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Elaboration of a tendency model and determination of optimal feed rate profiles for styrene/butyl acrylate semi-batch emulsion copolymerization reactor

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Abstract:
This paper concerns mathematical modeling and validation of a lab-scale semi-batch emulsion copolymerization of styrene and butyl acrylate in the presence of n-C12 mercaptan as transfer agent. The mathematical model is developed by using reaction rate laws available in polymerization literature. The population balance equations are based on a new approach which reduces significantly the number of the equations involved. 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 identified using a parameter estimation approach by minimizing the errors between the predicted and measured data. Some parameters are also obtained from literature. The model is then validated in order to be used to compute optimal profiles of monomers feed-rates which minimize an objective function, subject to a set of tight operational constraints.

Key words: Emulsion Copolymerization, Tendency Model, Population Balance, Parameters Estimation

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.
Molecular weight distribution (MWD), polymer microstructure, glass transition temperature (Tg), particle size distribution (PSD) and morphology are the main parameters which strongly govern the end use properties of the products (latex and polymer). For instance, the particle size distribution (PSD) is strongly correlated with rheological properties, adhesion and film-forming properties of the final products. On the other hand, MWD affects important end-use properties of the film, such as elasticity, strength, toughness, and solvent resistance. Average molecular weights are commonly controlled by means of chain-transfer agents. Although different chain-transfer agents can be used, mercaptans are by far the most important class in emulsion polymerization.

There is a rich literature on modeling emulsion polymerization processes, starting with the conventional Smith–Ewart model (1) which identified three stages in emulsion polymerization process (nucleation, particles growth and end of polymerization). The later models developed for emulsion polymerizations have varying degrees of complexity, depending upon their scope and application (2, 3). The most representative have been reviewed by Gao and Penlidis (4).

This paper deals with the elaboration of a tendency model for the emulsion copolymerization of styrene and butyl acrylate in the presence of n-C12 mercaptan as transfer agent. 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.

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 (5). 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. This approach reduces significantly the process model and gives a suitable average number of radicals per particle (\(\bar{n}\)), in conjunction with literature (6, 7).

In the next section, the features of the model will be described, highlighting the effect of the transfer agent and the novelties in the population balance. This will be followed by the description of a methodology for the parameter estimability. The subsequent section will discuss some simulation results and the validation of the model.

2. Emulsion polymerization model

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. In the case of homogenous nucleation, radicals propagate beyond their water solubility; they precipitate and are then stabilized by the available emulsifier present in the medium. In the case of the 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.
To enhance the speed of convergence, the model establishment is based on the following assumptions:

- Due to the high surfactant concentration used in this work, only micellar nucleation is considered.
- Propagation, chain transfer to monomer, transfer of monomer to transfer agent, and termination reactions in the aqueous phase are neglected.
- Chain transfer reactions to the polymer are not considered.
- Radical desorption is considered.
- The growing particles and the monomer droplets are 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

Initiation

\[ I_2 \xrightarrow{k_{I}} 2 I_{aq}^* \]

Inhibition

\[ R_{aq}^* + Z_{aq} \xrightarrow{k_{Z}} P + Z_{aq}^* \]

Nucleation

\[ R_{aq}^* + \text{micelle} \xrightarrow{k_N} \text{particle} + R_i^* \]

Radical absorption

\[ R_{aq}^* + \text{particle} \xrightarrow{k_p} \text{particle} + R_i^* \]

2.1.2. In the organic phase (particles)

Propagation

\[ R_i^* + M_j \xrightarrow{k_{M}} R_j^* \]

Termination by combination

\[ R_i^* + R_j^* \xrightarrow{k_{k}} P \]

Termination by disproportionation

\[ R_i^* + R_j^* \xrightarrow{k_{k'}} 2P \]

Inhibition

\[ R_i^* + Z_p \xrightarrow{k_{Z}} P + Z_p^* \]

Transfer to monomers

\[ R_i^* + M_j \xrightarrow{k_{M'}} P + R_j^* \]

Transfer to transfer agent

\[ R_i^* + TA_p \xrightarrow{k_{TA}} P + TA_p^* \]

Radical desorption

\[ R_i^* \xrightarrow{k_{desk}} R_{aq}^* \]

2.2. Reaction Rates

2.2.1. Initiator decomposition
The initiator is consumed by thermal decomposition in the aqueous phase with the following reaction rate

\[ R_j = k_j I \]  \quad (1)  

where \( I \) is the total number of moles of initiator in the aqueous phase.

2.2.2. Inhibition
The inhibitor, \( Z \), is consumed through reactions with radicals, in the aqueous phase and in the particles. The corresponding rates of consumption are as follows
• In the aqueous phase:

\[ R_{aqi} = \varepsilon k_{cpi} \frac{Z_{aq} R_{aqi}}{V_{aq}} \]  

(2)

• In the latex particles:

\[ R_{zpi} = k_{zpi} \frac{Z_{p} N_{p} \bar{\pi} P_{i}}{V_{p}} \]  

(3)

where \( \varepsilon k_{cpi} \) and \( k_{zpi} \) are the inhibition coefficient rates in the aqueous phase and in the latex particles for a radical \( i \), respectively, \( V_{aq} \) and \( V_{p} \) are the total volumes of the aqueous phase and the latex particles, \( Z_{aq} \) and \( Z_{p} \) are the total number of moles of inhibitor in the particles and in the aqueous phase, respectively, \( R_{aqi} \) is the total number of moles of free radicals (ended by a monomer unit \( i \)) in the aqueous phase, \( N_{p} \) is the number of particles expressed by the total number of moles, \( P_{i} \) is the fraction of free radicals ended by a monomer unit \( I \) in the particles, \( \bar{\pi} \) is average number of radicals in a particle.

