

SRC-TR-87-76

**CHEMICAL PROCESS SYSTEMS
LABORATORY**

Analysis of Steady State of Free Radical
Solution Polymerization in a Continuous
Stirred Tank Reactor

by

K. Y. Choi

RESEARCH REPORT

CHEMICAL PROCESS SYSTEMS ENGINEERING LABORATORY

ANALYSIS OF STEADY STATE OF FREE RADICAL SOLUTION
POLYMERIZATION IN A CONTINUOUS STIRRED TANK REACTOR

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**A CONSTITUENT LABORATORY OF
THE SYSTEMS RESEARCH CENTER**

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Analysis of Steady State of Free Radical Solution Polymerization in a Continuous Stirred Tank Reactor

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The steady state structure of non-isothermal free radical solution polymerization in a continuous stirred tank reactor is analyzed. With mean residence time as a bifurcation parameter, five regions of steady states are identified. The effect of reactor operating conditions on the structure and the stability of steady state is discussed.

INTRODUCTION

It has been well known that a class of continuous flow chemical reactors exhibits complex dynamic behavior for some operating and design conditions. Polymerization reactors are not exceptions. In recent years, considerable progress has been made in understanding the steady state characteristics and the dynamic behavior of various types of polymerization reactors (1-10). Notably, Hamer, *et al.* (5) performed a detailed analysis of the dynamic behavior of free radical solution polymerization in continuous stirred tank reactors (CSTR). They discovered that depending upon the solvent volume fraction and heat transfer parameter, quite complex dynamic behavior such as multiple steady states, limit cycles and oscillatory phenomena may occur. In particular, they showed that up to six different types of dynamic behavior are observed in a CSTR homopolymerization reactor. Schmidt, *et al.* (10) succeeded in confirming the isolated branch (isola) experimentally and illustrated that operating the polymerization reactor at the isolas may be advantageous in a sense that the reactor can be operated at very short residence times to obtain high monomer conversions. Their model simulations also indicate qualitatively that small variations in coolant temperature, reactor heat transfer coefficient, feed solvent concentration, or propagation rate constant can have enormous effects on the reactor behavior. An improved understanding of complex polymerization reactor behavior through such detailed analysis is of great practical importance in designing control systems for polymerization reactors.

In modeling a continuous non-isothermal free radical homopolymerization reactor, one needs

at least two material balance equations (monomer and initiator) and one energy balance equation to describe the macroscopic behavior of the reactor. The complexity of the reactor model increases further when the "gel effect" [reduction of polymer chain mobility at high conversions (high viscosities)] correlation is incorporated into the model to improve its accuracy. In common commercial practice, the effective initiator concentration in the reactor can be maintained nearly constant over a wide range of conversions by using a high feed concentration of slowly decomposing initiators or mixed initiators (11, 12). Previous reports on the free radical polymerization of acrylic and styrenic monomers in a CSTR indicate that the fractional conversion of initiator is quite small for some initiator systems (5). Jaisinghani and Ray (3) performed an analysis of reactor behavior for such conditions (constant initiator concentration). They showed the existence of multiple steady state and unstable limit cycles for some reactor operating conditions. It has also been shown in earlier studies that a varying Damköhler number (Da) will produce only S-shaped multiplicity patterns while a varying mean residence time can produce more complex multiplicity structures including isolated branches (isolas) (10, 13, 14).

In this paper, the steady state of free radical solution homopolymerization of methylmethacrylate in a CSTR is analyzed with a simplified model in which the initiator concentration is assumed to remain constant. Here the dimensionless groups are parameterized differently from that of (3), i.e. the residence time is used as a bifurcation parameter. By doing so, more detailed steady state structure can be identified. The validity of this simplifying approach will be

discussed by comparing the steady state structures predicted by a more detailed model (i.e. varying initiator concentration).

REACTOR MODEL

For classical free radical homopolymerization in a continuous stirred tank reactor of volume V , mass and energy balances are represented by the following form:

$$V \frac{dM}{dt'} = q(M_f - M) - V k_p M P \quad (1)$$

$$V \frac{dI}{dt'} = q(I_f - I) - V k_d I \quad (2)$$

$$\rho C_p V \frac{dT}{dt'} = \rho C_p q (T_f - T) + V(-\Delta H_r) k_p M P - hA(T - T_c) \quad (3)$$

Here M is the monomer concentration, I the initiator concentration, and T the reactor temperature. q denotes the volumetric flow rate of feed and product stream. The density of polymerization mixture (ρ) is assumed constant. The total concentration of growing free-radicals in the reactor is represented by

$$P = \left(\frac{2fk_d I}{k_{tc} + k_{td}} \right)^{1/2} \quad (4)$$

Here the rate constants (k_p , k_d , k_{tc} , and k_{td}) are of the Arrhenius form. It has been well known that termination and propagation reactions become diffusion controlled as the conversion of monomer increases. However, for solution polymerization of MMA with high solvent volume fraction (e.g. $f_s > 0.6$), the gel effect becomes insignificant (15, 16). Thus, for such operating condition which is adequate for continuous process we can neglect the gel effect even at high conversions.

