

# Irreversible Step Growth Polymerization Having Segmental Diffusion Limitations in HCSTRs—Simulation and Steady State Multiplicity

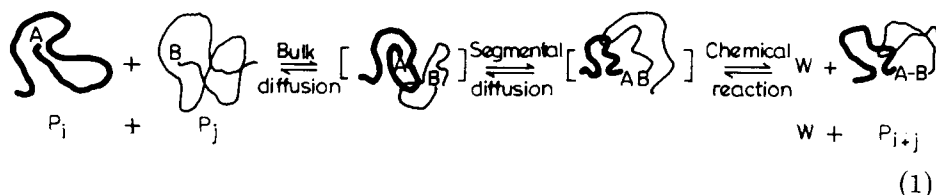
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## Synopsis

The effect of various parameters on the overall rate constant, number average chain length, and polydispersity index of isothermal, irreversible, step growth polymerization of ARB monomers, exhibiting segmental diffusional limitations and carried out in HCSTRs, are studied. A phenomenological model which has proved useful for chain polymerization is adapted for step growth polymerizations and simulations for several values of the different parameters are carried out. The number average chain length  $\mu_n$  and the polydispersity index  $\rho$  are obtained as a function of the dimensionless time  $t^*$ . It is found that, even though the behavior of  $\mu_n$  and  $\rho$  vs.  $t^*$  depends on the values of the parameters, the plot of  $\mu_n$  vs.  $\rho$  is unique as expected from statistical considerations. An attempt has been made to investigate the multiplicity of steady states under conditions of infinitely rapid heat transfer from a jacket, using singularity and bifurcation theory. It is found from the analysis that there is no multiplicity of steady states for this system, which is confirmed by simulations using a wide range of parameter values.

## INTRODUCTION

Step growth polymerization of ARB monomers occurs through several molecular steps. The schematic representation of the various steps can be written as<sup>1-4</sup>



Before chemical reaction between two polymer molecules  $P_i$  and  $P_j$  (having chain lengths  $i$  and  $j$ , respectively) actually occurs, the molecules must diffuse to within close proximity of each other in the reaction mixture. No reaction can occur as long as the functional groups A and B are buried inside the coiled molecules. Segmental diffusion brings these groups together, and a successful collision leads to chemical reaction between them.

The diffusional steps are rapid at low conversions since the viscosity of the reaction mass is low. Under these conditions, the overall reaction is controlled

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by the kinetics alone, without any diffusional influences. Assuming Flory's equal reactivity hypothesis,<sup>1-3</sup> the reaction process can be written as



where  $W$  is the condensation byproduct.

Segmental diffusional limitations are quite severe at high conversions. This effect in step growth polymerization is quite similar to the Tromsdorff or gel effect in chain polymerization. Some work has already been reported on the modeling of this effect<sup>5</sup> in batch reactors, using a simple phenomenological model. The model of Chiu et al.,<sup>6</sup> which has been developed for chain polymerization systems, has been adapted for this purpose due to its simplicity, even though other models have been proposed<sup>7-19</sup> for the gel effect. It is quite well known that all the models for the gel effect are equally good as regards explanation of experimental data, and so the simplest one was used in the earlier study,<sup>5</sup> as well as in the present one.

In this study, irreversible step growth polymerization of ARB type monomers exhibiting segmental diffusional resistances and carried out in isothermal, homogeneous, continuous-flow, stirred tank reactors (HCSTRs) is studied. Such a study is of importance because these reactors provide several advantages (e.g., continuous operation, excellent heat transfer characteristics, etc.) over other reactors. Moreover, several steady state polymerizations in HCSTRs have been found to be associated with interesting multiplicity features,<sup>20</sup> and it was of interest to find out if similar features are exhibited in the present case too. The technique suggested by Balakotaiah and Luss,<sup>21-26</sup> based on singularity theory, has been used to study the multiplicity of steady states for the present case of ARB polymerizations in HCSTRs.

## FORMULATION

In step growth polymerization, diffusion of two large macromolecules having functional groups at their ends towards each other takes place prior to chemical reaction. Due to this segmental diffusional limitation,  $k_p$  in eq. (2) decreases with conversion (or time). This situation is very similar to the effect of segmental diffusional limitations on the termination rate constants of free radical polymerizations, and so a similar model is postulated for the present case. A detailed description of the model is given by Kumar et al.<sup>5</sup> and only the final form of the expressions involving  $k_p$  are presented here for the sake of brevity.  $k_p$  can be written in terms of a reference value  $k_{p,0}$  as

$$\frac{1}{k_p} = \frac{1}{k_{p,0}} + \frac{r_m^2 [P]_b}{3D_o(D/D_o)} \quad (3)$$

where  $D_o$  is the overall (segmental) diffusivity of functional groups at some reference state and  $[P]$  represents the concentration of functional groups ( $\equiv \sum_{n=1}^{\infty} [P_n]$ ). Other terms are defined in Ref. 5. The ratio  $(D/D_o)$  depends

upon the bulk polymer concentration  $[P]_b$  and the temperature<sup>6,21</sup>:

$$\log(D/D_o) = \frac{V_f}{b_1(T) + b_2(T)V_f} \quad (4)$$

where  $V_f$  is the free volume fraction and  $b_1(T)$  and  $b_2(T)$  are empirically determined functions of the temperature  $T$ .  $V_f$ , in turn, is given as<sup>12</sup>

$$V_f = 0.025 + (\alpha_l - \alpha_g)(T - T_g) \quad (5)$$

where  $\alpha_l$  and  $\alpha_g$  are the volume-expansion coefficients of the liquid and glassy polymers, and  $T_g$  is the glass transition temperature of the polymer (a function of the average chain length). A commonly used equation for  $T_g^{2,27,28}$  is

$$\frac{1}{T_g} = \frac{1}{T_{g\infty}} + \frac{K[P]_b}{T_{g\infty}^2} \quad (6)$$

with  $T_{g\infty}$  and  $K$  being empirical constants.

