DOI: 10.1002/masy.200651112

Batch and Semicontinuous Styrene–Butadiene Emulsion Copolymerization Reactions

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Summary: In this work an experimental and simulation study of batch and semicontinuous styrene/butadiene emulsion copolymerization process was developed. The mathematical model combines the classical emulsion copolymerization equations, with mass balances, partitioning of components among all liquid phases, micellar and homogenous nucleation mechanisms and mass transfer equations between liquid and gaseous phases. Simulation results show good agreement with experimental measurements of conversion, average particle diameter and pressure.

Keywords: copolymerization; emulsion polymerization; gas-liquid mass transfer; modeling; semicontinuous; styrene/butadiene

Introduction

Chemical reactors that involve mass transfer between liquid and gas phases are common in many industrial applications. In all of them, the difficulties include not only the attainment of the concentrations in the gas phase, but also in the elaboration of models that are able to calculate the composition of both phases. This difficulty is attributed mainly to the lack of several thermodynamic and mass transfer parameters in literature. In the case of emulsion polymerization reactions this difficulty is enhanced by the additional partitioning of components among the different liquid phases (aqueous phase, monomer droplets and polymer particles).[1]

In the semicontinuous styrene/butadiene emulsion copolymerization process, which is widely applied for the production of paper and textile coatings, among other applications, due to the high vapor pressure of butadiene, reactor pressure profiles could be used to predict and control copolymer composition. In this direction, styrene/butadiene emulsion copolymerizations were modeled in this work taking the monomer mass transport between the gas and liquid phases into account. To our knowledge, mass transport between gas and liquid phases has not been taken into account in the few previous works[2–5] concerning the modeling of semicontinuous styrene/butadiene emulsion copolymerizations. The main advantage in including such a prediction is the possibility of relating the pressure in the reactor headspace with the monomer conversion, thus allowing one to infer conversion from fast and simple pressure measurements. The model presented in this work combines the classical emulsion copolymerization equations: mass balances, partitioning of components among all liquid phases, micellar and homogenous nucleation mechanisms with mass transfer equations between liquid and gaseous phases. Simulation results were compared with two groups of experiments: the experimental data from Araujo[6,7] (batch styrene/butadiene emulsion polymeriza-

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tions) and the data obtained in the automated unit described in this work (semicontinuous styrene/butadiene emulsion polymerizations).

Modeling

The mathematical model used in this work was based on the vinyl acetate/butyl acrylate emulsion copolymerization model of Araújo and Giudici[8] with modifications to describe styrene/butadiene (S/B) polymerizations. The modifications include the changes of kinetic constants and other system-dependent parameters (physical properties, partition coefficients, diffusion coefficients, ...), as well as the extensions to compute the partitioning (and mass transfer) of monomer between vapor and liquid phases.

For the sake of brevity in what follows only distinctive aspects of the modeling will be described. The mass balance equation for monomer i in the reactor headspace (vapor phase) is written as:

$$\frac{dm_i^V}{dt} = -K_L \cdot a \cdot (P \cdot y_i - P_i^{sat} \cdot \phi_i^w \cdot \gamma_i^w) \quad (1)$$

where m_i^v is the mass of monomer *i* in the vapor phase, K_L is the mass transfer coefficient, *a* is the gas-liquid interfacial area, y_i is the mole fraction of monomer *i* in the vapor phase, P_i^{sat} is the vapor pressure of monomer *i* at the reaction temperature, ϕ_i^w is the volume fraction of monomer i in the aqueous phase, and γ_i^w is the activity coefficient of monomer *i* in the aqueous phase. Equation (1) applies for all volatile species, including water. Activity coefficients were computed using Wilson equation with parameters estimated from head-space chromatography data.[9]

The mass balance for each monomer is calculated considering the feeding flow rate of monomer i ($\dot{m}_i^{feed}$) and the rate of polymerization occurring both in aqueous phase and in the polymer particles:

$$\frac{dm_i^{tot}}{dt} = \dot{m}_i^{feed} - MW_i(R_{p,i}^{aq} v_{aq} + R_{p,i}^{p} v_p) \quad (2)$$

where MW_i is the molecular weight of monomer i.

