

Analysis of Wiped Film Reactors Using the Orthogonal Collocation Technique

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Synopsis

Transport equation for ARB polymerization in wiped film reactors have been written. These have been reduced to the moment generation equations and using a suitable moment closure approximation, the zeroth and the second moments of the polymer have been numerically solved using the finite difference as well as the orthogonal collocation techniques. In the numerical solution by the finite difference technique, it is necessary to divide the dimensionless film thickness into at least 250 grid points to obtain stable results. The use of nine collocation points by the orthogonal collocation technique gives results close to those by the finite difference method and leads to considerable computational saving. The transport equations for the bulk and the film are found to involve four dimensionless parameters, and their effect upon the polymer formed at the end of the reactor has been studied.

INTRODUCTION

A considerable amount of work has been done on the simulation of step growth polymerization.¹ 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 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 condensation product, the most common of which is the wiped film reactor, shown in Figure 1. In this, a rotating blade applies a thin film of the reaction mass on the inside surface of a cylinder to which a high vacuum is applied.²⁻⁷ The reaction occurs primarily in the bulk while most of the condensation product is removed in the film.

Physically when the thin film of the polymer is applied on the surface of the cylinder in which the pressure is lowered, the condensation product formed by the chemical reaction is removed from the reaction mass both at the interface as well as product, in the form of small bubbles formed within the film which gradually rise to the interface. Mass transfer occurs in the bubbles from its adjoining areas, and this phenomenon has been analyzed in the literature.⁸⁻¹² The analysis of wiped film reactors, however, has been performed using simplified model, assuming that the mass transfer occurs *only* at the interface with the interface area taken as a parameter²⁻⁵ to correct for the formation of bubbles empirically.

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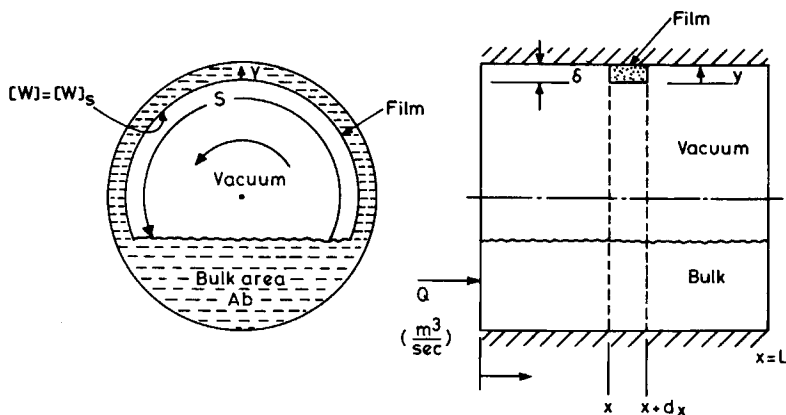


Fig. 1. Schematic diagram of the wiped film reactor.

There are two transport models of the wiped film reactors that exist in the literature, depending upon what fraction of the polymeric material in the bulk is applied as a film. In one model (called model 1),²⁻⁶ this fraction is assumed to be small and the reaction occurs primarily in the bulk, while most of the condensation product is removed in the film. On mixing, the film (scraped from the cylinder surface) with the bulk is assumed to produce negligible concentration changes in the bulk. In the other model^{5,12} (called model 2), it is assumed that the entire reaction mass is applied as a thin film and there is no separate bulk as in the earlier model. After a fixed time interval, the entire film is well mixed (instantaneously) by means of the blade of the reactor and applied once again.

Since the film is stationary, the mass transfer equations for the film would involve a partial differential equation. In model 1, since there is a bulk, the transport equation for this is an ordinary differential equation if axial diffusion is neglected. The solution of the film transport equations gives the amount of condensation product removed which is utilized in solving the bulk equations as a function of the axial position of the reactor. In model 2 since there is no bulk, the film equations are solved for the exposure time, starting from a known molecular weight of the polymer. However, the results from these two models do not differ significantly, and, as such, model 1 is used in this study.

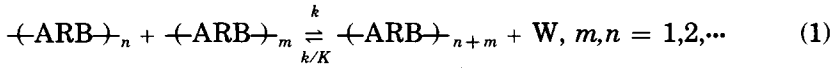
In our earlier studies of the simulation of wiped film reactors,^{3,4} we found that the numerical solution of the film transport equations using the finite difference method required that 1 cm thickness of the film must be divided in at least 250 divisions. This was necessary because the concentration profile of the condensation produce is extremely sharp and leads to numerical instability whenever the number of divisions are reduced below 250.

