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# Kinetics modeling of microemulsion copolymerization

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## Summary

A mathematical model for microemulsion copolymerization systems has been developed and compared with experimental conversion vs. time data for the vinyl acetate/butyl acrylate system. The main features of the model include micellar and homogeneous nucleation and thermodynamic equilibrium for the calculation of monomer partitioning between the phases. Simulations were made using this model with reported values for the kinetic parameters except for propagation rate constants in the water phase and radical capture by particles and micelles coefficients which were estimated. Simulations using the model showed good agreement with experimental data.

## Introduction

Microemulsion polymerization is a complex heterogeneous process where transport of monomers, free radicals and other species (such as chain transfer agent, co-surfactant and inhibitors) between the aqueous and organic phases, takes place. Compared with other heterogeneous polymerization processes (suspension or emulsion) microemulsion polymerization is a more complicated system. Polymerization rate is controlled by monomer partitioning between the phases, particle nucleation, and adsorption and desorption of radicals [1]. Particle stability is affected by the amount and type of surfactant and pH of dispersing medium.

The kinetics of microemulsion polymerization have much in common with emulsion polymerization kinetics, the most characteristic feature of which is the compartmentalization, where the radicals growing inside the particles are separated from each other, thus suppressing termination to a high extent and, as a consequence, providing high rates of polymerization. Only few works have been devoted to model kinetics of microemulsion copolymerization. Guo *et al.* [2,3] developed a model for polymerization of styrene in microemulsion media with four components. They considered that nucleation occurs in the microemulsion droplets and when these disappear, the nucleation can be continued by entry of a radical from the water phase to the so called *mixed micelles* formed with surfactant, co-surfactant and a small amount of monomer. This model is able to predict the experimental data only at low conversions. Morgan *et al.* [4] have discussed in detail a theoretical model for the

conversion and rate of polymerization of hexyl methacrylate. They assumed that the constants for capture of radicals by particles and micelles have the same value. Moreover, they suppose that all the radicals generated within particles by chain transfer to monomer are desorbed and the radicals remain active during all the reaction. This model predicts very well the experimental conversion and reaction rate data for the microemulsion polymerization of hexyl methacrylate, nevertheless, it does not predict the density in number of particles, or the size of particles and the molecular weight of the polymer. In addition, it predicts that the maximum polymerization rate always occurs at the same conversion value, independently of the monomer used, which is in opposition to what has been experimentally observed [5,6].

Mendizábal *et al.* [7] presented a model that describes conversion, average molecular weight, average particle size, and average number of polymer chains per particle as a function of time. In this model micellar and homogeneous nucleation are taken into account because the great amount of surfactant present in microemulsion polymerization makes possible the stabilization of precipitated oligomers through the reaction. This model predicts experimental data for the microemulsion polymerization of monomers with different water solubility but requires the estimation of parameters such as the propagation rate constants in the water phase as well as the constants of radicals capture by micelles and particles.

If the homopolymerization in microemulsion is considered a complex system, the modelling of microemulsion copolymerization is still more complex. Before 1980, few efforts were made for modelling emulsion copolymerization. Gilbert *et al.* [8] presented an extension of their emulsion homopolymerization model to copolymerization using Hamielec's pseudo-homopolymerization approach. This model neglects micellar nucleation because micelles are considered surfactant reservoirs. The partition of monomers between the phases was solved using empirical partition coefficients. Sanghvi *et al.* [9] used a mathematical method to represent the kinetics data of the microemulsion copolymerization for the styrene/acrylonitrile system. This model does not require the monomer partition calculation between each phase, it uses an overall monomer concentration and has one adjustable parameter. The model proposed by Sanghvi deviates significantly from the experimental data at high conversions.

In this paper a mathematical model for microemulsión copolymerization is presented which has been developed based on the work of Guo *et al.* [2,3] and of Mendizábal *et al.* [7]. Model predictions are compared with experimental work carried out in our laboratory [24] and with data reported by Sanghvi *et al*. [9].


