

# An Analytical Solution of the Molecular Weight Distribution of Reversible Step Growth Polymerization in Homogeneous Continuous Flow Stirred Tank Reactors

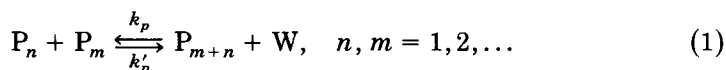
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## Synopsis

Mole balance for the molecular weight distribution in homogeneous continuous-flow stirred tank reactors (HCSTRs) for reversible step-growth polymerization has been written. The relation for the moment generating function  $G$  is found to be a nonlinear ordinary differential equation and has been solved analytically. The solution of the MWD of the polymer formed is shown to be valid even if the condensation product is removed. At equilibrium, the solution reduces to the Flory distribution. The computations show that the polydispersity of the polymer first increases with the residence time  $\theta$  of the reactor, but, for large  $\theta$ , it reduces to the equilibrium value after undergoing a maximum.

## INTRODUCTION

In step-growth polymerization, growth occurs through the reaction of reactive functional groups on the groups on the polymer.<sup>1-7</sup> If the starting monomer is bifunctional, the polymer formed is linear. If the monomer is multifunctional, the resulting polymer is either branched or a network. The step-growth polymerization of bifunctional monomers (schematically denoted as ARB type, where A and B are the reacting functional groups) can be represented as



In this representation,  $P_n$  is a polymer molecule having  $n$  repeat units and  $W$  is a low molecular weight condensation product. The reacting functional groups A and B on  $P_n$  are always found to be at chain ends and the molecule is strictly linear in structure.

Polymerization can either be carried out in batch or continuous reactors. As higher and higher throughputs are desired, the economy of large reactors demands that continuous reactors be used and usually either tubular reactors or a tank with agitators are employed.<sup>2-6</sup> These are idealized as plug reactors (PFRs) and homogeneous continuous-flow stirred tank reactors (HCSTRs). The performance of these ideal reactors has recently been reviewed.<sup>8-10</sup>

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The original analysis of Flory for the molecular weight distribution (MWD) of the polymer formed by the step-growth mechanism in batch reactors assumed an equal reactivity hypothesis. The polymerization is assumed to be irreversible in order to keep the analysis simple. Generalized kinetic balance relation valid for all oligomers is written. The infinite set of equations arising from this relation collapse into a single equation from which the net polymer concentration is analytically obtained.

Using this information the time-dependent MWD can, in principle, be solved sequentially. The MWD of the polymer is usually termed as Flory's most probable distribution and has been shown to be completely characterized by the conversion of functional groups. If the feed to the batch reactor is pure monomer, the polydispersity index ( $Q$ ) of the polymer is found to be limited to a maximum value of 2. Kilks<sup>11,12</sup> has subsequently analyzed a more general case of the recycle of the product stream of tubular reactors and showed that it is possible to get the value of  $Q$  greater than 2 in this case.

Irreversible ARB polymerization in HCSTRs have been analyzed.<sup>13</sup> For isothermal HCSTRs with monomer feed, unsteady state mole balance equations for various species have been written. Abraham<sup>14</sup> has also solved this problem using  $Z$  transforms, from which various moments of the MWD have been derived. For steady state operation of HCSTR with monomer feed and irreversible polymerization, Biesenberger<sup>15</sup> has derived analytical expressions of the MWD and the various moments of the polymer. He shows that the polydispersity index of the polymer is not limited to a maximum value of 2 and a designer can choose any desired level of  $Q$  by adjusting the reactor residence time.

The major difficulty of solving the MWD of reversible ARB polymerization lies in the fact that the growth step represented by eq. (1) consists of infinite elementary reactions.<sup>16-19</sup> In order to solve the concentration of any given species from mole balance equations, the concentrations of all other species must be known. In addition, the mole balance equations are nonlinear in nature. This implies that all these equations must be solved simultaneously, which is a difficult task even for a fast computer. If the mole balance relations are differential equations, which is the case for batch reactors, large numbers of equations must be solved such that the concentration of the last species is negligibly small in order to minimize the truncation error. As opposed to this, the MWD equations for HCSTRs are algebraic and, until now, have been solved only by using suitable numerical techniques, as discussed below.

The numerical determination of the MWD of the polymer formed in HCSTR can be done by using the Newton-Raphson or Brown's method.<sup>20</sup> The total number of equations to be solved must be kept large to minimize the truncation error and, for a finite reactor residence time, this can be as large as 300. Another major difficulty with these numerical techniques is the problem of providing a good initial guess.

The numerical techniques for determining MWD of polymer formed in HCSTR take considerable computation time. As the residence time increases, the CPU time required also increases and we have observed that the simulation of an industrial reactor could take as much as 5 CPU h on a DEC 1090.<sup>21</sup> In our earlier work, we attempted to decouple the MWD equations so that we could evaluate the concentrations of various species sequentially.<sup>21-24</sup> This leads to considerable reduction in the computation time.

Most of the studies reported on the reversible step-growth polymerization in HCSTR use numerical techniques due to the nonlinear nature of the governing equations. In this article, we have derived an expression for the moment generating function from the MWD equations and shown that for the reversible polymerization it is a Riccati differential equation. Under a transformation, this can be reduced to a linear second-order differential equation which can be solved analytically. From this, we have determined the MWD of the polymer formed in an HCSTR analytically. The technique of the solution presented in this article has been extended to determine the MWD under equilibrium. From this, the number and weight average chain length and the polydispersity index for any residence time of HCSTRs and under equilibrium condition have been determined. It is a common industrial practice to apply high vacuum to remove the condensation product from the fraction mass in order to push the overall polymerization in the forward direction. In this article, we have also examined the effect of vacuum upon the MWD of the polymer.

### MOLE BALANCE RELATIONS FOR HCSTRS

A schematic diagram of an HCSTR is shown in Figure 1, which has the reactor volume of  $V$  and the feed flow rate of  $F_0$ . The feed is assumed to consist of various oligomers at known concentrations  $[P_1]_0$ ,  $[P_2]_0$ , etc. and along with the condensation product  $W$ , oligomers  $P_i$  ( $i = 1, 2, \dots$ ) can flash from the reactor. Due to costs involved, it is desirable to separate the polymer in a suitable separator, as shown in Figure 1, and recycle. Assuming the HCSTR operating isothermally at steady state, for the nonflashing situation,

