

# Simulation of Reversible AA + B'B'' Polycondensations in Wiped Film Reactors

SANTOSH K. GUPTA, ANIL KUMAR, and ANUP K. GHOSH,  
*Department of Chemical Engineering, Indian Institute of Technology,  
Kanpur-208016, India*

## Synopsis

Wiped-film reactors carrying out AA + B'B'' type reversible polycondensations (where A, B', and B'' are functional groups, with B' and B'' reacting with A at different rates) have been simulated. The governing mass balance equations have been solved for two transport models of this reactor (one by Ault and Mellichamp and the other by Amon and Denson) using a combination of finite difference and the Runge-Kutta methods. The increase in the number-average chain length  $\mu_n$  of the polymer formed in the reactor is computed as a function of the various rate constants and the parameters characterizing the reactor.  $\mu_n$  is found to be most sensitive to the surface area of the film and to the temperature used, both for the equal reactivity as well as for the unequal reactivity cases. For the latter, the effect of the reactivity ratio for the forward rate constants is more significant than that of the equilibrium constants. Results of the two models are also compared under similar conditions and it is found that under equivalent conditions, the Amon-Denson model gives slightly higher  $\mu_n$  than the Ault-Mellichamp model.

## INTRODUCTION

A considerable amount of work has been done in the last decade on the simulation of step-growth polymerizations and has been reviewed recently.<sup>1</sup> Most of these studies have been confined to the study of isothermal polymerizations in sealed tubes, wherein functional groups are equally reactive.<sup>2,3</sup> These are idealizations since two major deviations occur in a real reactor, namely, the violation of the equal reactivity hypothesis and the role of diffusion in removing the condensation product out of the reaction mass in order to give high molecular weight products. To account for the former, attention has been focussed recently on polycondensations with chain-length-dependent reactivities,<sup>4-6</sup> with monomers AA + B'B'' (functional group A reacting with B' or B'' at different rates, called asymmetric monomers) and on AA + BB systems<sup>7-10</sup> wherein the reactivity of A on a molecule of AA changes once the other A has reacted (induced asymmetry). Some work has also been done<sup>10-12</sup> in the second category regarding the role of diffusion of the condensation product, and the effect of mass transfer in increasing the average molecular weight of the polymer formed in some idealized reactor geometries has been established.

In real reactors, as the viscosity of the reaction mass increases at high degrees of polymerization, mixing as well as diffusion become difficult and the buildup of the condensation product concentration in the reaction-mass favors the reverse reaction, thereby curtailing further polymer chain growth. Various types of continuous film-forming reactors have been developed to enhance the removal of the volatile byproduct and so obtain higher molecular weight product of

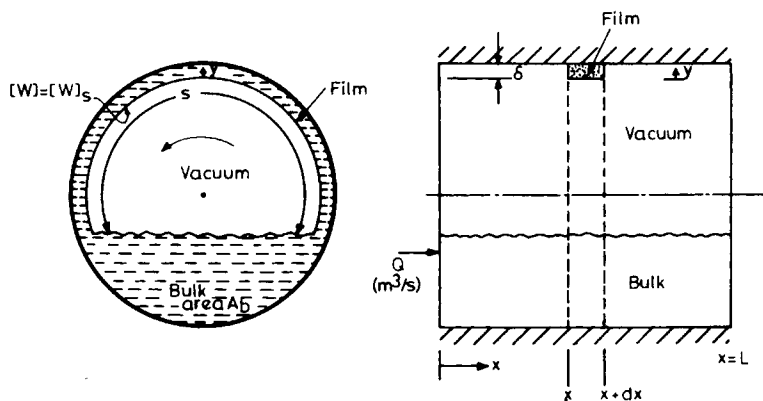


Fig. 1. Wiped film reactor.

commercial value. The most common is the wiped-film reactor, used extensively in the manufacture of PET. One model (henceforth referred to as model I) for such reactors has been presented by Amon and Denson.<sup>13</sup> In this model, shown in Figure 1, a rotating blade applies a thin "film" of the reaction mass on the surface of a cylinder to which a high vacuum is applied. The reaction occurs primarily in the "bulk" while most of the condensation product is removed in the film. The film is continuously applied on the walls, and after a certain time it is scraped and mixed with the bulk. Mass balance equations are written for both the bulk and the film and lead finally to a set of coupled partial differential equations. These have been solved using a combination of the finite difference technique and the Runge-Kutta method for a whole range of operating variables to give the conversion of functional groups and the number average molecular weight of the polymer formed. The work of Amon and Denson has been corrected and extended<sup>14</sup> to give the polydispersity index of the polymer formed also, using appropriate moment-closure approximations.<sup>15,16</sup>

Another mathematical model of the wiped-film reactor has been proposed by Ault and Mellichamp<sup>17</sup> (referred to as model II). In this model it is assumed that the entire reaction mass is applied as a thin film and there is no separate bulk as in model I. After a fixed time interval the entire film is well mixed (instantaneously) by means of the blade of the reactor and applied once again. This model thus has different axial mass balance equations than model I. The actual behavior of a wiped film reactor is expected to lie in between the results predicted by these two limiting models.

In this paper we have considered these two models of the wiped-film reactor and have studied their performance for reversible polymerizations wherein functional groups are not equally reactive, in particular, AA + B'B'' polycondensations. The basic principle of operation in the reactor has been kept the same as in the earlier models. It is assumed in this work that only the condensation product diffuses through the reaction mass. This assumption has been extensively used by earlier workers,<sup>10,11,18</sup> and, since the other species in the reaction mass usually are of much higher molecular weights, they are far less volatile. In fact, Nagasubramanian and Reimschuessel<sup>18</sup> have found experimentally that the diffusivity of the monomer  $\epsilon$ -caprolactam through the reaction mass is almost a hundredth of that of water in nylon 6 polymerization. The

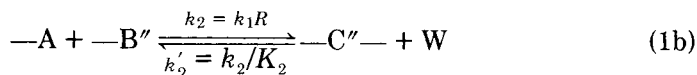
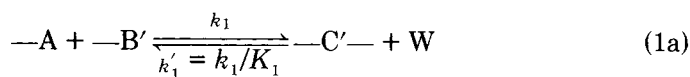
higher molecular weight products will also be physically entangled with other molecules in the reaction mass, and will thus have even lower diffusivities than the monomer.