**Experimental**

*Materials*

Vinyl acetate (VAc), butyl acrylate (BuA), sodium dodecyl sulfate (SDS), potassium persulfate (KPS, as initiator), and hydroquinone (HQ) were purchased from Aldrich. Bis (2-ethylhexyl) sodium sulfosuccinate (AOT) was from Fluka. VAc and BuA were dried with $CaCl_2$ and vacuum distilled at 30°C and 50°C, respectively, under reduced pressure and argon atmosphere, stored at 4°C in dark vials, and used within 15 days after distillation. SDS was recrystallized twice from methanol. The HQ and AOT were used as received. The water was deionized (tridistilled grade) and the argon ultra-high purity from Infra.

*Methods*

Polymerizations were carried out at 60°C in a 100 mL glass reactor with magnetic stirring. VAc and BuA total concentrations were 3.25 and 4.25% (w/w) respectively. The microemulsions were stabilized with a 3:1 (w/w) mixture of SDS/AOT and the ratio of surfactants to water was 5/95. KPS concentration was 1.0% with respect to the total monomers content. The mixture of VAc/BuA, 85:15 (w/w), and the micellar solution containing the KPS were degassed exhaustively before polymerization. Conversion was determined gravimetrically.

## Model development

*Physical picture*

The important physical and chemical processes in microemulsion polymerization include radical generation, chain propagation and termination in the aqueous phase. The following events can also occur in the water phase: radical capture by swollen monomer micelles and particles, and radical desorption from the polymer particles. There are two main mechanisms of particle nucleation: micellar and homogeneous. If a micelle captures a radical, this becomes an active particle (micellar nucleation). Hansen and Ugelstad in 1978 [10] stated that particles could be generated by oligomeric radicals precipitated in the water phase which are stabilized by surfactant molecules (homogeneous particle nucleation). A kinetic mechanism similar to the one presented by Mendizábal *et al.* [7] which considers both micellar and homogeneous nucleation was used for the mathematical model.

The model consists of a system of differential and algebraic equations based on mass and population balances. The following assumptions are made:

- i. The reactor is perfectly mixed.
- ii. Polymer particles contain only one radical (zero-one kinetics).
- iii. The particles are generated by micellar and homogeneous nucleation.
- iv. Monomer is in thermodynamic equilibrium in each phase.
- v. The non-initiated microemulsion droplets serve as monomer reservoirs.
- vi. The critical number of monomer units for precipitation of an oligomeric radical is independent of its composition.
- vii. Terminal kinetics model (Mayo-Lewis) is valid.

Balance equations of the model subjected to these assumptions are as follows.

*Micellar nucleation*

In micellar nucleation, a radical from the aqueous phase is captured by a microemulsion droplet to produce an active particle then the rate of micellar nucleation can be mathematically represented by:

$$\frac{dN_m}{dt} = \rho_m N_d = \left( k_{cmA} \sum_n^c P_{nA} + k_{cmB} \sum_n^c P_{nB} \right) N_d \tag{1}$$

where $t$ is the time, $N_m$ is the number of particles generated by micellar nucleation, $\rho_m$ is the first-order entry rate coefficient into microemulsion droplets, $N_d$ is the number

of microemulsion droplets, $P_{nA}$ and $P_{nB}$ are the total concentration of radicals type $A$ and $B$ in the water phase, and $k_{cmA}$ and $k_{cmB}$ are entry rate coefficients of radicals type $A$ and $B$ into microemulsion droplets respectively. Radicals type $A$ and $B$ are defined as the growing chains where the radical is $A$ or $B$.