The kinetic model considers initiator decomposition, propagation, chain transfer to chain transfer agent, chain transfer to monomer, chain transfer to polymer (for butadiene type radicals), reaction with internal double bonds, and termination by combination and by disproportionation.

The partitioning of monomer present in the liquid phase ($m_i^L = m_i^{tot} - m_i^V$) among aqueous phase, polymer particles, and monomer droplets, if present, is considered to be in equilibrium and the concentration in each of these phases is computed by the partition coefficient approach.[8,10,11] This partitioning calculation is performed using the amount of monomer in liquid phase (m_i^L) instead of the total amount of monomer present in the reactor (m_i^{tot}), as follows. The partition coefficients for each monomer i (i = A,B, i.e., styrene, butadiene) between monomer drops and aqueous phase (k_i^d) and between polymer particles and aqueous phase (k_i^p) are defined as:

$$k_i^d = \frac{v_i^d / v_d}{v_i^{aq} / v_{aq}} \quad (3)$$

$$k_i^p = \frac{v_i^p / v_p}{v_i^{aq} / v_{aq}} \quad (4)$$

where v_i^d, v_i^{aq} and v_i^p are the volumes of monomer i in droplets, aqueous phase, and polymer particles, respectively, and v_d, v_{aq}, and v_p are the total volume of droplets, aqueous phase and polymer particles, respectively, which are calculated, assuming volume additivity, as:

$$v_d = \sum_{i=A,B} v_i^d \quad (5)$$

$$v_{aq} = \sum_{i=A,B} v_i^{aq} + v_w \quad (6)$$

$$v_p = \sum_{i=A,B} v_i^p + v_{copol} \quad (7)$$

where v_w is the volume of water and v_{copol} is the volume of copolymer. The total volume of monomer *i* in liquid phase ($v_i = m_i^L / \rho_i$) is given by:

$$v_i = v_i^d + v_i^p + v_i^{aq} \quad (8)$$

Combining equations (3), (4) and (8) one obtains:

$$v_i^p = \frac{v_i}{1 + \frac{v_{aq}}{v_p k_i^p} + \frac{v_{aq} k_i^d}{v_p k_i^p}} \tag{9}$$

$$v_i^d = \frac{v_d}{v_p} \frac{k_i^d}{k_i^p} v_i^p \tag{10}$$

$$v_i^{aq} = \frac{v_{aq}}{v_p} \frac{1}{k_i^p} v_i^p \tag{11}$$

Knowing $v_i = (m_i^L/\rho_i)$, v_{copol}, v_w, k_i^d and k_i^p, it is possible to obtain v_i^d, v_i^{aq} and v_i^p by the following iterative procedure:[10,11]

i) set initial guesses for v_d, v_{aq} and v_p;
ii) calculate v_i^p using eq. (9);
iii) calculate v_i^d and v_i^{aq} using eq. (10) and eq. (11);
iv) calculate the new values of v_d, v_{aq} and v_p using eqs. (5), (6) and (7);
v) return to step i) with the new values of v_d, v_{aq} and v_p until convergence.

Once the volumes of each monomer in each phase are known, the concentrations are calculated by:

$$[M_i]_j = \frac{v_i^j}{v_j} \frac{MW_i}{\rho_i} \tag{12}$$

where ρ_i is density of monomer i.

By assuming that vapor phase behaves as ideal gas, the pressure can be readily calculated from temperature, volume, and mass of each volatile component in the reactor headspace.

$$P = \frac{\left(\frac{m_A^V}{MW_A} + \frac{m_B^V}{MW_B} + \frac{m_w^V}{MW_w} + \frac{m_{N_2}^V}{MW_{N_2}} \right) RT}{(V_R - (v_d + v_{aq} + v_p))} \tag{13}$$

where V_R is the total reactor volume and $(V_R - (v_d + v_{aq} + v_p))$ is the volume of gas phase in the reactor headspace.