To overcome the computational difficulty cited above, we have used the orthogonal collocation technique by which the partial differential equations for the film are reduced to ordinary differential equations at the collocation points.^{13,14} The results so computed are compared with those found from the finite difference method, and it is found that the use of nine collocation

points gives results within 2% of the exact solution. A considerable saving on the computational time results on using this technique.

FORMULATION

The kinetic scheme used in this work is the simple ARB polymerization, which can be written as



where W represents the condensation product. The rate of polymerization, r_p , can be written as

$$-r_p = k \left\{ -[\text{P}]^2 + \frac{[\text{W}][\text{M}]_0 - [\text{P}]}{K} \right\} \quad (2)$$

where [] represents the molar concentration, [P] is the bulk concentration of total polymer species, and [M]₀ is the initial monomer concentration. The rate of formation of the condensation product, r_w , is equal to r_p in magnitude but is of opposite sign. Mass balance equations for the bulk for P and W in a differential control volume of length dx , shown in Figure 1, can be written as

$$-Q d[\text{P}] - r_p A_b dx = 0 \quad (3a)$$

$$-Q d[\text{W}] + r_w A_b dx - \bar{n}_w s dx = 0 \quad (3b)$$

where A_b is the cross-sectional area of the bulk, Q is the volumetric flow rate of the material, \bar{n}_w is the time average flux of W at a given axial position x , and s is the film surface area per unit length.

To calculate \bar{n}_w , it is necessary that the mass balance equations for the film be solved. These are

$$-\frac{\partial[\text{P}]_0}{\partial t} = -r_p \quad (4a)$$

$$\frac{\partial[\text{W}]_f}{\partial t} = D \frac{\partial^2[\text{W}]_f}{\partial y^2} \quad (4b)$$

where D is the diffusivity of W through the reaction mass and the subscript f denotes that the concentrations have been evaluated for the film. The time averaged rate of diffusion of W from the film can be written as

$$\bar{n}_w = \frac{1}{T_f} \int_0^{T_f} \left. \frac{\partial[\text{W}]}{\partial y} \right]_{y=0} dt \quad (5)$$

where T_f is the exposure time of the film. The use of this equation for \bar{n}_w leads to severe instabilities in computations,² since it involves numerical

differentiation. However, eq. (5) can be reexpressed in a more convenient form as follows:

$$D \frac{\partial^2 [W]}{\partial y^2} = \frac{\partial [W]}{\partial t} = r_w = \frac{\partial}{\partial t} \left\{ [W] + [P] \right\} \quad (6)$$

On integrating this equation with respect to y using the appropriate boundary conditions, one obtains

$$\bar{n}_w = -\frac{1}{T} \int_{y=0}^{\delta} \left[\{ [W] + [P] \}_{t=0} - \{ [W] + [P] \}_{t=T} \right] dy \quad (7)$$

where δ is the film thickness.

The zeroth moment μ_0 of the MWD of the polymer formed can be computed as

$$\mu_0 = \sum_{n=1}^{\infty} [P_n] = [P] \quad (8)$$

The first moment μ_1 of the MWD of polymer formed represents the total number of repeat units and is time-invariant. The second moment μ_2 of the MWD can be found as follows: One first writes the mole balance equation for species P_n for the bulk as

$$-Q d[P_n] - r_{P_n} A_b dx = 0, \quad n = 1, 2, \dots \quad (9)$$

where r_{P_n} is the rate of formation of P and is given by

$$\begin{aligned} r_{P_n} &= k \sum_{n=1}^{n-1} [P_r][P_{n-r}] - k[P_n] \sum_{i=1}^{\infty} [P_i] \\ &\quad - \frac{k}{K} (n-1) [P_n][W] + \frac{k}{K} [W] \sum_{i=n+1}^{\infty} [P_i] \quad n \geq 2 \end{aligned} \quad (10a)$$

and

$$r_{P_1} = -k[P_1] \sum_{i=1}^{\infty} [P_i] + \frac{k}{K} [W] \sum_{i=2}^{\infty} P_i \quad (10b)$$

The second moment μ_2 is obtained by multiplying eq.(9) by n^2 and summing up the equations so obtained for all n . This leads to

$$-Q d\mu_2 - r_{\mu_2} \cdot A_b dx = 0 \quad (11)$$

where r_{μ_2} is given by

$$r_{\mu_2} = \sum_{n=1}^{\infty} n^2 r_{P_n} \quad (12)$$

It can easily be shown that r_{μ_2} is given by

$$r_{\mu_2} = k \left\{ 2 [M]_0^2 + \frac{[W][M]_0 - \mu_3}{3K} \right\} \quad (13)$$

where

$$\mu_3 = \sum_{n=1}^{\infty} n^3 [P_n] \quad (14)$$

To be able to solve for the various moments, it is necessary to use moment closure techniques to break the hierarchy of equations. The following closure relation has been used in this work:

$$\mu_3 = \frac{\mu_2(2\mu_2\mu_0 - \mu_1^2)}{\mu_1\mu_0} \quad (15)$$

This closure approximation has been found to be appropriate in earlier simulations of step-growth polymerizations, and the results have been found to match with those found from the exact MWDs.^{11,15,16}