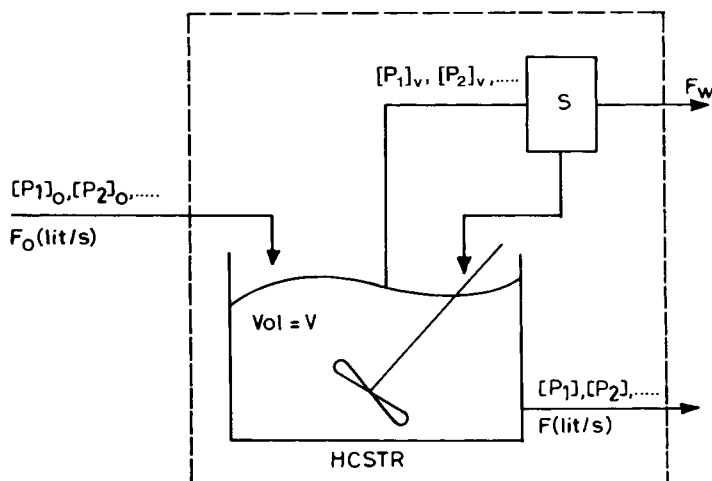


Fig. 1. Schematic diagram of a homogeneous continuous-flow stirred-tank reactor with flash: S = separator;  $F_0$  = input volumetric flow rate;  $F$  = output volumetric flow rate;  $F_w$  = volumetric flow rate of condensation product;  $[P_n]_0$  = molar concentration of species  $P_n$  in the feed,  $n = 1, 2, \dots$ ;  $[P_n]$  = molar concentration of species  $P_n$  in the exit  $n = 1, 2, \dots$ ;  $[P_n]_v$  = molar concentration of species  $P_n$  vaporizing from the reactor.

mole balance for various oligomers gives the following dimensionless relations:

$$\frac{P_1 - P_{10}}{\theta} = -2P_1P + 2\beta W \sum_{i=2}^{\infty} P_i \quad (2a)$$

$$\begin{aligned} \frac{P_n - P_{n0}}{\theta} = & -2P_nP + \sum_{i=1}^{n-1} P_iP_{n-i} \\ & + 2\beta W \sum_{i=n+1}^{\infty} P_i - \beta W(n-1)P_n, \quad n \geq 2, \end{aligned} \quad (2b)$$

$$\frac{W - W_0}{\theta} = P^2 - \beta W(\lambda_1 - P) \quad (2c)$$

where

$$\lambda_1 = \sum_{n=1}^{\infty} n[P_n]/\lambda_{10}^* \quad (3a)$$

$$P_n = [P_n]/\lambda_{10}^* \quad (3b)$$

$$P = \sum_{n=1} [P_n]/\lambda_{10}^* = \sum_{n=1}^{\infty} P_n \quad (3c)$$

$$P_0 = \sum_{n=1} [P_n]_0/\lambda_{10}^* = \sum_{n=1}^{\infty} P_{n0} \quad (3d)$$

$$W = [W]/\lambda_{10}^* \quad (3e)$$

$$W_0 = [W]_0/\lambda_{10}^* \quad (3f)$$

$$\lambda_{10}^* = \sum_{n=1}^{\infty} n[P_n]_0 \quad (3g)$$

$$\beta = k'_p/k_p \quad (3h)$$

$$\theta = k_p\lambda_{10}^*V/F_0 \quad (3i)$$

In these equations, the brackets indicate the concentrations of various species. Physically,  $\theta$  is the average residence time of the HCSTR and is a measure of the average time a fluid particle stays within the HCSTR. The total moles  $P$  of the polymer in the product stream is defined by eq. (3c) and can be obtained by adding eq. (2a) and (2b) for all possible values of  $n$ . On doing this, one obtains

$$\frac{P - P_0}{\theta} = -P^2 + \beta W(\lambda_1 - P) \quad (4)$$

In this relation the normalized first moment  $\lambda_1$  takes on the value of unity and  $P_0$  is the moles of polymer in the feed. Since  $\lambda_1$  represents the total number of repeat units, it remains time-invariant. It is desired to determine  $P_n$  for all  $n$ , which is done below.

### MOMENT-GENERATING FUNCTION FOR REVERSIBLE POLYMERIZATION IN HCSTRS

In order to determine the MWD of the polymer formed, we define a moment generating function  $G$ , as

$$G = \sum_{n=1}^{\infty} s^n P_n \quad (5a)$$

The value of  $G$  for the feed is thus given by

$$G_0 = \sum s^n P_{n0} \quad (5b)$$

The normalized first moment  $\lambda_1$ , as defined in eq. (3a), can be rewritten in terms of  $G$  as

$$\lambda_1 = \lim_{s \rightarrow 1^-} s \frac{\partial G}{\partial s} \quad (5c)$$

represents the total number of repeat units which must be time-invariant.

The relation for the moment-generating function  $G$  can be derived by multiplying eq. (2a) by  $s$  and eq. (2b) by  $s^n$  and then adding for all  $n$  to get

$$\frac{G - G_0}{\theta} = -2PG + G^2 + 2\beta W \frac{sP - G}{(1-s)} - \beta W \left( s \frac{\partial G}{\partial s} - G \right) \quad (6a)$$

where

$$\sum_{n=1}^{\infty} ns^n P_n = s \frac{\partial G}{\partial s} \quad (6b)$$

The details of this derivation are included in Appendix A. Equation (6a) can be rearranged as

$$\begin{aligned} \frac{\partial G}{\partial s} = & \frac{1}{\beta W s} G^2 - \frac{1}{\beta W s} \left( \frac{1}{\theta} + 2P + \beta W \frac{1+s}{1-s} \right) G \\ & + \frac{1}{\beta W s} \left( \frac{G_0}{\theta} + \frac{2\beta W P s}{1-s} \right) \end{aligned} \quad (6c)$$

This is a nonlinear first-order ordinary differential equation, which is transformed into a linear second-order differential equation by substituting

$$G = -\beta W s \frac{\partial y / \partial s}{y} \quad (7)$$

On doing so, one obtains the following:

$$s(1-s) \frac{d^2 y}{ds^2} + [\alpha'(1-s) + 2] \frac{dy}{ds} + [\alpha_0^2 \theta (1-s) R(s) + (\alpha - \alpha_0)] y = 0 \quad (8)$$

where

$$\alpha_0 = \frac{1}{\beta W \theta} \quad (9a)$$

$$\alpha = \alpha' = \frac{1}{\beta W} \left( 2P + \frac{1}{\theta} \right) \quad (9b)$$

$$R(s) = R_0 + sR_1 + s^2R_2 + s^3R_3 + \cdots + s^nR_n + \cdots \quad (9c)$$

where

$$R_0 = P_{10} \quad (9d)$$

$$R_n = P_{n+1,0}, \quad n \geq 1 \quad (9e)$$

Equation (8), which has singularities at  $s = 0$  and  $s = 1$ , can be solved by the extended power series method of Frobenius. The MWD is obtained as the coefficients of the power series in  $s$  as shown below.

### MOLECULAR WEIGHT DISTRIBUTION IN REVERSIBLE POLYMERIZATION IN HCSTRS

Let us assume that the solution of (8), around singularity  $s = 0$ , is of the form

$$y(s) = \sum_{m=0}^{\infty} C_m s^{m+\sigma} \quad (10a)$$

The first and second derivatives are given by

$$\dot{y}(s) = \sum (m + \sigma) C_m s^{m+\sigma-1} \quad (10b)$$

and

$$\ddot{y}(s) = \sum (m + \sigma)(m + \sigma - 1) C_m s^{m+\sigma-2} \quad (10c)$$

On substituting these in eq. (8) and collecting terms for the lowest order, we get the indicial relation

$$\sigma[(\sigma - 1) + \alpha' + 2] C_0 = 0 \quad (11)$$

For nonzero  $C_0$  the roots of  $\sigma$  give two exponents  $\sigma_1 = 0$  and  $\sigma_2 = -(\alpha' + 1)$ .

