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agent*

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**Citation:** BENYAHIA, B. ... et al., 2009. Modeling and optimization of fed-batch emulsion copolymerization of styrene and butyl acrylate in the presence of a chain transfer agent. IN: Proceedings of the 12th Congress of the French Society of Process Engineering 2009 (SFGP 2009), Marseille, France, Récents Progrès en Génie des Procédés, Paris, France, pp. Axx1 - Axx6

**Additional Information:**

- This is a conference paper.

**Metadata Record:** <https://dspace.lboro.ac.uk/2134/12416>

**Version:** Accepted for publication

Please cite the published version.

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## **Modelling and experimental analysis of fed-batch emulsion copolymerization of styrene and butyl acrylate in the presence of a chain transfer agent**

Benyahia Brahim <sup>a,b</sup>, Latifi Abderrazak <sup>a</sup>, Fonteix Christian <sup>a</sup>, Pla Fernand <sup>a</sup>

<sup>a</sup> Laboratoire des Sciences du Génie Chimique, CNRS-ENSIC

1 rue Grandville, BP 20451, 54001 Nancy Cedex, France

Tel : ++(33) 3 83 17 52 34, Fax : ++(33) 3 83 17 53 26

Email addresses : {brahim.benyahia, [latifi.fonteix.pla](mailto:latifi.fonteix.pla@ensic.inpl-nancy.fr)}@ensic.inpl-nancy.fr

<sup>b</sup> Département de Chimie, Faculté des Sciences et Sciences de l'Ingénieur

Université Mohamed Boudiaf, M'sila, Algérie

### **Abstract**

This paper deals with mathematical modeling and experimental validation of a fed-batch emulsion copolymerization reactor of styrene and butyl acrylate in the presence of n-C12 mercaptan as a chain transfer agent. The model is used to predict the global monomers conversion, the average molecular weights, the particle size distribution and the amount of residual monomers. A subset of the most influential parameters of the model is determined using a parameter estimability approach and identified by minimizing the errors between the predicted and measured data. Some parameters are also obtained from literature. The model is then validated by batch and fed-batch experimental measurements.

**Key words :** Fed-batch emulsion copolymerization, Modelling, chain transfer agent.

### **1. Introduction**

Emulsion polymerization is an important industrial process used to produce a great variety of polymers of multiple uses (e.g. paints, adhesives, coatings, varnishes...). Moreover, it has significant advantages over bulk and solution polymerization processes. These advantages result mostly from the multiphase and compartmentalized nature of the emulsion polymerization which allows the production of polymers of high molecular weight at high polymerization rates, delivering a high versatility to product qualities. However, the complexities of emulsion polymerization systems arising from factors such as the multiphase nature, nonlinear behaviour and sensitivity to disturbances induce more intense difficulties on modeling and make the development of optimization procedures of emulsion polymerization reactions a very challenging task.

There is a rich literature on modeling emulsion polymerization processes, starting with the conventional Smith–Ewart model (Smith and Ewart, 1948). The later models developed for emulsion polymerizations have varying degrees of complexity, depending upon their scope and application (Rawlings et al., 1988; Hoppe et al., 2005; Ginsburger et al., 2003). The most representative have been reviewed by Dube et al., 1997; Gao and Penlidis, 2002; Chern, 2006 and Thickett and Gilbert, 2007.

Chain transfer agents (CTAs) are commonly used to control the molecular weights in polymerization processes. However in emulsion polymerization both molecular weights and the rate of polymerization appeared to be affected by the CTA (Numura et al., 1994; Barudio et al., 1998 ; Salazar et al. 1998).

This paper deals with the elaboration of a mathematical model for the emulsion copolymerization of styrene and butyl acrylate in the presence of n-C12 mercaptan as a CTA. The objective was to predict the monomers global conversion, the average molecular weights of the resulting macromolecules, the average particles diameter and the amount of residual monomers. The process model developed is also able to handle the aforementioned effect of the CTA on the kinetic of the polymerization. This has been achieved by using a new approach for the desorption rate. On the other hand, a novel method is developed to carry

out population balance using two differential equations instead of large number of model equations for the same purpose.

Due the complexity of the phenomena involved in emulsion copolymerization, the major problem is the extensive number of parameters that must be considered and estimated. The key feature of the identification problem is to determine the subset of the most influential and potentially estimable parameters which allow reliable predictions of polymer properties.

In the next section, the main features of the model will be described briefly including the assumptions, the kinetic scheme and model equations. The parameter identification procedure is then introduced highlighting the results obtained. The model was validated by batch and fed-batch experimental measurements. The later results are not presented for the sake of brevity.

