

Molecular weight distribution of reversible ARB polymerization in homogeneous continuous flow reactors for monomer with reactivity different from higher homologues

Anil Kumar

Department of Chemical Engineering, Indian Institute of Technology, Kanpur-208, 016, India

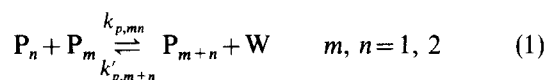
(Received 7 November 1985; revised 21 January 1986)

Mole balance equations for reversible step-growth polymerization in homogeneous continuous flow reactors are found to comprise a large set of interacting algebraic equations. These equations have been decoupled and made sequential under a transformation. The solution of these can now be adopted on any calculator and there is considerable computation saving using the technique presented in this paper. From the mole balance equations, the moment generating function has been derived to be a Riccati differential equation with its coefficients dependent on a variable s . Under a suitable transformation, it reduces into two linear ordinary differential equations. The latter has a solution in the vector-Volterra form and can be represented by an infinite series. Subsequently, for irreversible polymerization with unequal reactivity, an analytical solution of the *MWD* has been derived.

(Keywords: molecular weight distribution; reversible polymerization; step growth polymerization; unequal reactivity)

INTRODUCTION

Polymer formation from monomer occurs through the presence of growth centres. Polymerization is broadly classified into chain-growth and step-growth reactions, depending upon the nature of these growth centres¹⁻⁵. In step-growth polymerization, polymerization occurs through reaction of functional groups. Depending upon whether the starting monomer is bifunctional or multifunctional, the resulting polymer is either linear or branched (or network) in molecular structure. The step-growth polymerization of bifunctional monomers ARB, where A and B are reacting functional groups, can be schematically written as



where P_m is a polymer molecule with m repeat units, W is a low molecular weight condensation product, $k_{p,mn}$ and $k'_{p,m+n}$ are the rate constants for the forward and reverse reaction steps, which are in general chain-length dependent.

The forward and reverse rate constants in equation (1) are usually complex functions of chain lengths of the polymer molecules involved. Based on experimental results of Bhide and Sudborough⁶ on the esterification of aliphatic acids in presence of excess of ethanol, Flory was the first to propose the equal reactivity hypothesis^{7,8}. In this, $k_{p,mn}$ and $k'_{p,m+n}$ were assumed to be independent of chain lengths m and n . Under this assumption, the mole balance equations of various species collapse into one and the overall polymerization can be represented by reaction of functional groups. Industrially, polymerization can

either be carried out in batch or continuous reactors and the analysis of these reactors for step-growth polymerization has recently been reviewed⁹⁻¹³.

Mathematical results derived from the equal reactivity hypothesis have been used to explain the gross kinetic features. Comparison with experimental data shows that polymerization is far more complex than is represented by the equal reactivity hypothesis¹²⁻¹⁷. In literature, the discrepancy between the two is explained by the unequal reactivity hypothesis, which can arise either owing to the unequal reactivity of functional groups or the chain-length dependent reactivities in the forward and the reverse steps of equation (1). Case¹⁴ has analysed various situations of the former type using probabilistic arguments and derived the molecular weight distribution (*MWD*) in terms of the conversion of functional groups. The effect of unequal reactivity was then shown to have considerable effect on the *MWD* of the polymer.

Nanda and Jain¹⁸ have analysed the case of chain length dependent reactivity in irreversible step-growth polymerization. They assumed the forward rate constant to be falling linearly with chain length and derived the *MWD*. Recent experiments have shown that the change in the reactivity of functional groups with chain length is described by an S-shaped curve¹⁷. This reactivity change has been approximated by a step function in which the monomer is assumed to react differently to other oligomers¹⁸⁻²⁵. This can be idealized into two different limiting cases: in the first P_1 is assumed to react with P_1 alone with one (different) rate constant and in the second, P_1 reacts with all oligomers with another (different) rate constant. The reverse reaction involves the interaction of the condensation product W and a large polymer molecule. Since the latter is coiled the chain ends would be

buried within. It has been argued in the literature¹² that this might lead to some sort of molecular shielding, this giving lower reactivity to the end positions. In addition, if P₁ reacts with P₁ at a different rate constant, it may also be argued that P₂ may also react differently in the reverse reaction. The unequal reactivity in the reverse reaction makes the analysis extremely complex and in this paper we have ignored this effect to keep the analysis simple.

Polymerization can be carried out either in batch or continuous reactors. As higher and higher throughputs are desired, large continuous reactors are required and usually tubular reactors or tanks with agitators are employed. These are usually idealized as plug flow reactors (PFR) and homogeneous continuous flow stirred tank reactors (HCTR). Most of the studies existing in the literature on MWD of the polymer formed in HCTR, whether the hypothesis or equal reactivity or chain-length dependent reactivity is used, assumes that polymerization occurs under irreversible conditions.

The major difficulty of solving the MWD of reversible ARB polymerization with chain-length dependent reactivity lies in the fact that the growth step consists of infinite elementary reactions. Since the molar balance equations of individual polymer species do not collapse into one, the overall polymerization cannot be written in terms of the reaction of functional groups. In addition to these equations being non-linear in nature, to solve any given equation for the concentration of any given species, one must know the concentration of all other species. If the HCTR is operating at steady state, one obtains a large number of non-linear algebraic equations that must be solved simultaneously. The total number of such equations to be solved is chosen such that the concentration of the last species is negligibly small. One uses either the Newton-Raphson or Brown technique to determine the MWD of the polymer numerically²⁶. The computer calculation of MWD is tedious and requires considerable computation time.

