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Molecular Weight Distribution of Reversible ARB Polymerization in Homogeneous Continuous Flow Reactors with Monomers Exhibiting Unequal Reactivity

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ABSTRACT: Reversible step-growth polymerization with unequal reactivity of monomer in homogeneous continuous flow reactors (HCSTRs) has been modeled. The resulting mole balance relations are nonlinear interacting algebraic equations that must be solved simultaneously. These have been made noninteracting under transformation, which leads to considerable saving in computation time. Subsequently the mole balance equations have been properly combined to give a moment-generating function which is a Riccatti differential equation for reversible polymerization. This reduces to an algebraic equation for irreversible polymerization, and from the moment-generating function thus found, an analytical solution of the molecular weight distribution (MWD) has been derived. The moment-generating function has been solved by splitting the Riccatti differential equation under transformation into two linear differential equations. The solution of these is in the vector Volterra form and can be represented by a Neumann series. Two terms of the series were derived and were found to describe the MWD for low conversion very well. Finally the effect of the unequal reactivity and the equilibrium ratio has been examined on the equilibrium MWD and its moments.

Introduction

Polymer formation from its monomer occurs through the presence of growth centers, and polymerization is broadly classified into chain-growth and step-growth reactions, depending upon the nature of the growth center. In step-growth polymerization, growth of polymer chains 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

$$P_n + P_m \underset{k'_{p,m+n}}{\overset{k_{p,mn}}{\rightleftharpoons}} P_{m+n} + W \qquad m, n = 1, 2, ... \qquad (1)$$

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

The forward and reverse rate constants in eq 1 are usually complex functions of chain length of the polymer molecules involved. Flory was the first to propose the equal reactivity hypothesis[7,8] based on experimental results of Bhide and Sudborough[6] on the esterification of aliphatic acids in the presence of excess ethanol. 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 be carried out in either batch or continuous reactors, and the analysis of these reactors for step-growth polymerization has recently been reviewed.[9-13]

Mathematical results derived from the equal reactivity hypothesis have been used to explain the gross kinetic features. Comparison with experimental data shows that the polymerization is far more complex than that represented by the equal reactivity hypothesis.[12-17] In the literature, in the reaction-controlled polymerization, the discrepancy between the two is explained by the nonequal reactivity that can arise due to either the unequal reactivity of functional groups or the chain-length-dependent reactivities in the forward and the reverse steps of eq 1. Case[14] has analyzed various situations of the former 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 Jain[17] have analyzed the case of chain-length-dependent reactivity in irreversible step-growth polymerization. They assumed the forward rate constant to be falling linearly with the chain length and derived the MWD. Recent experiments have shown that the change in the reactivity in dilute Θ-solution of functional groups with chain length is described by an S-shaped curves.[18]

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This reactivity change has been approximated by a step function in which the monomer is assumed to react differently from other oligomers.[18-25] This can be idealized into two different limiting cases: in the first, P_1 is assumed to react only when P_1 having different rate constants, and in the second, P_1 reacts with all oligomers having different rate constants. In this paper, the unequal reactivity of the latter has been analyzed.

Polymerization can be carried out in either batch or continuous reactors. As higher and higher throughputs are desired, the economy of larger reactors demands that continuous reactors be used, and usually tubular reactors or tanks with agitators are employed. These are usually idealized as plug flow reactors (PFR) and homogeneous continuous flow reactors (HCSTRs). Most of the studies existing in the literature on MWD of the polymer formed in HCSTRs, whether under equal reactivity hypothesis or chain-length-dependent reactivity, assume the polymerization to occur under irreversible conditions.

The major difficulty of solving the MWD of reversible ARB polymerization under chain-length-dependent reactivity lies in the fact that the growth step consists of infinite elementary reactions. Since the mole 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, these equations are highly nonlinear in nature, and to solve any given equation for the concentration of any given species, one must know the concentration of all other species. If the HCSTR is operating at steady state, one obtains a large number of nonlinear 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 the Brown numerical technique to determine the MWD of the polymer formed. This computation of the MWD is tedious and requires considerable computation time.

As pointed out earlier, for reversible polymerization in HCSTRs with unequal reactivity, the mole balance equations are interconnected, which implies that the MWD can be found only through simultaneous solution of algebraic equations. In this paper, we have decoupled the mole balance equations and evolved an algorithm for sequential computation of the MWD of the polymer. Subsequently, we have determined an analytical expression of the MWD for irreversible polymerization in the presence of unequal reactivity. For reversible polymerization in HCSTRs operating at steady state, the moment-generating function has been found to be governed by an ordinary differential equation. This is a Riccattii equation which has been transformed into a set of linear ordinary differential equations. Its solution is in the vector Volterra form and is given by a Neumann series.