The value of mass transfer coefficient and interfacial area ($K_L a$) is estimated by fitting the model to pressure versus time data. Other model parameters that were determined by fitting the model to the experimental data included the rate constant of radical capture by micelles and the rate constant for radical capture by polymer particles, in a similar way as done by Casella et al.[12]

Experimental

Semicontinuous S/B emulsion copolymerizations were conducted in a 3-liter jacketed steel reactor equipped with stirrer and heating/cooling system, shown in Figure 1.

Reactant feeding was divided in three streams: 1) butadiene, 2) styrene, carboxylic monomer and chain transfer agent and 3) aqueous phase, composed of initiator, emulsifier and water.

After the end of the monomer feeding time (with constant feed rates), reaction temperature was increased from 85 °C to 100 °C and the aqueous phase feeding was maintained for one additional hour, as part of an investigation of possible strategies for reducing residual monomer content. Reaction temperature was controlled by a PID controller and agitation was maintained at 200 rpm. Additionally, nitrogen was used to remove the oxygen (that acts as an inhibitor) from the reaction medium and from the feeding tanks.

Monomer conversion was determined by gravimetry, styrene and butadiene concentrations were measured by headspace gas chromatography (HS-GC – Shimadzu) and average particle sizes were obtained by dynamic light scattering (Coulter N4 Plus).

Results and Discussion

Batch Styrene/Butadiene Reactions

In order to validate the styrene/butadiene emulsion copolymerization model simulation results were compared to experimental data from a previous work.[6] Results of ab-initio batch reactions were chosen for this purpose because they include all the emulsion polymerization steps. These experimental results of Araujo[6] evaluate the effect of initiator and emulsifier concentrations, as well as of the S/B molar ratio

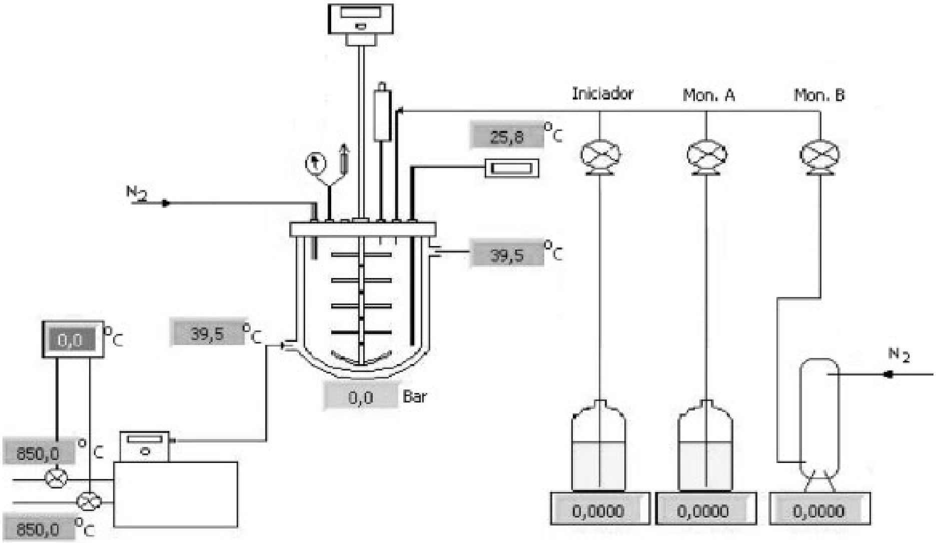

Figure 1.
Experimental unit used for semicontinuous styrene/butadiene emulsion copolymerization reactions.

on the evolution of conversion and average particle sizes, as shown in Table 1.