The modeling equations are reduced to dimensionless forms by using dimensionless variables and parameters:

$$X_1 = \frac{M_f - M}{M_f}, \quad X_2 = \frac{I_f - I}{I_f}, \quad X_3 = \frac{T - T_f}{T_f} \quad (5)$$

$$\alpha = \frac{hA}{\rho C_p V k(T_f)}, \quad \beta = \frac{(-\Delta H_r) M_f}{\rho C_p T_f}, \quad \gamma = \frac{E}{RT_f}$$

$$\delta = \frac{T_c - T_f}{T_f}, \quad \theta = \frac{V}{q}, \quad t = \frac{t'}{\theta}$$

$$D_a = \theta k(T_f), \quad K = k_{d0}/k(T_f), \quad \gamma_1 = \frac{E_d}{RT_f}$$

where

$$E^* E_p + (E_d - E_t)/2$$

$$k(T_f)^* k_{p0} e^{-E/RT_f} \left(\frac{2fk_{d0} I_f}{k_{t0} + k_{td0}} \right)^{1/2}$$

Then, the following dimensionless modeling equations are obtained.

$$\frac{dX_1}{dt} = -X_1 + D_a(1 - X_1)(1 - X_2)^{1/2} \cdot \exp\left[\frac{\gamma X_3}{1 + X_3} \right] \quad (6)$$

$$\frac{dX_2}{dt} = -X_2 + D_a K(1 - X_2) \exp\left[-\frac{\gamma_1}{1 + X_3} \right] \quad (7)$$

$$\frac{dX_3}{dt} = -X_3 + D_a \beta(1 - X_1)(1 - X_2)^{1/2} \cdot \exp\left[\frac{\gamma X_3}{1 + X_3} \right] - D_a \alpha (X_3 - \delta) \quad (8)$$

Here, θ is the mean residence time and D_a the dimensionless residence time. α is a measure of heat removal capacity of jacket cooling, β a measure of heat generated by polymerization, and δ a dimensionless coolant temperature. Note that the last term of Eq 8 contains two dimensionless parameters (D_a and α) which reflect the effect of mean residence time and heat removal capacity, respectively. According to (13, 14), the structure of the problem is greatly complicated by this type of parameterization.

MODEL ANALYSIS

Let us first assume that the initiator concentration in the reaction remains constant. Then, the modeling equations are greatly simplified and only Eqs 6 and 8 are to be solved (Model I). At steady state the following single equation is obtained by combining Eqs 6 and 8:

$$F(X_1, \mathbf{p}) = X_1 - D_a(1 - X_1) \cdot \exp\left[\frac{\beta \gamma X_1 + D_a \alpha \gamma \delta}{1 + \alpha D_a + D_a \alpha \delta + \beta X_1} \right] = 0 \quad (9)$$

where the parameter vector, \mathbf{p} , is defined as

$$\mathbf{p} = (D_a, \alpha, \beta, \gamma, \delta). \quad (10)$$

and the surface described by Eq 9 is called the steady state manifold. Here Damköhler number (D_a) represents dimensionless mean residence time and is chosen as a bifurcation parameter.

A surface in the parameter space \mathbf{p}^* ($\alpha, \beta, \gamma, \delta$) at which steady state multiplicity occurs is now sought. This surface is called the hysteresis variety and the following conditions are satisfied at this surface (17):

$$F(X_1, D_a, \mathbf{p}^*) = 0 \quad (11)$$

$$\frac{\partial F}{\partial X_1}(X_1, D_a, \mathbf{p}^*) = 0 \quad (12)$$

$$\frac{\partial^2 F}{\partial X_1^2}(X_1, D_a, \mathbf{p}^*) = 0 \quad (13)$$

A surface in the parameter space \mathbf{p}^* at which a continuous change in the parameters causes the appearance or disappearance of an isolated branch (isola) is called the isola variety. This is the surface at which Eqs 12, 13 and the following condition are satisfied.

$$\frac{\partial F}{\partial D_a}(X_1, D_a, p^*) = 0 \quad (14)$$

The technique developed by (17) leads to the following convenient analytical expressions for the hysteresis variety (multiple steady states) and isola variety:

Hysteresis variety (Multiple steady states)

$$\alpha = \frac{1 - \phi}{\phi} \left[\frac{4\beta\phi(1 - \phi)}{\gamma(1 - 2\phi)^2} - 1 \right] \cdot \exp \left\{ \gamma - \frac{2}{1 - 2\phi} \right\} \quad (15)$$

where

$$\phi = \frac{4\beta(1 + \delta) + 4\gamma\delta - \beta\gamma^{\pm} \sqrt{D}}{2[4\gamma\delta - 2\beta\gamma + 4\beta(1 + \delta)]} \quad (16)$$

$$D = [4\beta(1 + \delta) + 4\gamma\delta - \beta\gamma]^2 - 4\gamma\delta[4\gamma\delta - 2\beta\gamma + 4\beta(1 + \delta)] \quad (17)$$

Isola variety (Isolated branch)

$$\alpha = \frac{\beta(1 - \psi)^2}{\beta\psi^2 - \delta} \exp \left[\frac{\beta\gamma\psi^2}{1 + \beta\psi^2} \right] \quad (18)$$

where ψ is obtained by solving the following algebraic equation:

$$\psi^5\beta^3\gamma - \psi^3(1 - \psi + \delta\psi/\gamma - 2/\gamma)\beta^2\gamma^2 + \psi\{1 + \delta\gamma(1 - \psi) - 2\psi\delta\}\beta\gamma - \delta\gamma = 0 \quad (19)$$

$(0 < \psi < 1)$

As a model polymerization system, solution homopolymerization of methylmethacrylate with high solvent volume fraction ($f_s > 0.6$) is now considered. Under this condition, the gel effect is not significant at high conversion, making the continuous polymerization attractive. Figure 1 shows the hysteresis variety and isola variety on the α - β plane for a fixed value of δ . Here, $\delta = 0.01$ corresponds to $T_c = 303^\circ\text{K}$ for a cooling medium. Kinetic and physical constants of the polymerization are listed in Table 1. Note that there are five regions of dynamic behavior:

- Region I: Unique steady state
- Region II: Multiple steady state
- Region III: Isola and unique steady state
- Region IV: Isola and multiple steady stage (S-shaped curve)
- Region V: Mushroom

Figure 1 shows that for a highly exothermic reaction (large β) with high cooling capacity (large α), a region of isola/unique steady state (Region III) becomes broader. Since both Regions IV and V are small, it would be difficult to observe these regions experimentally. However, this diagram illustrates the complexity of steady state structure and dynamic behavior of free radical solution polymerization reactors even when the initiator concentration is constant and the gel effect is absent.

