Research Article

Modeling of the Penultimate Unit Effect in Chain-Growth Copolymerizations

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The present work addresses the modeling and simulation of the addition of copolymerizations of styrene and methyl methacrylate in batch mode, and the formation of tailored vinyl acetate/acrylic acid copolymers is evaluated through stochastic optimization procedures based on the Monte Carlo method. A kinetic model of the free-radical reaction was proposed in order to predict the behavior of the reaction system taking into consideration the presence of the penultimate unit effect. The profiles of conversion and copolymer composition were also evaluated considering the effect of the medium viscosity (kinetic phenomena related to gel and glass effects) on the reaction performance. It was shown that the proposed model for chain-growth copolymerization is able to describe strong nonlinear behaviors such as autoacceleration of the polymerization and drift of copolymer composition. It was also shown that copolymers with homogeneous composition can be successfully synthesized through manipulation of the monomer feed flow rate based on a stochastic optimization procedure.

1. Introduction

It is well-known that all reaction mechanism steps play an important role for the determination of copolymerization kinetic behavior. Despite this, the propagation step is fundamental for the proper description of the overall propagation rate coefficients, of polymer composition, and of the sequence distribution of final copolymer, important properties that define the material polymeric application.

In chain-growth polymerizations, two propagation models are normally used to describe the polymerization. The first one is the well-known *terminal model* [1], which assumes that the reactivity of the propagation reaction is governed only by the nature of the monomer and of the terminal unit of the growing polymer chain. The second one is known as the *penultimate model* [2], which considers the effect of both the terminal and penultimate monomeric units of the growing polymer chain. According to this assumption, electronic and geometric effects or steric interactions between the penultimate monomeric unit and reactant species (e.g., monomers, transfer agents, and solvents) can be

incorporated into the propagation model [3, 4]. As a consequence, one has to keep in mind that the *penultimate model* normally leads to a considerable increase in the number of model parameters, and for this reason, the *terminal model* is the most popular propagation model and is the starting point for most studies on polymerization kinetics.

The *penultimate model* is generally employed when the *terminal model* (first-order Markovian model) is not able to satisfactorily describe polymerization rates. Two types of the penultimate *model* have been proposed: (i) the first one is named the *explicit penultimate model* which assumes that both the terminal and penultimate units of the radical can affect both the reactivity and selectivity; (ii) the second one denominated the *implicit penultimate model* which considers that despite the terminal and penultimate units of the polymeric radical affect the reactivity, only the terminal unit affects the selectivity [5–13].

Coote and Davis [6] presented an extensive list of monomeric pairs, where the terminal model is not suitable to describe copolymerization kinetic, and the reader is referred to this publication for more detailed information. Although

the penultimate effect is important to describe both the composition and the polymerization kinetics in several polymer systems, only few kinetic parameters for the *penultimate model* are reported in the open literature. Recently, Deb [14] calculated the *penultimate model* reactivity ratios from different binary monomer mixtures employed in copolymerization systems.

Typically, polymerization systems comprising styrene/acrylonitrile [15–20], methyl methacrylate/n-butyl acrylate [21], ethylene/styrene [22], dimethyl itaconate/styrene [23], ethylene/4-methyl-1-pentene [24], α-alkylstyrenes/acrylonitrile [25], styrene/methyl methacrylate [26], p-chlorostyrene/methyl acrylate [27], styrene/isobutylene [28], methyl α-(trifluoromethyl)acrylate and α-(trifluoromethyl) acrylonitrile with styrene, p-chlorostyrene and methyl methacrylate [29], styrene/maleic anhydride [30], isobutyl methacrylate/-lauryl methacrylate [31], and styrene/fumaronitrile [32, 33] demonstrate a strong penultimate unit effect, representing good examples of the successful implementation of the *penultimate model* [9, 34].

The kinetic mechanism represented by the *penultimate model* (second-order Markovian model) is composed of four distinct radicals that can combine with monomeric species, generating eight distinct stages of propagation ($\sim M_{ij}^{.} + M_n \xrightarrow{k_{ijn}} \sim M_{ijn}^{.}$ with $i, j, n = 1, 2$, where k_{ijn} is the reaction rate constant that characterizes the addition of the monomer unit n to a growing polymer chain containing the monomeric units i and j). Given the complex nature of polymerization systems, the introduction of additional stages of propagation with a consequent increase in the number of kinetic parameters is the major practical limitation of employing the penultimate model in polymerization kinetic models intended to be used to describe the reaction behavior.

In spite of the popularity of the terminal model, it is generally agreed that the existence of the penultimate unit effect in important chain-growth polymerization systems seems to be general rather than an exception, which clearly indicates that this polymerization kinetic based on the terminal model oversimplifies actual polymerization reaction processes [8, 14]. Initial studies on the influence of the penultimate unit effect in free-radical copolymerizations date from 1940s. Among then, the pioneering works of Merz et al. [2], Barb [30], and Ham [33] must be highlighted.

The *penultimate model* was originally developed by Merz et al. [2] to predict the copolymer composition and sequence distribution of the final copolymer. This propagation model was extensively explored by Fukuda and coworkers [5, 9, 26, 27], some years later, in order to understand the deviations from the *terminal model*, showing that the *penultimate model* provides a good description of copolymer composition, distribution sequences, and rate of propagation. Fukuda and coworkers have distinguished the penultimate unit effect behavior, originating two distinct models: *explicit penultimate* and *implicit penultimate* models of copolymerization. Fukuda et al. [26] also demonstrated through measurements of average propagation rate constant from copolymerizations of styrene/methyl methacrylate that the terminal model was not suitable to appropriately describe the experimental data.

Li et al. [35, 36] have described the combined effect of depropagation and penultimate unit effect kinetic on the instantaneous copolymer composition and average copolymerization rate coefficients in styrene/butyl methacrylate reactions performed at elevated temperatures. According to the authors, when depropagation appears combined with the penultimate unit effect, the effective propagation rate coefficient deviates significantly from terminal model predictions regarding the copolymer composition.

Recently, Nikitin and Hutchinson [37] have evaluated the penultimate unit effect in homopolymerization of acrylates. According to the proposed kinetic mechanism, the differences in reactivity of radicals formed by monomer addition to midchain radicals are taking into consideration. Model calculations have shown that deviation from the terminal model may depend on the radical reactivity ratio s_i and monomer concentrations, which generally complicates the kinetic analysis of acrylate homopolymerizations.

