

## Dynamic Characteristics of a CSTR with MMA polymerization

Jong-Pill Ahn and Hyun-Ku Rhee

Department of Chemical Engineering, Seoul National University

**ABSTRACT** - A mathematical model is developed for a CSTR in which free radical solution polymerization of methyl methacrylate(MMA) takes place. It turns out that five ordinary differential equations are to be treated simultaneously in order to predict the reactor performance. Although the reaction proceeds under the conditions of relatively low temperature and pressure, the system shows very complex bifurcation features due to the diffusion limitation (gel effect) and the temperature dependence of the kinetic parameters and physical properties. The effects of various system parameters on the reactor performance as well as on the polymer properties are investigated by using the bifurcation analysis. The application of the singularity theory enables us to divide the parameter space into several different regions, in each of which the system takes a unique steady state structure. Under certain circumstances, complex dynamic features such as HB points and limit cycles are observed and these should be taken into consideration in the reactor design.

### INTRODUCTION

The steady state and dynamic behaviors of polymerization in CSTRs have attracted a great deal of research interest for many decades. Because of their inherent nonlinearities arising from complex kinetics, temperature effects and heat dissipation constraints, the reactor shows very complex features such as the steady state multiplicity and the oscillatory behavior[8]. Such behaviors are observed under both isothermal and nonisothermal operating conditions in various polymerization processes including bulk, solution, and emulsion polymerizations.

Reactor behavior arising from nonisothermal operation has notably been studied by Poore[11], Uppal et al.[16, 17], and Balakotaiah and Luss[2]. The experimental study of Schmidt and Ray[13] for the isothermal CSTR solution polymerization of MMA has demonstrated the existence of three steady states under the isothermal condition. The multiplicity observed in the isothermal reactor is attributed

to the autoacceleration caused by the gel effect [10, 15].

These results were further studied by Schmidt et al.[12], Hamer et al.[7], and Clinch [4]. In these studies, some very complex bifurcation features such as isola-type multiplicities, Hopf bifurcation, and stable and unstable limit cycles are examined. Adebekun et al.[1] showed some other behaviors such as two isolas and isola-tuck type multiplicities for the MMA system. The experimental study of Teymour and Ray[14] for the VA solution polymerization reactor has demonstrated the existence of periodic oscillatory behavior. Choi[3], and Kim and Choi[9] applied the singularity theory to MMA and styrene solution polymerization reactors and divided the parameter range into several regions in each of which the system shows a different multiplicity pattern.

In this study we develop a mathematical model for the solution polymerization for methyl methacrylate in a CSTR and introduce the singularity theory to analyze the steady state and dynamic characteristics of the reactor system. Some of the system parameters such as the residence time, the feed temperature, the solvent fraction and the thermal conductance are chosen as the bifurcation parameters and their effects on the steady state multiplicity and the dynamic behavior are investigated systematically.

### MODEL DEVELOPMENT

The solution polymerization of MMA in a CSTR with ethyl acetate solvent and benzoyl peroxide initiator is to be considered. The kinetics is assumed to follow the free radical polymerization mechanism including chain transfers to solvent and to monomer. From the mass and energy balances the following five ordinary differential equations can be derived for the concentrations of initiator(I), monomer(M), solvent(S), and living polymer(G), respectively, and the reactor temperature(T):

$$\frac{dI}{d\tau} = I_f - \epsilon I - \theta k_d I \quad (1)$$

$$\frac{dM}{d\tau} = M_f - \epsilon M - \theta(k_p + k_{trm})MG \quad (2)$$

$$\frac{dS}{d\tau} = S_f - \varepsilon S - \theta k_{tr,s} S G \quad (3)$$

$$\frac{dG}{d\tau} = -\varepsilon P + \theta(2fk_d I - k_t G^2) \quad (4)$$

$$\frac{d}{d\tau} \left[ \rho C_{p,mean}(T-T_f) \right] = -\varepsilon \rho C_{p,mean} (T - T_f) \quad (5)$$

$$+ \theta(-\Delta H)k_p MP - \theta UA/V \cdot (T - T_c)$$

where

$$\tau = \frac{t}{\theta}, \quad \theta = \frac{V}{q_f}, \quad \varepsilon = \frac{q}{q_f}$$