The various boundary and initial conditions can be written as follows:

Film

$$\text{at } t > 0: \quad y = 0, [W] = [W]_{f0} \quad (16)$$

$$y = \delta, \quad \frac{\partial [W]}{\partial y} = 0$$

$$\text{at } t = 0: \quad y \geq 0 \quad (17)$$

$$[P] = [P]_x, \quad [W] = [W]_x, \quad \mu_2 = \mu_{2x}$$

where $[P]_x$ and $[W]_x$ represent the concentrations of P and W in the bulk at axial position x .

These equations can be nondimensionalized using the following parameters:

$$\begin{aligned} C_1 &= K_p[M]_0 T_f \\ C_2 &= \frac{T_f D}{\delta^2} \\ C_3 &= K_p[M]_0 \tau \\ C_4 &= \frac{S\delta}{QT_f} \end{aligned} \quad (18)$$

$$W^* = \frac{[W]}{[M]_0} P^* = \frac{[P]}{[M]_0} \eta = \frac{y}{\delta}$$

$$\xi = \frac{x}{L} \theta = \frac{t}{T_f} \bar{N}_w = \frac{T_f \bar{n}_w}{\delta [M]_0}$$

where L is the length of the wiped film reactor.

These equations can be solved for given inlet conditions. The inlet polymer is assumed to have an average chain length of 50, which is fairly typical of PET reactors.

THE USE OF ORTHOGONAL COLLOCATION TECHNIQUE

The concentration of the condensation product in the film is assumed to be governed by following transformation

$$W^*(\eta) = \sum_{i=1}^{N+1} a_i(\eta^2)^{i-1} \quad (19)$$

where a_i are the undetermined coefficients and are a function of θ . This equation automatically satisfies the boundary conditions given in Table I.

TABLE I
Transport Equations for the Bulk and Film in Wiped-Film Reactor

Bulk

$$\begin{aligned} -\frac{dP^*}{d\xi} - (k[M]_0\tau) \left[P^{*2} - \frac{W^*(1-P^*)}{K} \right] &= 0 \\ -\frac{dW^*}{d\xi} + (k[M]_0\tau) \left[P^{*2} - \frac{W^*(1-P^*)}{K} \right] - \frac{S}{Q} \cdot \frac{\delta}{T_f} \bar{N}_w &= 0 \\ -\frac{d\mu^*_2}{d\xi} + (k[M]_0\tau) \left[2 + \frac{W^*(2-\mu^*_3)}{3K} \right] &= 0 \end{aligned}$$

$$\text{where } \mu^*_3 = \frac{\mu_3}{[M]_0}$$

The moment closure relation

$$\mu^*_3 = \mu_n \cdot \mu^*_2 \left(\frac{2\mu^*_2}{\mu_n} - 1 \right)$$

Initial condition for the bulk

$$\text{At } \xi = 0, W^* = \frac{K}{\mu_{n0}(\mu_{n0} - 1)}$$

$$P^* = \frac{1}{\mu_{n0}}$$

$$\mu^*_2 = 2\mu_{n0} - 1$$

Where μ_{n0} is the number average chain length of the feed to the reactor and is chosen to be 50

Film

$$\begin{aligned} \frac{\partial p^*}{\partial \theta} &= -(k[M]_0T) \left[P^{*2} - \frac{W^*(1-P^*)}{K} \right] \\ \frac{\partial W^*}{\partial \theta} &= \frac{T_f D \delta^2 W^*}{\delta^2 \partial \eta^2} + (k[M]_0T) \left[P^{*2} - \frac{W^*(1-P^*)}{K} \right] \end{aligned}$$

Initial conditions for film

$$\text{At } \theta = 0, \eta \geq 0$$

$$P^* = p^*|_{\xi=0}, W^* = W^*|_{\xi=0}, \mu^*_2 = \mu^*_2|_{\xi=0}$$

Boundary conditions for the film

$$\text{At } \theta > 0, \eta = 0, W^* = W^*,$$

$$\eta = 1, \frac{\partial W^*}{\partial \eta} = 0$$

The $(N + 1)$ collocation points, $(\eta_i, i = 1, 2, \dots, N + 1)$ lying between $\eta = 0$ and $\eta = 1$ are the roots of the equation $P_N(\eta^2) = 0$, where $P_N(\eta^2)$ is a polynomial of degree N in η^2 . The roots of this polynomial are tabulated in Ref. 13 for two different weighting functions. Equation (19) is applied at $(N + 1)$ collocation points, and in matrix notation this gives

