

Dynamic Behavior of a Continuous Autothermal Isobutylene Polymerization Reactor

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ABSTRACT: Industrial autothermal cationic isobutylene polymerization reactors may present very complex dynamic behavior and difficult operation. A mathematical model was developed to describe the operation of an autothermal solution industrial reactor, and some possible sources of complex dynamical behavior were analyzed. The results obtained indicate that the most probable source of the complex behavior observed industrially is the existence of adventitious impurities in the feed stream. The effects caused by the presence of adventitious impurities on process operation and product properties were investigated for both polymerization and oligomerization. In the first case, impurities influence the reactor productivity but do not change the polymer quality. In the oligomerization, both the polymer quality and the reactor productivity are seriously affected by the existence of impurities in the feed stream. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1403–1413, 1997

Key words: cationic; polymerization; autothermal reactor; dynamics; bifurcation; inhibitor

INTRODUCTION

The most important cationic polymerization process is the cationic isobutylene polymerization. Polyisobutylene resins may be used as additives, viscosity index improvers, elastomers, etc.,¹ and can be produced commercially in a large range of molecular weights, ranging from liquid oligomers (M_n around 500 g/mol) to high molecular weight elastomers (M_n ranging between 105 to 106 g/mol).

The initiating system used industrially normally comprises a solution of a Lewis acid (usually AlCl_3 or BF_3) and a protogenic species (as H_2O and HCl , for instance) in organic solvents.^{2,3} Depending on the final application, reaction temperatures range from -100°C to ambient temperature. For reaction to initiate, it is believed that

the Lewis acid reacts with the protogenic species forming a complex that reacts with the olefin, initiating the polymerization. The role of the protogenic species is, in fact, to generate the initiating proton, which in turn, completes the initiation by protonating the olefin.³ The protogenic material either is provided by ubiquitous impurities present in the system or is introduced on purpose.¹ Reaction takes place extremely fast and is very sensitive to impurities, especially water, even when impurities are present in very low amounts.

Polyisobutylene is manufactured continuously in solution or precipitation processes. As reaction rates are high, reaction heat has to be removed efficiently to allow the production of large amounts of polymer. The isobutylene polymerization reactors can be refrigerated by pumping the reacting mixture through external heat exchangers cooled by boiling ethylene at -100°C (EXXON process); by using cooling jackets and adding internal heat exchangers into the reactor; or by evaporating volatiles from the reacting mixture, condensing the vapor stream at the top of the

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Table I Isobutylene Polymerization Kinetic Scheme

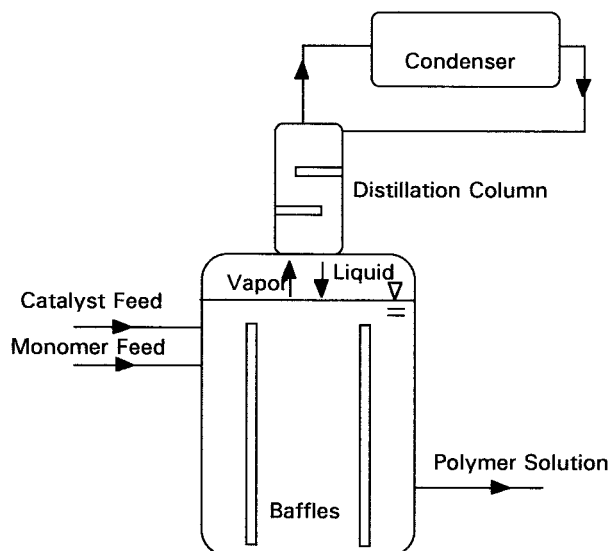
Initiation		
Initiator formation		$A + X \xrightleftharpoons{K} A^*$
Chain formation		$A^* + M \xrightarrow{k_i} P_i$
Propagation		
Activation-deactivation		$P_i \xrightleftharpoons[k_d]{k_a} P_i^*$
Chain growth		$P_i^* + M \xrightarrow{k_p} P_{i+1}^*$
Chain Transfer		
To monomer		$P_i^* + M \xrightarrow{k_m} \Lambda_i + P_i^*$
To solvent		$P_i^* + S \xrightarrow{k_s} \Lambda_i + P_i^*$
Termination		
Unimolecular		$P_i^* \xrightarrow{k_t} \Lambda_i$

reactor and recycling the condensed liquid stream back to the reaction environment. This last reactor configuration is known as the autorefrigerated or autothermal reactor. From the point of view of process control, the autorefrigerated configuration is very attractive, as the rate of heat exchange is not significantly affected by the increase of viscosity, which provides a robust temperature control even at high polymer concentrations.^{4,5} However, the heat exchange mechanism is more complex in this case.

Industrial cationic isobutylene polymerization reactors are subject to some serious operation problems. Kresge reports that in some industrial units the reactor can be operated intermittently for a maximum of 60 consecutive hours.¹ Industrial engineers have also observed oscillatory behavior and reaction extinction⁶ at plant site.

