

Nonisothermal Bulk Copolymerization of Styrene and Methyl Methacrylate in a CSTR: Multiplicity and Stability Analysis*

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Synopsis

A theoretical investigation of the nonisothermal bulk copolymerization of styrene and methyl methacrylate in a CSTR is reported. A modified framework of free volume theory is developed for a copolymerization system to account for the effect of concentration and temperature on the propagation and termination processes. The evolution of multiple steady states for a set of system parameters has been demonstrated. The stability of these steady states has also been examined.

INTRODUCTION

Polymerization reactions release large amounts of heat as the monomer is converted to polymer. In addition, the mechanical energy required for mixing may be converted to heat under highly viscous conditions. Removal of this heat is often difficult for high conversion polymerization because of high viscosity, heat transfer surface fouling, and change of phase during reaction. In many industrial situations, disastrous reactor run away is an ever present potential hazard because of these heat removal difficulties. This presents a great challenge to the process control engineer as well as to the reactor designer.

Recent studies of CSTRs for bulk or solution polymerization indicate the possibility of multiple steady states even under isothermal reactor conditions.^{1,2} Due to limited heat removal capacity of industrial reactors, heat evolution due to reaction is an additional source of autocatalytic behavior. These temperature effects produce even more interesting types of multiple steady state behavior. Almost all the previous analyses in the literature on nonisothermal multiplicity and stability of reactors have been restricted to homopolymerization systems. The dependence of the propagation and termination parameters on the nature and composition of monomer feed can lead to multiplicity of states under certain sets of operating conditions. There is a need to examine the stability of these states and product distribution corresponding to each of the steady states.

In this work, a comprehensive analysis is presented which reflects the effect of composition and temperature on the propagation and termination

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processes during copolymerization. The free volume framework³ as employed for the homopolymerization of Balke and Hamielec⁴ and Ross and Laurence⁵ has been extended to copolymerization. Using this model, the steady states behavior of the nonisothermal bulk copolymerization of styrene and methyl methacrylate (S-MMA) is investigated.

THEORETICAL DEVELOPMENT

Physical Phenomena of High Conversion Copolymerization

In the bulk free radical polymerization, the polymerization begins with pure monomers and the initiator. As the concentration of polymer chains increases, there is a relatively little increase in the termination processes. This is related to the effect of polymer concentration on the coil size. At conversions in the range of 15-20 mol %, polymer chains begin to entangle, causing a dramatic reduction in radical chain translational mobility, giving a rapid drop in the termination processes. In copolymerization, there are also changes in the propagation processes (as reflected in the reactivity ratios), and these changes are such as to enhance the overall rate of polymerization. An *a priori* knowledge of these effective groups is essential for any rational design of a copolymerization reactor. Additionally, at high levels of conversion, the heat effects of the exothermic reaction will become substantial, necessitating an exact accounting of the variation of the rate of polymerization and the effective rate groups. Virtually no published data are available on the influence of temperature on copolymerization rate parameters at high conversions. The overall activation energy for most free radical polymerizations is about 80-90 kJ/mol. This corresponds to a two- or threefold rate increase for a 10°C rise in temperature, resulting in increase of the viscosity of the reaction medium. The rise in temperature has an inverse effect on the viscosity of the medium. Hence in the absence of a feasible process to estimate the overall influence of temperature on the copolymerization rate parameters at higher conversions, the free volume theory of Bueche,³ which takes into account the effect of concentration and temperature on the propagation and termination processes, has been used. The success of the modeling of homopolymerization reactors shows that the free volume models^{6,7} do an adequate job of describing a rather broad range of phenomena that occur during polymerization processes. While developing the model based on free volume, it is assumed that the gel effect occurs at the point where the segmental motion of the polymer chains become equal to the translational diffusion of the chains, and it has a critical free volume given by V_{fc} .⁸

Kinetic Model for Copolymerization

Employing the classical model, the rate of copolymerization is expressed as⁹

$$R_p = \frac{(r_A C_A^2 + 2C_A C_B + r_B C_B^2) R_i^{1/2}}{[(r_A \delta_A C_A)^2 + 2\theta r_A r_B \delta_A \delta_B C_A C_B + (r_B \delta_B C_B)^2]^{1/2}} \quad (1)$$

Here R_p is the rate of copolymerization, C_A and C_B are the concentrations of monomers A and B, R_K is the rate of initiation ($2fk_dC_K$), f is the initiator efficiency, k_d is the rate constant for initiator decomposition, and C_K is the concentration of initiator K. The various rate groups appearing in eq. (1) are defined as

$$\begin{aligned}r_A &= k_{pAA}/k_{pAB} \\r_B &= k_{pBB}/k_{pBA} \\ \delta_A &= \left(2k_{tAA}/k_{pAA}^2\right)^{1/2} \\ \delta_B &= \left(2k_{tBB}/k_{pBB}^2\right)^{1/2} \\ \theta &= k_{tAB}/2\left(k_{tAA}k_{tBB}\right)^{1/2}\end{aligned}$$

