

Simulation of ARB Type Reversible Step Growth Polymerization in Semibatch Reactors

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Synopsis

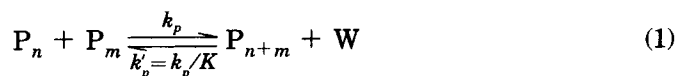
The polymerization of ARB type reversible step growth polymerization in semibatch reactors has been simulated. It is assumed that the condensation byproduct W and the monomer P_1 both can vaporize, but P_1 is refluxed back to the reactor. Raoult's law as well as Flory-Huggins theory have been used to account for vapor-liquid equilibrium. The degree of polymerization, μ_n , and the polydispersity index D_N have been computed for various situations. The results are found to be most sensitive to the total pressure and the equilibrium constant. A limiting total pressure history $P_T(t)$ has been obtained, going below which does not help to increase μ_n . The final set of equations incorporate both equalities as well as inequalities, and a simple and efficient computational scheme has been suggested to solve them.

INTRODUCTION

Several studies¹ on the simulation of *reversible* step growth polymerizations under various reactor conditions have been reported recently. This is because most commercial step growth polymerizations, e.g., PET, nylon 6, nylon-6,6, etc., are indeed reversible. Various physical phenomena like diffusion of the condensation byproduct and heat transfer are known to influence reactor performance significantly. In this paper, the role of diffusion on reactor performance under operating conditions usually encountered in the first stages of PET and nylon 6 manufacture is studied. The simplest reaction scheme, viz., starting from ARB monomer, with A and B being the reactive functional groups, is considered here; however, since the incorporation of other side reactions²⁻⁵ clouds away some important mathematical (both analytical and numerical) complexities. In our earlier work on the optimization of PET reactors with mass-transfer limitations,^{6,7} it has been found that these computational difficulties lead to serious problems, and it is necessary that one develops appropriate optimization algorithms using simplified kinetics before further progress can be made in that direction. This study on the simulation of such reactors, therefore, represents the first step in this direction.

The progress of reversible step growth polymerization reactions of ARB monomers in a closed reactor can be represented schematically by

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where P_n and P_m are the n - and m -mers, W is the low molecular weight condensation byproduct, and k_p and k'_p are the functional group reactivities. It can easily be shown¹ that p_A , the conversion of functional group A (or B), approaches an asymptotic (equilibrium) value $p_{A,e}$ given by

$$p_{A,e} = 1 - \frac{1}{\mu_{n,e}} = \frac{K}{K-1} - \frac{K^{1/2}}{K-1} \quad (2)$$

where $\mu_{n,e}$ is the equilibrium degree of polymerization. The value of the equilibrium constant K for some polymerizations of commercial interest are extremely unfavorable. For example, for the polymerization of PET from the monomer, bis hydroxyethyl terephthalate, the value of K is about 0.5, independent of temperature.² For this value of K , eq. (2) predicts the equilibrium degree of polymerization, $\mu_{n,e}$ as 1.71, which is too low a value to be of much interest. It is, therefore, evident that in order to obtain values of $\mu_{n,e}$ of about 100, which is of commercial importance, one must drive reaction (1) in the forward direction. One way of doing this is to remove the low molecular weight byproduct W by application of high vacuum (open reactors).

Several examples of industrial importance may be mentioned in which the byproduct W must be removed by some means. In nylon 6 polymerization, even though the value of K is several fold higher than for PET, optimal operation of the reactor requires that the condensation byproduct, water, be removed at some intermediate stage of polymerization.⁸ One way of achieving this is to bubble inert gas through the reaction mass.^{9,10} In nylon-6,6 polymerization too, the equilibrium constant is low, and vacuum is applied in order to obtain high molecular weight polymer.^{11,12} In all these cases, the condensation byproduct diffuses towards a liquid-vapor interface, where its concentration is lower and is determined by vapor-liquid equilibrium relations. A concentration gradient is established in the reaction mass, and concepts of mass transfer with simultaneous step growth polymerization are required to explain the performance of the reactor.

During the polymerization of PET, the viscosity of the reaction mass undergoes a significant increase from a few centipoise at low conversions to over about² 8000 P finally. The diffusivity of the small molecule W through the reaction mass towards the vapor-liquid interface, thus, varies over an extremely wide range^{13,14} and can, at times, be very low. This necessitates the use of special equipment which can enhance mass transfer rates. Also, depending upon the relative resistances of the mass transfer and the polymerization steps, different analytical models must be used for accounting for the mass transfer occurring in the specified geometry of the reactor. At one end of the spectrum lies the situation, where μ_n is about 100, the viscosity is of the order of 8000 P (for PET), and the mass transfer coefficient is extremely small compared to the reaction rate constant. The mass transfer resistance cannot then be neglected and spatial variations

of the concentration of W must be accounted for. Obviously, it is desirable to reduce the mass transfer resistance as much as possible by using special thin film reactors,¹⁵⁻¹⁹ in order to reduce the length of the diffusion path. Such *finishing* reactors have been modeled,^{19,22} but optimization studies for these have yet to be carried out.

At the other end of the spectrum of mass transfer with chemical reaction lies the situation where the viscosity of the reaction mass is low (for PET reactors,² till μ_n of about 30, when the viscosity is below about 40 P), and the diffusivity and the corresponding mass transfer coefficient are high compared to the rate of chemical reaction. It can then be easily assumed that there is no resistance to mass transfer. In fact, Ravindranath and Mashelkar² claim that the value of $k_L s$ (the product of the mass transfer coefficient k_L and the interfacial area per unit volume s) for a turbine-agitated PET reactor with $\mu_n \approx 30$ is about 10^{-2} s^{-1} while the pseudo-first-order reaction rate constant is about 10^{-3} s^{-1} , which is an order of magnitude lower. The rates of mixing under such situations are also very large compared to the rates of reaction. It can, therefore, be assumed that there are no spatial gradients present in the reaction mass in the concentration of W and the other species. The value of [W] (square brackets representing concentration) at any time t in the entire reaction mass is thus governed solely by vapor-liquid equilibrium conditions existing at the interface, which, in turn, are determined by the pressure and temperature applied. Turbine-agitated semibatch reactors are usually employed under such conditions wherein the mass transfer resistance is negligible. The removal of the volatile byproduct as well as the consequent reduction in the volume of the reaction mass must be correctly accounted for in the mole balance equations for such *semibatch* reactors. In this paper, we address ourselves to the simulation of such reactors. The polymeric oligomers, other than monomer molecules, are assumed not to vaporize, and the vapor and liquid phases are assumed to be in thermodynamic equilibrium at all times. It is further assumed for the sake of mathematical simplicity that the total pressure applied on the reactor is specified independently. In simulating industrial reactors, one must solve the reactor equations simultaneously with the "characteristic" equations of the vacuum-producing equipment. It is found that the resulting set of equations even with this simplification, incorporate some inequality constraints and special procedures have to be used to solve them.