Figure 2 shows the evolutions of conversion, average particle size and pressure during reactions conducted with molar comonomer ratio S/B = 70/30 (SSB1, SSB5 and SSB15) and varying amounts of initiator and emulsifier. The agreement between simulated and experimental results is quite good. The only exception refers to the average particle sizes in the low conversion region. The inflection points observed in the pressure evolutions (Figure 2c) coincide with the end of the interval II (disappearance of monomer droplets).

When the amount of butadiene is increased in the formulation (S/B = 30/70, reactions SSB2, SSB6 and SSB14) reaction rate decreases and the agreement between experimental and simulation results becomes slightly poorer, as shown in Figure 3 (it should be noted that the value of K_La was estimated for the run SSB1 in Figure 2, and then used to test the model prediction for reaction SSB2 in Figure 3). Nevertheless, major trends are still correctly predicted. In these reactions, the higher butadiene content leads to an increase of the initial reactor pressure and the disappearance of the monomer droplets was delayed as might be noted by the location of the inflection points of the pressure curves in Figure 3c. In addition, reactions with S/B = 30/70 (Figure 3c) showed higher final pressure than reactions with S/B = 70/30 (Figure 2c) indicating a higher amount of unreacted butadiene.

Table 1.
Batch styrene/butadiene emulsion copolymerizations.[6]

Reaction	Temperature (°C)	S/B (mol/mol)	S (g)	B (g)	I (g)	E (g)	W (g)
SSB1	70	70/30	361.53	80.47	0.594	5.157	1300
SSB2	70	30/70	199.84	242.16	0.594	5.157	1300
SSB5	70	70/30	361.53	80.47	1.187	9.846	1300
SSB6	70	30/70	199.84	242.16	1.187	5.157	1300
SSB14	70	30/70	199.84	242.16	1.187	10.10	1300
SSB15	70	70/30	361.53	80.47	0.594	9.846	1300