The mass balance equations for model I consist of a set of partial differential equations for the film and a set of ordinary differential equations for the bulk. The finite-difference and the Runge-Kutta methods are used to solve these equations simultaneously, and the number average degree of polymerization is obtained as a function of the various rate constants as well as the reactor parameters like residence time, film exposure time, mass transfer area, and the level of applied vacuum. In model II, however, a set of partial differential equations has to be solved using the finite-difference technique, and Simpson's rule is used to take care of the instantaneous mixing of the film.

### FORMULATION

The study of the kinetics of polymerization of AA and B'B'' type monomers is greatly simplified by working with the functional groups A, B', and B'' instead of dealing with the various molecular species present in the reaction mass. Both these representations are mathematically equivalent but the analysis in terms of functional groups can give the conversion of functional groups and the chain-length average only. In order to solve for higher moments of the chain length distribution, one must work with the individual molecular species and sum up the equations appropriately to give the various moments. Moment closure techniques are then required to solve the set of coupled equations obtained this way. Since there are only a few cases (e.g., nylon 6 polymerization with monofunctional acids) where the polydispersity index of the final polymer obtained is very different from the numerical value of 2, this restriction is relatively minor in importance.

In terms of functional groups the kinetic scheme studied here may be represented as



where  $-C'-$  and  $-C''-$  represent the reacted groups  $-AB'-$  and  $-AB''-$ , respectively, which are different structurally and, therefore, differ in their reactivities. W is the condensation byproduct. It is also assumed here that the reaction rates, equilibrium constants, and physical properties, particularly the diffusivity of W in the reaction mass, are independent of chain length. Of these, the last assumption is particularly important in view of the fact that the diffusivity of W in the reaction mass is expected to be a function of its viscosity, at least in cases where the average chain length is not very high (at higher chain lengths, the diffusivity of W is determined by segmental motions of the polymeric molecules and becomes independent of chain length<sup>19</sup>). The model presented herein can easily account for the variation of the diffusivity, but this has not been done in this work.

The rate of consumption,  $r$ , of the various functional groups by chemical reaction *alone* can be written as

$$r_A = -k_1\{-[A][B'] + [C'][W]/K_1 - R[A][B''] + R[C''][W]/K_2\} \quad (2a)$$

$$r_{B'} = -k_1\{-[A][B'] + [C'][W]/K_1\} \quad (2b)$$

$$r_{B''} = -k_1\{-R[A][B''] + R[C''][W]/K_2\} \quad (2c)$$

$$r_{C'} = k_1\{[A][B'] - [C'][W]/K_1\} \quad (2d)$$

$$r_{C''} = k_1\{R[A][B''] - R[C''][W]/K_2\} \quad (2e)$$

$$r_W = k_1\{[A][B'] - [C'][W]/K_1 + R[A][B''] - R[C''][W]/K_2\} \quad (2f)$$

where [ ] represents the molar concentration of any species.

### Model I

Using the rate expressions of eq. (2), mass balance equations may be written for the bulk of the reaction mixture (which is transported axially along the tubular reactor) as well as for the film (where the mixture is exposed to high vacuum in order to remove W). In the case of axial transport in the bulk, one considers a differential volume element shown in Figure 1 and the steady state mass balance equations are<sup>13</sup>

$$-Q \frac{d[A]}{dx} - r_A A_b \quad dx = 0 \quad (3a)$$

$$-Q \frac{d[B']}{dx} - r_{B'} A_b \quad dx = 0 \quad (3b)$$

$$-Q \frac{d[B'']}{dx} - r_{B''} A_b \quad dx = 0 \quad (3c)$$

$$-Q \frac{d[C']}{dx} + r_{C'} A_b \quad dx = 0 \quad (3d)$$

$$-Q \frac{d[C'']}{dx} + r_{C''} A_b \quad dx = 0 \quad (3e)$$

$$-Q \frac{d[W]}{dx} + r_W A_b \quad dx - \bar{n}_W s \quad dx = 0 \quad (3f)$$

where  $A_b$  is the cross-sectional area of the bulk,  $Q$ , the volumetric flow rate through the reactor,  $\bar{n}_W$  (defined later) is the average flux of W over the film perimeter at a given axial position  $x$ , and  $s$  is the film surface area per unit length, or the perimeter.

The amount of W diffusing out of the surface of the film can be obtained from the following set of mass balance equations for the film:

$$\frac{\partial[A]}{\partial t} = -r_A \quad (4a)$$

$$\frac{\partial[B']}{\partial t} = -r_{B'} \quad (4b)$$

$$\frac{\partial[B'']}{\partial t} = -r_{B''} \quad (4c)$$

$$\frac{\partial[C']}{\partial t} = r_{C'} \quad (4d)$$

$$\frac{\partial[C'']}{\partial t} = r_{C''} \quad (4e)$$

$$\frac{\partial[W]}{\partial t} = D \frac{\partial^2[W]}{\partial y^2} + r_w \quad (4f)$$

where  $D$  is the diffusivity of  $W$  through the reaction mass and is assumed to be constant and  $t$  is the time. In writing eq. (4), it is assumed that the effect of curvature is negligible and the film can be represented as an infinite flat plate.

