



THE DYNAMIC BEHAVIOR OF CONTINUOUS SOLUTION POLYMERIZATION REACTORS—VII. EXPERIMENTAL STUDY OF A COPOLYMERIZATION REACTOR

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Abstract—The dynamic behavior of continuous free-radical solution copolymerization reactors was studied, using VA (vinyl acetate) and MMA (methyl methacrylate) as comonomers. Due to the lack of data in the literature, a mathematical model was built and some kinetic parameters were determined for different operation conditions. This model was used to build a set of bifurcation diagrams, where oscillatory and ignition-extinction phenomena could be predicted as a function of operation conditions. Additional experiments validated the model predictions and showed that the dynamic behavior of these reactors may be extremely sensitive to changes in the feed composition.

1. INTRODUCTION

The first work to study the detailed dynamic structure of solution polymerization reactors was by Jaisinighani and Ray (1977). Based on literature data, part of the bifurcation structure of isothermal bulk MMA and styrene homopolymerization was determined in order to predict when multiple steady states and oscillatory behavior could be expected in certain ranges of the parameter space. This first model was extended by Schmidt and Ray (1981) to allow different solvent concentrations in the feed stream and multiple steady-state responses were then presented both theoretically and experimentally for homopolymerization. Hamer *et al.* (1981) extended the model to allow nonisothermal and copolymerization reactions. The monomers studied were VA and MMA and it was shown that the dynamics of VA homopolymerization was much richer than that of MMA homopolymerization. It was also predicted that the presence of small amounts of MMA could change the bifurcation structure of VA homopolymerization dramatically. Later, Schmidt *et al.* (1984) predicted the existence of isolated branches of steady-state solutions and confirmed the results experimentally. Most recently, Teymour and Ray (1989, 1991, 1992a, b) improved the mathematical model and extended the bifurcation diagrams for homopolymerization and successfully confirmed many of the predictions experimentally.

There are no reported experimental results on the dynamic behavior of continuous solution copolymer-

ization reactors. The closest results are those presented by Keane (1972) where it is shown how important the stability analysis of solution copolymerization reactors may be for proper control and safety design. Even the theoretical results seem to be of very limited scope, in spite of the industrial importance of such systems. For instance, Shastry and Fan (1973) and Balaraman *et al.* (1982, 1986) showed that copolymerization reactors could present multiple steady states in certain ranges of operation conditions, while Kuchanov *et al.* (1986) showed that self-sustained oscillations could occur in continuous bulk copolymerization processes. However, the only bifurcation analysis was that of Hamer *et al.* (1981) and this depended on rough estimates of some important kinetic parameters not available in the literature.

The main objective of the present work was to build a detailed mathematical model to describe a continuous solution copolymerization reactor and validate the model with experimental results. The system chosen for experimentation was VA/MMA copolymerization in tert-butanol (TB), due to its industrial importance. Homopolymer VA and copolymers with up to 2% MMA are made commercially under similar conditions in solution CSTRs as the first stage of polyvinyl alcohol production. Because of the lack of data in the literature, some kinetic parameters had to be evaluated from some experimental runs. After evaluating the parameters necessary for simulation, the model was used to predict conditions where VA homopolymerization and VA/MMA copolymerization would present qualitatively different dynamic characteristics. Additional experiments were then carried out to confirm the model predictions and show that the stability of such systems may be extremely sensitive to small changes in the feed composition.

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2. THE EXPERIMENTAL REACTOR SYSTEM

The basic experimental system and process operation have been described by Teymour and Ray (1989, 1992a) so that we emphasize only important points and constraints related to the experimental procedure. Figure 1 shows a diagram of the copolymerization process and general equipment. It is important to note that air was used as coolant medium, that the entire experimental setup was kept under inert (nitrogen) atmosphere to avoid oxygen inhibition, that the feed conditions were properly controlled and that reactor temperature and conversion were measured on-line. In the feed section two different containers were used to store a mixture of solvent (TB) and initiator (2,2'-azobis-2-methyl-propionitrile—AIBN) and the comonomer mixture (VA/MMA). The initiator was dissolved in the solvent alone to avoid polymerization in the storage tanks. The monomers were premixed because of the low MMA feed concentrations used in the experiments (below 2% in volume, as shown later), which made it difficult to control the feed composition otherwise.

In order to monitor conversion, an on-line process refractometer was used (model SSR-72, from Electron Machine Corporation). However, these dynamic conversion data were used for qualitative model analysis only. Whenever precise conversion data were needed, as in the analysis of steady-state conditions, where the reaction and heat transfer rates are uncoupled (from a parameter evaluation point of view), samples were taken from the output line and gravimetric analysis was performed. The technique consisted of taking samples of 50 ml, cooling the samples down to 15°C with cold water, weighting the samples in precision scale and drying them to constant weight under low temperature and vacuum conditions.

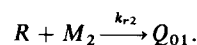
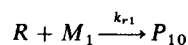
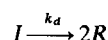
As in the earlier homopolymerization experiments, the experimental setup was designed for operation at atmospheric pressure, so that the reactor temperature was not allowed to rise above the boiling temperature of the reaction mixture. This is an important constraint to be included into the mathematical model.

Regarding the sources of the chemicals used, VA was bought from Pfaltz and Bauer, Inc., MMA and TB (99.5% + pure) from Aldrich Chemical Co., AIBN (99.0% + pure) from Eastman Kodak Co. and nitrogen (99.996% + pure) from Liquid Carbonic. VA and MMA were distilled under vacuum and inert atmosphere one day before the experiment was carried out and were stored in a refrigerator at 10–15°C. The other chemicals were used as received.

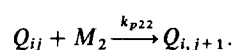
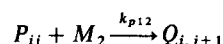
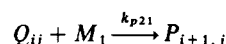
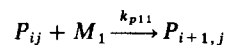
3. MATHEMATICAL MODELING

The mathematical model developed was based on the classical kinetic mechanism for free-radical solution copolymerization reactions, where the propagation and termination steps are extended to allow reactions between different types of monomer and living macro-radicals. The reaction mechanism is:

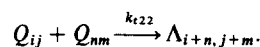
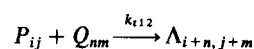
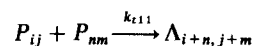
Initiation:



Propagation:



Termination:



It was assumed that transfer reactions could be neglected because our main interest was the dynamic behavior of global variables, such as reactor temperature and conversion. It is known (Ray, 1972) that these additional reactions are either uncoupled or very weakly coupled with the dynamics of these global variables.

In order to describe the cross-propagation and cross-termination kinetic constants, new variables are normally defined. The first ones are the reactivity ratios, that measure how much slower the cross-propagation is when compared to the the homopropagation. The reactivity ratios are defined as

$$r_{ij} = \frac{k_{pii}}{k_{pij}} \quad (1)$$

The other additional variable is the cross-termination constant, which measures how much faster the cross-termination is when compared to an ideal cross-termination value. It is defined as

$$\psi_{ij} = \frac{k_{tij}}{\sqrt{k_{tii}k_{tjj}}} \quad (2)$$

Although this is a quite standard kinetic mechanism for free-radical copolymerization, it has been criticized lately by different authors based on different arguments. The first type of argument is based on the fact that ψ depends strongly on the feed composition

Solution Polymerization

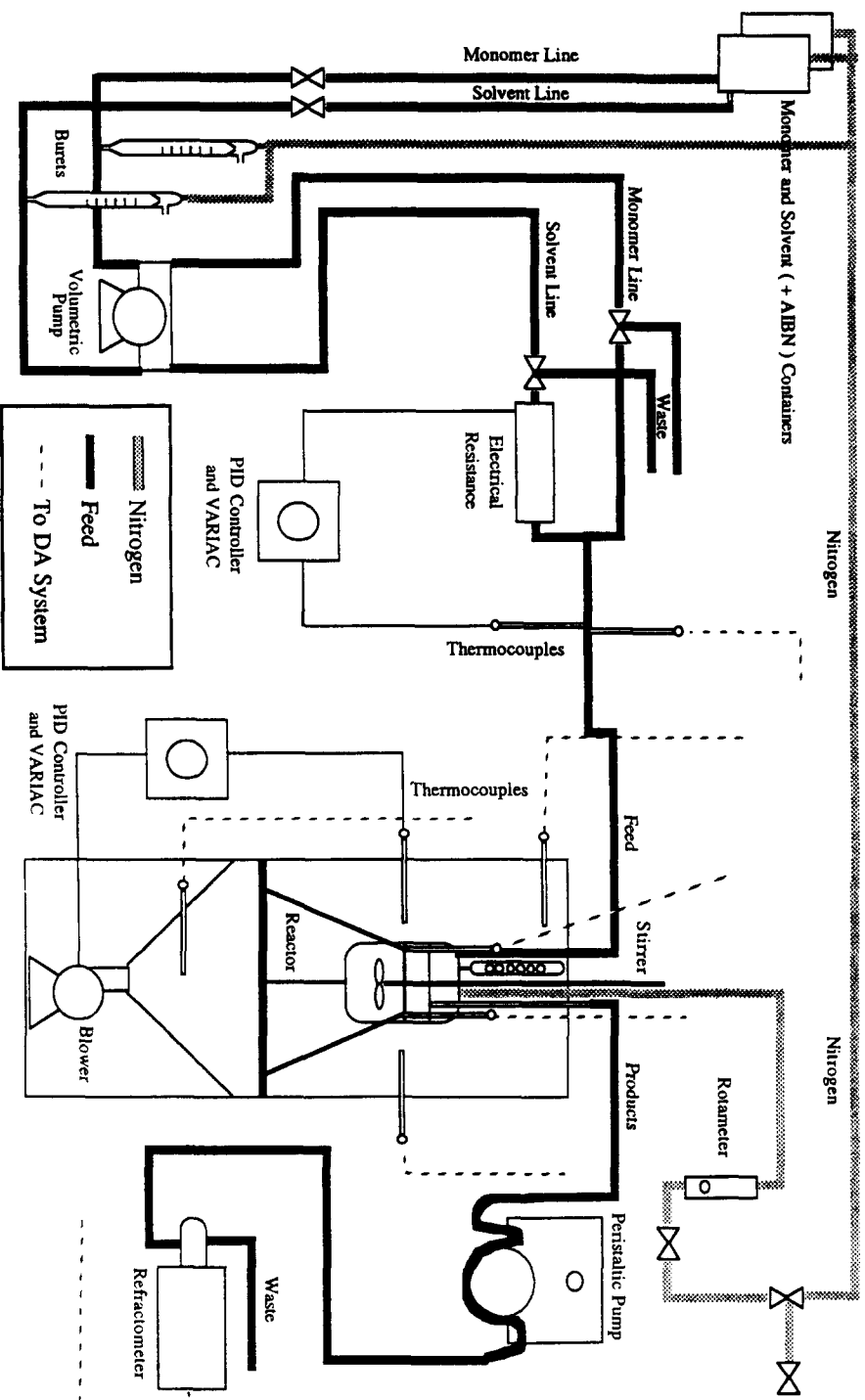


Fig. 1. Experimental Setup.

in many common copolymerization systems, including the system VA/MMA (Brandrup and Immergut, 1989). According to Atherton and North (1962) and more recently Procházka and Kratochvíl (1983) the termination step is not chemically controlled, but diffusion controlled. Thus ψ should be a function of feed composition, so that for the termination step k_t should have the form

$$k_t = \sum_i x_i k_{t,i} \quad (3)$$

where x_i is the mole fraction of species i in the polymer chain.