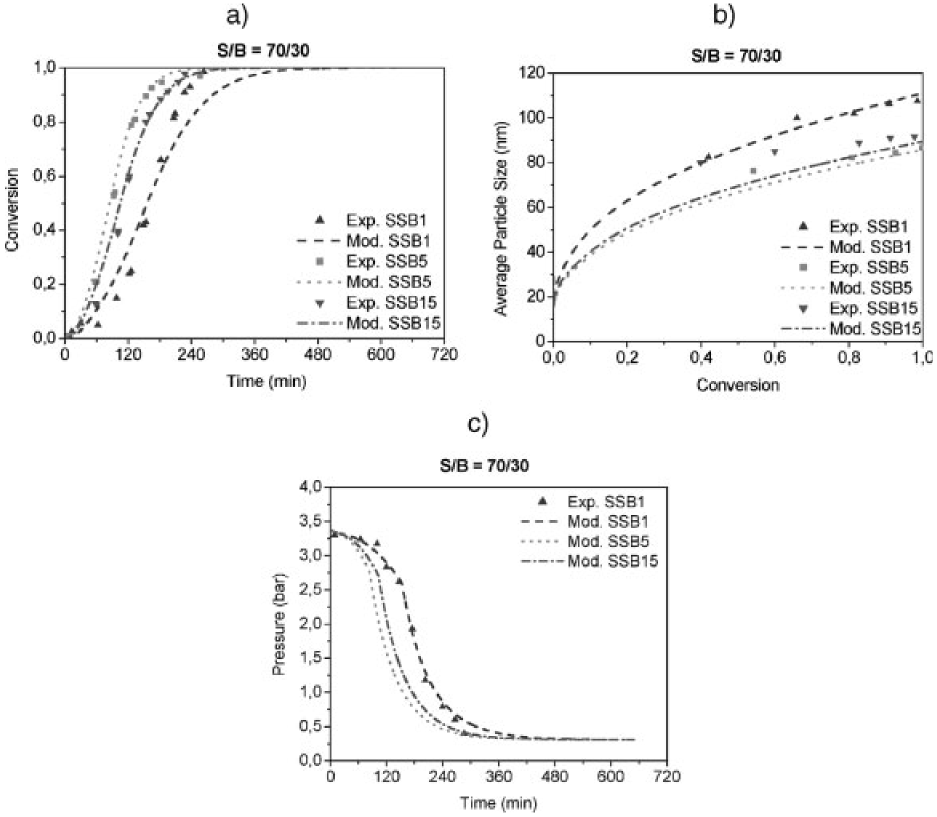

Figure 2.
Evolution of conversion, average particle diameter and pressure during batch styrene/butadiene emulsion copolymerization reactions with S/B = 70/30 (mol/mol) - comparison between experimental and simulation results.

Figure 4 shows the simulations of volumetric fraction of monomer in the liquid phase and mole fraction of monomer in the vapor phase regarding SSB1 styrene – butadiene batch reaction. In both variables, the observed inflection points – around 153 min – coincide with the end of the emulsion polymerization interval II (disappearance of monomer droplets), as shown in Figure 2-a. Prior to this point, the presence of the monomer droplets maintains the composition in both phases practically constant.

Good predictions of the pressure evolution show the possibility of using the model as a state estimator for monomer conversion (and reaction rate) from easily available pressure measurements in industrial styrene-butadiene copolymerization processes.

Figure 5 presents an analysis of sensitivity of the model predictions with respect to the value of the parameter $K_L \cdot a$. While the pressure evaluation is affected by changes in the mass transfer coefficient between gas and liquid phases, the monomer conversion profile is not affected at all. This is expected, as the amount of monomers in gas phase is quite small compared to the amount of monomers in the liquid phase. This also implies that the mass transfer parameter has to be fitted in order to have a reliable model to be used as a state estimator of conversion from pressure measurements.

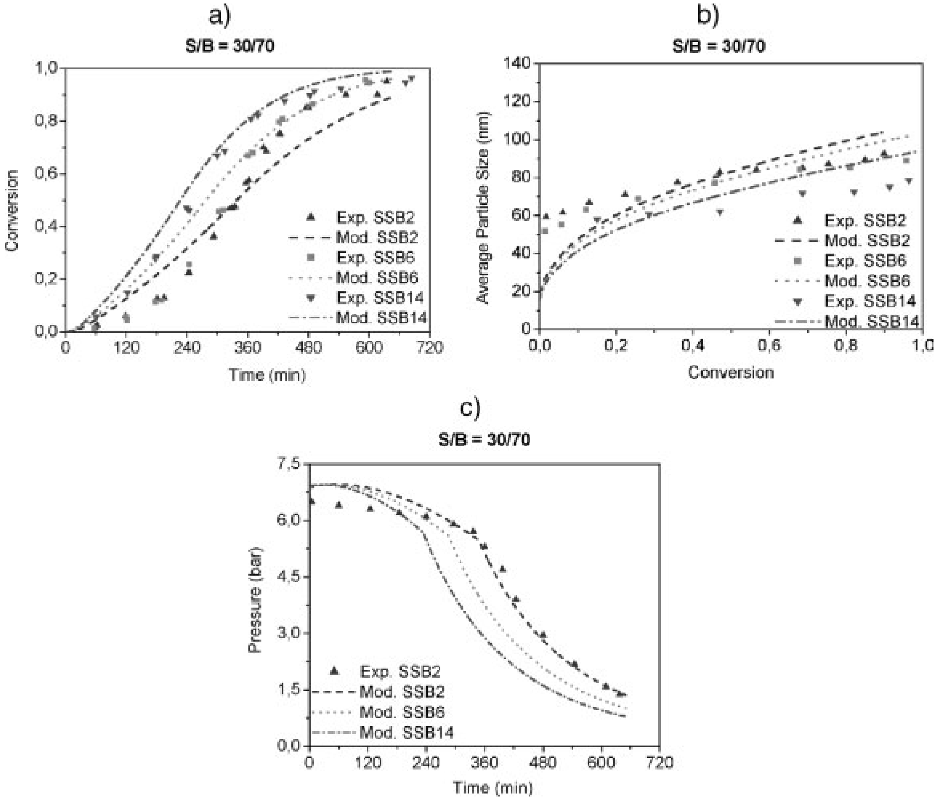

Figure 3.
Evolution of conversion, average particle diameter and pressure during batch styrene/butadiene emulsion copolymerization reactions with S/B = 30/70 (mol/mol) - comparison between experimental and simulation results.