The first solution for the exponent  $\sigma_1 = 0$  is

$$y_1(s) = C_0 \sum_{m=0}^{\infty} r_m s^m \tag{12}$$

and the coefficients  $r_m$  are obtained from the following recursive relationship found from eq. (8) as (details are included in Appendix B.)

$$r_{m+1} = \frac{m(m + \alpha' - 1) - (\alpha - \alpha_0)}{(m + 1)(m + \alpha' + 2)} r_m + \frac{\alpha_0^2 \theta (\sum_{m-1} - \sum_m)}{(m + 1)(m + \alpha' + 2)} \tag{13a}$$

where

$$r_0 = 1 \tag{13b}$$

$$\sum_m = \sum_{j=0}^m R_j r_{m-j} \tag{13c}$$

The  $R_j$  in eq. (13c) are the coefficients of the polynomial  $R(s)$  defined in eq. (9) and carry the information regarding the feed distribution.

Similarly, the second solution for  $\sigma_2 = -(\alpha' + 1)$  is determined and the general solution is written as a sum of these as

$$y(s) = y_1(s) + y_2(s) = C_0 \sum_{m=0}^{\infty} r_m s^m + C_0^* s^{-(\alpha'+1)} \sum_{m=0}^{\infty} r_m^* s^m \tag{14}$$

With the knowledge of  $y$ , the moment generating function can now be determined. It is observed that  $G$  is a series in  $s$  with integral powers only and exponent  $\sigma_2 = -(\alpha' + 1)$  in eq. (14) is a noninteger. This implies that  $C_0^*$  is necessarily zero. In view of this, the general solution of  $G$  is obtained by dropping the second series term altogether and is given by

$$G = -\beta W s \frac{r_1 (1 + a_1 s + a_2 s^2 + \dots)}{r_0 (1 + b_1 s + b_2 s^2 + \dots)} \tag{15a}$$

$$= -\beta W s \frac{r_1}{r_0} (1 + c_1 s + c_2 s^2 + \dots) \tag{15b}$$

where the  $a_i$ ,  $b_i$ , and  $c_i$  series are given by

$$a_n = (n + 1)r_{n+1}/r_1 \tag{16a}$$

$$b_n = r_n/r_0 \tag{16b}$$

$$c_n = a_n - b_n - \left( \sum_{j=1}^{n-1} b_j c_{n-j} \right) \tag{16c}$$

The  $r_n$  in these are given by the recursive relation given in eq. (13). Comparing the definition of  $G$  in (5a) with (15b) gives the MWD of the polymer as (since  $r_0$  is equal to unity)

$$P_1 = -\beta W r_1 \quad (17a)$$

$$P_n = -\beta W r_1 c_{n-1}, \quad n \geq 2 \quad (17b)$$

### MWD AT EQUILIBRIUM

The mole balance relations in eq. (2) at equilibrium (for  $\theta \rightarrow \infty$ ) reduces to

$$-2P_1P + 2\beta W \sum_{i=2}^{\infty} P_i = 0 \quad (18a)$$

$$-2P_nP + \sum_{i=1}^{n-1} P_i P_{n-i} + 2\beta W \sum_{i=n+1}^{\infty} P_i - \beta W(n-1)P_n = 0 \quad (18b)$$

Let us assume that the form of the solution satisfying eq. (18) is

$$P_n = xy^{n-1} \quad (19)$$

Since the first moment of the MWD is always unity, eq. (19) satisfies

$$\lambda_1 = x(1 + 2y + 3y^2 + \dots) = \frac{x}{(1-y)^2} = 1$$

Or

$$x = (1-y)^2 \quad (20)$$

In addition, the total moles of polymer,  $P_{\text{eq}}$ , in the reaction mass is given by

$$P_{\text{eq}} = x(1 + y + y^2 + \dots) = \frac{x}{(1-y)}$$

or

$$P_{\text{eq}} = (-y) \quad (21)$$

Consequently the MWD in eq. (19) is given by

$$P_n = P_{\text{eq}}^2(1 - P_{\text{eq}})^{n-1} \quad (22)$$

This is the Flory's distribution, which on substitution in eq. (18) is seen to satisfy it completely for any  $\beta$  and is consistent with observations made by Flory.  $P_{\text{eq}}$  above can be easily determined for given  $W$  in the reaction mass by

$$-P_{\text{eq}}^2 + \beta W(\lambda_1 - P) = 0 \quad (23)$$



One can obtain the same result by the solution of the differential equation given in eq. (6) for the limit of  $\theta \rightarrow \infty$ .

### MWD OF POLYMER IN THE PRESENCE OF FLASH

In the presence of flashing, the outlet flow rate of the HCSTR would differ from the inlet flow rate  $F_0$  by the amount of the condensation product evaporated. Assuming the density in the inlet stream and product stream remains unchanged (say it is  $\rho$ ), the mole balance relations for polymeric species get modified to

$$\frac{P_1 - P_{10}}{\theta} = -2P_1P + 2\beta W(P - P_1) + \frac{\rho_w}{\rho\theta_w}P_1 \quad (24a)$$

$$\begin{aligned} \frac{P_n - P_{n0}}{\theta} = & -2P_nP + \sum_{i=1}^{n-1} P_iP_{n-i} + 2\beta W \sum_{i=n+1}^{\infty} P_i \\ & - \beta W(n-1)P_n + \frac{\rho_w}{\rho\theta_w}P_n, \quad n \geq 2 \end{aligned} \quad (24b)$$

and the condensation product balance becomes

$$\frac{W - W_0}{\theta} = P^2 - \beta W(\lambda_1 - P) + \frac{\rho_w}{\rho\theta_w}W - \frac{\rho_w}{M_w\lambda_{10}^*\theta_w} \quad (25a)$$

where

$$\theta_w = k_p\lambda_{10}^*V/F_w \quad (25b)$$

Above,  $\rho_w$  and  $M_w$  are the mass density and molecular weight of the condensation product. The total moles  $P$  of the polymer are obtained by adding eqs. (24a, b) for all  $n$

$$\frac{P - P_0}{\theta} = -P^2 + \beta W(\lambda_1 - P) + \frac{\rho_w}{\rho\theta_w}P \quad (26)$$

Consequent to the above modification, the relation for the moment-generating function also changes—an additional term  $(\rho_w/\rho\theta_w)G$  shows up in eq. (6a). However, the transformed second-order differential equation in  $y$  remains identical to eq. (8) except that  $\alpha'$  is now defined as

$$\alpha' = \alpha - \frac{1}{\beta W\rho\theta_w} \quad (27)$$

This does not alter the analytical form of MWD and eq. (17) still remains valid.

Evaporation of the condensation product alters the concentrations of  $W$  and  $P$  in the product stream of the HCSTR because of  $\theta_w$  (or  $F_w$ ). Additional information on vapor-liquid equilibrium is needed in order to determine this.

In the following we consider two cases: In the first one we assume that only  $W$  leaves the reaction mass and, in the second, both  $P$  and  $W$  leave.