$$\mathbf{W}^* = \begin{bmatrix} W^*(\eta_1) \\ \vdots \\ W^*(\eta_{N+1}) \end{bmatrix} = \mathbf{Q} \cdot \mathbf{a} = \begin{bmatrix} 1 & \eta_1^2 & \dots & \eta_1^{2N} \\ \vdots & \vdots & \vdots & \vdots \\ 1 & \eta_{N+1}^2 & \dots & \eta_{N+1}^{2N} \end{bmatrix} \begin{bmatrix} a_1 \\ \vdots \\ a_{N+1} \end{bmatrix} \tag{20}$$

\mathbf{a} can now be solved to give

$$\mathbf{a} = \mathbf{Q}^{-1} \cdot \mathbf{W}^*$$

Taking the first derivative of the eq. (19) and evaluating them at the collocation points, one obtains

$$\frac{\partial \mathbf{W}^*}{\partial \eta} \equiv \begin{bmatrix} \frac{\partial W^*}{\partial \eta_1} \\ \vdots \\ \frac{\partial W^*}{\partial \eta_{N+1}} \end{bmatrix} = \mathbf{C} \mathbf{a} \equiv \begin{bmatrix} 0 & \frac{\partial}{\partial \eta} (\eta^2)_{\eta_1} & \dots & \frac{\partial}{\partial \eta} (\eta^{2N})_{\eta_1} \\ \vdots & \vdots & \vdots & \vdots \\ 0 & \frac{\partial}{\partial \eta} (\eta^2)_{\eta_{N+1}} & \dots & \frac{\partial}{\partial \eta} (\eta^{2N})_{\eta_{N+1}} \end{bmatrix} \begin{bmatrix} a_1 \\ \vdots \\ a_{N+1} \end{bmatrix} \tag{21}$$

which simplifies to

$$\frac{\partial \bar{\mathbf{W}}^*}{\partial \eta} = \mathbf{C} \mathbf{A}^{-1} \mathbf{W}^* \equiv \mathbf{U} \mathbf{W}^* \tag{22}$$

Again taking the Laplacian of eq. (19) at the collocation points, we obtain

$$\nabla^2 \mathbf{W}^* \equiv \begin{bmatrix} \frac{\partial^2 W^*}{\partial \eta^2} \Big|_{\eta_1} \\ \vdots \\ \frac{\partial^2 W^*}{\partial \eta^2} \Big|_{\eta_{N+1}} \end{bmatrix} = \mathbf{D} \mathbf{a} \equiv \begin{bmatrix} \nabla^2 \eta^0 \Big|_{\eta_1} & \dots & \nabla^2 \eta^{2N} \Big|_{\eta_1} \\ \vdots & & \vdots \\ \nabla^2 \eta^0 \Big|_{\eta_{N+1}} & \dots & \nabla^2 \eta^{2N} \Big|_{\eta_{N+1}} \end{bmatrix} \begin{bmatrix} a_1 \\ \vdots \\ a_{N+2} \end{bmatrix} \tag{23}$$

or

$$\nabla^2 W^* = \mathbf{D} \mathbf{a} = \mathbf{D} \mathbf{Q}^{-1} \mathbf{W}^* = \mathbf{V} \mathbf{W}^* \quad (24)$$

On substituting eqs. (20)–(24) in the film mass balance equations for the condensation product is obtained as

$$\left. \frac{\partial W^*}{\partial \theta} \right]_{\eta_j} = (k_{p0} T_f [M]_0) \left\{ [P^*]^2 - \frac{W^*(1-p^*)}{K} \right\}_{\eta_j} + \frac{T_f D}{\delta^2} \cdot \mathbf{V} \cdot \mathbf{W}^* \quad ; j = 1, 2, \dots, N+1 \quad (25)$$

The boundary condition of Table I are reduced to the following:

$$\text{at } \eta_{N+1} = 1: \quad W^*_{N+1} = W^*_j \quad (26)$$

Similarly for the polymer species, the following trial function can be assumed:

$$p^*(\eta) = \sum_{i=1}^{N+1} d_i \eta^{2i-2} \quad (27)$$

and \mathbf{d} can be solved as

$$\mathbf{d} = \mathbf{Q}^{-1} \mathbf{P}^* \quad (28)$$

The mass balance equation can be rewritten at the collocation points to give

$$\left. \frac{dp^*}{d\theta} \right]_{\eta_j} = - (k_p T_f [M]_0) \left(p^{*2} - \frac{W^*(1-p^*)}{K} \right)_{\eta_j}, \quad j = 1, 2, \dots, N+1 \quad (29)$$

The above set of equations are integrated using the fourth order Runge–Kutta method to get \mathbf{a} and \mathbf{d} at $\theta = 1$.

