

# Simulation of AA + B'B'' type reversible polymerizations with mass transfer of condensation product

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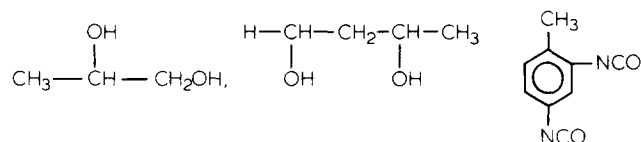
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Simulations have been carried out on AA + B'B'' type reversible polymerizations (where A, B' and B'' are functional groups, with B' and B'' reacting with A at different rates) with simultaneous removal of the condensation by-product. Three idealized models of industrial reactors have been considered. These include a wiped-film reactor, a pool-reactor with the reaction mass as the continuous phase and a pool-reactor with vapour as the continuous phase. The degree of polymerization and the concentration of functional groups are obtained as a function of the various rate constants as well as the parameters characterizing the reactor.

**Keywords** Simulation; unequal reactivity; mass transfer; polymerization; degree of polymerization; functional groups; conversion

## INTRODUCTION

Although the gross features of polymerization are explained fairly well by using Flory's equal reactivity (of functional groups) hypothesis<sup>1-3</sup>, several real systems violate this assumption. Different kinetic models have been proposed to explain the behaviour of such systems and these have been reviewed recently<sup>4</sup>. One common class of polymerization which is often encountered is the AA + B'B'' type, where A, B' and B'' are functional groups with B' and B'' reacting with A at different rates. Examples of this include the reaction of asymmetrical compounds like<sup>5-7</sup>



Some theoretical work has been reported recently on the kinetics of such polymerizations. Case<sup>5</sup> obtained the molecular weight distribution of the polymeric product in terms of the probabilities of reactions of the functional groups A, B' and B''. Gandhi and Babu<sup>6</sup> completed the analysis by obtaining these probabilities as functions of time for various values of the rate constants. Recently, Ozizmer and Odian<sup>7</sup> obtained the conversion of functional groups and the degree of polymerization as functions of time and confirmed their results. In all of these studies, however, the reactions were assumed to be irreversible. This is not so under practical situations and usually, a vacuum is applied to the reaction mass to remove the condensation by-product and thus drive the reaction in the forward direction. In this work, we have studied the effect of applying a vacuum to the reaction mass, with reversible polymerization of the AA + B'B''

type taking place. Three idealized reactor geometries shown in *Figure 1* have been chosen for this study. These correspond to three commonly encountered actual reactors<sup>8</sup>. In one reactor (wiped-film type), polymerization occurs in a thin film inside a cylindrical tank and a vacuum is applied inside. Since the film is thin, the effect of curvature is small and the reaction may be modelled as shown in *Figure 1(a)* where the cylindrical reactor mass is replaced by an infinite slab of thickness  $L$ . A pool-type reactor is another possibility in which an inert gas is bubbled through as in nylon-6 (or the condensation product may itself vaporize, forming gas bubbles which move towards the surface). In general, the gas bubbles will be of all sizes and will be randomly distributed. However, a simple model of such a reactor would be to assume equal-sized, spherical gas bubbles distributed uniformly. One can then associate with each bubble of radius  $R_1$ , a hollow spherical shell of the reaction mass extending over  $R_1 \leq r \leq R_2$  (*Figure 1(c)*) with the condensation product diffusing toward the hollow space, where its concentration is lower. At  $r = R_2$ , the outer surface of this hollow sphere, conditions are symmetrical on either side. The third system is a pool of polymerizing material with an extremely rapid vaporization of the reaction by-product, W. In such situations, the reaction mass is no more continuous but gets isolated into several small regions separated by the vaporized W, as shown in *Figure 1(b)*. A simple model of this situation would be to consider each reacting zone as a sphere of radius  $R_2$ , with diffusion of W from its interior to the surface  $r = R_2$ . The behaviour of real reactors will be fairly well described by these idealized geometries<sup>8</sup>. In the analysis of the various reactor geometries presented, the monomer and its higher oligomers are assumed not to diffuse, whereas the condensation product, W, diffuses through the reaction mass. A spatial concentration gradient of W is established, which varies with time. The mass balance equation for W is a nonlinear partial