In the present work, a phenomenological polymerization model is proposed based on the kinetic mechanism that takes into account the penultimate monomeric unit effect in chain-growth copolymerizations and simulations are performed based on a typical polymerization system (styrene/methyl methacrylate) governed by the penultimate kinetic model. Additionally, the penultimate model is also employed to describe the experimental data of vinyl acetate/acrylic acid suspension copolymerization carried out in a batch mode. It is also proposed strategies for controlling the copolymer composition based on stochastic optimization procedures with the Monte Carlo method.

2. Kinetic Mechanism and Polymerization Model

The kinetic mechanism proposed to describe the (e.g., bulk or suspension) copolymerizations comprises the following fundamental steps: initiation, propagation, transfer to monomer, and termination by disproportionation and combination, as follows:

Step 1. Initiation

$$
\begin{aligned}
I &\xrightarrow{k_D} 2Z, \\
Z + M_1 &\xrightarrow{k_1} P_{1,0}, \\
Z + M_2 &\xrightarrow{k_2} S_{0,1}.
\end{aligned}
\tag{1}
$$

Step 2. Propagation

$$
\begin{aligned}
P_{i,j} + M_1 &\xrightarrow{k_{P_{111}}} P_{i+1,j}, \\
P_{i,j} + M_2 &\xrightarrow{k_{P_{112}}} Q_{i,j+1}, \\
Q_{i,j} + M_1 &\xrightarrow{k_{P_{121}}} R_{i+1,j}, \\
Q_{i,j} + M_2 &\xrightarrow{k_{P_{122}}} S_{i,j+1},
\end{aligned}
$$