Theoretical Development

It is assumed that monomer (P_1) reacts with all species in the reaction mass with different rate constants (k_{11}), whereas all other higher homologues react with the rate constant k_p. This means that

$$k_{p,1n} = 2k_{11} \qquad n = 2, 3, ... \tag{2a}$$

$$k_{p,11} = k_{11} \tag{2b}$$

$$k_{p,mn} = 2k_p \qquad m \neq n;\ m, n = 2, 3, ... \tag{2c}$$

$$k_{p,mm} = k_p \qquad m = 2, 3, ... \tag{2d}$$

$$k_{p,m} = k'_p \qquad m = 2, 3, ... \tag{2e}$$

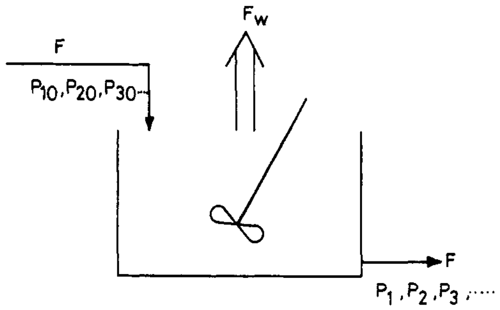

Figure 1. Schematic diagram of an HCSTR.

The schematic diagram of an HCSTR is shown in Figure 1. The feed is assumed to consist of oligomers at concentrations $[P_1]_0$, $[P_2]_0$, $[P_3]_0$, etc., and the reactor volume is V. For an isothermal HCSTR operating at steady state, the mole balances for various species are given by

$$([P_1] - [P_1]_0)/\theta_1 = -2k_{11}[P_1][P] + 2k'_p[W]\sum_{i=2}^{\infty}[P_i] \tag{3a}$$

$$([P_2] - [P_2]_0)/\theta_1 = k_{11}[P_1]^2 - 2(k_{11} - k_p)[P_1][P_2] - 2k_p[P_2][P] + 2k'_pW\sum_{i=3}^{\infty}P_i - k'_p[W][P_2] \tag{3b}$$

$$([P_n] - [P_n]_0)/\theta_1 = 2(k_{11} - k_p)[P_1]\{[P_{n-1}] - [P_n]\} + k_p\sum_{i=1}^{n-1}[P_i][P_{n-i}] - 2k_p[P_n][P] + 2k'_p[W]\sum_{i=n+1}^{\infty}[P_i] - k'_p[W](n-1)[P_n] \qquad n \geq 3 \tag{3c}$$

$$([W] - [W]_0)/\theta_1 = -F_w/\theta_1 + k_p[P]^2 - (k_{11} - k_p)[P_1]^2 + 2(k_{11} - k_p)[P_1][P] - k'_p[W]([P]_0 - [P]) \tag{3d}$$

where

$$\theta_1 = V/F \tag{4a}$$

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

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

V and F are the reactor volumes and the total flow rates, respectively. In cases where the reversible step is not favorable to the formation of the polymer, high vacuum is applied to remove the condensation product. In Figure 1, F_w represents the outflow of the condensation product due to the application of the vacuum.

For convenience, one defines the following dimensionless variables:

$$p_{n0} = [P_n]_0/[P]_0 \tag{5a}$$

$$p_n = [P_n]/[P]_0 \tag{5b}$$

$$P = [P]/[P]_0 \tag{5c}$$

$$W = [W]/[P]_0 \tag{5d}$$

$$\theta = k_p[P]_0{}^2\theta_1 \tag{5e}$$

$$\beta = k'_p[P]_0{}^2 \tag{5f}$$

$$R = k_{11}/k_p \tag{5g}$$

$$\gamma = 2k'_pW/k_p \tag{5h}$$

It is observed that at any given time of polymerization

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

which on substitution in eq (3) gives

$$\upsilon_n P_n = u_n + \sum_{r=1}^{n-1} P_r (P_{n-r} - \gamma) \tag{7}$$

where

$$u_2 = P_{2,0}/\theta + 2\beta WP + RP_1^2 \tag{8a}$$

$$u_n = 2(R-1)P_1P_{n-1} + P_{n0}/\theta + 2\beta WP \tag{8b}$$

and

$$\upsilon_n = \{1/\theta + 2(R-1)P_1 + 2P + \beta W(n+1)\} \tag{8c}$$

From these equations, it is thus seen that one can determine the entire molecular weight distribution sequentially if P and P_1 are known. These can be evaluated as follows. Equations 3a–d are added for all possible n to get

$$(P - P_0)/\theta = (R-1)P_1^2 - P^2 - 2(R-1)P_1P + \beta W(P_0 - P) \tag{9}$$

Between eq 3a,d and 9, P, P_1, and W can be solved exactly. If the reactor is operating strictly in the absence of by-product cross-flow (which means that $F_W = 0$ in eq 3d), then W in the reaction mass is exactly equal to the moles of functional groups reacted, i.e.

$$W - W_0 = 1 - p \tag{10}$$

where W_0 is the moles of condensation product present initially.