Here,  $q_f$  and  $q$  denote the volumetric flow rates of feed and product streams, respectively,  $UA$  thermal conductance and  $T_c$  the coolant temperature. The Greek letter,  $\varepsilon$ , represents the ratio of  $q$  to  $q_f$  which expresses the volume contraction factor,  $\theta$  the residence time, and  $\tau$  the dimensionless time. Because the solution polymerization reactor is run under atmospheric conditions, the reactor temperature can frequently reach the boiling point of the mixture. Once the boiling point is reached, the reactor operates under the isothermal condition.

Physical properties of the reaction mixture (e.g., density  $\rho$  and heat capacity  $C_p$ ) are considered to be dependent on the temperature and composition: i.e.,

$$\rho = \rho_m \nu_m + \rho_s \nu_s + \rho_p \nu_p \quad (6)$$

$$C_p = (C_{p,m} \rho_m \nu_m + C_{p,s} \rho_s \nu_s + C_{p,p} \rho_p \nu_p) / \rho \quad (7)$$

$$C_{p,mean} = \frac{\int_{T_f}^T C_p dT}{T - T_f} \quad (8)$$

where  $\nu$  denotes the volume fraction and the subscripts  $m$ ,  $s$ , and  $p$  represent monomer, solvent, and polymer, respectively.

To reflect the temperature dependence of the density and heat capacity of each component, it is convenient to use the densities and the volume fractions instead of the molar concentrations in Eqs. (1) ~ (5) by means of the relations:

$$M = \frac{\rho_m \nu_m}{w_m}, \quad S = \frac{\rho_s \nu_s}{w_s} \quad (9)$$

where  $w_m$  and  $w_s$  are the molecular weights of the monomer and solvent, respectively.

Because the concentrations of initiator and living polymer are very low, the temperature dependence of their densities may be neglected. This model is then similar to the one used by Teymour and Ray[14] - they neglected the temperature dependence of the physical properties. Detailed derivation is so complicated that complete set of equations are not presented here. The temperature dependence of the rate constants is assumed to follow Arrhenius law. The kinetic data and physical properties used for the simulation of this reactor system are given in Tables 1 and 2.

Table 1. Parameter values for the reaction rate constants

REACTION	FREQUENCY FACTOR (s <sup>-1</sup> , l/mol·s)	ACTIVATION ENERGY (cal/mol)
INITIATION(BPO)	$1.7 \times 10^{14}$ , $k_{d_0}$	30000, $E_d$
PROPAGATION	$4.92 \times 10^8$ , $k_{p_0}$	4353, $E_p$
TERMINATION	$9.8 \times 10^7$ , $k_{t_0}$	701, $E_t$
MONOMER TRANSFER	$4.39 \times 10^2$ , $k_{trm_0}$	6593, $E_{trm}$
SOLVENT TRANSFER	$4.08 \times 10^1$ , $k_{trs_0}$	4353, $E_{trs}$

Table 2. Thermodynamic data and conditions for the reactor

$f$	0.5	
$\rho_m$	$0.9654 - 0.00109 T - 9.7 \times 10^{-7} T^2$	g/cm <sup>3</sup>
$\rho_s$	$0.925 - 1.239 \times 10^{-3} T$	g/cm <sup>3</sup>
$\rho_p$	$\rho_m / [0.754 - 9.0 \times 10^{-4} (T - 70)]$	g/cm <sup>3</sup>
$C_{p,m}$	0.49	cal/g·K
$C_{p,s}$	0.457	cal/g·K
$C_{p,p}$	$0.339 + 9.55 \times 10^{-4} (T - 25)$	cal/g·K
$\Delta H_p$	-13800	cal/gmol
$V_{f,m}$	$0.025 + 0.001 \times (T + 106)$	
$V_{f,s}$	$0.025 + 0.001 \times (T + 92)$	
$V_{f,p}$	$0.025 + 0.00048 \times (T - 114)$	
$V$	0.5	$t$
$I_f$	0.032	mol/l
$T_c$	296.15	K