In this paper, the mole balance in HCTR for reversible ARB polymerization, with monomer reacting with itself at a different rate, has been written. The feed is assumed to consist of higher oligomers in addition to the monomer. Using a suitable transformation, the MWD equations are first decoupled and subsequently an analytical solution is found.

THEORY

It is assumed that P₁ reacts with itself with a different rate constant (i.e. k₁₁) whereas all other oligomers react with the same rate constant (i.e. k_p). To simplify the mathematics, we ignore the unequal reactivity in the reverse step. This means that

$$k_{p,11} = k_{11} \quad (2a)$$

$$k_{p,mn} = 2k_p; \quad m \neq n; \quad m, n = 1, 2, \dots \quad (2b)$$

$$k_{p,mn} = k_p; \quad m = 2, 3, \dots \quad (2c)$$

$$k'_{p,m} = k'_p; \quad m = 2, 3, \dots \quad (2d)$$

The schematic diagram of an HCTR is shown in Figure 1. The feed is assumed to have various oligomers at

concentrations [P₁]₀, [P₂]₀, [P₃]₀ etc. as shown. For an isothermal HCTR operating at steady state, one has

$$\frac{[P_1]}{\theta'} = \frac{[P_1]_0}{\theta'} - 2(k_{11} - k_p)[P_1]^2 - 2k_p[P_1][P] + 2k'_p[W] \sum_{r=2}^{\infty} [P_r] \quad (3a)$$

$$\frac{[P_2]}{\theta'} = \frac{[P_2]_0}{\theta'} + k_{11}[P_1]^2 - 2k_p[P_2][P] - k'_p[W][P_2] + 2k'_p[W] \sum_{r=3}^{\infty} [P_r] \quad (3b)$$

$$\frac{[P_n]}{\theta'} = \frac{[P_n]_0}{\theta'} + k_p \sum_{r=1}^{n-1} [P_r][P_{n-r}] - 2k_p[P_n][P] - k'_p(n-1)[W][P_n] + 2k'_p[W] \sum_{\substack{r=n+1 \\ n \geq 3}}^{\infty} [P_r] \quad (3c)$$

$$\frac{[W]}{\theta'} = \frac{[W]_0}{\theta'} - \frac{F_w}{\theta'} + (k_{11} - k_p)[P_1]^2 + k_p[P]^2 - k'_p[W]([P]_0 - [P]) \quad (3d)$$

where

$$\theta' = V/F \quad (4a)$$

$$[P] = \sum_{i=1}^{\infty} [P_i] \quad (4b)$$

$$[P]_0 = \sum_{i=1}^{\infty} [P_i]_0 \quad (4c)$$

Above V and F are the reactor volume and feed flow rate, respectively. One defines the following dimensionless variables

$$P_{n0} = \frac{[P_n]_0}{[P]_0} \quad (5a)$$

$$P_n = \frac{[P_n]}{[P]_0}; \quad n = 1, 2, 3, \dots \quad (5b)$$

$$P = \frac{[P]}{[P]_0} \quad (5c)$$

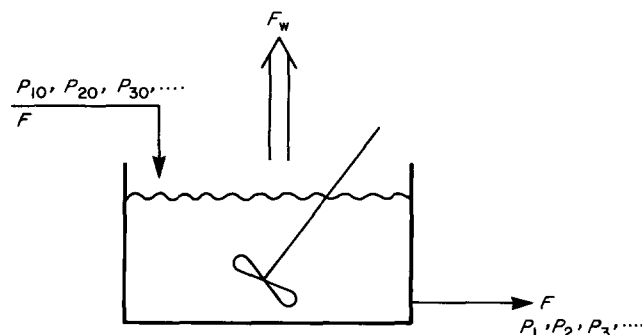


Figure 1 Schematic diagram of HCTR

$$W = \frac{[W]}{[P]_0} \quad (5d)$$

$$R = \frac{k_{11}}{k_p} \quad (5e)$$

$$\beta = 2k'_p/k_p \quad (5f)$$

$$\theta = k_p \theta' [P]_0^2 \quad (5g)$$

One observes that

$$\sum_{i=n+1}^{\infty} P_i = P - \sum_{i=1}^{n-1} P_i - P_n \quad (6)$$

On substituting this in equation (3), one obtains

$$v_n P_n = u_n + \sum_{r=1}^{n-1} P_r (P_{n-r} - \beta); \quad n \geq 2 \quad (7)$$

where

$$u_2 = \frac{P_{20}}{\theta} + 2\beta W P + (R-1)P_1^2 \quad (8a)$$

$$u_n = \frac{P_{n0}}{\theta} + 2\beta W P; \quad n \geq 3 \quad (8b)$$

and

$$v_n = \frac{1}{\theta} + P + \beta W(n+1); \quad n \geq 2 \quad (9)$$

On adding equations (3a), (3b) and (3c), for all values of n , one can obtain an expression for P which is found to involve W and P_1 in addition to P . It is thus seen that, one must solve the following equations simultaneously:

$$\left(\frac{1}{\theta} + 2P + 2\beta W\right)P_1 + 2(R-1)P_1^2 = \left(\frac{P_{10}}{\theta} + 2\beta W P\right) \quad (10a)$$

$$\frac{W}{\theta} = \frac{W_0}{\theta} - \frac{F_w}{\theta} + \{(R-1)P_1^2 + P^2 - \beta W(1-P)\} \quad (10b)$$

$$\frac{P}{\theta} = \frac{1}{\theta} + \{- (R-1)P_1^2 - P^2 + \beta W(1-P)\} \quad (10c)$$

If the reactor is operating strictly batchwise (which means that the condensation product is not allowed to leave the reaction mass), the moles of W in the reaction mass would be exactly equal to the moles of functional groups reacted, i.e.

$$(W - W_0) = (1 - P) \quad (11)$$

The solution of equation (10) can be found only by trial and error using any standard numerical technique. In this paper, we have used Newton-Raphson technique. After solving for P , P_1 and W , these are substituted in equation (7) and the MWD of the polymer is solved sequentially.