The relative rate groups represented by r_A , r_B , δ_A , δ_B , and θ in eq. (1) take into account the rate constants for the basic steps of initiation, propagation, and termination rate processes. Equation (1) is expressed in terms of the individual rates of reacting monomers as

$$R_A = \frac{-dC_A}{dt} = \alpha_A C_A C_K^{1/2} \quad \text{for monomer A} \quad (2)$$

$$R_B = \frac{-dC_B}{dt} = \alpha_B C_B C_K^{1/2} \quad \text{for monomer B} \quad (3)$$

Here α_A and α_B are the apparent rate functions and are given as

$$\alpha_A = [(r_A - 1)x + 1]/(T'_0)^{0.5} \quad (4)$$

and

$$\alpha_B = [(1 - r_B)x + r_B]/(T'_0)^{0.5} \quad (5)$$

here

$$x = C_A/(C_A + C_B) \quad (6)$$

$$(T'_0)^{0.5} = [T_0/(2fk_d)]^{0.5} \quad (7)$$

and

$$T_0 = (r_A \delta_A x)^2 + 2\theta r_A r_B \delta_A \delta_B x(1 - x) + [r_B \delta_B (1 - x)]^2 \quad (8)$$

The parameter T'_0 in eqs. (4) and (5) involves the constants corresponding to the termination rate processes.

Kinetic Data for the Copolymerization of Styrene Methyl Methacrylate and Estimation of the Rate Parameters

Although the set of equations (1)–(8) could be explored in their full generality, it was thought desirable that a specific system of pragmatic interest on which there exists a sound data base should be explored. Styrene–methyl methacrylate system was chosen for this purpose. Pertinent experimental data to enable model calculations were obtained by analyzing the data for this system studied by two different groups under identical reaction conditions.^{10,11} It is the only copolymerization system in which published reports on systematic studies have been reported till the limiting conversion (90 mol %) backed up by good kinetic data. In our earlier work¹² we had analyzed the data on this system to obtain generalized correlations for the variation of θ with the feed composition. In addition, the reactivity ratios for the individual monomers and the termination processes represented by T'_0 have been correlated with the extent of conversion. These correlations are now expressed in terms of the cumulative fractional free volume.

Estimation of Cumulative Fractional Free Volume

Free volume represents the space not occupied by the molecules themselves. As the polymerization mixture approaches the glass transition point, the free volume decreases, until there is a minimal free volume when macromolecular motion ceases. The minimal fractional free volume at the glass transition temperature was found to be close to 0.025.¹³ The cumulative fractional free volume may be defined³ from the various contributions of monomers and polymers as

$$V_f = V_{fp}\theta_p + V_{fA}\theta_A + V_{fB}\theta_B \quad (9)$$

where θ_p, θ_A , and θ_B are the volume fractions of polymer, monomer A, and monomer B in the mixture, respectively. The specific free volume contributions of the individual species are related to the glass transition temperature as

$$V_{fp} = 0.025 + \alpha_p(T - T_{gp}) \quad (10)$$

$$V_{fA} = 0.025 + \alpha_{MA}(T - T_{gA}) \quad (11)$$

$$V_{fB} = 0.025 + \alpha_{MB}(T - T_{gB}) \quad (12)$$

with

$$\begin{aligned} \alpha_p &= 4.8 \times 10^{-4}/\text{K} \\ \alpha_{MA} &= 1 \times 10^{-3}/\text{K} \\ \alpha_{MB} &= 1 \times 10^{-3}/\text{K} \end{aligned} \quad (13)$$

where α_p, α_{MA} , and α_{MB} are the coefficients of volumetric expansion. Equations (10)–(12) have been tested for several polymer diluent systems and

have been found to be fairly accurate. d_{mb} is the glass transition temperature of the copolymer and its variation with copolymer composition for styrene methylmethacrylate (S-MMA) is shown in Figure 1.¹⁴ The variation of T_{gp} with copolymer composition were correlated by us using linear regression and the coefficients deduced are given in Table II.

T_{gA} and T_{gB} are the glass transition temperatures of the monomers and are not reported in the literature. These were estimated by using the universal correlation developed by Fedors¹⁵:

$$\gamma_T = \frac{T_m + T_b}{T_g + T_b} \quad (14)$$

Here T_m is the melting point and T_b is the boiling point of the monomers, both being measured at atmospheric pressure. γ_T is a universal constant independent of the molecular structure of liquid and its value was found to be 1.15. Using eq. (14), T_{gB} of styrene was estimated to be 156.2 K. T_{gB} , the glass transition temperature of monomer B (MMA) is reported in the literature¹⁶ to be 167 K.