### CASE A: CONDENSATION PRODUCT FLASHING

It is assumed that the reaction mass consists of a binary mixture consisting of polymer  $P$  and the condensation product  $W$ . Their mole fractions,  $x_P$  and  $x_W$  are given as

$$x_P = \frac{P}{P + W} \quad (28a)$$

and

$$x_W = 1 - x_P \quad (28b)$$

If  $P_T$  is the pressure applied to the reactor,  $P_W^0(T)$  the vapor pressure of the condensation product, then

$$x_W = \frac{P_T}{P_W^0(T)} = \frac{W}{P + W} \quad (29)$$

It is assumed that the polymer cannot be in the vapor phase and the vapor liquid equilibrium is given by the Raoult's law. This is done to keep the analysis simple, even though the model presented here can be easily extended for more complex vapour liquid equilibrium relations. Equation (29) gives

$$W = P \frac{x_W}{1 - x_W} \triangleq kP \quad (30)$$

In eq. (29)  $x_W$  greater than 1 implies that the vapor pressure of the condensation product  $W$  is less than the applied pressure. This would mean that  $W$  would not distill and the  $W$  and  $P$  are the same as those for closed reactors. On substituting eq. (30) in eqs. (25) and (26), one can solve the following cubic equation for  $P$ :

$$aP^3 + bP^2 + cP + d = 0 \quad (31)$$

where

$$k = x_W / (1 - x_W) \quad (32a)$$

$$a = (1 + \beta k) \theta (k + 1) M_W \lambda_{10}^* \quad (32b)$$

$$b = -(1 + \beta k) \rho \theta + \beta k \theta (k + 1) M_W \lambda_{10}^* \quad (32c)$$

$$c = \beta k \theta \rho - \rho - k M_W \lambda_{10}^* P_0 + M_W \lambda_{10}^* W_0 \quad (32d)$$

$$d = \rho P_0 \quad (32e)$$

The moles of condensation product condensed from the HCSTR is then

computed, using eq. (26), as

$$F_w = \frac{k_p \lambda_{10}^{2*} V \rho M_w}{\theta \rho_w} \left( \frac{P(k+1) - (W_0 + P_0)}{P(k+1) M_w \lambda_{10}^* - \rho} \right) \quad (33)$$

### CASE B. POLYMER FLASHING WITH CONDENSATION PRODUCT

With the increase in chain length, it is known that the volatility of polymer molecules reduces sharply. As a first approximation, we assume that only monomer  $P_1$  leaves the reactor. Assuming that Raoult's law is valid, the vapor-liquid equilibrium is given by

$$\frac{P_{P_1}^0}{P_T} \frac{P_1}{P+W} + \frac{W}{P+W} \frac{P_W^0}{P_T} = 1 \quad (34)$$

Here  $P_{P_1}^0$  and  $P_W^0$  are the vapor pressures of  $P_1$  and  $W$ , respectively, and  $P_T$  the total reactor pressure. We can solve for the concentration of the condensation product in HCSTR using this relation. On substituting this in eqs. (25) and (26),  $\theta_w$  can again be evaluated.

### COMPUTATIONAL TECHNIQUE

For specified reactor temperature and pressure, it is first ascertained from eq. (29) [or eq. (34), in the case where monomer is also flashing] whether there is flashing. In case of condensation product flashing, one solves the cubic eq. (31) for  $P$ . If there is no flashing,  $W$  is given by the following stoichiometric relation:

$$W = (W_0 + P_0 - P) \quad (35)$$

Equation (4) can be solved for  $P$  without any trial and error. Once this is done,  $R_i$  and  $r_i$  can be evaluated sequentially from eqs. (9) and (13) respectively. Series  $a_i$ ,  $b_i$ ,  $c_i$  are then obtained from eq. (16) and the MWD of the polymer from eq. (17). The solution scheme is summarized in Table I.

### RESULTS AND DISCUSSION

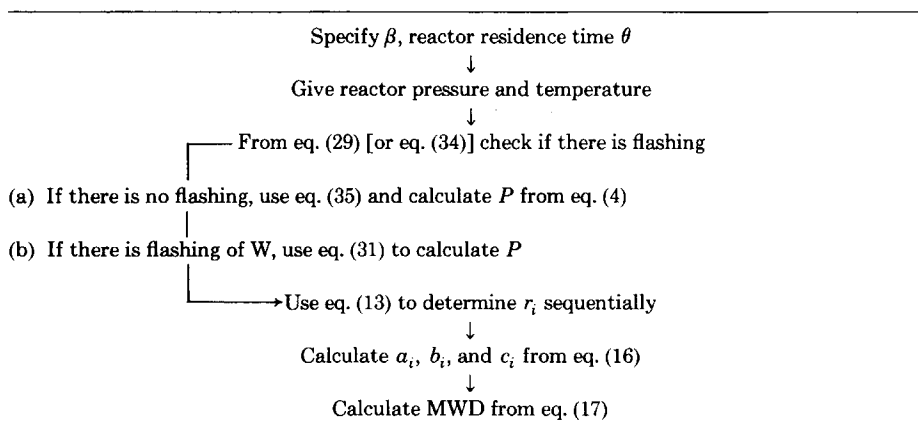
In several applications, polymerization is carried out in a train of reactors which can be any combination of batch and continuous reactors. When the HCSTR is placed somewhere in the middle of the train, its feed consists of higher oligomers. Since the analytical solution developed in this work is valid for any feed, it can be used to determine the characteristic of such reactors easily.

In order to demonstrate the effect of feed upon the polymerization in HCSTR, we assume that the feed has Flory's distribution given by

$$P_{n0} = P_0^2 (1 - P_0)^{n-1} \quad (36)$$

where  $P_0$  is the total moles of the polymer in feed. It is seen that the MWD of

TABLE I  
Algorithm for the Computation of MWD of the Polymer Formed  
in HCSTRs



the polymer is completely characterized by one variable  $P_0$  and  $P_0 = 1$  corresponds to the situation where the feed is pure monomer.

The analytical solution for the MWD of the polymer formed in HCSTRs involves only one recursive infinite series,  $r_i$  ( $i = 1, 2, \dots$ ) given in eq. (13). The  $a_i$ ,  $b_i$ , and  $c_i$  series appearing in eq. (15) are only a minor rearrangement as described therein. The  $r_1$  in eq. (17) is found to be negative and all terms of  $c_i$  series are positive. Since the first moment of the MWD of the polymer is always unity, the  $c_i$  must be a convergent series. In addition, we have carried out extensive computations of  $c_i$  series under all possible variation of reaction parameters and checked our analytical solution against the numerical computation of MWD.<sup>21-24</sup> We found the  $c_i$  series to be well behaved and never to lead to any instability of computation. The solution scheme developed in this work, this way, represents a convenient technique for determining the MWD of the polymer formed in HCSTRs and can easily be implemented even on a hand held calculator. The CPU time taken on DEC 1090 computer is less than 0.1 s. Most of the studies reported in the literature assume monomer feed and require numerical determination of the MWD which takes large CPU time (sometimes about 1 CPU h for large  $\theta$ ) due to excessive iterations. The analytical solution by Biesenberger assumes irreversible polymerization with monomer feed. In this paper we have relaxed all these assumptions and additionally present results in the presence of flashing.