Moment-Generating Function for Reversible Polymerization

Moment-generating function G is defined as

$$G(s,\theta) = \sum_{n=1}^{\infty} s^n P_n(\theta) \tag{11}$$

where s is a dummy variable whose numerical value is less than 1. Equations 3a–c are multiplied by s, s^2, and s^n, and the resulting equations are added for all values of n to obtain

$$(G - G_0)/\theta = (R-1)P_1^2(2s - s^2) - 2(R-1)P_1Ps - (R-1)p_1G(1-s) - 2PG + G^2 + 2\beta W\frac{sp - G}{1 - s} - \beta W\left(s\frac{\partial G}{\partial s} - G\right) \tag{12}$$

where

$$s\frac{\partial G}{\partial s} = \sum_{n=1}^{\infty} ns^nP_n \tag{13a}$$

and

$$G_0 = \sum_{n=1}^{\infty} s^n P_{n0} \tag{13b}$$

This equation can be rearranged to give

$$\beta Ws\frac{\partial G}{\partial s} = G^2 - G\left\{(R-1)(1-s)P_1 + P + \frac{2\beta W}{1-s} + \frac{1}{\theta} - \beta Ws\right\} + \left\{\frac{G_0}{\theta} + (R-1)p_1^2(2s - s^2) - 2(R-1)P_1Ps + \frac{2\beta Ws}{1-s}\right\} \tag{14}$$

This is an ordinary differential equation with the following boundary condition:

$$G(s,\theta) \to p \quad \text{for } s \to 1 \tag{15}$$

MWD in Irreversible Polymerization

For irreversible polymerization, the moment-generating relation, G, reduces to

$$(G - G_0)/\theta = (R-1)P_1^2(2s - s^2) - 2(R-1)P_1Ps - (R-1)P_1G(1-s) - 2PG + G^2 \tag{16}$$

or

$$G^2 - \{1/\theta + 2P + (R-1)P_1(1-s)\}G + \{(R-1)p_1^2(2s - s^2) + G_0/\theta - 2(R-1)P_1Ps\} = 0 \tag{17}$$

from which G can be easily solved as

$$G = (1/2)\{(\gamma_1 - \gamma_2 s) - [(\gamma_1 - \gamma_2 s)^2 - 4\{G_0/\theta - (R-1)P_1[(P - P_1)2s + s^2P_1]\}]^{1/2}\} \tag{18}$$

where

$$\gamma_1 = 1/\theta + 2P + (R-1)P_1 \tag{19a}$$

$$\gamma_2 = (R-1)P_1 \tag{19b}$$

Using the expression for G in eq 18, one can easily derive an analytical relation for various moments. Zeroth moment λ_0 is the same as P and is given by $\lim_{s\to1} G$, which was derived earlier. The first moment (λ_1) is given by

$$\lambda_1 = \sum nP_{n0} = s\frac{\partial G_0}{\partial s}\bigg|_{s\to1} \tag{20}$$

This is the same as the total number of repeat units in the reaction mass and is time invariant. To determine the number-average chain length (μ_n) and the polydispersity index (ρ), one needs information on λ_0, λ_1, and λ_2. The second moment (λ_2) is given by

$$\lambda_2 = \lim_{s\to1}\frac{\partial}{\partial s}\left(s\frac{\partial G}{s}\right) = \tfrac{1}{2}\{-\gamma_2 + [(\gamma_2 - \gamma_1\gamma_2) + 4(R-1)PP_1\}^2 - u_1\{(2\gamma_2^2 - \gamma_1\gamma_2) + 4(R-1)P_1(P + P_1)]/u_1^{3/2}\} \tag{21}$$

where

$$u_1 = [(\gamma_1 - \gamma_2)^2 - 4\{G_0/\alpha\theta - (R-1)P_1(2P - P_1)\}]^{1/2} \tag{22}$$

The molecular weight distribution of the polymer can be found by expanding eq 18 in powers of s and determining the coefficient of s^n as follows. Equation 18 is first rearranged as

$$G = \tfrac{1}{2}\{\gamma_1 - \gamma_2 s - \gamma_1(1 - y)^{1/2}\} \tag{23}$$

where

$$y = 1/\gamma_1^2\{\delta_1 s - \delta_2 s^2\} \tag{24a}$$

$$\delta_1 = 4P_{1,0}/\alpha\theta - 8(R-1)P_1(P - P_1) + 2\gamma_1\gamma_2 \tag{24b}$$

$$\delta_2 - 4(R-1)P_1^2 + (R-1)^2P_1^2 \tag{24c}$$

In eq 23, $(1 - y)^{1/2}$ is expanded in series first to get

$$G = \frac{1}{2}\{-\gamma_2 s + \sum_{n=1}^{\infty} d_n y^n\} \tag{25}$$

where

$$d_n = \prod_{i=0}^{n}(1/2 - i)/n! \qquad n = 1, 2, ... \tag{26}$$

Next, one expands $(\delta_1 s - \gamma_2 s^2)^n$ in eq 25 and then collects terms for s^n to get P_n as