It is well-known that polymerization kinetics exhibit a gel effect due to the increased diffusion limitation at higher viscosities accompanying high conversion. The termination step, which requires the participation of two large polymer molecules, is more affected by this limitation than the propagation step, in which the relatively small monomer molecule diffuses to meet a large polymer molecule. As a result the concentration of living polymer increases rapidly and the polymerization reaction is significantly accelerated as the conversion increases. There are a number of correlations reported for the gel effect in MMA polymerization, which are well summarized by Schmidt and Ray[13]. In this study we shall employ the following correlations for the gel effect ( $g_t = k_t/k_t'$ ,  $g_p = k_p/k_p'$ ) proposed first by Ross and Laurence and then extended by Schmidt and Ray[13].

$$g_t = \begin{cases} 0.10575 \exp[17.15 V_f - 0.01715 (T-273.2)] & (10a) \\ \text{for } V_f > 0.01856 - 2.965 \times 10^{-4} (T-273.2) \\ 2.3 \times 10^{-6} \exp[75 V_f] & (10b) \\ \text{for } V_f \leq 0.01856 - 2.965 \times 10^{-4} (T-273.2) \end{cases}$$

$$g_p = \begin{cases} 1 & \text{for } V_f > 0.05 \\ 7.1 \times 10^{-5} \exp[171.53 V_f] & \text{for } V_f \leq 0.05 \end{cases} \quad (11)$$

where  $k_t'$  denotes the termination rate constant at zero monomer conversion with  $k_p'$  similarly defined, and  $V_f$  is the free volume to be calculated from the volume fractions of monomer, polymer and solvent in the reactor (cf. Table 2).

## RESULTS AND DISCUSSION

In studying the dynamics of the continuous flow reactor, one may hope to obtain the complete solution covering all the system parameters. However, there are usually so many parameters in polymerization processes that it is almost impossible to consider all of these and we must choose several parameters to be treated. Hence, we shall choose four parameters, the feed temperature( $T_f$ ), the solvent fraction( $\phi_s$ ), the thermal conductance(UA) and the residence time( $\theta$ ) as the bifurcation parameter. For the parameter space classification we apply the singularity theory without making reduction of the system of equations to a single equation.

The analysis of steady state and dynamic behaviors has been carried out with the software package AUTO of Doedel[5]. The package was developed on the basis of the bifurcation theory along with numerical continuation technique in tracing branches of steady state as well as periodic solution for systems of ordinary differential equations.

In Fig. 1 the plane of the solvent fraction( $\phi_s$ ) and the thermal conductance(UA) is divided into five regions having different steady state structures. The diagram is constructed for a fixed value of  $T_f = 296.15$  K. It is noticed that for high heat transfer effect(large UA) and low solvent fraction(small  $\phi_s$ ), the region of isola/S-type steady state[Region III] becomes broader while the region of isola/unique type steady state[Region IV] tends to disappear.

For more detailed investigation, the steady state structure at  $UA = 0.05325$  cal/s·K is depicted in the  $(\phi_s, \theta)$ -plane as shown in Fig. 2. This figure shows the boundaries of the multiplicity regions of steady states and also the loci of Hopf bifurcation(HB) points, which are indicated by the solid lines and the dashed lines, respectively. The numbers in Fig. 2 indicate the number of steady states which increases or decreases by two when a solid line is crossed over. The Hopf bifurcation point appears over a wide range of residence time if the solvent fraction falls on the intermediate range(i.e., 0.43 ~ 0.49).

With the thermal conductance UA fixed at 0.05325 cal/s·K bifurcation diagrams are constructed for various values of the solvent fraction and presented in Fig. 3. In these diagrams the solid line represents the stable steady state solution branch, the dashed line the unstable branch, and the filled square the HB point. When the solvent fraction in the feed stream is low[less than 0.31; cf. Part(a)], five steady states can exist for a narrow range of the residence time and among these three solutions correspond to the boiling state(similar to the isothermal condition). As the solvent fraction increases, the solution branch develops to a typical S-type bifurcation[cf. Fig. 3(b)]. If the solvent fraction falls between 0.44 and 0.483, an isola type solution branch and an S-type curve coexist[cf. Fig. 3(c)]. Here we notice that an HB point is present on the isola branch. The isola and S-type branches are extinguished successively as the solvent fraction increases. In particular, it may be suggested that operation at the isola-type solution branch would be profitable for its high conversion with a low residence time[1].