The initial and boundary conditions used for the film are as follows:

**Initial Conditions for the Film:**

$$\text{at } t = 0, \quad y \geq 0$$

$$[A] = [A]|_x, \quad [B'] = [B']|_x, \quad [B''] = [B'']|_x \quad (5)$$

$$[C'] = [C']|_x, \quad [C''] = [C'']|_x, \quad [W] = [W]|_x$$

where  $[A]|_x, \dots$  represent the concentrations of  $A, \dots$  in the bulk at axial position  $x$ .

**Boundary Conditions for the Film:**

$$\text{at } t > 0, \quad y = 0, \quad [W] = [W]_s \quad (6a)$$

$$y = \delta, \quad \frac{\partial[W]}{\partial y} = 0 \quad (6b)$$

where  $\delta$  is the thickness of the film and  $[W]_s$  is the interfacial concentration of the condensation product. It may be mentioned that  $[W]_s$  is related by a thermodynamic equilibrium relationship to the level of vacuum applied in the wiped-film reactor. In this study,  $[W]_s$  is assumed as a constant and has been treated as a parameter. The second boundary condition in eq. (6) represents the fact that the flux of  $W$  at the impervious metal wall is zero. In writing eqs. (3) and (4) the contribution of mass transfer of  $W$  from the bulk has been neglected; so also the contribution of the polymerization in the film (other than in determining  $\bar{n}_w$ ) has been neglected. These are justified if the volume fraction of the reaction mass in the bulk is close to unity.

The time-averaged rate of diffusion of  $W$  from the film can be written as<sup>13</sup>

$$\bar{n}_w = \frac{1}{T} \int_0^T D \left. \frac{\partial[W]}{\partial y} \right|_{y=0} dt \quad (7)$$

where  $T$  is the exposure time of the film. The use of eq. (7) for  $\bar{n}_w$  leads to severe instabilities in calculations, since it involves numerical differentiation. However, Amon and Denson have reexpressed  $\bar{n}_w$  in an alternate form which avoids this problem. A similar simplification is tried here for the unequal reactivity polymerization of eq. (1). From eqs. (2) and (4), it is observed that

$$D \frac{\partial^2[W]}{\partial y^2} = \frac{\partial[W]}{\partial t} - r_w = \frac{\partial}{\partial t} ([W] + [A]) \quad (8)$$

On integrating this equation with respect to  $y$  using the boundary condition (6b) and simplifying, one obtains

$$\begin{aligned} \bar{n}_w &= -\frac{1}{T} \int_{t=0}^T \int_{y=0}^{\delta} \frac{\partial}{\partial t} ([W] + [A]) \, dy dt \\ &= \frac{1}{T} \int_{y=0}^{\delta} \{([W] + [A])_{t=0} - ([W] + [A])_{t=T}\} \, dy \quad (9) \end{aligned}$$

Equations (3), (4), and (9) represent a complete set of coupled ordinary (for the bulk) and partial (for the film) differential equations which must be solved simultaneously in order to simulate the wiped-film reactor.

The initial and boundary conditions to be used with the film equations are given in eqs. (5) and (6). The initial condition (at  $x = 0$ ) for the bulk equations were written, assuming that the feed to the reactor is an equilibrium prepolymer from the *previous* reactor. This assumption will be fairly close to real-life situations, specially in view of the findings of Ravindranath and Mashelkar<sup>20</sup> that the diffusional resistance of W is negligible till the number average chain length reaches the value of about 20–30. Also, this helps in comparing our results with those of reversible polymerizations characterized by the equal reactivity of functional groups in wiped-film reactors as studied earlier.<sup>1,14</sup> With the use of the stoichiometric relations, the conversion  $p$  of functional group A is related to the conversions  $p_1$  and  $p_2$  of functional groups B' and B'', respectively, as

$$\frac{[A]_0 - [A]}{[A]_0} \equiv p = \left( \frac{p_1}{2} + \frac{p_2}{2} \right) \equiv \frac{[B']_0 - [B']}{[B']_0} + \frac{[B'']_0 - [B'']}{[B'']_0} \quad (10)$$

for stoichiometric amounts of A, B', and B'' taken initially, i.e.,  $[B']_0 = [B'']_0 = [A]_0/2$ .

At equilibrium (at the end of the previous reactor), the following relationship must be satisfied:

$$K_1 = \frac{[C][W]}{[A][B']}, \quad K_2 = \frac{[C''][W]}{[A][B'']} \quad (11)$$

Using the following equation for the number average chain length  $\mu_n$ ,

$$\mu_n = [A]_0/[A] = 1/(1 - p) \quad (12)$$

we obtain, finally, at equilibrium,

$$\frac{[W]}{[A]_0} = \frac{-(\mu_n - 2)(K_1 + K_2) + \{\mu_n^2(K_1 + K_2)^2 - 4(\mu_n - 1)(K_1 - K_2)^2\}^{1/2}}{4\mu_n(\mu_n - 1)} \quad (13)$$

In this equation,  $[W]$  is the equilibrium concentration of W (corresponding to the vacuum applied on the *previous* reactor),  $[A]_0$  is the feed concentration of A for the *previous* reactor, and  $\mu_n$  is the corresponding equilibrium degree of polymerization. Equation (13) reduces to the expression used earlier,

$$[W]/[A]_0 = 1/\mu_n(\mu_n - 1) \quad (14)$$

when  $K_1 = 1$ ,  $K_2 = 1$ , and  $R = 1$ . The final equations for the initial values of the various dependent variables are given later in this paper in nondimensional form.

Equations (2)–(9) are nondimensionalized using the following dimensionless variables:

$$\begin{aligned} A^* &= [A]/[A]_0, & B'^* &= [B']/[A]_0, & B''^* &= [B'']/[A]_0, & C'^* &= [C']/[A]_0, \\ C''^* &= [C'']/[A]_0, & W^* &= [W]/[A]_0, & \eta &= y/\delta, \\ \xi &= x/L, & \theta &= t/T, & \bar{N}_W &= T\bar{n}_W/\delta[A]_0 \end{aligned} \quad (15)$$

where  $L$  is the length of the wiped film reactor and  $[A]_0$  the concentration of A corresponding to the feed to the *previous* reactor (or the sum of the concentrations of both the reacted and unreacted A).