FORMULATION

The mathematical model developed herein is for a semibatch reactor having negligible mass transfer resistance and short mixing times. Such models are useful to characterize the behavior of the reactors used in the first two stages of PET manufacture,^{2,3} or of batch nylon 6 reactors. In addition, the analysis can easily be modified to apply to continuous reactors, e. g., the top zone of the VK column used for nylon 6 production.^{10,23} The kinetic scheme used here, however, is that given by eq. (1). The reactor is shown schematically in Figure 1. It is assumed that the monomer P_1 and the volatile condensation byproduct W both can vaporize and are present

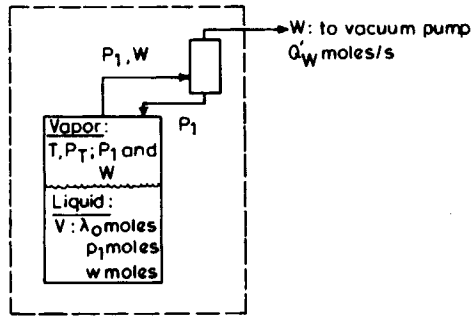


Fig. 1. A semibatch reactor with ARB polymerization.

above the liquid reaction mass at a concentration governed by vapor-liquid equilibrium. P_2, P_3, \dots , are assumed not to volatilize. The vapor consisting of P_1 and W is continuously removed, and the monomer is separated and refluxed back to the reactor completely. This approximates the situation present in PET and nylon 6 reactors closely. The total pressure above the reactor is assumed to be P_T , the temperature T , and the volume of the liquid phase (reactor volume) is V , all these being, in general, functions of time. The analysis given below can easily be extended to the case where more or fewer volatile components are present.³ Since the reactor volume V varies with time, mainly due to the vaporization of the condensation byproduct, it is more convenient to work in terms of the total moles of the various components than with their concentrations. Lower case symbols are used to represent these; for example, p_1 represents the total moles of species P_1 in the liquid phase at time t and w , the total moles of W in the liquid phase. Mole balance equations over the control volume shown by dotted lines in Figure 1 can easily be written and appropriately summed up to give

$$\frac{dp_1}{dt} = -V2k_p \left[\frac{p_1 \lambda_0}{V^2} - \frac{w(\lambda_0 - p_1)}{KV^2} \right] \quad (3a)$$

$$\frac{d\lambda_0}{dt} = -Vk_p \left[\frac{\lambda_0^2}{V^2} - \frac{w(\lambda_1 - \lambda_0)}{KV^2} \right] \quad (3b)$$

$$\frac{dw}{dt} = Vk_p \left[\frac{\lambda_0^2}{V^2} - \frac{w(\lambda_1 - \lambda_0)}{KV^2} \right] - Q_w \quad (3c)$$

$$\frac{d\lambda_2}{dt} = Vk_p \left(\frac{2\lambda_1^2}{V^2} + \frac{w(\lambda_1 - \lambda_3)}{3KV^2} \right) \quad (3d)$$

where it has been assumed that the reaction takes place only in the liquid phase. In eq. (3), $\lambda_0 \equiv V[P] = \sum_{n=1}^{\infty} p_n$, $\lambda_1 = \sum_{n=1}^{\infty} np_n = \lambda_{1,0}$ (since the total number of repeat units in the control volume remains constant), $\lambda_k = \sum_{n=1}^{\infty} n^k p_n$, $k = 2, 3, \dots$ and $Q_w (\geq 0)$ is the molar rate of removal of the by-product W from the control volume at time t . The volume V of the reactor can be written as

$$\frac{dV}{dt} = -v_w Q'_w \quad (4a)$$

or

$$V = V_0 - \int_{t=0}^t v_w Q'_w(t) dt \quad (4b)$$

where V_0 is the volume at $t = 0$ and v_w is the molar volume of (liquid) W which is, in general, a function of temperature.

Equations (3) and (4) constitute five simultaneous, ordinary differential equations for the six unknown variables p_1 , λ_0 , w , λ_2 , V , and Q'_w (since $\lambda_1 = \lambda_{1,0}$) provided the following commonly used moment closure equation is used:

$$\lambda_3 = \frac{\lambda_2 (2\lambda_2 \lambda_0 - \lambda_1^2)}{\lambda_1 \lambda_0} \quad (5)$$

Thus, one more equation is required. This is found by using vapor-liquid equilibrium conditions. If y_w and y_{P_1} represent the mole fractions of W and P_1 in the vapor phase and x_w , x_{P_1} , and x_P , the mole fractions of W, P_1 , and P in the liquid phase, Raoult's law can be used as a first approximation to give

$$y_{P_1} = x_{P_1} \frac{P_{P_1}^0}{P_T} = \frac{p_1}{\lambda_0 + w} \frac{P_{P_1}^0}{P_T} \equiv \frac{p_1}{\lambda_0 + w} K_{P_1} \quad (6a)$$

$$y_w = x_w \frac{P_w^0}{P_T} = \frac{w}{\lambda_0 + w} \frac{P_w^0}{P_T} \equiv \frac{w}{\lambda_0 + w} K_w \quad (6b)$$

In eq. (6), $P_{P_1}^0$ and P_w^0 are the vapor pressures of pure P_1 and W at the temperature T of the reaction mass, expressions for which are available in various handbooks,²⁴ while K_w ($\equiv y_w/x_w$) and K_{P_1} ($\equiv y_{P_1}/x_{P_1}$) are known as the partition coefficients. The mole fractions in the vapor phase must add up to unity in the absence of air. Equation (6) can be used to write, more generally,

$$y_{P_1} + y_w = \frac{p_1}{\lambda_0 + w} \frac{P_{P_1}^0}{P_T} + \frac{w}{\lambda_0 + w} \frac{P_w^0}{P_T} \leq 1 \quad (7)$$

Equation (7) gives the fifth equation which must be solved simultaneously with eqs. (3)–(5) in order to obtain the values of p_1 , λ_0 , w , λ_2 , V , and Q'_w as a function of time.