Rearrangements of eqs. (5) and (6) gives

$$V_f = 0.025 + [T_{g\infty}(\alpha_l - \alpha_g)] \left[ \frac{T}{T_{g\infty}} - \frac{T_g}{T_{g\infty}} \right] \quad (7)$$

$$\frac{1}{T_g/T_{g\infty}} = 1 + \frac{K[P]_b}{T_{g\infty}} \quad (8)$$

which are more convenient compared to eqs. (5) and (6).

Equations (3)–(8) involve several parameters. Most of them, however, may be obtained through *independent* experiments on *nonreacting* systems. In the present study (as in the previous one on batch reactors<sup>5</sup>), these parameters are varied one at a time, keeping others at some reference values and numerical results generated to study their effects. The reference values chosen are typical of some common step growth polymerization systems.<sup>5</sup>

(a) *Simulation*. Mole balance equations for an HCSTR (see Fig. 1) can be written as

$$[P_1]_{b,0} = [P_1]_b - 2k_p(\tau)\tau[P_1]_b[P]_b \quad (9a)$$

$$[P_n]_b = \tau k_p(\tau) \left[ \sum_{r=1}^{n-1} [P_r]_b [P_{n-r}]_b - 2[P_n]_b [P]_b \right] \quad (9b)$$

where the subscript 0 refers to the input-stream bulk values,  $b$  refers to the bulk values in the exit stream, as well as in the reactor, and  $\tau$  is the mean residence time ( $= V/Q$ ).  $k_p$  is a function of the conditions in the reactor, and so of the residence time, and is the same for all species,  $P_i$ , as given by eq. (3). The above equation can be appropriately summed up to give equations for the

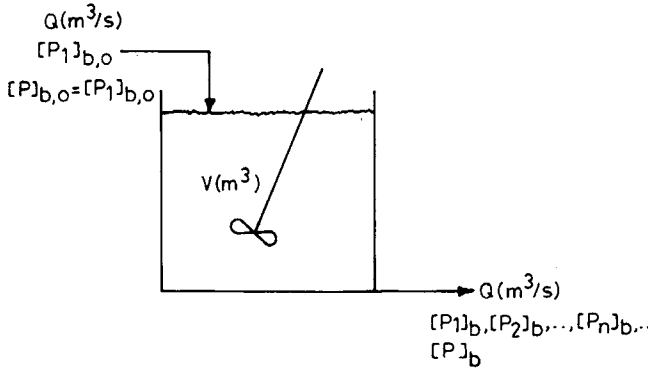


Fig. 1. Notation used for HCSTR.

various moments of the chain length distribution defined as

$$\lambda_i = \sum_{n=1}^{\infty} n^i [P_n]_b, \quad i = 0, 1, \dots \tag{10}$$

to give

$$\lambda_0 = [P]_b \tag{11a}$$

$$\lambda_1 = [P_1]_{b,0} \tag{11b}$$

$$\lambda_2 = 2k_p(\tau)\tau [P_1]_{b,0}^2 + [P_1]_{b,0} \tag{11c}$$

TABLE I  
Dimensionless Equations for Simulating HCSTR Behavior

$t^*(k_p/k_{p,0})[P]^*^2 + [P]^* - 1 = 0$	(a)
$\lambda_2^* = 2t^*(k_p/k_{p,0}) + 1$	(b)
$\mu_n = 1/[P]^*$	(c)
$\rho = [P]^*\lambda_2^*$	(d)
$\frac{1}{(k_p/k_{p,0})} = 1 + \frac{1}{3} \left( \frac{k_{p,0} r_m^2 [P_1]_{b,0}}{D_o} \right) \frac{[P]^*}{(D/D_o)}$	(e)
$\log \left( \frac{D}{D_o} \right) = \frac{V_j}{b_1 + b_2 V_j}$	(f)
$V_j = 0.025 + [T_{g\infty}(\alpha_l - \alpha_g)] \left[ \frac{T}{T_{g\infty}} - \frac{T_g}{T_{g\infty}} \right]$	(g)
$\frac{1}{T_g/T_{g\infty}} = 1 + \left( \frac{K [P_1]_{b,0}}{T_{g\infty}} \right) [P]^*$	(h)
where	
$t^* = \tau k_{p,0} [P_1]_{b,0}$	
$[P]^* = [P]_b / [P_1]_{b,0}$	
$\lambda_2^* = \lambda_2 / [P_1]_{b,0}$	
Functional group conversion, $x = 1 - [P]^*$	

These can be used to determine the polydispersity index  $\rho$  and the number average chain length  $\mu_n$  of the polymer, defined by

$$\rho = (\lambda_2/\lambda_1)/(\lambda_1/\lambda_0) \quad (12a)$$

$$\mu_n = \lambda_1/\lambda_0 \quad (12b)$$

The various equations can easily be made dimensionless, and the final forms of the equations as well as the definition of the variables are given in Table I for a feed stream of pure monomer.

These equations are solved using the following reference values suggested by Kumar et al.<sup>5</sup>:

$$\begin{aligned} \beta_1 &= K [P_1]_{b,0}/T_{g\infty} = 1.0 \\ \beta_2 &= (\alpha_l - \alpha_g)T_{g\infty} = 2.0 \\ \beta_3 &= T/T_{g\infty} = 1.06 \\ \beta_4 &= \frac{k_{p,0}r_m^2[P_1]_{b,0}}{D_0} = 10^6 \\ b_1 &= 0.05 \\ b_2 &= 0.04 \end{aligned} \quad (13)$$

For the above set of dimensionless parameters and for a given value of the dimensionless residence time  $t^*$  [eq. (a) of Table I] is solved for an *assumed* value of  $k_p/k_{p,0}$ . Only one value of  $[P]^*$  so obtained is physically meaningful (the other being negative). This computed  $[P]^*$  is used in eqs. (f)–(h) of Table I to get  $D/D_0$ . Equation (e) of Table I is then used to compute a new value of  $k_p/k_{p,0}$ , and, if this differs from the assumed value by more than some tolerance ( $10^{-5}$ ), it is used as a new estimate, and the computations are repeated. Thus, the method of successive substitutions is used to converge to the correct value of  $[P]^*$  for any  $t^*$ . Once convergence is attained, eqs. (b)–(d) of Table I are used to get the corresponding  $\mu_n$  and  $\rho$ . The CPU time on a DEC 1090 for a set of computations for one set of parameters [eq. (13)] but for a whole range of values  $t^*$  (with intervals of 100 for  $0 < t^* < 1000$ , and  $\Delta t^* = 1000$  for  $1000 \leq t^* \leq 20,000$ ) is 1.35 s. It may be added that eqs. (a) and (e)–(h) of Table I can also be analytically combined into a single nonlinear algebraic equation which can alternatively be solved to give identical numerical solutions. This has indeed been done in our study of the multiplicity of steady states, discussed below.