In terms of these, the initial conditions for the bulk in the wiped film reactor are given by

at  $x = 0$ :  $W^* =$

$$\frac{-(\mu_{n,0} - 2)(K_1 + K_2) + \{\mu_{n,0}^2(K_1 + K_2)^2 - 4(\mu_{n,0} - 1)(K_1 - K_2)^2\}^{1/2}}{4\mu_{n,0}(\mu_{n,0} - 1)} \quad (16a)$$

$$A^* = 1 - \frac{2K_1K_2 + \mu_{n,0}W^*(K_1 + K_2)}{2(K_1 + \mu_{n,0}W^*)(K_2 + \mu_{n,0}W^*)} \quad (16b)$$

$$B'^* = \frac{\mu_{n,0}W^*}{2(K_1 + \mu_{n,0}W^*)} \quad (16c)$$

$$B''^* = \frac{\mu_{n,0}W^*}{2(K_2 + \mu_{n,0}W^*)} \quad (16d)$$

$$C'^* = \frac{K_1}{2(K_1 + \mu_{n,0}W^*)} \quad (16e)$$

$$C''^* = \frac{K_2}{2(K_2 + \mu_{n,0}W^*)} \quad (16f)$$

where  $\mu_{n,0}$  is the number average chain length of the feed to the wiped-film reactor and is chosen as a parameter (in real situations,  $W^*$  at  $x = 0$  will be the *independent* parameter instead of  $\mu_{n,0}$ , its value being determined by the vacuum applied in the previous reactor).

The resulting equations are then solved numerically with the help of a combination of the fourth order Runge-Kutta and the explicit finite-difference techniques.<sup>21-24</sup> In finite-difference form the film mass balance equations simplify to

$$\begin{aligned} A_{i,n+1}^* &= A_{i,n}^* + k_1T[A]_0(-A^*B'^* - RA^*B''^* + C'^*W^*/K_1 + RC''^*W^*/K_2)_{i,n}\Delta\theta \\ B'_{i,n+1}^* &= B'_{i,n}^* + k_1T[A]_0(-A^*B'^* + C'^*B'^*/K_1)_{i,n}\Delta\theta \\ B''_{i,n+1}^* &= B''_{i,n}^* + k_1T[A]_0(-RA^*B''^* + RC''^*W^*/K_2)_{i,n}\Delta\theta \\ C'_{i,n+1}^* &= C'_{i,n}^* - k_1T[A]_0(-A^*B'^* + C'^*W^*/K_1)_{i,n}\Delta\theta \\ C''_{i,n+1}^* &= C''_{i,n}^* - k_1T[A]_0(-RA^*B''^* + RC''^*W^*/K_2)_{i,n}\Delta\theta \\ W_{i,n+1}^* &= -k_1T[A]_0(-A^*B'^* - RA^*B''^* + C'^*W^*/K_1 + RC''^*W^*/K_2)_{i,n}\Delta\theta \\ &\quad + (TD/\delta^2)(\Delta\theta/(\Delta\eta)^2)(W_{i-1,n}^* + W_{i+1,n}^*) + \{1-2(TD/\delta^2)\Delta\theta/(\Delta\eta)^2\}W_{i,n}^* \end{aligned} \quad (17)$$

where the subscripts  $i,n$  indicate the  $i$ th location in the film at the time  $n\Delta\theta$ . The symmetry boundary condition given by eq. 6(b) can be accounted for<sup>21</sup> by assuming  $W_{M-1,n}^* = W_{M+1,n}^*$  in eq. (17), where  $M$  is the number of finite-difference grid points into which the film is divided.

In order to assure convergence, the following set of increments was used for

the dimensionless independent variables:

$$\Delta\eta = \frac{1}{150}, \quad \Delta\theta = 0.1, \quad \Delta\xi = 10^{-2} \quad \text{or} \quad 10^{-3} \quad (18)$$

A further reduction in the values of these increments did not lead to significant changes in the final results. The results were found to be extremely sensitive to the choice of  $\Delta\xi$  and  $\Delta\eta$ . Higher values of  $\Delta\xi$  than  $1/100$  led to severe convergence problems while asymptotic results were attained only below  $\Delta\eta$  of about  $1/100$ . It may be mentioned here that Amon and Denson<sup>13</sup> used a semi-implicit finite-difference technique to solve the film equations instead of the explicit finite-difference method used here, which is mathematically simpler. Further, the computer program was run with  $K_1 = K_2 = R = 1$  and other parameters as in Ref. 14, and the results were found to match those reported earlier, thus confirming that the program was free of errors. The computer time (on a DEC 1090 system) taken for a typical run with the increments  $\Delta\eta = 1/150$ ,  $\Delta\theta = 0.1$ ,  $\Delta\xi = 10^{-3}$  was approximately 13 min.