Having a similar point of view but following a different approach, Hamielec and coworkers (Jones *et al.*, 1986; Bhattacharya and Hamielec, 1986; Yaras-kavitch *et al.*, 1987) emphasized the importance of the gel effect to describe copolymerization reactions. Briefly, the gel effect is the decrease of the termination rate observed when the reaction medium contains high polymer concentrations. This leads to an auto-catalytic reaction rate due to increasing concentrations of free-radical species. Eventually, at very high polymer concentrations, the rates of all different reactions involving macro-radicals also decrease. The gel effect is caused by the diffusion limitations that can be expected in a network of highly entangled polymer chains.

Fukuda *et al.* (1985) provided another point of view and suggested that eq. (2) is correct, but that the propagation step is incorrect. According to the authors, polymer chain composition and sequence length distribution obtained experimentally exhibit significant deviations from the theoretical results obtained with the classical kinetic model. However, the authors showed that experimental data for MMA/styrene copolymerization could be fitted extremely well by a model incorporating a penultimate effect, even when ψ was considered to be constant and equal to one.

It is clear that agreement has yet to be reached on how to describe copolymerization reactions properly. However, it is almost impossible to develop a modeling study based on any of the alternative kinetic schemes described in the last paragraphs without carrying out detailed kinetic studies, as additional kinetic constants and semi-empirical parameters not found in the literature are necessary to describe the system. Thus in our analysis here, we choose to use the standard kinetic mechanism and take most of the parameters necessary to describe the system from the literature and to determine the remaining ones experimentally.

Assuming that the reactive mixture occupies a constant volume (imposed experimentally), that volume additivity holds and that the quasi-steady-state approximation is valid for radicals R , P and Q , the following equations can be derived:

solvent mass balance:

$$\frac{dv_s}{d\tau} = \frac{\rho_{sf} v_{sf}}{\rho_s} - v_s \frac{q_o}{q_i} + \rho_s v_s \frac{dT}{d\tau} \frac{d(1/\rho_s)}{dT} \quad (4)$$

monomer 1 mass balance:

$$\begin{aligned} \frac{dv_1}{d\tau} = & \frac{\rho_{1f} v_{1f}}{\rho_1} - v_1 \left(\frac{q_o}{q_i} + \Theta \text{Rate}_1 \right) \\ & + \rho_1 v_1 \frac{dT}{d\tau} \frac{d(1/\rho_1)}{dT} \end{aligned} \quad (5)$$

monomer 2 mass balance:

$$\begin{aligned} \frac{dv_2}{d\tau} = & \frac{\rho_{2f} v_{2f}}{\rho_2} - v_2 \left(\frac{q_o}{q_i} + \Theta \text{Rate}_2 \right) \\ & + \rho_2 v_2 \frac{dT}{d\tau} \frac{d(1/\rho_2)}{dT} \end{aligned} \quad (6)$$

Initiator mass balance:

$$\frac{dc_i}{d\tau} = c_{if} - c_i \left(\frac{q_o}{q_i} + k_d \Theta \right) \quad (7)$$

energy balance:

$$\begin{aligned} (1 + \varepsilon) \frac{dT}{d\tau} = & \frac{\rho_f (T_f - T)}{\rho} + \frac{\Theta}{\rho c_p} (\Delta H_{11} v_1 \rho_1 k_{p11} P \\ & + \Delta H_{12} v_2 \rho_2 k_{p12} P + \Delta H_{21} v_1 \rho_1 k_{p21} Q \\ & + \Delta H_{22} v_2 \rho_2 k_{p22} Q) - \frac{\Theta}{\rho c_p} (UA(T - T_c) \\ & + \alpha UA(T - T_a) + Q_{lat}) \end{aligned} \quad (8)$$

where q_o/q_i is the ratio between the output and input volumetric flow rates, given by

$$\begin{aligned} \frac{q_o}{q_i} = & \frac{\rho_{sf} v_{sf}}{\rho_s} + \frac{\rho_{1f} v_{1f}}{\rho_1} + \frac{\rho_{2f} v_{2f}}{\rho_2} \\ & + \Theta (\text{Rate}_1 v_1 (\rho_1/\rho_p - 1) + \text{Rate}_2 v_2 (\rho_2/\rho_p - 1)) \\ & + \frac{dT}{d\tau} \left(\rho_s v_s \frac{d(1/\rho_s)}{dT} + \rho_1 v_1 \frac{d(1/\rho_1)}{dT} \right. \\ & \left. + \rho_2 v_2 \frac{d(1/\rho_2)}{dT} + \rho_p v_p \frac{d(1/\rho_p)}{dT} \right) \end{aligned} \quad (9)$$

The normalized rates of monomer consumption are given by

$$\text{Rate}_1 = k_{p11} P + k_{p21} Q + R_{ckr} \quad (10)$$

$$\text{Rate}_2 = k_{p12} P + k_{p22} Q + R_{ckr} \quad (11)$$

where R_{ckr} is the normalized rate of initiation, given by

$$R_{ckr} = \frac{2k_d c_i}{M_1/f_1 + M_2/f_2} \quad (12)$$

where the denominator accounts for changes in the initiation efficiency due to changes in the comonomer composition.

The concentration of species P and Q can be written as

$$Q = \sqrt{\frac{R_{ckr}(M_1 + M_2)}{k_{t11} k_s^2 + 2k_{t12} k_s + k_{t22}}} \quad (13)$$

$$P = k_s Q \quad (14)$$

where

$$k_s = (k_{p21}M_1)/(k_{p12}M_2). \quad (15)$$

The termination and propagation constants in eqs (8)–(15) include the gel effect and so have the general form

$$\begin{aligned} k_{tij} &= k_{tij}^0 g_{tij} \\ k_{pij} &= k_{pij}^0 g_{pij} \end{aligned} \quad (16)$$

where k_{tij}^0 and k_{pij}^0 are the kinetic constants at zero polymer concentration and g_{tij} and g_{pij} are the gel effect correlations that take into account the effects of increasing polymer concentration.

Some global variables in the energy balance are computed as

$$\rho = v_s \rho_s + v_1 \rho_1 + v_2 \rho_2 + v_p \rho_p \quad (17)$$

$$\begin{aligned} \rho C_p &= v_s \rho_s C_{ps} + v_1 \rho_1 C_{p1} + v_2 \rho_2 C_{p2} \\ &+ v_p \rho_p C_{pp} \end{aligned} \quad (18)$$

where

$$\rho_p = w \rho_{p1} + (1 - w) \rho_{p2} \quad (19)$$

$$C_{pp} = w C_{pp1} + (1 - w) C_{pp2} \quad (20)$$

and w is the polymer composition (mass fraction of structures of type 1). In the energy balance, ε is an additional term which accounts for extraneous heat capacity due to the reactor walls and additional equipment. The dynamic copolymer composition may be determined from

$$\begin{aligned} \frac{dw}{d\tau} &= (1 - w) \text{Rate}_1 \frac{v_1 \rho_1}{v_p \rho_p} \ominus \\ &- w \text{Rate}_2 \frac{v_2 \rho_2}{v_p \rho_p} \ominus. \end{aligned} \quad (21)$$

However, for most of our model calculations, simpler expressions were used because polymer composition does not vary much in continuous reactors and these variations have a negligible effect on the process dynamics. Thus copolymer composition was calculated by an approximate mass balance, based on the monomer compositions in the inlet and outlet streams these computations are exact at steady-state conditions). However, the total conversion (whether including or not the solvent) can be calculated exactly as

$$x = \frac{v_p \rho_p}{v_s \rho_s + v_1 \rho_1 + v_2 \rho_2 + v_p \rho_p} \quad (22)$$

and, as shown later, this is the important variable for the gel effect correlation.

Regarding the latent heat of vaporization in eq. (8), one could write

$$Q_{\text{lat}} = m_v \Delta H_v \quad (23)$$

where m_v is the rate of condensation and ΔH_v is the latent heat of condensation of the vapor phase. However, it is extremely difficult to evaluate m_v experimentally because part of the vapor condenses on the

internal walls of the reactor, before reaching the condenser. The theoretical solution for m_v is not available either without additional specification of the heat transfer areas and of the nitrogen flow through the condenser. The contribution of latent heat to the energy balance is not important except close to boiling conditions. Thus the effects were represented by

$$\begin{aligned} Q_{\text{lat}} &= 0, \quad T < T_b \\ \frac{dT}{d\tau} &= \frac{dT_b}{d\tau}, \quad T \geq T_b \end{aligned} \quad (24)$$

where T_b is the boiling temperature of the reacting solution and may be easily computed with a proper thermodynamic correlation. In order to avoid discontinuities in the model, which might not allow the use of continuation algorithms, eq. (24) was rewritten as

$$Q_{\text{lat}} = \begin{cases} 0, & T < T_b \\ \lambda(T - T_b)^2, & T \geq T_b \end{cases} \quad (25)$$

where λ is a numerical parameter that controls the strength of the boiling constraint. This same numerical approach was used successfully by Teymour (1989).

In order to calculate the boiling temperature, the classical Flory–Huggins equation for solvent activity in polymer solutions was used as

$$\ln \left(\frac{\Pi_i}{\Pi_{\text{sat}}} \right) = \ln(v_i) + v_p + \chi_i v_p^2 \quad (26)$$

with the additional assumption that the mixture of solvent and monomers behaved ideally.

4. PARAMETER EVALUATION

4.1. Parameters related to the heat transfer

In eqs (8) and (25) four different parameters related to the heat transfer mechanism are defined. Three of these (ε , UA, α UA) could be evaluated from independent heat transfer experiments, while the fourth one (λ) had to be fitted based on numerical experiments. λ should neither be too large, in order to allow the use of continuation algorithms for the computation of steady states, nor too small, in order to simulate the boiling constraint properly.

Figure 2 shows a typical temperature profile obtained from heat transfer experiments. A total of eight different heat transfer experiments were carried out for polymer solutions of different composition. In these experiments initiator was not added to the system and the monomers were inhibited with 5 ppm of hydroquinone to avoid spontaneous thermal polymerization. The overall results obtained after parameter estimation are shown in Table 1. It is important to emphasize that these numbers did not depend on the solution composition as the heat transfer to the coolant air jacket was the controlling step in the heat transfer mechanism. Additionally, no significant variation was observed in ε , although UA and α UA seemed to spread within a range of $\pm 10\%$, probably due to unavoidable changes in the arrangement of the