2.2.3. Transfer agent consumption

Only reactions with transfer agent in the particles are considered. The corresponding rate is given by:

\[ R_{zpi} = k_{TAp}, \frac{T_{Ap} N_{p} \bar{\pi} P_{i}}{V_{p}} \]  

(4)

where \( T_{Ap} \) is the total number of moles of the transfer agent in the particles and \( k_{TAp} \) is the transfer agent rate coefficient.

2.2.4. Micellar Nucleation

The micellar nucleation rate is given by:

\[ R_{N} = k_{N} \frac{N_{mic} R_{aq} d_{mic}}{V_{aq}} \]  

(5)

where \( N_{mic} \) is the total moles number of micelles, \( d_{mic} \) is the micellar diameter, \( k_{N} \) is the nucleation rate coefficient given by:

\[ k_{N} = \delta k_{cp} \quad \delta = \sum_{i=1,2} \delta_{i} f_{0i} \]  

(6)

where \( \delta \) is the ratio between the nucleation rate constant and the capture rate constant for radicals ending with monomer \( i \), \( \delta \) is the overall ratio of nucleation and capture rate coefficient, \( f_{0i} \) is the initial molar fraction of monomer \( i \) in the reactor, \( k_{cp} \) is the capture rate coefficient.

2.2.5. Radical Absorption

The classical absorption rate is given by:

\[ R_{absi} = k_{f} \delta_{m} \left( \frac{R_{aqi}}{V_{aq}} - \frac{N_{p} \bar{\pi} P_{i} \omega_{i}}{V_{p} m_{di}} \right) \pi d_{i}^{2} N_{p} N_{A} \]  

(7)
where $d_p$ is the average particle diameter, $N_A$ is Avogadro’s number, $\delta_{mi}$ is the ratio of the transfer resistance in the aqueous phase to the overall transfer resistance of free radicals ended by monomer unit $i$, $\omega_i$ is the fraction of radicals ended by monomer $i$ formed only by one monomer unit. $\delta_{wi}$ is the ratio of transfer resistance in aqueous phase on overall transfer resistance of free radicals ended by monomer unit $i$, $k_i$ is the transfer coefficient of free radicals formed by 1 monomer unit $i$

Since the particles have small diameters the corresponding Sherwood number is equal to 2:

$$Sh = \frac{k_i d_p}{D_{wi}} = 2$$  \hspace{1cm} (8)

where $D_{wi}$ is the diffusion coefficient of the free radicals ended by monomer unit $i$ in the aqueous phase.

The absorption rate could be written as follows:

$$R_{absi} = k_{cpi} \left( \frac{R_{aqi}}{V_{aq}} - \frac{N_p \bar{\pi} P_i \omega_i}{V_p m_{di}} \right) N_p d_p$$  \hspace{1cm} (9)

with $k_{cpi} = 2\pi N_A D_{wi} \delta_{mi}$

The absorption rate is the sum of the capture and desorption rates which are respectively given by:

$$R_{cpi} = k_{cpi} \frac{R_{aqi}}{V_{aq}} N_p d_p$$  \hspace{1cm} (10)

$$R_{desi} = k_{desi} \frac{N_p \bar{\pi} \chi_i}{V_p} N_p d_p$$  \hspace{1cm} (11)

such as: $k_{desi} = \frac{k_{cpi}}{m_{di}}$ and $\chi_i = P_i \omega_i$  \hspace{1cm} (12)

where $k_{desi}$ is the desorption rate coefficient of the radical ended by a monomer $i$.

2.2.6. Propagation

The propagation rate of monomer $j$ with a radical ended by $i$ is given by:

$$R_{prji} = k_{pij} \frac{M_{pi}}{V_p} R_{pi}$$  \hspace{1cm} (13)

where $M_{pj}$ is the total mole number of monomer $j$ in the particles, $R_{pi}$ is the total mole number of radicals ended by monomer $j$ in the particles, $k_{pij}$ is the propagation rate coefficient between a monomer $j$ and a free radical ended by a monomer $i$.

The total consumption rate of monomer $j$ through propagation is:

$$R_{p lj} = R_{prji} + R_{prjj}$$

$$= k_{pj} \frac{M_{pj}}{V_p} N_p \bar{\pi}$$  \hspace{1cm} (14)
such as: \( k_{pj} = \sum_{i=1,2} k_{pij} P_i \), \( \sum_{i=1}^2 P_i = 1 \)

The reactivity ratio is given by:

\[
r_{pj} = \frac{k_{pji}}{k_{pj}}
\]

The global propagation rate is finally as follows,

\[
R_{pr} = R_{pr1} + R_{pr2} = N_p \bar{\eta} \sum_{i=1,2} \sum_{j=1,2} k_{pij} \frac{M_{pj}}{\bar{V}_p} P_i
\]

2.2.7. Transfer to Monomer

As for propagation, the transfer to monomer rate of monomer \( j \) with a growing radical ended by monomer \( i \) is given by:

\[
R_{trmj} = k_{trmj} \frac{M_{pj}}{\bar{V}_p} R_{pi}
\]

where \( k_{trmj} \) is the transfer rate coefficient between monomer \( j \) and a growing radical ended by monomer \( i \).