Variation of the Propagation Processes with Free Volume

Propagation processes to which r_A and r_B refer do not proceed readily on encounter, since they are usually associated with energy of activation of 20 kJ mol⁻¹ or more. They are not expected to become diffusion-controlled until the mutual diffusivities of the reactants have fallen to very low values. But in the copolymerization of monomers with largely different chemical polarities, the probability of a change in the propagation processes will be

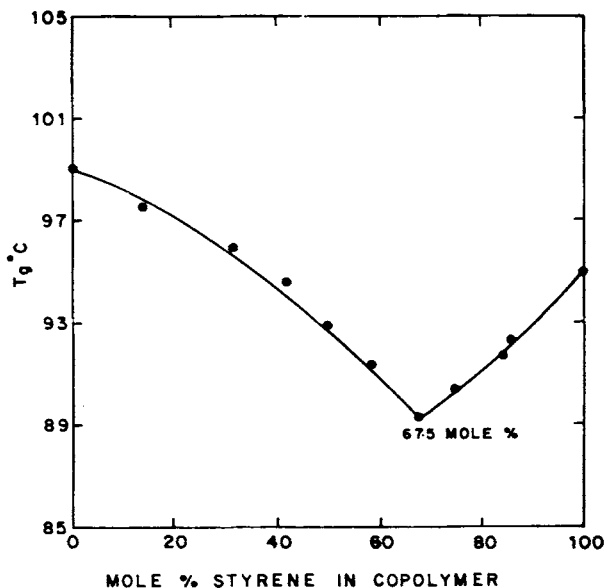


Fig. 1. Experimental T_g of S-MMA copolymer vs. mol % styrene in the copolymer (Johnston¹⁴).

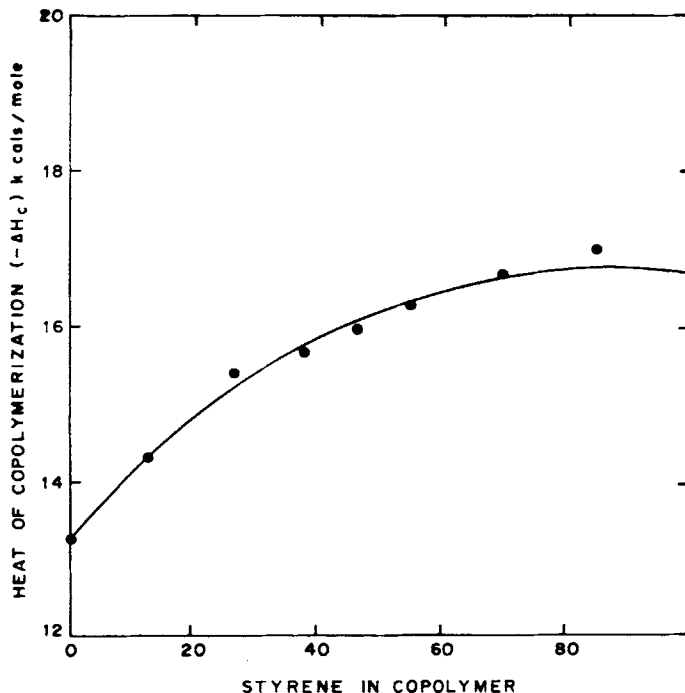


Fig. 2. Heat of S-MMA copolymerization as a function of styrene monomer concentration (Suzuki et al.³).

considerable. This arises mainly because the change in the rate constants of the chain propagation vary considerably between the monomers which become significant at higher conversions, leading to a decrease in r_A and an increase in r_B . This has been confirmed recently by Zilberman et al.¹⁷ in the solution copolymerization of methacrylamide with methacrylic acid or sodium methacrylate. The variation was quite considerable when acrylamide was copolymerized with acrylonitrile.¹⁸ The variation of r_A and r_B with free volume for S-MMA copolymerization is shown in Figures 3 and 4, and the correlations developed are given in Table II. It should be noted

TABLE I
Pertinent Physicochemical Data Used in the Study²²

	Styrene	Methyl methacrylate
	k_p $1.057 \times 10^7 \exp(-3557/T)$	$9 \times 10^5 \exp(-2365/T)$
	k_t $1.255 \times 10^9 \exp(-843/T)$	$1.1 \times 10^8 \exp(-604/T)$
Specific heat, c_p (cal/mol K)	0.4186	0.49
Density (g/cc)	0.9010	0.940
Mol wt (M)	104.14	100
Boiling point (K)	418.2	373
Melting point (K)	242.4	225
Initiator (Benzoyl peroxide)	k_d s^{-1} $2 \times 10^4 \exp(-15235/T)$	f 0.75

TABLE II
Copolymerization of Styrene-Methyl Methacrylate Data Used for Simulation

Feed to the reactor

- Styrene (C_{A_f}) = 5.35442 mol/L
- Methyl methacrylate (C_{B_f}) = 3.57464 mol/L
- Initiator (D_{R_f}) = 0.00826 mol/L

Cumulative fractional free volume corresponding to the gel point
(V_{f_c}) = 0.1596