Moment generating function

One defines moment generating function $G(s, \theta)$ as

$$G(s, \theta) = \sum_{n=1}^{\infty} s^n P_n \quad (12)$$

where s is a dummy variable which is less than 1 and P_n the

dimensionless variable defined in equation (5b). Multiplying equation (3a) by s , (3b) by s^2 and (3c) by s^n and summing for all possible values of n , one gets

$$\frac{G - G_0}{\theta} = - (R-1)P_1^2(2s - s^2) + G^2 - 2PG + 2W\beta \frac{sP - G}{(1-s)} - W\beta \sum_{n=1}^{\infty} s^n (n-1)P_n \quad (13)$$

It may be observed from equation (12) that

$$s \frac{\partial G}{\partial s} = \sum_{n=1}^{\infty} n s^n P_n \quad (14)$$

and in light of this equation (13) reduces to

$$\frac{G - G_0}{\theta} = - (R-1)(2s - s^2)P_1^2 + G^2 - 2PG + 2\beta W \frac{sP - G}{(1-s)} - W\beta \left(s \frac{\partial G}{\partial s} - G \right) \quad (15)$$

where

$$G_0 = \sum_{n=1}^{\infty} s^n P_{n0} \quad (16)$$

Irreversible polymerization

It is possible to derive the analytical solution of the MWD of the polymer formed in HCTR with unequal reactivity as follows. If the polymerization is irreversible, equation (15) yields the moment generating function

$$\frac{G - G_0}{\theta} = - (R-1)(2s - s^2)P_1^2 + G^2 - 2PG \quad (17)$$

From this G can be solved as

$$G = \frac{1}{2} \left[\left(2P + \frac{1}{\theta} \right) - \left\{ \left(2P + \frac{1}{\theta} \right)^2 - 4 \left\{ \frac{G_0}{\theta} - (R-1)(2s - s^2)P_1^2 \right\} \right\}^{1/2} \right] \quad (18)$$

Expressions of various moments can now be easily derived. The zeroth moment, λ_0 , is the same as P and its expression has already been derived earlier. The first moment, λ_1 , is equal to the number of units which is time invariant and is given by

$$\lambda_1(t) = \sum_{n=1}^{\infty} n P_{n0} = \lambda_{10} \quad (19)$$

The second moment, λ_2 , is given by

$$\lambda_2 = \lim_{s \rightarrow 1} \left\{ \frac{\partial}{\partial s} \left(s \frac{\partial G}{\partial s} \right) \right\} \quad (20)$$

and with the help of equation (18), one obtains

$$\lambda_2 = u_1^{-1/2} \left\{ \frac{\lambda_{20}}{\theta} - 2(R-1)P_1^2 \right\} + 2u_1^{-3/2} \left(\frac{\lambda_{10}}{\theta} \right)^2 \quad (21)$$

where

$$u_1 = \frac{1}{2} \left\{ \left(\frac{1}{\theta} + 2P \right)^2 - \frac{4P_0}{\theta} + (R-1)P_1^2 \right\} \quad (22)$$

The molecular weight distribution for a given feed can easily be found out with the help of equation (18), which needs to be expanded in a series and the multiplying factor of s^n collected. This gives P_n for the specified feed. Let us consider monomer as the feed, in which case G_0 is given as

$$G_0 = P_{10}s \quad (23)$$

Equation (18) gives G as

$$G = \frac{1}{2} \{ x - x\sqrt{1-y} \} \quad (24)$$

where

$$x = \left(\frac{1}{\theta} + 2P \right) \quad (25a)$$

$$y = \frac{4}{x^2} \left\{ \frac{P_{10}s}{\theta} - (R-1)P_1^2(2s-s^2) \right\} \quad (25b)$$

$$\equiv \delta_1 s + \delta_2 s^2 \quad (25c)$$

$$\delta_1 = \frac{4}{x^2} \left\{ \frac{P_{10}}{\theta} - 2(R-1)P_1^2 \right\} \quad (25d)$$

In equation (24), $\sqrt{1-y}$ can be expanded in series to obtain

$$G = \frac{1}{2} x \{ d_1 y + d_2 y^2 + d_3 y^3 + \dots \} \quad (26)$$

where

$$d_n = \frac{\prod_{i=0}^{n-1} \left(\frac{1}{2} - i \right)}{n!} \quad n = 1, 2, \dots \quad (27)$$

Next one makes y equal to $(\delta_1 s + \delta_2 s^2)$ in equation (26) and finds the coefficient of s^n as

$$P_n = \frac{1}{2} \sum_{i=0}^{(n-1)/2} \binom{(n-1)/2}{i} C_{[(n-1)/2]-i} d_{[(n+1)/2]+i} \delta_1^i \delta_2^{[(n-1)/2]-i} \text{ for odd } n$$

$$= \frac{1}{2} \sum_{i=0}^{n/2} \binom{n/2}{i} C_{(n/2)-i} d_{(n/2)+i} \delta_1^i \delta_2^{(n/2)-i} \text{ for even } n \quad (28)$$

Moment generating function for reversible polymerization

If equation (15) is differentiated with respect to s once, one obtains

$$\frac{1}{\theta} \left\{ \frac{\partial G}{\partial s} - \frac{\partial G_0}{\partial s} \right\} = - (R-1)(2-2s)P_1^2 + 2G \frac{\partial G}{\partial s} - 2P \frac{\partial G}{\partial s}$$

$$+ 2\beta W \frac{\partial}{\partial s} \left\{ \frac{sP-G}{1-s} \right\} - \beta W \left(\frac{\partial}{\partial s} \frac{\partial G}{\partial s} - \frac{\partial G}{\partial s} \right) \quad (29)$$

If the limit of this equation for $s \rightarrow 1$ is evaluated it is found that this equation is satisfied and it does not relate λ_2 to λ_1 and λ_0 . It is therefore necessary that the differential equation for G be solved first before an explicit relation for λ_2 is obtained.

