

# Analytical solution of molecular-weight distribution in reversible step-growth polymerization in homogeneous continuous-flow stirred tank reactors following unequal reactivity

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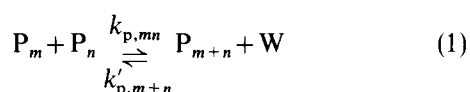
General unequal reactivity in reversible step-growth polymerization has been modelled by assuming that monomer reacts at different rates. The generation relation for the moment-generating function  $G$  has been derived for polymerization in homogeneous continuous-flow stirred tank reactors. It is a non-linear ordinary differential equation and has been solved analytically using the Frobenius method. Analytical solution of the molecular-weight distribution of the polymer is obtained from this in a natural way and is shown to be valid even when there is flashing of condensation product. Subsequently, the molecular-weight distribution at equilibrium has been derived.

(Keywords: step-growth polymerization; molecular weight distribution; modelling)

## INTRODUCTION

In step-growth polymerization chain growth occurs through the reaction of functional groups situated on polymer molecules. If the starting monomer is bifunctional (ARB), the resulting polymer is linear; and if it is multifunctional, the polymer acquires a branched or network structure.

Like all reactions in nature, step-growth polymerization for bifunctional (ARB-type) monomers is also reversible and can be represented by:



In this representation,  $P_m$  and  $P_n$  are molecules having  $m$  and  $n$  repeat units respectively, and  $W$  is the condensation product. Above  $k_{p,mn}$  is the rate constant for the forward step and  $k'_{p,m+n}$  is the rate constant for the reverse reaction between the condensation product  $W$  and a reacted  $-AB-$  bond on a  $P_{m+n}$  molecule.

Polymer formed by the step-growth mechanism always has a molecular-weight distribution ( $MWD$ ). Any molecular-weight distribution can be equivalently represented by its moments. The  $k$ th unnormalized moment  $\lambda_k^*$  is defined as

$$\lambda_k^* = \sum_{n=1}^{\infty} n^k [P_n] \quad k=0, 1, 2, \dots \quad (2)$$

It has been found that the physical properties of the polymer (for example, melt viscosity, tear strength, adhesive tack, friction, impact strength, etc.) are found to depend upon its  $MWD$ . Industrially, polymerization

is normally carried out in batch reactors<sup>1-3</sup>. However, as plant throughput increases, continuous<sup>4-6</sup> reactors are preferred over batch reactors. Among the various continuous reactor geometries, homogeneous continuous-flow stirred tank reactors (HCSTRs) are the most common, and their schematic diagram is shown in Figure 1.

As seen from equation (1), step-growth polymerization involves infinite elementary reactions, each having its own rate constant. The modelling of step-growth polymerization has been reviewed by several authors<sup>1,7-12</sup>, and the simplest among these is based upon the equal-reactivity hypothesis proposed by Flory<sup>11</sup>. In this it is assumed that all functional groups react with the same rate constant, independent of the chain length of the polymer on which they are situated.

There is evidence that the equal-reactivity hypothesis gives results that cannot explain experimental findings. Systems like phenylene sulphide<sup>13</sup>, polyimides<sup>14</sup>, polyurethanes<sup>15,16</sup>, divinylbenzene with *p*-cresol<sup>17</sup>, phenol-formaldehyde<sup>18-21</sup> and the ester interchange reaction on poly(ethylene terephthalate)<sup>22-24</sup> show either a chain-length-dependent reactivity or an induced asymmetry. In fact, recent experiments of Kuchanov *et al.*<sup>25</sup> have shown that, in polymerization under  $\theta$  conditions, several systems exhibit a chain-length-dependent unequal reactivity in which rate constant *versus* chain length  $n$  has an S shape.

Polymerization of asymmetric monomers and those exhibiting induced asymmetry have been analysed by several authors. Case<sup>26</sup> has used probabilistic arguments to derive the  $MWD$  and the moments of the polymer formed. Gandhi *et al.*<sup>27</sup> have used kinetic methods to analyse some of these systems and have derived results for HCSTRs.

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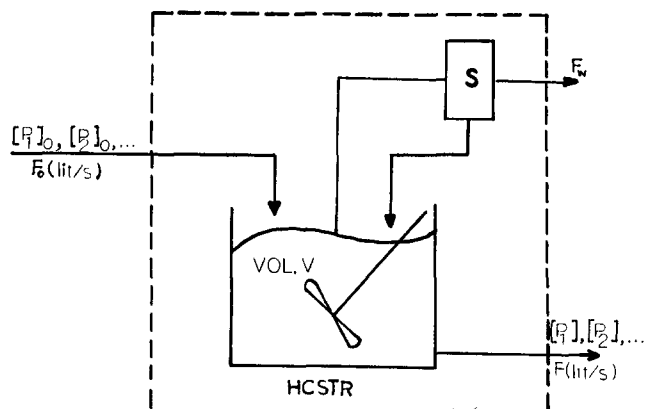


Figure 1 Schematic diagram of a homogeneous continuous-flow stirred tank reactor (HCSTR)

The most general chain-length-dependent reactivity (i.e. S-shaped form) has been more difficult to analyse mathematically. Nanda and Jain<sup>28</sup> have assumed all reactions in equation (1) to be irreversible and the forward rate constant to be decreasing with the chain length  $n$  following a linear relation. They have derived an analytical expression for the *MWD* and have curve-fitted the experimental *MWD* of nylon-6,6 using their results. Kumar<sup>29</sup> has modelled the S-shaped dependence of rate constants in equation (1) by assuming that monomer reacts with a different rate constant compared to other oligomers; all of which react with the same rate constant (different from that of the monomer).

In order to keep the mathematical analysis discussed above simple, step-growth polymerization has been assumed to be irreversible. The immediate effect of the chain-length-dependent unequal reactivity is that the mole balance equations for various species do not collapse into a single one as found for the equal-reactivity hypothesis. Kinetic equations for general reversible polymerization in HCSTRs with unequal reactivity in the forward step can be solved only numerically and have been solved in the literature using the following two techniques. In the first one, it is recognized that the *MWD* of the polymer is a solution of a set of coupled algebraic equations, which must be solved simultaneously. For this purpose, Brown's method is the most suitable, but in order to find the *MWD*, it is necessary to specify the total number of equations (say  $N_{max}$ ) and a good initial guess that is close to the actual solution. The  $N_{max}$  is decided by the fact that the concentration of the last species,  $P_{N_{max}}$ , must be less than the specified accuracy. However, a good initial guess poses considerable difficulty and is obtained by dividing the total residence time  $\theta$  into small increments  $\Delta\theta$ . For residence time  $\Delta\theta$ , the initial guess is taken as the conditions existing in the feed. The results for *MWD* calculated for time  $\Delta\theta$  serve as the initial guess for time  $2\Delta\theta$  and in this way the computation is stepped up to time  $\theta$ . Evidently the computations become extremely cumbersome for large residence times and in this regard the second numerical technique is a considerable improvement. In this the *MWD* equations are decoupled and the concentrations of various polymer species are computed sequentially<sup>30-32</sup>.