Glass transition temperature of monomers

- Styrene (T_{gA}) = 156.208 K
- Methylmethacrylate (T_{gB}) = 167 K

Variation of the glass transition temperature of the polymer (T_{gp}) with the composition of styrene in the copolymer (F_A)

$$T_{gp} \text{ (K)} = 132.8 - 1.732 \times 10^2 (F_A) + 2.144 \times 10^2 (F_A)^2 - 79.06(F_A)^3 + 273 \quad \text{for } F_A > 0.675$$

$$T_{gp} \text{ (K)} = 98.8 - 8.934(F_A) - 3.436(F_A)^2 - 6.821(F_A)^3 + 273 \quad \text{for } F_A \leq 0.675$$

Variation of the heat of copolymerization ($-\Delta H_c$) with the composition of styrene in the feed (x)

$$(-\Delta H_c) = 13.14 + 13.18(x) - 29.13(x)^2 + 35.82(x)^3 - 16.42(x)^4 \quad \text{(Ref. 21)}$$

Variation of r_A , r_B and $(T')^{1/2}$ with free volume

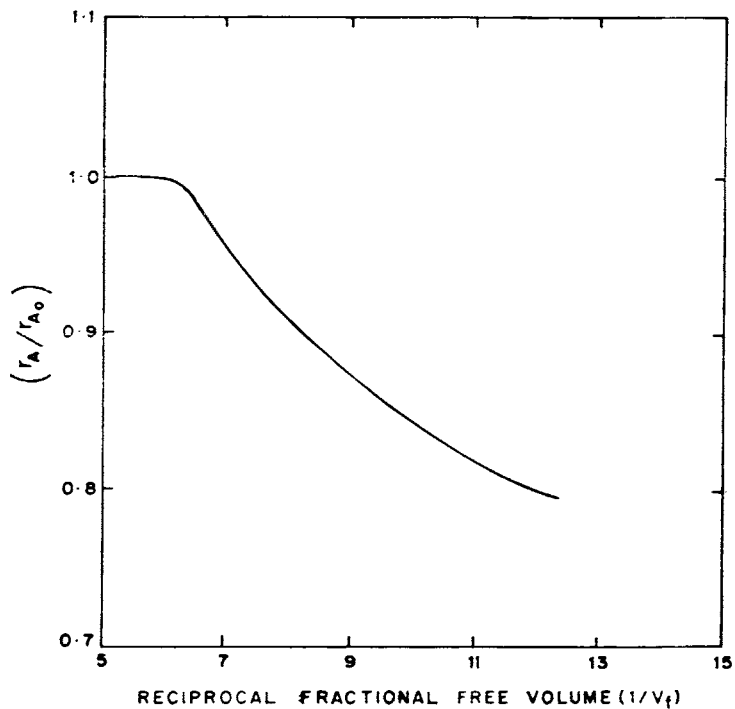
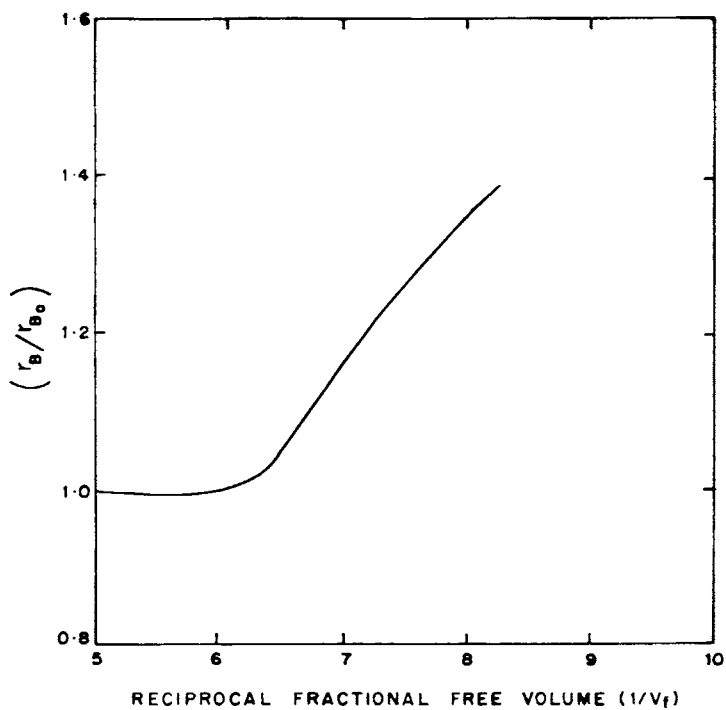
- (i) $V_f > V_{f_c}$
 - $r_{A0} = 1.83 \exp(-450/T)$
 - $wr_{B0} = 1.27 \exp(-340/T)$
 - $T_0 = (r_{A0}\theta_A x)^2 + 2\delta r_{A0}r_{B0}\theta_A x(1-x)$
 - $(T')^{1/2} = (T_0')^{1/2} = [T_0/(2fk_d)]^{1/2}$
- (ii) $V_f < V_{f_c}$
 - $r_A = r_{A0} + \sum_{i=1}^n a_i \left(\frac{1}{V_f} - \frac{1}{V_{f_c}} \right)^i$, $a_1 = -3.220 \times 10^{-2}$, $a_2 = 4.862 \times 10^{-3}$
 $a_3 = -4.672 \times 10^{-4}$, $a_4 = 1.8;6 \times 10^{-5}$
 - $r_B = r_{B0} + \sum_{i=1}^n b_i \left(\frac{1}{V_f} - \frac{1}{V_{f_c}} \right)^i$, $b_1 = 1.604 \times 10^{-1}$, $b_2 = -4.455 \times 10^{-2}$
 $b_3 = 5.405 \times 10^{-3}$, $b_4 = -2.331 \times 10^{-4}$