$$P_n = \sum_{i=0}^{(n-1)/2} {}^{((n+1)/2)+i}C_{((n-1)/2)-i}d_{((n+1/2)+i}\delta_1{}^i(-\delta_2)^{((n-1)/2)-i} \quad \text{for odd } n \tag{27a}$$

$$= \sum_{i=0}^{n/2} {}^{n/2+i}C_{n/2-i}d_{n/2+i}\delta_1{}^i(-\delta_2)^{((n-1)/2)-i} \quad \text{for even } n \tag{27b}$$

where ${}^nC_r$ is defined as

$${}^nC_r = n!/r!(n-r)! \tag{28}$$

Moment-Generating Function for Reversible Polymerization

To solve for the moment-generating function G, one defines x as

$$x = 1 - s$$

in terms of which eq 14 becomes

$$\frac{dG}{dx} = \frac{-1}{\beta W(1-x)}G^2 + 2\left(\frac{\gamma_3}{1-x} + \frac{1}{x} - \delta_4\right)G - \left\{\frac{\gamma_5}{(1-x)} + \frac{2}{x} + \gamma_6(1+x)\right\} \tag{29a}$$

$$\gamma_3 = \frac{(R-1)P_1P + 2P + 1/\theta}{2\beta W} + 1 \tag{29b}$$

$$\gamma_4 = \frac{(R-1)P_1P - \beta W}{2\beta W} \tag{29c}$$

$$\gamma_5 = G_0/\beta W\theta \tag{29d}$$

$$\gamma_6 = (R-1)P_1{}^2/\beta W \tag{29e}$$

If G is written as

$$G = y_2/y_1 \tag{30}$$

the Riccatti equation in (29a) can be written as a set of linear equations as

$$\dot{\mathbf{Y}} = \mathbf{A}(x)\mathbf{Y} \tag{31}$$

where $\mathbf{Y}$ and $\mathbf{A}$ are defined as

$$\mathbf{Y} = [y_1, y_2]^T \tag{32a}$$

$$\dot{\mathbf{Y}} = \begin{bmatrix} \dfrac{\partial y_1}{\partial x} & \dfrac{\partial y_2}{\partial x} \end{bmatrix} \tag{32b}$$

$$\mathbf{A}(x) = \begin{bmatrix} -\left(\dfrac{\gamma_3}{1-x} + \dfrac{1}{x} + \gamma_4\right) & \dfrac{1}{\beta W(1-x)} \\ -\left\{\dfrac{\gamma_5}{1-x} + \dfrac{2}{x} + \gamma_6(x+1)\right\} & \left\{\dfrac{\gamma_3}{1-x} + \dfrac{1}{x} + \gamma_4\right\} \end{bmatrix} \tag{32c}$$

The solution of eq 31 is a Neumann series whenever $\mathbf{A}$ is a function of x and is given by

$$\mathbf{Y}(x) = [\mathbf{I} + Q(\mathbf{A}) + Q(\mathbf{A}Q(\mathbf{A})) + Q(\mathbf{A}Q(\mathbf{A}Q(\mathbf{A}))) + ...]\mathbf{Y}(0) \triangleq \Phi(x)\mathbf{Y}(0) \tag{33}$$

Q is an integral operator defined as

$$Q(\cdots) = \int_0^x (\cdots)\, d\lambda \tag{34}$$

In eq 33 $\mathbf{Y}(0)$ is the initial condition on $\mathbf{Y}$, which is not known precisely. However, as shown below, it is not needed in order to find G. If one represents Φ as

$$\Phi = \begin{bmatrix} \phi_{11} & \phi_{12} \\ \phi_{21} & \phi_{22} \end{bmatrix} \tag{35}$$

then G is given by

$$G = \frac{\phi_{21}y_{10} + \phi_{22}y_{20}}{\phi_{11}y_{10} + \phi_{12}y_{20}} = \frac{\phi_{21} + P\phi_{22}}{\phi_{11} + P\phi_{12}} \tag{36}$$

We have evaluated the first three terms of Φ in eq 33, but we were unable to identify various terms in them converging to any known series. As a result, we found G using the first three terms, and then P_n was found as a coefficient of $(1-x)$. Results were found to be good for low conversions only. In view of this, the exact numerical computation is a convenient way of determining the MWD.

Results and Discussion

MWD for Finite Residence Time of HCSTR. As pointed out above, G can be found only as an infinite series, which would require a messy integration of eq 33. As opposed to this, the numerical computation outlined in this paper is straightforward without any trial and error.