$$R_{i,j} + M_1 \xrightarrow{k_{P_{211}}} P_{i+1,j},$$

$$R_{i,j} + M_2 \xrightarrow{k_{P_{212}}} Q_{i,j+1},$$

$$S_{i,j} + M_1 \xrightarrow{k_{P_{221}}} R_{i+1,j},$$

$$S_{i,j} + M_2 \xrightarrow{k_{P_{222}}} S_{i,j+1}.$$

$$(2)$$

Step 3. Transfer to monomer

$$P_{i,j} + M_1 \xrightarrow{k_{trM111}} \Theta_{i,j} + P_{1,0},$$

$$P_{i,j} + M_2 \xrightarrow{k_{trM112}} \Theta_{i,j} + S_{0,1},$$

$$Q_{i,j} + M_1 \xrightarrow{k_{trM121}} \Theta_{i,j} + P_{1,0},$$

$$Q_{i,j} + M_2 \xrightarrow{k_{trM122}} \Theta_{i,j} + S_{0,1},$$

$$R_{i,j} + M_1 \xrightarrow{k_{trM211}} \Theta_{i,j} + P_{1,0},$$

$$R_{i,j} + M_2 \xrightarrow{k_{trM212}} \Theta_{i,j} + S_{0,1},$$

$$S_{i,j} + M_1 \xrightarrow{k_{trM221}} \Theta_{i,j} + P_{1,0},$$

$$S_{i,j} + M_2 \xrightarrow{k_{trM222}} \Theta_{i,j} + S_{0,1}.$$

$$(3)$$

Step 4. Termination by disproportionation

$$P_{i,j} + P_{m,n} \xrightarrow{k_{TD11}} \Theta_{i,j} + \Theta_{m,n},$$

$$P_{i,j} + Q_{m,n} \xrightarrow{k_{TD12}} \Theta_{i,j} + \Theta_{m,n},$$

$$P_{i,j} + R_{m,n} \xrightarrow{k_{TD13}} \Theta_{i,j} + \Theta_{m,n},$$

$$P_{i,j} + S_{m,n} \xrightarrow{k_{TD14}} \Theta_{i,j} + \Theta_{m,n},$$

$$Q_{i,j} + Q_{m,n} \xrightarrow{k_{TD22}} \Theta_{i,j} + \Theta_{m,n},$$

$$Q_{i,j} + R_{m,n} \xrightarrow{k_{TD23}} \Theta_{i,j} + \Theta_{m,n},$$

$$Q_{i,j} + S_{m,n} \xrightarrow{k_{TD24}} \Theta_{i,j} + \Theta_{m,n},$$

$$R_{i,j} + R_{m,n} \xrightarrow{k_{TD33}} \Theta_{i,j} + \Theta_{m,n},$$

$$R_{i,j} + S_{m,n} \xrightarrow{k_{TD34}} \Theta_{i,j} + \Theta_{m,n},$$

$$S_{i,j} + S_{m,n} \xrightarrow{k_{TD44}} \Theta_{i,j} + \Theta_{m,n}.$$

$$(4)$$

Step 5. Termination by combination

$$P_{i,j} + P_{m,n} \xrightarrow{k_{TC11}} \Theta_{i+m,j+n},$$

$$P_{i,j} + Q_{m,n} \xrightarrow{k_{TC12}} \Theta_{i+m,j+n},$$

$$P_{i,j} + R_{m,n} \xrightarrow{k_{TC13}} \Theta_{i+m,j+n},$$

$$P_{i,j} + S_{m,n} \xrightarrow{k_{TC14}} \Theta_{i+m,j+n},$$

$$Q_{i,j} + Q_{m,n} \xrightarrow{k_{TC22}} \Theta_{i+m,j+n},$$

$$Q_{i,j} + R_{m,n} \xrightarrow{k_{TC23}} \Theta_{i+m,j+n},$$

$$Q_{i,j} + S_{m,n} \xrightarrow{k_{TC24}} \Theta_{i+m,j+n},$$

$$R_{i,j} + R_{m,n} \xrightarrow{k_{TC33}} \Theta_{i+m,j+n},$$

$$R_{i,j} + S_{m,n} \xrightarrow{k_{TC34}} \Theta_{i+m,j+n},$$

$$S_{i,j} + S_{m,n} \xrightarrow{k_{TC44}} \Theta_{i+m,j+n},$$

$$P = \sum_{i=1}^{\infty} \sum_{j=0}^{\infty} P_{i,j},$$

$$Q = \sum_{i=0}^{\infty} \sum_{j=1}^{\infty} Q_{i,j},$$

$$R = \sum_{i=1}^{\infty} \sum_{j=0}^{\infty} R_{i,j},$$

$$S = \sum_{i=0}^{\infty} \sum_{j=1}^{\infty} S_{i,j},$$

$$(5)$$
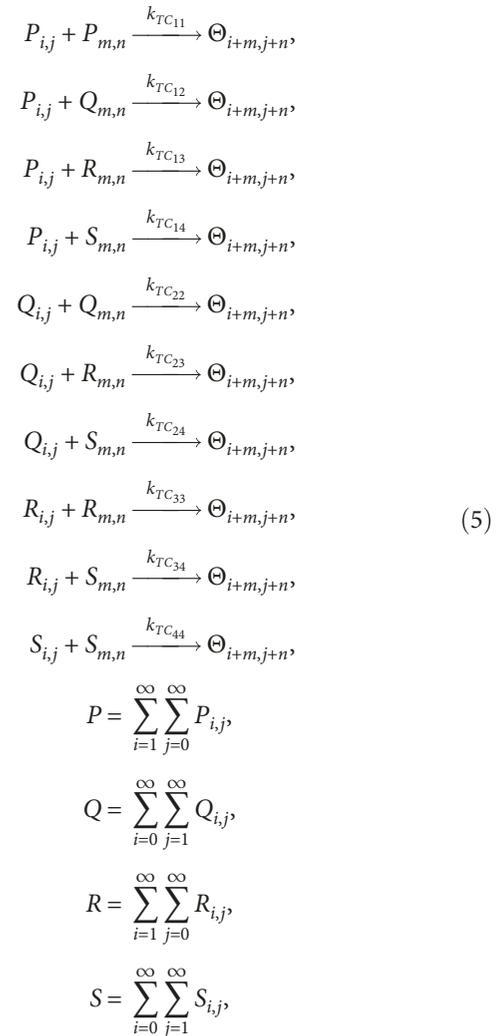
where I is the concentration of the initiator; k_D is the kinetic constant for initiator decomposition; Z is the concentration of free radical of the initiator; M_i is the concentration of monomer i; k_i is the kinetic constant for the formation of the first polymeric radical i; $P_{1,0}$ is the first polymeric radical containing 1 mer of species 1; $Q_{0,1}$ is the first polymeric radical containing 1 mer of species 2; $k_{P_{ijl}}$ is the kinetic constant for the propagation of polymeric radical containing the monomeric units i (penultimate) and j (terminal) with monomer unit l; $P_{i,j}$ is the growing polymeric chain containing the meric units i and j and species 1 at the active site (polymeric radical 1—$[P] = \sim M_1 M_1 \cdot$); $Q_{i,j}$ is the growing polymeric chain containing the meric units i and j and species 2 at the active site (polymer radical 2—$[Q] = \sim M_1 M_2 \cdot$); $R_{i,j}$ is the growing polymeric chain containing the meric units i and j and species 1 at the active site ($[R] = \sim M_2 M_1 \cdot$); $S_{i,j}$ is the growing polymeric chain containing the meric units i and j and species 2 at the active site ($[S] = \sim M_2 M_2 \cdot$); $\Theta_{i,j}$ is the dead polymer chain containing mer units i and j; $k_{trM_{ijl}}$ is the kinetic constant of transfer of

polymeric radical containing the monomeric units i and j to monomer l; $k_{TD_{ij}}$ and $k_{TC_{ij}}$ are the kinetic constants for termination by disproportionation and combination of growing polymeric radicals i and j, respectively; P, Q, R, and S represent the total concentration of growing polymeric radicals; $k_{T_{ij}}$ is the kinetic constant that characterizes the combined contribution of the termination by both disproportionation and combination ($k_{T_{ij}} = k_{TD_{ij}} + k_{TC_{ij}}$); and f is the initiator efficiency.

According to the proposed kinetic mechanism and assuming that the long-chain and *quasi*-steady-state hypotheses are valid for the polymer radicals and admitting that the propagation terms are much larger than the initiation, chain transfer, and termination terms, it is possible to write the following set of mass balance equations for the copolymerization process:

$$\frac{dI}{dt} = -k_D I,$$

$$\frac{dM_1}{dt} = -\left(k_{P_{111}}P\right)\left[1 + \Omega\left(\frac{1}{r_{11}} + \frac{r_{12}}{r_{11}}\frac{M_2}{M_1}\right) + \frac{M_2}{r_{11}M_1}\right]M_1,$$

$$\frac{dM_2}{dt} = -\left(k_{P_{111}}P\right)\left[\frac{1}{r_{11}} + \Omega\left(\frac{r_{12}}{r_{11}} + \frac{r_{22}r_{12}}{r_{11}}\frac{M_2}{M_1}\right) + \frac{M_2}{r_{21}r_{11}M_1}\right]M_2,$$

$$\frac{d\wp_1}{dt} = \left(k_{P_{111}}P\right)\left[1 + \Omega\left(\frac{1}{r_{11}} + \frac{r_{12}}{r_{11}}\frac{M_2}{M_1}\right) + \frac{M_2}{r_{11}M_1}\right]M_1,$$

$$\frac{d\wp_2}{dt} = \left(k_{P_{111}}P\right)\left[\frac{1}{r_{11}} + \Omega\left(\frac{r_{12}}{r_{11}} + \frac{r_{22}r_{12}}{r_{11}}\frac{M_2}{M_1}\right) + \frac{M_2}{r_{21}r_{11}M_1}\right]M_2,$$

$$(6)$$

where

$$\Omega = \left(\frac{M_2 + (1/r_{21})\left(M_2^2/M_1\right)}{M_1 + r_{12}M_2}\right),$$

$$r_{ii} = \frac{k_{P_{iii}}}{k_{P_{iij}}}, r_{ij} = \frac{k_{P_{ijj}}}{k_{P_{iji}}}, s_i = \frac{k_{P_{jii}}}{k_{P_{iii}}}, i = 1, 2(i \neq j),$$

$$\left(k_{P_{111}}P\right) = \left\{2fk_D I\left[\frac{1}{\psi_{11}} + \frac{1}{\psi_{22}}\left(\Omega\frac{r_{12}}{s_2 r_{11}}\right)^2 + \frac{1}{\psi_{33}}\left(\frac{M_2}{s_1 r_{11}M_1}\right)^2\right.\right.$$

$$+ \frac{1}{\psi_{44}}\left(\Omega\frac{r_{12}r_{22}M_2}{r_{11}M_1}\right)^2 + \frac{2\Omega\zeta_{12}}{\sqrt{\psi_{11}\psi_{22}}}\frac{r_{12}}{s_2 r_{11}}$$

$$+ \frac{2\zeta_{13}}{\sqrt{\psi_{11}\psi_{33}}}\frac{M_2}{s_1 r_{11}M_1} + \frac{2\Omega\zeta_{14}}{\sqrt{\psi_{11}\psi_{44}}}\frac{r_{12}r_{22}M_2}{r_{11}M_1}$$