The special form of eq. (7) and the requirement that $Q'_w \geq 0$ must be noted. The inequality in eq. (7) holds when, in addition to W and P_1 , there is some air present in the vapor space of the reactor. The special form of these equations leads to some interesting computational difficulties, which is best illustrated by discussing the strategy of solution. If the solution is

known at time t , one starts by assuming $Q'_w = 0$ and solving eqs. (3a-d) simultaneously with eq. (4), using the fourth order Runge-Kutta method to obtain p_1 , λ_0 , w , and λ_2 at $t + \Delta t$. These values are then substituted on the left-hand side (LHS) of eq. (7). If this LHS is ≤ 1 , this means that there is some air present in the system and the assumption of $Q'_w = 0$ is correct. If the LHS is > 1 , the assumption of $Q'_w = 0$ is incorrect, and one must assume a positive value of Q'_w , reintegrate eqs. (3a-d) along with eq. (4) and check the LHS of eq. (7) again. This is repeated till convergence is obtained. One must remember, however, that one cannot increase the value of Q'_w indefinitely to satisfy eq. (7), since a stage comes when the value of w becomes negative. Thus, it is observed that Q'_w can lie only between 0 and some maximum value, $Q'_{w,max}$, at which point $w = 0$, i.e., whatever W is produced by reaction, flashes. The LHS of eq. (7) at this point is > 1 . Physically this means that some air must leak into the vapor space to keep the total pressure at the specified value of P_T . In industrial situations, the pressure P_T will adjust itself based on the "characteristics" of the vacuum producing equipment, and so the violation of eq. (7) is a mathematical aberration arising from the fact that one is trying to solve the equations for the reactor independent of that of the vacuum producing device. Such nuances have probably not occurred in the earlier simulations of PET or nylon 6 semibatch reactors^{3-5,23} for the conditions studied, but have posed severe computational difficulties in the optimization studies carried out on PET reactors,^{6,7} and justifies the present, more fundamental though simplified analysis of semi-batch reactors.

The use of Raoult's law [eq. (6)] to describe vapor-liquid equilibrium can probably be justified only in the early stages of the reaction when there is very little polymer present in the reaction mass. As the polymer builds up, Raoult's law overestimates the vaporization and, consequently, overestimates the value of μ_n . An alternative approach is to use the Flory-Huggins theory^{25,26} to describe vapor-liquid equilibrium. Equation (6) must then be replaced by

$$\begin{aligned} y_{P_1} P_T &= \text{partial pressure of } P_1 \text{ in vapor} \\ &= P_{P_1}^0 \nu_{P_1} \exp \left\{ \nu_{P_2-P_\infty} \left(1 + \chi \nu_{P_2-P_\infty} - \frac{1}{\mu_n} \right) \right\} \simeq P_{P_1}^0 \nu_{P_1} e^{1+\chi} \quad (8a) \end{aligned}$$

$$\begin{aligned} y_W P_T &= \text{partial pressure of W in vapor} \\ &= P_W^0 \nu_W \exp \left\{ \nu_{P_2-P_\infty} \left(1 + \chi \nu_{P_2-P_\infty} - \frac{1}{\mu_n} \right) \right\} \simeq P_W^0 \nu_W e^{1+\chi} \quad (8b) \end{aligned}$$

where ν_{P_1} , ν_W , and $\nu_{P_2-P_\infty}$ are the *volume fractions* of P_1 , W, and the non-volatile species (P_2, P_3, \dots), respectively, in the liquid phase and χ is the Flory-Huggins interaction parameter (these equations are based on the Flory Huggins theory for a single "solvent" or a single volatile species). The approximate equations are valid for $\nu_{P_2-P_\infty} \simeq 1$ and when μ_n becomes large.

The volume fractions of W and P_1 can be related to the total moles w and p_1 as

$$v_{P_1} = \frac{p_1 v_{P_1}}{V} \quad (9a)$$

$$v_w = \frac{w v_w}{V} \quad (9b)$$

In these equations, v_{P_1} is the molar volume of the (liquid) monomer. Equation (9), when used with eq. (8), leads to the following relationships for the partition coefficients:

$$\frac{y_{P_1}}{x_{P_1}} \equiv K_{P_1} = \frac{P_{P_1}^0}{P_T} \left(\frac{w + \lambda_0}{V} \right) v_{P_1} e^{1+\chi} \quad (10a)$$

$$\frac{y_w}{x_w} \equiv K_w = \frac{P_w^0}{P_T} \left(\frac{w + \lambda_0}{V} \right) v_w e^{1+\chi} \quad (10b)$$

The partition coefficients are now observed to be functions of composition, as well as of T and P_T . Since y_w and y_{P_1} must sum up to unity in the absence of air, this gives

$$\left(\frac{p_1 v_{P_1}}{V} \frac{P_{P_1}^0}{P_T} + \frac{w v_w}{V} \frac{P_w^0}{P_T} \right) \exp(1 + \chi) \leq 1 \quad (11)$$

which must be used in place of eq. (7). The value of interaction parameter χ in eq. (11) is usually taken³ as 0.5 (which is the value corresponding to the Flory "theta" conditions), in the absence of any experimental information. The restriction on Q_w^* because of w becoming negative still applies.

The complete set of equations to be solved simultaneously may be non-dimensionalized, using

$$\begin{aligned} p_1^* &\equiv p_1 / \lambda_{1,0} \\ w^* &= w / \lambda_{1,0} \\ \lambda_k^* &= \lambda_k / \lambda_{1,0} \quad (k = 0, 1, 2, 3) \\ \tau^* &= \frac{k_p \lambda_{1,0} t}{V_0} \\ v_w^* &= v_w \lambda_{1,0} / V_0 \\ v_{P_1}^* &= v_{P_1} \lambda_{1,0} / V_0 \\ V^* &= V / V_0 \\ Q_w^* &= Q_w V_0 / (k_p \lambda_{1,0}^2) \end{aligned} \quad (12)$$

The final set of equations for isothermal reactor operation are summarized in Table I. It is observed that there are six independent dimensionless parameters: v_w^* , $v_{P_1}^*$, $P_{P_1}^0 / P_T$, P_w^0 / P_T , K , and χ . The effect of varying each of