We have observed earlier[22,23,25,26] that the MWD of the polymer formed in HCSTRs can be found from the numerical solution of algebraic equations that are nonlinear and interconnected in nature. Among the various numerical techniques used, Brown's technique was found to be the most efficient. To determine the MWD for a given residence time θ, one needs to provide a good guess of the molar concentrations of various species which is close to the actual solution. This was found to be the major problem and was overcome by dividing the residence time θ into small increments, $\Delta\theta$. At $\theta = 0$, we know that the MWD is the same as that of the feed, and providing this as the initial guess, the MWD at $\Delta\theta$ was computed. This served as the initial guess for the computation of the MWD at the reactor residence time of $2\Delta\theta$. By successive repetition of this process, one can find the MWD at any θ.

Another major difficulty faced in finding the MWD is that the number of equations that needs to be solved simultaneously must be increased with the residence time of polymerization. This is done because with increasing θ higher oligomers are formed in larger concentrations and the total number of equations, N_c, to be solved simultaneously is increased to minimize the truncation error. To give an idea of the difficulty, one needs about 170 equations at $\theta = 2$ and it takes about 70 min of CPU time on a DEC 1090.[23,26] As opposed to this, the computation technique of this paper takes only 0.25 s of CPU time.

In the method suggested herein there is no need for such successive computation. For a given θ, one solves eq 3a,d and 9 simultaneously for P, P_1, and W. If the reactor is operated in the absence of byproduct cross-flow, eq 10 would hold and the number of equations to be solved is only two. For the case of the equal reactivity hypothesis, $R = 1$, and one can solve for P straightaway using eq 9 because for this case the equation for P does not involve P_1. However, P_1 can be determined with the rest of the MWD by using eq 7.

To compute P and P_1, the Newton–Raphson technique can be used, which is found to converge always. If the HCSTR is operated in the absence of byproduct cross-flow, eq 10 holds. In terms of P, P_1 can be solved by using eq 3a to give

$$P_1 = \frac{P_{1,0}/\theta + 2\beta WP}{1/\theta + 2RP + 2\beta W} \tag{37}$$

This can be differentiated with respect to p:

$$\frac{\partial P_1}{\partial P} = \frac{\left(2\beta W + 2\beta P\dfrac{\partial W}{\partial P}\right) - P_1(2R + 2\beta\partial W/\partial P)}{1/\theta + 2RP + 2\beta W} \tag{38}$$

One subsequently defines $F(P)$ as

$$F(P) = (1 - P)/\theta + (R - 1)P_1^2 - P^2 - 2(R - 1)P_1P + \beta W(1 - P) \tag{39}$$

which can also be differentiated with respect to P to give

$$\frac{\partial F}{\partial P} = -\frac{1}{\theta} + 2(R - 1)P_1\frac{\partial P_1}{\partial P} - 2P - 2(R - 1)\left(P_1 + P\frac{\partial P_1}{\partial P}\right) + \beta\{(1 - p)(\partial W/\partial P) - W\} \tag{40}$$

The computation starts by giving an arbitrary value of P (say $P = 1$). The next trial value is determined by using the following recursive relation:

$$P^{k+1} = \frac{1}{2}\left[P^k + \left(p^k - \frac{F}{\partial F/\partial P}\right)\right] \tag{41}$$

If P^{k+1}, through this method, comes out to be greater than one, P^{k+1} is taken as $(P^k + 1)/2$ to keep its value between zero and one. Similarly, if P^{k+1} comes out to be less than zero, it is taken as $P^k/2$ and the computation from eq 41 is ignored.

We have computed the entire MWD for various values of R and in Figure 2 we have plotted the monomer concentration P_1 vs. θ for various P values of R and β. P_1 is found to reduce sharply at first, but for large θ, it takes an asymptotic value. For $R > 1$, for a given R, the asymptotic value is found to increase with increasing β. However, for $R < 1$, the asymptotic value is very small and is found to reduce with increasing β as seen from Figure 2. In Figure 3, the average chain length μ_n and the polydispersity index ρ have been plotted as a function of time. For the range of residence time θ shown in this diagram, μ_n is found to keep increasing, but for large θ, its rate of increase is found to reduce due to the presence of the reverse reaction. As R is increased, the curves shift upward as seen. The polydispersity index ρ first increases sharply, undergoes a maximum, and approaches an asymptotic value. As R increases, the peak value as well as the asymptotic value of ρ both fall.

Equilibrium Polymerization. At equilibrium, the rate of formation of P_n, $\mathcal{R}_{P_n}$, must be zero, or

$$\mathcal{R}_{P_n} = 0 \qquad n = 1, 2, ...$$

On doing this, one obtains F_w' and the left-hand side of eq 3 to be zero. Once again a set of nonlinear algebraic equations governing the MWD is obtained. One can solve these exactly the way HCSTR equations have been solved for finite θ, and requiring no trial and error procedure.