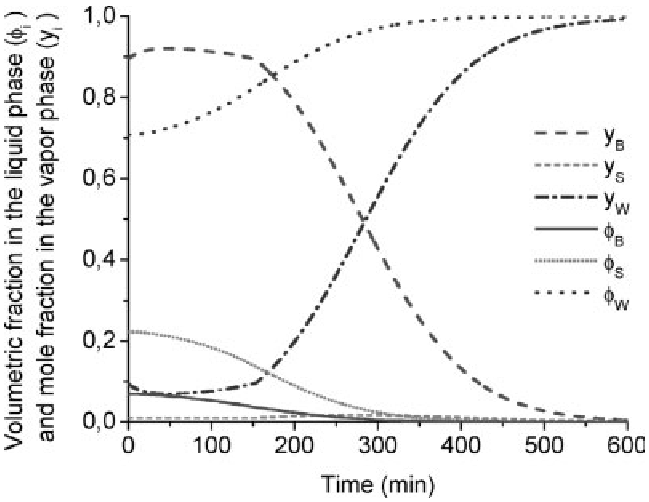

Figure 4.
Evolution volumetric fraction and mole fraction of monomers and water in liquid and vapor phase, respectively.

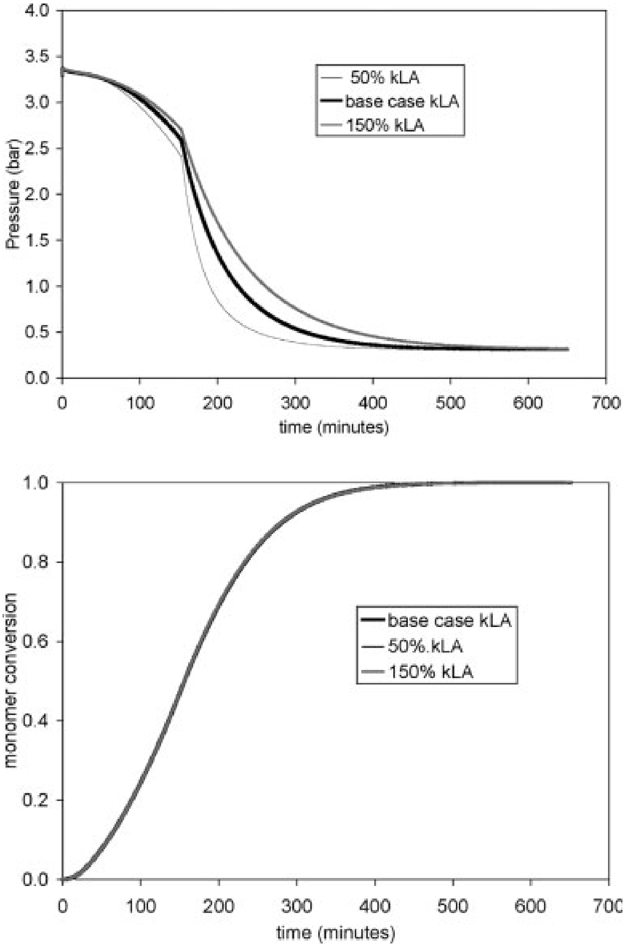

Figure 5.
Parametric sensitivity of parameter K_La. Effect on conversion versus time and pressure versus time.

The value of the mass transfer coefficient is assumed to be the same for all volatile components (butadiene, styrene and water). This simplifying assumption, which is reosanable for the system here studied, reduces the number of adjustable parameters to be determined as well as the necessity of more detailed experimental measurements otherwise required.