$$(T')^{1/2} = (T_0')^{1/2} v_f = v_{f_c}$$

where v is the gel effect parameter

$$\text{and } v = \left[1 + \sum_{i=1}^n c_i \left(\frac{1}{v_f} - \frac{1}{v_c} \right)^i \right]$$

- $c_1 = -0.482$, $c_2 = 0.1098$,
- $c_3 = -1.203 \times 10^{-2}$,
- $c_4 = 4.913 \times 10^{-4}$

Fig. 3. Variation of r_A with free volume.Fig. 4. Variation of r_B with free volume.

here that the free volume variation with composition of monomers is negligible (about 2% and well within the error for the determination of reactivity ratios). This implies that r_A and r_B though shown to be functions of the cumulative fractional free volume are approximately invariant with composition within the normal limits (between 30 and 70 mol % of monomer A) of the operation of the reactor.

Variation of the Termination Processes with Free Volume

During the bulk copolymerization of two monomers, if it is assumed that chain entanglement occurs soon after termination becomes diffusion controlled,¹⁹ then

$$T_e = k_1 D_p \quad (15)$$

where T_e is the effective variation of the termination rate processes alone, k_1 is the temperature-dependant proportionality constant, and D_p is the diffusion coefficient of the polymer molecule. According to Bueche,³ the diffusion coefficient of the polymer molecule is given as

$$D_p = \xi \exp(-A/V_f) \quad (16)$$

Combinations of eqs. (15) and (16) leads to

$$T_e = k_1 \xi \exp(-A/V_f) \quad (17)$$

In eq. (17), ξ and A are constants and V_f is the cumulative fractional free volume given by eq. (9).

A close examination of eq. (8) reveals that it contains the propagation parameters r_A , r_B , and x besides the termination rate parameters $\delta'_A = [\delta_A/(2f_{kd})^{1/2}]$, $\delta'_B = [\delta_B/(2f_{kd})]$, and θ , all of which vary with the extent of free volume or conversion. We can equivalently say that

$$\Delta T' = \frac{T'}{T'_0} = f(\Delta\delta'_A, \Delta\delta'_B, \Delta\theta, \Delta r_A, \Delta r_B, \Delta x) \quad (18)$$

where T'_0 and T' denotes the value of T_0 before and after the onset of gel effect respectively. As seen from eq. (18), it is apparent that it is not possible to evaluate the variation of $\Delta\delta'_A$, $\Delta\delta'_B$, and $\Delta\theta$ alone with the extent of free volume. The data given by Dionisio and O'Driscoll¹¹ for the S-MMA copolymerization system shows that up to about 50% conversion, the change in the concentration of styrene in the reactor (x) is only about 10% and in this range, the net effect of change of Δr_A , Δr_B , and x on $\Delta T'$ is negligible. and $T_e^*/T'_0 \simeq T'/T'_0$ as seen from the semilog plot shown in Figure 5. It is interesting to note from Figure 5 that it consists of three distinct phases of polymerization behavior. At low conversions, the course of polymerization is described by the conventional kinetics (phase I). After a certain conversion or free volume ($V_f < V_{fc}$), the well-known gel effect is observed and the termination processes obey eq. (17) and change exponentially with free

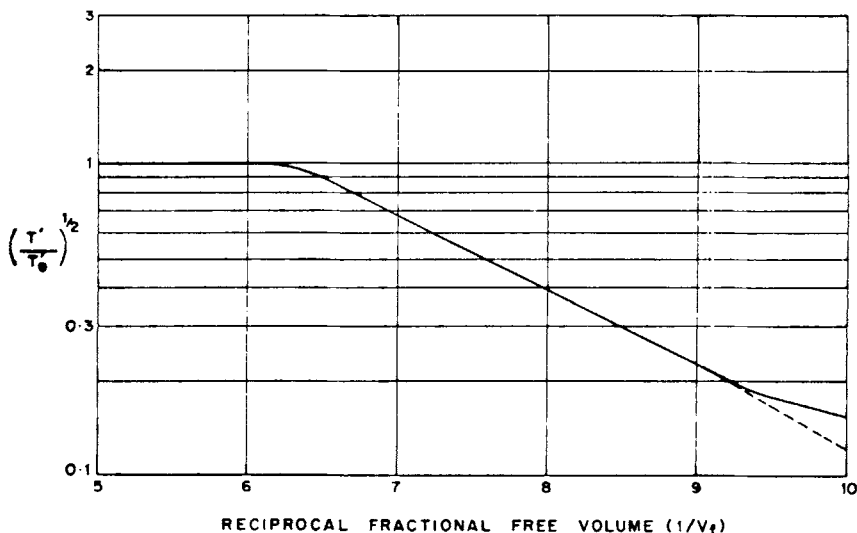


Fig. 5. Variation of the termination processes with free volume.