## 2. Modelling of the emulsion copolymerization process

Emulsion copolymerization is a radical polymerization, where the monomers are mainly located in droplets dispersed in an aqueous phase which are stabilized by a surfactant. The initiator is soluble in the water phase which contains an excess of surfactant mainly in its micellar form. The initiator decomposes in the aqueous phase and generates primary radicals. In conventional emulsion polymerizations, monomers with very low water solubility are used and lead to two kind of nucleation, homogenous and micellar nucleation. In the case of micellar nucleation, primary radicals enter to the micelle and lead to polymer particles in which propagation, termination, inhibition and chain transfer reactions take place. The monomers needed for the reactions are provided by the droplets.

The process model is based on the following assumptions:

- Due to the high surfactant concentration used in this work, only micellar nucleation was considered
- All reactions in the aqueous phase were neglected except initiation and inhibition.
- The chain transfer agent was subject to diffusional limitations mainly in the droplet-aqueous phase interface.
- The growing particles and the monomer droplets were considered to be monodisperse.
- The reactor is perfectly mixed and isothermal.

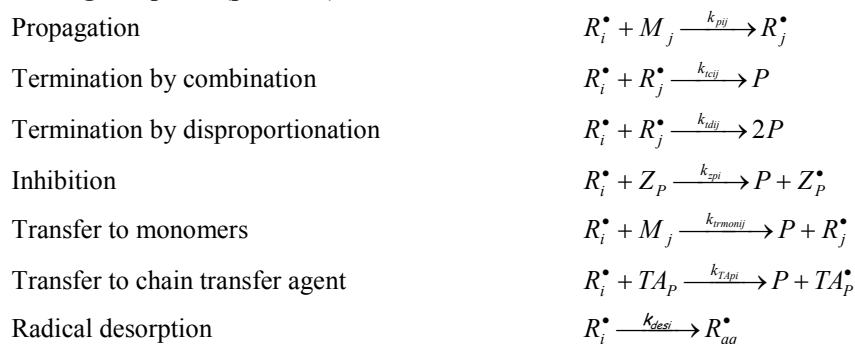
### 2.1. Kinetic Scheme

According to these assumptions, the model is based on the following elementary chemical reactions.

#### 2.1.1. In the aqueous phase



#### 2.1.2. In the organic phase (particles)



### 2.1. Mathematical model

The material balances are presented in a general form for semi-continuous process using expressions of the reaction rates based on the kinetic scheme presented above. These equations could be easily simplified for the case of a batch process. Equations 13 and 14 represent the population balance based on the assumption that the fraction of particles containing  $j$  free radicals follows Poisson's law. Equations (15-20) represent equations of moments necessary to assess the average molecular weights (Villermaux and Blavier, 1984).

$$\frac{dV_R}{dt} = Q_f + \sum_{i=1,2} \left( \frac{1}{\rho_{pi}} - \frac{1}{\rho_i} \right) M_M^i (R_{pi} + R_{irmi}) \quad (1)$$

$$\frac{dM_i}{dt} = -R_{pi} - R_{irmi} + Q_f [M_{fi}] \quad (2)$$

$$\frac{dM_{Ti}}{dt} = Q_f [M_{fi}] \quad (3)$$

$$\frac{dI}{dt} = -R_d + Q_f [M_{fi}] \quad (4)$$

$$\frac{dZ}{dt} = -(R_{Zp1} + R_{Zp2}) + Q_f [M_{fz}] \quad (5)$$

$$\frac{dT_A}{dt} = -R_{TAp1} - R_{TAp2} + Q_f [M_{fTA}] \quad (6)$$

$$\frac{dS}{dt} = Q_{sf} [M_{fs}] \quad (7)$$

$$\frac{dN_p}{dt} = R_N \quad (8)$$

$$\frac{dR_1}{dt} = (R_N + R_{cp}) f_{aq1} - R_{p12} + R_{p21} - R_{irm12} + R_{irm21} - R_{Zp1} - R_{des1} - (R_{T11} + R_{T12}) \quad (9)$$

$$\frac{dR_2}{dt} = (R_N + R_{cp}) f_{aq2} - R_{p21} + R_{p12} - R_{irm21} + R_{irm12} - R_{Zp2} - R_{des2} - (R_{T22} + R_{T21}) \quad (10)$$

$$\frac{d(N_p \bar{n} \chi_1)}{dt} = (R_N + R_{cp}) f_{aq1} + R_{irm21} + R_{irm11} + R_{TAp1} - R_{des1} - (R_{irm21} + R_{irm11} + R_{p11} + R_{p12} + R_{TAp1} + R_{Zp1}) \chi_1 - (R_{T11} - R_{T12}) \chi_1 \quad (11)$$