The total consumption rate of monomer \( j \) by transfer is then:

\[
R_{trmj} = R_{trmj} + R_{trmi}
\]

\[
= k_{trmj} \frac{M_{pj}}{\bar{V}_p} N_p \bar{\eta}
\]

such as:

\[
k_{trmj} = \sum_{i=1,2} k_{trmj} P_i
\]

The global transfer rate is finally given as follows:

\[
R_{trm} = R_{trm1} + R_{trm2} = N_p \bar{\eta} \sum_{i=1,2} \sum_{j=1,2} k_{trmj} \frac{M_{pj}}{\bar{V}_p} P_i
\]

The transfer to monomer rate coefficients \( k_{trmj} \) and \( k_{trmj} \) are defined, according to the corresponding homopolymerization transfer rate coefficients:

\[
k_{trmj} = k_{trmj} = \sqrt{k_{trmj} k_{trmj}}
\]

2.2.8. Termination

The termination rate between a radical ended by monomer \( i \) and a radical ended by monomer \( j \) is given by:

\[
R_{ij} = k_{ij} P_i P_j \frac{N_p^2}{\bar{V}_p} \bar{\eta}
\]

with \( \bar{\eta} = \sum_{h=2}^{\infty} h(h-1) \nu_h \), \( \sum_{h=0}^{\infty} \nu_h = 1 \), \( \sum_{h=0}^{\infty} h \nu_h = \bar{\eta} \)
where $k_{Tij}$ is the termination rate coefficient between two radicals ended by $i$ and $j$, $\bar{n}$ is the average number of pairs of radicals in a particle, $n$ is the number of free radicals in a particle, $v_h$ is the fraction of particles with $h$ free radicals.

The global termination rate can be defined as follows,

$$R_T = k_T \frac{N^2}{V_p}$$

with:

$$k_T = \sum_{i=1}^{2} \sum_{j=1}^{2} k_{Tij} P_i P_j$$

where $k_{Tij}$ is the overall termination rate coefficient.

According to the hypothesis assuming that the kinetic coefficients do not depend on the chain length, it is acceptable to consider that the termination rate coefficients between a radical ended by a monomer unit $i$ and a radical ended by a monomer unit $j$ are equal.

$$k_{Tij} = k_{Tji}$$

These coefficients can be calculated using the homopolymerization termination coefficients of the monomers concerned,

$$k_{Tij} = k_{Tji} = \sqrt{k_{Tii} k_{Tjj}}$$

The ratio between the rate of termination by disproportionation and the rate of termination by combination is defined by a coefficient $\tau$. Since the global termination rate is the sum of both mechanisms, the rates of termination by combination and by disproportionation are given respectively as follows

$$R_{TC} = \frac{R_T}{1 + \tau} \quad R_{TD} = \frac{\tau R_T}{1 + \tau}$$

2.2.9. Number of Radicals per Particle

In order to evaluate the reaction rates, one must also know the average number of radicals per particle. This was obtained by performing balances on the number of particles containing, at any instant, $j$ radicals. From the other hand and since the transfer agent reactions provide free radicals, they have no effect on the distribution of the radicals in the particle.

The balance equations of particles containing $j$ radicals are as follows:

$$\frac{d(N_p v_0)}{dt} = -R_{p} v_0 + \frac{3 v_R}{n} v_2 + \left(R_{2p} + R_{des}\right) v_1$$

$$\frac{d(N_p v_j)}{dt} = R_{p} v_j + 3 \frac{v_R}{n} v_3 - R_{p} v_1 + (R_{2p} + R_{des}) \left(\frac{2v_2 - v_j}{n}\right)$$

$$\frac{d(N_p v_{j+2})}{dt} = R_{p} (v_{j+2} - v_j) + \frac{R_{T}}{2n} \left((j+2)(j+1)v_{j+2} - j(j-1)v_j\right) + \left(R_{2p} + R_{des}\right) \left(\frac{(j+1)v_{j+1} - jv_j}{n}\right)$$

To determine the average number of radicals per particle ($\bar{n}$) and the average number of pairs ($\bar{n}$) necessary for the calculation of the termination rates, a maximum number of radicals per particle ($j_{\text{max}}$) was fixed (8). This approach implies to deal with $j_{\text{max}}$ differential
equations where the accuracy of the results depends on the choice of $j_{\text{max}}$. To avoid this procedure, we suppose that the fraction of particles containing $j$ free radicals follows Poisson’s law. Thanks to this approach, we obtain two differential equations as follows:

\[
\frac{d(N_p \tilde{n})}{dt} = R_{\lambda} + R_{zp} - (R_{zp} + R_T + R_{\text{des}}) \tag{26}
\]

\[
\frac{d(N_p \tilde{n})}{dt} = 2R_{zp} \tilde{n} - \left(\frac{2\tilde{n}}{\tilde{n} + 1}\right)R_T - \frac{2\tilde{n}}{\tilde{n}}(R_{zp} + R_{\text{des}}) \tag{27}
\]

where $\tilde{n} = \tilde{n} \left[\frac{\lambda \left(1 + \frac{\tilde{n}}{\tilde{n}} \right) + \frac{\tilde{n}}{\tilde{n}}}{\lambda + 2}\right]$ and $\lambda = \frac{\tilde{n}}{2\tilde{n}} - 1 + \sqrt{1 + \frac{\tilde{n}^2}{2\tilde{n}^2}} \tag{28}$

2.3. Surfactant Partition

The surfactant is distributed between the particles, droplets, aqueous phase and micelles. The total number of moles of surfactant in the reactor is given by:

\[
S = S_{\text{aq}} + S_{\text{mic}} + S_p + S_d \tag{29}
\]

where $S_p$, $S_{\text{mic}}$, $S_d$ and $S_{\text{aq}}$ are the number of moles of surfactant on the particles, in the micelles, on the droplets and dissolved in the aqueous phase, respectively.

\[
S_{\text{mic}} = N_{\text{mic}} n_s, \quad S_d = \frac{6V_d}{d_a a_s}, \quad S_p = \frac{6V_p}{d_p a_s} \tag{30}
\]

where $N_{\text{mic}}$ is the total number of moles of micelles, $n_s$ is the number of surfactant molecules per micelle, $a_s$ the surface covered by one mole of surfactant, $d_a$ is the average droplets diameter.