$$+ \frac{2\Omega\zeta_{23}}{\sqrt{\psi_{22}\psi_{33}}}\frac{r_{12}M_2}{s_1 s_2 r_{11}^2 M_1} + \frac{2\Omega^2\zeta_{24}}{\sqrt{\psi_{22}\psi_{44}}}\frac{r_{12}^2 r_{22}M_2}{s_2 r_{11}^2 M_1}$$

$$\left.\left.+ \frac{2\Omega\zeta_{34}}{\sqrt{\psi_{33}\psi_{44}}}\frac{r_{12}r_{22}}{s_1 r_{11}^2}\left(\frac{M_2}{M_1}\right)^2\right]^{-1}\right\}^{1/2},$$

$$\zeta_{ij} = \frac{k_{T_{ij}}}{\sqrt{k_{T_{ii}}k_{T_{jj}}}}, \quad i = 1, 2, j = 2, 4(i \neq j),$$

$$\psi_{ii} = \frac{k_{P_{iii}}^2}{k_{T_{ii}}}, \quad i = 1, 2(i \neq j),$$

$$\psi_{jj} = \frac{k_{P_{iii}}^2}{k_{T_{jj}}}, \quad i = 1, 2, j = 3, 4,$$

$$(7)$$

where r_{ij} is the reactivity ratio monomers i and j, s_i is the radical reactivity ratios for growing polymer chain i, ζ_{ij} is the cross-termination constant between polymer radicals i and j, and $\wp_i$ is the moles of monomer i incorporated into polymer chains.

3. Results and Discussion

3.1. Styrene/Methyl Methacrylate Copolymerization. Figure 1 shows the simulation result for the styrene (S)/methyl methacrylate (MMA) system, which is considered a typical polymerization where the penultimate effect has to be taken into account. All model parameters (see equations (6) and (7) and Table 1) used for simulations were obtained from Schmidt and Ray [38], Kalfas et al. [39], and Burke et al. [34], and the reader is referred to these works for more detailed information. Copolymerization model equations were implemented in FORTRAN and solved numerically with the integration package DDASSL [40]. A maximum reaction conversion of approximately 92% at the end of the reaction with a molar fraction of styrene in the copolymer equal to 17%, which is kept almost constant along the reaction time (Figure 1(b)) and reaction conversion (Figure 1(a)), is observed.

It is generally agreed that viscosity effects play a fundamental role in free-radical polymerization reactions, leading to strong diffusion limitations in the reaction medium. This particular and relevant nonlinear kinetic phenomenon is characterized by the glass and gel effects.

Additionally, for simulations of polymerization systems where glass and gel effects play a significant role, it is very important to consider correlations adopted to correct the propagation $[k_{P_{iii}}^{fv} = k_{P_{iii}}g_{P_i}(T)]$ and termination $[k_{T_{iii}}^{fv} = k_{T_{iii}}g_{T_i}(T)]$ constant deviations due to the diffusion limitations of both the monomer and growth polymer chain species. In this scenario, correlations based on the free volume theory are of fundamental importance [41].

It is widely adopted that the free volume of the polymerization system (v_f) can be expressed as the sum of the individual contribution of each species (v_{f_i}), as follows [38]:

$$v_f = \sum_i v_{f_i}\phi_i. \quad (8)$$

(a)

(b)
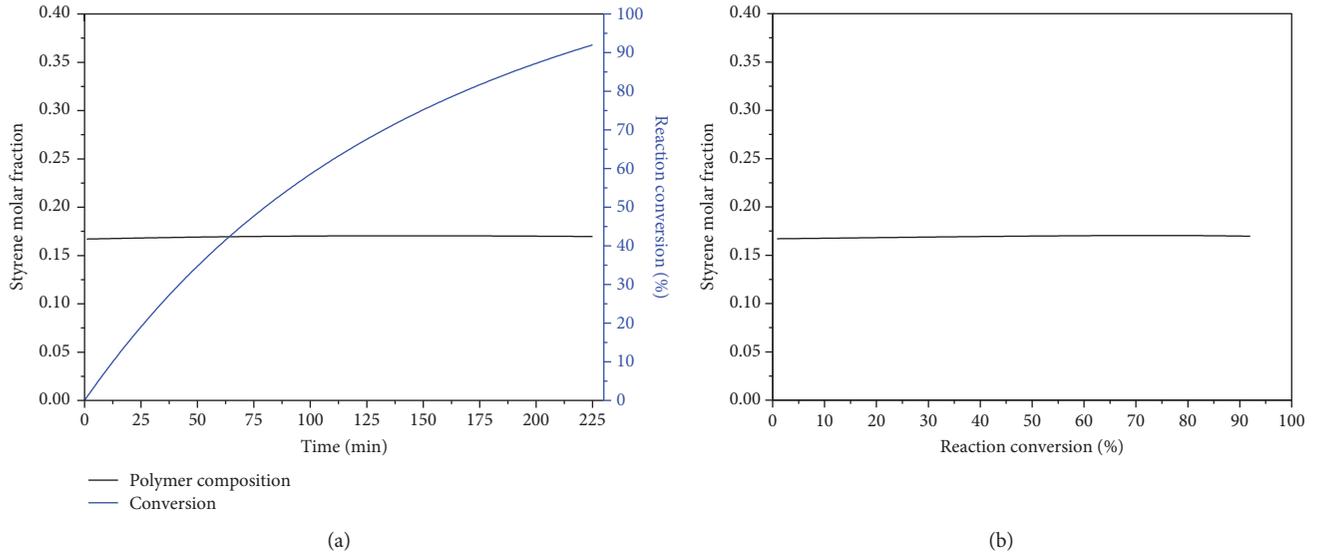
Figure 1: Conversion and copolymer composition profiles. $I = 0.17$ mol, $M_1 = 1.54$ mol, $M_2 = 5.00$ mol, $T = 85°$C, $r_{11} = 0.472$, $r_{12} = 0.454$, $r_{21} = 0.472$, $r_{22} = 0.454$, $s_1 = 0.412$, and $s_2 = 0.170$ [34].

Table 1: Model parameters used for simulation of styrene/methyl methacrylate system.