To solve for G from equation (15), one defines X as

$$X = (1-s) \quad (30)$$

in terms of which equation (15) becomes

$$-\beta W(1-X) \frac{\partial G}{\partial X} = \frac{G_0}{\theta} + G^2 - G \left\{ 2P + 2 \frac{\beta W G}{X} - \beta W + \frac{1}{\theta} \right\}$$

$$+ \left\{ 2 \frac{\beta W(1-X)}{X} P - (R-1)(1-X^2)P_1 \right\} \quad (31)$$

The boundary condition on equation (31) is obtained by observing that $G = P$ when $s \rightarrow 1$, or

$$\text{at } X=0, G=P \quad (32)$$

Equation (31) can be rearranged to give

$$\frac{\partial G}{\partial X} = \frac{-K_1}{(1-X)} G^2 + G \left\{ \frac{2\gamma_1}{(1-X)} + \frac{2}{X} \right\} - \left\{ \frac{\gamma_2}{(1-X)} + \frac{\gamma_3}{X} - \gamma_4(X+1) \right\} = 0 \quad (33)$$

where

$$K_1 = \frac{1}{\beta W} \quad (34a)$$

$$\gamma_1 = \frac{1/\theta + 2P}{2\beta W} + 1 \quad (34b)$$

$$\gamma_2 = G_0/\beta W \theta \quad (34c)$$

$$\gamma_3 = 2P \quad (34d)$$

$$\gamma_4 = \frac{(R-1)P_1^2}{\beta W} \quad (34e)$$

To solve for G from equation (33), one defines

$$G(\theta, s) = \frac{y_2(\theta, s)}{y_1(\theta, s)} \quad (35)$$

where $y_1(\theta, s)$ and $y_2(\theta, s)$ are given by

$$\frac{\partial y_1}{\partial s} = \left\{ \frac{\gamma_1}{(1-X)} + \frac{1}{X} \right\} y_1 + \frac{K_1}{(1-X)} y_2 \quad (36a)$$

$$\frac{\partial y_2}{\partial s} = - \left\{ \frac{\gamma_2}{1-X} + \frac{\gamma_3}{X} - \gamma_4(1+X) \right\} y_1 + \left(\frac{\gamma_1}{1-X} + \frac{1}{X} \right) y_2 \quad (36b)$$

These can now be written in the standard matrix equation form

$$\dot{y} = Ay \quad (37)$$

where

$$\dot{\mathbf{y}} = \begin{bmatrix} \frac{\partial y_1}{\partial s} \\ \frac{\partial y_2}{\partial s} \end{bmatrix} \quad (38a)$$

$$\mathbf{y} = \begin{bmatrix} y_1 \\ y_2 \end{bmatrix} \quad (38b)$$

$$\mathbf{A} = \begin{bmatrix} -\left(\frac{\gamma_1}{1-X} + \frac{1}{X}\right) & \frac{K_1}{(1-X)} \\ -\left\{\frac{\gamma_2}{(1-X)} + \frac{\gamma_3}{X} - \gamma_4(1+X)\right\} & \left\{\frac{\gamma_1}{1-X} + \frac{1}{X}\right\} \end{bmatrix} \quad (38c)$$

The solution of a matrix equation (of the form of equation (37)) is not straightforward wherever the components of matrix \mathbf{A} is function of X . In the case when \mathbf{A} is a function of X , the solution is of the vector-Volterra form and is given by an infinite series as follows. Matrix ϕ is defined as

$$\phi = \mathbf{I} + \mathbf{Q}(\mathbf{A}) + \mathbf{Q}(\mathbf{A}\mathbf{Q}(\mathbf{A})) + \mathbf{Q}(\mathbf{A}\mathbf{Q}(\mathbf{A}\mathbf{Q}(\mathbf{A}))) + \dots \quad (39)$$

where \mathbf{Q} is an operator given by

$$\mathbf{Q}(\cdot) = \int_{\tau}^X (\cdot) d\tau \quad (40)$$

The solution of equation (37) is then

$$\mathbf{y}(X) = \phi \mathbf{y}_0 \quad (41)$$

where \mathbf{y}_0 is the initial condition on \mathbf{y} . Some of the terms of equation (39) have been derived and are given in the Appendix, from which it is clearly seen that it is not possible analytically to get third terms and beyond. If one represents ϕ as

$$\phi = \begin{bmatrix} \phi_{11} & \phi_{12} \\ \phi_{21} & \phi_{22} \end{bmatrix} \quad (42)$$

then G is given by

$$G = \frac{\phi_{21}y_{10} + \phi_{22}y_{20}}{\phi_{11}y_{10} + \phi_{12}y_{20}} = \frac{\phi_{21} + P\phi_{22}}{\phi_{11} + \phi_{12}P} \quad (43)$$

Once G is obtained, one can in principle determine the entire MWD and the second moment λ_2 ; however it does not appear to be easy analytically.