The micelles disappeared when the concentration of surfactant in the aqueous phase go down the critical micelle concentration. Thus:

If \( S_{\text{aq}} < C_{MC} \cdot V_{\text{aq}} \) then \( N_{\text{mic}} = 0 \) \tag{31}

Otherwise \( N_{\text{mic}} = \frac{S - (S_d + S_p + C_{MC} \cdot V_{\text{aq}})}{n_s} \) \tag{32}

where $C_{MC}$ is the critical micelle concentration.

2.4. Influence of the temperature

The effect of the temperature on the kinetic constants is expressed by an Arrhenius’ law. On the other hand and according to Gilbert’s assumptions (9), the specific area of a surfactant molecule depends on the medium temperature and could be expressed by an exponential formula similar to Arrhenius’ law

\[
a_s(T) = a_s(T_o) \exp \left[-E_a \left(\frac{1}{T} - \frac{1}{T_o}\right)\right] \tag{33}
\]
where $E_v$ is the thermal expansion factor of a surfactant molecule.

2.5. Initiator efficiency
The initiator efficiency, $f$, can strongly depend on the type and on the monomer concentration in the reactor (7). Usually, efficiencies of 30% and 100% are attributed to persulphates, when they are used, respectively, with styrene and butyl acrylate. In order to describe the transition between these values, the following formula was used:

$$f = \exp\left(-f_a f_b\right)$$

where $f_a$ is an adjustment parameter and $f_b$ is the fraction of styrene in the reactor.

2.6. Glass and Gel Effects
The glass and gel effects equations used for propagation and termination reactions were those proposed by Nomura (6).

$$k_{ij} = k_{ij}^0 \left\{ \begin{array}{ll} k_{ij}^0 & \text{if } W_p \leq 0.7 \\ k_{ij}^0 \exp\left(-a_i^G (W_p - 0.7)\right) & \text{if } W_p > 0.7 \\ k_{ij}^0 \exp\left(-b_i^G (W_p - 0.32)\right) & \text{if } 0.32 < W_p \leq 0.8 \\ k_{ij}^0 \exp\left(-b_i^G (0.8 - 0.32) - b_i^G (W_p - 0.8)\right) & \text{if } W_p > 0.8 \end{array} \right. \quad (35)$$

where $b_i^G$ and $b_i^G$ are the gel and glass coefficients of termination reaction respectively and $W_p$ is the mass fraction of polymer in the particles.

$$W_p = \frac{\sum (M_{Ti} - M_i - R_{aq}) M_M}{\sum (M_{pi} + M_{Ti} - M_i - R_{aq}) M_M^i} \quad (36)$$

where $M_{Ti}$ is the total number of moles of monomer $i$ put in the reactor at time $t$, $M_i$ is the total number of moles of monomer $i$ left in the reactor at time $t$ and $M_M^i$ is the molecular weight of the monomer $i$.

2.7. Species partition
The partition of the different species between the aqueous phase, particles and droplets is needed to evaluate the reaction rates. This has been performed using the method of the partition coefficients developed by Gugliotta et al (10). Considering the thermodynamic equilibrium we obtain the following algebraic equations:

$$\begin{align*}
V_p &= \frac{\sigma}{\sigma - 1} V_{pol} \\
\frac{1}{\sigma} &= \rho_z (V_p - V_d \sigma - V_{aq} K_{pz}) + \frac{T_A M_M^{TA}}{\rho_{TA} (V_p - V_d \sigma - V_{aq} K_{TA})} + \sum_{i=1,2} \frac{M_i M_M^i}{\rho_i (V_p - V_d \sigma - V_{aq} K_{pi})}
\end{align*} \quad (37)$$
where $\sigma, K_{pZ}, K_{pTA}, K_{pi}$ are the partition coefficients and $V_{pol}$ is total polymer volume defined as follows,

$$V_{pol} = \sum_{i=1,2} (M_{Ti} - M_{i} - R_{aqi}) \frac{M^i_M}{\rho_i}$$

(38)

When the droplets disappeared the equilibrium algebraic equations become

$$\begin{cases}
V_d = 0 \\
1 - \frac{V_{pol}}{V_p} = \frac{Z M^Z_M}{\rho_Z (V_p - V_{aq} K_{pZ})} + \frac{TA M^TA_M}{\rho_{TA} (V_p - V_{aq} K_{pTA})} + \sum_{i=1,2} \frac{M_i M^i_M}{\rho_i (V_p - V_{aq} K_{pi})}
\end{cases}$$

(39)

On the other hand the volume balance gives:

$$V_{aq} = V_R - V_d - V_p$$

(40)

By solving the later algebraic equations we get partition of the species needed as follows

$$M^i_p = \frac{M_i V_p}{V_p + V_d \sigma + V_{aq} K_{pi}}$$

(41)

$$Z_p = \frac{V_p + V_d \sigma + V_{aq} K_{pZ}}{Z V_p}$$

(42)

$$TA_p = \frac{TA V_p}{V_p + V_d \sigma + V_{aq} K_{pTA}}$$

(43)

2.8. Molecular weight distribution

The physical and mechanical properties of polymers depend strongly on their molecular weight distributions (MWD). Therefore, one of the aims of the model was to determine this characteristic. This was achieved by using the method of the moments developed by Villermaux and Blavier (11). To apply this method, a description of the evolution of the instantaneous distributions of the degree of polymerization of both macroradicals and macromolecules is required.