Parameter	Unit	Reference
$\rho_1 = 0.9193 - 6.65 \cdot 10^{-4}(T - 273.15)$	g/cm^3	[39]
$\rho_2 = 0.9654 - 1.09 \cdot 10^{-3}(T - 273.15) - 0.970 \cdot 10^{-6}(T - 273.15)^2$	g/cm^3	[39]
$\rho_3 = 0.9926 - 2.65 \cdot 10^{-4}(T - 273.15)$	g/cm^3	[39]
$\rho_4 = 1.18 - 0.10 \cdot 10^{-2}(T - 273.15)$	g/cm^3	[39]
$k_{P_{111}} = 1.090 \times 10^7 \exp(-7051/RT)$	L/(mol·s)	[34]
$k_{T_{111}} = 1.703 \times 10^9 \exp(-2268/RT)$	L/(mol·s)	[34]
$k_{P_{222}} = 5.366 \times 10^5 \exp(-4353/RT)$	L/(mol·s)	[34]
$k_{T_{222}} = 9.800 \times 10^7 \exp(-701/RT)$	L/(mol·s)	[34]
$k_D = 1.7 \times 10^{14} \exp(-30000/RT)$	s^{-1}	[39]
$f = 0.80$	—	[48]

Subscript 1 for styrene and 2 for methyl methacrylate; subscripts 3 and 4 for the homopolymers based on styrene and methyl methacrylate, respectively.

The free volume contribution of methyl methacrylate ($v_{f_{\text{MMA}}}$) and its homopolymer ($v_{f_{\text{PMMA}}}$) is proposed by Schmidt and Ray [38] in the following form:

$$v_{f_{\text{MMA}}} = 0.025 + 0.0010\,(T - 167.15),$$

$$v_{f_{\text{PMMA}}} = 0.025 + 0.00048\,(T - 387.15),$$

$$\phi_i = \frac{\rho_i/m_i}{\sum_i \rho_i/m_i}, \tag{9}$$

where ρ_i is the pure density of species i and m_i is the mass of species i. It is also assumed that $g_{T_{\text{MMA}}}(T)$ can be expressed as [38, 39, 42]

$$g_{T_{\text{MMA}}}(T) = \begin{cases} 0.10575 \exp\left[17.15 v_f - 0.01715(T - 273.15)\right], & \text{for } v_f > v_{f_c}^T, \\ 2.3 \cdot 10^{-6} \exp\left(75 v_f\right), & \text{for } v_f \leq v_{f_c}^T, \end{cases} \tag{10}$$

(a)

(b)
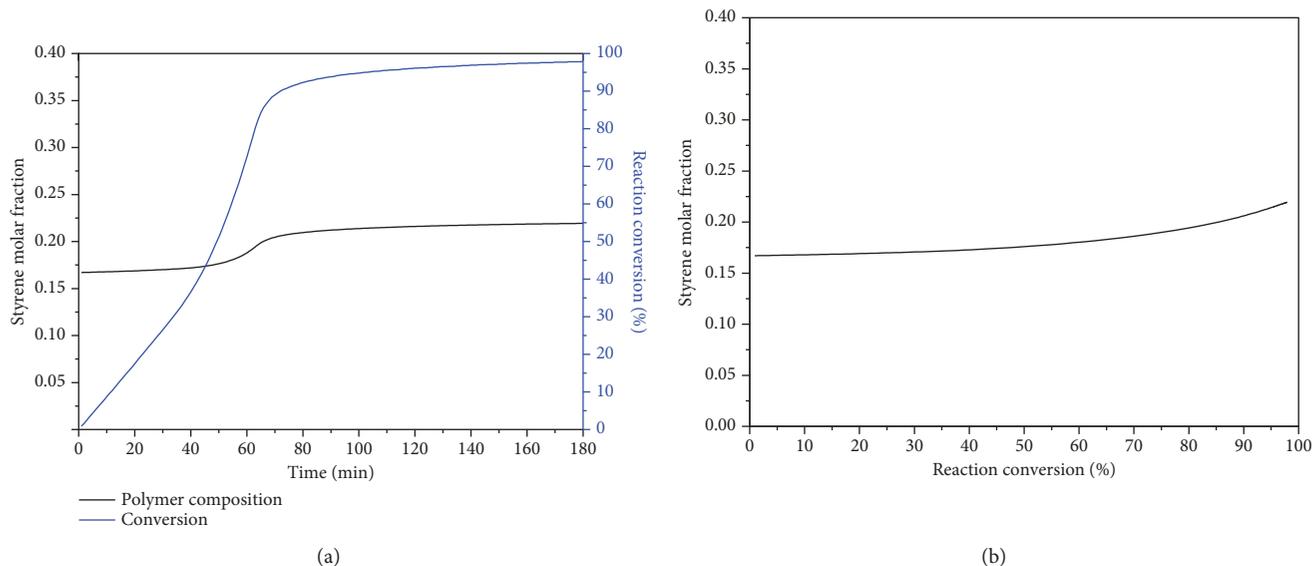
FIGURE 2: Conversion and composition profiles: gel and glass effects. $I = 0.17$ mol, $M_1 = 1.54$ mol, $M_2 = 5.00$ mol, $T = 85°C$, $r_{11} = 0.472$, $r_{12} = 0.454$, $r_{21} = 0.472$, $r_{22} = 0.454$, $s_1 = 0.412$, and $s_2 = 0.170$ [34].

where the critical free volume for termination is given by

$$v_{f_c}^T = 0.1856 - 0.2965 \cdot 10^{-3}(T - 273.15). \qquad (11)$$

In order to correct the propagation constant, $g_{P_{MMA}}(T)$ is expressed in the following form [38, 39, 42]:

$$g_{P_{MMA}}(T) = \begin{cases} 1, & \text{for } v_f > 0.05, \\ 7.1 \cdot 10^{-5} \exp\left(171.53 v_f\right), & \text{for } v_f \leq 0.05. \end{cases} \qquad (12)$$

For the styrene species, the gel effect correlation is expressed as a function of the styrene conversion (x_S), as follows [39]:

$$g_{T_S}(T) = \exp\left(-0.4404 x_S - 6.362 x_S^2 - 0.1704 x_S^3\right),$$
$$g_{P_S}(T) = 1.0. \qquad (13)$$

Figure 2 illustrates the simulation results for the S/MMA system. The copolymerization behavior is strongly affected when glass and gel effects are considered, exhibiting autoacceleration of the polymerization and copolymer composition drift. According to Figure 2(a), a maximum conversion limit equal to 98% is achieved and the molar fraction of styrene in the copolymer is lying in the interval from 17% to 22%. It is also observed that the copolymer composition slightly changes at the beginning of the reaction when the conversion is below 40% and the viscosity effects are not pronounced.