(b) *Multiplicity*. Recently, Choi<sup>29</sup> studied the multiplicity of steady states for free radical solution polymerizations in an HCSTR, in the presence of heat transfer to a coolant, using the mean residence time as the bifurcation parameter. He used the singularity theory as suggested by Balakotaiah and Luss<sup>21–26</sup> and neglected the presence of the gel effect. In this part of our work, an attempt has been made to investigate the possibility of multiple steady states in HCSTRs, for step growth polymerization of ARB monomers under conditions of infinitely rapid heat transfer (from a jacket) rate but in the presence of diffusional limitations. The dimensionless parameters used are

those given in eq. (13), and the residence time  $t^*$  is used as the bifurcation parameter. The equations of Table I are combined to give the following equation for the functional group conversion  $x$ :

$$F(x, t^*, \beta_1, \beta_2, \beta_3, \beta_4, b_1, b_2) \\ \equiv \frac{1}{3}\beta_4(x^2 - x) + [t^*(x - 1)^2 - x] \exp(d) = 0 \quad (14)$$

where

$$d \equiv 2.303 \left( \frac{0.025 + \beta_2\beta_3 - \beta_2/[1 + \beta_1(1 - x)]}{b_1 + 0.025b_2 + b_2\beta_2\beta_3 - b_2\beta_2/[1 + \beta_1(1 - x)]} \right) \quad (15)$$

The parameter space  $\mathbf{p}^*$  is defined as

$$\mathbf{p}^* = (\beta_1, \beta_2, \beta_3, \beta_4, b_1, b_2) \quad (16)$$

The surface defined by eq. (14) is called the steady state manifold. According to Ref. 26, the surface in the parameter space  $\mathbf{p}^*$  at which a continuous change of parameters causes the appearance or disappearance of a hysteresis type multiplicity is called the hysteresis variety. The following conditions are to be satisfied<sup>26</sup> for the hysteresis variety:

$$F(x, t^*, \mathbf{p}^*) = 0 \quad (17a)$$

$$\frac{\partial F}{\partial x}(x, t^*, \mathbf{p}^*) = 0 \quad (17b)$$

$$\frac{\partial^2 F}{\partial x^2}(x, t^*, \mathbf{p}^*) = 0 \quad (17c)$$

The isola variety<sup>26</sup> similarly defines a surface in the parameter space  $\mathbf{p}^*$ , where a continuous change of parameters causes the appearance or disappearance of an isolated branch and satisfies eqs. 17(a), 17(b), and

$$\frac{\partial F}{\partial t^*}(x, t^*, \mathbf{p}^*) = 0 \quad (18)$$

Similarly, the double limit variety is defined<sup>21</sup> in the parameter space  $\mathbf{p}^*$ , by the four equations

$$F(x_1, t^*, \mathbf{p}^*) = 0 \quad (19a)$$

$$F(x_2, t^*, \mathbf{p}^*) = 0 \quad (19b)$$

$$\frac{\partial F}{\partial x}(x_1, t^*, \mathbf{p}^*) = 0 \quad (19c)$$

$$\frac{\partial F}{\partial x}(x_2, t^*, \mathbf{p}^*) = 0; \quad x_1 \neq x_2 \quad (19d)$$

where  $x_1$  and  $x_2$  represent the relative range of limit points ( $0 < x_1, x_2 < 1$ ).

Details of the algebraic manipulations required for obtaining the hysteresis variety on a  $\beta_3$ - $\beta_4$  plane are given in the Appendix. For a given set of  $b_1, b_2, \beta_1, \beta_2$ , and  $x$  ( $0 < x < 1$ ), the sixth degree polynomial in  $\beta_3$ , as discussed in the Appendix, can be obtained. Real roots (values of  $\beta_3$ ) of this polynomial have been solved for, using the IMSL subroutine ZREAL 1, using the technique discussed. The remaining roots are complex and are not computed. At times two and at times only a single plausible value of  $\beta_3$  ( $\beta_3$  real and positive) are obtained, the remaining solutions being dropped. For each plausible value of  $\beta_3$ , eqs. (14) and (15) are used to obtain the corresponding  $\beta_4$  values. The results give the curve for the hysteresis variety on the  $\beta_3$ - $\beta_4$  plane.

The development of the final equations for the isola variety is far simpler, and is given in the Appendix again. In the double limit variety, one obtains eqs. (36) and (37) of the Appendix. By equating these two equations, a sixth degree polynomial is obtained in  $\beta_3$ , involving  $b_1, b_2, \beta_1, \beta_2, x_1$ , and  $x_2$ , with  $0 < x_1, x_2 < 1.0$ . We define a function  $G'(x_1, x_2, b_1, b_2, \beta_1, \beta_2, \beta_3) = t_1^* - t_2^*$ , where  $t_1^*$  and  $t_2^*$  are the right-hand sides of eqs. (36) and (37). For a given set of values of  $x_1, x_2$  ( $x_1 \neq x_2$ ) and  $0 < x_1/x_2 < \infty$ ,  $b_1, b_2, \beta_1$ , and  $\beta_2$ , an initial guess for  $\beta_3$  is supplied, and the subroutine ZREAL 1 of IMSL is again used to find the values of  $\beta_3$  which make  $G'$  zero.