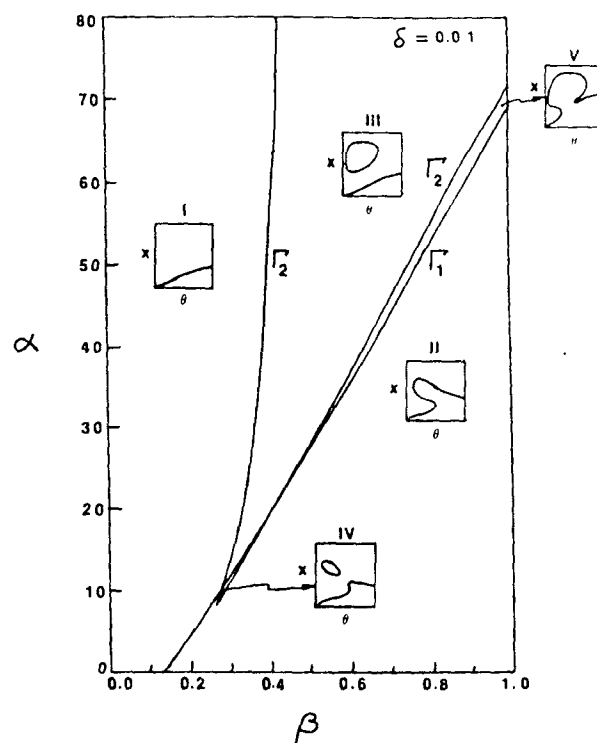


Fig. 1. Dynamic behavior regions for a continuous free radical solution polymerization reactor.

Table 1. Physical Constants and Standard Reactor Conditions (18).

k_p	$= 7.0 \times 10^8 e^{-6,300/RT}$ (l/mol·s)
k_d	$= 5.95 \times 10^{13} e^{-29,600/RT}$ (s ⁻¹) (AIBN)
k_{ic}	$= k_{id} = 1.76 \times 10^9 e^{-2,800/RT}$ (l/mol·s)
$(-\Delta H_r)$	$= 13.5$ Kcal/mol
f	$= 0.6$
T_r	$= 300^\circ\text{K}$
l_r	$= 0.05$ mole/l
ρC_p	$= 0.4$ Kcal/l ^o K

Figures 2a and b show the variations in the steady state profiles of monomer concentration (X_1) and reactor temperature (T ; X_3) as function of mean residence time $\theta (= D_a/k(T_r))$ for various values of α . As predicted in Fig. 1, both isola (curve C) and mushroom (curve B) structures are observed. The number average degree of polymerization (\bar{X}_N) is represented by the ratio of the sum of the first moments to the zeroth moments of live and dead polymer chains:

$$\bar{X}_N = \frac{\lambda_1^l + \lambda_1^d}{\lambda_0^l + \lambda_0^d}$$

$$= \frac{1 + \theta\{[k_{fs}S + k_{fT}W + k_fM + k_{id}P]\}(2 - \hat{\alpha})\hat{\alpha} + k_{ic}P}{(1 - \hat{\alpha})[1 + \theta\{k_{fs}S + k_{fT}W + k_fM + k_{id}P\}]\hat{\alpha} + \frac{1}{2}k_{ic}P} \quad (20)$$

where superscripts l and d denote live and dead polymers, respectively, $\hat{\alpha}$ represents the probability of propagation

$$\hat{\alpha} = \frac{k_p M}{[k_p M + k_{fs}S + k_{fT}W + k_f M + (k_{ic} + k_{id})P]} \quad (21)$$

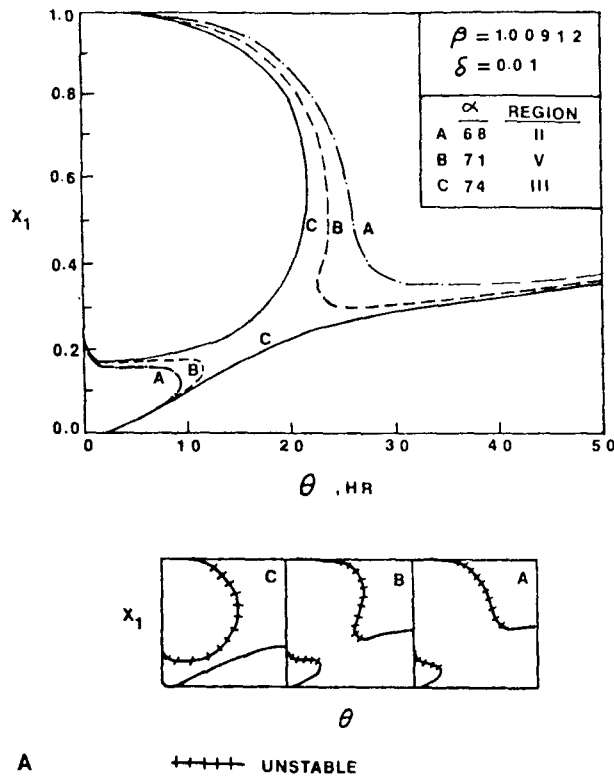


Fig. 2a. Variation of steady state monomer conversion profiles for varying heat removal capacity parameters.