RESULTS AND DISCUSSION

The numerical technique of sequential computation of MWD is easy to implement. Earlier^{22,23,25,26} we have treated the various mole balance relations as a set of non-linear algebraic equations and solved them using the Brown technique; to get the MWD for a given residence

time θ , the time of polymerization was divided into small increments, $\Delta\theta$. This was done owing to the difficulty of providing a good initial guess which is close to the actual solution for every computation step. At $\theta=0$, the outlet of the reactor would have polymer molecules at the concentrations as in feed. Therefore the MWD of the polymer at $\Delta\theta$ was computed using feed values as the initial guess, that as $2\Delta\theta$ was determined using the MWD at $\Delta\theta$ as the initial guess and so on.

While using the Brown technique to get the MWD, $\Delta\theta$ and the maximum number of equations, N_c , that has to be solved simultaneously to obtain a stable numerical solution must be chosen. Preferably $\Delta\theta$ is kept as large as possible, but then the constraint of the initial guess being close to the actual solution cannot be satisfied. Simultaneously, the value of N_c chosen should be such that the truncation error arising due to neglecting concentrations of higher oligomers should be small. This would imply that N_c should increase with time of polymerization and would depend upon the current value of P_N , which can be neglected. To obtain MWD using the Brown technique is time consuming and the approximate CPU time required for the Dec. 1090 computer, with $\theta=1.5$ and $\Delta\theta=0.5$ for 153 equations, is about 70 minutes.

The numerical technique outlined in this paper is extremely efficient and the MWD of the polymer at any given reactor residence time θ can be obtained without making any sequential computation scheme as outlined above. For example for $\theta=100$, the entire MWD was obtained in 0.25 s CPU time. Equations (10a), (10b) and (10c) are first solved using the Newton-Raphson method as follows. For a batch reactor the concentration of the condensation product is given by equation (11), which means that

$$\frac{\partial W}{\partial P} = -1 \quad (44)$$

$(\partial P_1/\partial P)$ can be found using equation (10a) to get

$$\frac{\partial P_1}{\partial P} = \frac{1}{2A} \left\{ -\frac{\partial B}{\partial P} + \frac{B \frac{\partial B}{\partial P} + 2A \frac{\partial C}{\partial P}}{\sqrt{B^2 + 4AC}} \right\} \quad (45)$$

where

$$A = 2(R-1)P_1^2 \quad (46a)$$

$$B = \frac{1}{\theta} + 2P + 2\beta W \quad (46b)$$

$$C = \frac{P_{10}}{\theta} + 2\beta WP \quad (46c)$$

$$\frac{\partial B}{\partial P} = 2 + 2\beta \frac{\partial W}{\partial P} \quad (46d)$$

$$\frac{\partial C}{\partial P} = 2\beta P \frac{\partial W}{\partial P} + 2\beta W \quad (46e)$$

To apply the Newton-Raphson technique an initial guess of P is made (i.e. $P=1$). Using this, P_1 and $(\partial P_1/\partial P)$ are computed and then:

$$F(P) = \frac{1-P}{\theta} - (R-1)P_1^2 - P^2 + \beta W(1-P) \quad (47a)$$

and

$$\frac{\partial F}{\partial P} = -\frac{1}{\theta} - 2(R-1)P_1 \frac{\partial P_1}{\partial P} - 2P + \beta(1-P) \frac{\partial W}{\partial P} - \beta W \quad (47b)$$

The next trial value of P is calculated, $P^{(k+1)}$; the following relation is always found to lead to convergence

$$P^{k+1} = 1/2 \left\{ P^k + \left(P^k - \frac{F}{(\partial F/\partial P)} \right) \right\} \quad (48)$$

If P^{k+1} is more than one, to keep the guess value of P between 0 and 1, P^{k+1} is taken as $(1+P^k)/2$ and the computation from equation (48) is ignored. Similarly if equation (48) gives P^{k+1} less than 0, P^{k+1} is taken as $P/2$ and the computation from equation (48) is ignored.

The entire *MWD* has been computed for several values of the reverse rate constant, β , the unequal reactivity ratio, R , and reactor residence times, θ . The method consists of first determining P and P_1 and then using equation (9) for all values of n . In generating results presented in this paper it has been assumed that feed consists of monomer only, even though the scheme presented here is valid for any feed. Unlike the irreversible case, the polymer chains stop growing as equilibrium is approached and the equilibrium *MWD* can be easily obtained by putting $1/\theta = 0.0$ in equations (7)–(9). Finally, by substituting $R=1$ above, results for the case of equal reactivity can be derived. The results are then considerably more simplified because P can be solved from equation (10c) without any trial and error. Once P is computed, the entire *MWD* can be easily determined from equations (7)–(9).

The *MWD* of the polymer from HCFR for irreversible polymerization has been studied earlier¹². It has been found that the *MWD* splits into two curves for the odd and even n for $R > 1$. For $R < 1$, substantial amounts of unreacted monomer are present in the product stream

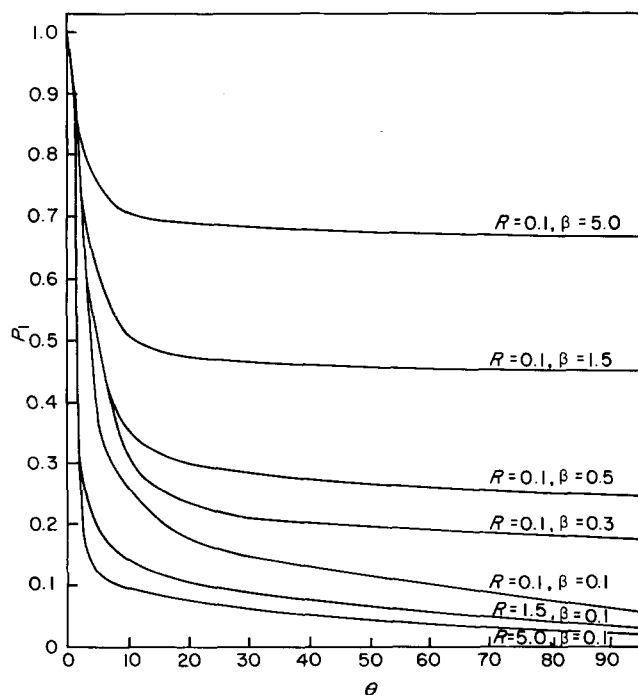


Figure 2 Effect of R and β on the concentration of monomer P_1 versus reactor residence time θ . Parameters R , θ and β as defined in equation (5)