volume (phase II). At conversions higher than 60 mol % (phase III) a deceleration in the value of T'/T_0 is observed as shown in Figure 5. A similar observation in the high conversion region (60–65 mol %) was made recently by Soh and Sunderberg^{20,21} in their studies on diffusion-controlled vinyl polymerization. They attributed the deceleration to the cumulative molecular weight averages (except the number average molecular weight) beginning to decrease slightly. The variation of T'/T_0 with free volume till limiting conversion is correlated by a polynomial and the individual coefficients deduced by linear regression are given in Table II.

In summary, we have analyzed the data on the high conversion copolymerization of styrene and methyl methacrylate available in the literature and developed a model based on the free volume framework. The model takes into account the effect of concentration and temperature on the termination and propagation processes. This model forms the basis for our subsequent analysis of the steady state behavior of the nonisothermal bulk copolymerization of S-MMA in a CSTR to be discussed in detail.

STEADY STATE MULTIPLICITY AND STABILITY ANALYSIS

Multiplicity Analysis

The system under consideration is a CSTR in which the copolymerization of the monomers takes place. If we allow a fresh feed of monomer A to be mixed with monomer B containing the initiator K, then the system can be described by the following material and energy balance equations:

$$V \frac{dC_A}{dt} = F(C_{A_f} - C_A) - V\alpha_A C_A C_K^{1/2} \quad (19)$$

$$V \frac{dC_B}{dt} = F(C_{B_f} - C_B) - V\alpha_B C_B C_K^{1/2} \quad (20)$$

and

$$V\rho C_p \frac{dT}{dt} = F\rho C_p(T_f - T) + V(-\Delta H_c) \quad (21)$$

$$[(\alpha_A C_A + \alpha_B C_B)C_K^{1/2}] - UA(T - T_c)$$

In eqs. (19)–(21), the initiator concentration C_K is given by

$$C_K = \frac{C_{K_f}}{1 + 2fk_d \theta} \left\{ 1 - \exp\left[-\left(\frac{1}{\theta} + 2fk_d\right)t\right] \right\} \quad (22)$$

$$+ C_{k_0} \left\{ \exp\left[-\left(\frac{1}{\theta} + 2fk_d\right)t\right] \right\}$$

where $\theta = V/F$.

At a given temperature T and residence time θ , eqs. (19) and (20) are solved numerically with the initial conditions, $t = 0$ $C_A = C_{A_0}$, $C_B = C_{B_0}$, and $C_K = C_{K_0}$ by the fourth-order RKG integration method. For every new value of x and F_A , the corresponding C_p , ρ , $\theta(-\Delta H_c)$, and T_g are evaluated by the correlations given in Table II. The variation of $(-\Delta H_c)$ with the composition of styrene in the monomer mixture for the system S–MMA is shown in Figure 2.²³ The cumulative free volume fraction was then calculated using eq. (9). The reactivity ratios r_A , r_B , and the termination parameters T' were then determined. The variations of r_A , r_B , and T' depend on the critical free volume V_{fc} . The computations were continued till the concentrations of the monomers in the reactor reached a steady state value. At steady state, the combination of eqs. (19) and (20) gives

$$\frac{m}{\Theta} = \frac{R_p}{(C_{A_f} + C_{B_f})} \quad (23)$$

In eq. (23), $R_p = [\alpha_A C_A + \alpha_B C_B]C_K^{1/2}$ and

$$m \text{ is the total conversion} = 1 - \left(\frac{C_A + C_B}{C_{A_f} + C_{B_f}} \right)$$

Substituting eq. (23) in eq. (22) gives at steady state,

$$F(C_{A_f} + C_{B_f})(-\Delta H_c)m = F\rho C_p(T - T_f) + UA(T - T_c) \quad (24)$$

The lhs of eq. (24) represents the rate of heat generation. θ_g which is proportional to be heat of copolymerization and the degree of conversion

m which in turn is determined by the residence time θ . The two rhs terms in eq. (24) represent the rate of heat removal, Q_R as a result of the heat absorbed by the cold feed and the heat transformed to the cooling medium, respectively. Using the numerical values of the system parameters given in Tables I and II in the steady state, expression (24) shows the possibility of the existence of multiple steady states, when the slope of the heat generating line (Q_g vs. T) is greater than the slope of the heat removal line ($FpC_p + UA$), as shown in Figure 6. Figures 7-9 show schematically the effect of the operating variables on the heat generation rate and the heat removal rate.