We first determine the MWD of the polymer when the feed to the HCSTR is polydispersed. This is obtained by varying  $P_0$  in eq. (36) and results have been plotted in Figure 2. Results have been reported for two residence times,  $\theta = 1$  and  $\theta = 15$ , and the MWD is seen to become broad as  $\theta$  increases. We also find that as  $\beta$  increases, the conversion of functional groups reduces and some of higher oligomers depolymerize to give a sharper distribution. It is sometimes difficult to compare two MWD; however, its moments can be compared as done in Figures 3 and 4.

In Figure 3, we have plotted the average chain length of the product stream as a function of residence time of HCSTR. It is seen that for  $\beta = 0.1$  and  $P_0$

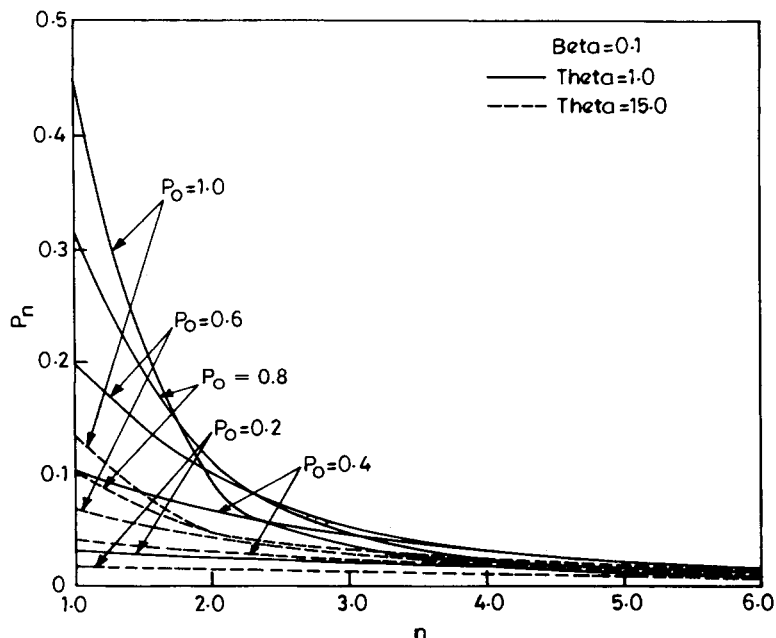


Fig. 2. The effect of residence time ( $\theta$ ) [(—) 1.0; (---) 15.0] and the nature of initial feed  $P_0$  (characterized by Flory's distributions) on molecular weight distribution.

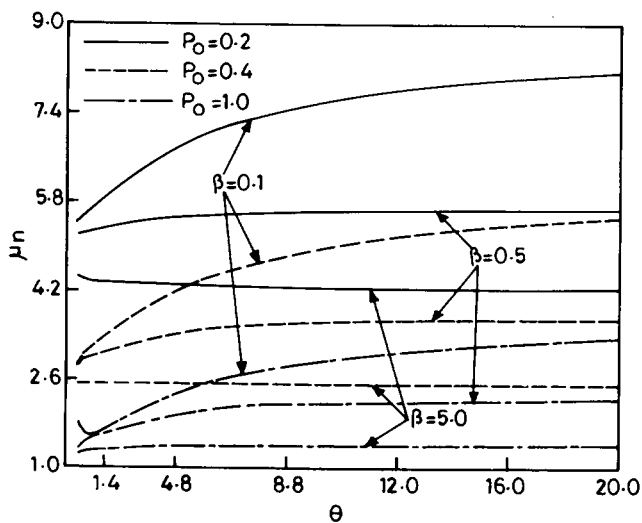


Fig. 3. The effect of the kinetic parameter  $\beta$  and  $P_0$  [(—) 0.2; (---) 0.4; (-·-·-) 1.0], total moles of polymer in the feed, on the chain length vs. residence time.

as 0.2, the starting chain length is 5.0 and it rises to a value of 8.4 and is still rising at  $\theta = 20$ . As opposed to this for  $P_0 = 0.4$ , the starting chain length is 2.5 and it goes up to 5 only, which is a smaller increase. This is because, for small  $P_0$ , the reaction mass consists of higher oligomers in considerably larger concentration. Any growth reaction of these would lead to larger chain length, as observed in this figure.

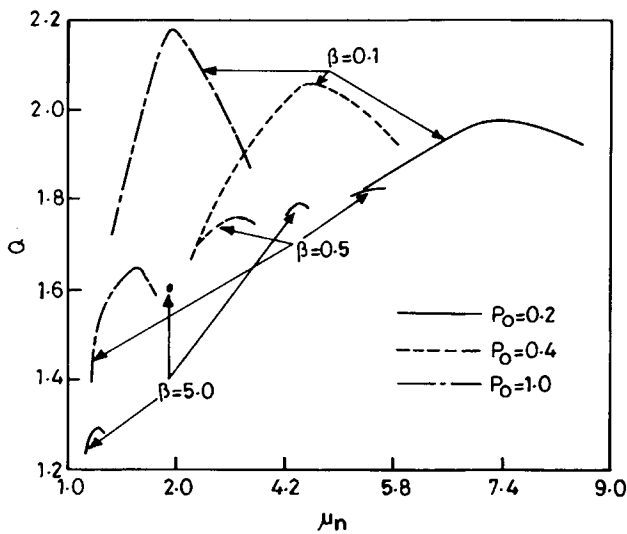


Fig. 4. The effect of the kinetic parameter  $\beta$  and total moles of polymer in the feed,  $P_0$  (—) 0.2; (---) 0.4; (- - -) 1.0], on polydispersity index vs. average chain length.

We have defined polydispersity index  $Q$  as the ratio of number- and weight-average chain length,  $\mu_n$  and  $\mu_w$ , given by

$$Q = \mu_w / \mu_n \quad (37a)$$

where

$$\mu_w = \lambda_2 / \lambda_1 \quad (37b)$$

$$\mu_n = \lambda_1 / \lambda_0 \quad (37c)$$

Flory has analyzed step-growth polymerization in the batch reactor with monomer as its feed and shown through statistical arguments that the MWD of the polymer formed has a binomial distribution. He further showed that the polydispersity index is proportional to conversion of functional groups and is inversely proportional to  $\mu_n$ . For irreversible step-growth polymerization carried out in HCSTR, having finite residence time, we find that the MWD of the polymer formed is significantly different.