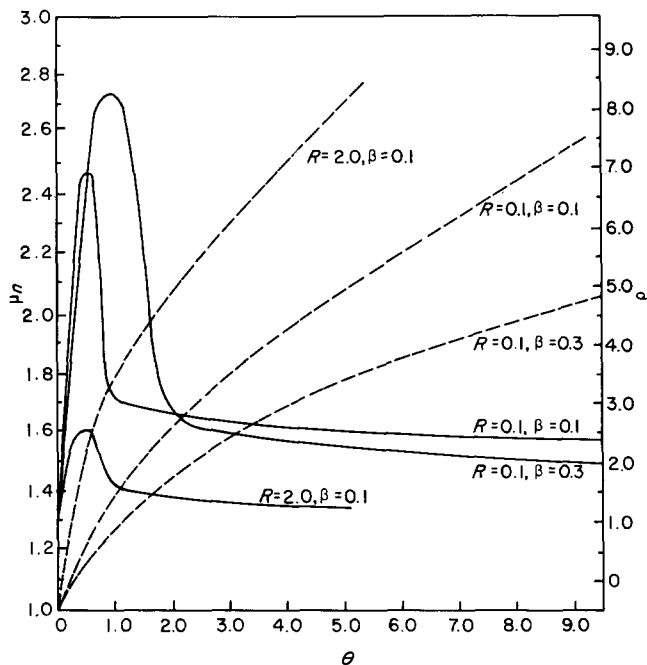


Figure 3 Effect of R and β on the average chain length, μ_n , and polydispersity index, ρ , versus θ : (—), ρ ; (---), μ_n . Parameters R , θ and β as defined in equation (5)

and curve splitting does not occur. We have derived an analytical expression of the *MWD* given in equation (29) which involves rate constant, θ , P and P_1 . The presence of the reverse reaction does not change the nature of the *MWD*, which splits exactly as earlier. The presence of the reverse reaction only reduces the amount of the split for the odd and even n compared with that found for the irreversible case.

In Figure 2, P_1 as a function of θ has been plotted for various R and β . For $R=0.1$, β has been increased. As θ increases, P_1 falls sharply first but for large θ it approaches an asymptotic value. For any R , as β increases, the asymptotic value of P_1 is found to increase. This is expected because as β increases, more unreacted monomer is going to be present in the reaction mass. As R is increased, no matter what the value of β is, the tendency of the monomer to react is expected to increase, this way raising the asymptotic P_1 in the reaction mass. Figure 3 gives the average chain length, μ_n , and the polydispersity index, ρ , in the reaction mass. In this figure we have plotted results up to $\theta=9$ to bring out the effect of R and β on the polydispersity index, ρ , which is found to increase sharply first for small θ , then to fall after passing through a maximum. The fall in ρ slows down considerably for $\theta > 3$ for the ranges of β and R studied here. The maximum value of ρ is found to fall when either β or R or both are increased. For the range of θ plotted in this graph, the average chain length μ_n is found to increase; however its rate of increase slows down as θ increases. This is due to the fact that, for large θ , the reverse reaction gains in importance and polymerization begins to slow down as equilibrium is approached.

In Figures 4, 5 and 6, results for equilibrium polymerization are given. Figure 4 gives the equilibrium molecular weight distribution, MWD_{equil} . MWD_{equil} is found to split even though for large n , curves for even and odd n merge. Even though MWD_{equil} is affected by R , the effect is small and cannot be shown in Figure 4. In Figure 5 the equilibrium P and P_1 (denoted by P_{eq} and $P_{1\text{eq}}$) is

CONCLUSIONS

The computations of *MWD* of reversible step-growth polymerization for a given residence time is a solution of a large number of interacting non-linear algebraic equations. This takes a considerable amount of computation time on fast computers. It is possible to rearrange these algebraic equations in such a way that they become non-interacting in nature. A computation scheme has been developed in which concentrations of monomer, P_1 and that of functional groups in the reaction mass, P , are first solved using the Newton-Raphson technique. The entire *MWD* can be determined in terms of P and P_1 .

The moment generating function for reversible polymerization in HCFR has been derived and is found to be a Riccati equation. Under a transformation, it is found to reduce into two linear differential equation whose coefficients are functions of a variable, s . The solution of these is not straightforward and has been suggested to be in vector-Volterra form. On further manipulations, the solution of G is obtained as an infinite series.

For irreversible polymerization with unequal reactivity, the equation governing G reduces to an algebraic equation. From this, the *MWD* for monomer feed has been derived, and the concentration of P_n is found to be given by an infinite series. The expressions for odd and even n are found to be different, thus explaining the split in the *MWD* as found in an earlier analysis.