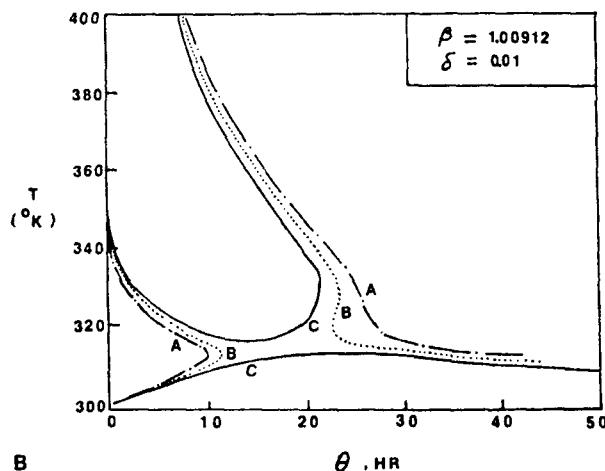


Fig. 2b. Variations of steady state reactor temperature profiles for varying heat removal capacity parameters.

and S and W represent solvent and chain transfer agent, respectively. Figure 2c illustrates the steady state values of \bar{X}_N as a function of mean residence time (θ) for three different values of α . Here, chain transfer reactions to solvent, monomer, and chain transfer agent are neglected. Note that \bar{X}_N decreases initially with an increase in θ , but \bar{X}_N increases with a further increase in θ (Case c). Although Fig. 2a suggests that operating the reactor at isolas can reduce the reactor residence time considerably while obtaining high conversion, Fig. 2c indicates that such reactor operation may result in a production of polymers having very low molecular weight. Therefore, it is suggested that the

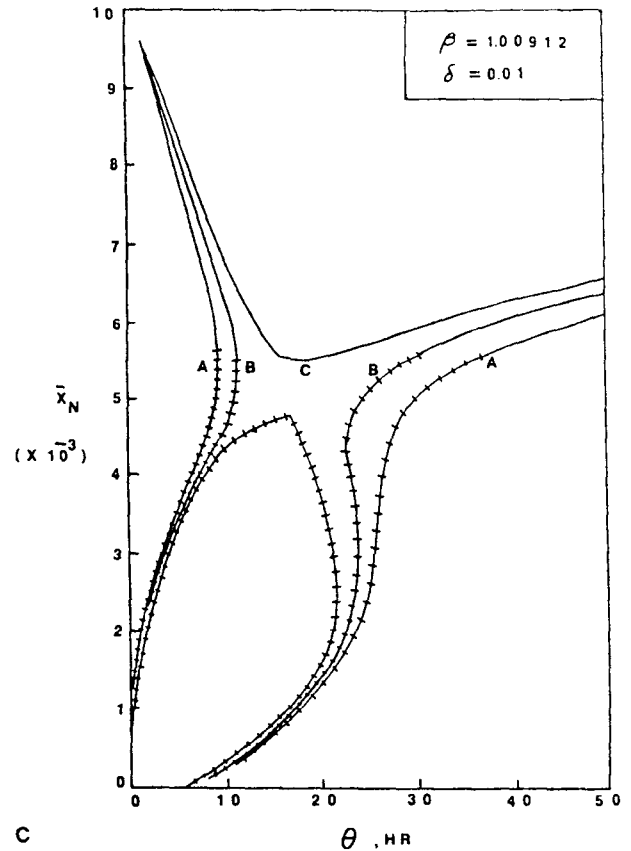


Fig. 2c. Variations of steady state degree of polymerization profiles for varying heat removal capacity parameters; ++++++ unstable branch.

polymer reactor designer should consider not only the monomer conversion and temperature but also the molecular weight of the resulting polymer in determining the proper reactor operating conditions.

The local stability of the steady state is important for the design of control systems and is determined by the roots of the characteristic equation

$$|A - \lambda I| = 0 \quad (22)$$

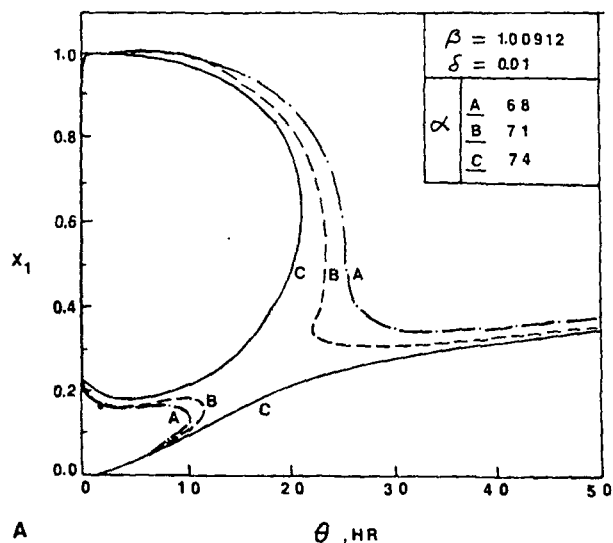
where A denotes the Jacobian of the linearized modeling equations and λ the eigenvalues of A . If the real part of λ is positive, the system is unstable. The stability analysis shows (see lower diagrams of Fig. 2a) that only the lower steady states are stable.