TABLE I
Final Set of Equations for Semibatch Reactors

Mole balance

$$\frac{dV^*}{d\tau^*} = -Q_w^* v_w^* \quad (\text{a})$$

$$\frac{dp_1^*}{d\tau^*} = -\frac{2}{V^*} \left[p_1^* \lambda_0^* - \frac{w^* (\lambda_0^* - p_1^*)}{K} \right] \quad (\text{b})$$

$$\frac{d\lambda_0^*}{d\tau^*} = -\frac{1}{V^*} \left[\lambda_0^{*2} - \frac{w^* (1 - \lambda_0^*)}{K} \right] \quad (\text{c})$$

$$\frac{dw^*}{d\tau^*} = \frac{1}{V^*} \left[\lambda_0^{*2} - \frac{w^* (1 - \lambda_0^*)}{K} \right] - Q_w^* \quad (\text{d})$$

$$\frac{d\lambda_2^*}{d\tau^*} = \frac{1}{V^*} \left[2 + \frac{w^* (1 - \lambda_2^*)}{3K} \right] \quad (\text{e})$$

Moment closure

$$\lambda_3^* = \frac{\lambda_2^* (2\lambda_2^* \lambda_0^* - 1)}{\lambda_0^*} \quad (\text{f})$$

Equilibrium

$$\frac{p_1^* (P_{P_1}^0/P_T) + w^* (P_W^0/P_T)}{\lambda_0^* + w^*} - 1 \leq 0 \quad (\text{g}_1)$$

or

$$\frac{p_1^* (P_{P_1}^0/P_T) v_{P_1}^* + w^* (P_W^0/P_T) v_w^*}{V^*} \exp(1 + \chi) - 1 \leq 0 \quad (\text{g}_2)$$

Physical constraint

$$w^* > 0 \quad (\text{h})$$

Initial conditions

$$\tau^* = 0: \quad w^* = 0, \quad p_1^* = \lambda_0^* = \lambda_1^* = \lambda_2^* = \lambda_3^* = V^* = 1 \quad (\text{i})$$

these around some reference values is studied here in order to determine the sensitivity of the performance of the reactor to these parameters.

The initial conditions given in Table I [eq. (i)] correspond to the case when pure monomer (P_1) is fed to the reactor at temperature T . The values of the independent parameters are estimated based on conditions existing in the first stage of PET reactors (it being emphasized that ARA + BR'B polymerization occurs in these, instead of ARB polymerization being studied herein). These are called as reference values hereafter and are

$$\begin{aligned} v_w^* &= 0.5 \\ v_{P_1}^* &= 1.0 \\ P_{P_1}^0/P_T &= 0.2161 \\ P_W^0/P_T &= 7.6965 \\ K &= 1.0 \\ \chi &= 0.5 \end{aligned} \quad (\text{13})$$

The value of v_w^* of 0.5 has been obtained assuming $\lambda_{1,0}/V_0$ of 10 mol/L (the mean of the values for pure DMT and pure ethylene glycol at 200°C) and v_w of 0.0476 L/mol (for methanol at 200°C).²⁴ Similarly, the reference value of $v_{p_1}^*$ has been taken as unity since the feed is assumed to be pure monomer. The values of $P_{p_1}^0/P_T$ and P_w^0/P_T have been estimated as 0.2161 and 7.6965 using the vapor pressure of ethylene glycol²⁷ at 200°C as 1.0806 atm, that of methanol⁸ as 38.483 atm and P_T as 5 atm. The value of P_T has been assumed to be higher than 1 atm since it was found that if P_T was taken as 1 atm, the entire feed vaporizes instantaneously as soon as it enters the reactor.

RESULTS AND DISCUSSION

The numerical technique used for integrating the equations in Table I has already been discussed earlier in this paper [below eq. (7)]. The binary chop method²⁸ has been used to estimate the value of Q_w^* if it is above zero, and convergence is assumed to occur when the absolute value of the LHS of eq. (g₁) or (g₂) in Table I is less than a value $\epsilon = 0.0001$. This method of integration is different from that used in the literature³ in which the operation of the reactor with simultaneous chemical reaction and vaporization was modeled as a sequence of two steps: chemical reaction without any vaporization is assumed to occur for a time $\Delta\tau^*$, and this is followed by an instantaneous flashing operation, in which the volatile component, if in excess, vaporizes and the system attains thermodynamic equilibrium. Even though these two numerical techniques are expected to give identical results as $\Delta\tau^*$ approaches zero, the technique developed in this paper is far easier to enmesh with reactor optimization algorithms in addition to being fundamentally rigorous.

Several tests were made to ensure that our computer program was free of errors. The value of the time increment, $\Delta\tau^*$, was reduced from 0.01 to 0.0001 and the results were found to be independent of the step size. On running the program at a very high total pressure, P_T , of 50 atm, when evaporation is not expected to occur it was found that Q_w^* was zero throughout, and V^* was unity. In addition to this, the results obtained with this run matched earlier results²⁹ on reversible ARB polymerization in closed reactors. Reduction of the value of ϵ from 0.0001 to 0.00001 also did not alter the results significantly. In view of this, all runs made hereafter used $\epsilon = 0.0001$ and $\Delta\tau^* = 0.01$. The computer (DEC 1090) time required for one set of parameter values was about 45 s.

The number average chain length, $\mu_n (= \lambda_1^*/\lambda_0^*)$ and the polydispersity index $D_N \{ = (\lambda_2^*/\lambda_1^*)/(\lambda_1^*/\lambda_0^*) \}$ for the reference conditions [eq. (13)] are shown in Figure 2 as a function of the dimensionless time τ^* . In the absence of any vaporization, eq. (2), along with l'Hospital's rule, gives the equilibrium value of μ_n as 2.0. The vaporization of W leads to higher values of μ_n than this, depending on the extent of vaporization. Use of the Flory-Huggins theory for vapor-liquid equilibrium leads to lower evaporation of W and therefore gives polymer having lower μ_n than predicted by the use of Raoult's law. It is found that the values of μ_n are quite sensitive to the value of χ , the interaction parameter. Indeed, Figure 2 predicts that the better the solvent W (the lower the value of χ), the lower its vaporization