The $k^{th}$ normalised moments of the macroradicals and the macromolecules are given by:

$$\lambda_k = \sum_{j=1}^{\infty} j^k \bar{w}_j$$

$$L_k = \sum_{j=1}^{\infty} j^k w_j$$

(44)

where $\bar{w}_j$ and $w_j$ are the fraction of macroradicals and macromolecules with a degree of polymerization $j$, with

$$\sum_{j=1}^{\infty} \bar{w}_j = 1$$

$$\sum_{j=1}^{\infty} w_j = 1$$

(45)
The corresponding balance equations are:

\[
\begin{align*}
\frac{d(N_p \bar{n})}{dt} &= R_N + R_{cp} - (R_{zp} + R_T + R_{des}) \\
\frac{d(N_p \bar{\lambda}_1)}{dt} &= R_N + R_{cp} - R_{des} + R_p + (R_{rm} + R_T) (1 - \lambda_i) - (R_{zp} + R_T) \lambda_i \\
\frac{d(N_p \bar{\lambda}_2)}{dt} &= R_N + R_{cp} - R_{des} + R_p (1 + 2 \lambda_2) + (R_{rm} + R_T) (1 - \lambda_2) - (R_{zp} + R_T) \lambda_2 \\
\frac{d(N_m)}{dt} &= R_{zp} + R_{rm} + R_T + R_{TAp} + \frac{R_c}{2} \\
\frac{d(N_m L_1)}{dt} &= (R_{zp} + R_{rm} + R_T + R_{TAp}) \lambda_i \\
\frac{d(N_m L_2)}{dt} &= (R_{zp} + R_{rm} + R_T + R_{TAp}) \lambda_2 + R_{TC} \left( \lambda_2 + \lambda_i \right)
\end{align*}
\]

Therefore, the number and weight average molecular weights, \( \bar{M}_n \) and \( \bar{M}_w \), can easily be calculated by using the following equations:

\[
\bar{M}_n = \bar{M} L_i \quad \bar{M}_w = \bar{M} \frac{L_i}{L_j}
\]

where \( \bar{M} \) is the average molecular weight of the monomeric unit given by

\[
\bar{M} = \sum_{i=1,2} \frac{(M_{Ti} - M_i - R_{aqi}) M^i}{(M_{Ti} - M_i - R_{aqi}) M^i}
\]

**2.9. Glass transition temperature**

The control of the product quality during emulsion polymerization requires the monitoring of a large set of parameters related to end-use properties. Some of these properties are often described through distributed characteristics such as the molecular weight distribution (MWD) and/or the copolymer composition distribution (CCD). This is, for example, the case for the glass transition temperature, \( T_g \), which depends strongly on the microstructure of the macromolecules, particularly for copolymers. To complete the model, the glass transition temperature is evaluated according to Fox’s equation.

\[
\left[ T_g + \frac{a}{\bar{M}_n} \right]^{-1} = \sum_{i=1,2} W_i \frac{T_{gi}}{T_{gi}}
\]

where \( a \) is an adjustment parameter, \( T_{gi} \) is the glass transition temperature of the homopolymer of monomer \( i \) and \( W_i \) is the mass fractions of monomer \( i \) in the copolymer defined as:

\[
W_i = \frac{(M_{Ti} - M_i - R_{aqi}) M^i}{\sum_{i=1,2} (M_{Ti} - M_i - R_{aqi}) M^i}
\]
2.10. Conversion and Copolymer Composition

The global mass conversion is:

\[ X = \frac{\sum_{i=1,2}(M_{Ti} - M_i)M'_M}{\sum_{i=1,2}M_{Ti}M'_M} \]  \hspace{1cm} (50)

The residual mass fraction of monomer i is

\[ F_i = \frac{M_i M'_M}{\sum_{i=1,2}M_i M'_M} \]  \hspace{1cm} (51)

2.11. Mass and population balance

The balance equations used to describe the semi-continuous emulsion copolymerization reactor are:

**Volume balance**

\[ \frac{dV_f}{dt} = Q_f + \sum_{i=1,2} \left( \frac{1}{\rho_{pi}} - \frac{1}{\rho_i} \right) M'_i \left( R_{pi} + R_{rau} \right) \]  \hspace{1cm} (52)

**Monomers**

\[ \frac{dM_i}{dt} = -R_{pi} - R_{rau} + Q_f \left[ M_f \right] \]  \hspace{1cm} (53)

\[ \frac{dM_{Ti}}{dt} = Q_f \left[ M_f \right] \]  \hspace{1cm} (54)

**Initiator**

\[ \frac{dI_f}{dt} = -R_d + Q_f \left[ M_f \right] \]  \hspace{1cm} (55)

**Inhibitor**

\[ \frac{dZ}{dt} = -\left( R_{zp1} + R_{zp2} \right) + Q_f \left[ M_f^z \right] \]  \hspace{1cm} (56)

**Chain transfer Agent**

\[ \frac{dT_A}{dt} = -R_{T_Ap1} - R_{T_Ap2} + Q_f \left[ M_{fT_A} \right] \]  \hspace{1cm} (57)

**Surfactant**

\[ \frac{dS_f}{dt} = Q_f \left[ M_f^s \right] \]  \hspace{1cm} (58)

**Number of particles:**

\[ \frac{dN_p}{dt} = R_N \]  \hspace{1cm} (59)

**Radicals in the Particles**

\[ \frac{dR}{dt} = \left( R_N + R_{rp} \right) f_{aq1} - R_{p12} - R_{p21} - R_{Zp} - R_{T_A} - R_{des} - \left( R_{T_f11} + R_{T_f12} \right) \]  \hspace{1cm} (60)
Radicals formed only by one monomer (necessary for the radical desorption)

\[
\frac{dR_i}{dt} = \left( R_N + R_{cp} \right) f_{aq2} - R_{p21} + R_{p12} - R_{tm21} + R_{tm12} - R_{dpl2} - \left( R_{T22} + R_{T21} \right)
\]