*Homogeneous nucleation*

In this process, a particle is formed by the precipitation of a radical of larger size than the critical, $P_{c+1}$, and its rate of formation is given by:

$$\frac{dN_H}{dt} = \left( k_{pwAA}\ P_{cA}M_{Aw} + k_{pwAB}\ P_{cA}M_{Bw} + k_{pwBA}\ P_{cB}M_{Aw} + k_{pwBB}\ P_{cB}M_{Bw} \right) N_{AV}$$

$$= \left[\ P_{cA}(k_{pwAA}M_{Aw} + k_{pwAB}M_{Bw}) + P_{cB}(k_{pwBA}M_{Aw} + k_{pwBB}M_{Bw}) N_{AV} \right. \quad \textbf{(2)}$$

where $N_H$ is the number of particles generated by homogeneous nucleation, $N_{AV}$ is Avogadro's number, and $k_{pwAA}$ and $k_{pwAB}$ are the propagation constants in the aqueous phase for radicals terminated in monomer A which reacts with monomer $A$ and $B$, respectively. $k_{pwBA}$ and $k_{pwBB}$ are the radicals propagation constants in the aqueous phase type $B$ that reacts with monomer $A$ and $B$, respectively. $M_{Aw}$ and $M_{Bw}$ are concentrations of monomers $A$ and $B$ in the water phase, respectively. The total rate of formation of polymer particles, $N$, is given by $dN/dt = dN_m/dt + dN_H/dt$ .

For a zero-one kinetics, the particle population balance for particles containing one radical is:

$$\frac{dN_1}{dt} = -(k_{dA} + k_{dB})N_1 + (N_0 - N_1)(k_{cpA}P_A + k_{cpB}P_B) + \frac{dN_H}{dt} + \frac{dN_m}{dt} \quad \textbf{(3)}$$

Where $N_1$ and $N_0$ are the number of particles containing one and zero chains in propagation ($N = N_1 + N_0$), respectively, $k_{dA}$ and $k_{dB}$ are desorption rate coefficients of radicals type $A$ and $B$ from active particles, respectively, and $k_{cpA}$ and $k_{cpB}$ are entry rate coefficients of radicals type $A$ and $B$ into polymer particles, respectively.

*Mass balance for radicals in water phase*

The mass balance for radicals containing one monomer unit in the water phase is given by:

$$\frac{dP_{1i}}{dt} = \left(2fk_I I\right) + \left(k_{di}\frac{N_1}{N_{AV}}\right) - \left(\frac{k_{cmi}N_d + k_{cpi}N}{N_{AV}}\right)P_{1i} - \left(k_{pwii}M_{iw} + k_{pwij}M_{jw}\right)P_{1i}$$

$$-2k_{twii}P_{1i}P_i - k_{twij}P_{1i}P_j \quad \textbf{(4)}$$

where $P_i = \sum_{n=1}^{c} P_{ni}$ , $I$ is the initiator concentration, $k_I$ is the rate coefficient of initiator decomposition, $f$ is the initiator efficiency, and $k_{twii}$ and $k_{twij}$ are the radicals termination constants in water phase type $i$ that reacts with monomer $i$ and $j$, respectively.

Mass balance for radicals containing $n$ monomer units in the water phase is given by

$$\frac{dP_{ni}}{dt} = \left(k_{pwii}M_{iw}P_{n-1i} + k_{pwji}M_{iw}P_{n-1j}\right) - \left(k_{cmi}N_d + k_{cpi}N\right)\frac{P_{nj}}{N_{AV}}$$

$$- \left(k_{pwii}M_{iw}P_{ni} + k_{pwijB}M_{jw}P_{ni}\right) - 2k_{twii}P_{ni}P_i - k_{twij}P_{ni}P_j \quad \text{(5)}$$

where $2 \leq n \leq c$.

The reaction rate of each monomer is given by:

$$\frac{dx_i}{dt} = \frac{\left(k_{pii}N_{1i}M_{ip} + k_{pji}N_{1j}M_{ip}\right)/N_{AV} + \left(k_{pwii}M_{iw}P_i + k_{pwji}M_{iw}P_j\right)}{M_{i0}} \quad \text{(6)}$$

where $i, j = A, B$ and $i \neq j$, $x_i$ is the fractional conversion, $k_{pii}$ and $k_{pij}$ are the radicals propagation constants type $i$ inside the particles that reacts with monomer $i$ and $j$, respectively; $M_{ip}$ is monomer $i$ concentration in the particles, $N_{1i}$ and $N_{1j}$ are de number of active particles containing radicals type $i$ and $j$, respectively, and $M_{i0}$ is the amount of monomer $i$ initially charged into the reactor.