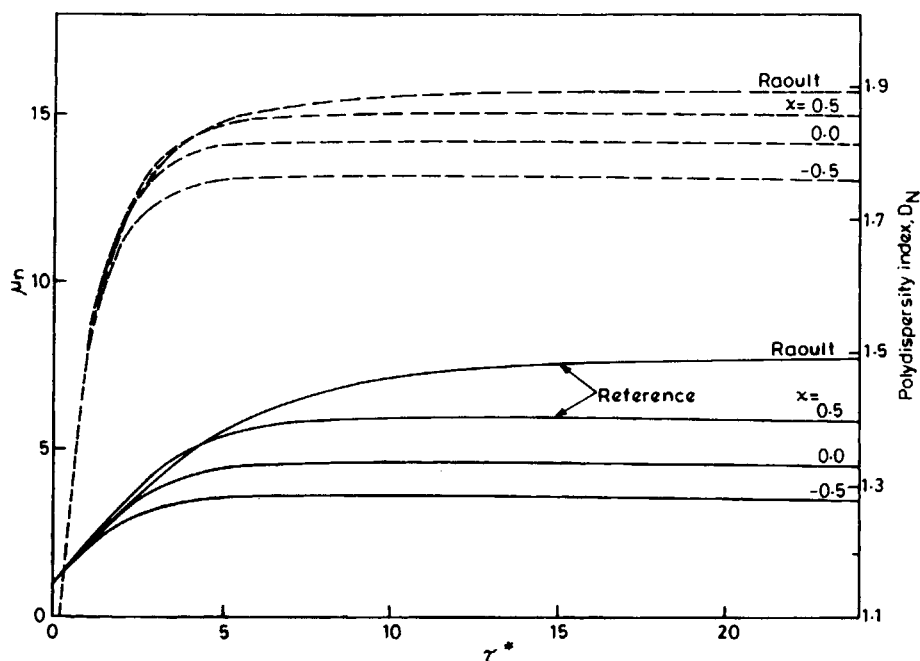


Fig. 2. Number average chain length (—) and polydispersity index (---) as a function of dimensionless time.

and the lower the value of μ_n . This is consistent with intuitive expectations. The lower values of D_N when χ is reduced are *partly* because of the lower conversions attained.

An interesting feature for polymerization in semibatch reactors is demonstrated by Table II. In this table, the value of D_N obtained in semibatch reactors is compared to the value of D_N at the same functional group conversion, p_A , for irreversible ARB polymerization. In all the cases, it is found that these two values of D_N are within about 1.5%, an error which is attributable to the use of the moment closure equation (5). Thus, it can be inferred that, in semibatch reactors, the time history of μ_n (or p_A) depends

TABLE II
 D_N for the Semibatch Reactors Compared with D_N for Irreversible ARB Polymerization at the Same Conversion

	Semibatch reactor (ref. run) $\tau^* = 20$		Irreversible ARB polymerization (p_A same as semibatch reactor)	
	μ_n	$p_A = 1 - \frac{1}{\mu_n}$	D_N (computed)	$D_N = 1 + p_A$
Raoult	7.835	0.872	1.889	1.872
FH, $\chi = 0.5$	6.008	0.833	1.855	1.833
FH, $\chi = 0.0$	4.673	0.786	1.813	1.786
FH, $\chi = -0.5$	3.634	0.7250	1.758	1.725

on the conditions present in the reactor, but the value of D_N is almost uniquely determined once p_A is known, and Flory's most probable distribution with the appropriate value of p_A applies.

Figure 3 shows plots of Q_w^* as a function of τ^* for the reference conditions. For the case of Raoult's law, it is found that $Q_w^* = 0$ for some time at the beginning, when there is some air present in the vapor space (in fact, P_T has been deliberately chosen to be high so that vaporization is prevented at $\tau^* = 0$). Q_w^* shoots up soon thereafter and then decreases slowly with τ^* . At large values of τ^* (~ 40) near equilibrium conditions prevail with $Q_w^* = 0$ and the LHS of eq. (g₁) (Table I) equal to zero. A similar qualitative behavior is found for Q_w^* when the Flory-Huggins (FH) theory is used with $\chi = 0.5$. It is interesting to observe that at small τ^* , the value of Q_w^* predicted by the FH theory is higher than that predicted by Raoult's law. This explains the higher μ_n for the FH ($\chi = 0.5$) case in Figure 2, than for the Raoult's law case. At larger τ^* , the FH theory predicts lower Q_w^* , and so, lower μ_n .

The sensitivity of the final properties of the polymer to the parameters is now studied by systematically varying them around the reference values given in eq. (13). Figure 4 shows the effect of P_T (both $P_{p_1}^0/P_T$ and P_w^0/P_T are simultaneously changed). At higher pressures, the vaporization is suppressed and equilibrium conditions are attained at lower values of μ_n and D_N . It is interesting to observe that the FH theory gives higher Q_w^* and so, higher μ_n , compared to Raoult's law when values of μ_n are low. The effect of varying K is shown in Figure 5. Increasing K favors the forward reaction in eq. (1) and leads to higher values of μ_n . The values of D_N are found to

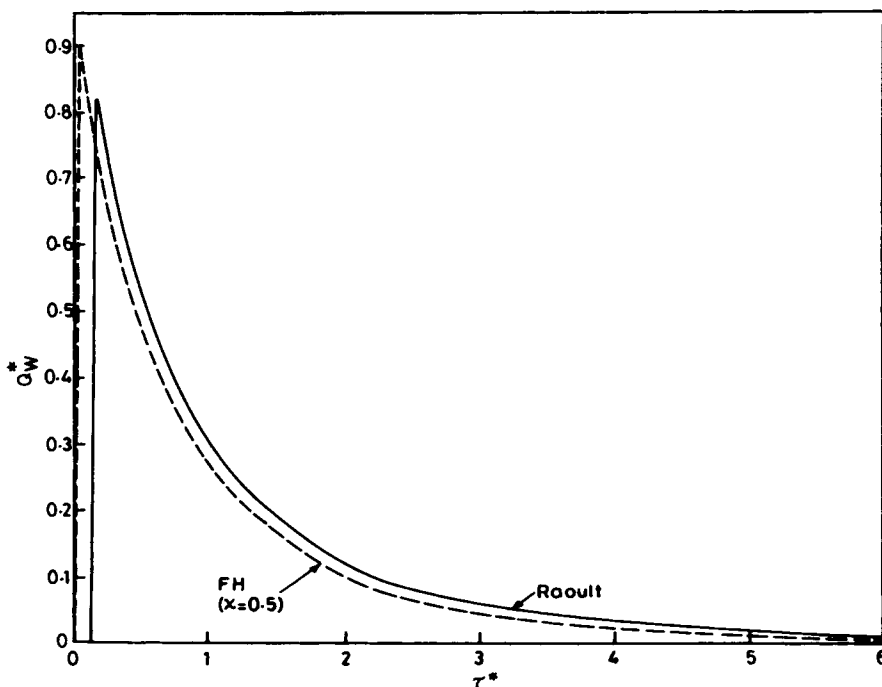


Fig. 3. Q_w^* as a function of τ^* for the reference conditions.