In this paper, we have analysed the unequal-reactivity model proposed by Kumar<sup>31</sup>. We have written down the *MWD* relations for reversible polymerization in HCSTRs and from these we have derived an expression for the

moment-generating function,  $G(s, \theta)$ , which is a non-linear ordinary differential equation. Under a mathematical transformation, this is reduced to a linear ordinary second-order equation, which has been solved to obtain an analytical expression for the *MWD* of the polymer formed in HCSTRs with specified residence time. Reversible polymerization is limited by equilibrium, as a result of which the condensation product must be removed from the reaction mass in order to obtain polymer of high molecular weight. Industrially this is done by applying high vacuum on the reactor to drive out  $W^{10}$ . Depending upon the level of vacuum applied, at times, smaller oligomers like  $P_1, P_2$ , etc., are also vaporized. In this paper, we have examined the effect of vacuum on reactor performance and evaluated an analytical expression of the *MWD* for a given vacuum level.

## KINETIC MODEL

Experiments of Kuchanov<sup>25</sup> have shown that the forward rate constants in equation (1) are chain-length-dependent and exhibit an S-shaped curve as discussed earlier. In this paper this has been approximated by assuming that the monomer reacts differently and various rate constants in equation (1) are given by:

$$\begin{aligned} k_{p,11} &= 2(k_{11}/2) \\ k_{p,mn} &= 2k_p \quad m \neq n \quad m, n = 1, 2, 3, \dots \\ k_{p,mn} &= 2(k_p/2) \quad m = n, \quad m, n > 1 \\ k'_{p,m} &= k'_p \quad m \geq 2 \end{aligned} \quad (3)$$

Herein, it is assumed that the reactivity of a reacted bond  $-AB-$  is the same whether it is at the chain end or at an internal site of  $P_m$ .

The schematic diagram of a HCSTR is shown in Figure 1. The feed is assumed to consist of oligomers at concentrations  $[P_1]_0, [P_2]_0, \dots$ , etc. The reactor volume is  $V$ , with the feed flow rate as  $F_0$ . Mole balance relations for  $P_1, P_2, \dots, P_n$  and  $W$ , at the exit of an isothermal HCSTR operating at steady state, can be written for the kinetic model given in equation (3) in the following dimensionless form:

$$(P_1 - P_{10})/\theta = -2(R-1)P_1^2 - 2P_1\lambda_0 + 2\beta W \sum_{r=2}^{\infty} P_r \quad (4a)$$

$$(P_2 - P_{20})/\theta = -2P_2\lambda_0 + RP_1^2 + 2\beta W \sum_{r=3}^{\infty} P_r - \beta WP_2 \quad (4b)$$

$$(P_n - P_{n0})/\theta = \sum_{r=1}^{n-1} P_r P_{n-r} - 2P_n\lambda_0 + 2\beta W \sum_{r=n+1}^{\infty} P_r - (n-1)\beta WP_n \quad (4c)$$

$$(W - W_0)/\theta = (R-1)P_1^2 + \lambda_0^2 - \beta W (\lambda_1 - \lambda_0) \quad (4d)$$

where

$$P_n = [P_n]/\lambda_{10}^* \quad (5a)$$

$$P_{n0} = [P_n]_0/\lambda_{10}^* \quad (5b)$$

$$\lambda_0 = [\lambda_0^*]/\lambda_{10}^* = \sum_{i=1}^{\infty} [P_i]/\lambda_{10}^* \quad (5c)$$

$$W = [W]/\lambda_{10}^* \quad (5d)$$

$$\lambda_{00} = [\lambda_0^*] / \lambda_{10}^* = \sum_{i=1}^{\infty} [P_i]_0 / \lambda_{10}^* \quad (5e)$$

$$W_0 = [W]_0 / \lambda_{10}^* \quad (5f)$$

$$\lambda_{10}^* = \sum_{n=1}^{\infty} n[P_n] = \sum_{n=1}^{\infty} n[P_n]_0 = \lambda_1^* \quad (5g)$$

$$\theta = k_p \lambda_{10}^* V / F_0 \quad (5h)$$

$$R = k_{11} / k_p \quad (5i)$$

$$\beta = k'_p / k_p \quad (5j)$$

On adding mole balance relations for all species,  $P_1, P_2, \dots, P_n, \dots$ , the mole balance for the polymer ( $= \sum_{i=1}^{\infty} P_i$ ) can be obtained as the zeroth moment  $\lambda_0$  from:

$$(\lambda_0 - \lambda_{00}) / \theta = -(R-1)P_1^2 - \lambda_0^2 + \beta W(\lambda_1 - \lambda_0) \quad (6)$$

The first moment  $\lambda_1$  of the polymer formed within the reactor represents the total count of repeat units, which is found to be invariant, i.e. it is equal to  $\lambda_{10}$ , the value for the feed; and it is equal to unity when there is no vacuum on the reactor.

### MOMENT-GENERATING FUNCTION FOR REVERSIBLE POLYMERIZATION

Moment-generating function  $G$  is defined as:

$$G(s, \theta) = \sum_{n=1}^{\infty} s^n P_n(\theta) \quad (7)$$

where  $s$  is a dummy variable whose numerical value is less than 1. The generation relation for  $G$  is obtained by multiplying equations (4a), (4b) and (4c) by  $s, s^2$  and  $s^n$ , and adding them for all  $n$  gives:

$$(G - G_0) / \theta = -(R-1)P_1^2(2s - s^2) - 2\lambda_0 G + G^2 + 2\beta W(s\lambda_0 - G) / (1-s) - \beta W(s \partial G / \partial s - G) \quad (8)$$

where

$$s \partial G / \partial s = \sum_{n=1}^{\infty} n s^n P_n \quad (9a)$$

and

$$G_0 = \sum_{n=1}^{\infty} s^n P_{n0} \quad (9b)$$

This is rearranged to give:

$$\partial G / \partial s = \frac{1}{\beta W s} G^2 - \frac{1}{\beta W s} \left( 2\lambda_0 + \frac{2\beta W}{1-s} + \frac{1}{\theta} - \beta W \right) G + \frac{1}{\beta W s} \left( \frac{G_0}{\theta} + P_1^2(R-1)(s^2 - 2s) + \frac{2\beta W s \lambda_0}{1-s} \right) \quad (10)$$

This differential equation should satisfy:

$$\lim_{s \rightarrow 1^-} G = \lambda_0 \quad (11a)$$

and

$$\lim_{s \rightarrow 1^-} s \partial G / \partial s = \lambda_1 = 1 \quad (11b)$$

The analytical solution of equation (10) can be obtained by using the following transformation:

$$G = \frac{-\beta W s}{y} \frac{\partial y}{\partial s} \quad (12)$$

which on substitution reduces to:

$$s(1-s) d^2 y / ds^2 + [\alpha'(1-s) + 2] dy / ds + [\alpha_0^2 \theta (1-s) R(s) + (\alpha - \alpha_0)] y = 0 \quad (13)$$

where

$$\alpha' = \alpha = (\theta^{-1} + 2\lambda_0) / \beta W \quad (14a)$$

$$\alpha_0 = 1 / \beta W \theta \quad (14b)$$

$$R_0 = P_{10} - 2P_1^2(R-1)\theta \quad (14c)$$

$$R_1 = P_{20} + P_1^2(R-1)\theta \quad (14d)$$

$$R_i = P_{i+1,0} \quad i=2, 3, \dots \quad (14e)$$

$$R(s) = R_0 + R_1 s + R_2 s^2 \dots \quad (14f)$$

Equation (13) has singularities at  $s=0$  and at  $s=1$  and can be solved using the extended power series method of Frobenius<sup>33</sup>. It has at least one solution, which can be represented in the form:

$$y(s) = s^\sigma \sum_{m=0}^{\infty} C_m s^m \quad (15)$$

where the exponent  $\sigma$  may be any real or complex number and is chosen so that  $C_0 \neq 0$ .

