

## Multiple Steady-State Solutions in an Isothermal Perfectly Mixed Flow Reactor

ABU AHMAD, MIKE N. TREYBIG, and RAYFORD G. ANTHONY,  
*Department of Chemical Engineering, Texas A&M University, College  
Station, Texas 77843*

### Synopsis

The effect of multiple steady solutions in isothermal perfectly mixed flow reactors is illustrated for polymerizations which have autocatalytic rates of initiation and no termination reactions. For feed conditions where more than one steady condition can exist, longer holding times may not necessarily yield higher molecular weight polymer or higher monomer conversions.

### INTRODUCTION

The existence of multiple steady states is well documented for isothermal perfectly mixed flow reactors. Matsuura and Kato<sup>1</sup> discuss the existence of multiple steady states in an isothermal reactor for autocatalytic and heterogeneous reactions. Knoor and O'Driscoll<sup>2</sup> have considered the multiple steady-state conditions for free-radical polymerization in isothermal perfectly mixed flow reactors. They show that monomer conversions obtained at short residence times may be greater than those obtained at long residence times, and that putting perfectly mixed flow reactors (PMFR) in series may not increase production. Gerrens et al.<sup>3</sup> have experimentally verified the existence of multiple steady states for the emulsion polymerization of styrene. For the free-radical polymerization, the possibility of multiple steady states, which is called "concentration stability," is due to the Tromsdorf, or gel effect.

In this work, the effect of concentration stability on monomer and initiator conversions, molecular weights, residence times, and times required to reach steady state is illustrated for anionic polymerizations. Lower molecular weights and monomer conversions are obtained for long residence time, whereas higher molecular weights and conversions are obtained at shorter residence times. In addition, the time required to achieve steady state for the longer residence times may be 15 to 20 times the steady-state residence time.

### THEORY AND DISCUSSION

Bywater et al.<sup>4,5</sup> have suggested that the initiation reaction for polymerization of isoprene or styrene in hydrocarbon solvents with butyllithium may be autocatalytic. As indicated by these investigators, the mechanism for the initiation

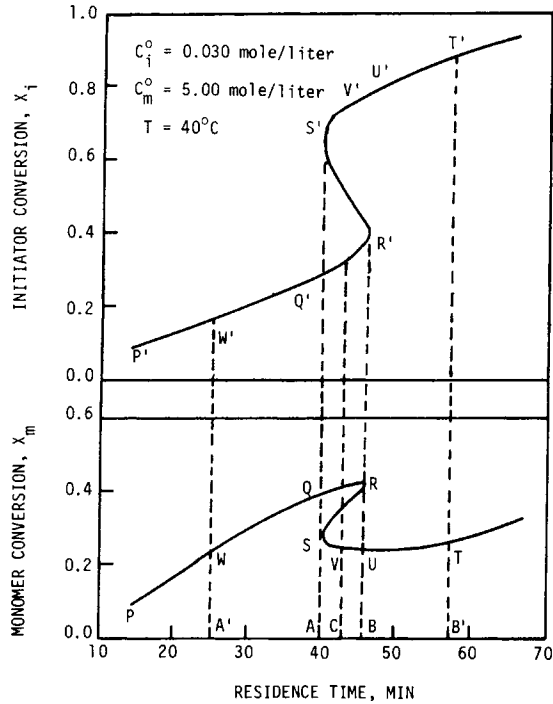


Fig. 1. Effect of residence time on monomer and initiator conversions for polymerization of isoprene in a perfectly mixed flow reactor.

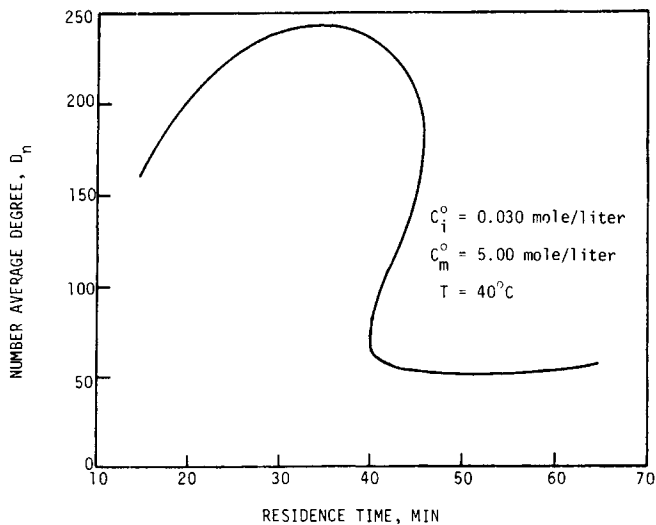


Fig. 2. Effect of residence time on number-average degree for polymerization of isoprene in a perfectly mixed flow reactor.