## RESULTS AND DISCUSSION

In order to test out the computer program for simulation, results were generated for the case of no diffusional limitations ( $k_p/k_{p,0} = 1.0$ ) and the numerical results compared with the analytical solution<sup>3</sup>:

$$\mu_n = \frac{2t^*}{(1 + 4t^*)^{1/2}} \quad (20a)$$

$$= \frac{(2t^* + 1)(\sqrt{1 + 4t^*} - 1)}{2t^*} \quad (20b)$$

Excellent agreement was found. The computer program was then used to generate results for the case when diffusional limitations were present, using the reference values of the parameters [eq. (13)].

A parametric study was performed by varying one parameter at a time, keeping the remaining at their reference values. Figures 2-4 show the influence of the parameter  $\beta_4 (= -k_{p,0}r_m^2[P_1]_{b,0}/D_0)$ . The trend is quite similar to that obtained for batch reactors,<sup>5</sup> although the values of  $t^*$  are much higher in the case of HCSTRs, as expected (see Fig. 5). Figure 2 shows the variation of  $k_p/k_{p,0}$  with  $t^*$ . The change is most significant for values of  $\beta_4$  varying between  $10^5$  and  $10^6$  for conversions of around 97% ( $t^* \sim 2000$ ). Figure 3 shows the variation of the number average chain length  $\mu_n$  with  $t^*$ . It is observed that diffusional limitations start playing a role at conversions of about 93-95% ( $\mu_n > 15-20$ ) for the reference run. These conversions are low enough for HCSTRs to be used commercially, and indeed these reactors are used under such conditions for polyesterifications. The variation of the polydispersity index  $\rho$  is shown in Figure 4. Unlike in batch reactors, the maxi-

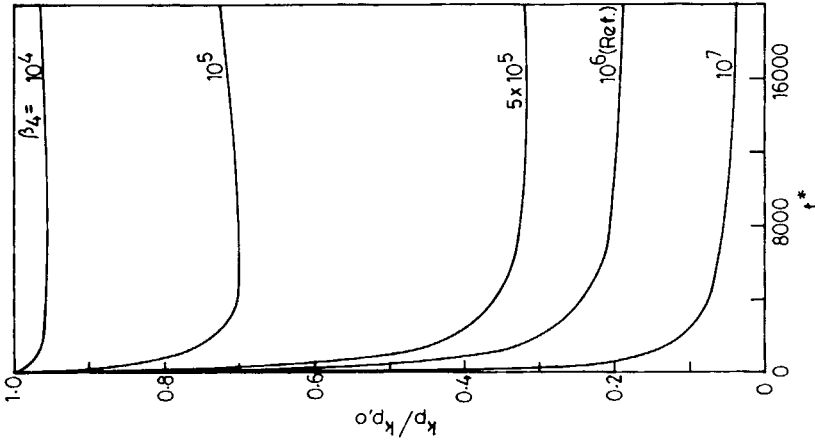


Fig. 2.  $k_p/k_{p,0}$  vs.  $t^*$  with  $\beta_4$  varying. All other parameters at their reference values [eq. (13)].

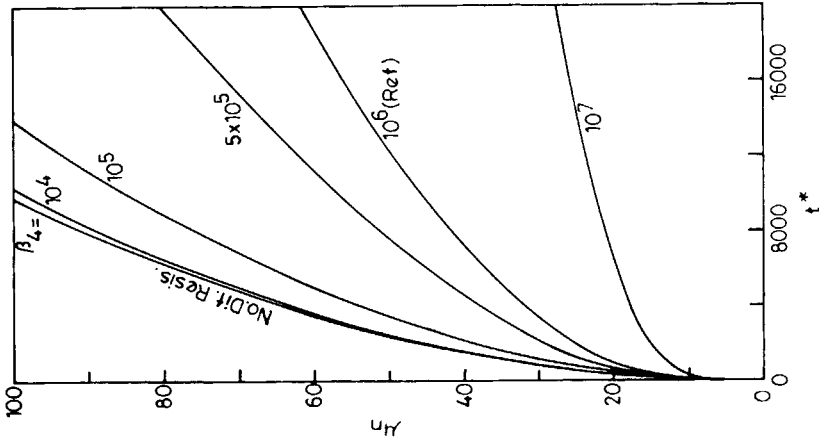


Fig. 3.  $\mu_n$  vs.  $t^*$  with  $\beta_4$  varying.

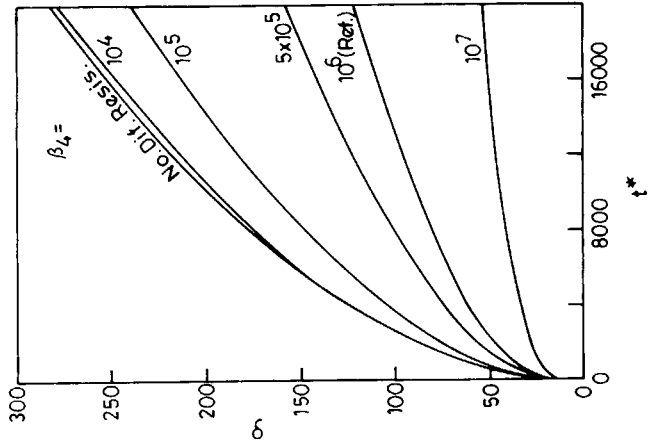


Fig. 4.  $\rho$  vs.  $t^*$  with  $\beta_4$  varying.