In Figure 4 we find that  $Q$  increases first but, after some time, it begins to fall, which can be explained as follows. Biesenberger<sup>15</sup> has studied irreversible step-growth polymerization in HCSTRs and has shown that, for the same chain length, the polymer formed in the HCSTR always has a higher  $Q$ . Since the feed to the HCSTR is assumed to have Flory's distribution, it can be safely assumed that this is the product stream of some fictitious batch reactor with monomer as a feed to the latter. Flory has shown that  $Q$  for the batch reactor is never more than 2 while Biesenberger has shown that  $Q$  increases linearly with conversion. In our studies of reversible polymerization,  $Q$  rises for small  $\theta$  simply because the reaction mass is closer to the irreversible case and therefore  $Q$  rises with  $\mu_n$ . We have clearly shown that the polymer at equilibrium always has Flory's distribution. This means that, as  $\theta$  increases,

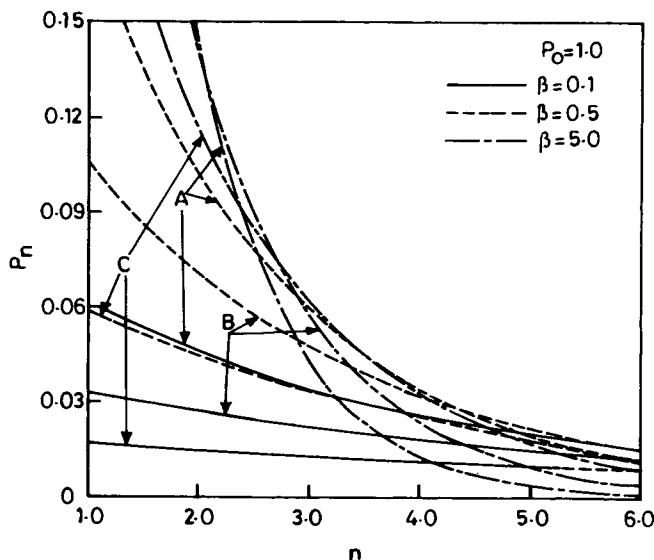


Fig. 5. The effect of the kinetic parameter  $\beta$  [(—) 0.1; (---) 0.5; (- - -) 5.0] and the extent of flashing on the equilibrium MWD: (A) no flashing; (B)  $0.5W_{\max}$  removed; (C)  $0.75W_{\max}$  removed.  $P_0 = 1.0$ .

the reaction mass is closer to the equilibrium and, consequently,  $Q$  falls as observed in the figure. It is interesting to observe that, for  $\beta = 0.5$  and  $P_0 = 0.4$ , the change in  $\mu_n$  or  $Q$  is small during polymerization and it appears as a point on the figure.

We have shown that, under the equilibrium condition, the polymer always has Flory's distribution. When the average chain length of the polymer

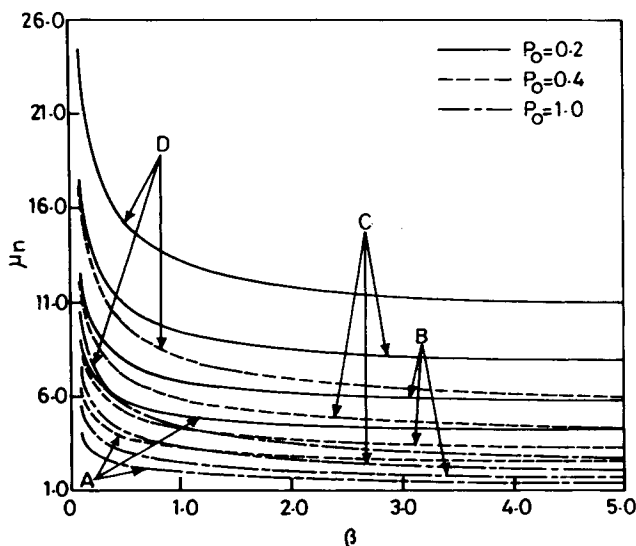


Fig. 6. The effect of total moles of polymer in the feed  $P_0$  [(—) 0.2; (---) 0.4; (- - -) 1.0], and the extent of flashing on equilibrium average chain length vs. kinetic parameter  $\beta$ : (A) no flashing; (B)  $0.5W_{\max}$  removed; (C)  $0.75W_{\max}$  removed; (D)  $0.875W_{\max}$  removed.

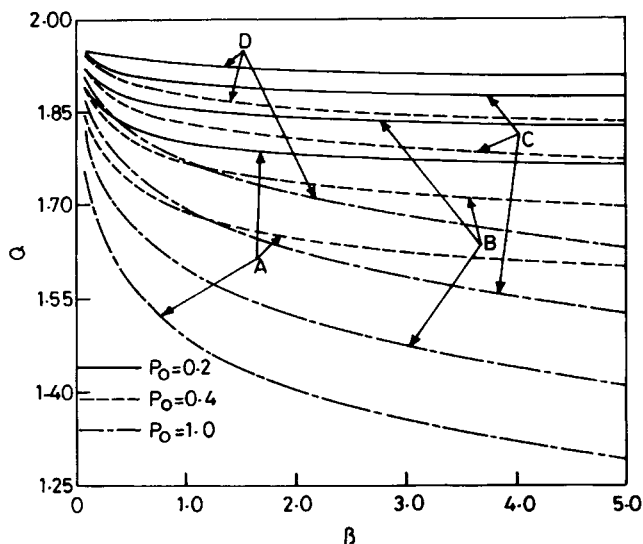


Fig. 7. The effect of total moles of polymer in the feed  $P_0$  [(—) 0.2; (---) 0.4; (- - -) 1.0] and the extent of flashing on equilibrium polydispersity index vs. kinetic parameter  $\beta$ : (A) no flashing; (B)  $0.5W_{\max}$  removed; (C)  $0.75W_{\max}$  removed; (D)  $0.875W_{\max}$  removed.

becomes large (corresponding to about 90% conversion of functional groups), the overall polymerization can be taken as mass transfer (for the condensation product) controlling. When this is so, polymeric part of the reaction mass can be assumed to be in equilibrium at the concentration of the condensation product within the reactor. It is thus seen that with the analytical solution of the equilibrium MWD in this work, one needs to solve only one diffusion equation for the condensation product. In generating Figures 5–7 for the MWD,  $\mu_n$  and  $Q$  for the equilibrium polymerization, we observe that for specified  $W_0$  and  $P_0$  in the feed, maximum  $W$ ,  $W_{\max}$ , in the reaction mass is given by

$$W_{\max} = W_0 + P_0 - P_{\text{eq}} \quad (38)$$

$P_{\text{eq}}$  is the moles of total polymer formed at the equilibrium in a closed reactor. On application of a vacuum, moles of condensation product fall due to flashing from this  $W_{\max}$  and can in principle be reduced to any level. In Figure 5, we have presented MWD for three levels and we find that the MWD becomes broader. It is seen in Figure 6 that this corresponds to a considerable increase in chain length and, in Figure 7, that it corresponds to a higher polydispersity index.

### CONCLUSIONS

In this article, we have analyzed reversible step-growth polymerization in homogeneous continuous-flow stirred tank reactors. Assuming the equal reactivity hypothesis proposed by Flory, we have established mole balance relations for the MWD of the polymer formed in it. These represent infinite algebraic expressions which can be combined into one equation by the use of the moment-generating function  $G(s, \theta)$ . The generation relation for  $G$  is a first-order nonlinear ordinary differential equation which has been reduced to



a second-order linear ordinary differential equation under a transformation. The latter can be solved using the Frobenius method of series solution; from this the analytical solution of the MWD is determined in a natural way. We have examined the effect of flashing of the condensation product as well as polymer and have derived results for equilibrium polymerization. We find that, in the case of the latter, the MWD is given by Flory's distribution, which is expected.