The time average rate of diffusion equation (7) can be rewritten in terms of these trial functions as*

$$\bar{N}_w = (W^* + P^*)_{\theta=0} - \sum_{i=1}^{N+1} \left(\frac{a_i - d_i}{d_{i-1}} \right) \Big]_{\theta=1} \quad (30)$$

Knowing \bar{N}_w , the mass balance equations for the bulk are solved by the fourth-order Runge–Kutta method.

RESULTS AND DISCUSSION

The solution of the film transport equation in Table I is computationally difficult because of the steep concentration profiles of the condensation product near the interface. We varied the total number of divisions M in

TABLE II
Effect of M on Degree of Polymerization Polydispersity Index and Time Average Flux of Byproduct ($\theta = 0.1$, $\Delta\xi = 0.001$) at End of Reactor^a

M	$\mu_{n,L}$	ρ_L	$\bar{N}_{w,L} \times 10^5$
10	81.967	1.9895	0.982603
50	56.394	1.9847	0.417748
100	53.612	1.9839	0.261408
150	52.831	1.98367	0.211033
250	52.369	1.9836	0.179821
300	52.317	1.98361	0.178427

^a $K = 1.0$, $\mu_{n,0} = 50.0$, $C_1 = 1$, $C_2 = 10^{-5}$, $C_3 = 2000$, $C_4 = 500$.

the film and used the finite difference technique to compute the number average chain length and the polydispersity index of the polymer as a function of the axial position. The results have been summarized in Table II for various values of M . It can be seen that at least 250 divisions of the dimensionless film thickness are necessary to obtain numerically stable results. The concentration profiles of the condensation product at the end of the reactor (i.e., $\xi = 1.0$), for various θ 's are given in Figure 2.

From this figure it is obvious that the total number of division of the film thickness into finite difference end points should be large so that the steep rise in the concentration of the condensation product could be sensed. In the orthogonal collocation technique, the total number of orthogonal collocation points is a parameter which should be adjusted in such a way

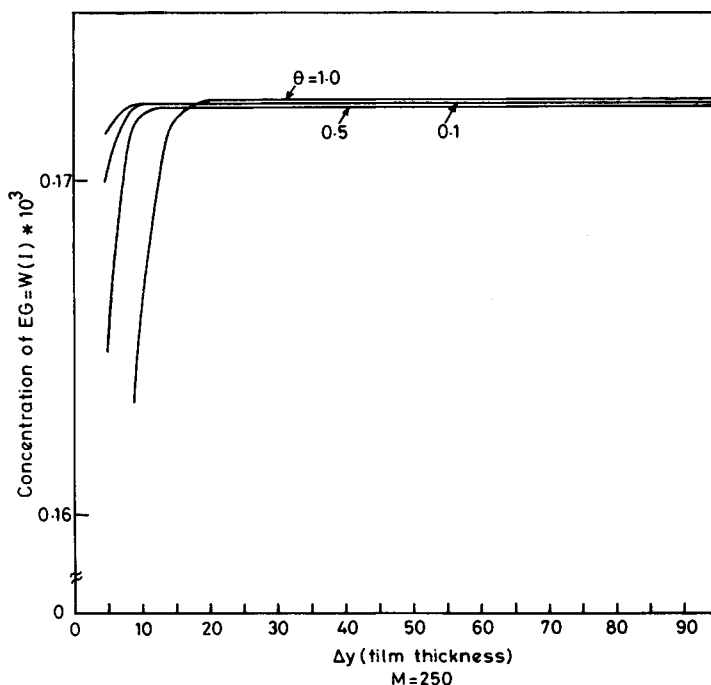


Fig. 2. Concentration profile of ethylene glycol in the film: $C_1 = 2.0$, $C_2 = 10^{-5}$, $C_3 = 2000$, $C_4 = 1000$, $K = 0.5$. Interfacial concentration $C^* = 0$, $\mu_{n,0} = 50$.