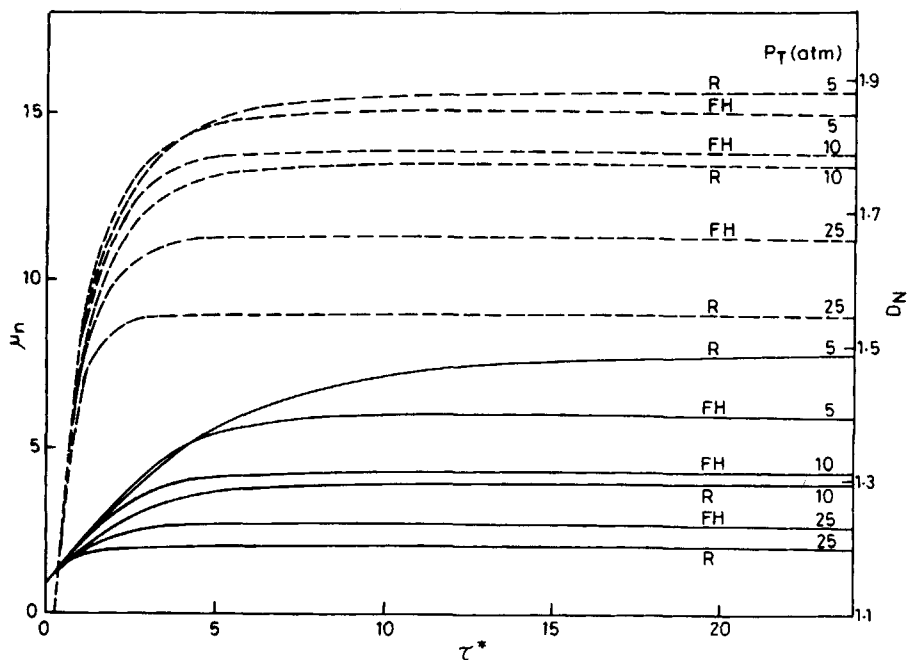


Fig. 4. Effect of varying P_T on μ_n (—) and D_N (---). R and FH denote Raoult's law and Flory-Huggins theory, respectively. All parameters except P_T are at their reference values.

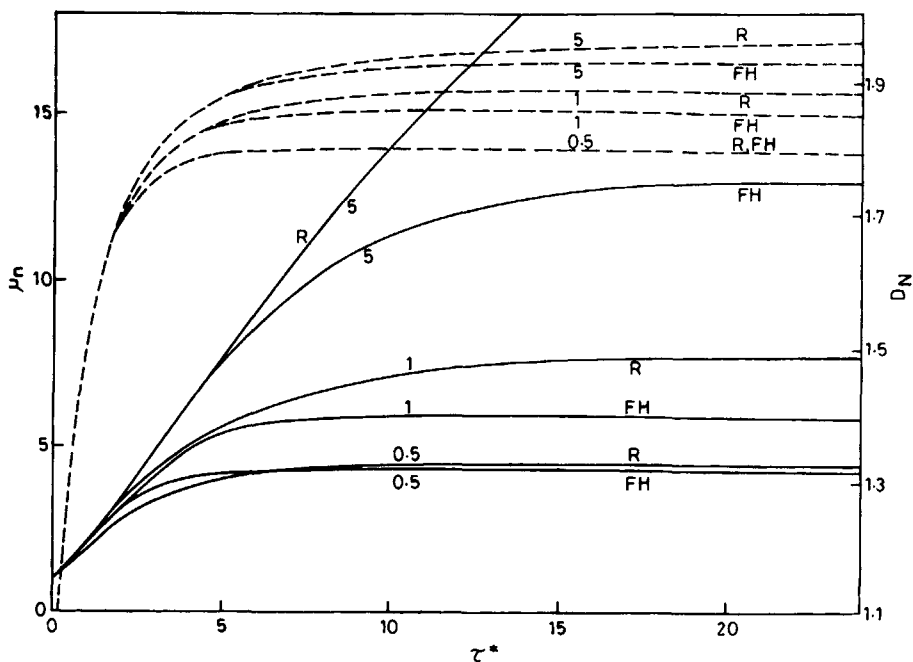


Fig. 5. Effect of varying K on μ_n (—) and D_N (---). All parameters except K are at their reference values. R and FH denote Raoult's and Flory-Huggins theories, respectively. Values of K are indicated.

get closer to the value of 2.0 characterizing irreversible ARB polymerization at complete conversion. Once again, the higher values of μ_n for the FH case at low values of τ^* are to be noted. Figure 6 similarly illustrates the effect of varying the physical properties of W, viz., v_w^* . The equations of Table I indicate that when Raoult's law is used, v_w^* enters only in the equation for V^* . Thus, it would be expected that the effect of altering v_w^* would not be significant, and would be associated with the change in the concentrations of the various species as W vaporizes. This is indeed found to be true. On using the FH theory, however, v_w^* enters in the vapor-liquid equilibrium equation as well, and influences μ_n more significantly. The higher is v_w^* , the larger is found to be μ_n . The effect of varying $v_{p_1}^*$ is not studied since pure monomer feed is assumed in this study, for which $v_{p_1}^* = 1$. Figure 7 shows that altering the parameter $P_{p_1}^0/P_T$ has relatively little effect on μ_n and D_N at least over the ranges studied. However, Figure 8 shows that P_W^0/P_T does influence the results significantly.