We have shown that the reversibility of polymerization and the polydispersity of the feed has a great effect upon the MWD of polymer formed in HCSTRs. It is observed that as the reactor residence  $\theta$  is increased, the polydispersity index  $Q$  vs. chain length  $\mu_n$  first rises and then falls, giving a maximum. This result must be contrasted with that found by Biesenberger<sup>15</sup> for irreversible polymerization, in which case  $Q$  increases linearly with  $\mu_n$  without any limit. This has been explained by the fact that as  $\theta$  increases, HCSTR operates closer to equilibrium and the MWD would then be closer to Flory's distribution. The nature of the feed is found to have a great effect upon the chain length of the polymer formed. As the concentration of higher oligomers in feed increases, the growth of the polymer chains would be larger for every functional group reacted. As a result, the gain in chain length is found to be larger as the average chain length of polymer in feed increases.

**APPENDIX A: DERIVATION OF EQ. (6A) FOR THE MOMENT GENERATING FUNCTION  $G$**

Multiply eq. (2a) by  $s$  and eq. (26) by  $s^n$  (for  $n \geq 2$ ) and on adding:

$$\frac{\sum_{n=1}^{\infty} s^n P_n - \sum_{n=1}^{\infty} s^n P_{n0}}{\theta} = -2 \sum_{n=1}^{\infty} s^n P_n P + \sum_{n=2}^{\infty} s^n \sum_{i=1}^{n-1} P_i P_{n-i} + 2\beta W \sum_{n=1}^{\infty} s^n \sum_{i=n+1}^{\infty} P_i - \beta W \sum_{n=2}^{\infty} s^n (n-1) P_n \tag{39}$$

The term on the left-hand side is  $(G - G_0)/\theta$ . The first term on right-hand side (rhs) is  $-2PG$ . The second term on the rhs is

$$\begin{aligned} \sum_{n=2}^{\infty} s^n \sum_{i=1}^{n-1} P_i P_{n-i} &= s^2 P_1^2 + s^3 (P_1 P_2 + P_2 P_1) \\ &+ s^4 (P_1 P_3 + P_2 P_2 + P_3) \\ &+ s^5 (P_1 P_4 + P_2 P_3 + P_3 P_2 + P_4 P_1) + \dots \\ &= s P_1 [s P_1 + s^2 P_2 + s^3 P_3 + \dots] \\ &+ s^2 P_2 [s P_1 + s^2 P_2 + s^3 P_3 + \dots] \\ &+ s^3 P_3 [s P_1 + s^2 P_2 + s^3 P_3 + \dots] \\ &+ \dots \\ &= \left( \sum_{n=1}^{\infty} s^n P_n \right) \left( \sum_{n=1}^{\infty} s^n P_n \right) = G^2 \tag{40} \end{aligned}$$

The third term on the rhs is given by

$$\begin{aligned}
 2\beta W \sum_{n=1}^{\infty} s^n \sum_{i=n+1}^{\infty} P_i &= 2\beta W \left[ s \sum_{i=2}^{\infty} P_i + s^2 \sum_{i=3}^{\infty} P_i + s^3 \sum_{i=4}^{\infty} P_i + s^4 \sum_{i=5}^{\infty} P_i + \dots \right] \\
 &= 2\beta W \left[ sP_2 + (s + s^2)P_3 + (s + s^2 + s^3)P_4 \right. \\
 &\quad \left. + (s + s^2 + s^3 + s^4)P_5 + \dots \right] \\
 &= 2\beta Ws \left[ P_2 + (1 + s)P_3 + (1 + s + s^2)P_4 \right. \\
 &\quad \left. + (1 + s + s^2 + s^3)P_5 + \dots \right] \\
 &= 2\beta Ws \left[ \frac{(1-s)}{(1-s)} P_2 + \frac{(1-s^2)}{1-s} P_3 + \frac{(1-s^3)}{1-s} P_4 \right. \\
 &\quad \left. + \frac{(1-s^4)}{(1-s)} P_5 + \dots \right] \\
 &= \frac{2\beta Ws}{(1-s)} \sum_{n=2}^{\infty} (1-s^{n-1})P_n = \frac{2\beta Ws}{(1-s)} \sum_{n=1}^{\infty} (1-s^{n-1})P_n \\
 &= \frac{2\beta W}{(1-s)} \left[ \sum_{n=1}^{\infty} sP_n - \sum_{n=1}^{\infty} s^n P_n \right] \\
 &= \frac{2\beta W}{(1-s)} (sP - G) \tag{41}
 \end{aligned}$$

The last term on the rhs is

$$\begin{aligned}
 -\beta W \sum_{n=2}^{\infty} s^2(n-1)P_n &= -\beta W \left[ \sum_{n=2}^{\infty} ns^n P_n - \sum_{n=2}^{\infty} s^n P_n \right] \\
 &= -\beta W \left[ s \sum_{n=1}^{\infty} ns^{n-1} P_n - \sum_{n=1}^{\infty} s^n P_n \right] \\
 &= -\beta W \left( s \frac{\partial G}{\partial S} - G \right) \tag{42}
 \end{aligned}$$

Hence the relation in (39) becomes

$$\frac{G - G_0}{\theta} = -2PG + G^2 + 2\beta W \frac{sP - G}{(1-s)} - \beta W \left( s \frac{\partial G}{\partial S} - G \right) \tag{6a}$$

## APPENDIX B: DERIVATION OF THE RECURSIVE RELATIONSHIP OF EQ. (13a)

$$y(s) = \sum_{m=0}^{\infty} C_m S^{m+\sigma} \tag{43a}$$

$$\frac{dy}{ds} = \sum (m + \sigma) C_m S^{m+\sigma-1} \tag{43b}$$

and

$$\frac{d^2y}{ds^2} = \sum (m + \sigma)(m + \sigma - 1)C_m s^{m+\sigma-2} \quad (43c)$$

Substituting these into eq. (8):

$$\begin{aligned} & (s - s^2) \left[ \sum (m + \sigma)(m + \sigma - 1)C_m s^{m+\sigma-2} \right] + (\alpha' - \alpha's + 2) \\ & \times \sum (m + \sigma)C_m s^{m+\sigma-1} \\ & + \{ (\alpha_0^2\theta - \alpha_0^2\theta s)(R_0 + sR_1 + s^2R_2 + s^3R_3 + \dots) + (\alpha - \alpha_0) \} \\ & \times \sum C_m s^{m+\sigma} = 0 \end{aligned} \quad (44)$$

or

$$\begin{aligned} & \sum (m + \sigma)(m + \sigma - 1)C_m s^{m+\sigma-1} - \sum (m + \sigma)(m + \sigma - 1)C_m s^{m+\sigma} \\ & + (\alpha' + 2) \sum (m + \sigma)C_m s^{m+\sigma-1} - \alpha' \sum (m + \sigma)C_m s^{m+\sigma} \\ & + \alpha_0^2\theta R_0 \sum C_m s^{m+\sigma} + \alpha_0^2\theta R_1 \sum C_m s^{m+\sigma+1} + \dots \\ & + \theta \alpha_0^2 R_j \sum C_m s^{m+\sigma+j} \\ & - \alpha_0^2\theta R_0 \sum C_m^{m+\sigma+1} - \alpha_0^2 R_1 \sum C_m s^{m+\sigma+2} - \dots \\ & - \alpha_0^2\theta R_j \sum C_m s^{m+\sigma+j+1} \\ & + (\alpha - \alpha_0)C_m s^{m+\sigma} = 0 \end{aligned} \quad (45)$$