Table II Kinetic Constant Ratios¹⁴

Kinetic Constant Ratio	Estimated Value
$\frac{k_a}{k_d}$ mol/L	$29.768 \exp\left(\frac{-5163}{RT}\right)$
$\frac{k_m}{k_a}$ L/mol	$0.0142 \exp\left(\frac{-9736}{RT}\right)$
$\frac{k_s}{k_a}$ L/mol	$0.0102 \exp\left(\frac{-13593}{RT}\right)$
$\frac{k_t}{k_a}$ L/mol	$0.3153 \exp\left(\frac{-14483}{RT}\right)$

**Figure 1** Reactor configuration.

In spite of the huge amount of work regarding isobutylene cationic polymerizations and the well-known operation problems observed in industrial units, much of the research in the area has been focused on describing the kinetics and mechanism of the isobutylene polymerization. There are just a few works dealing with the polymerization engineering and process analysis of these systems. Giusti et al.⁷ analyzed the batch isothermal solution polymerization of isobutylene in order to find the operation conditions where transfer reactions would be minimum, and the polymerization would be "more" living. Mashio et al.⁸ extended the previous model by adding the molecular weight distribution (MWD) moment equations for dead and growing polymer chains in order to describe monomer conversion and polymer molecular weight distribution. The unimolecular termination step was not taken into account in these works, which might explain the fact that the conversion curve predicted by their model was always above the experimental curve.

Freitas and Pinto⁹ investigated the dynamic behavior of continuous solution and continuous precipitation nonisothermal cationic isobutylene polymerization and showed that oscillatory behavior is not inherent to the kinetic mechanism that describes such reactors. They suggested that possible sources of process instabilities might be the presence of feed impurities or a more complex heat transfer mechanism, as in autorefrigerated reactors.

In this work, the dynamic behavior of an autothermal solution isobutylene polymerization re-

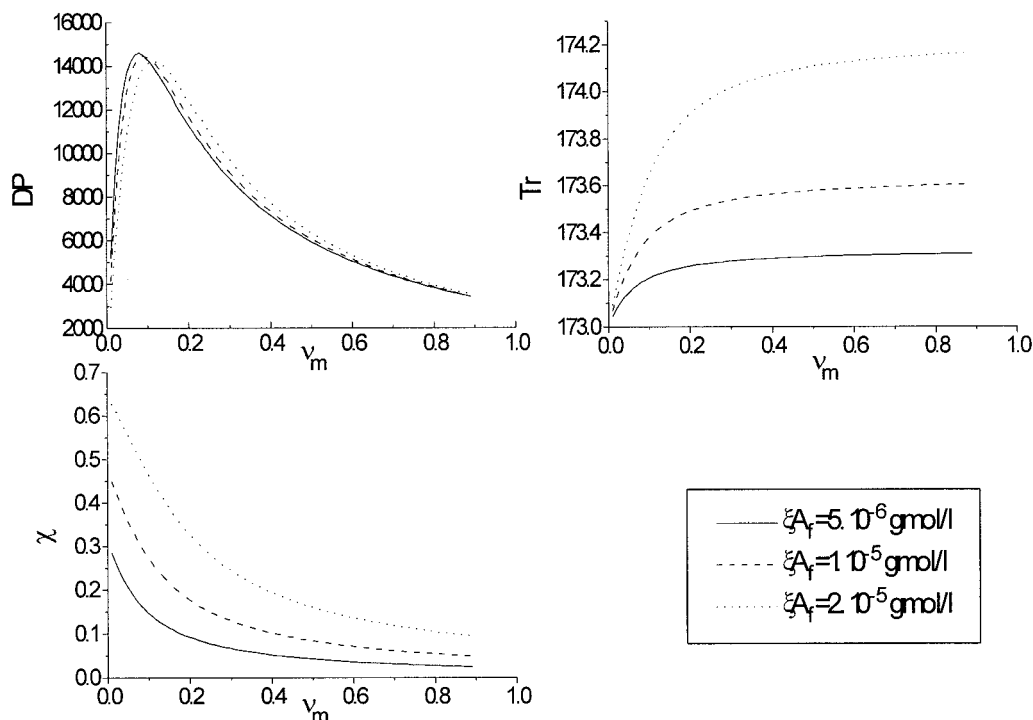


Figure 2 Steady-state reactor response as a function of monomer concentration in the feed stream. Conditions: $T_f = 173.15$ K; $\theta_f = 2$ h; $\nu_m = 0.2$.

actor is investigated in order to find out whether this more complex heat transfer configuration may be a source of process instabilities. The reactor sensitivity to changes of the feed composition is also analyzed in order to find out how reactor operation responds to feed perturbations and how important feed perturbations may be to describe oscillatory operation.

KINETIC SCHEME

Based on the studies of Kennedy and co-workers,^{10–13} a kinetic scheme for the isobutylene polymerization was suggested, as presented in Table I, and the kinetic constant ratios were estimated.¹⁴ The kinetic constant ratios are presented in Table II.

The initiation step of cationic polymerizations is believed to involve two stages: the ion generation and the cationation of an olefin. Initiation is not completely understood though, and the identity of the “real” initiating species has not yet been determined. However, it is generally accepted that the role of the protogenic species is to provide the initiating entity and that the role of the Lewis acid is to facilitate the initiation step.³

The most accepted initiation scheme involves

the interaction between the protogenic species and the Lewis acid, forming a complex that protonates the olefin and produces the true initiating species.³ However, Plesh¹⁵ reports that AlCl_3 is easily complexed by monomer when they are mixed, which inhibits the initiation step. To take into account the lack of understanding of the initiation process, the true catalyst concentration is represented here as a fraction (catalyst efficiency) of the total amount of AlCl_3 fed into the reactor. It is also assumed that initiator is formed outside the reactor. A similar procedure was adopted successfully by Freitas and Pinto⁹ to describe the behavior of such reactors.