Stability Analysis

The local stability character of the steady states of the reactor has been determined by examining the transient eqs. (19)-(21) linearized around the steady state. For this purpose, the Jacobian matrix is formulated as

$$\bar{A} = \begin{vmatrix} \frac{\partial f_1}{\partial C_A} & \frac{\partial f_1}{\partial C_B} & \frac{\partial f_1}{\partial T} \\ \frac{\partial f_2}{\partial C_A} & \frac{\partial f_2}{\partial C_B} & \frac{\partial f_2}{\partial T} \\ \frac{\partial f_3}{\partial C_A} & \frac{\partial f_3}{\partial C_B} & \frac{\partial f_3}{\partial T} \end{vmatrix} \quad (25)$$

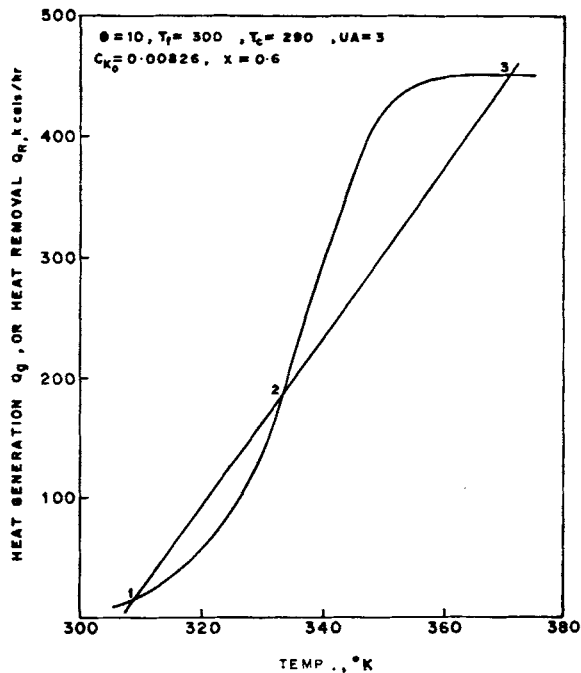


Fig. 6. Predicted multiplicity of states in exothermic copolymerization of S-MMA.

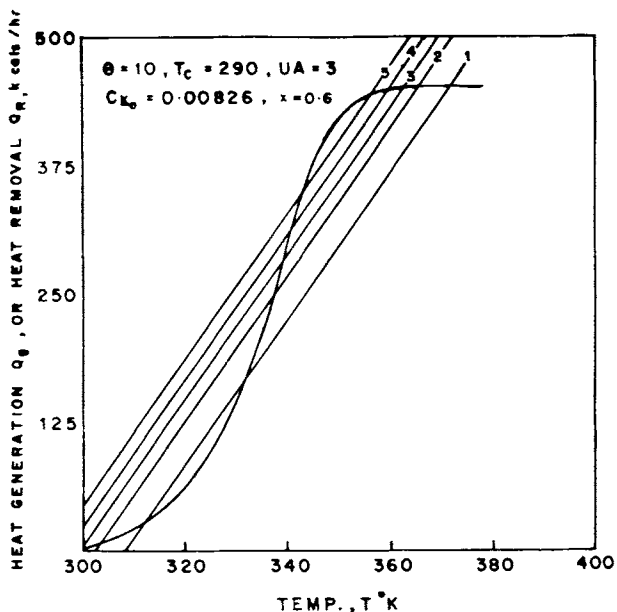


Fig. 7. Effect of feed temperature on heat removal. T_f (K): (1) 320; (2) 310; (3) 300; (4) 305; (5) 295.

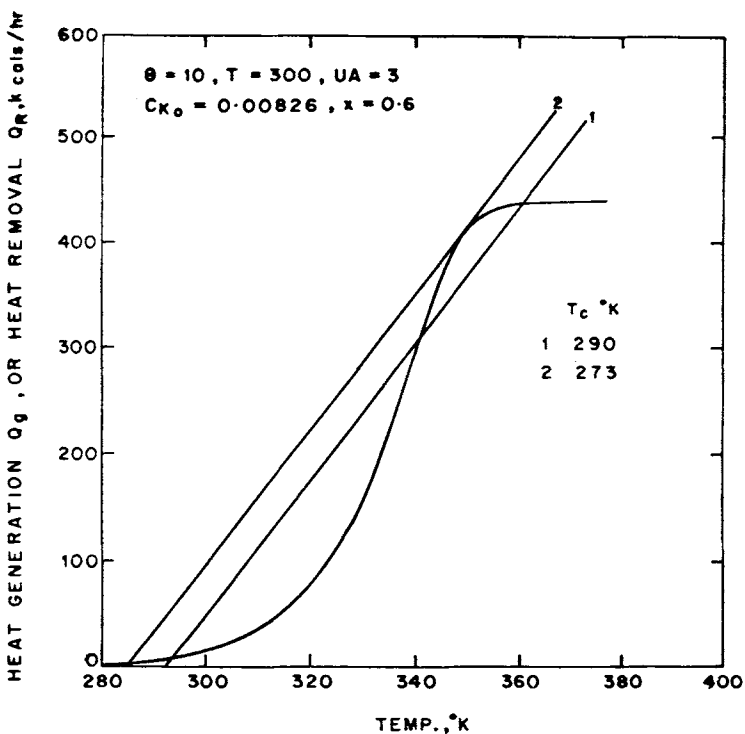


Fig. 8. Effect of coolant temperature on heat removal. T_c (K): (1) 290; (2) 273.