### Model II

In the mixing film model, the polymerization reactions have been assumed to occur only in the film and  $A_b$  is zero. Thus only the film mass balance equations (17) need to be solved numerically using the finite-difference technique. At the end of a cycle, when  $\theta = 1$ , the entire film is mixed together and reapplied instantaneously. Thus the starting concentrations in the film at  $\theta = 0$  (beginning of a cycle) are related to the conditions at  $\theta = 1$  of the previous cycle by the following mixing equations:

$$\begin{aligned} A^*(\theta = 0, \eta)_{N+1} &= \overline{A^*}(\theta = 1)_N = \int_{\eta=0}^{\eta=1} A^*(\theta = 1, \eta)_N \, d\eta \\ B^*(\theta = 0, \eta)_{N+1} &= \overline{B^*}(\theta = 1)_N = \int_{\eta=0}^{\eta=1} B^*(\theta = 1, \eta)_N \, d\eta \\ B''^*(\theta = 0, \eta)_{N+1} &= \overline{B''^*}(\theta = 1)_N = \int_{\eta=0}^{\eta=1} B''^*(\theta = 1, \eta)_N \, d\eta \\ C^*(\theta = 0, \eta)_{N+1} &= \overline{C^*}(\theta = 1)_N + \int_{\eta=0}^{\eta=1} C^*(\theta = 1, \eta)_N \, d\eta \\ C''^*(\theta = 0, \eta)_{N+1} &= \overline{C''^*}(\theta = 1)_N = \int_{\eta=0}^{\eta=1} C''^*(\theta = 1, \eta)_N \, d\eta \\ W^*(\theta = 0, \eta)_{N+1} &= \overline{W^*}(\theta = 1)_N = \int_{\eta=0}^{\eta=1} W^*(\theta = 1, \eta)_N \, d\eta \quad (19) \end{aligned}$$

where  $W^*(\theta, \eta)_N, \dots$  represent the dimensionless concentrations  $W^*, \dots$  at time  $\theta$  and position  $\eta$  in the film in the  $N$ th cycle and  $\overline{W^*}(\theta)_N, \dots$  are the spatial average values of  $W^*, \dots$  at time  $\theta$  in the film in the  $N$ th cycle. These equations have also been solved on the DEC 1090 system for several cycles using  $\Delta\eta = 1/150$  and  $\Delta\theta = 0.1$ . The computer time for  $N = 100$  cycles was 3 min.



## RESULTS AND DISCUSSIONS

Six nondimensional parameter,  $k_1(LA_b/Q)[A]_0$ ,  $k_1T[A]_0$ ,  $(sL/Q)(\delta/T)$ ,  $TD/\delta^2$ ,  $W_s^*/W_0^*$  and  $\mu_{n,0}$ , characterize the reactor system in the set of dimensionless equations for model I. Here,  $W_s^*$  is  $[W]_s/[A]_0$  and  $W_0^*$  is the nondimensional concentration of W in the feed and is given by eq. (16a). These parameters, along with the values of the rate parameters  $K_1$ ,  $K_2$ , and  $R$  are sufficient to determine the dependent variables  $A^*$ ,  $B'^*$ ,  $B''^*$ ,  $C'^*$ ,  $C''^*$ ,  $W^*$  and the number average chain length  $\mu_n \equiv 1/A^*$  as a function of the dimensionless axial location  $\xi$  in the reactor.

In order to study the effect of various reactor design and kinetic parameters systematically, several computer runs were made using the following reference set of values for the parameters<sup>13,14</sup>:

**Reactor Design Parameters:**

$$k_1(LA_b/Q)[A]_0 = 2000, \quad TD/\delta^2 = 10^{-4}$$

$$k_1T[A]_0 = 2, \quad W_s^*/W_0^* = 0$$

$$(sL/Q)(\delta/T) = 1000, \quad \mu_{n,0} = 50$$

**Rate Parameters:**

$$K_1 = 1, \quad K_2 = 1, \quad R = 1 \quad (20)$$

The various parameters were varied one by one, keeping all others at these reference values.

The axial variation of  $\mu_n$  for the reference set of parameters given in eq. (20) is shown in Figure 2. When  $R$  is unity, identical results are obtained for  $\mu_n$  using either  $K_1 = 0.5$ ,  $K_2 = 1$ , or  $K_1 = 1$ ,  $K_2 = 0.5$ , etc. This is consistent with the

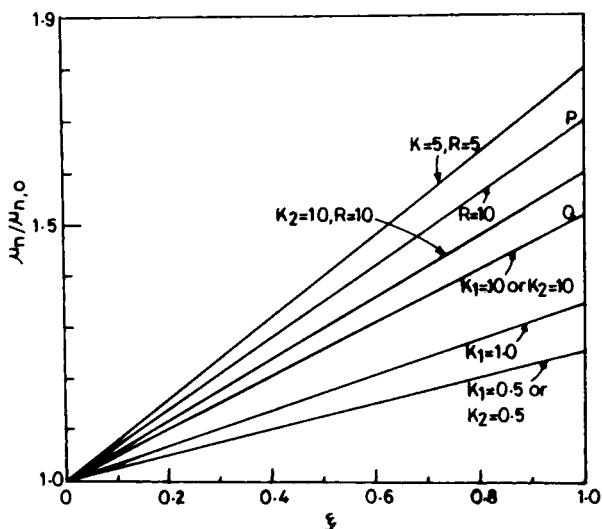


Fig. 2. Axial variation of  $\mu_{n,L}/\mu_{n,0}$  for model I.  $k_1(LA_b/Q)[A]_0 = 2000$ ,  $k_1T[A]_0 = 2$ ,  $(sL/Q)(\delta/T) = 1000$ ,  $TD/\delta^2 = 10^{-4}$ ,  $W_s^*/W_0^* = 0$ ,  $\mu_{n,0} = 50$ ; rate parameters varied one-by-one about the following set of reference values:  $K_1 = 1$ ,  $K_2 = 1$ ,  $R = 1$ .