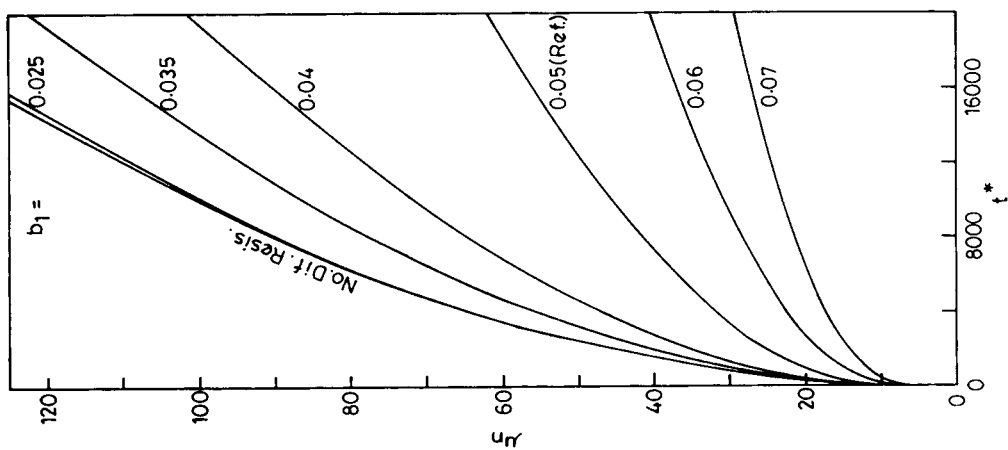


Fig. 7.  $\bar{\mu}_n$  vs  $t^*$  with  $b_1$  as parameter.

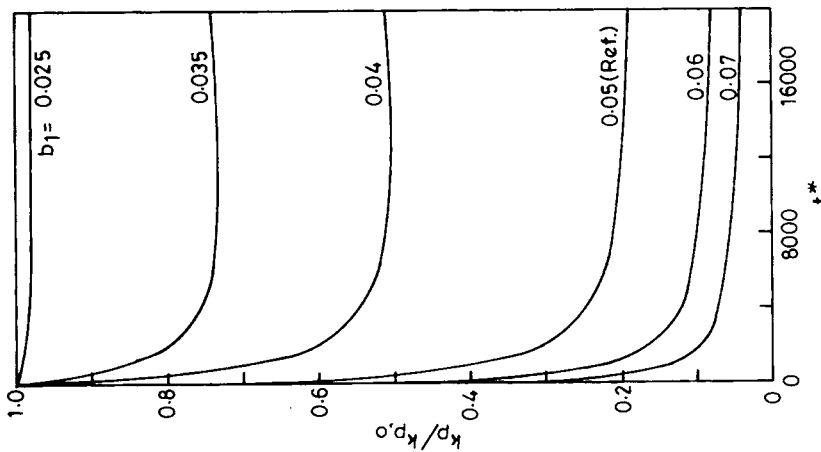


Fig. 6.  $k_p/k_{p,0}$  vs.  $t^*$  with  $b_1$  as parameter.

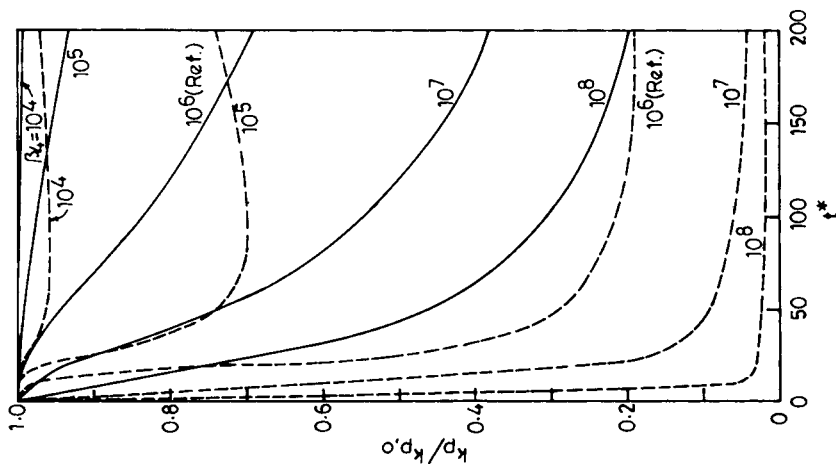


Fig. 5. Comparison of batch reactor<sup>5</sup> (---) and HCSTR (—). Result for different values of  $\beta_4$ . Other parameters have the values given in eq. (13).

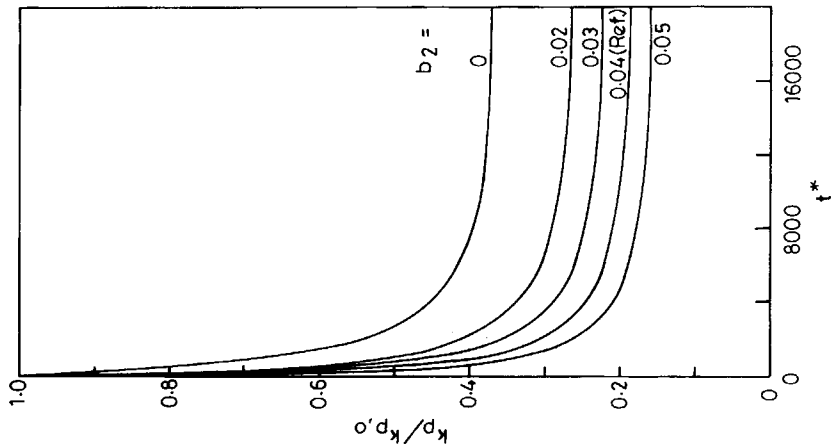


Fig. 8.  $k_p/k_{p,0}$  vs.  $t^*$  with  $b_2$  as parameter.

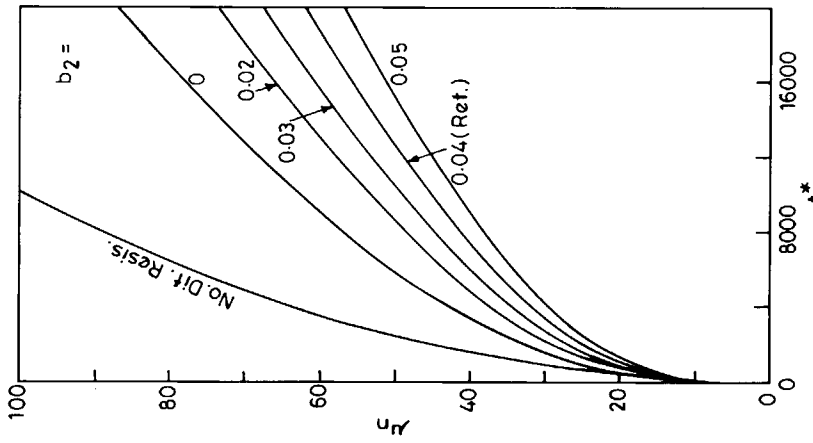


Fig. 9.  $\mu_n$  vs.  $t^*$  with  $b_2$  as parameter.