Figure 3 illustrates the effect of the reaction temperature and the initiator concentration on the global conversion behavior. According to Figure 3(a) the conversion is significantly affected by the temperature, exhibiting a strong gel effect as the medium temperature is increased from 70°C to 90°C. Simulations presented in Figure 3(b) were performed at 80°C and show that the global conversion is slightly affected by the initiator (benzoyl peroxide (BPO)) concentration, lying in the range from 85% to 91% when the BPO concentration is increased from 0.10 mol to 0.2 mol.

Figure 4 illustrates the ability of the penultimate model to predict the experimental data of the bulk copolymerization of styrene and methyl methacrylate as provided by Jalili et al. [43]. According to Figure 4, the reaction conversion profile is satisfactory predicted by the penultimate model, which is able to represent typical monomer mass-transfer limitation that is responsible for a strong nonlinear kinetic behavior closely related to gel and glass effects.

3.2. Vinyl Acetate/Acrylic Acid Copolymerization. The effect of the penultimate monomeric unit of the growing polymer chains might also be important in vinyl acetate (VAc)/acrylic acid (AA) copolymerizations performed in dispersed medium such as suspension polymerization process. In a series of articles, Silva and coworkers [44–46] evaluated the suspension copolymerization of VAc/AA. According to the authors, the role of the penultimate effect in the kinetic mechanism of VAc/AA must be considered.

In order to evaluate the ability of equations (6) and (7) to predict the kinetic behavior of VAc/AA, copolymerization is fundamental to describe the partition of AA between the organic phase and the aqueous phase. For this reason, the AA partition coefficient must be included into the copolymerization model to determine the AA concentration throughout the reaction. Equations (14) and (15) represent the solubility of AA in water. It is very important to keep in mind that the amount of AA available for polymerization inside the organic droplets (dispersed into the aqueous phase) is different from the total amount of monomer added into the reactor ($M_2 = M_2^{aqueous} + M_2^{organic}$). The amounts of

(a)

(b)
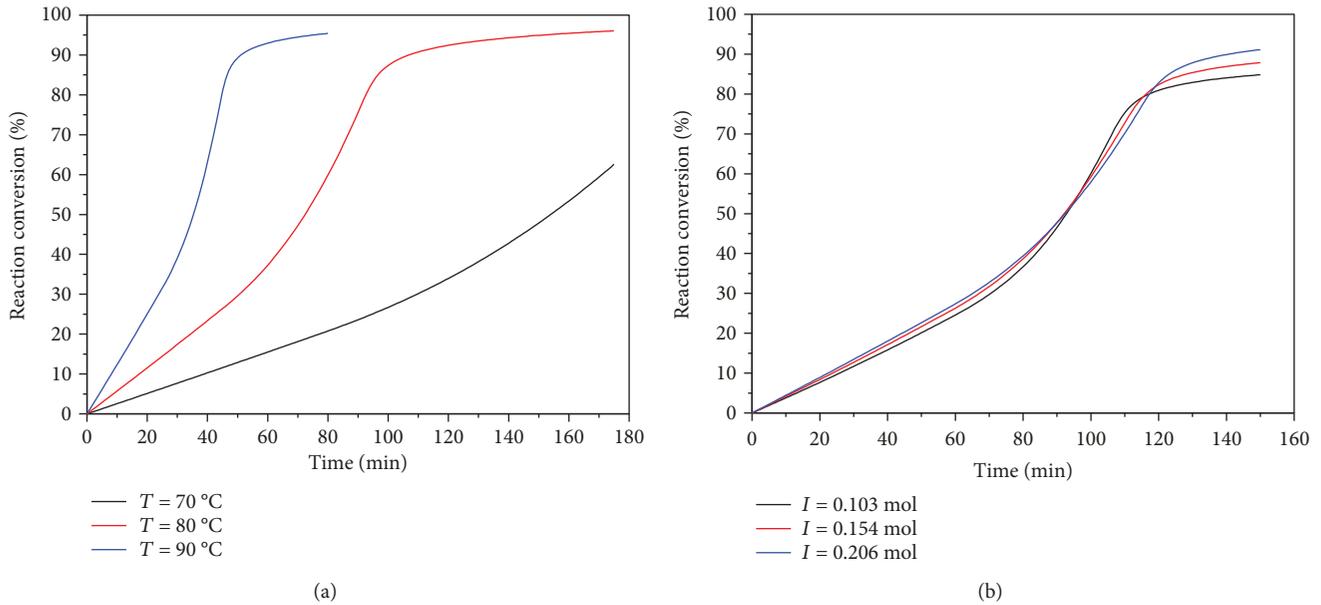
Figure 3: Effect of (a) temperature and (b) initiator concentration on the conversion profiles. $M_1 = 2.4$ mol, $M_2 = 9.25$ mol, $T = 80°$C, $r_{11} = 0.472$, $r_{12} = 0.454$, $r_{21} = 0.472$, $r_{22} = 0.454$, $s_1 = 0.412$, and $s_2 = 0.170$ [34].

AA in the organic ($M_2{}^{\text{organic}}$) and aqueous ($M_2{}^{\text{aqueous}}$) phases is given as follows [46]:

$$M_2{}^{\text{organic}} = \frac{M_2}{1 + K},$$
$$M_2{}^{\text{aqueous}} = \frac{K}{1 + K}M_2, \tag{14}$$

where

$$K = \alpha\frac{V^{\text{aqueous}}}{V^{\text{organic}}}, \tag{15}$$

where V^{organic} is the volume of the organic phase and V^{aqueous} corresponds to the volume of the aqueous phase.

The partition coefficient of AA considering the system in the system AA/VAc/water is represented as a function of both the aqueous AA composition and temperature in the following form [46]:

$$\alpha\left(T, [M_2]^{II}\right) = \left[A + B[M_2]^{II} + \frac{C}{\left([M_2]^{II}\right)^2}\right]^{-1}, \tag{16}$$

where coefficients A, B, and C are temperature-dependent adjustable parameters, expressed as follows [46]:

$$A = -16.67 + 0.455(T - 273.15) - 2.92 \cdot 10^{-3}(T - 273.15)^2,$$
$$B = 23.02 - 0.594(T - 273.15) + 3.96 \cdot 10^{-3}(T - 273.15)^2,$$
$$C = 0.317 - 9.02 \cdot 10^{-3}(T - 273.15) + 6.04 \cdot 10^{-5}(T - 273.15)^2. \tag{17}$$
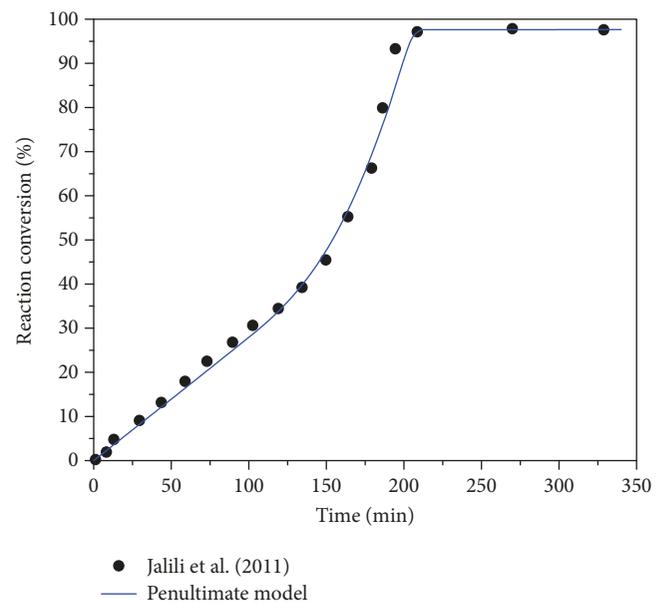
Figure 4: Penultimate model prediction of the styrene/methyl methacrylate bulk copolymerization carried out with BPO [43].

Table 2 presents the model parameters, and Figure 5 shows the prediction of the penultimate model (equations (6) and (7)) in comparison to experimental data provided by Silva et al. [45]. As depicted in Figure 5, the proposed model is able to describe experimental data of conversion and AA composition. Figure 6 illustrates the effect of the initiator amount on the kinetic behavior, when BPO inside the organic phase was varied from 0.004 mol to 0.021 mol. The copolymerization conversion is significantly affected by the BPO concentration. According to simulation results, this

TABLE 2: Model parameters used for simulation of vinyl acetate/acrylic acid system.

Parameter	Unit	Reference
$\rho_1 = 0.9584 - 1.3276 \cdot 10^{-3}(T - 273.15)$	g/cm^3	[48]
$\rho_2 = 1.0821 - 1.1969 \cdot 10^{-3}(T - 273.15)$	g/cm^3	[45]
$\rho_3 = 1.211 - 8.496 \cdot 10^{-4}(T - 273.15)$	g/cm^3	[48]
$\rho_4 = 1.22$	g/cm^3	[49]
$\rho_w = 1.00066 - 7.35 \cdot 10^{-5}(T - 273.15) - 3.5 \cdot 10^{-6}(T - 273.15)$	g/cm^3	[50]
$k_{P_{11}} = 3.2 \times 10^7 \exp(-6300/RT)$	L/(mol·s)	[48]
$k_{T_{11}} = 3.7 \times 10^9 \exp(-3200/RT)$	L/(mol·s)	[48]
$k_{P_{22}} = 8.4 \cdot 10^2$	L/(mol·s)	In this work
$k_{T_{22}} = 3.2 \cdot 10^7$	L/(mol·s)	In this work
$k_D = 1.7 \times 10^{14} \exp(-30000/RT)$	s^{-1}	[51]
$f = 0.8$	—	[48]

Subscript 1 is reserved for vinyl acetate, and subscript 2 is for acrylic acid. Subscripts 3 and 4 for the homopolymers based on vinyl acetate and acrylic acid, respectively.
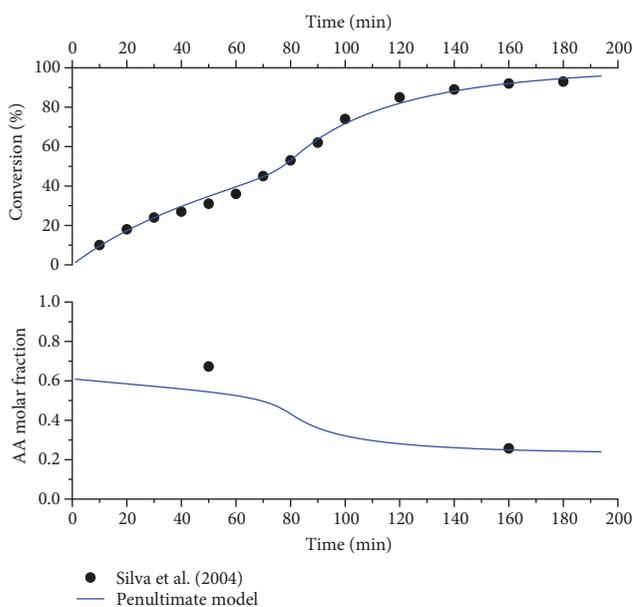
FIGURE 5: Penultimate model prediction for the vinyl acetate/acrylic acid copolymerization. $M_1 = 1.67$ mol, $M_2 = 0.50$ mol, $T = 70°$C, $r_{11} = 0.054$, $r_{12} = 2.927$, $r_{21} = 0.032$, $r_{22} = 1.902$, $s_1 = 0.412$, and $s_2 = 1.0$ [52].

FIGURE 6: Effect of the initiator amount on the conversion and composition profiles. $M_1 = 1.67$ mol, $M_2 = 0.50$ mol, $T = 70°$C, $r_{11} = 0.054$, $r_{12} = 2.927$, $r_{21} = 0.032$, $r_{22} = 1.902$, $s_1 = 0.412$, and $s_2 = 1.0$ [52].

kind of reaction is characterized by presenting an autoacceleration of the polymerization and significant drift of copolymer composition.

The synthesis of copolymer materials presenting homogeneous chemical composition throughout the reaction may be regarded as an important challenge in the polymerization field mainly when the copolymerization is carried out with from monomers that present very different reactivities. In order to avoid composition drift control, composition strategies should be implemented. In the particular case of VAc/AA copolymerization because of the complete solubility

of AA in the aqueous phase (AA is partitioned between the organic and the aqueous phases during the reaction course), semibatch operation mode can be successfully performed, as the aqueous phase can be used as a reservoir, supplying AA for the organic phase.