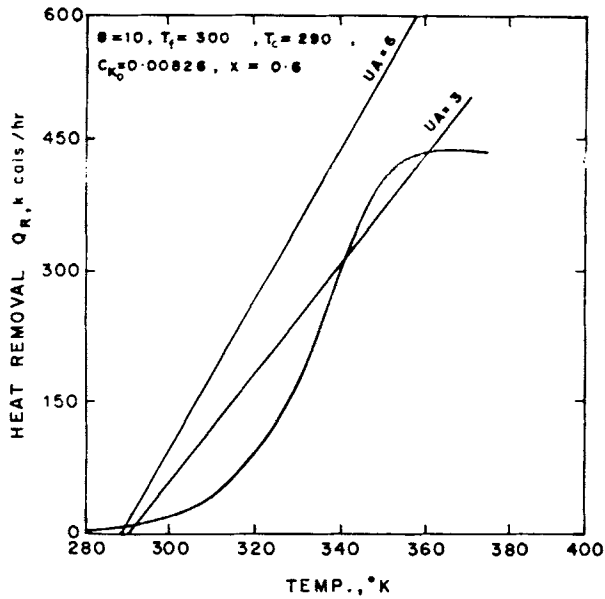


Fig. 9. Effect of reactor cooling capacity on heat removal.

The conditions for the steady state to be a asymptotically stable are well known²⁴

$$(-\text{tr } \bar{A}) > 0$$

$$\frac{\sum \text{minors of diag elements} (-\text{tr } \bar{A}) + (\det \bar{A})}{\sum \text{minors of diag elements}} > \theta \quad (26)$$

$$-(\det \bar{A}) > 0$$

The analysis indicates the existence of only two stable states, the lower and the upper one, the middle one being unstable.

The present study thus provides the influence of concentration, temperature, heat of reaction, and residence time on the region of multiplicity of the nonisothermal bulk copolymerization of S-MMA in a CSTR. For a set of fixed parameter values, the region of multiplicity has been identified by numerically solving eqs. (19)–(21). In the region of multiplicity, the stability of each solution is ascertained by performing linear stability analysis.

CONCLUSIONS

In this work we have used the framework of free volume theory and presented a comprehensive approach to determine the influence of reactor operating conditions on the type of steady state behavior and also the overall performance expected for the nonisothermal bulk copolymerization of styrene and methyl methacrylate in a CSTR. The results suggest that the control of a copolymerization reactor at high conversions in a CSTR may offer some unique problems. Better understanding of the dynamics of com-

plex copolymerization processes such as the one considered in this paper can enable to define the directions for developments in reactor control theory and improve dramatically our ability to design and control copolymerization reactors with a variety of in built feedback loops.

APPENDIX: NOMENCLATURE

\underline{A}	reactor jacket area for heat transfer
A	Jacobian matrix defined by eq. (25)
C_A	concentration of monomer A
C_B	concentration of monomer B
C_K	concentration of initiator K
C_p	specific heat of the reactants
D_p	diffusion coefficient of the polymer molecule
f	initiator efficiency
f_1, f_2, f_3	functions of jacobian matrix defined by eqs. (19)–(21)
F	flow rate of reactants
F_A	composition of monomer A in the copolymer
k_1	temperature dependent proportionality constant
k_d	rate constant for initiator decomposition
$k_{pAA}, k_{pAB}, k_{pBA}, k_{pBB}$	rate constants for propagation
$k_{tAA}, k_{tAB}, k_{tBB}$	rate constants for termination
m	conversion of monomers
r_A, r_B	reactivity ratios
R_A	rate of polymerization of monomer A
R_B	rate of polymerization of monomer B
R_K	rate of initiation
R_p	total rate of copolymerization
t	reaction time
T	temperature
T_0	termination rate parameter defined by eq. (8)
T	termination rate parameter defined by eq. (7)
T_b	boiling point of the monomer
T_c	coolant temperature
T_e	effective termination rate processes defined by eq. (17)
T_f	feed temperature
T_g	glass transition temperature
T_m	melting point of the monomer
U	overall heat transfer coefficient
V	effective reactor volume
V_f	cumulative fractional free volume
x	mole fraction of monomer A defined by eq. (6)

Greek Symbols

α_A, α_B	apparent rate functions
α_m, α_p	coefficients of volumetric expansion
γ_T	universal constant defined by eq. (14)
ΔH_f	heat of copolymerization
δ_A, δ_B	defined by eq. (1)
Θ	residence time
θ	defined by eq. (1)
θ_m	volume fraction
ρ	density
ξ	constant defined by eq. (17)

Subscripts

A	monomer A
B	monomer B
K	initiator K
<i>f</i>	feed
p	polymer

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