Radicals formed only by one monomer (necessary for the radical desorption)

\[
\frac{d(N_p \bar{X}_1)}{dt} = \left( R_N + R_{cp} \right) f_{aq1} + R_{tm12} + R_{tm21} + R_{dpl1} - \left( R_{tm21} + R_{tm11} + R_{p11} + R_{p12} + R_{zpl1} + R_{rpl2} \right) X_1 - \left( R_{T11} + R_{T12} \right) X_1
\]

\[
\frac{d(N_p \bar{X}_2)}{dt} = \left( R_N + R_{cp} \right) f_{aq1} + R_{tm12} + R_{tm21} + R_{dpl2} - \left( R_{tm12} + R_{tm22} + R_{p22} + R_{p21} + R_{TAp1} + R_{TAp2} \right) Z_2 - \left( R_{T11} - R_{T12} \right) Z_2
\]

where \( Q_f \) is the feed rate (monomers, inhibitor, transfer agent and surfactant), \( \rho_{pi} \) the density of the homopolymer \( i \), \( [M_{f1}], [M_{f2}], [M_{f3}], [M_{f4}] \) the concentration of monomer \( i \), initiator, inhibitor, surfactant and transfer agent in the feed.

3. Estimability analysis of the parameters

A first step, prior to parameter identification is to evaluate the estimability of the model parameters and to determine the subset of potentially estimable parameters.

A non-linear multi-response model described by ordinary differential equations (ODEs) can be represented as follows:

\[
y_{rn} = \eta_r(x, t_n, z_n, p) + \varepsilon_{rn} \quad r = 1, 2, \ldots R \quad n = 1, 2, \ldots N
\]

where \( N \) is the number of observations, \( R \) is the number of response variables and \( t_n \) is the time corresponding to the \( n \)th observation, \( y_{rn} \) is the measured value of the \( n \)th observation of the \( r \)th response variable; \( \eta_r \) is the corresponding expected value of that response variable determined by the settings of the operating variables, \( z_n \), and specified values of the model parameters, \( p \). \( x \) is a vector of state variables, which are functions of time, initial conditions, inputs and parameters, \( \varepsilon_{rn} \) is a random error term.

The parametric sensitivity coefficients are defined as follows:

\[
\frac{\partial \eta_r(x, t_n, z_n, p)}{\partial p_i} \quad i = 1, 2, \ldots n_p
\]

Note that sensitivity coefficients are dependent on the parameter considered and the time of the corresponding observation \( t_n \). These coefficients are linearly independent for a particular set of parameters, \( \hat{p} \), then there exists only one unique set of optimal parameter values. If, on the other hand, the sensitivity functions are linearly dependent at all values of \( p \), then the model parameters are non-estimable (5).

A sensitivity coefficient matrix, \( Z \), could then be formed from the individual coefficients as follows:
There are two features that govern the estimability of a parameter: the strong influence of this parameter on one or more of the measured responses and the correlation between the effects of that parameter on model predictions and the corresponding effects of all other estimable.

The first feature can be determined by examining the magnitude of the column of $Z$ that corresponds to the particular parameter. The second feature demands that we examine whether the columns corresponding to the set of estimable parameters are linearly dependent. This requires some form of orthogonalization algorithm explained by Yao et al., (5).

This approach has been applied to the parameter identification of 32 parameters which gave a subset of the most influential 18 parameters. The rest of parameters have been set to their nominal values according to the literature (8).

4. Experimental part

4.1. Compounds

Monomers: Styrene (STY) and butyl acrylate (ABu) previously stabilized with 15 ppm of 4-tertbutylcatechol (inhibitor)
Initiator: Ammonium persulphate ($\text{(NH}_4\text{)}_2\text{S}_2\text{O}_8$).
Surfactant: REWOPOL SBFA 50 (sulfo succinate polyetherglycol and alcohol disodium)
Chain transfer agent: n-C12 mercaptan.

4.2. Equipment

The reactor used was a 1 l jacketed glass batch reactor equipped with a stirrer, a reflux condenser, a cryostat, and an inlet system for nitrogen. Samples were withdrawn from the reactor at appropriate time intervals and polymerization was short stopped with hydroquinone.

4.3. Characterization of Latex and Macromolecules

In order to follow the polymerization, analytical methods have been developed to obtain experimental data.

The global monomer conversion was determined gravimetrically using a Mettler Toledo HG 53 halogen moisture analyzer.
For a better control of the consumption of each monomer during polymerization, a more precise titration of the monomers was made using a DELSI NERMAG DN 200 gas chromatograph equipped with a capillary column (length :10 m ; diameter : 0.53μm) and with a stainless precolumn filled up with glass fiber. Analyses were carried out under the following operating conditions:
- Injection temperature : 175°C
- Column temperature : 80°C
- Detector temperature : 175°C
- Gas vector : Helium ; flow-rate : 3ml.min⁻¹

The average particles diameters were determined by use of a Malvern 4700 quasi-elastic light scattering apparatus. After dilution of the samples with deionized water, the unswollen particles diameters were measured.

The average molecular weights were determined by size exclusion chromatography (SEC) using a double detection: a multi-angle laser light scattering (MALLS) apparatus (Dawn DSP-F) and a differential refractometer (Waters 410, Millipore). Elutions were performed at 35°C with tetrahydrofuran (THF) containing di-tertiary-butyl-2.6 methyl-4 phenol as stabilizer. The flow-rate was 1 ml.min⁻¹. The concentration of the polymer solutions and the corresponding injected volume were 1 g.l⁻¹ and 25 μl respectively. Prior to chromatography, THF and polymer solutions were passed through a Nylon filter of 0.45 μm porosity. The SEC assembly consisted of a degasser, a Waters 510, Millipore pump, a U6K, Millipore injector, a precolumn, two chromatographic columns assembled in series and filled with linear ultragel and an electric oven to control the temperature of the columns.