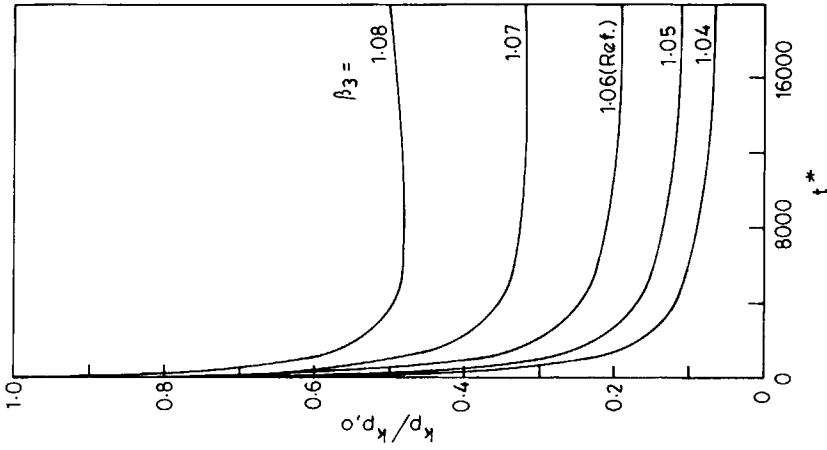


Fig. 10.  $k_p/k_{p,0}$  vs.  $t^*$  with  $\beta_3$  as parameter.

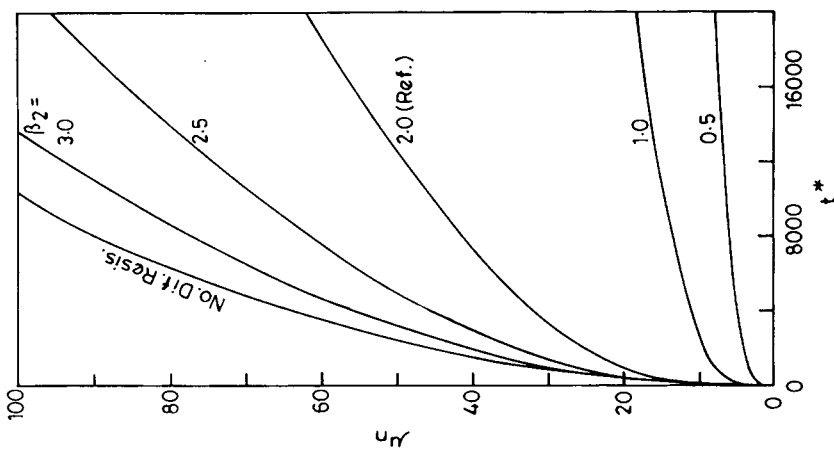


Fig. 13.  $\mu_n$  vs  $t^*$  with  $\beta_2$  as parameter.

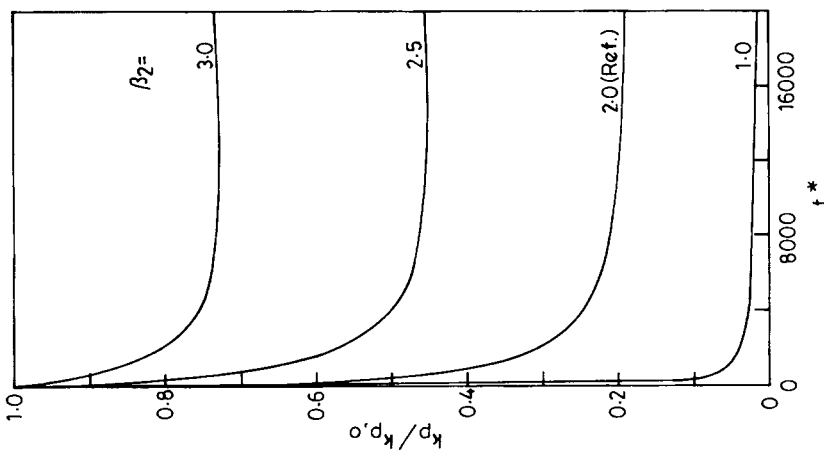


Fig. 12.  $k_p/k_{p,0}$  vs.  $t^*$  with  $\beta_2$  as parameter.

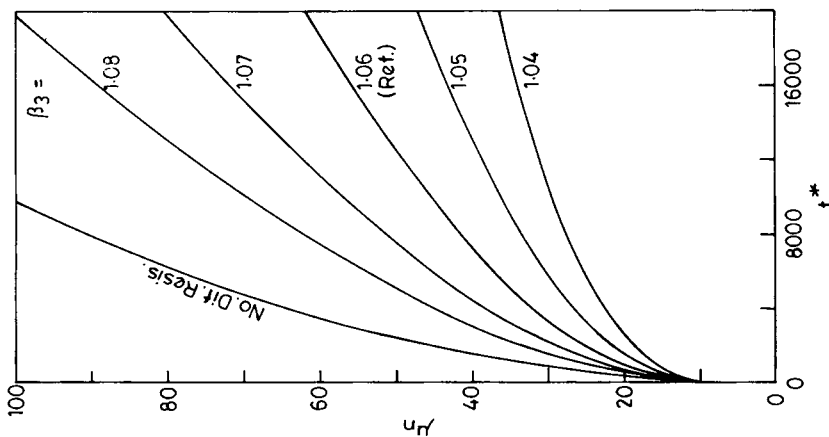


Fig. 11.  $\mu_n$  vs.  $t^*$  with  $\beta_3$  as parameter.