### MOLECULAR-WEIGHT DISTRIBUTION IN REVERSIBLE POLYMERIZATION

The solution of the hypergeometric equation (13) around the singularity at  $s=0$  gives the molecular-weight distribution in a natural fashion. Assuming a power series solution as in equation (15) gives the indicial equation:

$$\sigma[(\sigma-1) + \alpha' + 2] = 0 \quad (16a)$$

which gives the roots of  $\sigma$  as:

$$\sigma_1 = 0 \quad \sigma_2 = -(\alpha' + 1) \quad (16b)$$

The solution corresponding to  $\sigma_1 = 0$  is given by:

$$y_1(s) = \sum_{m=0}^{\infty} C_m s^m = C_0 \sum_{m=0}^{\infty} r_m s^m \quad (17)$$

where

$$r_m = C_m / C_0 \quad (18a)$$

and

$$r_0 = 1 \quad (18b)$$

The coefficients  $r_m$  for any  $m$  are obtained recursively from:

$$r_{m+1} = \{ [m(m + \alpha' - 1) - (\alpha - \alpha_0)] r_m + [\alpha_0^2 \theta (\Sigma_{m-1} - \Sigma_m)] \} / (m+1)(m + \alpha' + 2) \quad (18c)$$

where

$$\Sigma_{m-1} = \sum_{j=0}^{m-1} R_j r_{m-1-j} \quad (18d)$$

$$\Sigma_m = \sum_{j=0}^m R_j r_{m-j} \quad (18e)$$

The  $R_j$  in equation (18) are the coefficients of polynomial  $R(s)$  in equation (13) and are given as in equations (14c, d, e). The solution corresponding to  $\sigma_2 = -(\alpha' + 1)$  is also obtained similarly:

$$y_2(s) = C_0^* \sum_{m=0}^{\infty} r_m^* s^{m-\alpha'-1} \quad (19)$$

The general solution for  $y$  is given by:

$$y(s) = y_1(s) + y_2(s) \\ = C_0 \sum_{m=0}^{\infty} r_m s^m + C_0^* \sum_{m=0}^{\infty} r_m^* s^{m-\alpha'-1} \quad (20)$$

However, since  $G$  is a series in  $s$  with integer exponents,  $y_2(s)$  cannot exist and  $C_0^*$  must be zero. Therefore:

$$y = C_0 \sum_{m=0}^{\infty} r_m s^m \quad \dot{y} = C_0 \sum_{m=1}^{\infty} m r_m s^{m-1} \quad (21)$$

On reversing the transformation we get the solution for equation (10) and  $G$  is given by:

$$G = -\beta W s \dot{y}(s)/y(s) \quad (22a)$$

$$= -\beta W \frac{r_1 s + 2r_2 s^2 + 3r_3 s^3 + \dots}{r_0 + r_1 s + r_2 s^2 + \dots} \quad (22b)$$

$$= -\beta W r_1 s \frac{1 + a_1 s + a_2 s^2 + a_3 s^3 + \dots}{1 + b_1 s + b_2 s^2 + b_3 s^3 + \dots} \quad (22c)$$

$$= -\beta W r_1 s (1 + c_1 s + c_2 s^2 + c_3 s^3 + \dots) \quad (22d)$$

The coefficients  $c_i$  in the series of equation (22d) are obtained from:

$$c_0 = 1 \quad (23a)$$

$$c_1 = a_1 - b_1$$

$$c_n = a_n - \sum_{j=1}^n b_j c_{n-j} \quad n \geq 2 \quad (23b)$$

$$a_n = (n+1)r_{n+1}/r_1 \quad (23c)$$

and

$$b_n = r_n \quad (23d)$$

On comparing with the definition of  $G$  in equation (7) we get:

$$P_1 = -\beta W r_1 \quad (24a)$$

$$P_n = -\beta W r_1 c_{n-1} \quad n \geq 2 \quad (24b)$$

where

$$r_1 = -[1/\alpha' + 2][(\alpha - \alpha_0) + \alpha_0^2 \theta R_0] r_0 \quad (24c)$$

### EQUILIBRIUM MOLECULAR-WEIGHT DISTRIBUTION

The equilibrium  $MWD$  is obtained by considering the limit  $\theta \rightarrow \infty$ . Under these conditions, the moment-generating relation in equation (10) reduces to:

$$\frac{\partial G}{\partial s} = \frac{1}{\beta W s} G^2 - \frac{1}{\beta W s} \left( 2\lambda_0 + \beta W \frac{1+s}{1-s} \right) G \\ + \frac{1}{\beta W s} \left( P_1^2 (R-1) (s^2 - 2s) + \frac{2\beta W s \lambda_0}{1-s} \right) \quad (25)$$

and the corresponding transformed equation (using the

transformation  $G = -\beta W s (\partial y / \partial s) / y$ ) is written as:

$$s(1-s) d^2 y / ds^2 + [\alpha(1-s) + 2] dy / ds \\ + [R(s)(1-s) + \alpha] y = 0 \quad (26)$$

where

$$\alpha = 2\lambda_0 / \beta W \quad (27a)$$

$$R_0 = -[2P_1^2 / (\beta W)^2] (R-1) \quad (27b)$$

$$R_1 = P_1^2 (R-1) / (\beta W)^2 \quad (27c)$$

$$R(s) = R_0 + R_1 s \quad (27d)$$

The indicial equation and its roots remain the same as  $\sigma_1 = 0$  and  $\sigma_2 = -(\alpha + 1)$ . As before,  $y_1(s)$  alone exists and the complete series solution is:

$$y(s) = C_0 \sum_{m=0}^{\infty} r_m s^m \quad (28a)$$

which yields:

$$\dot{y}(s) = C_0 \sum_{m=0}^{\infty} m r_m s^{m-1} \quad (28b)$$

The recursive relations for the  $r$ 's changes to:

$$r_{m+1} = \frac{(m+\alpha)(m-1)}{(m+1)(m+\alpha+2)} r_m + \frac{\Sigma_{m-1} - \Sigma_m}{(m+1)(m+\alpha+2)} \quad (29)$$