Assuming steady-state for radicals into the particles:

$$k_{pBA}M_{Ap}N_{1B} = k_{pAB}M_{Bp}N_{1A} \quad \text{(7)}$$

or

$$N_{1B}/N_{1A} = k_{pAB}M_{Bp}/k_{pBA}M_{Ap} = \alpha \quad \text{(8)}$$

where $N_{1A} + N_{1B} = N_1$

After algebraic manipulations, we can obtain

$$\frac{dx_A}{dt} = \frac{\left(\frac{1}{1+\alpha}\right)\left(k_{pAA}M_{Ap} + k_{pAB}M_{Bp}\right)N_1/N_{AV} + \left(k_{pwii}M_{iw}P_i + k_{pwji}M_{iw}P_j\right)}{M_{i0}} \quad \text{(9)}$$

and

$$\frac{dx_B}{dt} = \frac{\left(\frac{\alpha}{1+\alpha}\right)\left(k_{pBB}M_{Bp} + k_{pBA}M_{Ap}\right)N_1/N_{AV} + \left(k_{pwii}M_{iw}P_i + k_{pwji}M_{iw}P_j\right)}{M_{i0}} \quad \text{(10)}$$

The rate of disappearance of microemulsion droplets is

$$-\frac{dN_d}{dt} = \rho_m N_d \quad \text{(11)}$$

This equation is valid as long as the monomer concentration in the microemulsion droplets is greater than zero.

The variation in initiator concentration with time is:

$$\frac{dI}{dt} = -k_I I \quad \text{(12)}$$

*Monomer partitioning in microemulsion copolymerization*

Before a monomer molecule from a microemulsion droplet could reach a growing particle to participate in the polymerization it must cross the droplet/water interphase, diffuse through the aqueous phase, cross the water/particle interphase, and diffuse into the polymer-monomer particle. Therefore, to be able to model the microemulsion copolymerization it is necessary to know the equilibrium concentrations of monomers in each phase. These can be determined with the Morton theory [11]. The monomer partitioning was calculated using equations similar to those presented by Guo, *et al.* [2], in terms of three domains in thermodynamic equilibrium (organic phase, water phase and polymer phase) and material balances for each component.

The equations of thermodynamic equilibrium will give the volume fraction ($\phi_{iQ}$) of each component (*i*) in each phase (*Q*), and the volume of the phases in thermodynamic equilibrium as a function of conversion. The concentrations will be given as:

$$M_{Aw} = \frac{\phi_{Aw}}{\overline{V}_A}, \quad M_{Ba} = \frac{\phi_{Bw}}{\overline{V}_B}, \quad M_{Ap} = \frac{\phi_{Ap}}{\overline{V}_A}, \quad M_{Bp} = \frac{\phi_{Bp}}{\overline{V}_B} \tag{13}$$

Where $\overline{V}_A$ and $\overline{V}_B$ are the molar volumes of A and B.

*Average particle volume*

The average particle volume can be calculated with [7]:

$$V_{part} = \frac{V_p}{N} \tag{14}$$

where $V_p$ is the total polymer volume.

*Numerical implementation*

The equations describing particle nucleation and reaction rate were integrated numerically by means of the fifth order Runge-Kutta method. This set of ordinary differential equations was coupled with the equations that describe the monomer partitioning between each phase, and solved by means of Newton's method [14].

**Results and discussion**

To test the model a simulation of the microemulsion copolymerization at 60°C of vinyl acetate and butyl acrylate (VAc:BuA, 85:15 w/w) for a monomer content of 3.25% w/w with respect to the total reaction mixture was made. The values of the parameters used in the simulation are shown in Table I. The results of this run are presented in Figures 1-4. Figure 1 shows the change of total volume of the three phases as a function of time. The total volume of monomers in noninitiated microemulsion droplets drops to zero around 10% of overall conversion, in contrast to emulsion polymerization where the depletion of monomer in the reservoirs (monomer drops) occurs generally between 20% and 40% of total conversion [15]. The total volume of aqueous phase does not change through the reaction.