The propagation step comprises two stages¹³: the activation of the growing chain and the monomer insertion. In the first stage, the negative counterion is set apart from the cationic chain end by natural oscillations, which facilitates the monomer incorporation in the second stage. The first stage is represented as an equilibrium process due to the ionic nature of the growing species.⁹

Chain transfer occurs to both monomer and solvent,¹⁰ which poses a limit on the maximum attainable polymer average molecular weight. Spontaneous unimolecular termination is also expected to occur,¹⁶ which poses a limit on the maximum attainable monomer conversion.

REACTOR MODEL

The reaction system consists of a continuous stirred tank reactor, a distillation column with two equilibrium stages, and a total condenser placed at the top of the column. The schematic diagram of the autorefrigerated solution isobutylene homopolymerization reactor is shown in Figure 1.

It is assumed here that polymerization occurs in a solution of *n*-pentane and that AlCl_3 is the initiator. Reactor volume is kept constant due to proper control of reactor level, but density variations have to be taken into account due to significant differences between polymer and monomer densities. The reactor is fed by two streams: a stream that contains a mixture of monomer and solvent, and a stream that contains the catalyst solution. Both streams are admitted into the reactor at the same reactor position.⁹ Compared to the amounts of monomer and solvent fed into the reactor, the amount of catalyst may be regarded as negligible.

The reactor vessel is assumed to be perfectly isolated, so that the reaction heat is completely removed by evaporating volatiles from the reacting mixture. Volatiles are then condensed at the top condenser and pumped back into the reaction environment. The contribution of shaft work to the energy balance may be neglected.

Based on the assumptions presented above, the following equations can be written to describe the reactor reaction zone:

$$Vr \frac{d\rho}{dt} = \rho_f q_f - \rho q + L_2 - V_1 \quad (1)$$

$$Vr \frac{dM}{dt} = M_f q_f - M q - V_1 y_{m_1} + L_2 x_{m_2} - \left[1 + \frac{k_a k_p M}{k_t (k_d + k_p M)} + \frac{k_m M}{k_t} \right] \xi A_f q_f \quad (2)$$

$$Vr \frac{dS}{dt} = S_f q_f - S q - \left[\frac{k_s S}{k_t} \right] \xi A_f q_f - V_1 y_{s_1} + L_2 x_{s_2} \quad (3)$$

$$\rho c_p Vr \frac{dT_1}{dt} = \rho_f c_p q_f (T_f - T_1) - V_1 \lambda_v + L_2 c_p p_2 (T_2 - T_1) + (-\Delta H_p) \times \left[1 + \frac{k_a k_p M}{k_t (k_d + k_p M)} + \frac{k_m M}{k_t} \right] \xi A_f q_f \quad (4)$$

where it is assumed that the first equilibrium stage is the reaction vessel and that only monomer and solvent can be vaporized. The heat of polymerization is equal to -54 kJ/mol .¹⁷

It is convenient to express monomer and solvent concentrations in terms of the monomer feed volume concentration ($\nu_{M,f}$).

$$M_f = \frac{\rho_{M,f}}{PM_M} \nu_{M,f} \quad (5)$$

$$S_f = \frac{\rho_{S,f}}{PM_S} (1 - \nu_{M,f}) \quad (6)$$

The density of the reacting mixture is a function of temperature and concentration of the reacting species present in the reaction environment. So, the global mass balance can be written as

$$Vr \frac{d\rho}{dt} = Vr \left[\left(\frac{\partial \rho}{\partial T} \right) \frac{dT}{dt} + \left(\frac{\partial \rho}{\partial M} \right) \frac{dM}{dt} + \left(\frac{\partial \rho}{\partial S} \right) \frac{dS}{dt} \right] = \rho_f q_f - \rho q + L_2 - V_1 \quad (7)$$

and the reactor model can be rewritten in terms of charging time ($\theta_f = V/q_f$), discharging time ($\theta = V/q$), and monomer feed volume concentration as

$$\left[\left(\frac{\partial \rho}{\partial T} \right) \frac{dT}{dt} + \left(\frac{\partial \rho}{\partial M} \right) \frac{dM}{dt} + \left(\frac{\partial \rho}{\partial S} \right) \frac{dS}{dt} \right] = \frac{\rho_f}{\theta_f} - \frac{\rho}{\theta} + \frac{L_2}{Vr} - \frac{V_1}{Vr} \quad (8)$$

$$\frac{dM}{dt} = \frac{\rho_{M,f}}{PM_M \theta_f} \nu_{M,f} - \frac{M}{\theta} - \left[1 + \frac{k_a k_p M}{k_t (k_d + k_p M)} + \frac{k_m M}{k_t} \right] \times \frac{\xi A_f}{\theta_f} - \frac{V_1}{Vr} y_{m_1} + \frac{L_2}{Vr} x_{m_2} \quad (9)$$

$$\frac{dS}{dt} = \frac{\rho_{S,f}}{PM_S \theta_f} (1 - \nu_{M,f}) - \frac{S}{\theta} - \left[\frac{k_s S}{k_t} \right] \frac{\xi A_f}{\theta_f} - \frac{V_1}{Vr} y_{s_1} + \frac{L_2}{Vr} x_{s_2} \quad (10)$$

$$\begin{aligned} \rho c_p V_r \frac{dT_1}{dt} &= \frac{\rho_f c_p P_f}{\theta_f} (T_f - T_1) \\ &- V_1 \lambda_v + L_2 c_p p_{12} (T_2 - T_1) + (-\Delta H_p) \\ &\times \left[1 + \frac{k_a k_p M}{k_t (k_d + k_p M)} + \frac{k_m M}{k_t} \right] \frac{\xi A}{\theta_f}. \quad (11) \end{aligned}$$