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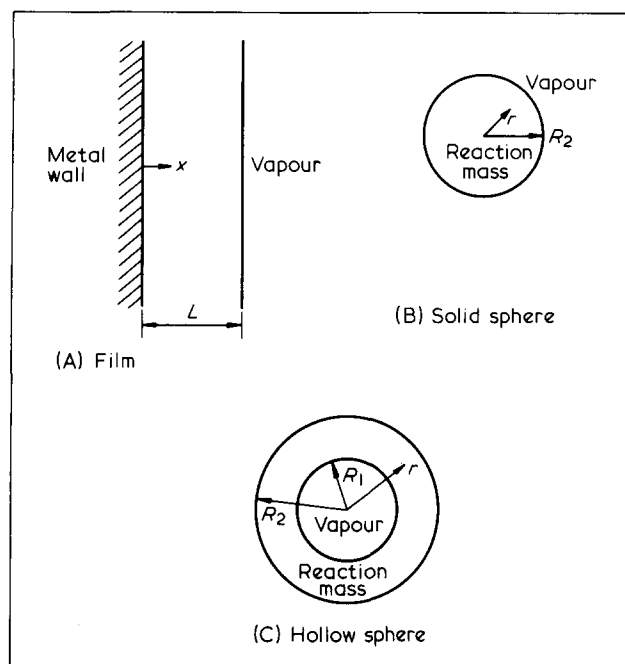
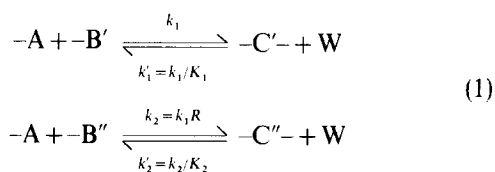


Figure 1 Three idealized models of polymerization reactors

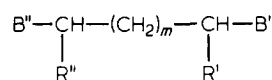
differential equation which is coupled with the balance equations of the other species in the reaction mass. The finite difference method is used to solve these equations simultaneously and the degree of polymerization,  $\mu_n$ , and the conversion of functional groups are determined as a function of the reaction time and of the various reaction parameters.

## FORMULATION

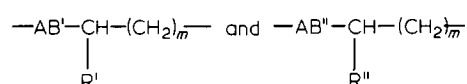
The kinetic scheme chosen for this study is represented in terms of functional groups as



where  $-C'$  and  $-C''$  represent the reacted groups  $-AB'$  and  $-AB''$  respectively and  $W$  is the condensation by-product. In writing equation (1), it is assumed that because the two groups  $-AB'$  and  $-AB''$  are structurally different, the reactivity of  $W$  with these is going to be different. For example, if one uses the following monomer



where  $R'$  and  $R''$  differ, then  $-AB'$  and  $-AB''$  will also differ kinetically since the 'local' structures as shown below are different:



Mass balance equations may now be written for the various geometries of Figure 1 assuming that only the condensation by-product can diffuse through the reaction

mass. This assumption has been justified and used by earlier workers<sup>8-12</sup> to study other reaction schemes. The equations to be solved simplify to the following set of coupled partial differential equations:

$$\begin{aligned}
 \frac{\partial [A]}{\partial t} &= -k_1[A][B'] + k_1[C'][W] \\
 &\quad -k_2[A][B''] + k_2[C''][W] \\
 \frac{\partial [B']}{\partial t} &= -k_1[A][B'] + k_1[C'][W] \\
 \frac{\partial [B'']}{\partial t} &= -k_2[A][B''] + k_2[C''][W] \\
 \frac{\partial [C']}{\partial t} &= k_1[A][B'] - k_1[C'][W] \\
 \frac{\partial [C'']}{\partial t} &= k_2[A][B''] - k_2[C''][W] \\
 \frac{\partial [W]}{\partial t} &= D_w \left\{ \frac{\partial^2 [W]}{\partial \zeta^2} + \frac{\lambda}{\zeta} \frac{\partial [W]}{\partial \zeta} \right\} \\
 &\quad + k_1[A][B'] + k_2[A][B''] \\
 &\quad - k_1[C'][W] - k_2[C''][W]
 \end{aligned} \quad (2)$$