Based on the previous assumptions, semibatch copolymerization can be performed to keep the copolymer composition constant at the desired setpoint ($y_{AA}{}^d$) value throughout reaction through manipulation of the feed flow rate of AA (F_{AA}). AA feed rate profiles required to maintain AA molar fraction constant into the copolymer chains were
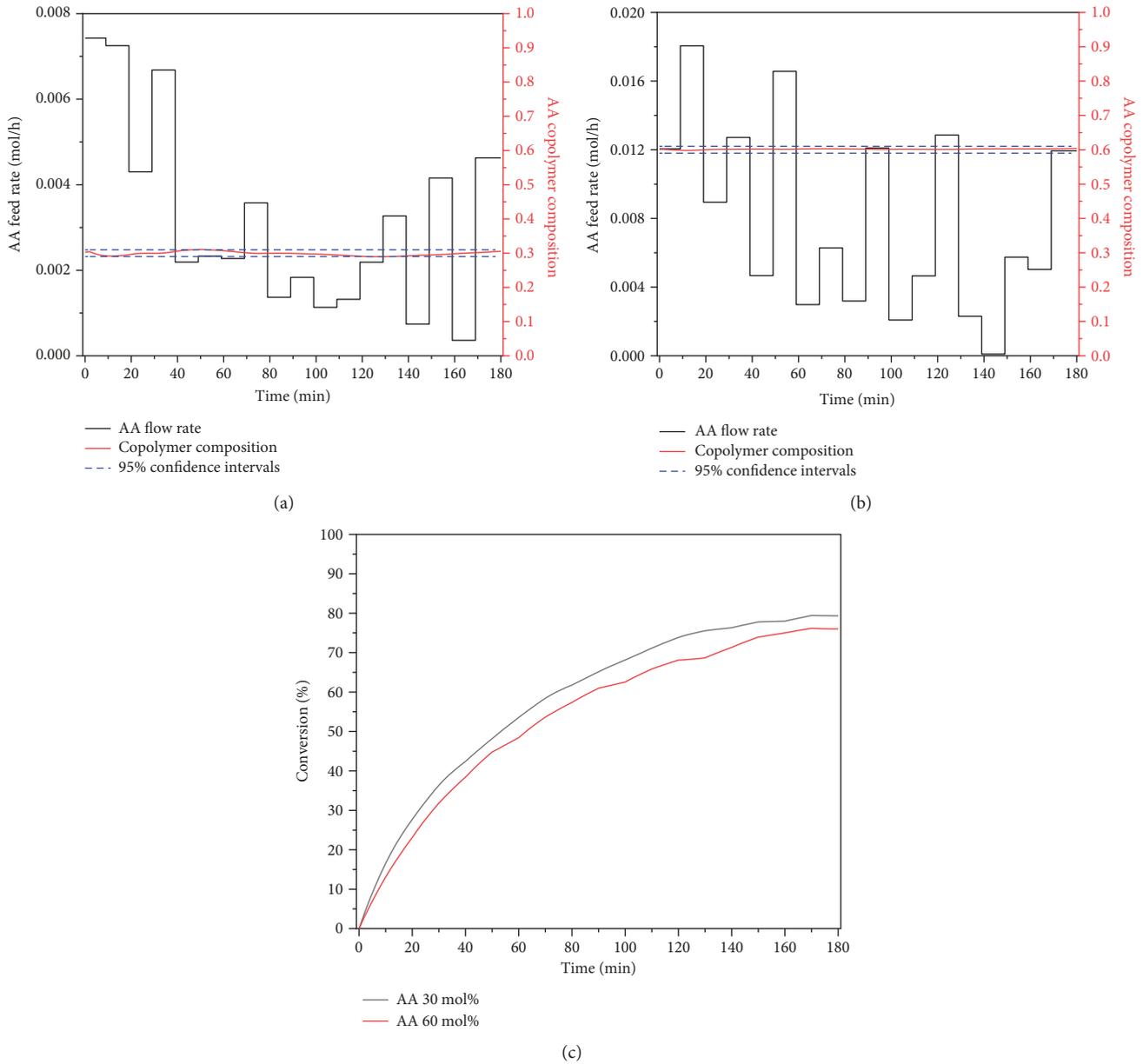
FIGURE 7: Dynamic behavior of vinyl acetate/acrylic acid suspension copolymerizations in semibatch operation mode. AA feed flow rate and AA copolymer composition profile for y_{AA} = 30 mol% (a) and y_{AA} = 60 mol% (b) and conversion profiles (c).

determined for discretized time intervals of 10 minutes. The optimization problem can be defined as follows:

$$\min_{\underline{F_{AA}}} \quad f = \sum_{i=1}^{ND} \left(y_i - y_i^d\right)^2,$$

$$\text{subject to} \quad l_i \le x_i \le u_i, \quad i = 1, 2, \ldots, m, \tag{18}$$

where y_i corresponds to the cumulative copolymer composition at each discretized sampling time i, y_i^d is the desired copolymer composition at each discretized sampling time i, ND is the number of discretized sampling times in the control window of 10 minutes, x_i is the manipulated variable at each discretized sampling time i, f is the objective function

that must be minimized, u_i is the upper limit of the constraints, and l_i is the lower limit of the constraints.

AA feed rate profiles were estimated based on stochastic optimization procedures with the Monte Carlo method [47]. Optimum candidates were estimated by generating random numbers in the following form:

$$x_{i,j} = x_{i,j-1} + r_{i,j}\,\Delta_{i,j}, \quad i = 1, \ldots, ND, j = 1, \ldots, NITER, \tag{19}$$

where $r_{i,j}$ are pseudorandom numbers uniformly distributed in the interval (-1,1) and $\Delta_{i,j}$ defines a search interval for variable i at iteration j. Dynamic trajectories of conversion and copolymer composition were computed after the generation

of the candidate optimum solutions at iteration j, and the objective function was minimized.

Figure 7 shows the optimum AA feed rate profiles generated to keep the AA copolymer composition equal to 30 mol% and 60 mol% as well as global conversions predicted by the penultimate polymerization model. According to Figures 6(a) and 6(b), copolymers with homogeneous chemical composition at the desired setpoint values are easily obtained based on the proposed optimization procedure. The copolymer composition is kept within the upper control (UCL) and lower control (LCL) limits considering a 95% confidence interval and standard deviation equal to 1% related to the setpoint value of the AA molar fraction. It is important to note that because of the high consumption rates of the AA, the conversion trajectories are not affected by fluctuation of the AA feed operation, as shown in Figure 7(c).

4. Conclusion

A kinetic model of free-radical copolymerization of styrene and methyl methacrylate was proposed, taking into account the penultimate unit effect. It was shown that the addition copolymerization reactions can be properly simulated by using the proposed penultimate polymerization model, being suitable to evaluate strong nonlinear behavior that takes place due to the presence of viscosity effects related to important kinetic phenomena such as autoacceleration of the polymerization, copolymer composition drift, diffusion, and heat-transfer limitations. Copolymer with homogeneous composition along the whole polymerization time can be successfully obtained through manipulation of the AA feed flow rate based on stochastic optimization procedures.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The author declares no conflict of interest.

Acknowledgments

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