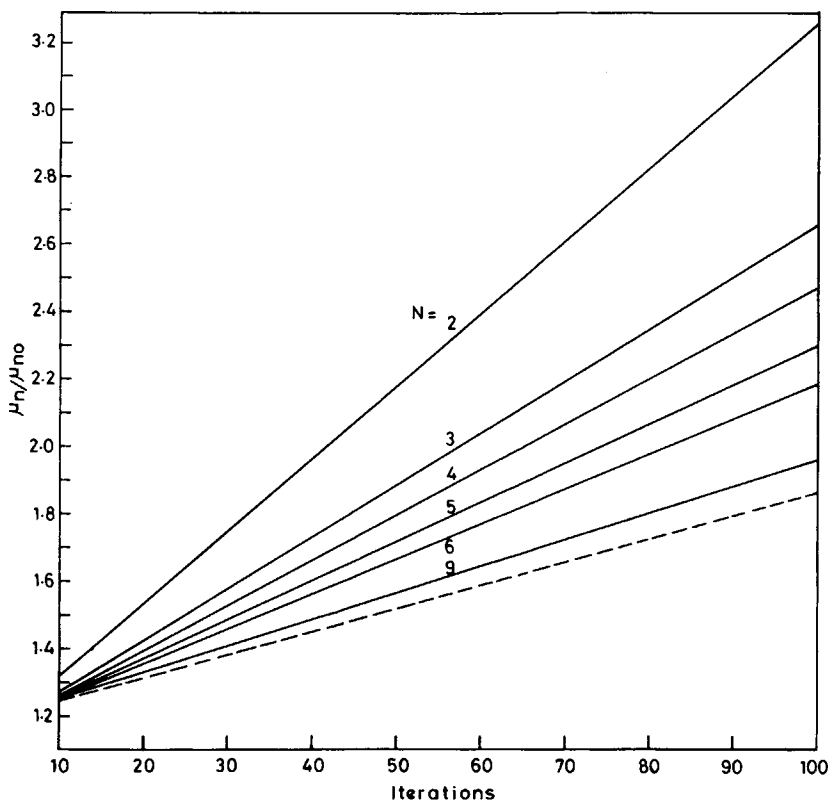


Fig. 3. Effect of the number of collocation points upon the molecular weight vs. ξ : $C_1 = 2.76 \times 10^{-3}$, $C_2 = 10^{-5}$, $C_3 = 5.526$, $C_4 = 4000$, $\mu_{n0} = 50.0$; (—) collocation; (- - -) finite difference.

that the computed results are close to those found from the finite difference method. In Figure 3, the results calculated from the finite difference technique are shown by the dotted line, and the results for various values of the number of collocation points N are shown in the same graph for comparison. For small N , the difference between the two techniques is extremely large whereas for $N = 9$ results diverge only by about 5%. If N is increased beyond 9, it is found that for a stable solution $\Delta\theta$ must also be reduced, this way reducing the computational advantage of the collocation technique. In this paper we have used nine collocation points for generating the various figures.

The various transport equations for the film and the bulk involve four parameters C_1 – C_4 as defined in Table I. In the variation of C_1 , the exposure time and temperature are the only design parameters which change, and its systematic variation has been studied in Figure 4. As the exposure time (or the Temperature) is reduced, the time average flux is found to increase which, in turn, increases the average chain length of the polymer formed at the end of the reactor as plotted in Figure 4. On the same figure, the polydispersity index ρ (PDI) has also been plotted, and it is found that the change in ρ is very small for the range of C_1 studied.

Parameter C_2 is composed of two film variables: the film thickness δ and the exposure time T_f . When C_2 is increased, it amounts to an increase in

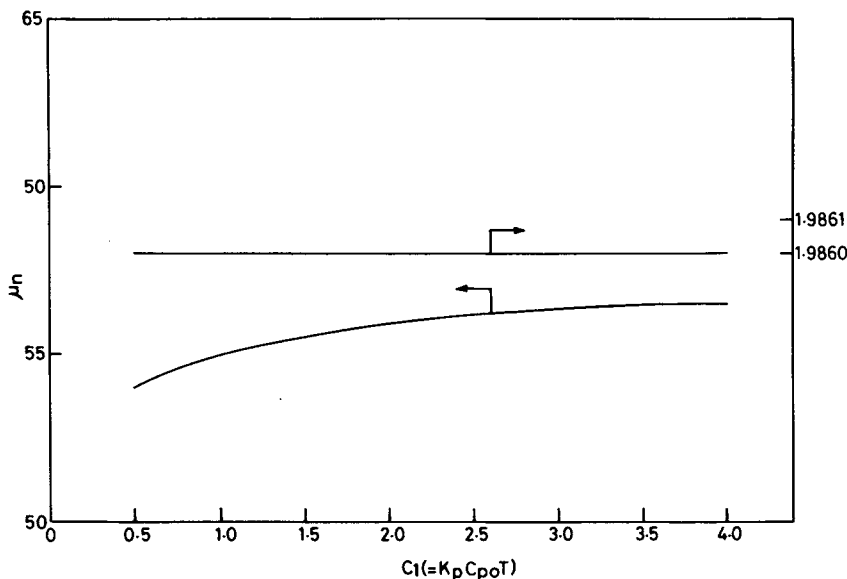


Fig. 4. Effect of C_1 on chain length average and polydispersity index at $\xi = 1$: $C_2 = 10^{-5}$, $C_3 = 2000$, $C_4 = 1000$.