In Figures 4–6, the equilibrium polymerization has been studied to examine the effect of various parameters on it. In Figure 4, the equilibrium MWD has been plotted for various R. The split in MWD for odd and even n for $R < 1$ is similarly obtained as found for irreversible polymerization except for the fact that the difference between these curves is smaller. For higher n (for $n \geq 6$ in Figure 4), the curves for odd and even n merge. In addition, the MWD curves become broader as R is increased.

In Figure 5, equilibrium P and P_1 have been plotted for various values of R. For $R < 1$, P and P_1 both increase, reaching some plateau values for large β. This plateau value is found to reduce as R is increased. However, for $R > 1$, for any given R, there is a value of β for which p increases sharply to a value of one while the value of P_1 plunges to zero. Evidently this cannot be true because P can be one only when P_1 is also equal to one. This implies that there is no solution of P_1 after certain β for $R > 1$. For $R > 1$, P_1 would preferably react to form higher oligomers, and if one waits long enough for equilibrium, P_1 should be in negligible concentration. On the other hand, if β is increased to higher values, smaller conversion of functional groups would occur, which would lead to a preponderance of monomer. In Newton–Raphson's technique used here, we have forced P and P_1 to be between zero and one. As a result of this artificiality, P_1 is found to settle on zero, which is not the correct solution.

In Figure 6, μ_n and ρ have been plotted as a function of β and R. The average chain length of the polymer at equilibrium falls with β, but for large β the rate of fall

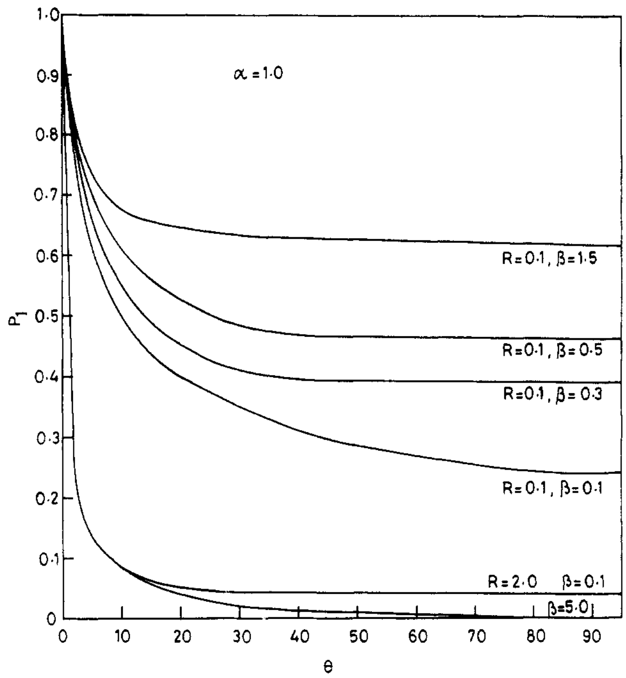

Figure 2. Monomer concentration (P_1) vs. θ for various R and β.

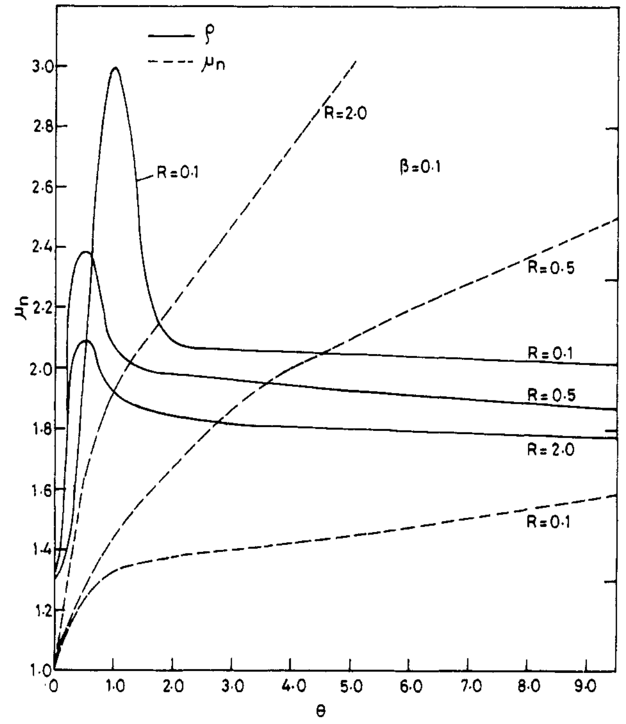

Figure 3. Average chain length (μ_n) and polydispersity index (ρ) vs. θ.