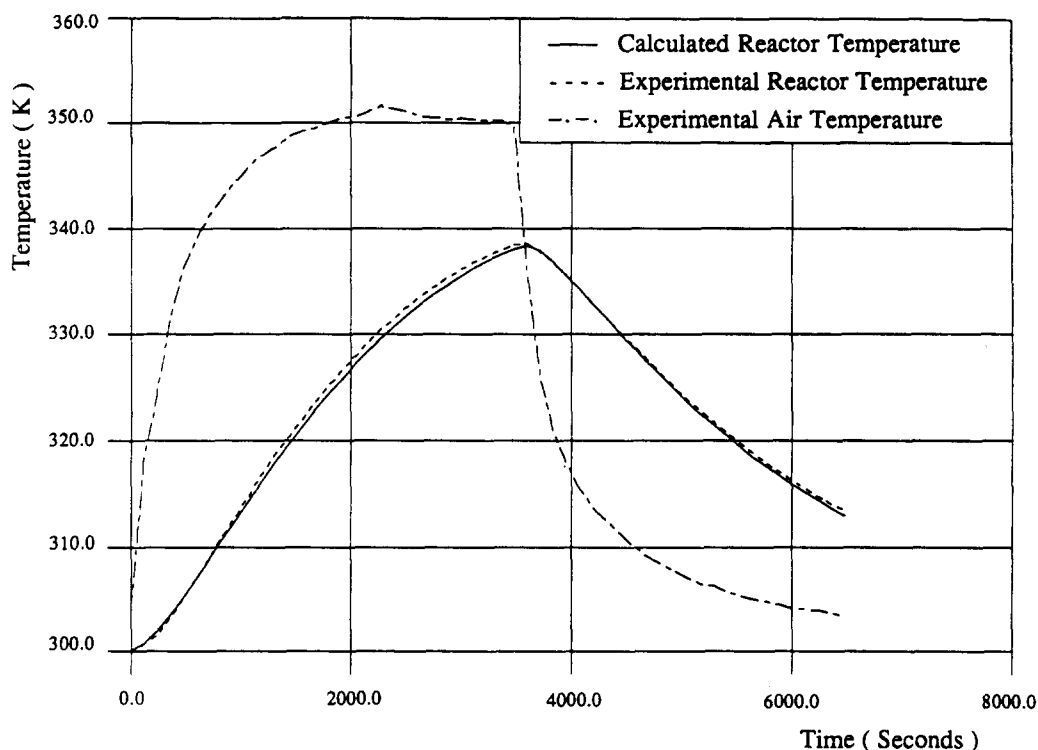


Fig. 2. Results from a heat transfer experiment (results obtained for a mixture of 60% VA and 40% TB in volume, with 5 ppm of hydroquinone. $\varepsilon = 0.55$, $UA = 0.858 \text{ J/kg m}^2 \text{ K}$, $\alpha UA = 0.0746 \text{ J/kg m}^2 \text{ K}$, $V = 500 \text{ ml}$, $T_a = 298 \text{ K}$).

Table 1. Parameters describing heat transfer phenomena

Parameter	Value
UA	0.836 J/K s
αUA	0.07315 J/K s
ε	0.55
V	500 ml

experimental setup that occurred from experiment to experiment.

4.2. Parameters for VA homopolymerization

Table 2 presents all parameters necessary to describe the VA homopolymerization. As it can be seen, most of the data are the same as used by Teymour (1989). One important change, however, regards the definition of the individual kinetic constants k_p and k_t , necessary for copolymerization studies. The gel effect correlation was also taken from Teymour (1989), and is of the form

$$g_{p11} = 1$$

$$g_{t11} = \exp(-0.4407x - 6.7530x^2 - 0.3495x^3) \quad (27)$$

where x is the total conversion (including solvent) as defined in eq. (22). Parameter fitting was not necessary for VA homopolymerization.

4.3. Parameters for MMA homopolymerization

Although a large collection of kinetic data is available for MMA homopolymerization (Brandrup and Immergut, 1975, 1989), two problems had to be faced in order to define the set of kinetic equations *a priori*. The first one was related to the kinetic constants. Basically, two sets of parameters have been used recently in the literature. The first set (called SET 1 from now on) seems to have originated from kinetic data presented by different authors and listed in Brandrup and Immergut (1989) for MMA polymerization initiated by AIBN. This set of parameters was used by Hamer *et al.* (1981) and more recently by Choi and Butala (1991). The second set of parameters (called SET 2 from now on) seems to have originated by kinetic data presented by Mahabadi and O'Driscoll (1977) and was used by Schmidt and Ray (1981) and more recently by Maschio and Moutier (1989). Both sets of parameters (presented in Table 3) have been successful in representing experimental data, although it may be hard to understand how the reactivity ratios for the system VA/MMA can be constant, as usually reported in the literature, if SET 2 is correct, since the activation energy of the propagation constant for MMA is very different from the activation energy of the propagation constant for VA.

A second important issue is the gel effect correlation. The gel effect is extremely important for the description of MMA homopolymerization (Hamer

Table 2. Parameters describing VA homopolymerization

Parameter	Reference
$\rho_s = \frac{74.12}{60.21 + 0.116 T} \text{ g/ml}$	Teymour (1989)
$\rho_1 = 0.9584 - 1.3276 \times 10^{-3} (T - 273.15) \text{ g/ml}$	Teymour (1989)
$\rho_p = 1.211 - 8.496 \times 10^{-4} (T - 273.15) \text{ g/ml}$	Teymour (1989)
$c_{ps} = 0.716 \text{ cal/g K}$	Teymour (1989)
$c_{p1} = 0.4479 + 5.625 \times 10^{-4} (T - 273.15) \text{ cal/g K}$	Kroschwitz (1986)
$c_{pp} = 0.3453 + 9.55 \times 10^{-4} (T - 298.15) \text{ cal/g K}$	Teymour (1989)
$\Pi_s^{\text{sat}} = \exp\left(16.8548 - \frac{2658.29}{T - 95.5}\right) \text{ mmHg}$	Reid <i>et al.</i> (1986)
$\Pi_1^{\text{sat}} = \exp\left(16.1003 - \frac{2744.68}{T + 37.32}\right) \text{ mmHg}$	Reid <i>et al.</i> (1986)
$\Delta H_{11} = 87.78 \text{ kJ/mole}$	Kroschwitz (1986)
$k_{p11} = 3.2 \times 10^7 \exp(-6300/RT) \text{ l/mol s}$	Kroschwitz (1986)
$k_{t11} = 3.70 \times 10^9 \exp(-3200/RT) \text{ l/mol s}$	Kroschwitz (1986)
$k_d = 1.58 \times 10^{15} \exp(-30800/RT) \text{ l/s}$	AIBN
$f_i = 0.8$	Mean value from various references in Brandrup and Immergut (1975)
$g_{11} = \text{empirical correlation}$	Eq. (27)
$\chi_s = 0.5$	For lack of data, as suggested by Allcock and Lampe (1981)
$\chi_1 = 0.5$	

Table 3. Kinetic constants for MMA homopolymerization

Set 1	$k_{p22} = 7.0 \times 10^6 \exp(-6300/RT) \text{ l/mol s}$ $k_{t22} = 1.76 \times 10^9 \exp(-2800/RT) \text{ l/mol s}$ $f_2 = 0.6$
Set 2	$k_{p22} = 4.92 \times 10^5 \exp(-4353/RT) \text{ l/mol s}$ $k_{t22} = 9.80 \times 10^7 \exp(-701/RT) \text{ l/mol s}$ $f_2 = 0.5$

$$g_{p22} = \begin{cases} 1, & v_f > v_{fpc} \\ 7.1 \times 10^{-5} \exp(171.53 v_f), & v_f \leq v_{fpc} \end{cases} \quad (29)$$

where

$$v_{fpc} = 0.1856 - 2.965 \times 10^{-4} (T - 273.15) \quad (30)$$

$$v_{fpc} = 0.05 \quad (31)$$

and the total free volume v_f is given by

$$v_f = v_{f1} v_1 + v_{f2} v_2 + v_{fs} v_s + v_{fp} v_p \quad (32)$$

where

$$v_{fi} = 0.025 + \alpha_i (T - T_{gi}) \quad (33)$$

et al., 1981) and no kinetic data are available for MMA polymerization in TB. This lack of data is easily understood if one realizes that PMMA is not soluble in TB even at low polymer concentration and moderate temperatures (around 50°C), although the presence of MMA enhances the polymer solubility. As TB is extremely beneficial for VA polymerization (Teymour, 1989), it was decided to adjust the gel effect correlation for MMA homopolymerization in TB, using the well known Ross and Laurence equation (Ross and Laurence, 1976) as a basis. Thus, the gel effect correlation for MMA can be written as:

$$g_{t22} = \begin{cases} 0.10575 \exp(17.15 v_f - 0.01715 (T - 273.15)), & v_f > v_{frc} \\ 2.3 \times 10^{-6} \exp(75 v_f), & v_f \leq v_{frc} \end{cases} \quad (28)$$

Table 4. Parameters for MMA gel effect correlations

Parameter	Chemical species			
	VA	MMA	PMMA	EA
α	0.001	0.001	0.00048	0.001
$T_g \text{ (K)}$	173	167	387	181

Figures 3–5 show experimental and simulation results for MMA homopolymerization in TB at steady-state conditions when the SET 1 of kinetic constants and T_{sTB} equal to 181 K were used for simulation. These parameters were much better at predicting a wide large range of experiments for MMA (Pinto, 1991) than other parameter choices. Thus these were used in all model calculations. The complete set

of parameters necessary to describe the system is presented in Table 5.

4.4. Parameters for VA/MMA copolymerization

In our study here, we will be operating with low MMA content in the polymer and this influences our choice of model parameters. The additional parameters needed to describe the copolymerization reac-

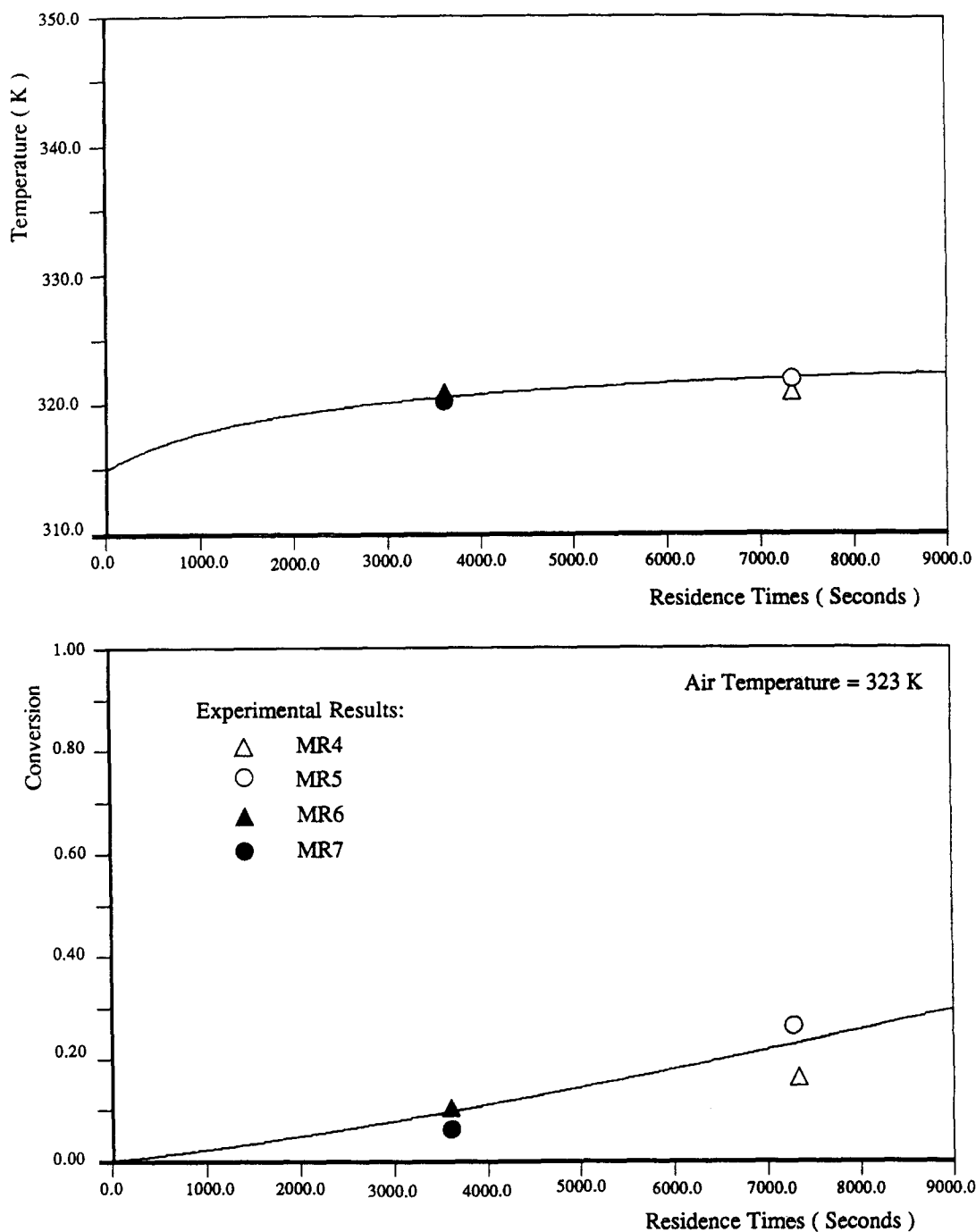


Fig. 3. Steady-state conditions for MMA homopolymerization at $T_c = 50^\circ\text{C}$ ($v_{2f} = 0.40$, $v_{3f} = 0.60$, $c_{if} = 0.04$ gmol/l, $T_a = 298$ K, kinetic parameters from SET 1 and $T_{gs} = 181$ K).