$$\frac{d(N_p \bar{n} \chi_2)}{dt} = (R_N + R_{cp}) f_{aq2} + R_{irm12} + R_{irm22} + R_{TAp2} - R_{des2} - (R_{irm12} + R_{irm22} + R_{p22} + R_{p21} + R_{TAp2} + R_{Zp2}) \chi_2 - (R_{T11} - R_{T12}) \chi_1 \quad (12)$$

$$\frac{d(N_p \bar{n})}{dt} = R_N + R_{cp} - (R_{Zp} + R_T + R_{des}) \quad (13)$$

$$\frac{d(N_p \tilde{n})}{dt} = 2R_{cp} \bar{n} - \left( \frac{2\tilde{n}}{\bar{n}} + 1 \right) R_T - 2 \frac{\tilde{n}}{\bar{n}} (R_{Zp} + R_{des}) \quad (14)$$

$$\frac{d(N_p \bar{n})}{dt} = R_N + R_{cp} - (R_{Zp} + R_T + R_{des}) \quad (15)$$

$$\frac{d(N_p \bar{n} \lambda_1)}{dt} = R_N + R_{cp} - R_{des} + R_p + (R_{irm} + R_{TAp}) (1 - \lambda_1) - (R_{Zp} + R_T) \lambda_1 \quad (16)$$

$$\frac{d(N_p \bar{n} \lambda_2)}{dt} = R_N + R_{cp} - R_{des} + R_p (1 + 2\lambda_2) + (R_{irm} + R_{TAp}) (1 - \lambda_2) - (R_{Zp} + R_T) \lambda_2 \quad (17)$$

$$\frac{d(N_m)}{dt} = R_{Zp} + R_{irm} + R_{TD} + R_{TAp} + \frac{R_{TC}}{2} \quad (18)$$

$$\frac{d(N_m L_1)}{dt} = (R_{Zp} + R_{irm} + R_T + R_{TAp}) \lambda_1 \quad (19)$$

$$\frac{d(N_m L_2)}{dt} = (R_{Zp} + R_{irm} + R_{TD} + R_{TAp}) \lambda_2 + R_{TC} (\lambda_2 + \lambda_1^2) \quad (20)$$

### 3. Results and Discussion

#### 5.1. Parametric Identification

A first step, prior to parameter identification problem is to evaluate the estimability of the model parameters and to determine the subset of potentially estimable parameters. Due to the model structure and possible lack of measurements, estimation of some parameters may be impossible regardless of the amount of data available. The main limitations to the parameters estimability are the weak effect of the parameter on the measured outputs and the correlation between the parameters effects. Estimation of these parameters can lead to significant degradation in the predictive capability of the model.

The development of an effective solution to the parameter selection problem required establishing a methodology based on the magnitude of the individual effect of each parameter on the measured outputs (Yao et al., 2003). This approach has been applied to the 48 parameters of the model leading to a subset of 21 parameters.

The aim of the model was to predict satisfactorily and simultaneously the global conversion ( $X_{ove}$ ), the fraction of residual styrene ( $Fr_2$ ), the number- and weight-average molecular weights ( $\bar{M}_n, \bar{M}_w$ ) and the average particle diameter ( $d_p$ ). The model parameters were determined by minimization of the maximum likelihood criterion,  $J$ , with the experimental data.

$$J = \sum_{k=1}^5 N_k \cdot \ln \left( \sum_{l=1}^{N_k} (x_k(t_{kl}) - \hat{x}_k(t_{kl}, \theta))^2 \right) \quad (21)$$

where  $N_k$  is the number of measurements of the variables  $x_k$ ,  $t_{kl}$  is the  $l$ th time of measurement of the variable  $x_k$  and  $\hat{x}_k$  is the value of  $x_k$  predicted by the model using the values  $\theta$  of the unknown parameters. In this relation, the five variables  $x_k$  were :  $X_{ove}$ ,  $\bar{M}_n, \bar{M}_w$ ,  $d_p$  and  $Fr_2$ .

#### 5.2. Associated results

The measured data were obtained from several batch emulsion copolymerization runs. The experiments were carried out with an initial initiator mass of 1 g, initial styrene mass of 60 g, initial Butyl acrylate 60 g. Different CTA concentrations and temperatures were used.

Figure 1a shows the time evolution of the global conversion for experiments carried out at two different temperatures (60 and 70 °C) and different concentrations of chain transfer agent. As expected, when the temperature is increased the conversion rate is higher. On the other hand, the effect of the CTA on the global conversion is quite clear in spite of the weak differences between experimental and simulated values due to the CTA concentrations used in this work.