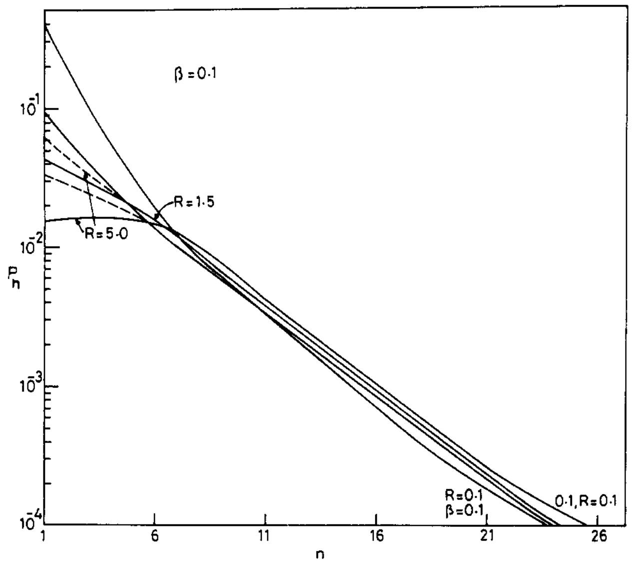

Figure 4. Equilibrium MWD.

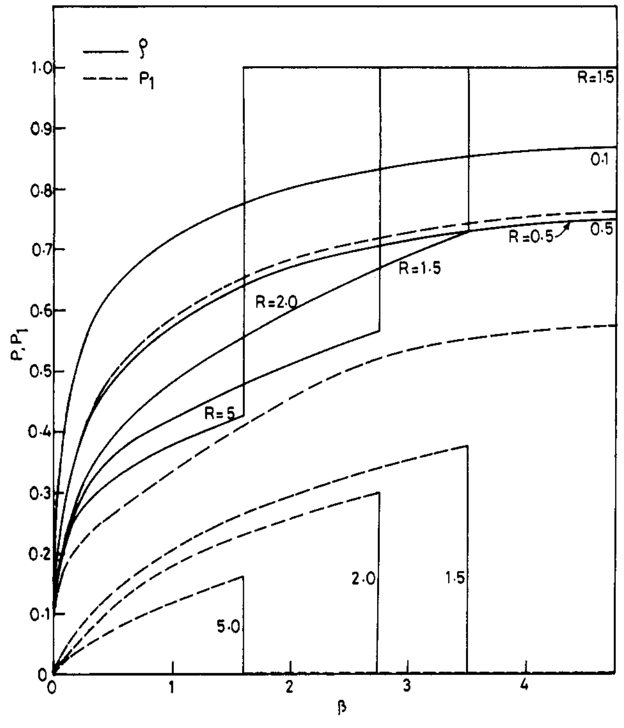

Figure 5. Equilibrium P and P_1 vs. β.

reduces considerably. For $R > 1$, μ_n approaches one much faster compared to when $R < 1$. Similar observation is made for the polydispersity index. Lastly, In Figure 5 we have observed instability in the computation of P_1, but the effect of this instability on μ_n and ρ is not noticeable in Figure 6.

Conclusions

In this paper we have modeled the reversible step-growth polymerization in HCSTRs. The mole balance relations were found to be nonlinear interacting algebraic expressions that must be solved simultaneously to determine the MWD of the polymer. We have rearranged these equations so that the MWD can be solved sequentially, and in doing this there is a considerable saving in computation time.

From the MWD equations, one can derive an expression for the moment-generating function, and it is found to be a Riccatti differential equation for reversible polymerization. For irreversible polymerization, this reduces to an algebraic expression from which an analytical expression of the MWD and its moment have been derived. The solution of the Riccatti differential equation is considerably more involved because its coefficients are functions of s. Under a certain transformation, this differential equation can be split into two linear differential equations that have a solution in the vector Volterra form. The complete solution is a Neumann series, whose first two terms have been derived in this paper.

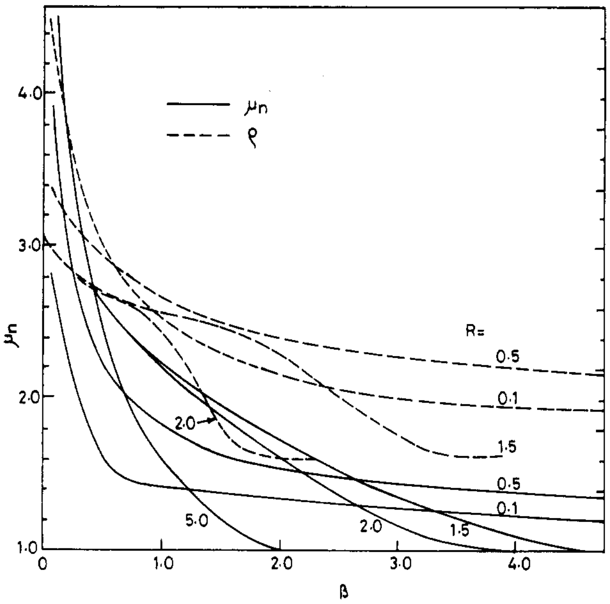

Figure 6. Equilibrium μ_n and ρ vs. β.