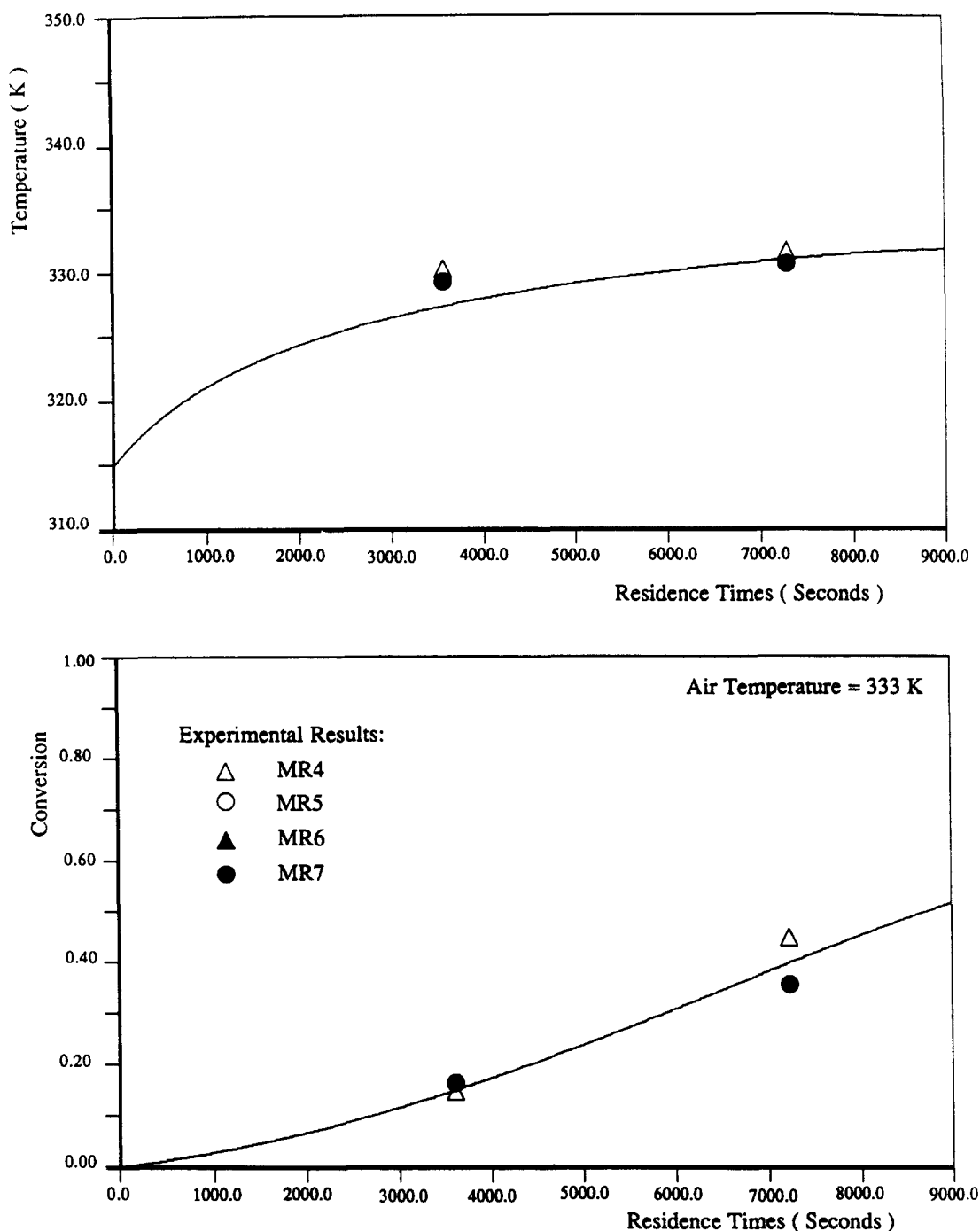


Fig. 4. Steady-state conditions for MMA homopolymerization at $T_c = 60^\circ\text{C}$ ($v_{2f} = 0.40$, $v_{3f} = 0.60$, $c_{if} = 0.04$ gmol/l, $T_a = 298$ K, kinetic parameters from SET 1 and $T_{gs} = 181$ K).

tions are shown in Table 6, except for the ones related to the cross-termination step.

Table 7 shows typical values of ψ reported in the literature. It seems that ψ has been always reported for batch reactors and high amounts of MMA. In the first case, due to the composition drift, ψ is obtained as an average for the batch and not pointwise as a function of MMA composition as needed for con-

tinuous polymerization. In the second case, ψ is expected to assume different values at the low MMA concentrations used in this study. For these reasons, experiments were designed to allow the evaluation of ψ from dynamic and steady-state experiments for different MMA feed concentrations.

Before evaluating ψ , the proper gel effect correlation had to be defined. Two different assumptions

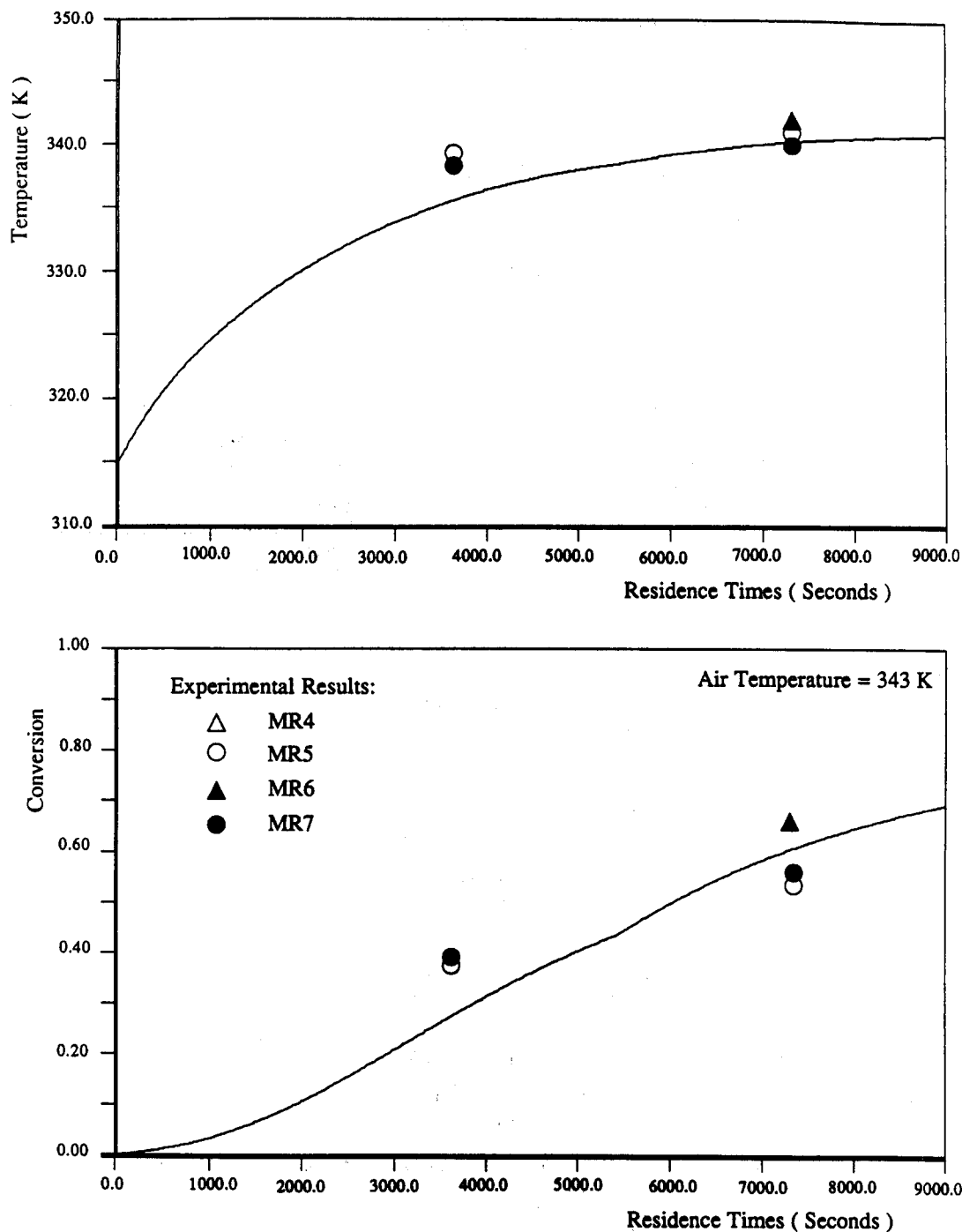


Fig. 5. Steady-state conditions for MMA homopolymerization at $T_c = 70^\circ\text{C}$ ($v_{2f} = 0.40$, $v_{3f} = 0.60$, $c_{1f} = 0.04$ gmol/l, $T_a = 298$ K, kinetic parameters from SET 1 and $T_{gs} = 181$ K).

seemed to be reasonable. The first one would extend the definition of k_{i12} to the gel effect correlation, so that g_{i12} would be defined as:

$$g_{i12} = \sqrt{g_{i11}g_{i22}}. \quad (34)$$

The second assumption was based on the fact that when the MMA feed concentration is low the polymer

produced is mostly composed of VA molecules. So, g_{i11} should describe the diffusion limitations properly for all k_{ij} .

Table 8 and Figs 6–9 show the results obtained when the gel effect was computed as in eq. (34). The theoretical profiles were obtained assuming that the heat transfer coefficients were subject to small variations within the range $\pm 10\%$.

