervals of conversion, one should find that the result converges into a constant MWD. This converged MWD should then represent the true MWD under the variable reactivity conditions. The number of repetitive calculations may be large but it should not be a problem on a minicomputer or a main frame computer.

LIMITED MONOMER SOLUBILITY

Limited monomer solubility is equivalent to the condition of continuous addition of monomer during

a polymerization. Treatment for this case can be illustrated by a two-step polymerization with a part of the monomer added at the second step. Let M_1 be the amount of monomer used in the first step, and M_2 , the amount of monomer added at the second step. The conversion p_2 for the second polymerization step is

$$p_2 = \frac{p(M_1 + M_2) - p_1 M_1}{M_1(1 - p_1) + M_2} \quad (14)$$

The N_1 function calculated from the first step should be modified by the following equations:

$$N'_1(1) = \frac{N_1(1)M_1(1 - p_1) + M_2}{M_1(1 - p_1) + M_2} \quad (15)$$

$$N'_1(x) = \frac{N_1(x)M_1(1 - p_1)}{M_1(1 - p_1) + M_2}, \quad \text{for } x > 1 \quad (16)$$

The function N'_1 is then used in eqs. (9) and (10) to calculate the B array.

Table III is the result for $M_1 = 0.6$, $M_2 = 0.4$, $p = 0.9$ and $p_1 = 0.67$. As expected, the two-step monomer addition left more unreacted monomer in the distribution. The condition of limited monomer solubility can be simulated by subdividing the polymerization into more steps and by using eqs. (14)–(16) to modify p and N_1 for each of the steps.

END-CAPPING REACTION

The effect of end-capping agent addition at different stages of polymerization can also be treated by the stepwise scheme. Let C represent the mole fraction of the end-capping agent, and F , the mole fraction of the monomer. When the reaction is carried to completion, the probability of a chain of DP x is

Table III Comparison of the Distribution Function $N(x)$ for the First 10 DPs Calculated for the One-step Polymerization and Those Calculated for Monomer Added in Two Steps: Conversion p Was 0.9

x	$N_1(x)$	$N_2(x)$	$N(x)$ Two-step	$N(x)$ One-step
1	.7781605	.1672242	.1301273	.1
2	7.320702E-02	.1392602	9.656876E-02	9.000002E-02
3	4.904871E-02	.1159726	7.871512E-02	8.100002E-02
4	3.286263E-02	9.657915E-02	6.770802E-02	7.290001E-02
5	2.201797E-02	8.042878E-02	5.986357E-02	6.561001E-02
6	1.475204E-02	6.697915E-02	5.363238E-02	5.904901E-02
7	9.883865E-03	5.577862E-02	4.834715E-02	.0531441
8	6.62219E-03	4.645108E-02	4.370662E-02	4.782969E-02
9	4.436867E-03	3.868334E-02	3.956279E-02	4.304672E-02
10	2.972701E-03	3.221455E-02	.035833	3.874205E-02

For the split monomer addition, 0.6 mol was added first; 0.4 mol was added at a p_1 of 0.67; and p_2 as calculated from eq. (14) was 0.8327758.

$$N(x) = F^{x-1}C = F^{x-1}(1 - F) \quad (17)$$

Equation (17) is identical to eq. (2) except that the conversion p is replaced by the mole fraction of the monomer. For the case when the end-capping agent is added after the conversion reaches p_1 , the N_1 function for the first stage should be identical to that calculated from eq. (3). Let F denote the mole fraction of monomer in the overall reaction; the mole fraction of the monomer for the second reaction F_2 is then

$$F_2 = \frac{F(1 - p_1)}{1 - Fp_1} \quad (18)$$

The distribution for the second step is then

$$N_2(x) = F_2^{x-1}(1 - F_2) \quad (19)$$

The overall N function for the two-step distribution is different from that given by eqs. (6)–(8). Because the end unit of each chain must be the end-capping agent, only those chains with $N_1(1)$ at the ends are allowed. Since $N_1(1)$ is the end-capping agent at the chain end and it is already considered in the calculation of N_2 by eq. (19), the equations for $N(x)$ should be as follows:

$$N(1) = N_2(1) \quad (20)$$

$$N(2) = N_2(2)N_1(1) \quad (21)$$

$$N(3) = N_2(2)N_1(2) + N_2(3)N_1(1)N_1(1)$$

$$N(4) = N_2(2)N_1(3) + N_2(3)N_1(1)N_1(2) + N_2(3)N_1(2)N_1(1) + N_2(4)N_1(1)N_1(1)N_1(1) \quad (22)$$

The general expression for the N function becomes

$$N(1) = N_2(1)$$

$$N(x) = \sum_{i=2}^x N_2(i)B(x-1, i-1) \text{ for } x > 1 \quad (23)$$

The B array is the same as that defined by eq. (10).