The density and specific heat of the reacting mixture can be evaluated by

$$\rho = \sum_{i=S,M,P} \nu_i \rho_i(T) \quad (12)$$

$$c_p = \sum_{i=S,M,P} w_i c_{p_i} \quad (13)$$

where ν_i and w_i are the volume fraction and the mass fraction of species i . The physical constants of individual species can be found in ref. 9.

As the dynamics of the column stages is much faster than the dynamics of the reaction vessel, due to their much smaller volumes, the quasi steady-state assumption was made for the column stages. It was also assumed that the column stages were in thermodynamic equilibrium. Therefore, the mass and heat balances for the first column stage can be written as

$$V_1 + L_3 = L_2 + V_2 \quad (14)$$

$$y_{m_1} V_1 + x_{m_3} L_3 = x_{m_2} L_2 + y_{m_2} V_2 \quad (15)$$

$$c_{p_{v_1}} V_1 T_1 + c_{p_{l_3}} L_3 T_3 = c_{p_{l_2}} L_2 T_2 + c_{p_{v_1}} V_1 T_1 \quad (16)$$

where it was assumed that the heat of vaporization does not significantly depend on composition.

Mass and energy balance equations for the second column stage are similar to the ones presented before.

The quasi steady-state assumption was also made to describe the dynamics of the condenser. This assumption is based on the fact that condenser level is carefully controlled to avoid both flooding and emptying of the condenser and that the vapor that reaches the condenser contains mostly isobutylene, as it is more volatile than n -pentane and much more volatile than other oligomeric species. Besides, no significant change of the heat transfer coefficient is expected to take place when small changes of the vapor concentration occurs. Therefore, the condenser heat and mass balances may be written as

$$UA(T_c - T_3) = V_3 \lambda_v \quad (18)$$

$$L_4 = V_3 \quad (19)$$

where it was assumed that the liquid stream that leaves the condenser is at the bubble point.

The reactor pressure may be obtained by assuming that liquid and vapor phases are in equilibrium in the reaction vessel. In this case, the Flory–Huggins equation¹⁸ may be used to describe the thermodynamic equilibrium. So, the activity coefficient of solution components may be calculated as

$$a_i = \nu_i \exp(\nu_p + \varphi_i \nu_p^2) \quad (20)$$

The vapor phase was assumed to be an ideal gas. The Flory–Huggins interaction parameters were evaluated by Freitas and Pinto⁹ using literature data:

$$\varphi_s = -1.631 + 706/T \quad (21)$$

$$\varphi_M = 0.249 + 17.3/T \quad (22)$$

The polymer molecular weight distribution can be described using the classical method of moments.¹⁹ In this case, the following equations may be written:

$$\frac{d\lambda_0}{dt} = \left[\frac{k_m M + k_s S + k_t}{k_t} \right] \frac{\xi A_f}{\theta_f} - \frac{\lambda_0}{\theta} \quad (23)$$

$$\frac{d\lambda_1}{dt} = \left[\frac{k_m M + k_s S + k_t}{k_t} \right] \frac{\xi A_f}{(1 - \alpha)\theta_f} - \frac{\lambda_1}{\theta} \quad (24)$$

$$\frac{d\lambda_2}{dt} = \left[\frac{k_m M + k_s S + k_t}{k_t} \right] \frac{\xi A_f}{(1 - \alpha)^2 \theta_f} - \frac{\lambda_2}{\theta} \quad (25)$$

where λ_0 , λ_1 , λ_2 are the zeroth, first, and second moments of the dead polymer molecular weight distribution; and α is the propagation probability, defined as

$$\alpha = \frac{k_a k_p M}{k_a k_p M + (k_m + k_s S + k_t)(k_d + k_p M)} \quad (26)$$

If the concentration of growing chains is much lower than the concentration of dead chains, the number average degree of polymerization is