Periodic oscillation phenomenon, which is observed by many

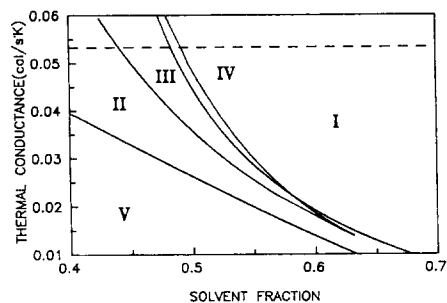


Fig. 1 Division of the  $(\phi_s, UA)$ -plane into regions of different multiplicity patterns when  $T_f = 296.15$  K (I: Unique steady state; II: S-type steady state; III: Isola/S-type steady state; IV: Isola/Unique steady state, and V: five steady states).

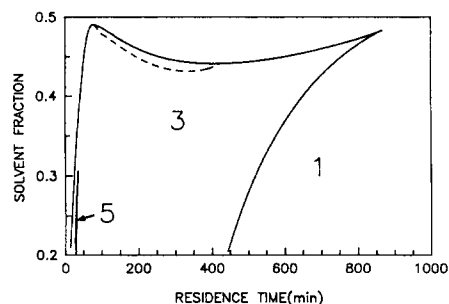


Fig. 2 Multiplicity regions of the steady state in the  $(\theta, \phi_s)$ -plane when  $T_f = 296.15$  K.

other workers, is found over a wide range of the residence time. Figure 4 shows the periodic solution branch emanating from the S-type branch when  $\phi_s = 0.436$ . The upper and lower branches indicate the maximum and minimum values of the conversion, respectively. As illustrated in Fig. 4, the periodic solution grows subcritically and then develops supercritically passing through the periodic limiting point(PLP). The periodic solution branch is generated from the HB point and terminates in a homoclinic. The trajectory of periodic solution and its phase plane portrait are shown in Figs. 5 and 6, respectively. The period of stable limit cycle is about 2 times the residence time and this result is in good agreement with the experimental observation[14].

If the reactor is operated with a higher feed temperature, the dynamic behavior of the reactor becomes even more complex. Figure 7 shows the hysteresis variety and isola variety on the  $(\phi_s, UA)$ -plane for a fixed value of  $T_f = 335.15$  K. Under this condition the parameter space can be divided into eleven regions. In Fig. 8 some of the interesting bifurcation features are presented excluding those similar to Fig. 3. These diagrams are constructed for various values of the solvent fraction with the thermal conductance UA fixed at 0.023 cal/s·K. We notice the mush-room type bifurcation diagram found by Choi[3] and double isola type bifurcation diagram similar to that observed by Adebekun et al.[1]. However, isola in the S-type bifurcation diagram[cf. Fig. 8