Table 5. Parameters describing MMA homopolymerization

Parameter	Reference
$\rho_s = \frac{74.12}{60.21 + 0.116 T} \text{ g/ml}$	Teymour (1989)
$\rho_2 = 0.9654 - 0.00109 (T - 273.15) - 9.7 \times 10^{-7} (T - 273.15)^2 \text{ g/ml}$	Schmidt <i>et al.</i> (1984)
$\rho_p = \frac{\rho_2}{0.754 - 9.0 \cdot 10^{-4} (T - 343.15)} \text{ g/ml}$	Schmidt <i>et al.</i> (1984)
$c_{ps} = 0.716 \text{ cal/g K}$	Teymour (1989)
$c_{p2} = 0.490 \text{ cal/g K}$	Schmidt <i>et al.</i> (1984)
$c_{pp} = 0.339 + 9.55 \times 10^{-4} (T - 298.15) \text{ cal/g K}$	Schmidt <i>et al.</i> (1984)
$\Pi_s^{\text{sat}} = \exp\left(16.8548 - \frac{2658.29}{T - 95.5}\right) \text{ mmHg}$	Reid <i>et al.</i> (1986)
$\Pi_2^{\text{sat}} = \exp\left(19.8567 - \frac{5441.04}{T + 37.32}\right) \text{ mmHg}$	From experimental data in Brandrup and Immergut (1975)
$\Delta H_{22} = 57.7 \text{ K J/mol}$	Kroschwitz (1986)
$k_{p22} = 7.0 \times 10^6 \exp(-6300/RT) \text{ l/mol s}$	Brandrup and Immergut (1975)
$k_{t22} = 1.76 \times 10^9 \exp(-2800/RT) \text{ l/mol s}$	Brandrup and Immergut (1975)
$k_d = 1.58 \times 10^{15} \exp(-30800/RT) \text{ l/s}$	AIBN
$f_2 = 0.6$	Mean value from various references in Brandrup and Immergut (1975)
$g_{22} = \text{free-volume theory}$	Hamer <i>et al.</i> (1981)
$\chi_s = 0.5$	For lack of data, as suggested by Allcock and Lampe (1981)
$\chi_2 = 0.5$	

Table 6. Additional parameters describing VA/MMA copolymerization

Parameter	Reference
$\Delta H_{12} = \Delta H_{21} = 72.0 \text{ kJ/mol}$	Geometric mean of ΔH_{11} and ΔH_{22}
$r_{12} = 0.015$	Kroschwitz (1986)
$r_{21} = 20$	Kroschwitz (1986)
Ψ	Table 8
g_{12}	Geometric mean of g_{11} and g_{22}

Table 7. Ψ as reported by different authors

Ψ	Source	Remarks
120	Choi and Butala (1991)	Batch reaction with high MMA concentration (0.10–0.50 mole fraction). $49^\circ\text{C} < T < 65^\circ\text{C}$
150	Kuo <i>et al.</i> (1976a)	Batch reaction with 30% MMA (molar basis). $T = 60^\circ\text{C}$
170	Kuo <i>et al.</i> (1976b)	Batch reaction with high MMA concentration (0.30–0.50 mole fraction). $T = 60^\circ\text{C}$
400	Chen <i>et al.</i> (1981)	Batch reaction with 30% MMA (molar basis). $T = 60^\circ\text{C}$
400	Burnett and Gersmann (1958)	Batch reaction with high MMA concentration (0.10–0.30 mole fraction). $40^\circ\text{C} < T < 60^\circ\text{C}$

Table 8. Ψ Evaluated in this work

% MMA monomer feed volume basis	% Q^* solution molar basis	% MMA [†] polymer molar basis	Ψ
0.00	0.00	0.00	1.00 [‡]
0.25	17.0	0.26	1.45
0.375	22.0	0.40	1.95
0.50	32.0	0.54	5.25
2.00	73.0	2.50	30.0

[†]From simulation.[‡]Extrapolated from data.

It can be seen from Table 8 that ψ increases steadily when MMA feed concentration increases and that it may eventually reach the range of values shown in Table 7 for higher MMA feed compositions. Note that ψ tends to the ideal value of 1 as the MMA feed composition tends to zero.

Regarding the gel effect, using the VA value, g_{111} , as a global correlation for all compositions always led to poor results. Thus, it was decided to use eq. (34) in all our model computations.

Although ψ must be a function of the internal reactor composition, no attempt was made to model

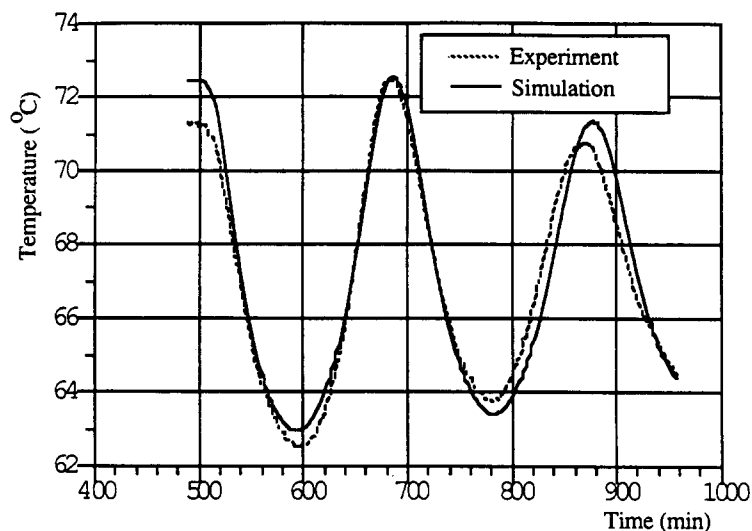


Fig. 6. Dynamic temperature profile following a perturbation in T_c ($v_{1f} = 0.3990$, $v_{2f} = 0.0010$, $v_{3f} = 0.6000$, $c_{if} = 0.04$ gmol/l, $T_a = 298$ K, $\Theta = 90$ min, $UA = 1.00(UA)_0$, $\psi = 1.45$, T_c changed from 53 to 48°C at steady-state conditions).

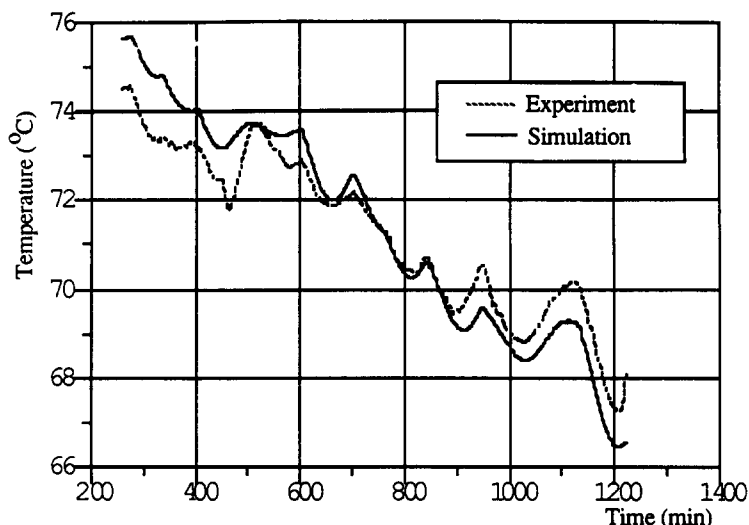


Fig. 7. Dynamic temperature profile following a perturbation in T_c ($v_{1f} = 0.3985$, $v_{2f} = 0.0015$, $v_{3f} = 0.6000$, $c_{if} = 0.04$ gmol/l, $T_a = 298$ K, $\Theta = 90$ min, $UA = 0.95(UA)_0$, $\psi = 1.95$, T_c changed from 55 to 48°C in a series of small step changes).

ψ . In our calculations here, ψ was taken as the function of MMA comonomer feed composition, shown in Table 8.

5. BIFURCATION ANALYSIS

Using the mathematical model and parameters described in the previous sections, a series of bifurcation diagrams was built with the capabilities of the continuation routines of AUTO (Doedel, 1986). More details of this analysis will be presented in a companion paper (Pinto and Ray, 1995). The bifurcation diagrams are shown in Fig. 10 for different comonomer feed compositions at certain standard

operation conditions. In order to show how sensitive these structures are to changes in the heat transfer mechanism, Figs 11–14 show how the bifurcation diagrams change when the coolant air temperature changes by $\pm 2^\circ\text{C}$ or the heat transfer coefficients change by $\pm 10\%$.

Figures 10–14 also indicate that VA/MMA copolymerization dynamics may be extremely sensitive to small changes in the feed composition. Particularly, it may be seen that:

(1) At the experimental conditions analyzed, VA homopolymerization is always stable in the whole range of residence times.

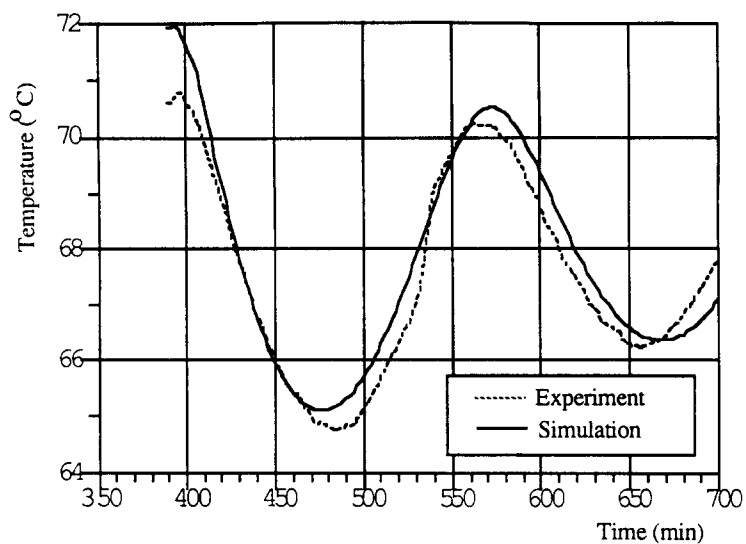


Fig. 8. Dynamic temperature profile following a perturbation in T_c ($v_{1f} = 0.3980$, $y_{2f} = 0.0020$, $v_{sf} = 0.6000$, $c_{if} = 0.04$ gmol/l, $T_a = 298$ K, $\Theta = 120$ min, $UA = 1.00(UA)_o$, $\psi = 5.20$, T_c changed from 57 to 52°C at steady-state conditions).

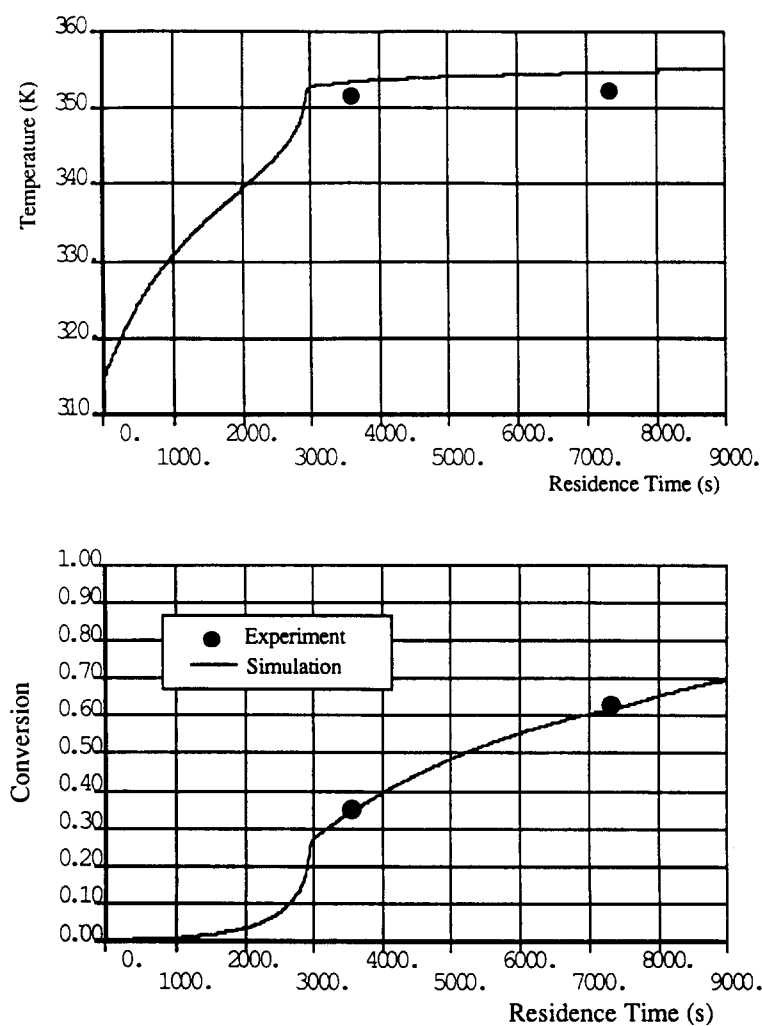


Fig. 9. Steady-state conditions for VA/MMA copolymerization at $T_c = 90^\circ\text{C}$ ($v_{1f} = 0.3920$, $v_{2f} = 0.0080$, $v_{sf} = 0.6000$, $c_{if} = 0.04$ gmol/l, $T_a = 298$ K, $UA = 1.00(UA)_o$, $\psi = 30$).