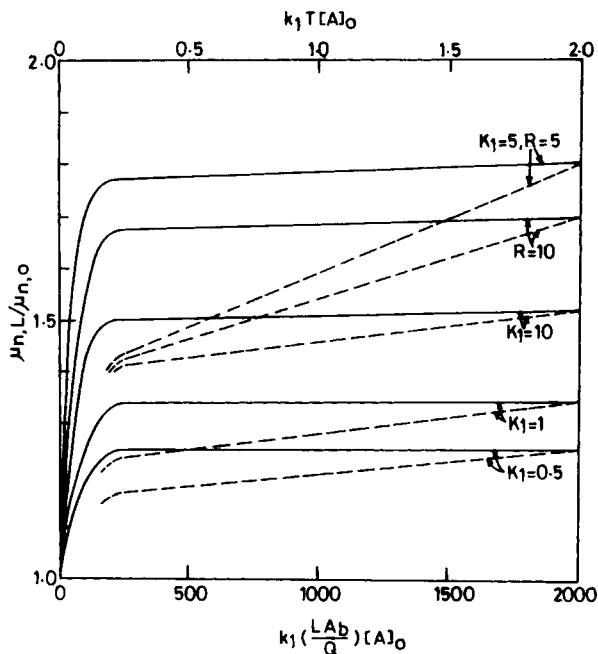


Fig. 3. Reactor efficiency vs.  $k_1(LA_b/Q)[A]_0$  (—) and  $k_1T[A]_0$  (---) for model I. Values of parameters not specified are given in eq. (20).

symmetry associated with the reaction scheme between —A and —B' or between —A and —B'' as shown in eq. (1). The increase in  $\mu_n$  with the rate parameters  $K_1$ ,  $K_2$ , and  $R$  are consistent with intuitive expectations since increasing the forward rate constants in the scheme shown in eq. (1) leads to more production of W and thus to higher removal of W by diffusion and higher chain lengths. It is interesting to observe that  $\mu_n$  is more affected by an increase in the value of  $R$  than by an increase in  $K_1$  or  $K_2$ , as can be observed by comparing curves P and Q in Figure 2. It is also observed that for the case when  $K_1 = 1$ ,  $K_2 = 1$ ,  $R = 1$ , the results on AA + B'B'' polymerization match with earlier results<sup>14</sup> on equal reactivity ARB polymerizations.

Figure 3 shows the effect of varying the dimensionless residence time  $k_1(LA_b/Q)[A]_0$  in the reactor and the dimensionless film exposure time,  $k_1T[A]_0$  on the reactor efficiency (defined as  $\mu_{n,L}/\mu_{n,0}$ ). On increasing  $k_1(LA_b/Q)[A]_0$ ,  $\mu_{n,L}/\mu_{n,0}$  is observed to rise sharply to its asymptotic value, the asymptotic value again depending on the rate parameters—they being higher when the forward reactions are favored. It is observed that there is relatively little change in the value of  $\mu_{n,L}/\mu_{n,0}$  as the residence time,  $LA_b/Q$  in the reactor is increased. This is because the driving force for the mass transfer of W becomes very small as  $[W]$  approaches  $[W]_s$  in the reactor. It also illustrates the futility of increasing product molecular weights by increasing the length of the reactor. This conclusion is further supported by the trend shown by the  $\mu_{n,L}/\mu_{n,0}$  vs.  $k_1(LA_b/Q)[A]_0$  plots for  $K_1 = 5$ ,  $R = 5$  wherein more W is produced and there is a continual rise in the reactor efficiency. The reactor efficiency is also found to increase greatly on varying  $k_1T[A]_0$ . This diagram illustrates the effect of varying the rate constant  $k_1$  and does not indicate the influence of increasing  $T$  among

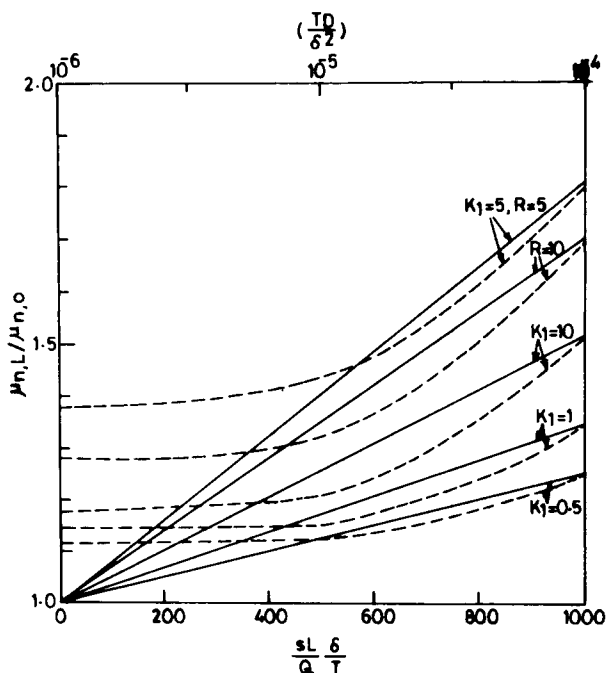


Fig. 4. Reactor efficiency vs.  $(sL/Q)(\delta/T)$  (solid lines) and  $TD/\delta^2$  (dotted line) for model I. Values of parameters not specified are given in eq. (20).

the variables since the parameters  $TD/\delta^2$  and  $(sL/Q)(\delta/T)$  are simultaneously kept unchanged in Figure 3. Once again, higher reactor efficiencies are observed as the rate parameters are increased to favor the forward reactions in eq. (1). It may be mentioned that the reactor efficiency will reduce as  $T$  increases, keeping  $D$  and  $\delta$  fixed, indicating the usefulness of the rapid application and removal of the film.