Data from the two detectors were acquired and computed by use of the software Astra from Wyatt Technology which allowed determining the molecular weight distribution and the number and weight average molecular weights of the samples.

5. Results and Discussion
5.1. Parametric Identification
The aim of the model was to predict satisfactorily and simultaneously the global conversion (X), the fraction of residual styrene (Fr₂), the number- and weight-average molecular weights (Mₙ, Mₙ�) and the average particle diameter (dₚ). The model parameters were determined by minimization of the maximum likelihood criterion, J, with the experimental data.

$$J = N_x \cdot \ln \left( \sum_{\text{données}} \left( X_{\text{exp}} - X_{\text{mod}} \right)^2 \right) + N_{d_p} \cdot \ln \left( \sum_{\text{données}} \left( d_{\text{exp}} - d_{\text{mod}} \right)^2 \right) + N_{M_n} \cdot \ln \left( \sum_{\text{données}} \left( M_{n\text{exp}} - M_{n\text{mod}} \right)^2 \right)$$

$$+ N_{M_w} \cdot \ln \left( \sum_{\text{données}} \left( M_{w\text{exp}} - M_{w\text{mod}} \right)^2 \right) + N_{Fr_2} \cdot \ln \left( \sum_{\text{données}} \left( Fr_{2\text{exp}} - Fr_{2\text{mod}} \right)^2 \right)$$

where $X_{\text{exp}}, d_{\text{exp}}, M_{n\text{exp}}, M_{w\text{exp}}, Fr_{2\text{exp}}$ the measured values and $X_{\text{mod}}, d_{\text{mod}}, M_{n\text{mod}}, M_{w\text{mod}}, Fr_{2\text{mod}}$ the model predicted values. N is the number of measurements of a given variable.

The subsets of the eighteen parameters identified were simultaneously obtained by the minimization of J using a genetic algorithm using DASSL to solve model problem.
5.1.1. Associated results

The measured data were obtained from several batch emulsion copolymerizations. 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 chain transfer agent concentrations and temperatures were used.

Figure 1 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 chain transfer agent concentration has no effect on the experimental conversions where the simulated data are slightly different for lowest temperature (60 °C). Figure 2 and 3 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 4 which shows that small particles are produced when the temperature is increased.

![Graph showing average particles diameter curves](image)

**Fig.5. Styrene residual fraction**

Figure 5 shows the residual fraction of styrene. Due to the difference between the reactivity ratios of butylacrylate 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 chain transfer agent mass of 0.45 g are shown in figures 6, 7, 8, 9, and 10.

![Graph showing overall conversion](image)

**Fig.6. Overall conversion**

![Graph showing number average molecular weight](image)

**Fig.7. Number average molecular weight**
Fig. 8. Weight average molecular weight
Fig. 9. Average particles diameter
Fig. 10. Styrene residual fraction

6. Conclusion

In this work, a dynamic reactor model has been developed for the batch and semi 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. A subset of the most influential parameters of the model has been distinguished using the parameter estimation approach. These parameters were estimated by minimization of the maximum likelihood criterion with well designed experiments. Good agreement between simulated and experimental data was achieved.
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Symbols
\( a \) : Flory adjustment parameter (K kg kmol\(^{-1}\))
\( a_s \) : surface covered by one kmole of surfactant. (m\(^2\) kmol\(^{-1}\))
\( b^{Gl} \) : Glass coefficient of termination reaction
\( b^{Ge} \) : Gel coefficient of termination reaction
\( d_d \) : average droplets diameter (m)
\( d_{mic} \) : average micelles diameter (m)
\( d_p \) : average particles diameter (m)
\( D_{wi} \) : diffusion coefficient of the free radicals \( i \) in the aqueous phase (m\(^2\) s\(^{-1}\))
\( E_e \) : thermal expansion factor of a surfactant molecule.
\( f \) : free radical efficiency in aqueous phase
\( f_b \) : fraction of styrene in the reactor
\( f_{0i} \) : initial molar fraction of monomer \( i \) in the reactor
\( F_i \) : residual mass fraction of monomer \( i \)
\( h \) : number of free radicals in particular particle.
\( I \) : total number of moles of initiator in the aqueous phase (kmol)
\[ k_{cp} \] : capture rate coefficient of free radicals from monomer \( i \) by particles (m\(^2\) kmol\(^{-1}\) s\(^{-1}\))
\[ k_d \] : initiator decomposition constant (s\(^{-1}\))
\[ k_{des} \] : desorption rate coefficient of the radical ended by a monomer \( i \) (m\(^2\) kmol\(^{-1}\) s\(^{-1}\))
\[ k_i \] : transfer coefficient of free radicals formed by one monomer unit \( i \) (m s\(^{-1}\))
\[ k_N \] : nucleation rate coefficient (m\(^2\) kmol\(^{-1}\) s\(^{-1}\))
\[ k_{pij} \] : propagation rate coefficient of monomer \( j \) with free radical ended by \( i \) (m\(^3\) kmol\(^{-1}\) s\(^{-1}\))
\[ K_{pi} \] : partition coefficient of monomer \( i \) between the droplets and the aqueous phase
\[ K_{pTA} \] : partition coefficient of the transfer agent between the droplets and the aqueous phase
\[ K_{pZ} \] : partition coefficient of the inhibitor between the droplets and the aqueous phase
\[ k_{rmij} \] : transfer to monomer rate coefficient (radicals ended by \( i \)-monomer \( j \)) (m\(^3\) kmol\(^{-1}\) s\(^{-1}\))
\[ k_{zp} \] : inhibition rate coefficient in particles (m\(^3\) kmol\(^{-1}\) s\(^{-1}\))
\[ L_k \] : normalised moments of the macromolecules
\[ M \] : average molecular weight of the monomeric unit (kg kmol\(^{-1}\))
\[ M_a \] : number average molecular weight (kg kmol\(^{-1}\))
\[ M_w \] : weight average molecular weight (kg kmol\(^{-1}\))
\[ M_i' \] : total number of moles of monomer \( i \) in the particles (kmol)
\[ M_{pi} \] : total mole number of monomer \( i \) in the particles (kmol)
\[ M_{Ti} \] : total number of moles of monomer \( i \) (initial and fed to the reactor) (kmol)
\[ M_i \] : total number of moles of monomer \( i \) left in the reactor (kmol)
\[ M_i^m' \] : molecular weight of the monomer \( i \). (kg kmol\(^{-1}\))
\[ M_i^Z \] : molecular weight of the inhibitor. (kg kmol\(^{-1}\))
\[ M_{TA}' \] : molecular weight of the transfer agent (kg kmol\(^{-1}\)).
\[ [M_i] \] : concentration of monomer \( i \) in the feed (kmol m\(^{-3}\))
\[ [M_p] \] : concentration of the initiator in the feed (kmol m\(^{-3}\))
\[ [M_I] \] : concentration of the inhibitor in the feed (kmol m\(^{-3}\))
\[ [M_S] \] : concentration of the surfactant in the feed (kmol m\(^{-3}\))
\[ [M_{TA}] \] : concentration of the transfer agent in the feed (kmol m\(^{-3}\))
\[ m_{di} \] : equilibrium constant of free radicals ended by \( i \) between aqueous and particle phases
\[ N_A \] : Avogadro number (kmol\(^{-1}\))
\[ N_p \] : total number of moles of particles (number of particles/N\(A\)) (kmol)
\[ N_{mic} \] : total number of moles of micelles (number of micelles/N\(A\)) (kmol)
\[ N_m \] : total number of macromolecules (kmol)
\[ \bar{n} \] : average number of free radicals in a particle
\[ \bar{n} \] : average number of pairs of free radicals in a particle
\[ n_s \] : number of surfactant molecules per micelle.
\[ P_i \] : fraction of free radicals ended by a monomer unit \( i \) in the particles.
\[ Q_f \] : total feed rate of monomers, inhibitor, transfer agent and surfactant (m\(^3\) s\(^{-1}\))
\[ Q_{ft} \] : feed rate of initator (m\(^3\) s\(^{-1}\))
\[ R_{aq} \] : the number of moles of free radicals in the aqueous phase (kmol)
$R_d$: thermal decomposition of initiator in the aqueous phase (kmol s$^{-1}$)