In equation (2),  $[ ]$ , represents molar concentrations,  $D_w$  is the diffusivity of the condensation product,  $\zeta = x$ ,  $\lambda = 0$  is used for the film (Figure 1a) and  $\zeta = r$ ,  $\lambda = 2$  for the solid (Figure 1b) and hollow-sphere (Figure 1c) idealizations of the polymerization reactor.

The initial and boundary conditions used in this study are taken as follows.

Initial conditions: at  $t = 0$ :  $0 \leq x \leq L$  or  $0 \leq r \leq R_2$  or  $R_1 \leq r \leq R_2$

$$\begin{aligned}
 [A] &= [A]_0 \\
 [B''] &= [B'] = \frac{1}{2}[A]_0 \\
 [C'] &= [C''] = [W] = 0
 \end{aligned} \quad (3a)$$

Boundary conditions: at  $t > 0$ :

$$\begin{aligned}
 [W] &= [W]_s \quad \text{at } x = L \text{ (film)} \\
 &\quad \text{or} \\
 &\quad \text{at } r = R_2 \text{ (solid sphere)} \\
 &\quad \text{or} \\
 &\quad \text{at } r = R_1 \text{ (hollow sphere)}
 \end{aligned}$$

$$\begin{aligned}
 \text{(i)} \quad \frac{\partial [W]}{\partial x} &= 0 \quad \text{(no flux) at } x = 0 \text{ (film)} \\
 &\quad \text{or} \\
 \text{(ii)} \quad \frac{\partial [W]}{\partial r} &= 0 \quad \text{at } r = 0 \text{ (solid sphere)} \\
 &\quad \text{or} \\
 &\quad \text{at } r = R_2 \text{ (hollow sphere)}
 \end{aligned} \quad (3b)$$

The initial conditions represent the use of stoichiometric amounts of the pure monomers as the feed.

This has been selected in order to facilitate comparison of our results with those of irreversible polymerization studied by Ozizmer and Odian<sup>7</sup>. Other workers<sup>10</sup> who have studied mass transfer effects in polycondensation reactors have assumed an equilibrium prepolymer as the starting material which is closer to the operations carried out industrially.

In the boundary conditions used, symmetry has been assumed at the centre of the solid sphere or at  $R = R_2$  in the hollow sphere and  $[W]_s$  is the equilibrium concentration in the liquid phase at the surface at which the vacuum is applied.  $[W]_s$  is related to the partial pressure of W in the gas phase through some thermodynamic relationship. In most physical situations, a constant vacuum is applied on the reaction mass and so, rigorously,  $[W]_s$  should change with time as the degree of polymerization and the concentration vary with time but this effect has been ignored to keep the analysis simple. An improved model would be to assume Flory-Huggin's theory<sup>1,2</sup> and use the characteristics of the vacuum pump (usually constant pumping speeds<sup>13</sup>) to obtain  $[W]_s$  as a function of time.

The average value of the concentration of any species, for example, W, is obtained by using the following equation:

$$\begin{aligned} [\bar{W}] &= \frac{1}{L} \int_0^L [W] dx \text{ (film)} \\ &= \frac{3}{R_2^3} \int_0^{R_2} [W] r^2 dr \text{ (solid sphere)} \\ &= \frac{3}{R_2^3 - R_1^3} \int_{R_1}^{R_2} [W] r^2 dr \text{ (hollow-sphere)} \end{aligned} \quad (4)$$

The number average chain length,  $\mu_n$ , at any position in the reaction mass is given by<sup>7</sup>

$$\mu_n = \frac{[A]_0}{[A]} \quad (5)$$

An alternative method of defining  $\mu_n$  in an AA + B'B'' type system would be to equate it to the average number of -AB'- or -AB''- linkages per molecule in the reaction mass. This gives

$$\mu_n^* = \frac{[A]_0 - [A]}{[A]} \quad (6)$$

Again, the definition in equation (5) is used in order to facilitate comparison with results of Ozizmer and Odian<sup>7</sup>. The spatial average value,  $\bar{\mu}_n$ , can be obtained using equation (5) with  $[\bar{A}]$  used instead of  $[A]$ .