Figure 4 shows the effect of  $(sL/Q)(\delta/T)$  and  $TD/\delta^2$  on the reactor efficiency. Once again, neither of these two sets of graphs can give the effect of varying the film thickness directly, since the other parameters involving  $\delta$  are kept constant as these are varied. However, the graphs corresponding to  $(sL/Q)(\delta/T)$  represent the effect of the film perimeter  $s$ , and it is observed that the reactor efficiency increases as  $s$  increases, as expected intuitively, since more surface area is available for the removal of  $W$ . This effect is higher when the rate constants favor the forward reaction—the effect of increasing  $R$  being more substantial than that of increasing  $K_1$ . The graphs corresponding to  $TD/\delta^2$  in Figure 4 can be interpreted as those representing the effect of the diffusivity  $D$  of  $W$  through the reaction mass. It is observed that the reactor efficiency is not very sensitive to  $TD/\delta^2$  when this parameter varies from about  $10^{-6}$  to  $10^{-5}$ , but beyond  $TD/\delta^2$  of about  $10^{-5}$ , the reactor efficiency increases very rapidly, specially when the rate parameters favor the forward reaction. This is consistent with our earlier explanation that for  $TD/\delta^2$  around  $10^{-5}$ , the driving force for the mass transfer of  $W$  is relatively small. This effect is thus very similar to the asymptotic nature of the reactor efficiency vs.  $k_1(LA_b/Q)[A]_0$  curves. For values of  $TD/\delta^2$  above about  $10^{-4}$ , it appears that these mass transfer limitations diminish in impor-

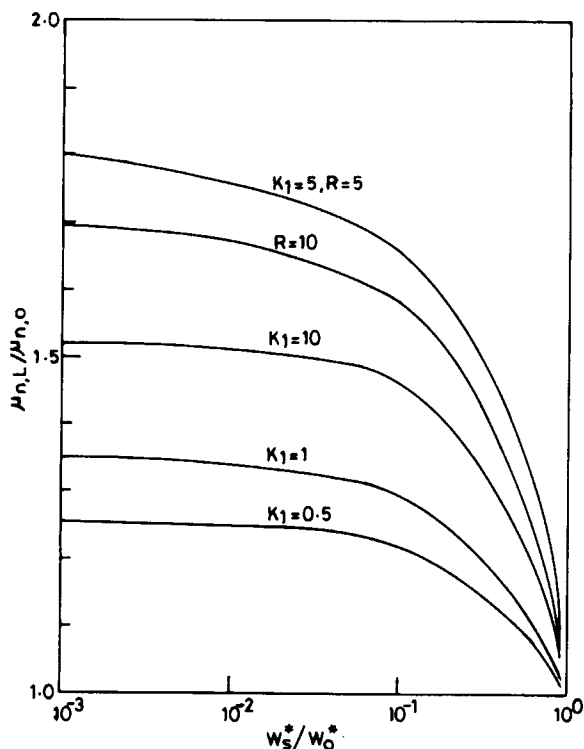


Fig. 5. Effect of  $W_s^*/W_0^*$  on the reactor efficiency for model I.

tance, and there is a very sharp increase in the reactor efficiency. It is found that the reactor efficiency vs.  $k_1(LA_b/Q)[A]_0$  curves for these ranges of  $TD/\delta^2$  also show an increasing trend in contrast to their sharp rise to an asymptotic value as in Figure 3 for lower values of  $TD/\delta^2$ . However, such ranges of  $TD/\delta^2$  would probably not be physically meaningful.

Figure 5 shows the effect of the degree of vacuum applied on the film. A lowering of the reactor efficiency has been found as  $W_s^*/W_0^*$  is increased, specially when the latter is above about  $10^{-1}$ . A reduction in the vacuum level below this level does not lead to significant improvements in the reactor efficiency and again illustrates the futility of applying much higher vacuum. A similar effect for the equal reactivity case was reported by Amon and Denson. It is observed from Figure 5, however, that the limiting *useful* value of  $W_s^*/W_0^*$  depends on the rate parameters and, for unequal reactivity polycondensations, one can get substantially higher reactor efficiencies by increasing the level of vacuum to below  $W_s^*/W_0^*$  values of  $10^{-1}$ .

Model I of the wiped-film reactor thus predicts the following two major qualitative effects:

(a) There always arises a point of diminishing returns when one tries to get improvements in the product molecular weights by going to longer reactors or by applying higher vacuum. It is always more profitable to increase the surface area of the film (per unit flow rate of the reaction mass) or the temperature of the reactor (through  $k_1$ ) to maximize the reactor efficiency.

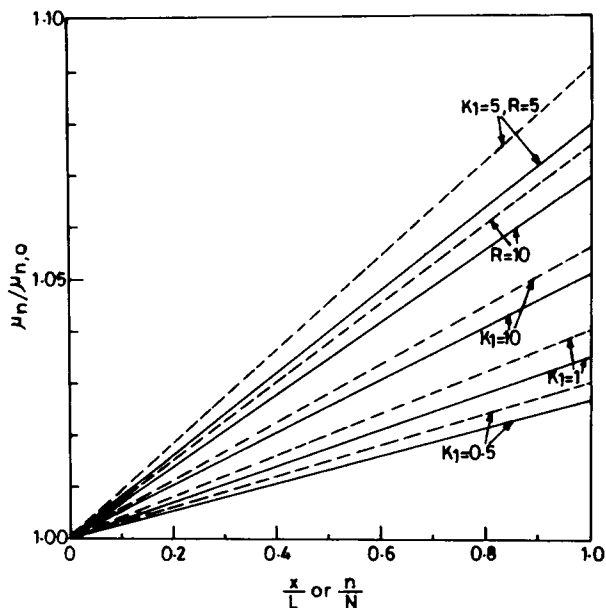


Fig. 6.  $\mu_n/\mu_{n,0}$  as a function of the axial location  $n/N$  or  $x/L$ . (—) Model II using  $k_1T[A]_0 = 2$ ,  $TD/\delta^2 = 10^{-4}$ , and  $N = 100$ ; (---) model I using  $k_1(LA_b/Q)[A]_0 = 2000$ ,  $k_1T[A]_0 = 2$ ,  $TD/\delta^2 = 10^{-4}$ ,  $(sL/Q)(\delta/T) = 100$ .  $\mu_{n,0} = 50$  and  $W_s^*/W_0^* = 0$  for both cases. Rate parameters are unity unless specified otherwise.