The equilibrium molecular weight distribution and its properties have been investigated for step growth polymerization with unequal reactivity. The equilibrium *MWD* is affected by the unequal reactivity ratio, R , as well as by the equilibrium rate constant, β . The effect of R is found to be small, but increasing β makes the *MWD* sharper because of smaller conversion. For a given R , μ_n and ρ both fall drastically as β is increased from a small value; however for large β , this change is small. For a given β , as R is increased, μ_n as well as ρ both fall.

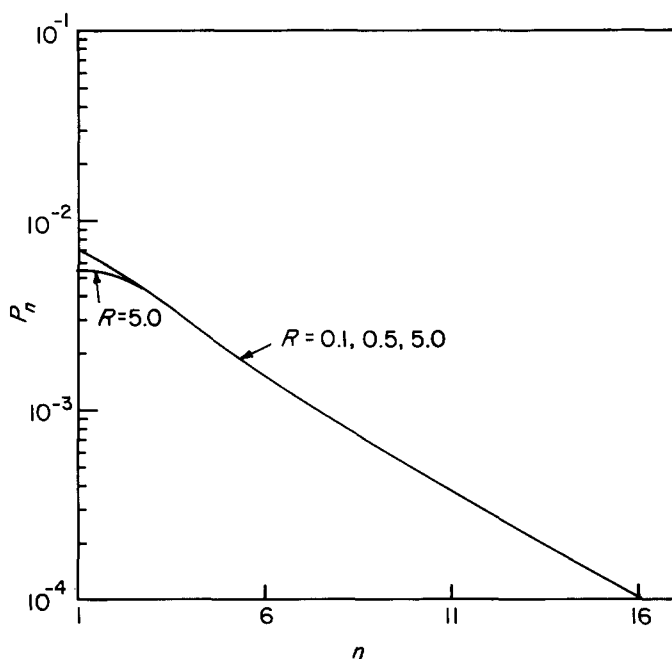


Figure 4 Effect of R on the equilibrium *MWD* for $\beta = 0.1$. Parameters R , θ and β as defined in equation (5)

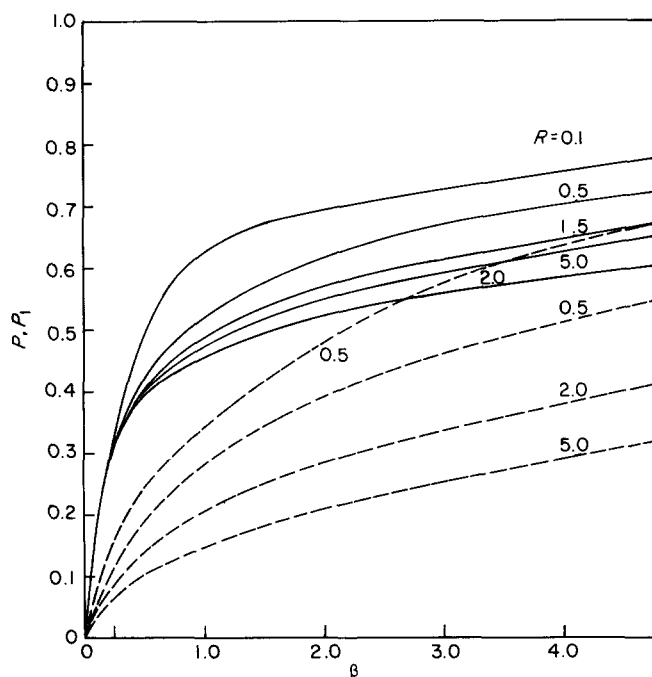


Figure 5 Effect of R and β on equilibrium P and P_1 : (—), P ; (---), P_1 . Parameters R , θ and β as defined in equation (5)

shown as a function of β for various values of R . For a given R , as β is increased, the reverse reaction gains in importance and P_{eq} and P_{1eq} are found both to increase as seen. For a given β , as R is increased, P_{eq} and P_{1eq} are found both to decrease. This is expected because on increasing R , monomer reacts to form higher oligomers, thus giving reduced P and P_1 in the reaction mass. In Figure 6 equilibrium values of μ_n and ρ have been plotted as a function of β for various values of R . For the same reasons, μ_n and ρ both fall monotonically as β or R is reduced.

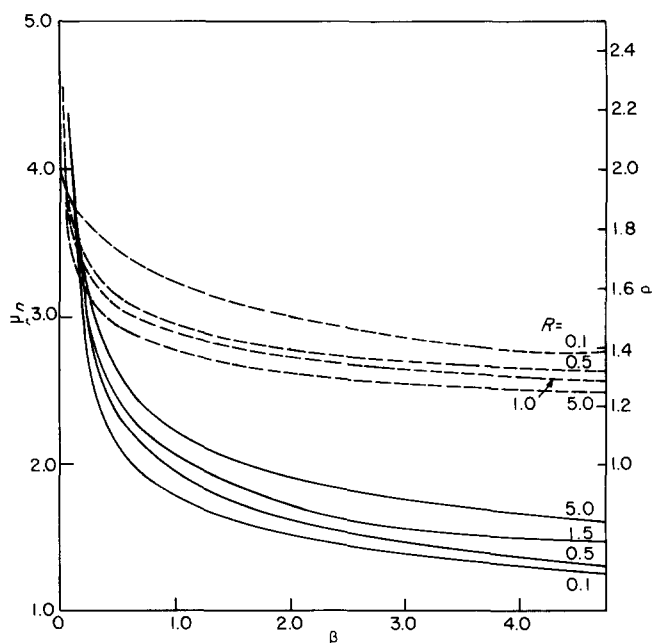


Figure 6 Effect of R and β on equilibrium μ_n and ρ : (—), μ_n ; (---), ρ . Parameters R , θ and β as defined in equation (5)