Equations (2) were non-dimensionalized by using the following variables:

$$R = k_2/k_1, K_1 = k_1/k'_1, K_2 = k_2/k'_2, C_s = [W]_s/[A]_0$$

$$a = [A]/[A]_0, b' = [B']/[A]_0, b'' = [B'']/[A]_0,$$

$$c' = \frac{[C']}{[A]_0}, c'' = \frac{[C'']}{[A]_0}, w = [W]/[A]_0,$$

$$\theta = k_1[A]_0 t, \xi = \{k_1[A]_0/D_w\}^{1/2} \zeta \quad (7)$$

and the forward finite difference technique<sup>8,14,15</sup> was used to obtain the concentrations of the various species at any location  $\{\xi = (J-1)\Delta\xi\}$  at time  $\theta + \Delta\theta$  in terms of the values at time  $\theta$ . The simplified equations were as follows<sup>16</sup>:

$$\begin{aligned} {}^{\theta+\Delta\theta}w_J &= {}^\theta w_{J+1} \left\{ 1 + \frac{\lambda}{(J-1)} \right\} \frac{\Delta\theta}{(\Delta\xi)^2} \\ &\quad - {}^\theta w_J \left\{ 2 \left( 1 + \frac{\lambda}{J-1} \right) \frac{\Delta\theta}{(\Delta\xi)^2} - 1 \right\} \\ &\quad + {}^\theta w_{J-1} \frac{\Delta\theta}{(\Delta\xi)^2} + \Delta\theta \left\{ {}^\theta a_J {}^\theta b'_J + R {}^\theta a_J {}^\theta b''_J - \frac{{}^\theta w_J {}^\theta c'_J}{K_1} - \frac{R}{K_2} {}^\theta c''_J {}^\theta w_J \right\} \\ {}^{\theta+\Delta\theta}a_J &= \Delta\theta \left\{ - {}^\theta a_J {}^\theta b'_J + \frac{{}^\theta w_J {}^\theta c'_J}{K_1} - R {}^\theta a_J {}^\theta b''_J + \frac{R}{K_2} {}^\theta c''_J {}^\theta w_J \right\} + {}^\theta a_J \\ {}^{\theta+\Delta\theta}b'_J &= \Delta\theta \left\{ - {}^\theta a_J {}^\theta b'_J + \frac{{}^\theta w_J {}^\theta c'_J}{K_1} \right\} + {}^\theta b'_J \\ {}^{\theta+\Delta\theta}b''_J &= \Delta\theta \left\{ - R {}^\theta a_J {}^\theta b''_J + \frac{R}{K_2} {}^\theta c''_J {}^\theta w_J \right\} + {}^\theta b''_J \\ {}^{\theta+\Delta\theta}c'_J &= \Delta\theta \left\{ {}^\theta a_J {}^\theta b'_J - \frac{{}^\theta w_J {}^\theta c'_J}{K_1} \right\} + {}^\theta c'_J \\ {}^{\theta+\Delta\theta}c''_J &= \Delta\theta \left\{ R {}^\theta a_J {}^\theta b''_J - \frac{{}^\theta c''_J {}^\theta w_J}{K_2} \right\} + {}^\theta c''_J \end{aligned} \quad (8)$$

where the notation  ${}^\theta p_J$  indicates the values of  $p$  at the spatial location  $J\{\xi = (J-1)\Delta\xi\}$  and at time  $\theta$ . L'Hospital's rule and symmetry are applied to obtain expression for the values of  ${}^{\theta+\Delta\theta}w_0$  (centre of sphere or at  $x=0$  for the slab) to give