Collecting terms for the lowest power of  $s$ , which is  $(\sigma - 1)$  at  $m = 0$ , gives the indicial eq. (11). Similarly collecting terms for an arbitrary power  $(n + \sigma)$  of  $s$  gives

$$\begin{aligned} & (n + 1 + \sigma)(n + 1 + \sigma - 1)C_{n+1} - (n + \sigma)(n + \sigma - 1)C_n \\ & + (\alpha' + 2)(n + 1 + \sigma)C_{n+1} - \alpha'(n + \sigma)C_n + \alpha_0^2\theta \sum_{j=0}^n R_j C_{n-j} \\ & - \alpha_0^2\theta \sum_{j=0}^{n-1} R_j C_{n-1-j} + (\alpha - \alpha_0)C_n = 0 \end{aligned} \quad (46)$$

or

$$\begin{aligned} & [(n + 1 + \sigma)(n + \sigma) + (\alpha' + 2)(n + 1 + \sigma)]C_{n+1} \\ & = [(n + \sigma)(n + \sigma - 1) + \alpha'(n + \sigma) - (\alpha - \alpha_0)]C_n \\ & + \alpha_0^2\theta \sum_{j=0}^n R_j C_{n-1-j} - \alpha_0^2\theta \sum_{j=0}^n R_j C_{n-j} \end{aligned} \quad (47)$$

or

$$C_{n+1} = \frac{[(n + \sigma)(n + \sigma - 1) + \alpha'(n + \sigma) - (\alpha - \alpha_0)]C_n}{(n + 1 + \sigma)(n + \sigma + \alpha' + 2)} + \frac{\alpha_0^2 \theta (\sum_{n-1} - \sum_n)}{(n + 1 + \sigma)(n + \sigma + \alpha' + 2)} \quad (48)$$

where

$$\sum_n \equiv \sum_{j=0}^n R_j C_{n-j} \quad (49)$$

Additionally, if we define

$$r_n \equiv C_n / C_0 \quad (50a)$$

then

$$r_0 \equiv 1 \quad (50b)$$

and the above recursive relationship is written for  $r_{n+1}$  when  $\sigma = 0$  as

$$r_{n+1} = \frac{\{[n(n + \alpha' - 1) - (\alpha - \alpha_0)]r_n + \alpha_0^2 \theta (\sum_{n-1} - \sum_n)\}}{(n + 1)(n + \alpha' + 2)} \quad (51)$$

### APPENDIX C: NOMENCLATURE

|                        |  |
|------------------------|--|
| $a_i, i = 1, 2, \dots$ | coefficient in the infinite numerator series for $G$ [as given by eq. (15a), expressed in terms of the recursive ratio series $r_i$ by eq. (16a)]    |
| $b_i, i = 1, 2, \dots$ | coefficient in the infinite denominator series for $G$ [as given by eq. (15a)], expressed in terms of the recursive ratio series $r_i$ by eq. (16b)] |
| $c_i, i = 1, 2, \dots$ | coefficient in the infinite series for $G$ [as given by eq. (15b)], expressed in terms of $a_i$ and $b_i$ , by eq. (16c)]                            |
| $C_M$                  | coefficient of the $m$ th power in the power series of $y$ [eq. (10a)]   |
| $C_0, C_0^*$           | coefficients for the zeroth power in the power series of the two solutions of $y$ : $y_1$ and $y_2$ [eq. (14)]                                       |
| $F_0$                  | inlet flow rate to CSTR (L/s)  |
| $F$                    | outlet flow rate from CSTR (L/s)   |
| $F_W$                  | flow rate of condensation product W from separator S (L/s)   |
| $G$                    | moment generating function based on feed conditions [given by eq. (5b)]  |
| $k_p$                  | forward reaction rate constant   |
| $k'_p$                 | reverse reaction rate constant   |
| $M_W$                  | molecular weight of condensation product   |
| $[P_n]$                | molar concentration of oligomeric species $P_n$  |
| $[P_{n0}]$             | molar concentration of oligomeric species $P_n$ in the feed  |
| $P_n$                  | dimensionless concentration of oligomeric species $P_n$ in the reactor   |
| $P_{n0}$               | dimensionless concentration of oligomeric species $P_n$ in the feed  |
| $P$                    | dimensionless molar concentration of total polymer in the reactor  |
| $P_0$                  | dimensionless molar concentration of total polymer in the feed   |
| $P_{eq}$               | dimensionless molar concentration of total polymer at equilibrium  |
| $P_T$                  | total pressure at which the reactor is operating   |
| $P_W^0$                | vapor pressure of condensation product at reactor temperature corresponding to $P_T$   |

|                          |   |
|--------------------------|---|
| $P_{P_1}^0$              | vapor pressure of monomer $P_1$ at reactor temperature corresponding to $P_T$   |
| $Q$                      | polydispersity index  |
| $R_i, i = 0, 1, 2 \dots$ | input feed distribution of species $P_1, P_2, \dots, P_{n+1}$ [eq. (9e)]  |
| $r_m, r_m^*$             | coefficient ratio in recursive series for $y_1$ and $y_2$ : $r_m = C_m/C_0$ and $r^* = C_m^*/C_0^*$                             |
| $V$                      | volume of the reaction mass in the reactor (L)  |
| $[W]$                    | molar concentration of condensation product in reactor (mol/L)  |
| $[W_0]$                  | molar concentration of condensation product in feed (mol/L)   |
| $W$                      | dimensionless molar concentration of condensation product in the reactor  |
| $W_0$                    | dimensionless molar concentration of condensation product in feed   |
| $W_{\max}$               | dimensionless maximum concentration of $W$ at equilibrium   |
| $x$                      | parameter in equilibrium feed distribution  |
| $x_P$                    | molar fraction of polymer in CSTR   |
| $x_W$                    | molar fraction of condensation product  |
| $y_1, y_2$               | the two particular solutions of the "transformed" second-order hypergeometric differential eq. (8)                              |
| $y$                      | transformed variable of moment generating function $G$ , according to eq. (7)   |
| $\alpha$                 | parameter in the hypergeometric differential equation   |
| $\alpha'$                | parameter in the hypergeometric differential equation   |
| $\alpha_0$               | parameter in the hypergeometric differential equation   |
| $\beta$                  | kinetic parameter = $k'_p/k_p$  |
| $\theta$                 | dimensionless residence time of CSTR  |
| $\theta_w$               | dimensionless residence time of flashing condensation product   |
| $\sigma$                 | exponent for the power series solution  |
| $\sigma_1, \sigma_2$     | roots of the indicial equation  |
| $\lambda_0$              | normalized zeroth moment of MWD   |
| $\lambda_1$              | normalized first moment of MWD  |
| $\lambda_2$              | normalized second moment of MWD   |
| $\Sigma_m$               | function defined in terms of recursive ratio series ( $r_m$ ) and inlet feed distribution variable $r_m$ according to eq. (13c) |
| $\mu_n$                  | number average chain length   |
| $\mu_w$                  | weight average chain length   |
| $\rho$                   | mass density of polymer (g/L)   |
| $\rho_W$                 | mass density of condensation product (g/L)  |

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