reaction is very complicated and unknown. Porter et al.<sup>6,7</sup> studied the polymerization of isoprene with butyllithium in the solvent hexane in batch reactors and developed rate equations for the initiation and propagation reactions. The rate equations for the initiation reaction included a term for autocatalytic initiation. Both the initiation and propagation rate equations had the same form

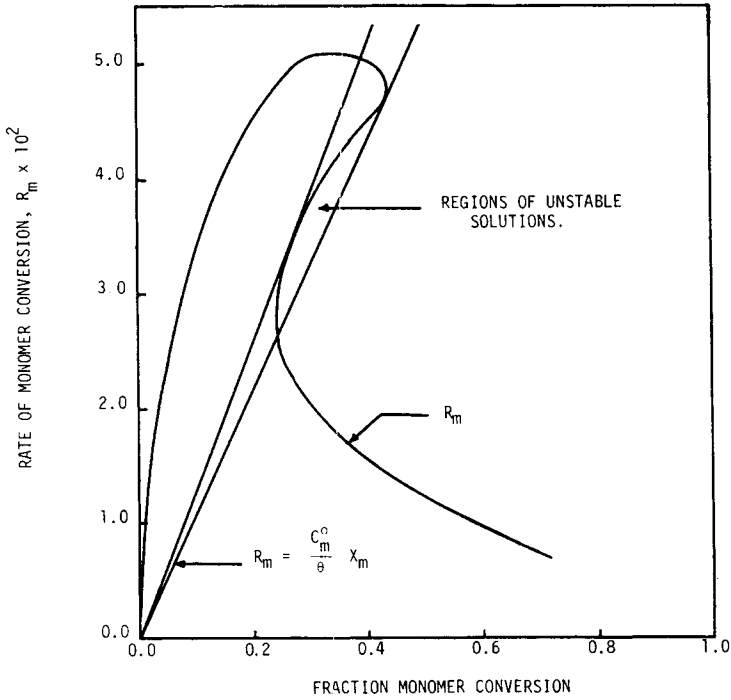


Fig. 3. Rate Function for monomer in an isothermal perfectly mixed flow reactor,  $C_i^0 = 0.03$ ,  $C_m^0 = 5.0$ .

as those obtained by use of the active-site theory in heterogeneous catalysts. Landon et al.<sup>8</sup> obtained similar results for the batch polymerization of styrene with butyllithium in cyclohexane. For these rate equations, which have an autocatalytic term and are of the form obtained for heterogeneous catalyst, the possibility of concentration stability or multiple steady states is suggested.

The rate equations developed by Porter et al.<sup>6,7</sup> are used to illustrate the effect of multiple steady states on monomer and initiator conversions, molecular weights, and the times required to obtain the steady-state solutions. These rate equations are

$$R_i = \frac{k_a(1 + \phi C_p)}{1 + K_1 C_i^2} C_i C_m = \beta_i C_i C_m \quad (1)$$

$$R_p = \frac{k_p}{1 + K_2 C_i^{3/4} + K_3 C_p^3} C_p C_m = \alpha C_p C_m \quad (2)$$