$R_N$: total micellar nucleation rate (kmol s$^{-1}$)

$R_{pr}$: total propagation rate (kmol s$^{-1}$)

$R_{TAp}$: transfer agent consumption rate in particles (kmol s$^{-1}$)

$R_T$: total termination rate (kmol s$^{-1}$)

$R_{TC}$: total termination rate by combination (kmol s$^{-1}$)

$R_{TD}$: total termination rate by disproportionation (kmol s$^{-1}$)

$R_{trm}$: total transfer to monomer rate (kmol s$^{-1}$)

$R_{Zaq}$: inhibitor consumption rate in the aqueous phase (kmol s$^{-1}$)

$R_{Zp}$: inhibitor consumption rate in particles (kmol s$^{-1}$)

$S_{aq}$: number of moles of surfactant in the aqueous phase (kmol)

$S$: total number of moles of surfactant in the reactor (kmol)

$S_d$: number of moles of surfactant on the droplets (kmol)

$S_p$: number of moles of surfactant on particles (kmol)

$S_{mic}$: number of moles of surfactant in micelles (kmol)

$TA_p$: total number of moles of the transfer agent in the particles (kmol)

$T$: temperature of the reaction mixture (K)

$T_g$: glass transition temperature (K)

$V_{aq}$: total volume of the aqueous phase (m$^3$)

$V_p$: total volume of the particles (m$^3$)

$V_{pol}$: total volume of the polymer in the particles (m$^3$)

$V_R$: total volume engaged in the reactor (m$^3$)

$v_h$: fraction of particles with $h$ free radicals.

$W_p$: mass fraction of polymer in the particles

$W_i$: mass fractions of the monomer $i$ in the copolymer

$X$: overall mass conversion

$Z_{aq}$: total number of moles of the inhibitor in the aqueous phase (kmol)

$Z_p$: total number of moles of the inhibitor in the particles (kmol)

$\varepsilon$: ratio of inhibition in aqueous phase and capture rate coefficients (m)

$\omega_i$: fraction of radicals ended by monomer $i$ formed only by one monomer unit

$\delta$: overall ratio of nucleation and capture rate coefficients

$\delta_i$: ratio of nucleation and capture coefficients due to monomer unit $i$

$\delta_{mi}$: ratio of transfer resistance in aqueous phase on overall transfer resistance of free radicals ended by monomer unit $i$

$\tau$: ratio of the termination rates by disproportionation and combination

$\rho_i$: density of monomer $i$ (kg m$^{-3}$)

$\rho_{Pi}$: density of polymer $i$ (kg m$^{-3}$)

$\rho_{Z}$: density of monomer $i$ (kg m$^{-3}$)

$\rho_{TA}$: density of the transfer agent (kg m$^{-3}$)

$\sigma$: coefficient related to the saturation degree of the particle

$\lambda_k$: normalised moments of the macroradicals

$\widetilde{w}_j$: fraction of macroradicals with a degree of polymerization $j$

$w_j$: fraction of macromolecules with a degree of polymerization $j$