$$DP \equiv \frac{\lambda_1}{\lambda_0} \quad (27)$$

The number average and weight average molecular weights are

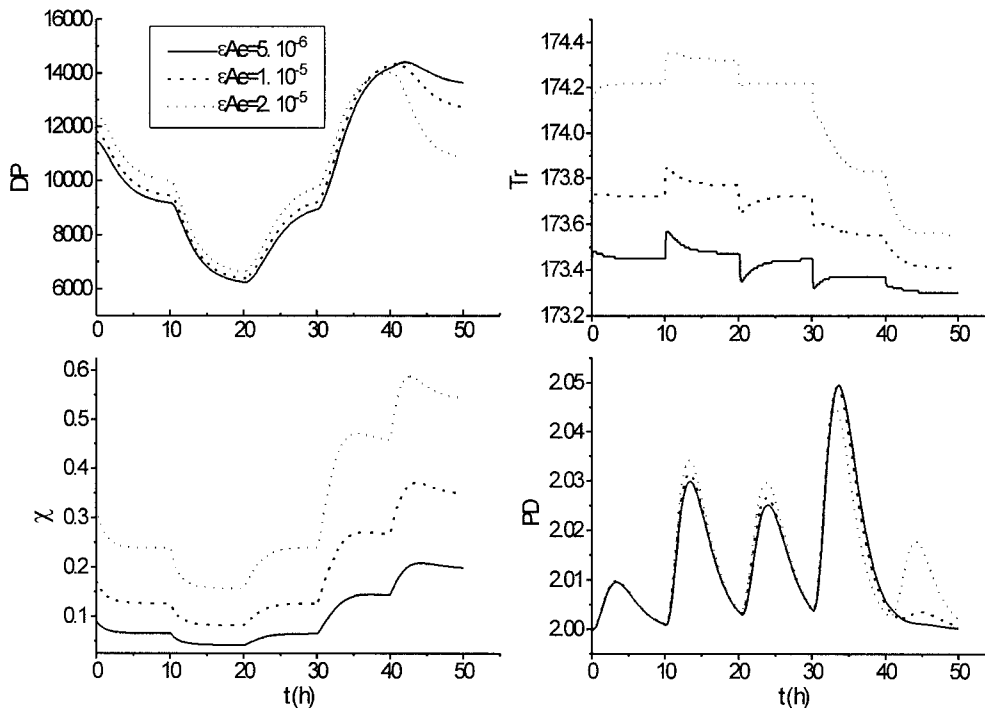


Figure 3 Open loop reactor response to monomer feed concentration step changes: $t = 0$ h, $\nu_m = 0.3$; $t = 10$ h, $\nu_m = 0.5$; $t = 20$ h, $\nu_m = 0.3$; $t = 30$ h, $\nu_m = 0.1$; $t = 40$ h, $\nu_m = 0.05$; other conditions: $T_f = 173.15$ K; $\theta_f = 2$ h.

$$\bar{M}_n \equiv PM_M \frac{\lambda_1}{\lambda_0} \quad (28)$$

$$\bar{M}_w \equiv PM_M \frac{\lambda_2}{\lambda_1} \quad (29)$$

The monomer conversion is

$$\chi \equiv \frac{\lambda_1}{\lambda_1 + M} \quad (30)$$

The polydispersity is

$$PD \equiv \frac{\bar{M}_w}{\bar{M}_n} = \frac{\lambda_2 \lambda_0}{\lambda_1^2} \quad (31)$$

STEADY-STATE AND DYNAMIC REACTOR BEHAVIOR

The system of algebraic-differential equations that constitute the reactor model was solved numerically using the code DASSL.²⁰ DASSL uses a BDF (backward differentiation formula) method to solve systems of algebraic differential equations.

The control of the degree of polymerization can be achieved by manipulating the reactor tempera-

ture and initiator feed concentration. At low temperatures (around -100°C) high molecular weight polymers are produced, while at higher temperatures (in the range between -40 and 20°C) low molecular polyisobutylenes are produced ($M_n < 10,000$). The open loop reactor response to step changes in the feed temperature was investigated, but the results were very similar to the ones obtained by Freitas and Pinto⁹ and will not be presented here. As shown by Freitas and Pinto,⁹ although reactor responses are nonlinear, they never lead to oscillatory behavior, and new steady-state conditions are reached smoothly after the perturbation.

The molecular weight control can also be achieved by manipulating the monomer feed concentration, as shown in Figure 2. As the monomer feed concentration increases, the degree of polymerization goes through a maximum, which is attained when the monomer feed volume fraction is around 0.20. At lower monomer feed concentrations, the degree of polymerization is very sensitive to small changes of the monomer concentration. At higher monomer concentrations, the polymer molecular weight decreases continuously as the monomer feed volume fraction increases. Figure 2 also shows that monomer conversion de-