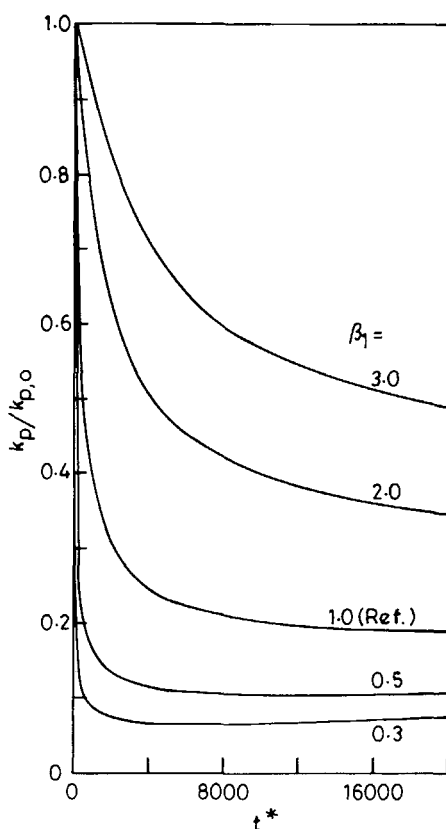


Fig. 14.  $k_p/k_{p,0}$  vs.  $t^*$  with  $\beta_1$  as parameter.

imum value of  $\rho$  is not limited to 2.0 in this case, and the value of  $\rho$  increases continuously as  $t^*$  increases. It may be noted that the plot for  $\beta_4 = 0$  in all these cases corresponds to the results of Biesenberger.<sup>30</sup> Thus, it is observed that lower  $\mu_n$  and  $\rho$  products are formed at any specified  $t^*$  in the presence of diffusional limitations than in their absence. However, eqs. (a)–(d) of Table I can be easily rearranged to show that there is a unique value of  $\rho$  for a given  $\mu_n$ , irrespective of diffusional limitations. This is an interesting, though not surprising (it may be proved statistically), result, and the plot is the same as given by Tadmor and Biesenberger.<sup>31</sup>

The effect of the parameters  $b_1$  and  $b_2$  are shown in Figures 6–9. The results are found to be less sensitive to changes in  $b_2$ , the maximum sensitivity with respect to  $b_1$  being observed in the range  $0.035 < b_1 < 0.05$ .

Figures 10 and 11 show the influence of the parameter  $\beta_3 (= T/T_{g\infty})$ . As expected, lowering the value of  $T_{g\infty}$  or increasing  $T$  reduces the diffusional limitations.

Figures 12–15 shows the effects of the parameters  $\beta_2 [= (\alpha_l - \alpha_g)T_{g\infty}]$  and  $\beta_1 [= K[P_1]_{b,0}/T_{g\infty}]$ , respectively. The trends are again as expected intuitively.

In order to study the multiplicity of steady states in the polymerization of ARB monomers in HCSTRs (under infinitely rapid heat transfer conditions),

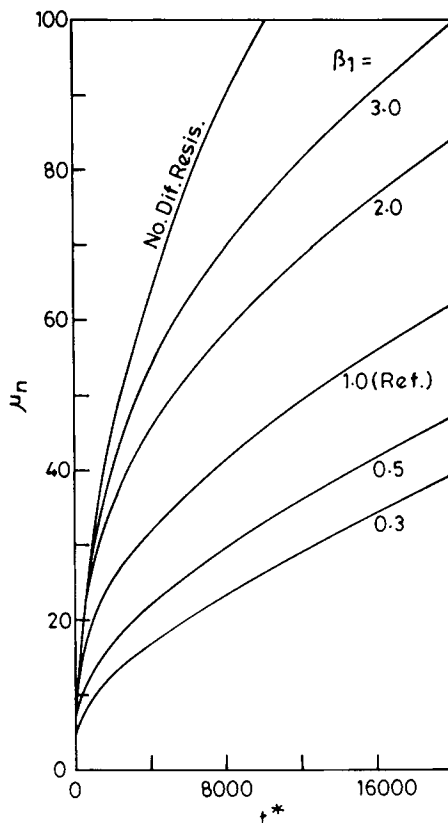


Fig. 15.  $\mu_n$  vs  $t^*$  with  $\beta_1$  as parameter.

the hysteresis, isola and double limit varieties are obtained for the reference values of the parameters  $b_1$ ,  $b_2$ ,  $\beta_1$ , and  $\beta_2$ , as given in eq. (13), and referred to a  $\beta_3$ - $\beta_4$  plane. Numerical results for  $0 < x < 1$  show that the hysteresis variety plot on a  $\beta_3$ - $\beta_4$  plane is as follows:

$$\beta_4 = 0 \quad \text{for } 0 < \beta_3 < 1.4 \tag{21a}$$

$$\beta_4 \ll 0 \text{ (large negative)} \quad \text{for } \beta_3 > 1.4 \tag{21b}$$

Negative values of  $\beta_4$  are physically unrealizable. This suggests that there is no physically meaningful hysteresis variety. Similar results were obtained when  $b_1$ ,  $b_2$ ,  $\beta_1$ , and  $\beta_2$  were changed from their reference values within reasonable limits.

The isola variety is given by eq. (31) of the Appendix. It is found that for all practical values of the parameters  $b_1$ ,  $b_2$ ,  $\beta_1$ ,  $\beta_2$ , and  $\beta_3$ , eq. (31) is not satisfied. This implies that there is no isola variety as well for the present example. In our study of the double limit variety, it was found that, for the entire range of  $x_1$  and  $x_2$  values,  $\beta_3$  values were either zero or negative, which is not plausible. This implies that there is no physically plausible double limit variety either for the parameter values of interest. This system thus exhibits

unique steady states. In fact, numerical simulations for several sets of values of the parameters always led to unique steady states, with no hysteresis, isola, or double limit varieties. It is possible that multiple steady states may be exhibited when one incorporates energy balance equations into the modeling equations as in the case of Choi<sup>29</sup> for chain polymerization (in absence of the gel effect). Work along these lines will require precise functionalities for  $b_1(T)$  and  $b_2(T)$ , which are not yet known for step growth polymerization systems of industrial interest. The equation for the diffusional limitations are indeed available for poly(methyl methacrylate) (PMMA) chain polymerization, and study of multiplicity of steady states for these systems in the presence of the gel effect is continuing.