where

$$r_0 = 1 \quad (30a)$$

$$\Sigma_0 = R_0 r_0 \quad (30b)$$

$$\Sigma_1 = R_0 r_1 + R_1 r_0 \quad (30c)$$

$$\Sigma_m = R_0 r_m + R_1 r_{m-1} \quad m \geq 2 \quad (30d)$$

With these, the  $MWD$  is determined by equation (24) except that now:

$$r_1 = -[(\alpha - R_0) / (\alpha + 2)] r_0 \quad (30e)$$

### EFFECT OF VACUUM ON THE MOLECULAR-WEIGHT DISTRIBUTION

As observed earlier, in order to obtain a polymer of high molecular weight, a vacuum is applied to push the polymerization in the forward direction. In the presence of flashing, the outlet flow rate would differ from the inlet flow rate by  $F_w$ , the amount of condensation product lost in evaporation. Assuming the density of the product remains unchanged (say it is  $\rho$ ), the modified  $MWD$  equations are:

$$(P_1 - P_{10}) / \theta = -2(R-1)P_1^2 - 2P_1 \lambda_0 + 2\beta W \sum_{r=2}^{\infty} P_r \\ + (\rho_w / \theta_w) P_1 \quad (31a)$$

$$(P_2 - P_{20}) / \theta = -2P_2 \lambda_0 + R P_1^2 + 2\beta W \sum_{r=3}^{\infty} P_r - \beta W P_2 \\ + (\rho_w / \rho \theta_w) P_2 \quad (31b)$$

$$(P_n - P_{n0}) / \theta = \sum_{r=1}^{n-1} P_r P_{n-r} - 2P_n \lambda_0 + 2\beta W \sum_{r=n+1}^{\infty} P_r \\ - (n-1)\beta W P_n + (\rho_w / \rho \theta_w) P_n \quad (31c)$$

where  $\theta_w$  has the definition:

$$\theta_w \equiv k_p \lambda_{10}^* V / F_w \quad (32)$$

The balance for condensation product is given by:

$$(W - W_0) / \theta = (R - 1)P_1^2 + \lambda_0^2 - \beta W(\lambda_1 - \lambda_0) + (\rho_w / \rho \theta_w)W - \rho_w / M_w \lambda_{10}^* \theta_w \quad (33)$$

and the mole balance for the total polymer is given as:

$$(\lambda_0 - \lambda_{00}) / \theta = -(R - 1)P_1^2 - \lambda_0^2 + \beta W(\lambda_1 - \lambda_0) + (\rho_w / \rho \theta_w)\lambda_0 \quad (34)$$

The generation relation for the moment-generating function  $G$  is derived as:

$$(G - G_0) / \theta = -(R - 1)P_1^2(2s - s^2) - 2\lambda_0 G + G^2 + 2\beta W(s\lambda_0 - G) / (1 - s) - \beta W(s \partial G / \partial s - G) + (\rho_w / \rho \theta_w)G \quad (35)$$

This is rearranged to give:

$$\frac{\partial G}{\partial s} = \frac{1}{\beta W s} G^2 - \frac{1}{\beta W s} \left( 2\lambda_0 + \frac{2\beta W}{(1-s)} + \frac{1}{\theta} - \beta W - \frac{\rho_w}{\rho \theta_w} \right) G + \frac{1}{\beta W s} \left( \frac{G_0}{\theta} + P_1^2(R-1)(s^2 - 2s) + \frac{2\beta W s \lambda_0}{1-s} \right) \quad (36)$$

Using the earlier transformation  $G = -\beta W s (\partial y / \partial s) / y$  the above equation again reduces to equation (13) except that now  $\alpha$  and  $\alpha'$  are different:

$$\alpha' = \alpha - \rho_w / \rho \theta_w \beta W \quad (37)$$

The  $MWD$  is, therefore, again given by equation (24). The following three situations may arise in the presence of a vacuum.

#### Closed reactor

If the pressure in the reactor is large, there is no cross-flow of the by-product and  $F_w = 0$ . The concentration of  $W$  in HCSTR is then given by the stoichiometry, i.e.:

$$W = W_0 + \lambda_{00} - \lambda_0 \quad (38)$$

where  $W_0$  is the molar concentration of  $W$  in the feed. It is further observed that in equation (4a):

$$\sum_{i=2}^{\infty} P_i = (\lambda_0 - P_1) \quad (39)$$

On substituting this,  $P_1$ ,  $\lambda_0$  and  $W$  can be calculated by solving equations (4a), (6) and (38). Once these are determined, the  $MWD$  is found from equation (24), as derived in the earlier section.

#### Only condensation product flashing

When the vacuum applied is large, the condensation product  $W$  begins to flash and  $\theta_w$  in equations (31) to (37) is a finite quantity. The solution procedure in the presence of  $W$  flashing consists of solving for  $P_1$ ,  $\lambda_0$  and  $W$  using equations (31a), (33) and (34). However,  $\theta_w$  is unknown and is determined by assuming a vapour-liquid equilibrium between the reaction mass and the escaping vapour. The mole fractions of polymer and condensation product are given by:

$$x_w = W / (W + \lambda_0) \quad (40a)$$

and

$$x_p = \lambda_0 / (W + \lambda_0) \quad (40b)$$

Since the polymer is assumed not to flash, we can write the following relationship using Raoult's law:

$$W / (\lambda_0 + W) = P_T / P_w^0 \quad (40c)$$

where  $P_T$  is the total pressure of the reactor and  $P_w^0$  the vapour pressure of the condensation product.

#### Condensation product and $P_1$ flashing

As the chain length of the polymer increases, its relative volatility falls. As a first approximation, it is assumed that only  $P_1$  evaporates. Normally monomer is expensive, and it is desirable to recycle it after condensation as shown in Figure 1. When  $W$  and  $P_1$  leave the reaction mass, there is a change in volume, which is usually small. If it is assumed to be small, then the mole balance for  $P_1$ ,  $P_2$ , etc., in the broken square in Figure 1 can easily be shown to be the same as given in equation (31). If the vapour-liquid equilibrium is given by Raoult's law then the following relation is satisfied:

$$\frac{P_{P_1}^0}{P_T} \frac{P_1}{\lambda_0 + W} + \frac{W}{\lambda_0 + W} \frac{P_w^0}{P_T} = 1 \quad (41)$$

Herein,  $P_{P_1}^0$  and  $P_w^0$  are the vapour pressures of  $P_1$  and  $W$  respectively and  $P_T$  the total reactor pressure. Equation (41) can be used to determine the concentration of  $W$  in the HCSTR, which on substitution in equation (33) yields the moles of  $W$  flashed or  $F_w$ . Since the transformed equation in  $y$  does not change, the  $MWD$  given in equation (24) also remains unaltered, except that  $W$  appearing in it must be properly evaluated in the presence of flashing.