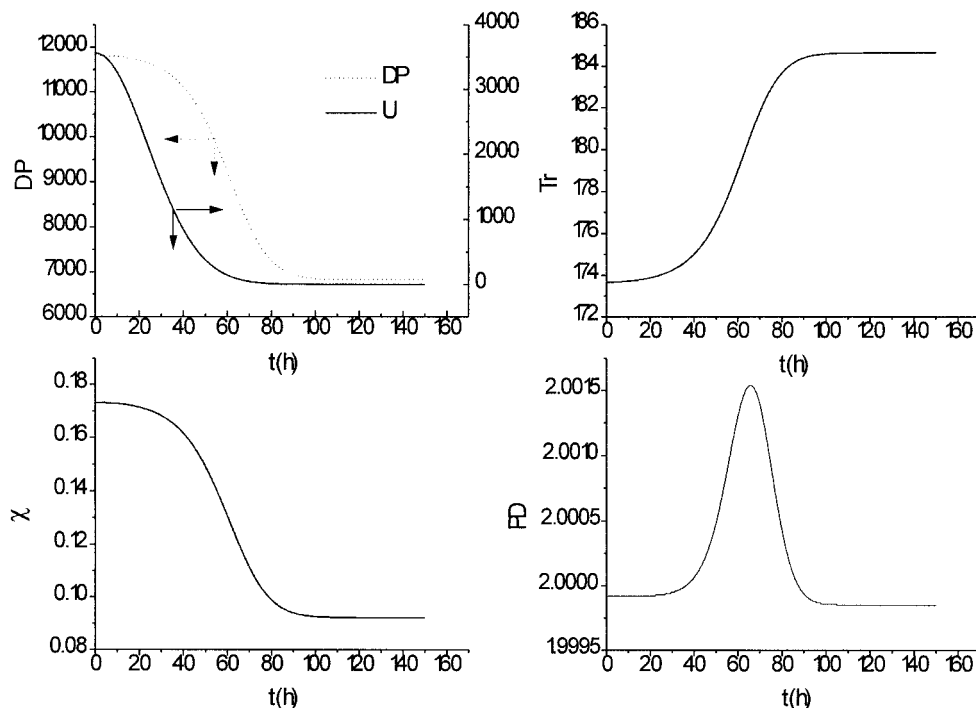


Figure 4 Open loop reactor response to an exponential decrease of the global heat transfer coefficient. Conditions: $T_f = 173.15$ K; $\xi A_f = 1 \times 10^{-5}$; $\theta_f = 2$ h; $\nu_m = 0.2$.

crases monotonously as the monomer fraction increases.

The steady-state response to changes of the monomer feed concentration is due to the fact that the rate of monomer addition increases sharply as the monomer concentration increases at low monomer concentration, reaching a practically constant at higher monomer concentrations. However, the sum of termination and transfer rates increases linearly and steadily with the monomer feed concentration. The effect of the monomer feed concentration on the reactor temperature (Fig. 2) is very low, due to the robust temperature control provided by the autorefrigerated configuration.

The open loop response of the reactor (initially at steady-state conditions) to step changes of the monomer feed concentration is shown in Figure 3. The reactor is more sensitive to changes of the monomer feed concentration than to changes of the feed temperature. Figure 3 indicates that steady states are stable and that the process dynamics is nearly linear. It may be concluded that changes of the monomer feed concentration is not responsible for the complex behavior observed in industrial units. However, it may also be concluded that proper characterization of the feed stream is extremely important to describe reactor responses. It is a common industrial practice to feed the reactor with an isobutylene stream that also contains sig-

nificant amounts of other butenes, coming from a distillation column that fractionates the effluents of a cracking unit. Given the sensitivity of the reactor responses to changes of the feed composition, this procedure may be unwise.

A possible source of complex dynamics is the isobutylene polymerization inside the condenser, which may cause the decrease of the heat transfer efficiency, leading the reactor to an unstable operational condition. In order to investigate this hypothesis, it may be assumed that the global heat transfer coefficient decreases exponentially with time. It can be observed in Figure 4, however, that the reactor can be operated adiabatically without any sort of unstable behavior. This is due to the decrease of the monomer conversion with the increase of the reactor temperature. It must also be said that the most important function of the internal equilibrium stages placed between the reaction vessel and the condenser is removing initiator residue from the vapor stream, to prevent polymerization to occur inside the condenser, so that U is not expected to decrease significantly as time goes on. Thus, it may be concluded that the reduction of the heat transfer rates in the condenser does not compromise the stability of the reactor operation.

Similar results may be obtained when the bubble point constraint is removed from the liquid