Since the initiator concentration has been assumed constant, it will be instructive to check the validity of this approximation by comparing Fig. 2 with the steady state profiles obtained by solving the original three modeling equations (Eq 6-8) (Model II). Figure 3a shows the steady state monomer conversion (X_1) vs. residence time (θ) curves for varying values of α when the original steady state modeling equations are solved. When compared with Fig. 2a for the simplified model, the overall structure is almost identical with only minor differences. Note that both isola and mushroom shape steady state profiles are also predicted with Model II (varying

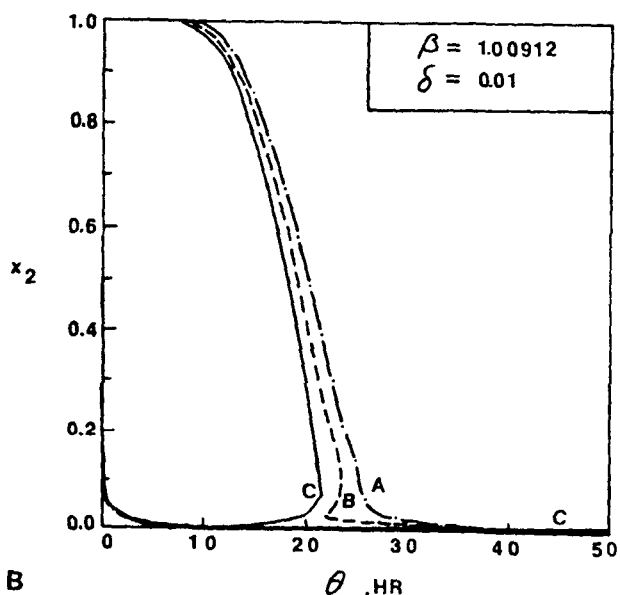
initiator) for the same set of parameter values used in the simplified model. Figures 3b and c show the steady state profiles of initiator conversion and reactor temperature, respectively. As expected, initiator conversion at stable steady state (e.g.; lower branch of A, B, and C) is very low. It is also interesting to note that even when the initiator conversion is high (upper and middle branches of A, B, and isola (C)), the overall steady state structure (e.g.; monomer conversion and temperature) predicted by the model is quite similar to that predicted by the simplified model (see Figs. 2a and b). This implies that for the solution polymerization system considered, the simplified model predicts the steady state characteristics of the polymerization reactor reasonably well. This is an interesting result indicating that one can conduct a quick but still quite accurate analysis of the

dynamic behavior of free radical homopolymerization in a CSTR with simplified reactor model. In other words, one can first obtain the analytical bifurcation map such as Fig. 1 using the simplified model and then determine the approximate range of operating parameters for more complex model.

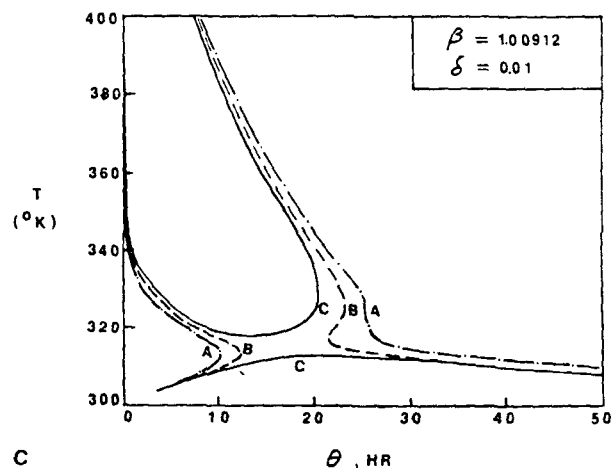
Figures 4a, b, and c show the steady state profiles of monomer conversion, temperature, and degree of polymerization in different regions (I($\alpha = 9.6$), II($\alpha = 8.0$), III($\alpha = 9.4$), and IV($\alpha = 9.28$)) with the simplified model. Note that the upper portion of the S-shaped curve ($\alpha = 8.0$) and isolas ($\alpha = 9.28$ and 9.4) are less exaggerated than in Fig. 2a. As α (dimensionless heat transfer coefficient) increases from 9.4 to 9.6, the isola "evaporates", resulting in a unique steady state. Figures 5a and b represent the steady state conversions of monomer and initiator with Model II (varying initiator concentration). Again, there exists only a slight difference between Fig. 4a and Fig. 5a. Figure 5b also shows that the initiator conversions at lower stable branches are very low.



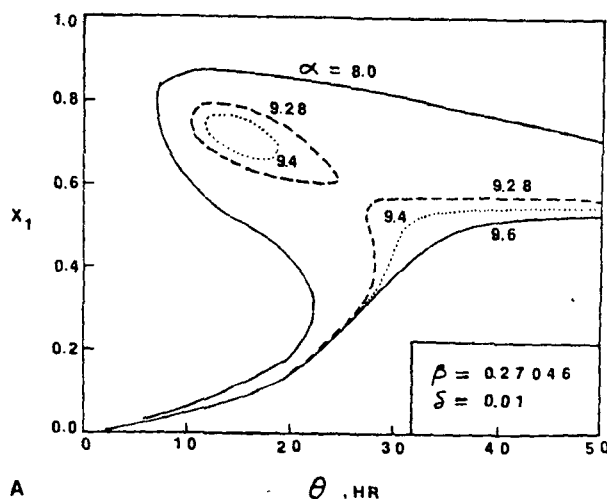
A
Fig. 3a. Steady state monomer conversion profiles for the case of varying initiator concentration (Model II).



B
Fig. 3b. Steady state initiator conversion profiles (Model II).



C
Fig. 3c. Steady state reactor temperature profiles for the case of varying initiator concentration (Model II).



A
Fig. 4a. Steady state monomer conversion profiles at constant initiator concentration: $\alpha = 8.0$ (Region II), $\alpha = 9.28$ (Region IV), $\alpha = 9.4$ (Region III), $\alpha = 9.6$ (Region I).

initiator) for the same set of parameter values used in the simplified model. Figures 3b and c show the steady state profiles of initiator conversion and reactor temperature, respectively. As expected, initiator conversion at stable steady state (e.g.; lower branch of A, B, and C) is very low. It is also interesting to note that even when the initiator conversion is high (upper and middle branches of A, B, and isola (C)), the overall steady state structure (e.g.; monomer conversion and temperature) predicted by the model is quite similar to that predicted by the simplified model (see Figs. 2a and b). This implies that for the solution polymerization system considered, the simplified model predicts the steady state characteristics of the polymerization reactor reasonably well. This is an interesting result indicating that one can conduct a quick but still quite accurate analysis of the