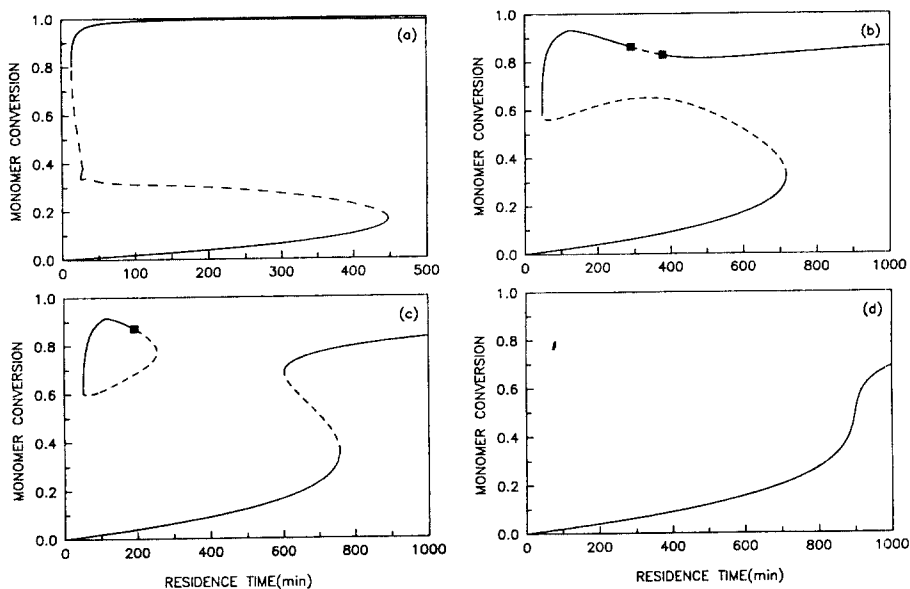


Fig. 3 Bifurcation diagrams when  $UA = 0.05325 \text{ cal/s}\cdot\text{K}$ ,  $T_r = 296.15 \text{ K}$ , and the solvent fractions are (a) 0.2, (b) 0.436, (c) 0.45, and (d) 0.49, respectively.

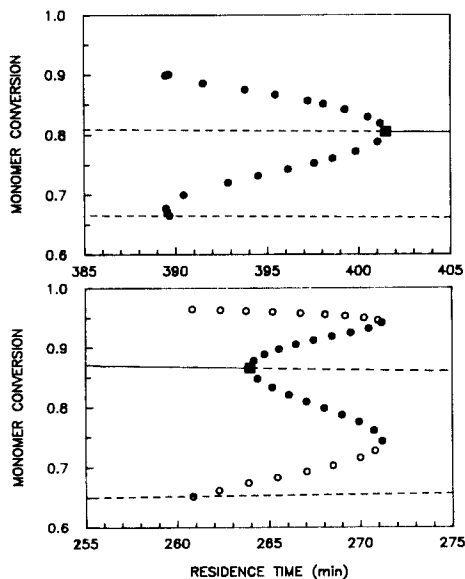


Fig. 4 Bifurcation diagram showing the steady state branch and the periodic solution branch when  $\phi_s = 0.436$  and  $T_f = 296.15 \text{ K}$ .

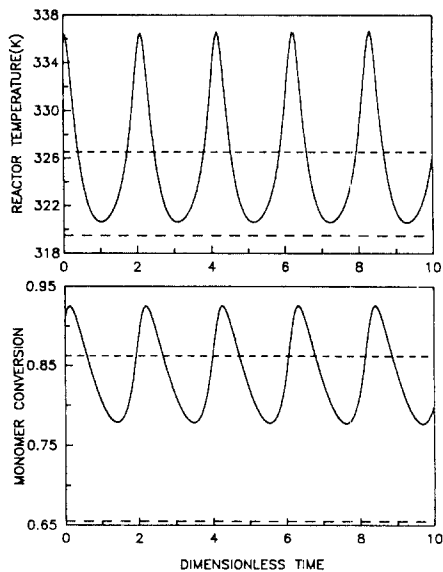


Fig. 5 Steady states and the periodic solution when  $\theta = 270 \text{ min}$  and  $T_f = 296.15 \text{ K}$ .

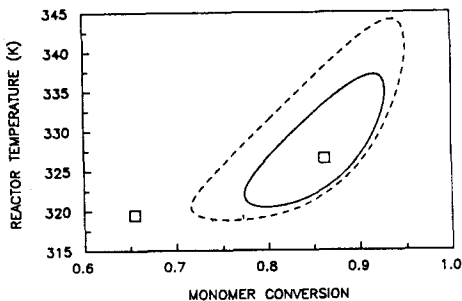


Fig. 6 Phase plane plot of the limit cycles when  $\theta = 270$  min and  $T_f = 296.15$  K.

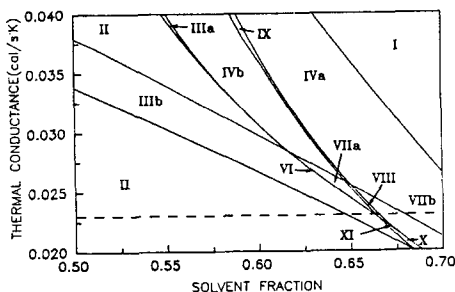


Fig. 7 Division of the  $(\phi_s, UA)$ -plane into regions of different multiplicity patterns when  $T_f = 335.15$  K (VI: Isola in mush-room; VII: Mush-room; VIII: Mush-room/isola; IX: Double isola; X: Mush-room/S-type; XI: Double mush-room type branch; For I through V, see the caption of Fig. 1).