#### COMPUTATIONAL SCHEME

The  $MWD$  of the polymer formed in HCSTRs of given residence time is given by equation (24), which involves the concentrations of species  $\lambda_0$ ,  $P_1$  and  $W$ . We first consider the case where  $P_1$  does not flash and the condensation product  $W$  may. In order to calculate the  $\lambda_0$  and  $P_1$ , we substitute equation (39) into equation (31a):

$$(P_1 - P_{10}) / \theta = -2(R - 1)P_1^2 - 2P_1\lambda_0 + 2\beta W(\lambda_0 - P_1) + (\rho_w / \rho \theta_w)P_1 \quad (42)$$

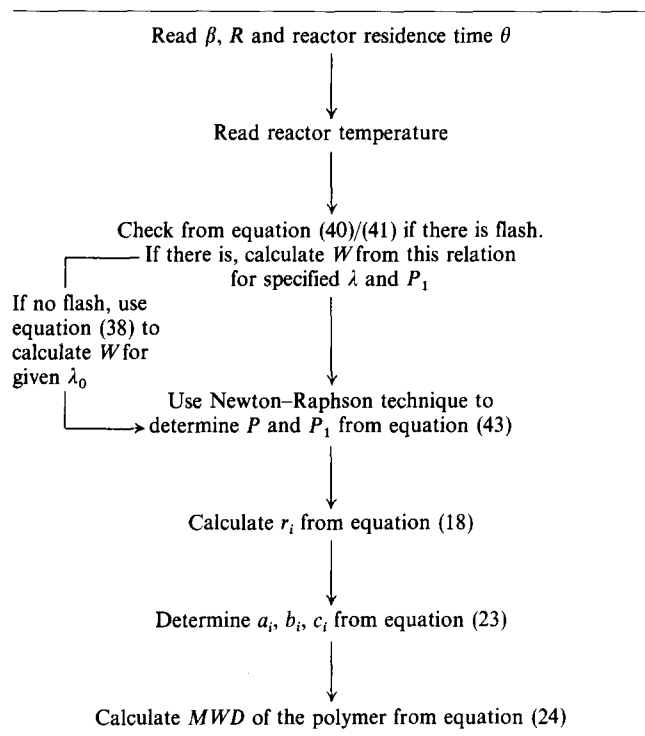
Equations (34) and (42) can now be solved simultaneously for  $\lambda_0$  and  $P_1$ . However, it needs information on  $W$ . If the condensation product does not evaporate,  $W$  is determined by equation (38), otherwise equation (40) or (41) is used to find  $W$ .

One of the convenient methods to find roots of equations (34) and (42) is to use the Newton-Raphson method in which these are rearranged as:

$$F_1 = (P_{10} - P_1) / \theta - 2(R - 1)P_1^2 - 2P_1\lambda_0 + 2\beta W(\lambda_0 - P_1) + (\rho_w / \rho \theta_w)P_1 \quad (43a)$$

$$F_2 = (\lambda_{00} - \lambda_0) / \theta - (R - 1)P_1^2 - \lambda_0^2 + \beta W(\lambda_1 - \lambda_0) + (\rho_w / \rho \theta_w)\lambda_0 \quad (43b)$$

where for the correct values of  $P_1$  and  $\lambda_0$ ,  $F_1$  and  $F_2$  would be identically equal to zero. The procedure of computation consists of starting with a guess of  $\lambda_0$  and determining  $P_1$  analytically using equation (42). Equation (43b) is checked if these  $\lambda_0$  and  $P_1$  satisfy equation (34). While guessing the next plausible value

**Table 1** Algorithm for computation of *MWD* of polymer formed in HCSTRs

of  $\lambda_0$ , one moves along the gradient, keeping in mind that both  $\lambda_0$  and  $P_1$  must be less than 1. The Newton-Raphson technique of solution of these equations has been discussed in our earlier publications and we find that convergence always occurs<sup>29-32</sup>. A general computer program has been developed and its flow chart is summarized in *Table 1*.

## RESULTS AND DISCUSSION

The solution of the *MWD* of the polymer formed in HCSTRs, derived in this work, is in the most general form and can handle feed having higher oligomers. The analytical solution given in equation (24) involves three infinite series,  $a_i$ ,  $b_i$  and  $c_i$ ,  $i = 1, 2, \dots$ , and it is important that they all be convergent; that is the feed to the HCSTR consists of oligomers  $P_{10}$ ,  $P_{20}$ ,  $P_{30}$ , etc., such that:

$$\lambda_{00} = \sum_{n=1}^{\infty} P_{n0} \quad (44a)$$

and

$$P_{n0} = \lambda_{00}^2 (1 - \lambda_{00})^{n-1} \quad n = 1, 2, \dots \quad (44b)$$

This has been derived by Flory for the case of equal-reactivity hypothesis (i.e. parameter  $R = 1$ ) as the *MWD* of the polymer formed in batch reactors with monomer as feed. It is thus seen that the feed is completely characterized by the zeroth moment  $\lambda_{00}$ , which gives the total moles of polymer in it. Equation (44) satisfies the condition that the first moment  $\lambda_1$  is always unity.

Earlier techniques of computing the *MWD* of the polymer consisted of solving a large number of mole balance equations simultaneously for various species. This was found to take considerable computation time. The present analytical solution given in equation (24) requires that the total moles  $\lambda_0$  and the concentration of

monomer  $P_1$  must be known. Equations (34) and (42) governing these are quadratic and in principle can be solved analytically. However, the use of the Newton-Raphson method is considerably more convenient. The computations for  $\lambda_0$  and  $P_1$  can be made to an accuracy of  $10^{-5}$  within 15 to 20 iterations, which does not take more than 0.01 s of CPU time on a DEC 1090. In order to determine the *MWD* of the polymer, series  $b_i$  given in equation (23) can be determined even by a desk calculator. The  $a_i$  and  $c_i$  series are only a linear combination of the terms of the  $b_i$  series and can also be easily evaluated, in this way giving the *MWD* of the polymer.

We have carried out extensive computations with the variation of the reaction parameters using the analytical solution presented in this paper. We have also determined the *MWD* of the polymer using some of the numerical techniques described in the literature and we found a perfect match between the two, in this way ensuring the convergence of the  $c_i$  series.

There have been a few studies reported in the literature on the unequal reactivity of monomer, and the *MWD* of the polymer formed in HCSTRs has been computed by one of the recommended numerical techniques. These studies assume the feed to consist of monomer only, with the condensation product not flashing from the reaction mass. We have relaxed both these assumptions and show that they serve as important engineering parameters having considerable ramifications upon the *MWD* of the polymer. We divide our discussion in the following into steady-state and equilibrium polymerization and present results to show how a polymer of the desired property can be made by suitably operating the HCSTR.