It is possible to determine the total-pressure history, $P_T(\tau^*)$, required to give the maximum μ_n in a semibatch reactor. This is the situation when w^* in the liquid phase is zero at all times, i.e., whatever W is produced by chemical reaction, is flashed instantaneously. Under these conditions, $Q_w^* = \lambda_0'^2/V^*$ and the LHS of eqs. (g₁) and (g₂) of Table I are zero. If $P_T(\tau^*)$ is lowered still further, air must leak into the vapor space, but μ_n would remain unchanged. This $P_T(\tau^*)$ thus represents the limiting conditions for operating an isothermal semibatch reactor. Figure 9 shows this limiting

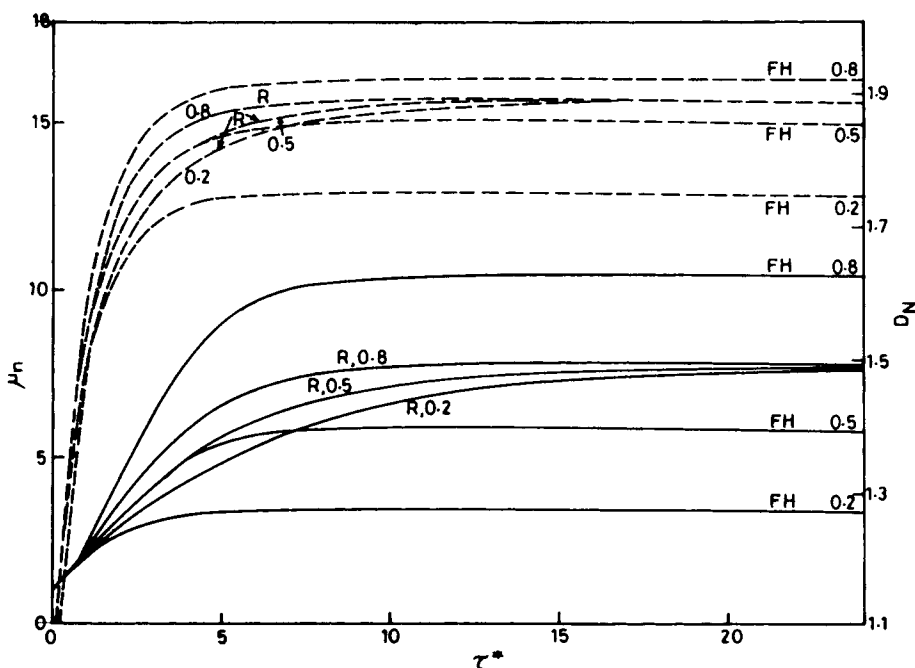


Fig. 6. Effect of varying v_w^* on μ_n (—) and D_N (---). R and FH denote Raoult and Flory-Huggins. All other parameters are at their reference values. Values of v_w^* are indicated on the graphs.

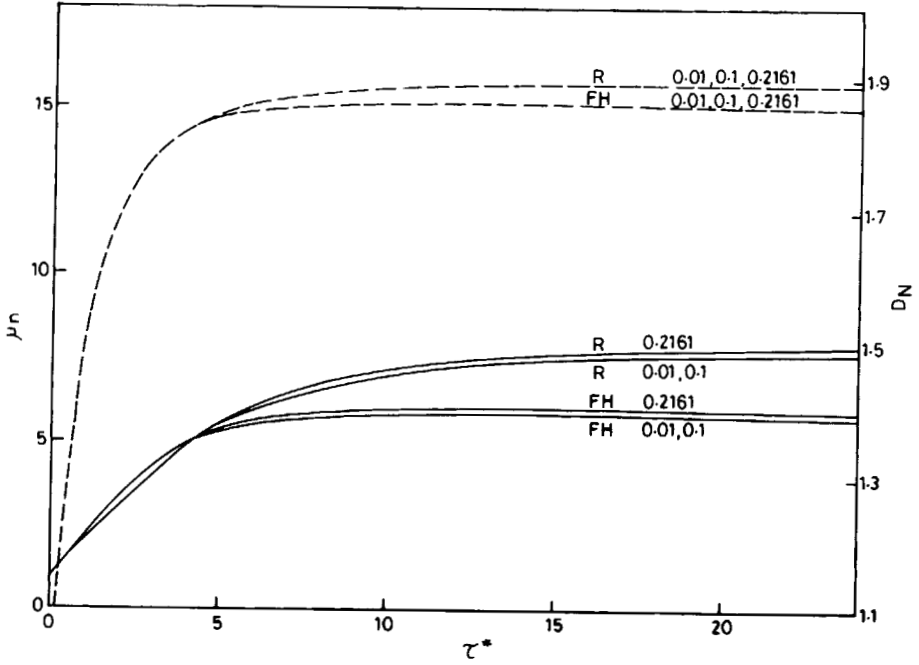


Fig. 7. Effect of P_{P_1}/P_T on μ_n (—) and D_N (---). Values of P_{P_1}/P_T are indicated on the graphs.

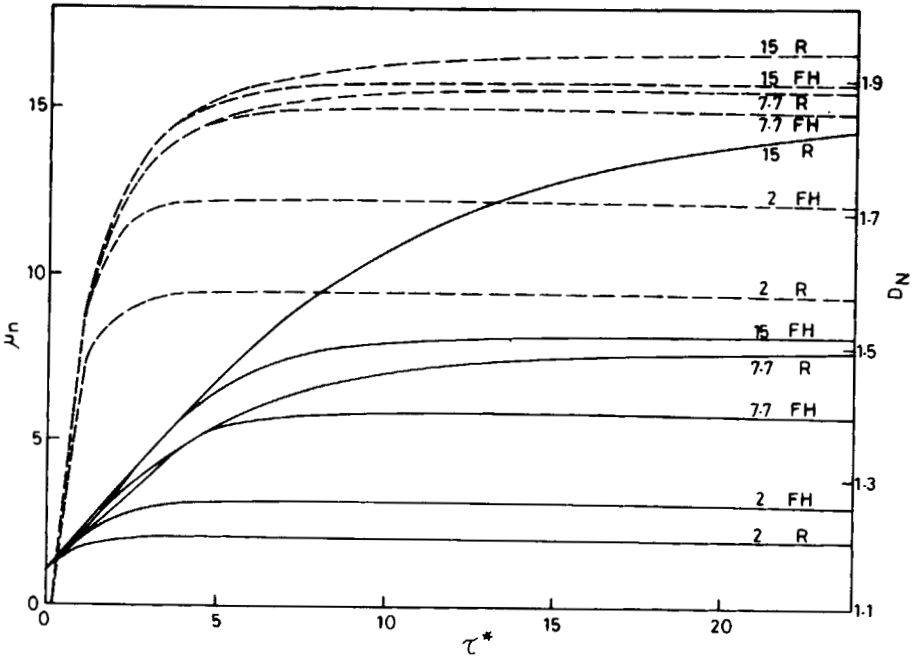


Fig. 8. Effect of P_W/P_T on μ_n (—) and D_N (---). Values of P_W/P_T are indicated.