(a)], isola with mush-room type bifurcation diagram [cf. Fig. 8(c)], and double mush-room type bifurcation diagram [cf. Fig. 8(f)] are found for the first time in this study. It is to be noted that the isola branch in Fig. 8 (a) exhibits unusual stability nature; i.e., the upper branch is unstable while the lower one is stable. This is due to the fact that the upper branch of isola in (a) comes from the lower branch of isola in (c).

## CONCLUSIONS

Non-isothermal solution polymerization of MMA in a CSTR with benzoyl peroxide initiator has been analyzed to identify the complex structure of the steady states. In this system a variety of complex behaviors such as steady state multiplicity, multiple Hopf bifurcation (HB) points and limit cycles have been observed.

With the residence time as the bifurcation parameter, five different types of steady state structure can be identified in the  $(\phi_s, UA)$ -plane when the feed temperature is 296.15 K. Under this condition isola-type steady state branch predicted by Schmidt et al. [12] is found and at low values of the solvent fraction five steady states are observed.

When the feed temperature increases to 335.15 K, the structure of the parameter space becomes very complex and eleven different types of steady state pattern are found. In particular, peculiar steady state features such as mush-room/isola type and double mush-room type solution branches are found when the heat transfer rate is low.

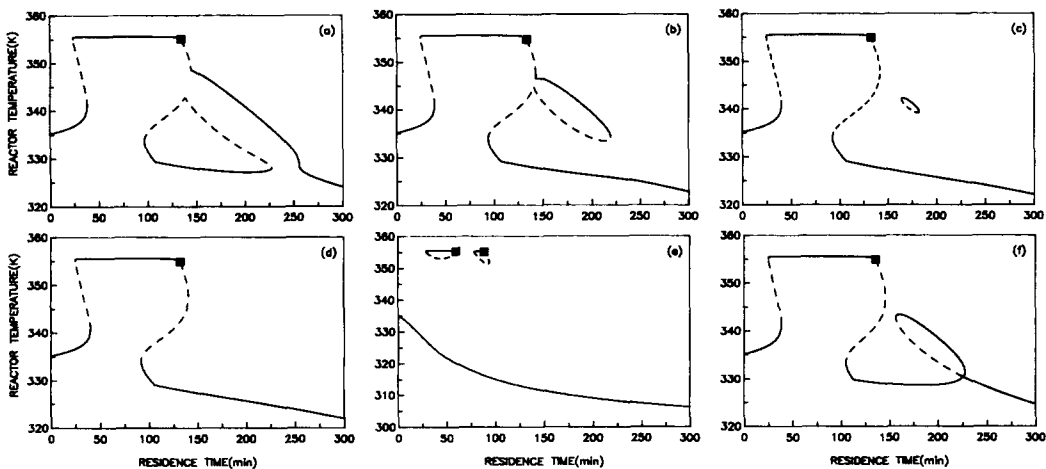


Fig. 8 Bifurcation diagrams for  $UA = 0.023$  cal/s.K,  $T_f = 335.15$  K when  $\phi_s =$  (a) 0.6618, (b) 0.66334, (c) 0.6647, (d) 0.665, (e) 0.55 ( $UA=0.05325$  cal/s.K), and 0.6708 ( $UA=0.021$  cal/s.K), respectively.