**Table I.** Parameters and reaction conditions used in simulations of microemulsion copolymerization of VAc (A) and BuA (B).

| | | | |
|---|---|---|---|
| $k_{pAA}^{25}, k_{pBB}^{25}, k_{pAB}^{25*}$ (cm³/mol s) | 2.30x10⁶ | 1.26x10⁵ | 6.35x10⁷ |
| $k_{pBA}^{25}, k_{pwAA}^{a}, k_{pwBB}^{a}$ (cm³/mol s) | 1.98x10⁴ | 2.339x10⁶ | 1.2x10⁶ |
| $k_{pwAB}^{a}, k_{pwBA}^{a}\ k_{twAA}^{25}$ (cm³/mol s) | 6.259x10⁷ | 1.88x10⁴ | 0.29x10¹¹ |
| $k_{twBB}^{25}, k_{twAB}^{25}, k_{twBA}^{25}$ (cm³/mol s) | 0.625x10⁶ | 0.135x10⁹ | 0.135x10⁹ |
| $k_{cmA}^{b}, k_{cmB}^{b}, k_{cpA}^{b}$ (cm³/mol s) | 1.0x10⁸ | 1.0x10⁸ | 6.49x10⁹ |
| $k_{cpB}^{b}$ (cm³/mol s)$^{b}$ | 6.49x10⁹ | | |
| $k_{I}(\text{s}^{-1})^{1}$ | 0.35x10⁻⁵ | | |
| $\chi_{BW}^{25}, \chi_{AB}^{25}, \chi_{BA}^{25}$ | 4.2 | 0.15 | 0.45 |
| $\chi_{AW}^{25}$ | 2.1 | | |
| $m_{AW}^{25}, m_{BW}^{25}, m_{AB}^{25}$ | 0.37 | 1.31 | 0.33 |
| $m_{AP}^{25}, m_{BP}^{25}, m_{BA}^{25}$ | 0.0 | 0.0 | 3.03 |
| $\chi_{APA}^{25}, \chi_{BPB}^{25}, \chi_{APB}^{25}$ | 0.37 | 0.35 | 0.36 |
| $\chi_{BPA}^{25}, c^{c}, f^{1}$ | 0.46 | 50 | 0.5 |

\* The superscript in the first column are reference number, ᵃ estimated value, ᵇ calculated value, ᶜ assumed value.

Although the microemulsion droplets disappear at around 10% conversion, the total volume of polymer particles increases until 80% overall conversion is reached. This behavior can be explained by the high VAc water solubility ($\approx$ 2.5 g/100 mL water) which, as reaction in particles occurs, migrates to the particles to replace the consumed monomer. Figure 2 displays the swollen polymer particle average radius. A drastic increase in particle radio is observed at the beginning of polymerization due to monomer diffusion from the microemulsion droplets toward the particles through the water phase.

The model was also used to investigate the effect of initiator concentration on overall conversion (Figure 3). In this figure it is observed that as the initiator concentration increases reaction rate also increases because there is a greater flow of radicals, this result agrees with experimental observations [5, 7, 16]. Individual conversions for the microemulsion copolymerization of VAc/BuA are shown in Figure 4, where it can be observed that the first monomer to be depleted is BuA (after ~15 min reaction) because of the high tendency for the VAc to react with BuA radical and the small reactivity of BuA towards VAc radical, combined with the high water solubility of VAc which causes that VAc concentration in the particles to be low. Monomer reactivity ratios for emulsion copolymerization of VAc and BuA are 0.08 and 7.2, respectively [22] and because it is not expected that these values change in microemulsion copolymerization, these values were used. Consequently, since the macromolecules are formed within a very short time, chains rich in BuA are formed early, whereas those appearing later are increasingly richer in VAc. These results have been confirmed earlier in an independent NMR study in our laboratory [21]. The resulting latex is a complex mixture of macromolecules, which can lead to heterogeneous material by phase segregation [17].