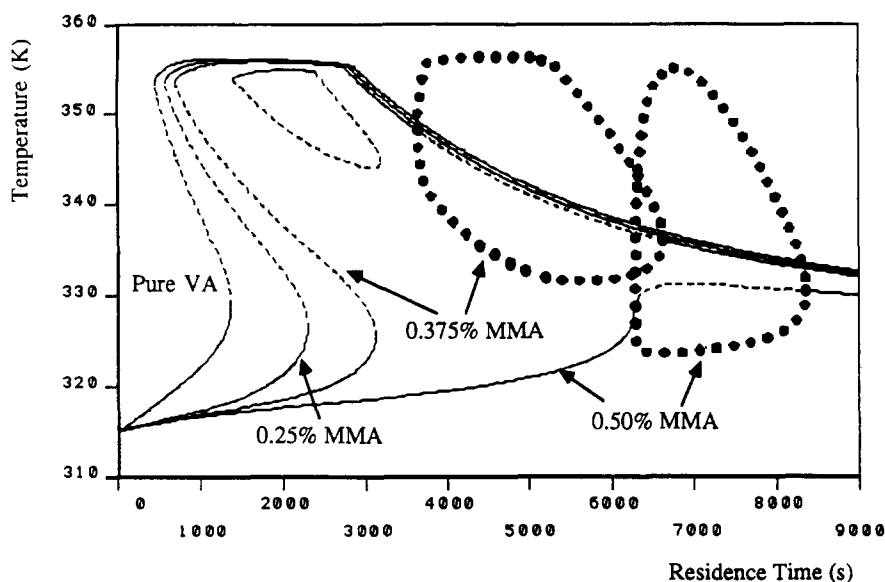


Fig. 10. Bifurcation diagrams for different MMA comonomer feed concentrations ($v_{sf} = 0.6000$, $c_{if} = 0.04$ gmol/l, $T_a = 298$ K, $T_c = 48^\circ\text{C}$, $UA = 1.00$ (UA)₀).

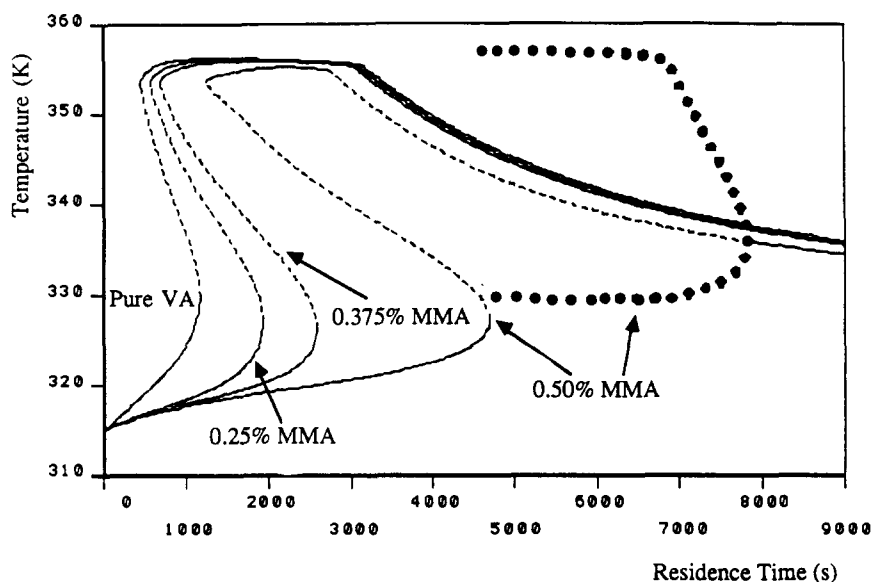


Fig. 11. Bifurcation diagrams for different MMA comonomer feed concentrations ($v_{sf} = 0.6000$, $c_{if} = 0.04$ gmol/l, $T_a = 298$ K, $T_c = 50^\circ\text{C}$, $UA = 1.00$ (UA)₀).

(2) VA/MMA copolymerization with comonomer feed composition of 0.25% in volume of MMA must always be stable, unless the heat transfer to the surroundings is larger than at the standard conditions. In this case, oscillations may develop around residence times of 90 min.

(3) VA/MA copolymerization with comonomer feed composition of 0.375% in volume of MMA must lead to unstable operation at residence times around 90 min. If the heat transfer to the surroundings is lower than expected, however, the oscillations may disappear.

(4) VA/MMA copolymerization with comonomer feed composition of 0.50% in volume of MMA shows that the upper steady state for VA homopolymerization disappears, so that reaction extinction may be expected; also at residence times around 120 min oscillatory behaviour may be expected. However, if heat transfer to the surroundings is higher than at standard conditions, the self-sustained oscillations may disappear.

Figures 15–19 show experimental results that confirm the theoretical predictions. Figure 15 shows

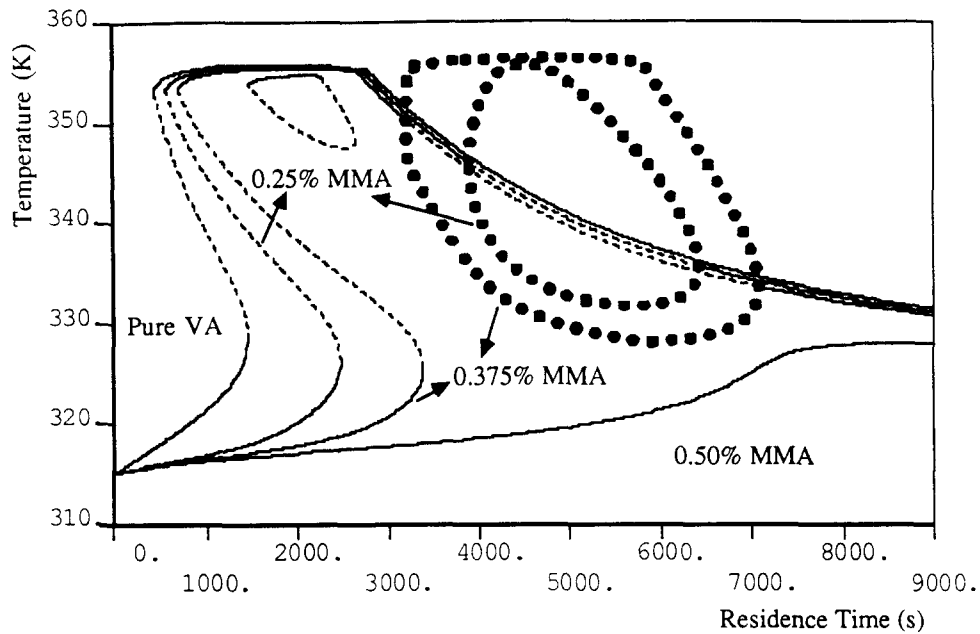


Fig. 12. Bifurcation diagrams for different MMA comonomer feed concentrations ($v_{sf} = 0.6000$, $c_{if} = 0.04$ gmol/l, $T_a = 298$ K, $T_c = 46^\circ\text{C}$, $UA = 1.00$ (UA)_o).

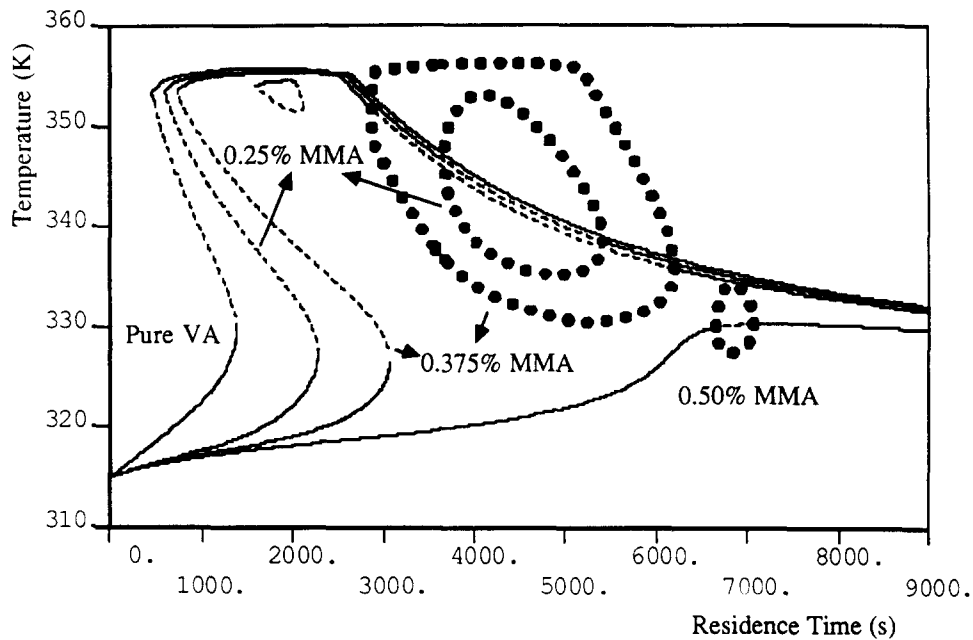


Fig. 13. Bifurcation diagrams for different MMA comonomer feed concentrations ($v_{sf} = 0.6000$, $c_{if} = 0.04$ gmol/l, $T_a = 298$ K, $T_c = 48^\circ\text{C}$, $UA = 1.10$ (UA)_o).

a typical dynamic pattern that developed when the comonomer feed composition was changed from pure VA to 99.75% VA and 0.25% MMA in volume, at steady-state conditions. The oscillations are damped and eventually lead to a new steady state or to a very shallow limit cycle.

Figures 16 and 17 show the development of self-sustained oscillations when the comonomer feed composition was initially equal to 99.625% VA and 0.375% MMA in volume and that fast convergence to stable operation occurs when the feed composition was changed to pure VA.