Figure 1b and 1c present the evolution of the number and weight average molecular weights versus the global conversion for experiments carried out at different temperatures and with different concentrations of transfer agent. As expected, the average molecular weights decrease when the concentration of the transfer agent increases. On the other hand they decrease when the temperature is increased.

Average particles diameter curves are plotted in figure 1d which shows that small particles are produced when the temperature is increased. As mentioned before for the global conversion, the CTA has a weak effect on the particles average diameters.

Figure 1e shows the residual fraction of styrene. Due to the difference between the reactivity ratios of butyl acrylate and styrene, styrene is more consumed during the polymerization process. The composition drifts till the total consumption of styrene. Since the initial composition ratio between styrene and butyl acrylate is not changed during the experiments, the evolution of the residual composition is almost the same for different temperatures.

Globally the results show an acceptable agreement between the simulated and experimental data.

#### 5.2. Model validation

The model was then validated using new experimental conditions. The different results obtained for a temperature of 65 °C and a CTA mass of 0.45 g are shown in figure 2. The results show good agreement. The model has been validated under semi batch conditions and the results are not presented here for the sake of brevity.

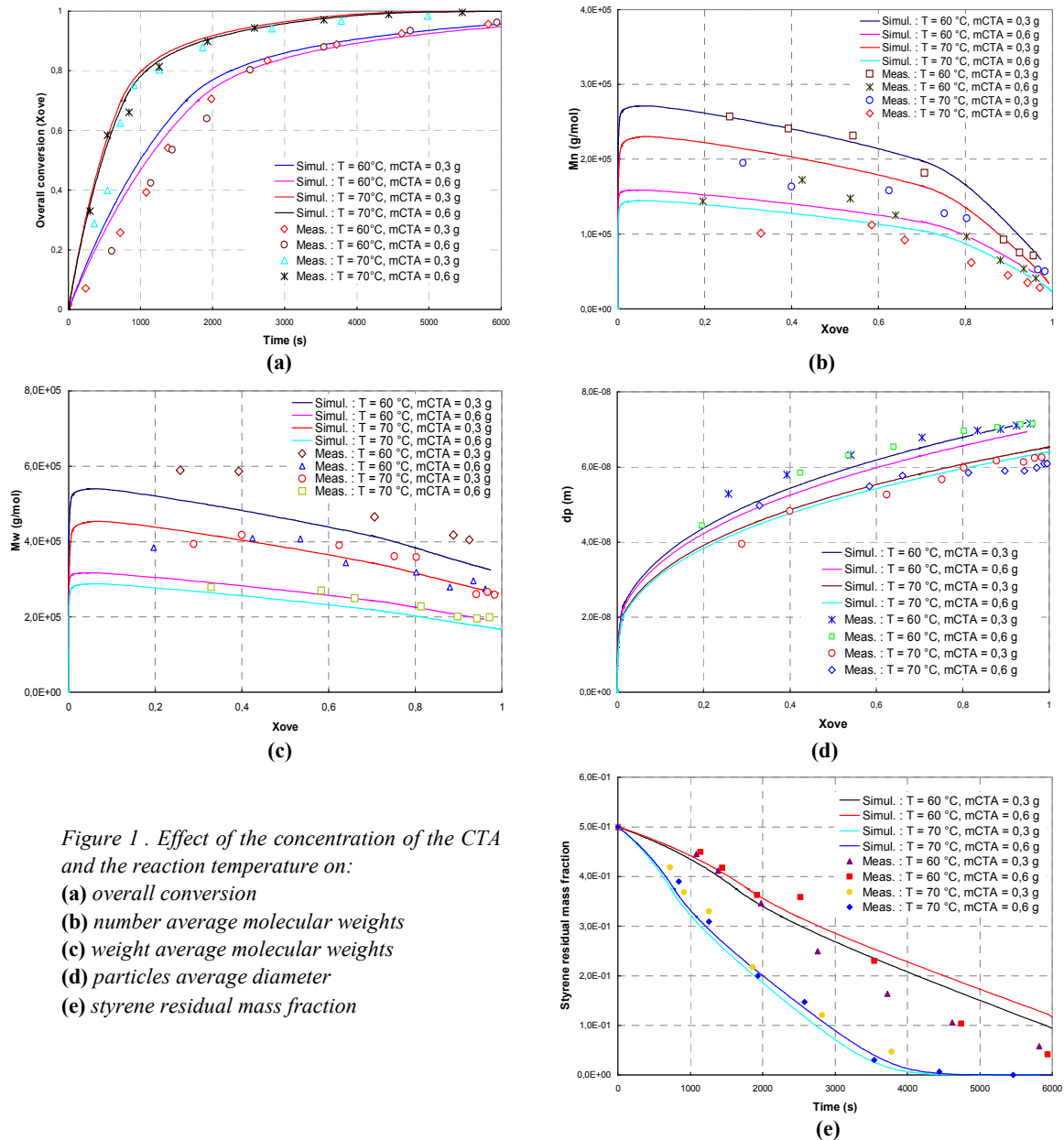


Figure 1. Effect of the concentration of the CTA and the reaction temperature on:  