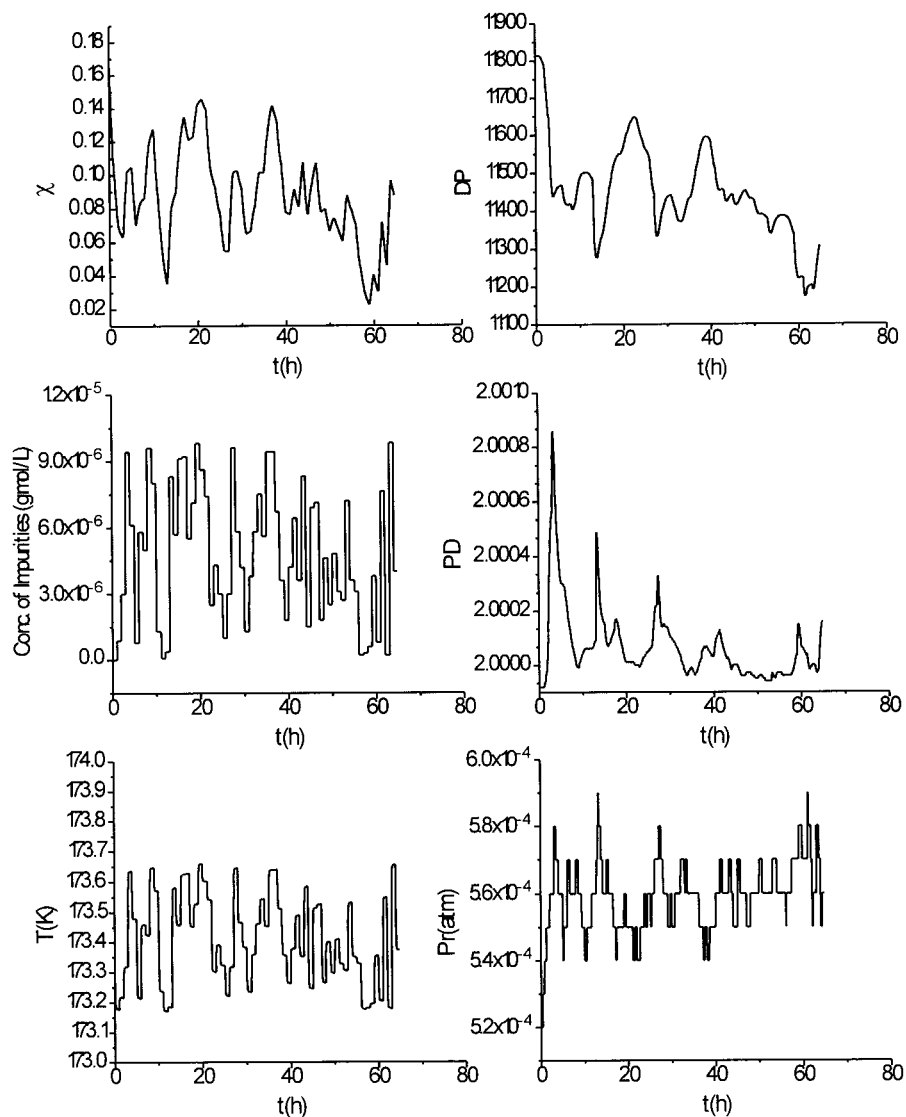


Figure 5 Open loop reactor response to random step perturbation of the inhibitor feed concentration. Conditions: $T_f = 173.15$ K; $\theta_f = 2$ h; $\nu_m = 0.2$.

that leaves the condenser. When the condenser liquid stream is supercooled, an even tighter temperature control is possible, as the recycled liquid stream contributes to reducing reactor temperature operation.

Another possible source of complex behavior at actual plant site is the adventitious presence of impurities in the feed stream. As discussed before, the composition of the feed stream may change from time to time, depending on the performance of the cracking and fractionation units. Besides, it was shown previously that reactor responses are sensitive to changes of the feed composition. Figures 5 and 6 show the effect of feeding a random amount of impurities into the reactor. It is assumed here that each inhibitor molecule is able

to deactivate one initiator molecule. If inhibition is caused by water, for instance, according to the concentration range presented in Figures 5 and 6, the inhibitor concentration will lie in the range between 0 and 200 ppm.

As shown in Figures 5 and 6, the polymerization reactor may present a very complex behavior when impurities are present in the feed stream and when inhibitor feed concentrations are subject to random fluctuations within intervals of 30 min. Reactor responses do not filter the noisy feed perturbations because reaction rates are too high and very sensitive to small changes of the feed composition. It must be noticed that it is well known that cationic polymerizations are very sensitive to impurities,³ which does not necessarily mean that the continu-

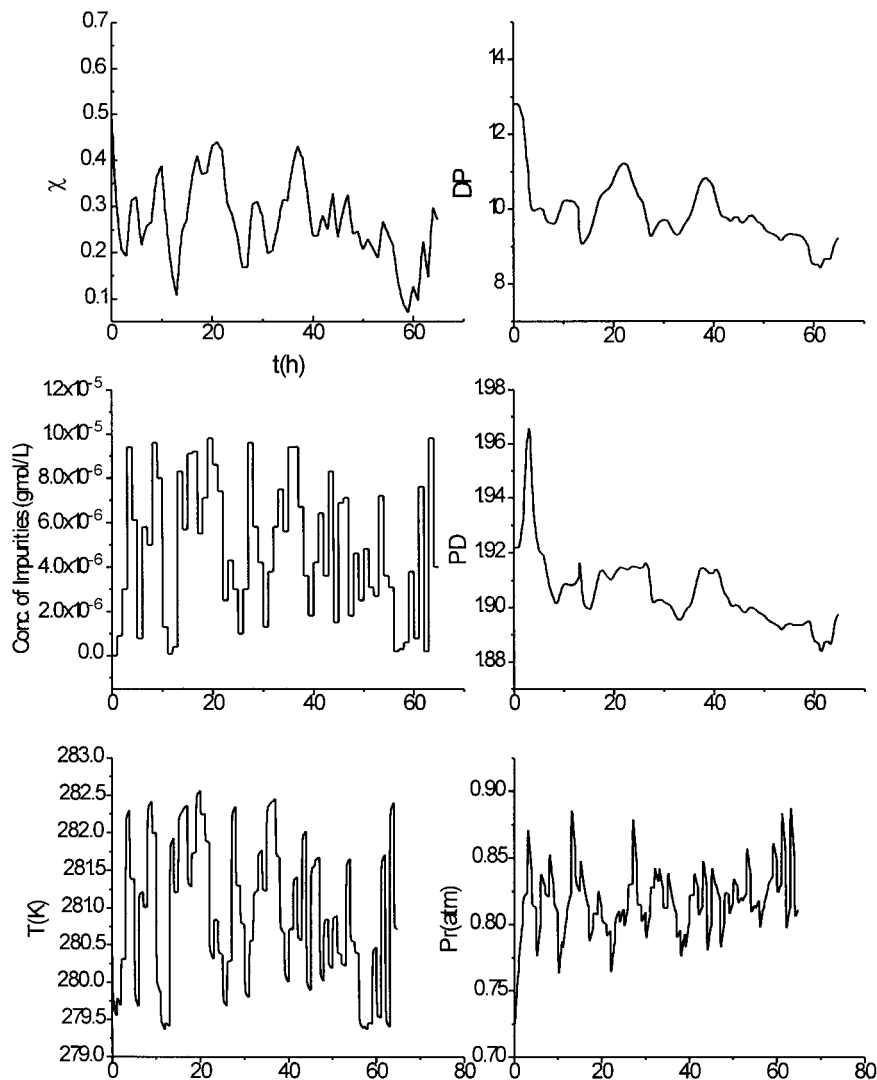


Figure 6 Open loop reactor response to random step perturbation of the inhibitor feed concentration: $T_f = 298.15$ K; $\theta_f = 2$ h; $\nu_m = 0.4$.