T_f or a decrease in the film thickness. In Figure 5, the effect of the variation of C_2 on the number-average chain length and the PDI of the polymer has been studied, and both these quantities are found to decrease as C_2 is increased. From Figure 4 it has already been demonstrated that on the reduction of T_p , the terminal molecular weight increases. Therefore, from

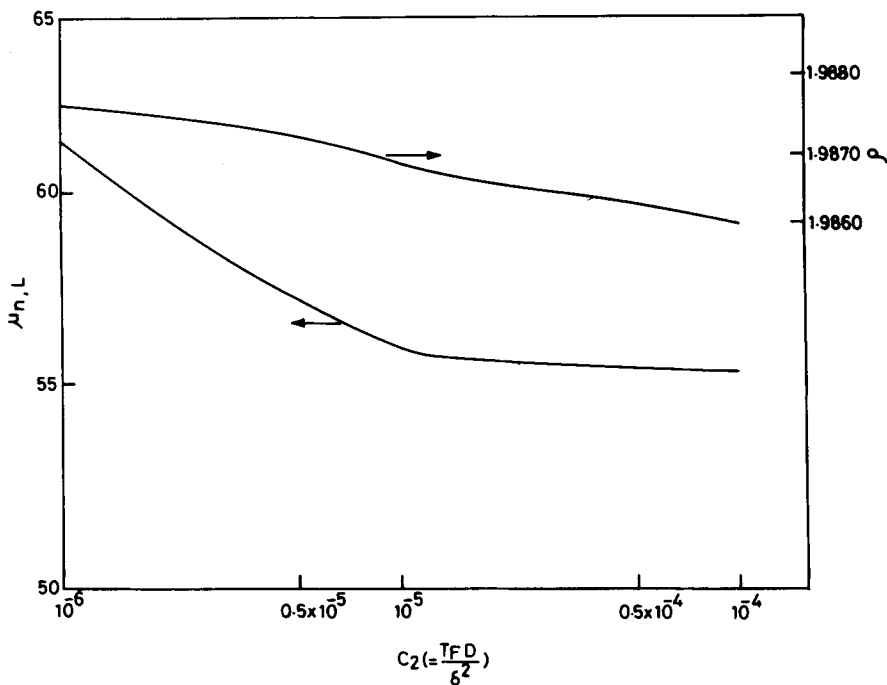


Fig. 5. Effect of C_2 on μ_n and ρ at $\xi = 1$: $C_1 = 2$, $C_3 = 2000$, $C_4 = 1000$.

Figure 5, it is inferred that, as the film thickness is increased, the terminal molecular weight (as well as the PDI) increases. Physically the amount of material exposed to the vacuum in the film increases with increasing δ , and, consequently, the amount of condensation product removed also increased.

Among the various parameters in this formulation, C_4 is found to be the most important one. This is because it involves the surface area S . While generating Figure 6, S has been taken as a parameter. It may be recognized that in the strictest sense S is the area offered by the interface. This implies that S can be increased only by an increase in the diameter of the wiped film reactor. While modeling the film by a flat plate, we have ignored the bubble formation in the film completely. An order of magnitude calculation easily reveals that the value of the surface area S required to attain experimentally attained values of μ_n in pilot experiments exceeds the actual film interface by a few orders of magnitude. It is well known that in the film there are small-size bubbles which are generated at the metallic drum surface and they move towards the interface. The condensation product diffuses from the adjoining areas to these bubbles which grow in size because of this mass transfer. The approximation of the film by a flat plate introduces an artificiality in the sense that only a very small fraction of the film (Fig. 1) is active in mass transfer as opposed to the actual situation where the entire film is active. The mass transfer to a single bubble has been a subject of several earlier studies⁸⁻¹² and is complex. In the present model, the surface area S has been taken as a parameter just to account for the mass transfer to the bubbles in the film. This is consistent with earlier studies of wiped film reactors,²⁻⁴ but whether we can actually do this or not would depend whether the domains associated with a given