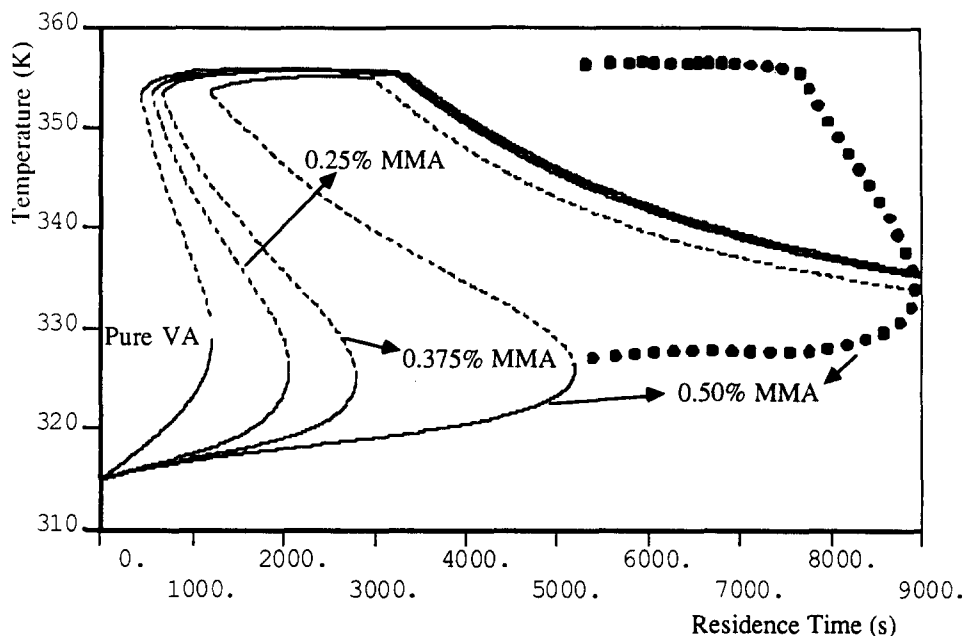


Fig. 14. Bifurcation diagrams for different MMA comonomer feed concentrations ($v_{sf} = 0.6000$, $c_{if} = 0.04$ gmol/l, $T_a = 298$ K, $T_c = 48^\circ\text{C}$, $UA = 0.90$ (UA)₀).

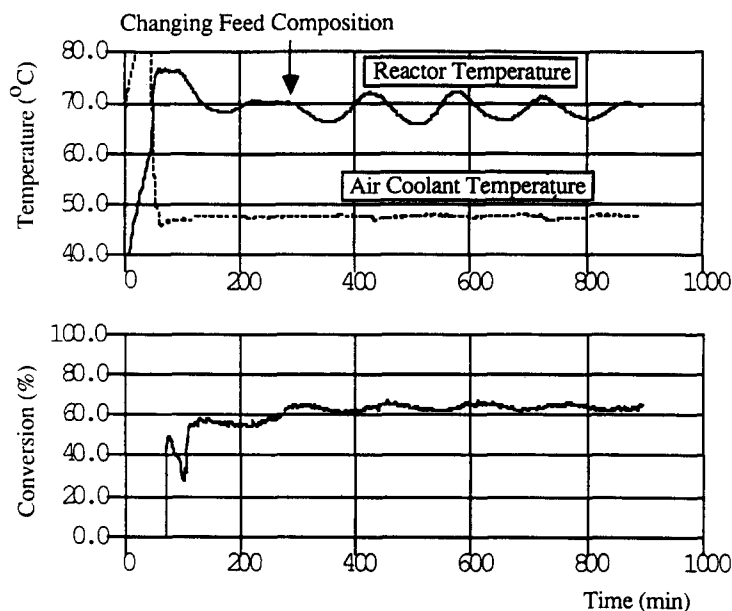


Fig. 15. Dynamic temperature profile following a step change in the feed composition ($v_{sf} = 0.6000$, $c_{if} = 0.04$ gmol/l, $T_a = 298$ K, $T_c = 48^\circ\text{C}$, $\Theta = 90$ min, v_{2f} changed from 0.0000 to 0.0010 after steady state).

Figure 18 shows a dying reaction. The extinction occurred when the comonomer feed composition was changed from pure VA to 99.50% VA and 0.50% MMA in volume at the steady state obtained at residence time of 90 min.

Finally, Fig. 19 shows the development of self-sustained oscillations at a residence time of 120 min when the comonomer feed composition was equal to

99.50% VA and 0.50% MMA in volume. The oscillations disappeared very fast when the feed composition was changed to pure VA.

Figures 20 and 21 show that the theoretical predictions are not only good from a qualitative point of view, but are also quantitatively correct. These figures show theoretical and experimental profiles for experiments where self-sustained oscillations were present.

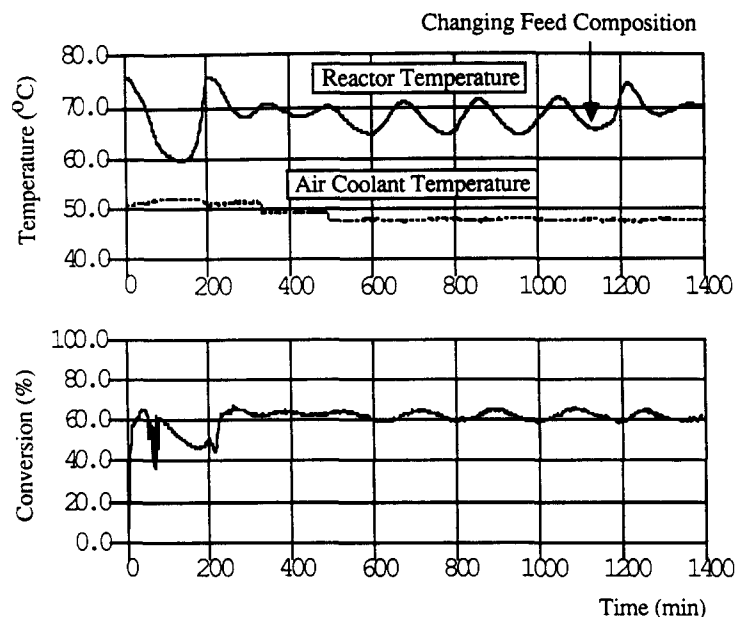


Fig. 16. Dynamic temperature profile following a step change in the feed composition ($v_{sf} = 0.6000$, $c_{if} = 0.04$ gmol/l, $T_a = 298$ K, $T_c = 48^\circ\text{C}$, $\Theta = 90$ min, v_{2f} changed from 0.0015 to 0.0000 during oscillatory state).

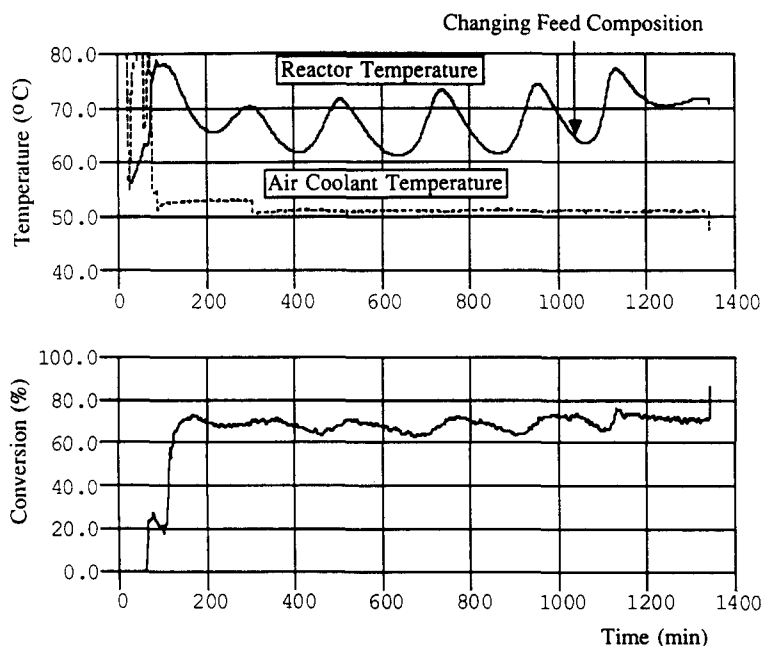


Fig. 17. Dynamic temperature profile following a step change in the feed composition ($v_{sf} = 0.6000$, $c_{if} = 0.04$ gmol/l, $T_a = 298$ K, $T_c = 51^\circ\text{C}$, $\Theta = 90$ min, v_{2f} changed from 0.0015 to 0.0000 during oscillatory state).

It can be seen that the temperature profiles agree very well. As discussed before, the experimental conversion profiles evaluated by the on-line refractometer sometimes presented deviations to lower values, although they might be reasonably good as in Fig. 21.

6. DISCUSSION

From previous theoretical and experimental results it seems clear that the dynamics of solution VA homopolymerization is extremely sensitive to addition of small amounts of MMA. In a more general

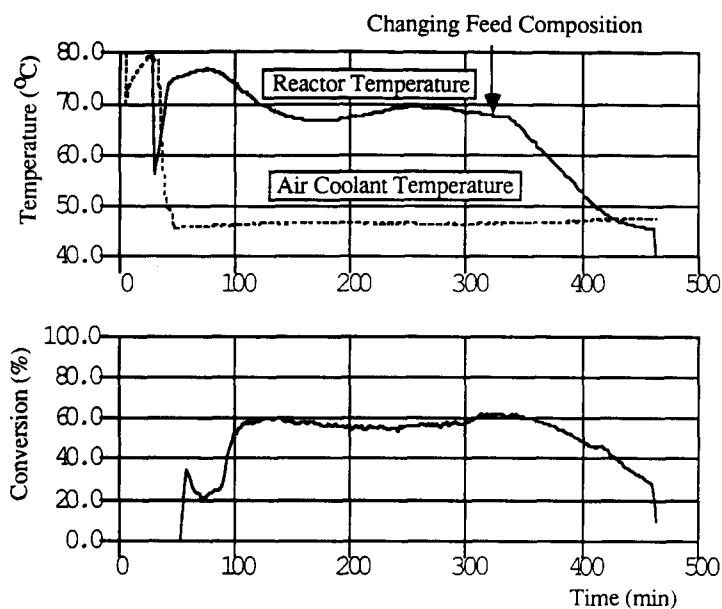


Fig. 18. Dynamic temperature profile following a step change in the feed composition ($v_{sf} = 0.6000$, $c_{if} = 0.04$ gmol/l, $T_a = 298$ K, $T_c = 48^\circ\text{C}$, $\Theta = 90$ min, v_{2f} changed from 0.0000 to 0.0020 after steady state).

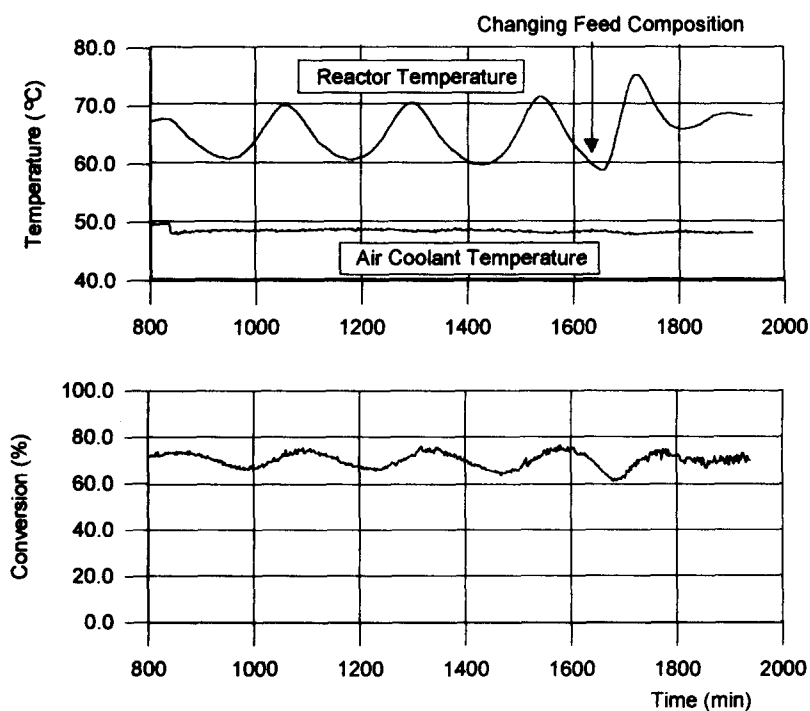


Fig. 19. Dynamic temperature profile following a step change in the feed composition ($v_{sf} = 0.6000$, $c_{if} = 0.04$ gmol/l, $T_a = 298$ K, $T_c = 50^\circ\text{C}$, $\Theta = 90$ min, v_{2f} changed from 0.0020 to 0.0000 during oscillatory state).

sense, the stability of continuous polymerization reactors may be very sensitive to changes in the feed composition.