(b) The effect of the reactivity ratio  $R$  on the reactor efficiency is more pronounced than that of the equilibrium constants.

The dimensionless reactor parameters associated with model II, the mixing-film model<sup>17</sup> of the wiped film reactor, are  $k_1T[A]_0$ ,  $TD/\delta^2$ ,  $W_s^*/W_0^*$ ,  $\mu_{n,0}$ , and the total number of cycles  $N$ . It is thus observed that there is one less independent parameter in this model than in model I and a good comparison of the two models is difficult. A rough idea of the conditions under which the two models are equivalent, may be obtained by discretizing the operation of model II. In this model, an amount of material equal to  $QT$  is fed in time  $T$ . We may imagine that all of this material is spread out instantaneously as a film of thickness  $\delta$ , over a length  $x^*$ . After time  $T$ , this film is mixed and moved forward by a distance  $x^*$ , while another film of volume  $QT$  is applied at its original position, these steps occurring instantaneously. If the perimeter of the film is  $s$ , we can write

$$sx^*\delta = QT \quad (21)$$

which gives  $x^*$  as  $QT/s\delta$ . Thus, the number of contacts,  $N$ , in length  $L$  of the reactor is  $L/x^*$  or  $Ls\delta/QT$ . No independent equivalence relationship can be obtained relating  $k_1(LA_b/Q)[A]_0$  of model I to parameters associated with model II. However, as depicted in Figure 3, results of model I are insensitive to the value of  $k_1(LA_b/Q)[A]_0$  and a reasonably high value of 2000 is used.

In order to compare the two models under the above-mentioned equivalent conditions, the following set of parameter values were used to generate results for model II:

$$\begin{aligned}
 k_1 T[A]_0 &= 2, \quad W_s^*/W_0^* = 0 \\
 TD/\delta^2 &= 10^{-4}, \quad \mu_{n,0} = 50 \\
 N &= 100
 \end{aligned}
 \tag{22}$$

Higher values of  $N$  were not used because of the excessive computer times involved. Figure 6 shows the results for various values of the rate constants. Results for model I using the equivalent set of parameters:

$$\begin{aligned}
 k_1 T[A]_0 &= 2, \quad TD/\delta^2 = 10^{-4}, \quad (sL/Q)(\delta/T) = 100 \\
 k_1(LA_b/Q)[A]_0 &= 2000, \quad W_s^*/W_0^* = 0, \quad \mu_{n,0} = 50
 \end{aligned}
 \tag{23}$$

are also shown for comparison by dotted lines. It is observed that slightly higher values of  $\mu_n$  are obtained for model I than for the mixing-film model. Since actual reactors are expected to lie in between these two limiting behaviors, and, since the results do not differ significantly, one may claim that either of the two models are good enough to predict the actual behavior.

### References

1. S. K. Gupta and A. Kumar, *Chem. Eng. Commun.*, to appear.
2. P. J. Flory, *Principles of Polymer Chemistry*, 1st ed., Cornell University Press, Ithaca, N.Y., 1953.
3. A. Kumar and S. K. Gupta, *Fundamentals of Polymer Science and Engineering*, 1st ed., Tata McGraw-Hill, New Delhi, 1978.
4. V. S. Nanda and S. C. Jain, *J. Chem. Phys.*, **49**, 1318 (1968).
5. S. K. Gupta, N. L. Agarwal, P. Rajora, and A. Kumar, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 933 (1982).
6. S. K. Gupta, P. Rajora, N. L. Agarwal, and A. Kumar, *Polymer*, **23**, 222 (1982).
7. L. C. Case, *J. Polym. Sci.*, **29**, 455 (1958).
8. K. S. Gandhi and S. V. Babu, *AIChE J.*, **25**, 266 (1979).
9. E. Ozizmer and G. Odian, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 1089 (1980).
10. R. M. Secor, *AIChE J.*, **15**, 861 (1969).
11. S. K. Gupta, N. L. Agarwal, and A. Kumar, *J. Appl. Polym. Sci.*, **27**, 1217 (1982).
12. S. K. Gupta, S. S. Rao, R. Agarwal, and A. Kumar, *Ind. Chem. Eng.*, to appear.
13. M. Amon and C. D. Denson, *Ind. Eng. Chem. Fundam.*, **19**, 415 (1980).
14. S. K. Gupta, A. Kumar, and A. K. Ghosh, *Ind. Eng. Chem. Fundam.*, to appear.
15. S. K. Gupta, A. Kumar, and K. K. Agarwal, *J. Appl. Polym. Sci.*, **27**, 3089 (1982).
16. A. Ramgopal, A. Kumar, and S. K. Gupta, *Polym. Eng. Sci.*, to appear.
17. J. W. Ault and D. A. Mellichamp, *Chem. Eng. Sci.*, **27**, 1441 (1972).
18. K. Nagasubramanian and H. K. Reimschuessel, *J. Appl. Polym. Sci.*, **17**, 1663 (1973).
19. J. S. Vrentas and J. L. Dudas, *AIChE J.*, **25**, 1 (1979).
20. K. Ravindranath and R. A. Mashelkar, *J. Appl. Polym. Sci.*, to appear.
21. H. S. Mickley, T. K. Sherwood, and C. E. Reed, *Applied Mathematics in Chemical Engineering*, 2nd ed., McGraw-Hill, New York, 1957.
22. A. S. Foust, L. A. Wenzel, C. W. Clump, L. Maus, and L. B. Anderson, *Principles of Unit Operations*, 2nd ed., Wiley, New York, 1980.
23. B. Carnahan, H. A. Luther, and J. O. Wilkes, *Applied Numerical Methods*, Wiley, New York, 1969.
24. W. F. Ames, *Numerical Methods for Partial Differential Equations*, 2nd ed., Academic, New York, 1977.

Received August 13, 1982

Accepted October 6, 1982