Semicontinuous Styrene/Butadiene Reactions – Effect of Reactant Feeding Time

Table 2 shows the major characteristics and differences among the semicontinuous styrene/butadiene emulsion copolymerization reactions carried out at the experimental unit previously described. These reactions verify the effect of different reactant feeding times on the process.

Figure 6 compares experimental and simulated evolutions of conversion and average particle diameter during semicontinuous styrene/butadiene (S/B = 45/55 mol/mol) emulsion copolymerizations conducted with different reactant feeding times as shown in Table 2. Model predictions of conversion evolution (Figure 5a) are rather good. Average particle sizes for the reactions with shorter feeding times

Table 2.
Semicontinuous styrene/butadiene emulsion copolymerizations.

Reaction**	Temperature (°C)	S/B (mol/mol)	Monomer feed time (min)	Aqueous phase feed time (min)	Total reaction time (min)
SB1	85/100*	45/55	300	360	420
SB2	85/100*	45/55	240	300	360
SB3	85/100*	45/55	180	240	300

* Reaction temperature increase after the end of the monomer feed time (post polymerization strategy for residual monomer reducing).

** All reactions were performed with solid content of 50%, polystyrene seeds of average diameter 22 nm, 1.7wt% of acrylic acid and 0.6wt% of TTDM as chain transfer agent.

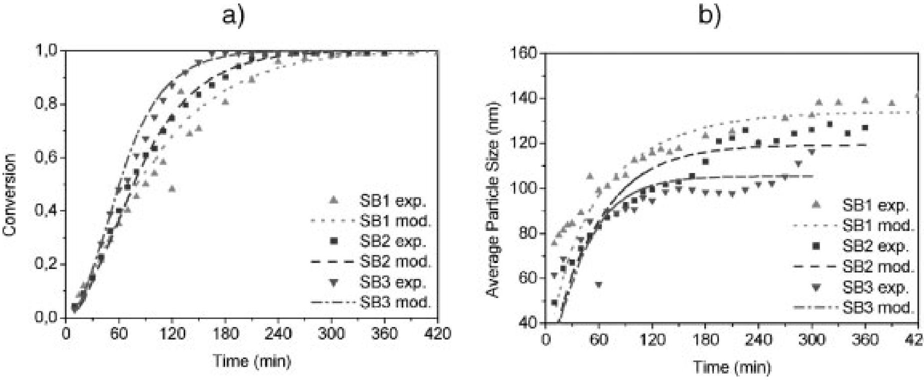

Figure 6.
Evolution of conversion and average particle diameter during semicontinuous styrene/butadiene emulsion copolymerization reactions with S/B = 45/55 (mol/mol) - comparison between experimental and simulation results.

(SB2 and SB3) showed an increase towards the end of the reactions indicating the formation of particle aggregates, which, however, was not predicted by the simulations since the model does not include a particle coalescence mechanism. The decrease of latex stability with the increase of reaction temperature has already been observed previously.[13,14]

Conclusions

Experimental and analytical procedures were established to allow for the conduction of semicontinuous styrene-butadiene emulsion copolymerization reactions in a lab-scale reactor under safe and reproducible conditions.

A previously developed emulsion copolymerization model was modified to predict the evolution of pressure and composition of the gas in the reactor headspace along the reaction, accounting for the gas-liquid mass transfer and the phase equilibrium thermodynamics. This model, that takes into account the mass transfer resistance between gas and liquid phases, is more general than other approaches previously presented[15–17] that assume equilibrium between gas and liquid phases. The model was able to represent experimental results of batch and semicontinuous reactions conducted under different conditions.

Acknowledgements: The financial support from FAPESP - Fundação de Amparo à Pesquisa do Estado de São Paulo and CNPq - Conselho

Nacional de Desenvolvimento Científico e Tecnológico is gratefully appreciated. The authors also thank CIBA Specialty Chemicals for monomer supply.

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