In Figure 5 the experimental curves of conversion vs. time are compared with the simulated results using the model for the microemulsion copolymerization of VAc/BuA at 60°C. Conversions and polymerization rate increase with total monomers concentration as expected. Overall conversions after 40 minutes were between 90 and 97%. The results obtained applying the model published by Sanghvi e*t al.* [9] are also shown in this figure. Sanghvi *et al.*'s model is unable to represent the experimental data of the VAc/BuA system. It is also observed that the model proposed by us deviates slightly from the experimental data at high conversions. This is probably due to the fact that desorption coefficients were treated as constants in the simulations; an improvement to the model would be to treat the desorption coefficients as Nomura *et al.* propose [1]. Figure 6 shows two rate periods (*Rp*) during the reaction which is characteristic of microemulsion homopolymerization of these and other monomers [18, 19, 20]. The first period is characterized by a very rapid increase in $R_p$ due to the increase in the number of particles and ends when the conversion is around 10%. The second period shows a constant decrease in reaction rate and presents a change in slope at around 25% conversion. This change in slope can be attributed to the change in monomer ratio in the particles because of the more rapid depletion of BuA.
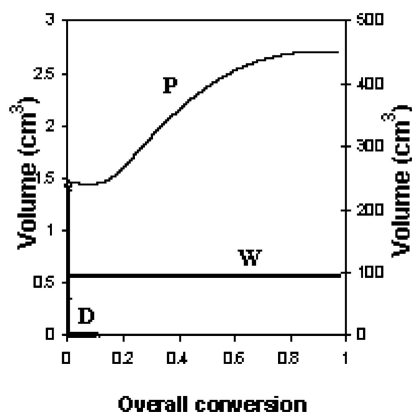


**Figure 1.** Total volume of all three phases in VAc/BuA microemulsion copolymerization. W: water phase; P: polymer particles phase and D: microemulsion droplets phase.
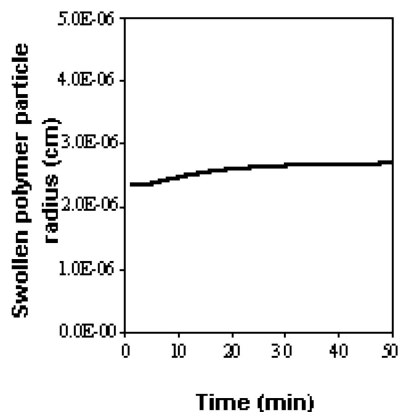


**Figure 2.** Simulation of the radius of the swollen polymer particles versus time for VAc/BuA microemulsion copolymerization.

*Simulations of copolymerization of styrene/acrylonitrile in microemulsion*

Sanghvi *et al.* [9] performed experiments of microemulsion copolymerization of styrene (S) with acrylonitrile (AN) under various reaction conditions and used their model to simulate the experimental kinetics data. Results using their reported values and the model presented here are shown in Figure 7. The values of the parameters used in the simulation are shown in Table II. In this figure it can be seen that both models reproduce very well the experimental data up to about 70% conversion, but at higher conversions the model proposed by Sanghvi deviates significantly from the experimental observations.
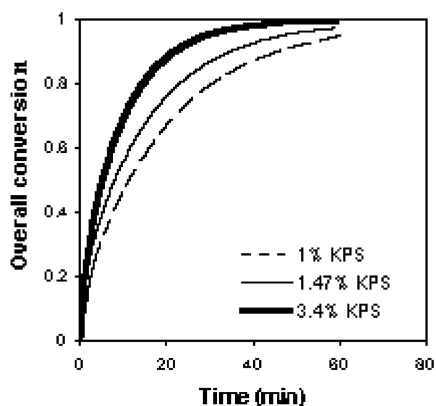
**Figure 3.** Model predictions of the kinetics of VAc/BuA (85:15 w/w) microemulsion copoly-merization with different KPS concentrations at 60 °C.
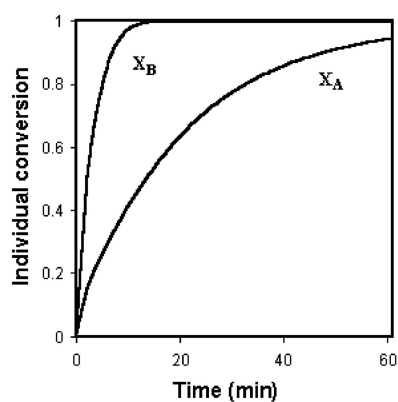
**Figure. 4.** Individual monomer conversion, at 60 °C for microemulsion copolymeri-zation of VAc (A)/BuA (B) (85:15 w/w).
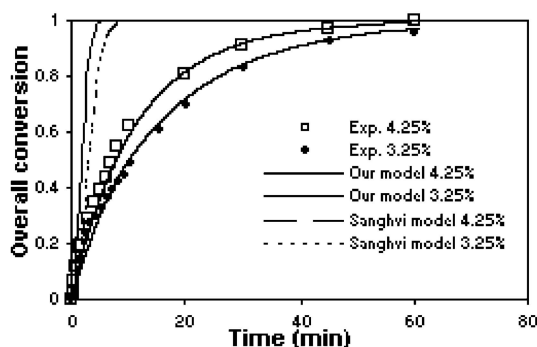