$$\begin{aligned} {}^{\theta+\Delta\theta}w_0 &= 2 {}^\theta w_1 \frac{\Delta\theta}{(\Delta\xi)^2} (1 + \lambda) + {}^\theta w_0 \left\{ 1 - \frac{2(\lambda+1)}{(\Delta\xi)^2} \Delta\theta \right\} \\ &\quad + \Delta\theta \left\{ {}^\theta a_0 {}^\theta b'_0 + R {}^\theta a_0 {}^\theta b''_0 - \frac{{}^\theta w_0 {}^\theta c'_0}{K_1} - \frac{R}{K_2} {}^\theta c''_0 {}^\theta w_0 \right\} \end{aligned} \quad (9)$$

For assuring proper convergence of the numerical results, we have taken<sup>14,15</sup>

$$(\Delta\xi)^2 = (2 + \lambda)\Delta\theta \quad (10)$$

The dimensionless concentration profile of the various species in the reaction mass and  $\mu_n$  were computed as a function of the dimensionless time for several values of  $R$ ,  $K_1$ ,  $K_2$  and  $C_s$ . The values chosen for the other 'size' parameters appearing in the analysis were as follows:

$$\text{Film:} \quad \{k_1[A]_0/D_w\}^{1/2} L = 2$$

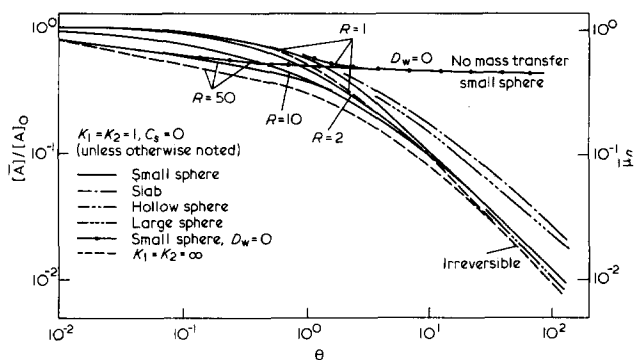


Figure 2 Effect of reactor parameters on  $\bar{\mu}_n$  for  $K_1 = K_2 = 1$ . Curves for  $R = 1$  and 50 only shown for cases other than the small solid sphere with mass transfer

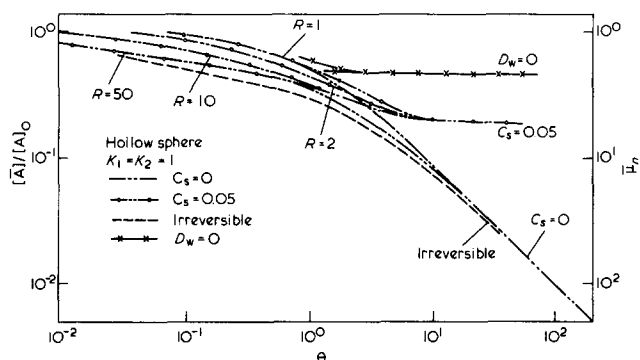


Figure 3 Effect of vacuum on  $\bar{\mu}_n$  for  $K_1 = K_2 = 1$  for the hollow sphere

Solid sphere:  $\{k_1[A]_0/D_w\}^{1/2}R_2 = 2$  (small sphere)  
 $\{k_1[A]_0/D_w\}^{1/2}R_2 = 4$  (large sphere)

Hollow sphere:  $\{k_1[A]_0/D_w\}^{1/2}R_1 = 2$   
 $\{k_1[A]_0/D_w\}^{1/2}R_2 = 2.52$   
 (same mass as small sphere) (11)

These values of the dimensionless parameters represent commonly encountered range of values in polymerization reactors, as discussed by Gupta *et al.*<sup>8</sup> and Amon and Denson<sup>10</sup>.