## NOTATION

$C_p$	Heat capacity of reaction mixture	[cal/g·°C]
$E$	Activation energy	[cal/mol]
$f$	Initiator efficiency	[ - ]
$\Delta H_p$	Heat of polymerization	[cal/mol]
$I$	Initiator concentration	[mol/l]
$k$	Reaction rate constant	[s <sup>-1</sup> , l/mol·s]
$k_0$	Pre-exponential factor	[s <sup>-1</sup> , l/mol·s]
$k_p$	Propagation rate constant	[l/mol·s]
$M$	Monomer concentration	[mol/l]
$G$	Living polymer concentration	[mol/l]
$q$	Volumetric flow rate	[l/s]
$S$	Solvent concentration	[mol/l]
$T$	Reactor temperature	[K]
$T_c$	Coolant temperature	[K]
$UA$	Thermal conductance	[cal/s·K]
$V$	Reactor volume	[l]

### Greek letters

$\epsilon$	Volume contraction factor	[ - ]
$\theta$	Reactor residence time	[s]
$\nu$	Volume fraction in the reactor	[ - ]
$\rho$	Density of reaction mixture	[g/l]
$\phi$	Volume fraction in feed stream	[ - ]

### Subscripts

$f$	Feed condition
$m$	Monomer(MMA)
$p$	Polymer(PMMA)
$s$	Solvent

## REFERENCE

1. A.K. Adebekun, K.M. Kwalik and F.J. Schork, "Steady-state multiplicity during solution polymerization of methyl methacrylate in a CSTR," *Chem. Engng Sci.*, **44**, 2269-2281(1989).
2. V. Balakotaiah and D. Luss, "Analysis of the multiplicity patterns of a CSTR," *Chem. Engng Commun.*, **13**, 111-132(1981).
3. K.Y. Choi, "Analysis of steady state of free radical solution polymerization in a continuous stirred tank reactor," *Polymer Engng and Sci.*, **26**, 975-981(1986).
4. A.B. Clinch, Master's thesis, University of Wisconsin(1983).
5. E.J. Doedel, AUTO: Software for Continuation and Bifurcation Problems in Ordinary Differential Equations, California Institute of Technology, Pasadena, CA(1986).
6. M. Golubitsky and D.G. Schaeffer, *Singularity and Groups in Bifurcation Theory*, Vol. 1, Springer-Verlag, New-York (1985).
7. J.W. Hamer, T.A. Akramov and W.H. Ray, "The dynamic behavior of continuous polymerization reactors-II. Nonisothermal solution homopolymerization and copolymerization in a CSTR," *Chem. Engng Sci.*, **36**, 1897-1914(1981).
8. R. Jaisinghani and W.H. Ray, "On the dynamic behavior of a class of homogeneous continuous stirred tank polymerization reactors," *Chem. Engng Sci.*, **32**, 811-825(1977).
9. K.J. Kim and K.Y. Choi, "Steady state behavior of a continuous stirred tank reactor for styrene polymerization with bifunctional free radical initiators," *Chem. Engng Sci.*, **43**, 965-977(1988).
10. G. Odian, *Principles of Polymerization*, John Wiley, New York(1981).
11. A.B. Poore, "A model equation arising from chemical reactor theory," *Archs ration. Mech. Analysis*, **52**, 358-388(1973).
12. A.D. Schmidt, A.B. Clinch and W.H. Ray, "The dynamic behavior of continuous polymerization reactors-III. An experimental study of multiple steady state in solution polymerization," *Chem. Engng Sci.*, **39**, 419-432(1984).
13. A.D. Schmidt and W.H. Ray, "The dynamic behavior of continuous polymerization reactors-I. Isothermal solution polymerization in a CSTR," *Chem. Engng Sci.*, **36**, 1401-1410(1981).
14. F. Teymour and W.H. Ray, "The dynamic behavior of continuous solution polymerization reactors-IV. Dynamic stability and bifurcation analysis of an experimental reactor," *Chem. Engng Sci.*, **44**, 1967-1982(1989).
15. T.J. Tulig and M. Tirrel, "Toward a molecular theory of the Trommsdorff effect," *Macromolecules*, **14**, 1501-1511(1981).
16. A. Uppal, W.H. Ray and A.B. Poore, "The classification of the dynamic behavior of continuous stirred tank reactors-influence of reactor residence time," *Chem. Engng Sci.*, **31**, 205-214(1976).
17. A. Uppal, W.H. Ray and A.B. Poore, "On the dynamic behavior of continuous stirred reactors," *Chem. Engng Sci.*, **29**, 967-985(1974).