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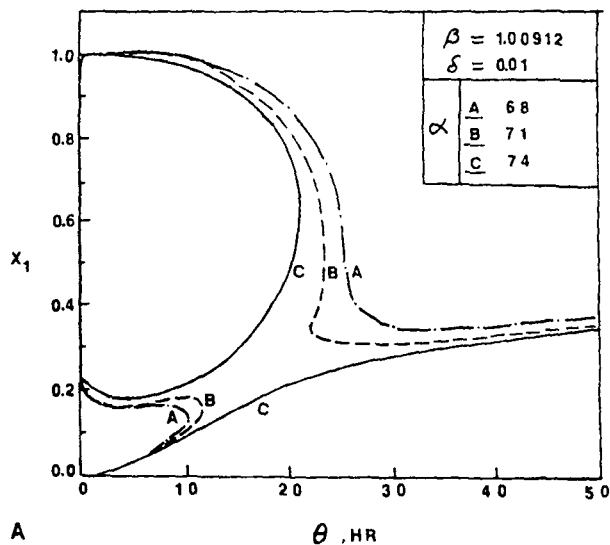


Fig. 3a. Steady state monomer conversion profiles for the case of varying initiator concentration (Model II).

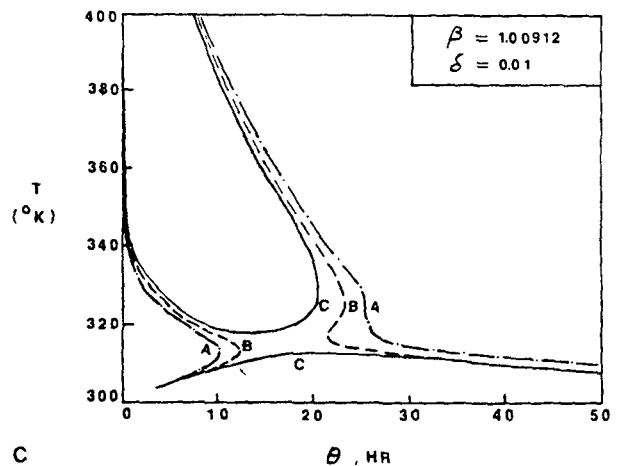


Fig. 3c. Steady state reactor temperature profiles for the case of varying initiator concentration (Model II).

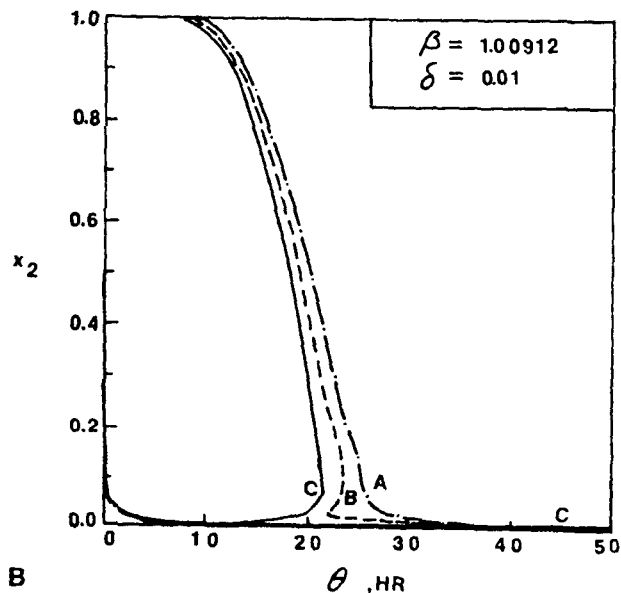


Fig. 3b. Steady state initiator conversion profiles (Model II).

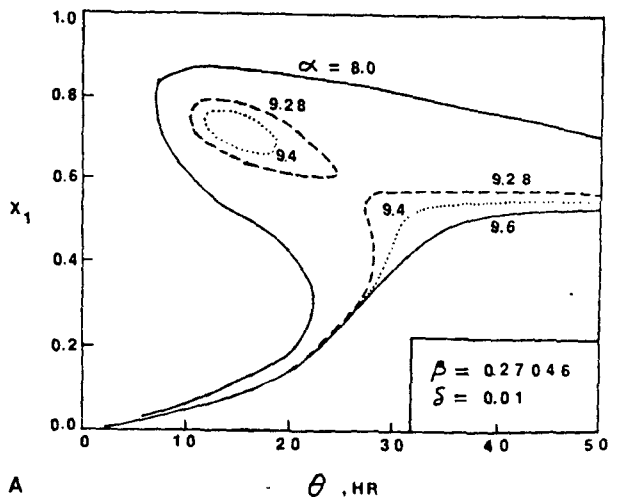


Fig. 4a. Steady state monomer conversion profiles at constant initiator concentration; $\alpha = 8.0$ (Region II), $\alpha = 9.28$ (Region IV), $\alpha = 9.4$ (Region III), $\alpha = 9.6$ (Region I).

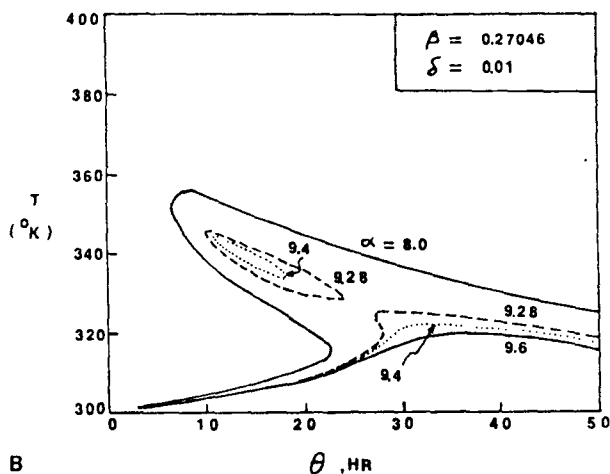


Fig. 4b. Steady state reactor temperature profiles at constant initiator concentration.