**Figure 5.** Overall conversions of VAc/BuA (85:15 w/w) microemulsion copolymerization with 4.25 and 3.25% of monomer contents.

*Analysis of residuals*

Figure 8 compares the distribution of the residuals (defined as $\delta x = x_{exp.} - x_{calc.}$) for the two models discussed here using the experimental overall conversion data for the 4.25% VAc/BuA monomers concentration microemulsión system. It is seen that Sanghvi *et al.*'s model gives higher values (an order of magnitude) for the residuals than the model described here. However, both models show deficiencies in explaining the experimental data fully: the residuals are not randomly distributed. Application of the Durbin-Watson statistic test [23] to both models gives $d$ values of 0.086 for Sanghvi *et al.*'s and 0.176 for the model described in this paper, respectively. The values of $d$ indicate that the residuals in both models are correlated (Figure 8) although the model reported here gives better estimates of the conversion data. Sinusoidal variation of the residuals is a clear indication that the model needs an

additional parameter that seems to be important at low conversions as can be observed in Figure 8. The value of $d$ is calculated as follows:

$$d = \sum_1^n \frac{(\delta x_t - \delta x_{t-1})^2}{\sum_1^n \delta x_t^2} \tag{15}$$

**Table II.** Parameters used in simulations of microemulsion copolymerization of AN (A) and S (B).

| | | | |
|---|---|---|---|
| $k_{pAA}{}^{27}$, $k_{pBB}{}^{27}$, $k_{pAB}{}^{27}$ (cm$^3$/mol s)$^*$ | 3.3983x10$^7$ | 2.832x10$^4$ | 4.357x10$^8$ |
| $k_{pBA}{}^{27}$, $k_{pwAA}{}^{a}$, $k_{pwBB}{}^{a}$ (cm$^3$/mol s) | 7.8665x10$^4$ | 3.3983x10$^7$ | 2.8658x10$^5$ |
| $k_{pwAB}{}^{a}$, $k_{pwBA}{}^{a}$, $k_{twAA}{}^{27}$ (cm$^3$/mol s) | 4.3568x10$^8$ | 7.8665x10$^6$ | 1.502x10$^{12}$ |
| $k_{twBB}{}^{27}$, $k_{twAB}{}^{27}$, $k_{twBA}{}^{27}$ (cm$^3$/mol s) | 1.1503x10$^{11}$ | 1.925x10$^{13}$ | 3.195x10$^{11}$ |
| $k_{cmA}{}^{b}$, $k_{cmB}{}^{b}$, $k_{cpA}{}^{b}$ (cm$^3$/mol s) | 1.0x10$^8$ | 1.0x10$^8$ | 1.0x10$^9$ |
| $k_{cpB}{}^{b}$ (cm$^3$/mol s) | 1.0x10$^9$ | | |
| $k_I{}^{1}$ (s$^{-1}$) | 0.35x10$^{-5}$ | | |
| $\chi_{BW}{}^{26}$, $\chi_{AB}{}^{26}$, $\chi_{BA}{}^{26}$ | 7.39 | 0.23 | 0.4 |
| $\chi_{AW}{}^{26}$ | 2.39 | | |
| $m_{AW}{}^{26}$, $m_{BW}{}^{26}$, $m_{AB}{}^{26}$ | 0.50 | 1.30 | 0.57 |
| $m_{AP}{}^{26}$, $m_{BP}{}^{26}$, $m_{BA}{}^{26}$ | 0.0 | 0.0 | 1.74 |
| $\chi_{APA}{}^{26}$, $\chi_{BPB}{}^{26}$, $\chi_{APB}{}^{26}$ | 0.88 | 0.40 | 0.42 |
| $\chi_{BPA}{}^{26}$, $c^{c}$, $f^{1}$ | 1.58 | 50 | 0.5 |