The equilibrium step-growth polymerization in the presence of unequal reactivity has been studied and is found to be considerably affected by both the unequal reactivity ratio R and the reverse rate constant β. The equilibrium becomes broader as R is increased. It is seen that for $R > 1$, the computation of P_1 undergoes an instability; however, those of P, μ_n, ρ, P_2, P_3, etc. are stable. This is explained as being due to the fact that by having $R > 1$ monomer would form oligomers with higher likelihood, whereas by having large β monomer should be present in the reaction mass with greater preponderance.

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Effect of Cross-Linking on the Degree of Molecular Level Mixing in a Polymer Blend

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ABSTRACT: The results of a Fourier transform infrared study of different phenolic resin blends containing an ethylene–vinyl acetate (EVA) copolymer are presented. The EVA carbonyl stretching vibration is employed as a probe of molecular mixing through its sensitivity to intermolecular hydrogen-bonding interactions. In the absence of cross-linking, novolac and model poly(vinylphenol) blends with EVA form essentially single-phase systems. These blends may be cycled up and down in temperature, and the fraction of hydrogen-bonded carbonyl groups observed is determined primarily by the strength of the intermolecular interaction, the blend composition, and the temperature, in other words, an equilibrium process. In contrast, when the phenolic resin undergoes reactions leading to increases in molecular weight, branching, and cross-linking during the heating cycle, phase separation occurs. The fraction of hydrogen-bonded EVA carbonyl groups observed is significantly less than that expected from equilibrium considerations. The ramifications of these results to semiinterpenetrating networks and polymer mixing in general are discussed.

Introduction

Although we have a vested interest in infrared spectroscopy and might be excused for some slight bias in favoring the technique, under advantageous conditions it is undeniably an excellent method for studying the mixing of polymers at the molecular level in the condensed state. The infrared probe size is at the level of a few angstroms, and information concerning the extent of mixing may be gained from an analysis of isolated normal modes that are sensitive to perturbations arising from specific intermolecular hydrogen-bonded interactions. The carbonyl stretching vibration, for example, has proven to be an excellent probe of molecular mixing for a number of polymer blends.[1] In poly(4-vinylphenol) (PVPh) blends with poly(vinyl acetate), ethylene–vinyl acetate copolymers, and polylactones,[2-4] it was a reasonably straightforward task to distinguish between and quantitatively measure those carbonyl groups that were and were not hydrogen bonded to the phenolic hydroxyl groups. The fraction of hydrogen-bonded carbonyl groups was measured as a function of temperature, and these results compare favorably to those calculated from a simple equilibrium model.[5]

The studies presented in this paper, which concern blends composed of an ethylene–vinyl acetate copolymer containing 70 wt % vinyl acetate (EVA[70]) with different phenol–formaldehyde (PF) resins, represent a logical, albeit rather complicated, extension to our previous work. The EVA[70] carbonyl stretching vibration will still be our infrared probe of molecular mixing through its sensitivity to intermolecular hydrogen bonding to the PF phenolic hydroxyl group. In this case, however, the PF resins may be cross-linked, potentially forming a semiinterpenetrating network (semi-IPN).[6,7] Somewhat naively, we postulated that, given the relatively strong intermolecular interaction involved (about -5 kcal mol^{-1}),[2] it should be possible to form a truly "miscible" semi-IPN, where, conceptually, the linear EVA[70] chains would "snake" in and out of the three-dimensional network, forming, at any instant of time, the maximum number of intermolecular hydrogen-bonding interactions dictated by equilibrium considerations. We recognized that the small entropy of mixing that occurs in high molecular weight linear polymer–polymer blends will be even less if one of the polymers undergoes cross-linking. Nevertheless, we were optimistic that a miscible semi-IPN could be formed, given the favorable enthalpy of mixing. As we will see, this optimism was unfounded.

Homogeneous IPNs have been reported for epoxy/acrylic systems[8,9] on the basis of thermal analysis and dielectric relaxation studies. This system should not be confused, however, with an interpenetrating network of an acrylic polymer intertwined with a cross-linked epoxy resin. In our opinion, it is better described as an epoxy–epoxy IPN where two different epoxy networks are formed by dissimilar chemical mechanisms, a free-radical reaction through an acrylic end group and a condensation reaction through an epoxy end group. A semi-IPN based upon an epoxy resin with polycaprolactone (PCL) has also been studied,[10] and infrared spectroscopy was one of the techniques employed. For the amine-cured epoxy system it was concluded that the semi-IPN with PCL was partially miscible.

Miscible IPNs have been reported by Frisch and coworkers,[11,12] who prepared linear blends, semi-IPNs, and IPNs of polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) which exhibited single T_gs that varied systematically with composition. In addition, no evidence of phase separation was seen in the electron microscope. To a large extent, however, the probe size of the experimental method used to study these complex mixtures dictates whether or not a system is deemed

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