A comparison of $N(x)$ calculated for the end-capping agent added at the beginning of the polymerization and that for the end-capping agent added at 50% conversion is shown in Table IV. The end-capping agent used was 10 mol %. The last column is the distribution calculated directly from eq. (17). The next to the last column is the distribution calculated from eq. (23). The $N_1(x)$ used in the calculation of the B array was from eq. (3) with $p_1 = 0.5$. The N_2 function was calculated from eq. (19) with an F_2 value of 0.8181818 calculated from eq. (18). As expected, the two distributions are not the same.

The three applications discussed above show that the present stepwise scheme is adaptable to various polymerization conditions. Also, it is unlikely that a general computer program can be written for all cases. Each case requires a slightly different treatment but with the same stepwise concept.

EXTENSION TO BIMOLECULAR CONDENSATION

For A–A, B–B bimolecular condensation under equal reactivity conditions, Flory used three expressions to describe the distributions of three different polymer molecules; $N_e(x)$, for polymer of even numbers

Table IV Comparison of the Distribution Function $N(x)$ for the First 10 DPs Calculated for the End-capping Agent Added at the Beginning of the Polymerization and Those Calculated for The Addition of the End-capping Agent Later at 50% Conversion

x	$N_1(x)$	$N_2(x)$	$N(x)$ Cap at $p_1 = 0.5$	$N(x)$ Direct
1	.5	.1818182	.1818182	.1
2	.25	.1487604	7.438019E-02	9.000002E-02
3	.125	.121713	6.761835E-02	8.100002E-02
4	.0625	9.958338E-02	6.147122E-02	7.290001E-02
5	.03125	.0814773	5.588293E-02	6.561001E-02
6	.015625	6.666324E-02	5.080266E-02	5.904901E-02
7	.0078125	5.454265E-02	4.618423E-02	.0531441
8	3.90625E-03	.0446258	4.198566E-02	4.782969E-02
9	1.953125E-03	3.651201E-02	3.816879E-02	4.304672E-02
10	9.765625E-04	2.987346E-02	.0346989	3.874205E-02

of DP with A functionality at one end and B at the other end; $Noa(x)$, for polymer of odd numbers of DP with A at both ends; and $Nob(x)$, for polymer of odd numbers of DP but with B at both ends:

$$Ne(x) = p^{x-1} r^{x/2} \left[\frac{2(1-p)(1-rp)}{(1+1/r-2p)r} \right] \quad (24)$$

$$Noa(x) = p^{x-1} r^{x/2} \left[\frac{(1-p)^2 r^{-1/2}}{1+1/r-2p} \right] \quad (25)$$

$$Nob(x) = p^{x-1} r^{x/2} \left[\frac{(1-rp)^2 r^{-3/2}}{1+1/r-2p} \right] \quad (26)$$

where r is the mole ratio of A-A to B-B with B-B the excess monomer.

Extension of the present scheme to the bimolecular case will not be trivial. The starting reaction mixture that led to the distributions in eqs. (24)–(26) consists of two types of monomers: A-A and B-B. For the intermediate steps, three types of monomers must be considered: A-A, B-B, and A-B. The corresponding equations for N_2 will be more complex than eqs. (24)–(26) and have to be derived. Evidently, more than one B array will be needed. Whether the B arrays can be expressed by the simple recurring relation in eqs. (9) and (10) is also problematic. For these reasons, the bimolecular case is treated separately.⁴

CONCLUSIONS

1. A stepwise scheme based on probabilistic considerations for the calculation of MWD in the condensation of the A-B monomer was formulated and demonstrated to be valid.
2. The scheme was shown to be adaptable to treat polymerizations under the condition of unequal reactivity, to treat polymerizations with limited monomer solubility, and to treat the late introduction of the end-capping reagent in a polymerization. Each application, however, requires a slightly different treatment. Numerical calculations are relatively simple.
3. Extension of the stepwise scheme to the treatment of the more complicated bimolecular A-A, B-B condensation will not be trivial.

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