Computations were carried out using several values of the time increment, each half the value of the previous run, till a further reduction did not yield any different results. The longest run (going till  $\theta = 100$  and with 11 spatial grid points) took about 7 minutes computer time.

### RESULTS AND DISCUSSION

Several simulation runs were carried out to study the effect of various kinetic and reactor design parameters. Runs were made assuming the reactions in equation (1) to be irreversible ( $K_1 = K_2 = \infty$ ) and results were found to match those of Ozizmer and Odian<sup>7</sup> and Gandhi and Babu<sup>6</sup>. As expected, the reactor design parameters studied here had no effect on these results.

Figures 2 and 3 show the effects of some reactor design parameters on  $\bar{\mu}_n$  for  $K_1 = K_2 = 1$  and different values of  $R$ . For the small solid sphere, it is observed that because of

the application of a high vacuum, the  $\bar{\mu}_n$  versus  $\theta$  curve shifts towards the curve for the irreversible case<sup>6,7</sup> from that corresponding to the no-mass-transfer case. For the latter, equilibrium is attained at a fairly low value of  $\bar{\mu}_n$ . It is also observed that the effect of the forward-reaction unequal reactivity ( $R$ ) persists till larger times for the irreversible reactions than it does for the no-mass-transfer situation, and lies intermediate between these two, depending on the level of vacuum applied. A comparison of the results on the small sphere with those for a slab having the same  $\xi$  gives the effect of reactor geometry. There is very little difference in the values of  $\bar{\mu}_n$  at low values of  $\theta$  for the sphere and the slab, but at larger  $\theta$  the sphere, which has more surface area per unit volume of the reaction mass than the slab (but has the same distance through which  $W$  has to diffuse), gives higher  $\bar{\mu}_n$ . Similarly, for the hollow sphere described in equation (11), having the same mass as the small sphere, but having a shorter path for  $W$  to diffuse through, there is little difference in  $\bar{\mu}_n$  at low  $\theta$ , but at larger times, higher  $\bar{\mu}_n$  are observed for the hollow sphere than for the solid one. The effect of the degree of vacuum applied is observed to be far more pronounced and is shown in Figure 3 for the hollow sphere.

Figure 4 shows the dimensionless spatial average concentration of B'' as a function of the dimensionless time for various values of the parameters. The trends are the same, i.e., the curves shift from the curve for the no-mass-transfer situation towards that for the irreversible case, the amount of this shift depending upon the resistance offered to mass transfer. Thus, for any  $R$ , the curve for the hollow sphere is the nearest to that for irreversible reactions (due to minimum mass transfer resistance present in this system) while the curve for the infinite slab is the closest to the no-mass-transfer curve for the small sphere. The spread of these curves, specially for  $R = 50$ , are far more than those for  $\bar{\mu}_n$ . Plots for  $[B']/[A]_0$  are not shown since the behaviour of these may be inferred from that of  $[A]/[A]_0$  and  $[B'']/[A]_0$  and the fact that

$$[B'] + [B''] = [A] \quad (12)$$

Figure 5 shows the effect of the kinetic parameters on the spatial average degree of polymerization for the hollow sphere. At high degrees of the applied vacuum

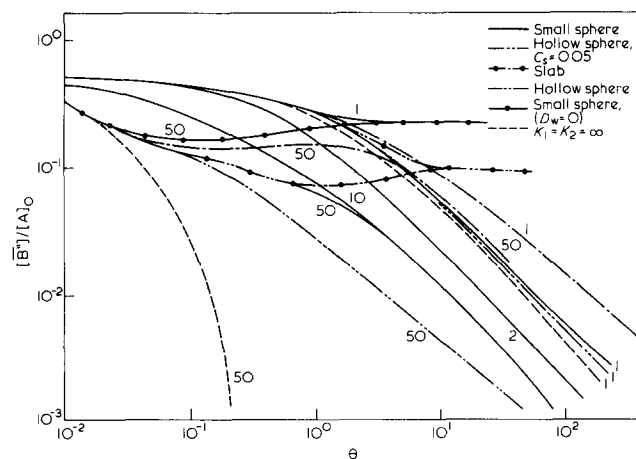


Figure 4 Effect of reactor parameters on  $[B'']$ . Curves for  $R = 1$  and 50 only shown for cases other than the small solid sphere with mass transfer