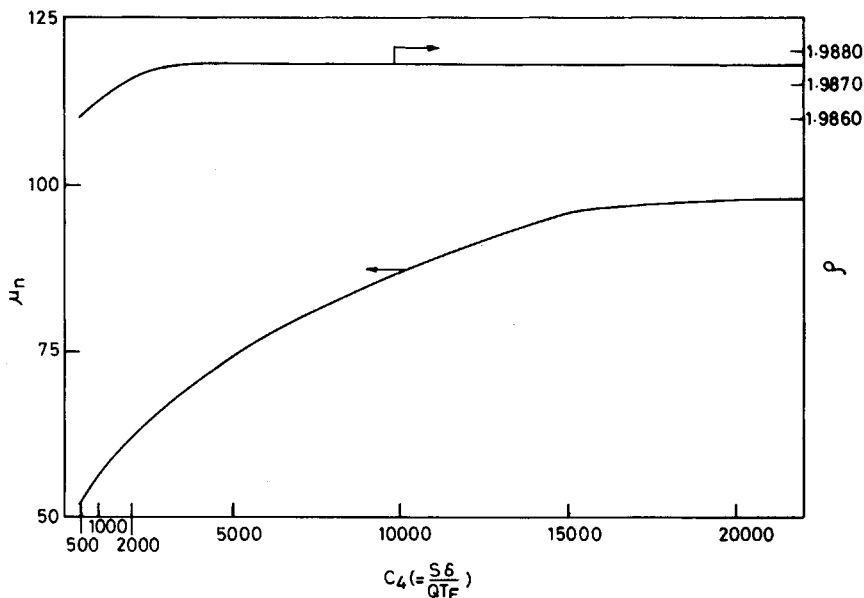


Fig. 6. Effect of C_4 on μ_n and p at $\xi = 1$: $C_1 = 2$, $C_2 = 10^{-5}$, $C_4 = 2000$.

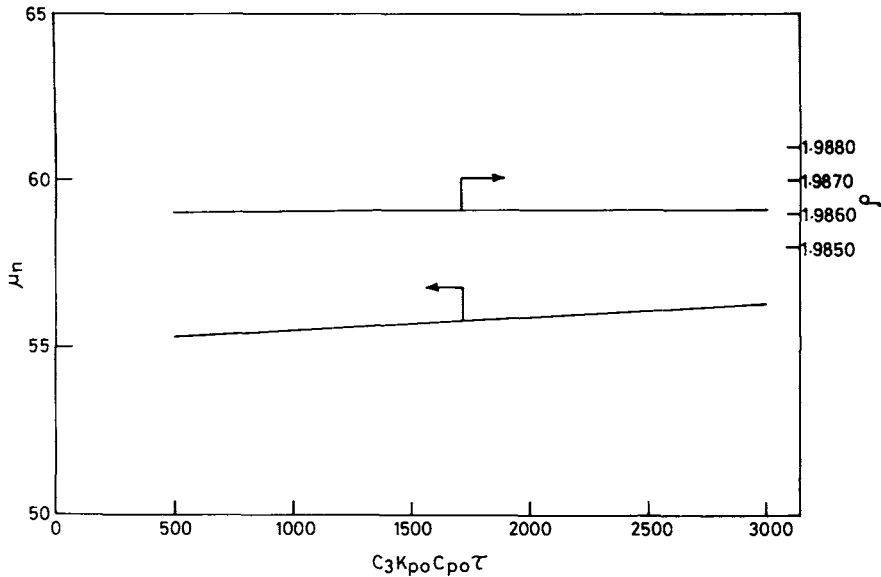


Fig. 7. Effect of C_3 on μ_n and ρ at $\xi = 1$: $C_1 = 2$, $C_2 = 10^{-5}$, $C_4 = 1000$.

bubble does not interact with those of neighboring ones. When the overall polymerization is mass transfer controlled, the increase in S is found to promote polymer formation as seen in Figure 6. However, as S is increased beyond a certain value in this figure, the curve is found to level at an asymptotic value where the overall reaction once again becomes reaction controlled.

In Figure 7, we have varied C_3 , which involves the reactor residence time τ only. As C_3 is increased, higher conversions of functional groups are attained, which is reflected as a higher average chain length at the exit of the reactor. On comparison with the variation of the parameter C_4 , it appears that C_3 has comparatively a much smaller effect on the reactor performance.

CONCLUSIONS

The wiped film reactor for A-R-B polymerization has been modeled and the transport equations for the film and bulk phases have been written. In view of the fact that the transport equations for the film are partial differential equations, the numerical solution of these by the finite difference technique requires considerable computer time. To reduce this, we have used the orthogonal collocation technique by which the partial differential equations can be converted into ordinary differential equations at the collocation points. In doing this, the total number of collocation points is an adjustable parameter, and, on comparison with the finite difference solution, nine collocation points are found to be adequate. The computer time using this technique is found to be halved.

The transport equations for the film and bulk are found to involve four nondimensional parameters C_1 - C_4 , and among these C_4 ($= S\delta/QT_p$) is found to be the most important, thus indicating that the total interphase surface

area, i.e., the film surface as well as those for vapor bubbles formed within the film, is an extremely important modeling parameter.

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