In order to analyze the source of instabilities in the VA/MMA copolymerization, one should recall that Table 8 shows that ψ depends strongly on the MMA

feed concentration and that it increases steadily as the MMA concentration increases. As the rate of cross-termination is proportional to ψ , an increase in the MMA feed concentration causes an increase in the rate of termination and a consequent decrease in the concentration of free-radical species. The net result is

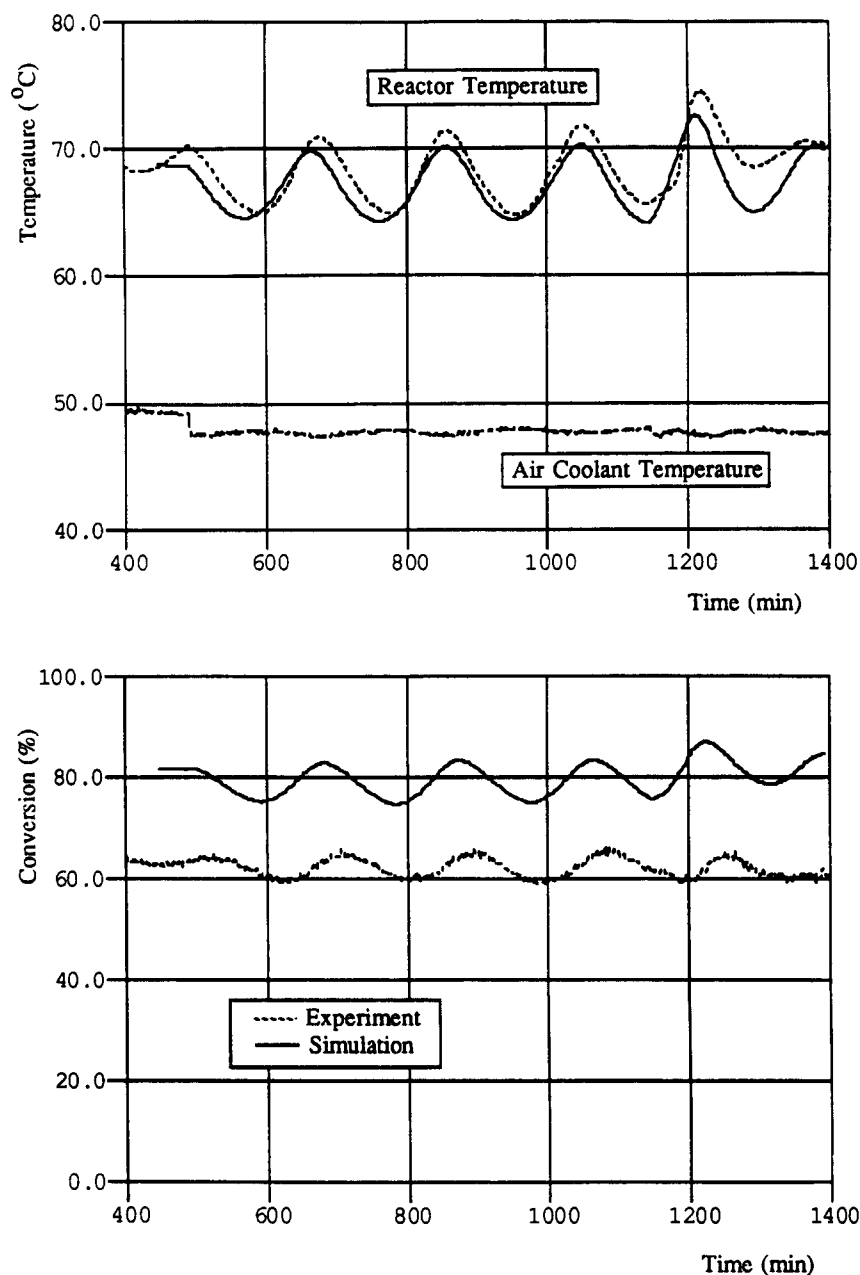


Fig. 20. Theoretical dynamic temperature profile (conditions as in Fig. 16, $UA = 1.01 (UA)_0$).

a decrease in the rate of reaction. So, from this point of view, MMA molecules inhibit the VA homopolymerization. Therefore, similar results may be expected in other types of free-radical copolymerization where ψ depends strongly on the feed composition, for example MMA/styrene and VA/styrene.

7. CONCLUSION

The stability of free-radical solution copolymerization may be extremely sensitive to changes in the feed composition. Using the system VA/MMA as an

example, it was shown that changes in the MMA comonomer feed concentration in the range 0.00–0.50% in volume could change the stability of VA homopolymerization, leading to self-sustained oscillations and extinction. A mathematical model was developed to describe the dynamic behavior of continuous free-radical solution copolymerization reactors and, after preliminary evaluation of some kinetic parameters, it was able to predict changes in the stability of VA homopolymerization when very small amounts of MMA are added to the system. The theoretical results were confirmed experimentally.

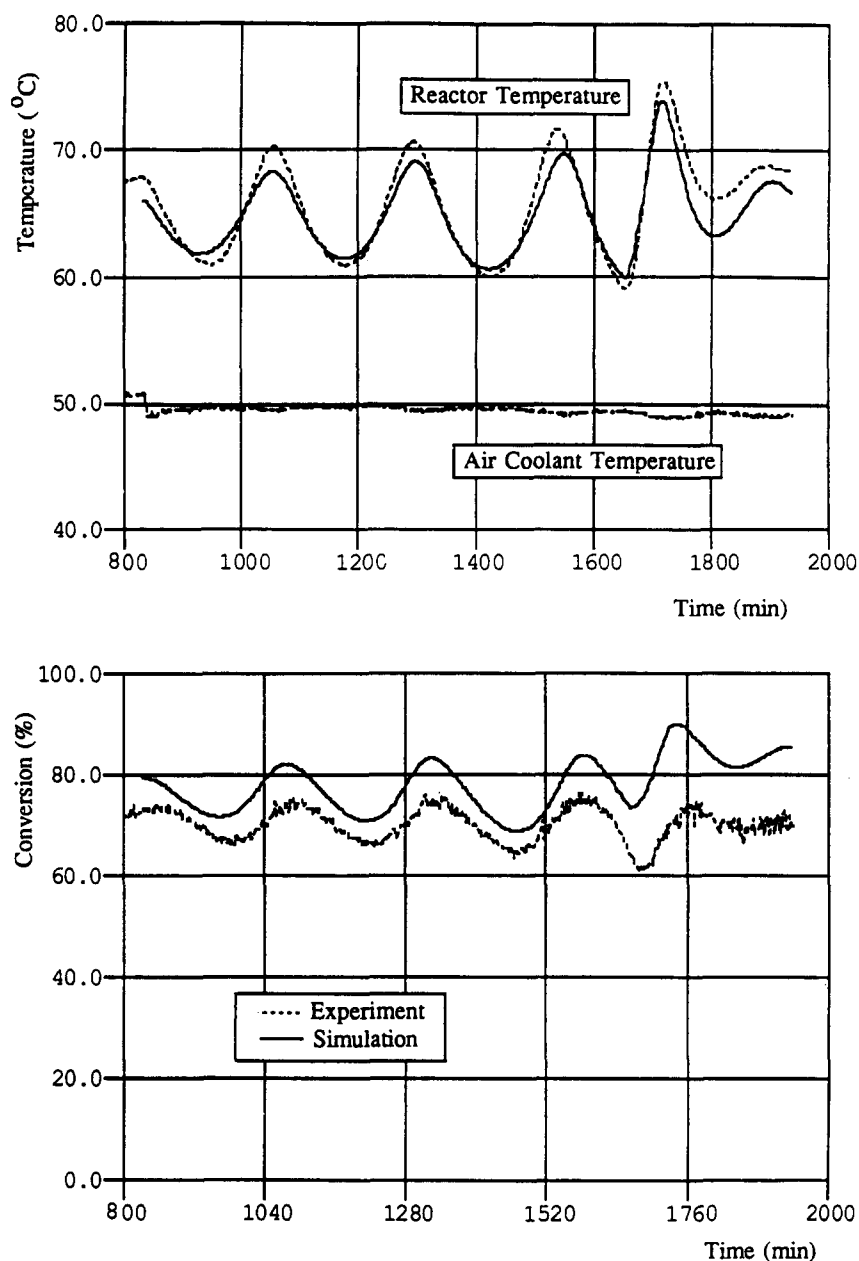


Fig. 21. Theoretical dynamic temperature profile (conditions as in Fig. 19, $UA = 0.95 (UA)_0$).

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NOTATION

c_i molar concentration of initiator
 c_p heat capacity
 f_i initiator efficiency for initiation of monomer i

g_{pij} gel effect correlation for k_{pij}
 g_{tij} gel effect correlation for k_{tij}
 I initiator
 k_d kinetic constant for initiator decomposition
 k_{pij} kinetic constant for propagation of free radical i with monomer j
 k_{ri} kinetic constant for initiation of free-radical i
 k_s kinetic 'equilibrium constant', as defined in eq. (15)
 k_t kinetic constant for termination, as defined in eq. (3)
 k_{tij} kinetic constant for termination of free radical i with free radical j

m_v	rate of vapor condensation
M_i	monomer i , molar concentration of monomer i
P	total molar concentration of free radicals P_{ij}
P_{ij}	molar concentration of free-radical 1 (having monomer 1 at the active site), containing i units of monomer 1 and j units of monomer 2
q_o/q_i	volume shrinkage, as in eq. (9)
Q	total molar concentration of free-radicals Q_{ij}
Q_{ij}	molar concentration of free-radical 2 (having monomer 2 at the active site), containing i units of monomer 1 and j units of monomer 2
Q_{lat}	rate of heat removal due to condensation
r_{ij}	reactivity ratio, as defined in eq. (1)
R	initiator fragment
$Rate_i$	normalized rate of reaction of monomer i
R_{ckr}	normalized rate of initiation
T	temperature
T_a	ambient temperature
T_b	boiling temperature
T_c	coolant air temperature
T_{gi}	glass transition temperature of species i
UA	global heat transfer coefficient to coolant jacket
v_f	free volume
v_{fpc}	critical free volume for propagation
v_{fte}	critical free volume for termination
V	reactor volume
x	total monomer conversion
x_i	molar fraction of species i
w	polymer composition (mass fraction of species 1)

Greek letters

α_i	expansion coefficient of species i , for free volume calculation
α_{UA}	global heat transfer coefficient to the ambient
ΔH_{ij}	heat of reaction for propagation k_{pij}
ΔH_v	latent heat of vaporization
ε	external capacitance
Θ	residence time
λ	numerical constant in eq. (25)
v_i	volume fraction of species i
Π_i	partial pressure of species i
Π_i^{sat}	saturation pressure of species i
ρ	density
τ	dimensions time (t/Θ)
χ_i	interaction parameter for species i
ψ_{ij}	cross-termination constant, as defined in eq. (2)

Special subscripts

1	monomer 1
2	monomer 2
f	feed
p	polymer
s	solvent

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