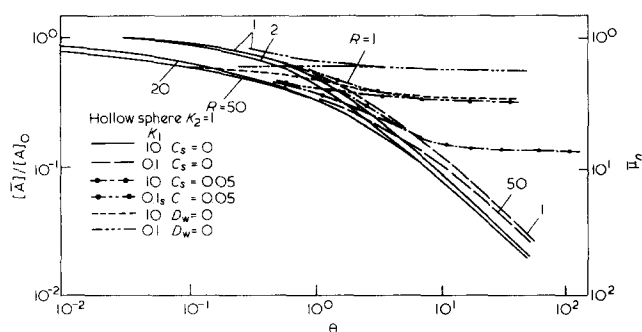


Figure 5 Effect of kinetic parameters on  $\bar{\mu}_n$  for the hollow sphere

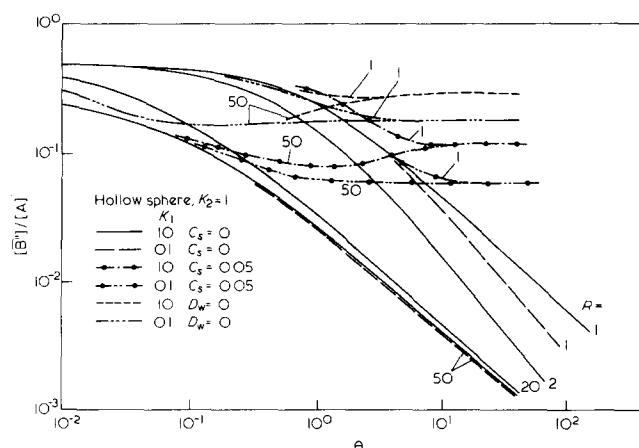


Figure 6 Effect of kinetic parameters on  $[B'']$  for the hollow sphere

( $C_s = 0$ ) the results are not very sensitive to changes in the values of the equilibrium constants  $K_1$  and  $K_2$ . In fact, values of  $\bar{\mu}_n$  for  $K_1 = 10$ ,  $K_2 = 1$  are almost indistinguishable from those corresponding to  $K_1 = K_2 = 1$  and the irreversible cases. At lower vacuum (e.g.,  $C_s = 0.05$ ), speeding up the forward reaction associated with B' ( $K_1 = 10$ ,  $K_2 = 1$ ) leads to higher equilibrium values of  $\bar{\mu}_n$ , as expected intuitively. It may be noted that changing  $K_2$  keeping  $K_1$  fixed would lead to similar results since the roles of B' and B'' get interchanged.

Figure 6 shows the dependence of  $[B'']/[A]_0$  on the kinetic parameters. The concentration of B'' turns out to be more sensitive to these parameters than does  $\bar{\mu}_n$  and even at high vacuums, there is a difference between the concentrations for  $K_1 = 10$  and  $K_1 = 0.1$  with  $K_2 = 1.0$ . Equilibrium concentrations of B'' are lower when  $C_s$  is 0.05 and  $K_1 = 0.1$  than when  $K_1 = 10$ , as expected from the kinetic scheme.

Figure 7 shows the effect of mass-transfer on the spatial dependence of  $\bar{\mu}_n$  for  $R = K_1 = K_2 = 1$ . Substantial variation of  $\bar{\mu}_n$  is observed at different positions of the small sphere. This effect is less at  $C_s = 0.05$  and for the hollow sphere, wherein the driving force for mass transfer is smaller.