### HCSTRs operating under steady state

The equations governing the *MWD* of the polymer formed in HCSTRs involve parameters  $R$  and  $\beta$ , which are temperature-dependent. In generating *Figure 2*, we assumed  $R$  to be greater than unity and calculated the *MWD* for different values of  $\beta$  and  $\lambda_{00}$ . It has already been discussed that the feed is assumed to have the Flory distribution, which means that the value of  $\lambda_{00}$  completely characterizes it;  $\lambda_{00}$  is equal to unity for pure monomer feed while higher oligomers are present in larger concentrations as  $\lambda_{00}$  decreases to smaller values. In *Figure 2*, the molecular-weight distributions of polymer for three  $\lambda_{00}$  and three  $\beta$  values are given for a reactor residence time of  $\theta = 1$ . The results in this figure reveal that the relative change in the *MWD* is smaller as  $\lambda_{00}$  is reduced. As an example, for  $\lambda_{00} = 0.4$ , the moles of monomer in the feed is 0.16, and this figure reveals that for  $\beta = 5.0$  there is almost no change in monomer concentration at  $\theta = 1$ ; and for  $\lambda_{00} = 0.2$ , higher oligomers depolymerize to give  $P_1$  in the outgoing stream at more than 0.04 concentration. This figure also reveals that as  $\beta$  is increased, there is less polymerization. Higher oligomers tend to depolymerize.

*Figure 3* gives the *MWD* of the polymer for  $R$  less than unity. Since  $R < 1$ , the monomer has the tendency to react less than higher oligomers. As a consequence, for monomer feed (i.e.  $\lambda_{00} = 1$ ), there is small polymerization, which is indicated by a sharp *MWD* as shown. On comparing this with *Figure 2*, it is found that about 80% monomer remains unreacted as opposed to 50% for  $R = 2$ . The change in *MWD* curves is also found to be

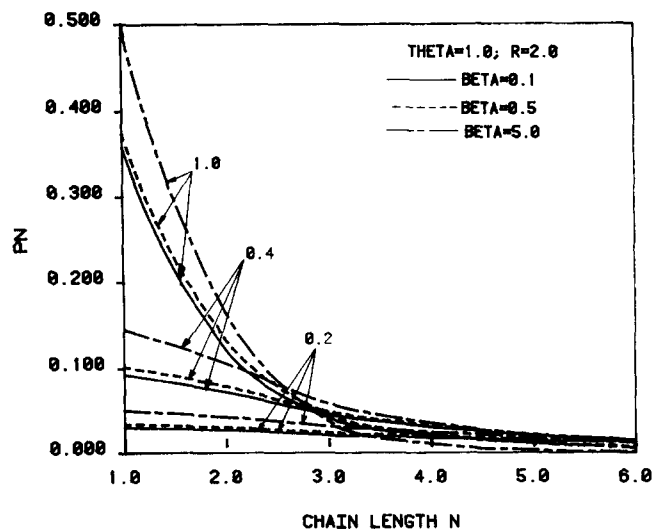


Figure 2 Effect of  $\beta$  and  $\lambda_{00}$  on molecular-weight distribution at  $\theta = 1.0$ ,  $R > 1$  ( $= 2$ )

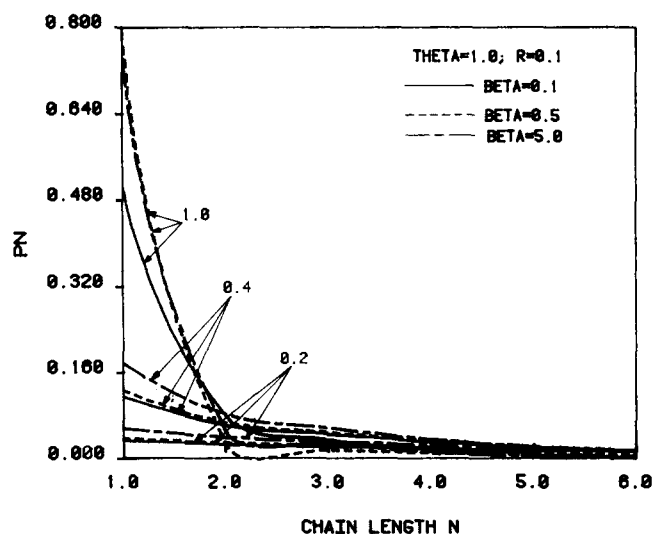


Figure 3 Effect of  $\beta$  and  $\lambda_{00}$  on molecular-weight distribution at  $R < 1$

smaller with change in  $R$  as  $\lambda_{00}$  for the feed reduces. This is expected because unequal reactivity has been assumed to be restricted to the monomer only. As the feed to the HCSTR becomes more polydisperse, the effect of  $R$  is small simply because of the reduced concentration of the monomer in it. As a consequence, the  $MWD$  of the product deviates only little from the Flory distribution, except that the conversion of functional groups has increased.

Sometimes it is easier to compare the molecular-weight distributions by examining the moments. The average chain length  $\mu_n$  of the polymer is defined as the ratio of the first and the zeroth moments, and the results have been plotted in Figure 4. The residence time  $\theta$  has been varied up to the value of 20, and for small  $\beta$  the chain length is found to increase continually. However, as  $\beta$  is increased, the conversion reduces and consequently the chain length of the polymer is limited by the equilibrium value as shown. Figure 4 shows results for three  $R$  values for every  $\beta$  and, as  $R$  increases for a given  $\beta$ ,  $\mu_n$  is found to increase. As has been observed earlier, when  $R$  is less than unity, there is a preponderance of unreacted monomer. This would in turn imply smaller  $\mu_n$ , which is indeed observed in Figure 4. In Figure 5,  $\mu_n$  versus

residence time has been plotted for  $\lambda_{00} = 0.4$ , which is compared with Figure 4. The kinetic model proposed in this work assumes unequal reactivity in monomer only. Consequently when  $\lambda_{00}$  is lowered, the moles of monomer in the reaction mass reduces (0.16 moles) and the effect of  $R$  on the chain length is small, as seen in this figure.

In his analysis of step-growth polymerization, Flory suggested a binomial distribution (sometimes called a Flory distribution) for the polymer formed in batch reactors. This in turn implies that the polymer formed is completely characterized by the conversion (and therefore the chain length,  $\mu_n$ ) of the functional groups. The polydispersity index ( $PDI$ ) of the polymer is defined as the ratio of the weight-average chain length  $\mu_w$  ( $= \lambda_2/\lambda_1$ ) and the number-average chain length  $\mu_n$  ( $= \lambda_1/\lambda_0$ ) as:

$$PDI = \mu_w/\mu_n \quad (45)$$

In the case of the Flory distribution, a plot of  $PDI$  versus  $\mu_n$  should be independent of  $\beta$ . For the kinetic model discussed here,  $PDI$  versus  $\mu_n$  has been plotted in Figure 6, and it is observed that  $PDI$  depends not only on  $\mu_n$  but also on  $\beta$  and  $R$ . Assuming the equal-reactivity