**(a)** overall conversion  
**(b)** number average molecular weights  
**(c)** weight average molecular weights  
**(d)** particles average diameter  
**(e)** styrene residual mass fraction

#### 4. Conclusion

In this work, a dynamic reactor model has been developed for the batch and fed-batch emulsion copolymerization of styrene and butyl acrylate in the presence of n- C12 mercaptan as chain transfer agent. This model is based on the kinetics of the complex elementary chemical reactions occurring both in the aqueous phase and in the particles, the particle nucleation, radical absorption and desorption, and the gel and glass effects. The effect of the CTA on the kinetic of the polymerization has been investigated experimentally and included in the mathematical model by using a new approach on the desorption rate. The diffusional limitations of the CTA from the droplets were considered to improve the explanation of the efficiency of the CTA throughout the polymerization process.

A subset of the most influential parameters of the model has been distinguished using the parameter estimability approach. These parameters were estimated by minimization of the maximum likelihood criterion with well designed experiments. The good agreement between simulated and experimental data achieved in this work shows the predictive capability of the process model.

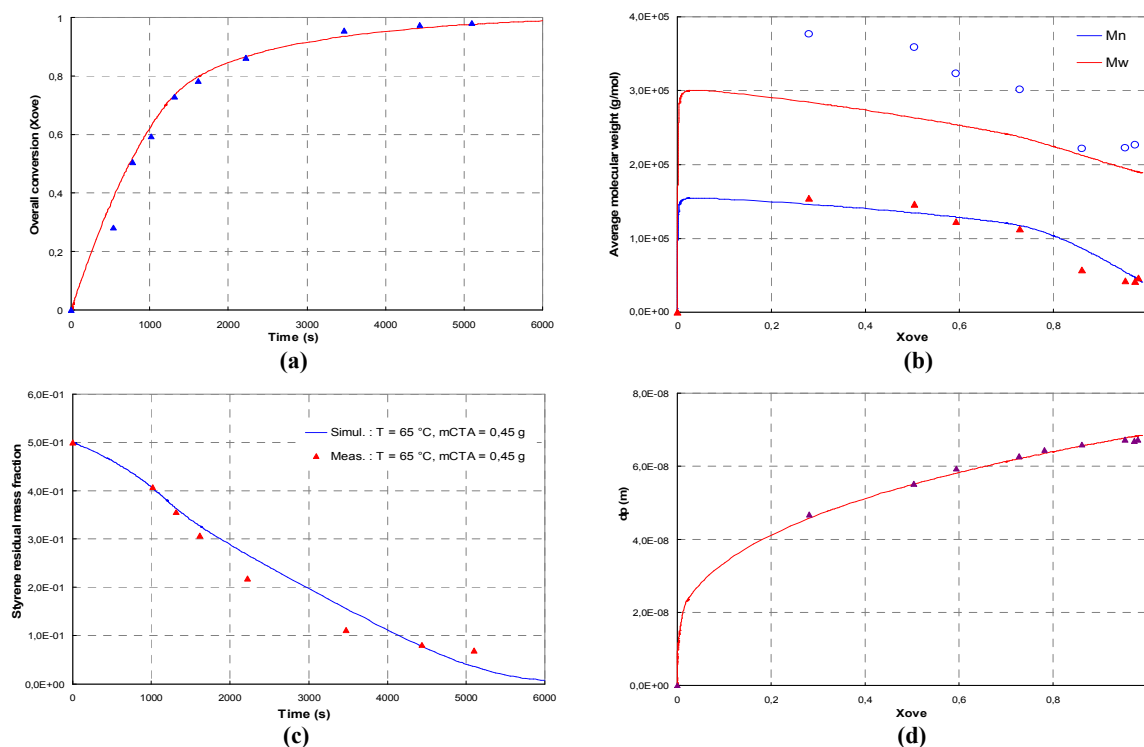


Figure 2 . validation of the process model in batch conditions (a) overall conversion, (b) number and weight average molecular weights, (c) particles average diameter (d) styrene residual mass fraction

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