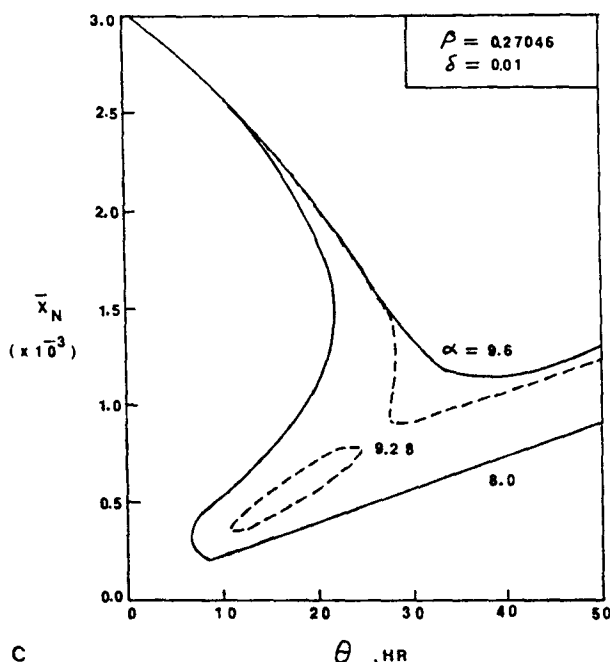


Fig. 4c. Steady state profiles of the degree of polymerization at constant initiator concentration.

CONCLUDING REMARKS

Non-isothermal solution polymerization of methylmethacrylate in a CSTR has been analyzed to identify the complex structure of steady states. With mean residence time as a bifurcation parameter, five types of steady states have been identified for the cases of constant initiator concentration and varying initiator concentration. The steady state structures predicted by the simplified model (constant initiator concentration) and the original model (varying initiator concentration) have been found to be quite similar qualitatively and quantitatively. This suggests that one can use this simplifying approach for a rapid analysis of a free radical solution polymerization in a CSTR without making significant errors. However, when the solvent volume fraction is low, diffusion controlled chain termination ("gel effect") should be

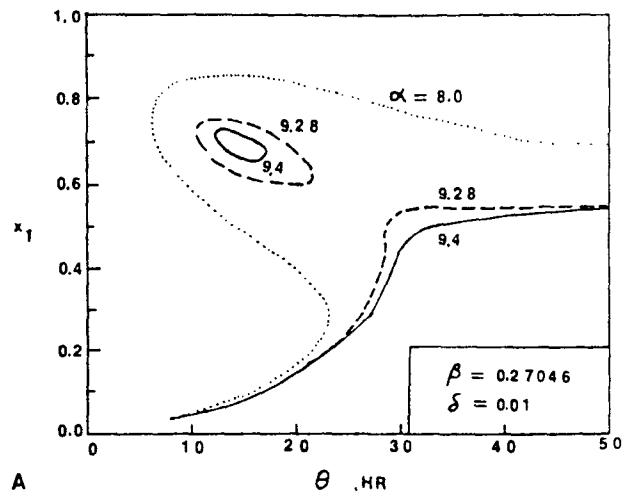


Fig. 5a. Steady state monomer conversion profiles for the case of varying conversion profiles for the case of varying initiator concentration.

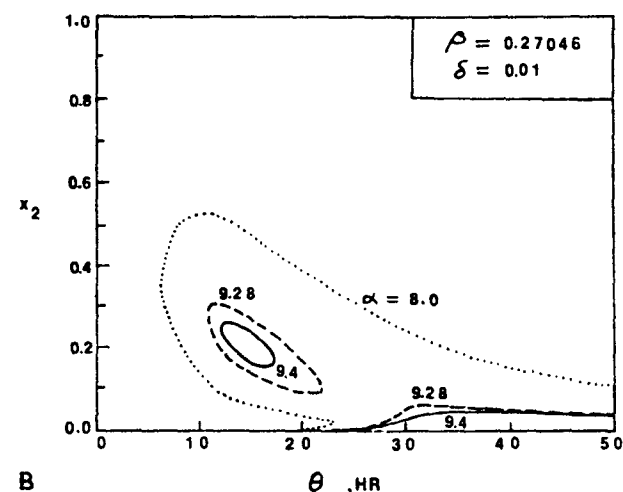


Fig. 5b. Steady state initiator conversion profiles for the case of varying initiator concentration.

incorporated into the model to characterize the detailed structure and stability of steady states.

ACKNOWLEDGMENTS

The author is indebted to the DuPont Company for research support through DuPont Young Faculty Award and to the University of Maryland Computer Science Center for computing time. Partial support by the Systems Research Center at the University of Maryland is also gratefully appreciated.

NOMENCLATURE

C_p	= Heat capacity of reaction mixture.
D_a	= Damköhler number.
E_a	= Activation energy of initiator decomposition.
E_p	= Activation energy of propagation.
E_t	= Activation energy of chain termination.
f	= Initiator efficiency.
f_s	= Solvent volume fraction in the feed.
h	= Heat transfer coefficient to reactor.