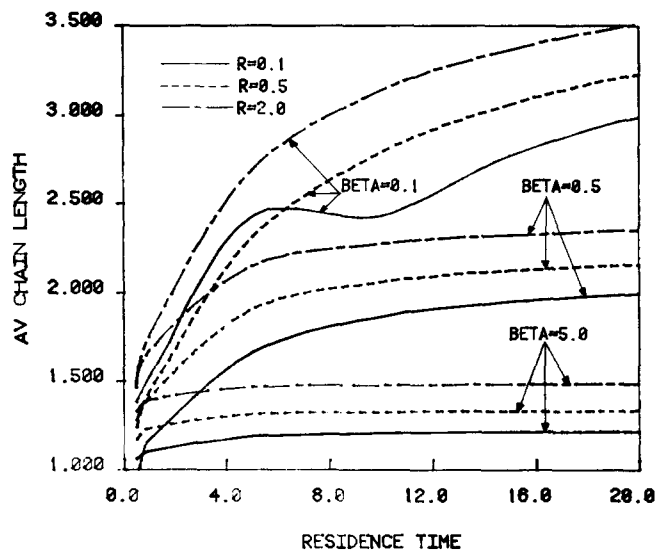


Figure 4 Effect of varying  $\beta$  and  $R$  on  $\mu_n$  versus  $\theta$  at  $\lambda_{00} = 1.0$

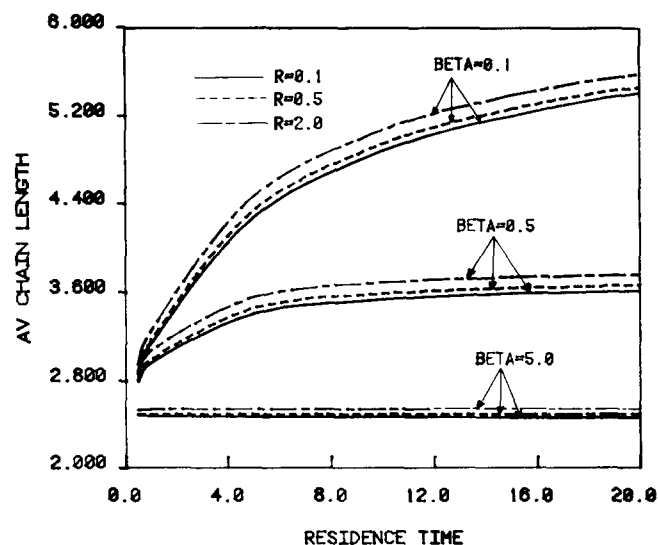


Figure 5 Effect of  $\beta$  and  $R$  on number-average chain length versus residence time for feed with  $\lambda_{00} = 0.4$

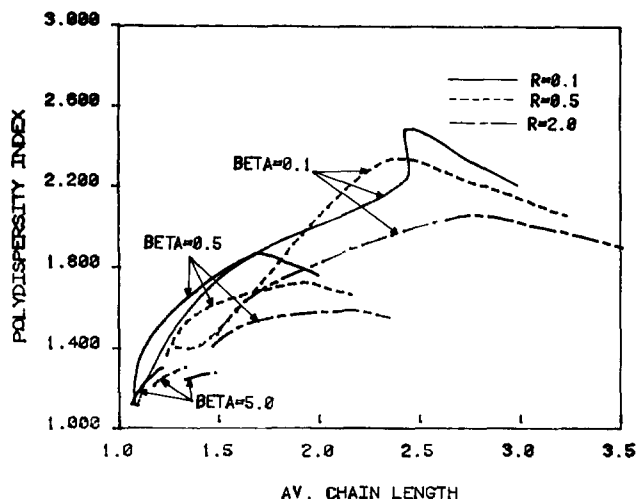


Figure 6 Effect of  $\beta$  and  $R$  on polydispersity index versus number-average chain length at  $\lambda_{00}=1.0$

hypothesis, for polymerization in a batch reactor with monomer feed, Flory has shown that the  $PDI$  is limited to a maximum value of 2. Beisenberger<sup>4</sup> has analysed irreversible step-growth polymerization in HCSTRs for monomer feed and shown that polydispersity index is not limited to 2, but can reach any value. As opposed to all these, reversible polymerization in HCSTRs exhibits an entirely different behaviour. The  $PDI$  undergoes a maximum, which depends on  $\beta$  as well as  $R$  as seen in Figure 6. We find that, as  $\beta$  is reduced, the  $PDI$  takes on a larger value. When  $R$  is small for given  $\beta$ , the reaction mass has a large amount of unreacted monomer, due to which  $PDI$  is increased.

#### Equilibrium polymerization

On careful examination of the mole balance relation for the equilibrium case, we find that the  $MWD$  is independent of the type of reactor. If we charge the reactor with  $\lambda_{00}$  moles of feed and  $W_0$  moles of condensation product, then the following stoichiometric relation is valid:

$$W_{eq} = \lambda_{00} + W_0 - \lambda_{0eq} \quad (46)$$

provided there is no flashing of the condensation product. Herein  $\lambda_{0eq}$  and  $W_{eq}$  represent the total moles of polymer and condensation product in the reaction mass at equilibrium. When there is a flashing,  $W$  in the reaction mass can be reduced to any level and serves as a degree of freedom for tailoring the polymer to the requirements. Results for the  $MWD$  of the polymer have been generated for equilibrium polymerization, and are plotted in Figures 7 and 8 for  $R$  less than and greater than unity, respectively. In these figures,  $W_{eq}$  serves as the maximum moles of condensation product in the reaction mass and curves marked A represent the computed  $MWD$  for this case. The moles of condensation product can be conveniently reduced by lowering the pressure of the reactor, and the curves marked B and C have been generated assuming that the condensation product has fallen to one-half and one-quarter of the maximum  $W_{eq}$  calculated by equation (46), respectively. On doing this, we find that the monomer concentration falls from 0.75 to 0.45 moles for curve B and to 0.28 for curve C. This represents a considerable reduction especially when the monomer must be separated because of its carcinogenic nature. In Figure 8, similar behaviour is observed except

for the fact that  $R=2$  represents the case when monomer reacts preferentially to form higher oligomers. This would lead to larger chain length and polydispersity index, as seen in Figures 9 and 10, where these have been plotted as a function of  $\beta$ . As the contribution of the reverse reaction increases with increasing  $\beta$ , the chain length  $\mu_n$  falls sharply and afterwards its sensitivity reduces. At a given  $\beta$ , it is always possible to attain any  $\mu_n$ , which can be obtained by lowering the concentration of the condensation product in the reaction mass.