* The superscript in the first column are references number, [a] estimated value, [b] calculated value, [c] assumed value.
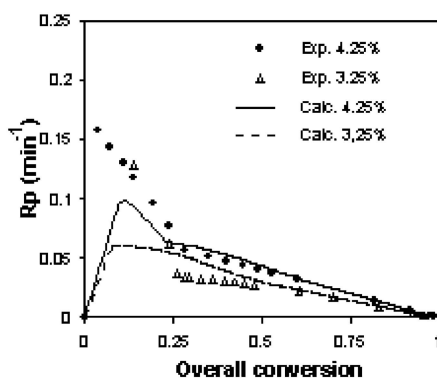


**Figure 6.** Polymerization rate vs. overall conversion for the microemulsion copolymerization of VAc/BuA (85:15 w/w) as a function of monomer contents with respect to the total mixture at 60°C. Symbols represent experimental values and solid curves are model predictions.

## Conclusions

The mathematical model proposed here satisfactorily predicts the VAc/BuA conversion vs. time data, although there are slight deviations at high conversions. Two rate periods are present during the reaction, however the decreasing rate period shows a change in slope when the kinetics is modified by the change in monomers ratio in the particles due to the early consumption of BuA. The model developed here is able to predict other microemulsion copolymerizations. Further improvement of the model is needed to have a better representation of the kinetic data.
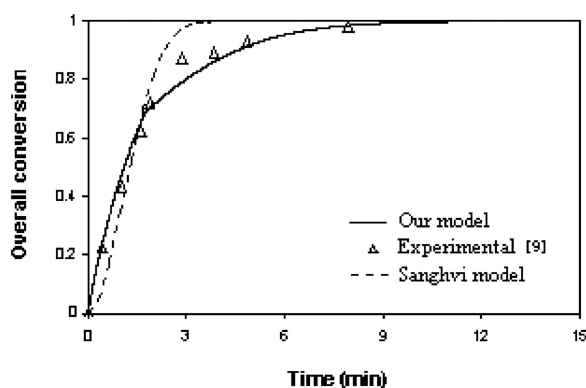


**Figure 7.** Overall conversion of S/AN (1:1 mol/mol) microemulsion copolymerization with 0.37 mM of KPS as initiator at 80 °C (5% of monomer mixture, 81% of water and 14% of SDS).
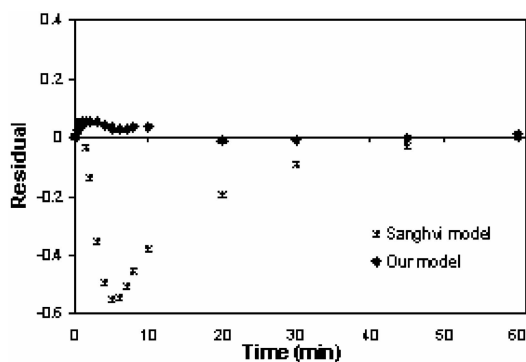


**Figure 8.** Residuals distributions for the two models discussed here using the experimental overall conversion data of VAc/BuA system (4.25% monomers concentration).

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