ous process should be unable to filter random fluctuations of the feed inhibitor concentration. Monomer conversion is strongly affected by the presence of impurities. Depending on the amount of impurities in the feed stream, reaction can even be extinguished. Figure 5 shows that, at lower temperatures, the effect of random fluctuations of the inhibitor concentration on molecular weight is less pronounced. This filtering of the molecular weight is mostly due to the large differences between the characteristic reaction time and the residence time, which allows the mixing of the polymer produced at different moments and the averaging of the polymer molecular weight.

When operation is carried out at higher temperatures to produce low molecular weight polymers or oligomers, the effects caused by the pres-

ence of impurities in the feed stream on other state variables is more pronounced. In this case, Figure 6 shows that similar amounts of impurities may cause monomer conversion to oscillate in the range between 0.1 and 0.6. Similarly, the degree of polymerization oscillates between 9 to 14. In this case, the presence of impurities causes not only fluctuations of polymer productivity, but also causes serious problems in product quality and unit performance. A much tighter control scheme must be implemented in this case to assure polymer quality.

Although variations of the feed inhibitor concentration may cause huge fluctuations in monomer conversion and in the average polymer molecular weight (for the oligomerization), reactor temperature and pressure are not significantly af-

ected by them. From a practical point of view, though, reactor temperature and pressure are the most important operation variables, as they can be measured easily and frequently at the plant site. In this case, however, monitoring process operation by measuring reactor temperature and pressure may be inadequate and may lead to control failures, as these variables are not very sensitive to feed disturbances, which are the variables that affect the reactor performance most significantly. Therefore, control strategies based on monitoring reactor temperature and/or pressure may also contribute to the development of oscillatory behavior in actual reactors.⁶

Regarding the effects of impurities in other polymerization systems, Pinto and Ray²¹ showed that the reactor dynamics in free radical polymerizations is very sensitive to the presence of inhibitors in the feed stream, which might lead the reactor operation to unstable conditions. In that case, though, the reactor response is able to filter fluctuations of the inhibitor concentration, given the much slower reaction rates, and/or lead to temperature oscillations of large amplitude, which certainly allows the implementation of more efficient control strategies.²² In the case studied here, reactor operation is not unstable, as oscillatory behavior ceases if the inhibitor concentration is kept at a constant value. However, one may wonder whether the feed purification in industrial units is able to keep the impurity levels at sufficient low and constant levels to maintain the process stable.

Based on the results presented, it can be concluded that the most likely source of oscillatory behavior in continuous industrial isobutylene cationic polymerization reactors is the presence of impurities in the feed stream.

CONCLUSIONS

The dynamic behavior of a continuous autorefrigerated solution isobutylene polymerization reactor was investigated in order to find the sources of oscillations observed in industrial reactors. It was shown that such reactors do not present unstable steady states or self-sustained oscillatory behavior. However, it was shown that they are very sensitive to changes of the inhibitor feed concentrations and unable to fast filter random fluctuations of the inhibitor levels. Therefore, the most likely source of complex behavior in this system is the fluctuation of the impurity feed concentration. Regarding other process variables, such

as feed temperature and heat transfer rates, reactor responses are extremely well behaved, so that changes of these variables cannot lead the process to unstable operation. It is important to notice, however, that reactor responses are sensitive to changes of the monomer feed composition, so that proper characterization of the feed stream must be carried out.

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NOMENCLATURE

a	activity coefficient
A_f	initiator concentration
A	effective heat transfer area
cp	specific heat of the reacting mixture
cp_v	specific heat of the vapor phase
cp_L	specific heat of the liquid phase
DP	number average degree of polymerization
L	molar rate of liquid leaving an equilibrium stage
M	monomer concentration
\bar{M}_n	number average molecular weight
\bar{M}_w	weight average molecular weight
PD	polydispersity index
PM_M	monomer molecular weight
Pr	reactor pressure
q	volumetric flow rate
S	solvent concentration
T_j	temperature of j th equilibrium stage
U	global heat transfer coefficient
V	molar rate of vapor leaving an equilibrium stage
V_r	reactor volume
x	liquid molar fraction
y	vapor molar fraction

Greek Symbols

α	propagation probability
χ	monomer conversion
$(-\Delta HP)$	heat of polymerization
φ	Flory–Huggins interaction parameter
λ_k	k th moment of dead polymer molecular weight distribution
$(-\lambda_v)$	heat of vaporization
ν	volume fraction

θ	reactor discharging time
θ_f	reactor charging time
ρ	density of the reacting mixture
ρ_j	density fraction of species j
ω_j	mass fraction of species j
ξ	catalyst efficiency
ξA_f	"effective" initiator feed concentration

Special Subscripts

1	reaction vessel (first equilibrium stage)
2	first column stage (second equilibrium stage)
3	second column stage (third equilibrium stage)
4	condenser (fourth equilibrium stage)
c	coolant
f	feed
L	liquid stream
M	monomer
P	polymer
S	solvent
V	vapor stream

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