The unsteady-state material balances for a perfectly mixed flow reactor at constant density are as follows:

$$\theta \frac{dC_i}{dt} = C_i^0 - C_i - \beta_i C_i C_m \theta \quad (3)$$

$$\theta \frac{dC_m}{dt} = C_m^0 - C_m - (\beta_i C_i C_m + \alpha C_m C_p) \theta \quad (4)$$

$$\theta \frac{d\lambda_0}{dt} = -\lambda_0 + \beta_i C_i C_m \theta \quad (5)$$

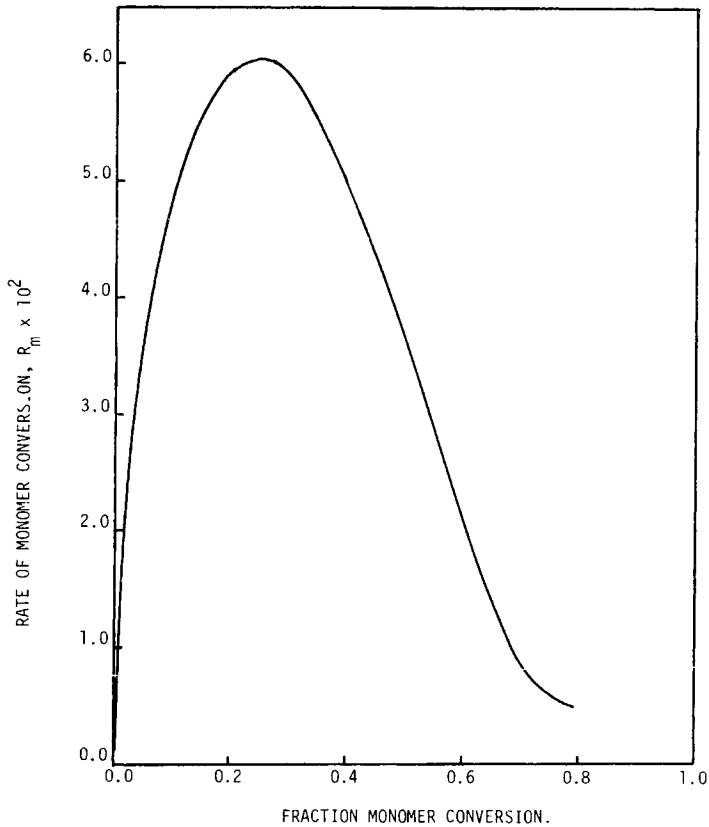


Fig. 4. Rate function for monomer in an isothermal batch reactor,  $C_i^0 = 0.03$ ,  $C_m^0 = 5.0$

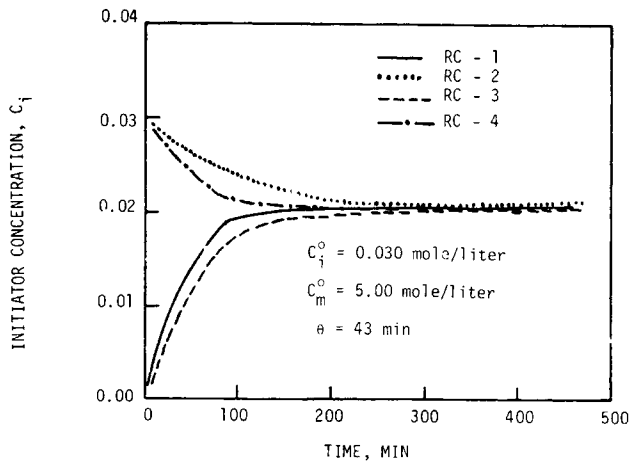


Fig. 5. Unsteady-state trajectory of  $C_i$  showing the effect of initial condition for polymerization of isoprene in a perfectly mixed flow reactor.

$$\theta \frac{d\lambda_1}{dt} = -\lambda_1 + (\beta_i C_i C_m + \alpha C_m C_p) \theta \quad (6)$$

$$\theta \frac{d\lambda_2}{dt} = -\lambda_2 + (\beta_i C_i C_m + \alpha C_m C_p) \theta + 2\alpha f_2 \lambda_1 C_m \theta \quad (7)$$