### CONCLUSIONS

The isothermal polymerization of ARB monomers exhibiting segmental diffusional limitation in HCSTRs is simulated. The effect of various dimensionless parameters are obtained. A study of the multiplicity of steady states using the singularity theory approach of Balakotaiah and Luss<sup>21-26</sup> reveals the absence of hysteresis or isolated branches under physically reasonable values of the various parameters and points to the existence of unique steady states under the conditions studied.

### APPENDIX: DERIVATION OF HYSTERESIS AND ISOLA VARIETIES

#### Hysteresis Variety

Equations (14), (15), and (17b) give

$$\frac{1}{3}\beta_4(2x - 1)(c - gx)^2 = - \left[ (2xt - 2t - 1)(c - gx)^2 + (tx^2 - 2tx - x + t)(ag - bc) \right] \exp(d) \quad (22)$$

and eqs. (17c) and (22) give

$$\begin{aligned} & \frac{2}{3}\beta_4(c - gx)^4 \\ &= -\exp(d) \left\{ 2t(c - gx)^4 + 2(ag - bc)(c - gx)^2(2tx - 2t - 1) \right. \\ & \quad \left. + [2g(c - gx)(ag - bc) + (ag - bc)^2][t(x - 1)^2 - x] \right\} \quad (23) \end{aligned}$$

where

$$a = 2.303[(0.025 + \beta_2\beta_3)(1 + \beta_1) - \beta_2] \quad (24)$$

$$b = 2.303\beta_1(0.025 + \beta_2\beta_3) \quad (25)$$

$$c = (b_1 + 0.025b_2 + b_2\beta_2\beta_3)(1 + \beta_1) - b_2\beta_2 \quad (26)$$

$$g = \beta_1(b_1 + 0.025b_2 + b_2\beta_2\beta_3) \quad (27)$$

Eliminating  $\exp(d)$  between eqs. (14) and (22) and solving for  $t^*$ , one gets

$$t^* = \frac{x^2c[(ag - bc)(x - 1) - (c - gx)^2]}{(x - 1)^2[(c - gx)^2 + x(x - 1)(ag - bc)]} \tag{28}$$

Eliminating  $\exp(d)$  between eqs. (14) and (23), and solving for  $t^*$ ,

$$\begin{aligned} t^* = & x\{2(c - gx)^2[(c - gx)^2 - (x - 1)(ag - bc)] \\ & - x(x - 1)(ag - bc)[2g(c - gx) + ag - bc]\} \\ & \times \{(x - 1)[2(c - gx)^4(x - 1) - 2x(c - gx)^4 \\ & - 4x(x - 1)(ag - bc)(c - gx)^2 - 2gx(c - gx)(ag - bc)(x - 1)^2 \\ & - x(ag - bc)^2(x - 1)^2]\}^{-1} \end{aligned} \tag{29}$$

Equating equations (28) and (29), a sixth degree polynomial in  $\beta_3$ , involving  $b_1, b_2, \beta_1, \beta_2$ , and  $x$  can be obtained.

Instead of actually solving the sixth-degree polynomial in  $\beta_3$ , we defined a function  $G$

$$G(x, b_1, b_2, \beta_1, \beta_2, \beta_3) = t_1^* - t_2^* \tag{30}$$

where  $t_1^*$  and  $t_2^*$  are the expressions on the right-hand sides of eqs. (28) and (29). For a given set of values of  $x, b_1, b_2, \beta_1$ , and  $\beta_2$  an initial guess for  $\beta_3$  is supplied and the subroutine ZREAL 1 tries to improve  $\beta_3$  so that  $G$  becomes zero (within a tolerance of  $10^{-6}$  for  $\beta_3$ ), even if the initial guess is a poor one.

### Isola Variety

For the isola variety, eqs. (14), (15), and (18) give

$$(x - 1)^2 \exp(d) = 0, \quad 0 < x < 1 \tag{31}$$

where  $d$  is given by eq. (15).

### Double Limit Variety

From eq. (19),

$$\frac{1}{3}\beta_4(x_1^2 - x_1) + [t^*(x_1 - 1)^2 - x_1] \exp\left(\frac{a - bx_1}{c - gx_1}\right) = 0 \tag{32}$$

$$\frac{1}{3}\beta_4(x_2^2 - x_2) + [t^*(x_2 - 1)^2 - x_2] \exp\left(\frac{a - bx_2}{c - gx_2}\right) = 0 \tag{33}$$

$$\frac{1}{3}\beta_4(2x_1 - 1) + \left\{ (2x_1t^* - 2t^* - 1) + [t^*x_1^2 - (2t^* + 1)x_1 + t^*] \right. \\ \left. \times \frac{(ag - bc)}{(c - gx_1)^2} \right\} \exp\left(\frac{a - bx_1}{c - gx_1}\right) = 0 \quad (34)$$

$$\frac{1}{3}\beta_4(2x_2 - 1) + \left\{ (2x_2t^* - 2t^* - 1) + [t^*x_2^2 - (2t^* + 1)x_2 + t^*] \right. \\ \left. \times \frac{(ag - bc)}{(c - gx_2)^2} \right\} \exp\left(\frac{a - bx_2}{c - gx_2}\right) = 0 \quad (35)$$

Eliminating  $\exp[(a - bx_1)/(c - gx_1)]$  between eqs. (32) and (34) and solving for  $t^*$ , we get

$$t^* = \frac{x_1^2}{(x_1 - 1)^2} \cdot \frac{(c - gx_1)^2 - (x_1 - 1)(ag - bc)}{x_1(1 - x_1)(ag - bc) - (c - gx_1)^2} \quad (36)$$

Similarly, eliminating  $\exp[(a - bx_2)/(c - gx_2)]$  between eqs. (33) and (35) and solving for  $t^*$ , we get

$$t^* = \frac{x_2^2}{(x_2 - 1)^2} \cdot \frac{(c - gx_2)^2 - (x_2 - 1)(ag - bc)}{x_2(1 - x_2)(ag - bc) - (c - gx_2)^2} \quad (37)$$

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