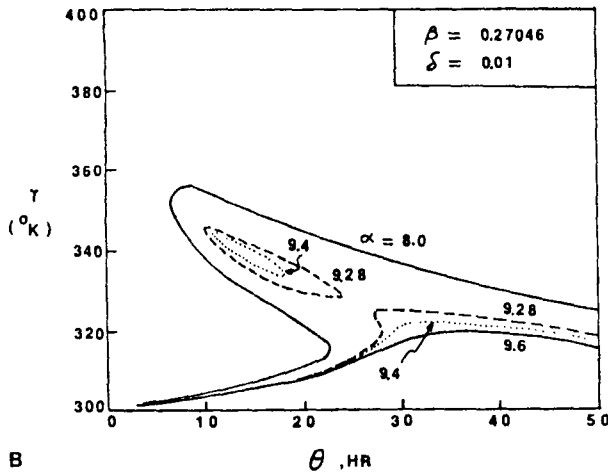


Fig. 4b. Steady state reactor temperature profiles at constant initiator concentration.

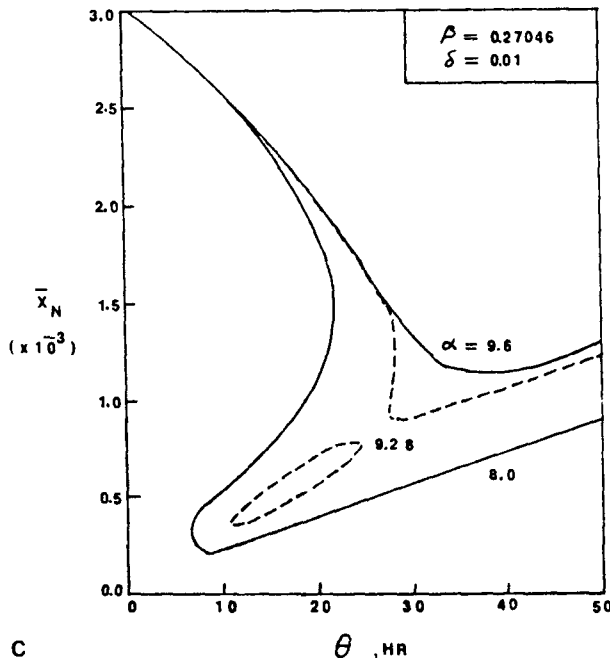


Fig. 4c. Steady state profiles of the degree of polymerization at constant initiator concentration.

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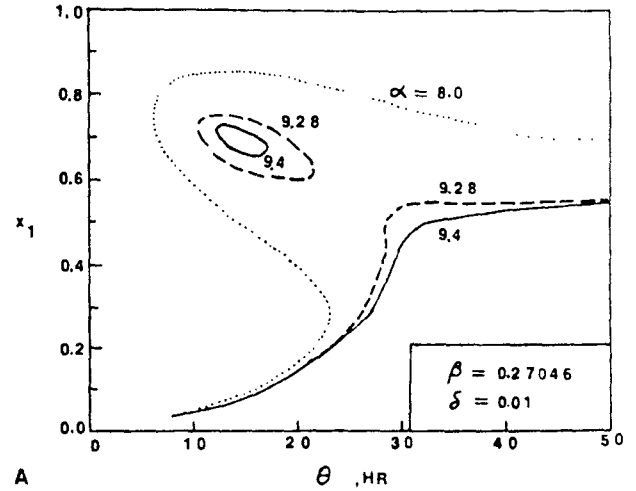


Fig. 5a. Steady state monomer conversion profiles for the case of varying conversion profiles for the case of varying initiator concentration.

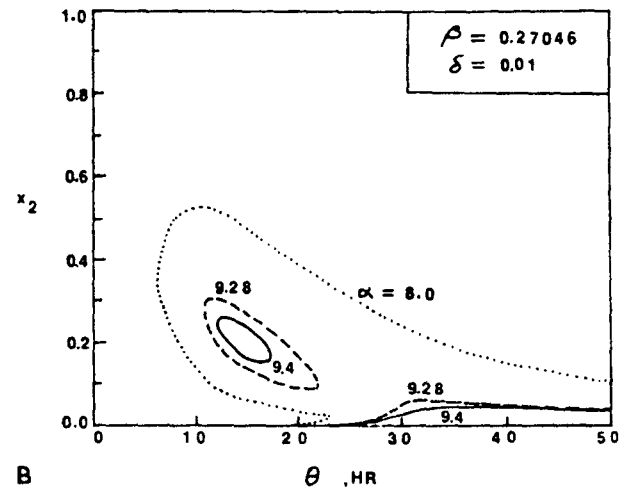


Fig. 5b. Steady state initiator conversion profiles for the case of varying initiator concentration.

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Analysis of Steady State of Free Radical Solution

$(-\Delta Hr)$	= Heat of polymerization.
I	= Initiator concentration.
I_f	= Feed initiator concentration.
k_d	= Initiator decomposition rate constant.
k_{do}	= Pre-exponential factor of initiator decomposition rate constant.
k_j	= Monomer chain transfer rate constant.
k_{js}	= Solvent chain transfer rate constant.
k_{jT}	= Chain transfer agent chain transfer rate constant.
k_p	= Propagation rate constant.
k_{po}	= Pre-exponential factor of propagation rate constant.
k_t	= Termination rate constant.
k_{tco}	= Pre-exponential factor of consideration termination rate constant.
k_{td}	= Pre-exponential factor of disproportionation termination rate constant.
M	= Monomer concentration.
M_f	= Feed monomer concentration.
P	= Total concentration of live polymer.
q	= Volumetric flow rate.
R	= Gas constant.
T	= Reactor temperature.
T_c	= Coolant temperature.
T_f	= Feed temperature.
t	= Dimensionless time.
t'	= Time.
X_1	= Conversion of monomer to polymer.
X_2	= Fractional conversion of initiator.
X_3	= Dimensionless temperature.

Greek Symbols

α	= Dimensionless heat transfer capability.
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β	= Dimensionless heat of reaction.
γ	= Dimensionless activation energy.
δ	= Dimensionless coolant temperature.
θ	= Mean residence time.
ρ	= Density of reaction mixture.

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