#### CONCLUSIONS

Unequal reactivity in reversible step-growth polymerization was observed to be more of a rule and it was modelled by assuming monomer reacting differently from higher oligomers. The mole balance relations for various oligomers were established for the case when reversible polymerization is being carried out in a homogeneous continuous-flow stirred tank reactor. From these, the generation relation for the moment-generating function

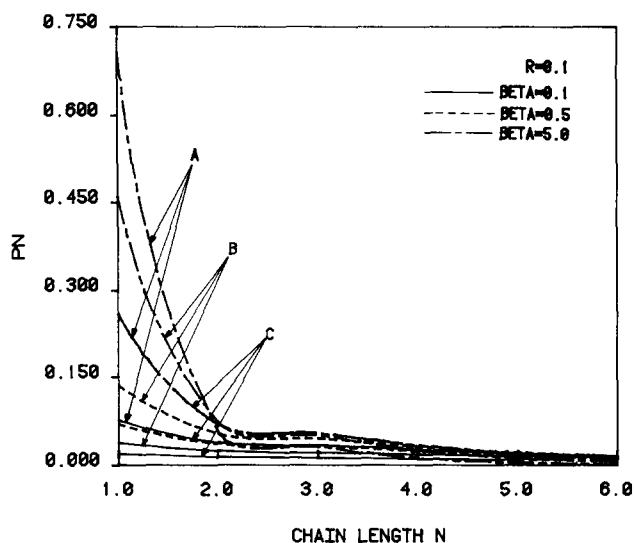


Figure 7 Effect of  $\beta$  and extent of flashing on equilibrium molecular-weight distribution for  $R < 1$  at  $\lambda_{00}=1.0$ : (A) no flashing; (B) 0.050  $W_{eq}$  removed; (C) 0.75  $W_{eq}$  removed

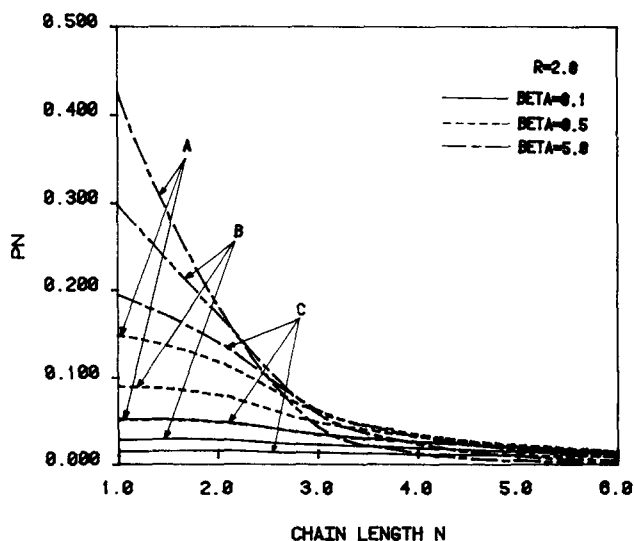


Figure 8 Effect of  $\beta$  and extent of flashing on equilibrium molecular-weight distribution for  $R > 1$  at  $\lambda_{00}=1.0$ : (A) 0.5  $W_{eq}$  removed; (C) 0.75  $W_{eq}$  removed



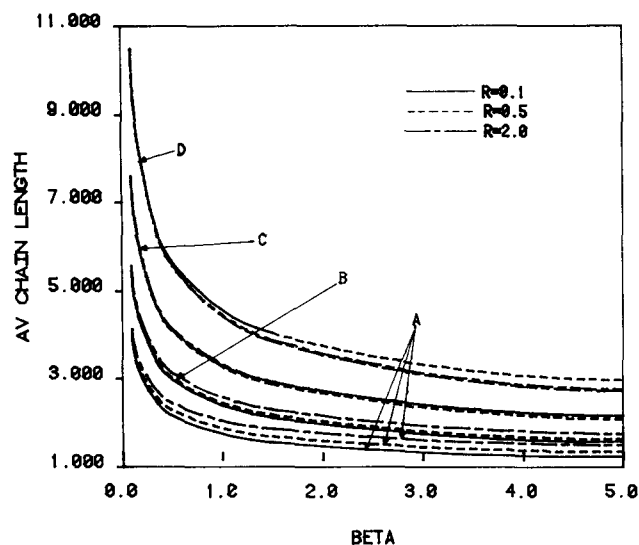


Figure 9 Effect of  $R$  and extent of flashing on equilibrium  $\mu_n$  versus  $\beta$  at  $\lambda_{00}=1.0$ : (A) no flashing; (B)  $0.5 W_{eq}$  removed; (C)  $0.75 W_{eq}$  removed; (D)  $0.875 W_{eq}$  removed

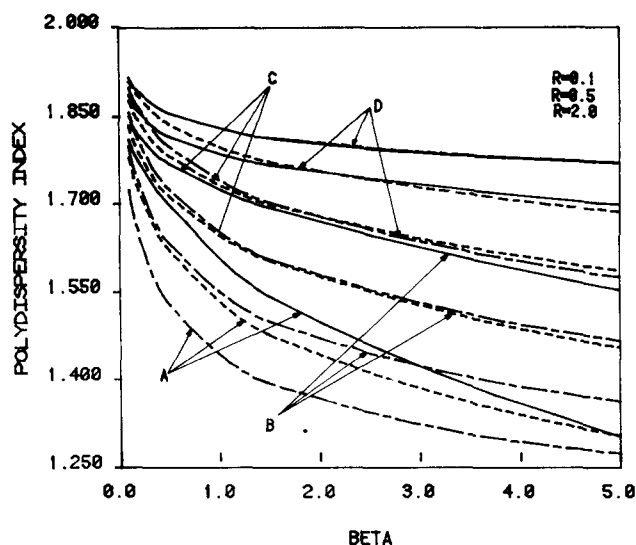


Figure 10 Effect of  $R$  and extent of flashing on equilibrium polydispersity index versus  $\beta$  for monomer feed at  $\lambda_{00}=1.0$ : (A) no flashing; (B)  $0.5 W_{eq}$  removed; (C)  $0.75 W_{eq}$  removed; (D)  $0.875 W_{eq}$  removed

has been derived, which is a non-linear, first-order ordinary differential equation. We have proposed a mathematical transformation under which it reduces to a linear second-order ordinary differential equation. We have subsequently derived the analytical solution of this, from which we determined the expression for  $MWD$  of the polymer formed in HCSTRs. We have critically examined the effect of vacuum upon the solution of the  $MWD$  and analysed several special cases of polymerization in HCSTRs with condensation product and polymer flashing. Polymerization at equilibrium has also been analysed, in this way developing the complete solution of reversible polymerization in HCSTRs.

In this paper we analyse the situation when the HCSTR is part of a train of polymerization reactors, where its feed need not necessarily be pure monomer. We show that the nature of the feed has a considerable effect on the final product, which is due to the fact that the polydispersed feed has a smaller amount of unreacted monomer. Flory has shown that the  $MWD$  of polymer formed by step-growth polymerization in batch reactors is binomially distributed. This implies that the plot of polydispersity index versus average chain length must be independent of  $\beta$ . Under reversible polymerization in HCSTRs, we show that the situation is considerably more complex, and depending upon the values of  $\beta$  and  $R$ , polydispersity undergoes a maximum before settling upon the equilibrium value.

We have subsequently presented results for equilibrium polymerization, which are independent of the type of reactor as well as the nature of the feed. We observe that if  $W_0$  and  $\lambda_{00}$  in the feed are given, then either  $W$  or  $\lambda_0$  can be specified in the product stream independently. This introduces a degree of freedom that can be utilized to get any desired property of the polymer formed in HCSTRs.

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