## CONCLUSION

Reversible AA + B'B' type condensation polymerizations have been simulated with the condensation by-product diffusing through the reaction mass. Results on functional

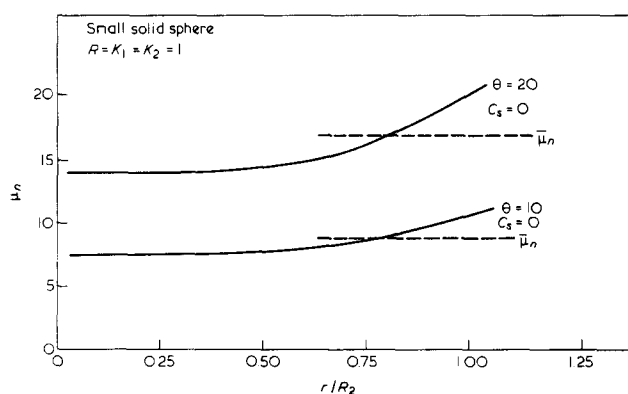


Figure 7 Spatial variation of  $\bar{\mu}_n$  for the small solid sphere.  $K_1 = K_2 = R = 1$ ,  $C_s = 0$

group concentrations and  $\bar{DP}$  are found to lie between two limiting solutions—one corresponding to polymerization in sealed tubes and the other corresponding to irreversible polymerization. Higher  $\bar{DP}$  are obtained when the mass transfer driving force is higher as in the case where higher vacuums are present or when the mass transfer resistance is lower as in geometries with higher surface to volume ratio or shorter diffusion paths. Sparged reactors with several small-size gas bubbles (of the type used for nylon-6<sup>17,18</sup>) are thus superior to wiped-film reactors for manufacturing higher  $\bar{DP}$  polymer. Also, the sensitivity of  $\bar{DP}$  to these reactor variables emphasizes the need for estimating correctly the surface area present in commercial reactors which usually operate under conditions where boiling takes place<sup>10</sup>.

## REFERENCES

- Flory, P. J. Principles of Polymer Chemistry, 1st ed. Cornell University Press, Ithaca 1953
- Kumar, A. and Gupta, S. K. Fundamentals of Polymer Science and Engineering, 1st ed. Tata McGraw Hill, New Delhi, 1978
- Odian, G. Principles of Polymerization, 1st ed. McGraw Hill, New York 1970
- Gupta, S. K. and Kumar, A. Chem. Eng. Commun. in press
- Case, L. C. J. Polym. Sci. 1958, **29**, 455
- Gandhi, K. S. and Babu, S. V. A. I. Ch. E. J. 1979, **25**, 266
- Ozizmer, E. and Odian, G. J. Polym. Sci., Polym. Chem. Edn 1980, **18**, 1089
- Gupta, S. K., Agarwalla, N. L. and Kumar, A. J. Appl. Polym. Sci. in press
- Secor, R. M. A. I. Ch. E. J. 1969, **15**, 861
- Amon, M. and Denson, C. D. Ind. Eng. Chem. 1980, **19**, 415
- Nagasubramanian, K. and Reimschuessel, H. K. J. Appl. Polym. Sci. 1973, **17**, 1663
- Hoflyzer, P. J. and Van Krevelen, D. W. Proc. 4th Eur. Symp. Chem. Reaction Eng., Brussels, 9-11 Sept. 1968, Pergamon Press, New York (1971), p. 139
- Gupta, S. K. Momentum Transfer Operations, 1st ed. Tata McGraw Hill, New Delhi, 1979
- Mickley, H. S., Sherwood, T. K. and Reed, C. E. Applied Mathematics in Chemical Engineering, 2nd ed. McGraw Hill, New York, 1957
- Foust, A. S., Wenzel, L. A., Clump, C. W., Maus, L. and Anderson, L. B. Principles of Unit Operations, 2nd ed. Wiley, New York, 1980
- Agrawal, K. K. M. Tech. Dissertation, Indian Institute of Technology, Kanpur (1981)
- Gupta, S. K., Kumar, A. and Agrawal, K. K. J. Appl. Polym. Sci. in press
- Jacobs, H. and Schweigman, C. Proc. 5th Eur. 2nd Int'l. Symp. Chem. Rxn. Eng., Amsterdam, 2-4 May, 1972, p. B7.1