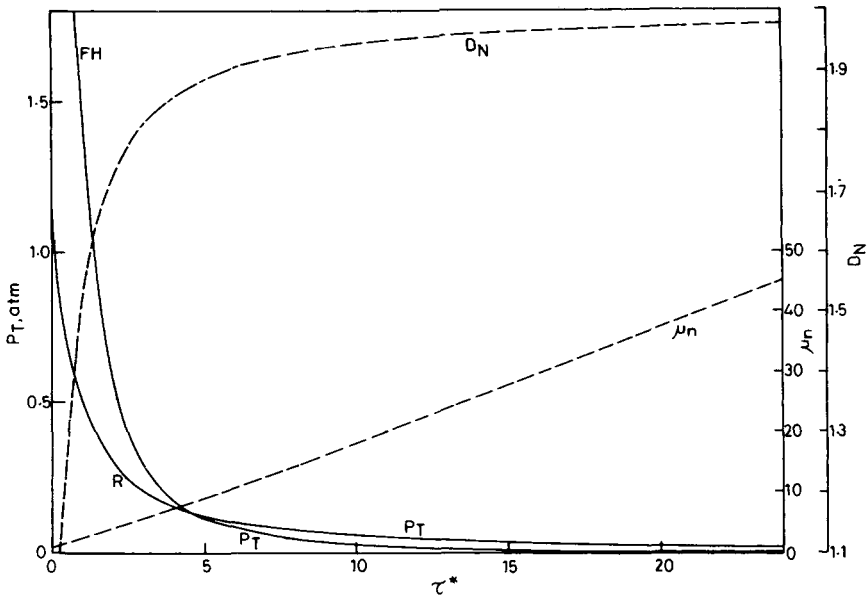


Fig. 9. $P_T(\tau^*)$ to give maximum $\mu_n(\tau^*)$ in a semibatch reactor. $P_{p_1}^0 = 1.0806$ atm, $P_w^0 = 38.483$ atm. All other parameters are at their reference values. P_T for the FH case as $\tau^* = 0$ is 4.843 atm. It is assumed that the feed does not flash at $\tau^* = 0$.

pressure history for reference conditions for both the cases when Raoult's law is used as well as when the FH theory is used. It turns out that in this computation, the equations for p_1^* , λ_0^* , λ_2^* , and V^* are uncoupled and can be solved independently, while the equation for w^* can be used to compute Q_w^* and the thermodynamic equilibrium condition can be used to compute P_T . The values of μ_n and D_N are thus independent of the relation used to predict vapor liquid equilibrium. Figure 9 also shows plots of $\mu_n(\tau^*)$ and $D_N(\tau^*)$ obtained when this computed $P_T(\tau^*)$ is applied to the reactor, and represent the maximum permissible values (under the values of the other operating parameters).

CONCLUSIONS

Semibatch reactor operation has been modeled in this study for simple ARB step growth polymerization. It is found that the total-pressure and the equilibrium constant are the most significant operating variables. The limits of reactor operation have also been worked out. The formulation presented herein can easily be extended and optimization algorithms developed which can overcome the special problems posed by the inequality conditions in the mathematical model.

References

1. S. K. Gupta and A. Kumar, *Chem. Eng. Commun.*, **20**,1 (1983).
2. K. Ravindranath and R. A. Mashelkar, *Polym. Eng. Sci.*, **22**, 619 (1982).
3. R. Ravindranath and R. A. Mashelkar, *J. Appl. Polym. Sci.*, **26**, 3179 (1981).

4. D. A. Mellichamp, *Chem. Eng. Sci.*, **24**, 125 (1969).
5. J. W. Ault and D. A. Mellichamp, *Chem. Eng. Sci.*, **27**, 2219 (1972).
6. A. Kumar, S. N. Sharma, and S. K. Gupta, *Polym. Eng. Sci.*, **24**, (1984), to appear.
7. A. Kumar, S. N. Sharma, and S.K. Gupta, *J. Appl. Polym. Sci.*, **29**, 1045 (1984).
8. H. K. Reimschuessel and K. Nagasubramanian, *Chem. Eng. Sci.*, **27**, 1119 (1972).
9. Vereinigte Glanzstoff Fabriken, *Ger. Pat.* 1167021 (1962).
10. S. K. Gupta, A. Kumar, and K. K. Agarwal, *J. Appl. Polym. Sci.*, **27**, 3089 (1982).
11. H. Gerrens, *Germ. Chem. Eng.*, **4**, 1 (1981).
12. W. H. Li (Du Pont), U. S. Pat. 3113843 (1959/63).
13. J. S. Vrentas and J. L. Duda, *AIChE J.*, **25**, 1 (1979).
14. J. L. Duda, J. S. Vrentas, S. T. Ju, and H. T. Liu, *AIChE J.*, **28**, 279 (1982).
15. R. A. Mashelkar, *Chem. Ind. Dev.*, **10**(9), 17 (1976).
16. F. Windmer, *Adv. Chem. Ser.*, **128**, 51 (1973).
17. G. A. Latinen, *Adv. Chem. Ser.*, **34**, 325 (1962).
18. D. B. Todd and H. F. Irving, *Chem. Eng. Prog.*, **65**(9), 84 (1969).
19. M. Amon and C. D. Denson, *Ind. Eng. Chem. Fundam.*, **19**, 415 (1980).
20. J. W. Ault and D. A. Mellichamp, *Chem. Eng. Sci.*, **27**, 1441 (1972).
21. S. K. Gupta, A. Kumar, and A. K. Ghosh, *J. Appl. Polym. Sci.*, **28**, 1063 (1983).
22. A. Kumar, S. K. Gupta, S. Madan, N. G. Shah, and S. K. Gupta, *Polym. Eng. Sci.*, **24**, 194 (1984).
23. A. Ramagopal, A. Kumar, and S. K. Gupta, *Polym. Eng. Sci.*, **22**, 849 (1982).
24. J. H. Perry and C. H. Chilton, Eds., *Chemical Engineers' Handbook*, 5th ed., McGraw-Hill, New York, 1973.
25. P. J. Flory, *Principles of Polymer Chemistry*, 1st ed., Cornell University Press, Ithaca, NY, 1953.
26. A. Kumar and S. K. Gupta, *Fundamentals of Polymer Science and Engineering*, 1st ed., Tata McGraw-Hill, New Delhi, 1978.
27. C. M. Fontana, *J. Polym. Sci., A-1*, **6**, 2343 (1968).
28. E. J. Henley and E. M. Rosen, *Material and Energy Balance Computations*, 1st ed., Wiley, New York, 1969.
29. S. K. Gupta, N. L. Agarwal, P. Rajora, and A. Kumar, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 933 (1982).

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