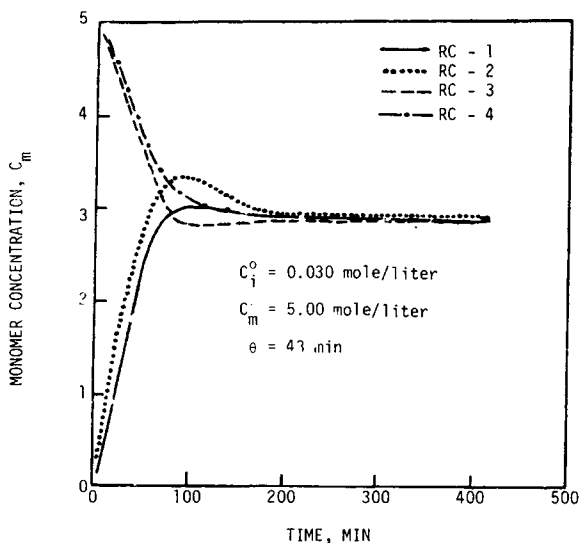


Fig. 6. Unsteady-state trajectory of  $C_m$  showing the effect of initial condition for polymerization of isoprene in a perfectly mixed flow reactor.

$$D_n = \frac{\lambda_1}{\lambda_0} \quad (8)$$

$$D_w = \frac{\lambda_2}{\lambda_1} \quad (9)$$

where  $C_i$ ,  $C_m$ , and  $C_p$  ( $C_p = \lambda_0$ ) are concentrations of initiator, monomer, and polymer, respectively;  $\lambda_1$  and  $\lambda_2$  are the first and second moments of the distribution, respectively;  $D_n$  and  $D_w$  are number- and weight-average degrees of polymerization, respectively;  $\lambda_0 = C_i^0 X_i$  at steady state; and  $\theta = V/v =$  residence time. If the derivatives with respect to time are set equal to zero, eqs. (3)–(7) become the steady-state balances.

For  $C_i^0 = 0.03$  and  $C_m^0 = 5.0$  g moles/liter, the steady-state solutions are shown in Figures 1 and 2. The values of  $X_i$  and  $X_m$  between  $R'$  and  $S'$  and  $R$  and  $S$  are unstable solutions, whereas the values of  $X_i$  and  $X_m$  at all other points on Figure 1 represent stable solutions. The fact that monomer conversions and molecular

TABLE I  
Initial Conditions for a PMFR

Condition	Description
RC-1	Reactor full of solvent at time $t = 0$ $\{C_i\}_{t=0} = 0$ , $\{C_m\}_{t=0} = 0$
RC-2	Reactor at initiator feed concentration at time $t = 0$ $\{C_i\}_{t=0} = C_i^0$ , $\{C_m\}_{t=0} = 0$
RC-3	Reactor at monomer feed concentration at time $t = 0$ $\{C_m\}_{t=0} = C_m^0$ , $\{C_i\}_{t=0} = 0$
RC-4	Reactor at initiator and monomer feed concentration at time $t = 0$ $\{C_i\}_{t=0} = C_i^0$ , $\{C_m\}_{t=0} = C_m^0$

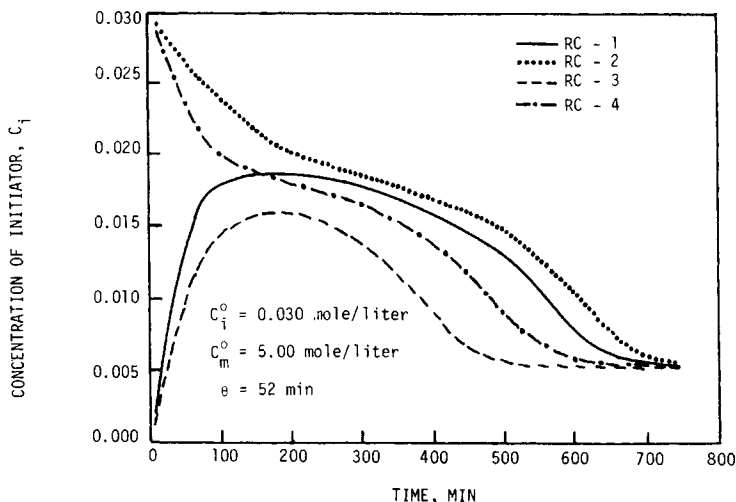


Fig. 7. Trajectory of  $C_i$  showing the effect of initial condition for polymerization of isoprene in a perfectly mixed flow reactor.

weights may decrease with increased residence time is apparent. Hence, for some feed concentrations, an increase in residence time will result in low molecular weight polymer as well as a low production rate of polymer.