REFERENCES

- 1 Flory, P. J. 'Principles of Polymer Chemistry', 1st Edn., Cornell University Press, Ithaca, New York, 1953
- 2 Odian, G. 'Principles of Polymerization', 2nd Edn., Wiley, New York, 1981
- 3 Throne, J. L. 'Plastics Process Engineering', 1st Edn., Marcell Dekker, New York, 1979
- 4 Kumar, A. and Gupta, S. K. 'Fundamentals of Polymer Science and Engineering', 1st Edn., Tata McGraw Hill, New Delhi, 1978
- 5 Biesenberger, J. A. and Sebastian, D. H. 'Polymer Reaction Engineering', 1st Edn., Wiley, New York, 1983
- 6 Bhide, B. V. and Sudborough, J. J. *J. Ind. Inst. Sci.* 1925, **8A**, 89
- 7 Flory, P. J. *J. Am. Chem. Soc.* 1939, **61**, 3334
- 8 Flory, P. J. *J. Am. Chem. Soc.* 1940, **62**, 2261
- 9 Solomon, D. H. (Ed.), 'Step Growth Polymerization', Marcell Dekker, New York, 1978
- 10 Ray, W. H. *Macromol. Sci., Rev. Macromol. Chem.* 1972, **C8**, 1
- 11 Ray, W. H. and Laurence, R. L. in 'Chemical Reactor Theory', (Eds. L. Lapidus and N. R. Amundson), 1st Edn., Prentice Hall, Englewood Cliff, NJ, 1977
- 12 Gupta, S. K. and Kumar, A. *Chem. Eng. Commun.* 1983, **20**, 1
- 13 Gupta, S. K. and Kumar, A. 'Reaction Engineering of Step Growth Polymerization, Plenum, New York, in press
- 14 Case, L. C. *J. Polym. Sci.* 1958, **29**, 455
- 15 Hodkin, J. H. *J. Polym. Sci., Polym. Chem. Edn.* 1976, **14**, 409
- 16 Lenz, R. W., Handlovitz, C. E. and Smith, H. A. *J. Polym. Sci.* 1962, **58**, 351
- 17 Kuchanov, S. I., Keshtov, M. L., Halatur, P. G., Vasnev, V. A., Vinogradova, S. V. and Korshak, V. V. *Macromol. Chem.* 1983, **184**, 105
- 18 Nanda, V. S. and Jain, S. C. *J. Chem. Phys.* 1968, **49**, 1318
- 19 Goel, R., Gupta, S. K. and Kumar, A. *Polymer* 1977, **18**, 851
- 20 Gupta, S. K., Kumar, A. and Bhargava, A. *Europ. Polym. J.* 1979, **15**, 557
- 21 Gupta, S. K., Kumar, A. and Bhargava, A. *Polymer* 1979, **20**, 305
- 22 Kumar, A., Gupta, S. K. and Saraf, R. *Polymer* 1980, **21**, 1323
- 23 Gupta, S. K., Kumar, A. and Saraf, R. *J. Appl. Polym. Sci.* 1980, **25**, 1049
- 24 Gupta, S. K., Agarwalla, N. L., Rajora, P. and Kumar, A. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 933
- 25 Kumar, A., Rajora, P. and Bhargava, A. *Polymer* 1979, **20**, 305
- 26 Ramagopal, A., Kumar, A. and Gupta, S. K. *Polym. Eng. Sci.* 1982, **22**, 849

APPENDIX

Some terms of equation (39)

$$\mathbf{A} = \begin{bmatrix} -\left(\frac{\gamma_1}{1-X} + \frac{1}{X}\right) & \frac{K}{(1-X)} \\ -\left\{\frac{\gamma_2}{1-X} + \frac{\gamma_3}{X} - \gamma_4(1-X)\right\} & \left(\frac{\gamma_1}{1-X} + \frac{1}{X}\right) \end{bmatrix}$$

$$\mathbf{Q}(\mathbf{A}) = \begin{bmatrix} \gamma_1 \ln(1-X) - \ln X & -K \ln(1-X) \\ \gamma_2 \ln(1-X) - \gamma_3 \ln X + \gamma_4 \left(X + \frac{X^2}{2}\right) & -\gamma_1 \ln(1-X) + \ln X \end{bmatrix}$$

$$\mathbf{A}\mathbf{Q}(\mathbf{A}) = \begin{bmatrix} \left\{\frac{\gamma_1}{1-X} + \frac{1}{X}\right\} \left\{\gamma_1 \ln(1-X) - \ln X\right\} + \frac{K}{1-X} \left\{\gamma_2 \ln(1-X) - \gamma_3 \ln X + \gamma_4 \left(X + \frac{X^2}{2}\right)\right\}, & -\left(\frac{\gamma_1}{1-X} + \frac{1}{X}\right) K \ln(1-X) \\ + \frac{K}{(1-X)} \left\{-\gamma_1 \ln(1-X) + \ln X\right\} & \\ -\left\{\frac{\gamma_2}{1-X} + \frac{\gamma_3}{X} - \gamma_4(1-X)\right\} \left\{\gamma_1 \ln(1-X) - \ln X\right\} + \left(\frac{\gamma_1}{1-X} + \frac{1}{X}\right) \left\{\gamma_2 \ln(1-X) - \gamma_3 \ln X + \gamma_4 \left(X + \frac{X^2}{2}\right)\right\}, & \\ \left\{\frac{\gamma_2}{1-X} + \frac{\gamma_3}{X} - \gamma_4(1-X)\right\} K \ln(1-X) - \left\{\frac{\gamma_1}{1-X} + \frac{1}{X}\right\} \left\{-\gamma_1 \ln(1-X) + \ln X\right\} & \end{bmatrix}$$