The existence of operating conditions which will give problems with concentration stability for a given set of feed concentrations may be determined by plotting the rates as given by eqs. (1) and (2) as a function of conversion. Because of the interdependence of these two equations, the type of plot obtained is a function of reactor type. A comparison of Figures 3 and 4 for  $R_m$  calculated for a PMFR and a batch reactor illustrates this point. Similar results are obtained for the initiation rate equation. (The fact that the shape of the rate function becomes a function of reactor type is significant because for single reactions the shape of the rate function is considered to be a function only of temperature pressure and concentration.) Unstable solutions exist between the two material balance lines in Figure 3.

Reactor performance for unsteady-state conditions was obtained by numerically integrating eqs. (3)–(7). Initial conditions which were considered are listed in Table I. Figures 5 and 6 illustrate the trajectories obtained for the different initial conditions for  $\theta = 43$  min. In general, for the initial conditions, listed in Table I, and for residence times less than point  $B$  on Figure 1, the steady-state solutions on  $PR$  and  $P'R'$  were obtained in four to five residence times as indicated in Figures 5 and 6. For values of  $\theta$  greater than  $B$  on Figure 1 and the initial conditions shown in Table I, 15 to 20 residence times were required to achieve the steady-state solution. The trajectories of initiator concentration and weight-average molecular weight are shown in Figures 7 and 8. Hence, an increase in residence time has not only resulted in a lower molecular weight polymer and lower production rate, but a longer time is required to achieve steady-state.

To obtain the steady-state solutions for  $\theta$ 's between  $A$  and  $B$  on  $SU$  and  $S'U'$  in Figure 1, it was necessary to start with the steady-state solution for  $\theta = B'$  (or any other value higher than  $B$ ). By using the steady solutions at  $B'$  as the initial

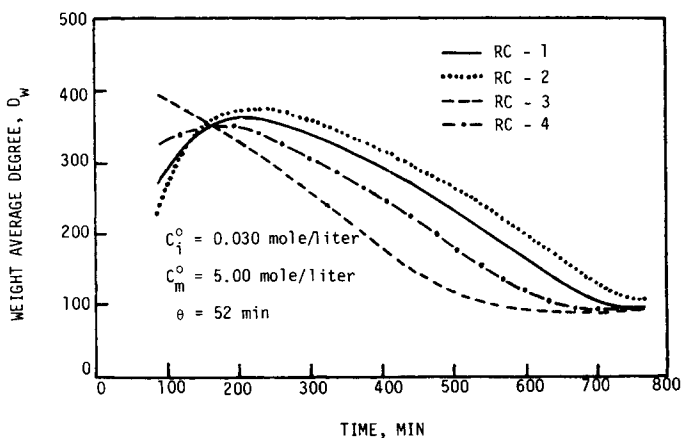


Fig. 8. Trajectory of  $D_w$  showing the effect of initial condition on polymerization of isoprene in a perfectly mixed flow reactor.

condition in a PMFR, monomer, and initiator feed concentrations of 0.03 and 5.0, and a  $\theta$  at point C, a steady-state condition was reached after about four residence times which corresponded to  $X_m$  and  $X_i$  of  $V$  and  $V'$ , respectively. A solution in the  $SU$  and  $S'U'$  region was also obtained by starting as a batch reactor. Steady-state solutions in the  $SU$  and  $S'U'$  region could be obtained also, provided the initial polymer concentration was high and the initial initiator concentration was low.

For the rate equations used, multiple steady-state solutions did not exist for  $C_i^0 \leq 0.02$  g-moles/liter and  $C_m^0 \leq 4$  g-moles/liter. These limits, would, of course, vary for each type of polymerization and set of rate equations.

### LIMITATIONS

No experiments were performed to verify these theoretical findings owing to excessive time and material requirements. Further, the feed concentrations used in these calculations are not within the range studied by Porter et al. However, this should not detract from the fact that concentration stability may be encountered for these types of rate equations.

### CONCLUSIONS

The effect of multiple steady states for the anionic polymerization of isoprene has been illustrated. The existence of such states suggest a means of testing rate equations experimentally. For feed conditions where these states may exist, a continued increase in residence time may reduce molecular weight and polymer production and require abnormally long times to achieve the steady-state condition.

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