POPULATION BALANCE EQUATIONS FOR PARTICLE SIZE DISTRIBUTIONS IN SEMIBATCH EMULSION POLYMERIZATIONS

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***Abstract*— In a previous work of this group, theoretical studies and stability measurements were performed in order to describe the particle coagulation provoked by electrolytes. The work of the current paper concerns the development of mathematical models based on the DLVO theory and on population balance equations (PBE), which involve highly complex integro-differential equations. This model includes particle coagulation, particle nucleation, the polymerization kinetics and monomer partitioning among the many phases of the system. The model ensured a proper description of butyl acrylate/methyl methacrylate emulsion copolymerizations reactions, and related phenomena such as coagulation and particle nucleation in the presence of large seed particles. These latter systems are very important to the multimodal latexes production. Finally, simulation studies were performed in order to test the model ability to follow the competitive growth of polymer particles during semibatch operations.**

***Keywords*— emulsion polymerization, particle size distribution, population balance equations.**

I. INTRODUCTION

Emulsion polymerization processes present a great importance as they allow the production of polymers with specific properties. Due to its multiphase and compartmentalized nature, the emulsion polymerization process offers the possibility of preparing polymers with unique properties that cannot be produced by other polymerization techniques (El-Aasser and Sudol, 1997). One of the variables that determines the final latex properties (stability, film-forming ability, covering capacity, "brushability", viscosity, opacity, and texture among others) is the particle size distribution (PSD) (Flores-Cerrillo and MacGregor, 2002). As a consequence, in the design and study of emulsion polymerization processes, knowledge of the factors governing the average size and size distribution of particles is an important consideration.

The emulsion polymerization has been described as a three stage process involving, (i) particle nucleation, (ii) particle growth in the presence of monomer droplets and (iii) monomer depletion in the polymer particles once the monomer droplets have disappeared (El-Aasser and Sudol, 1997). In fact, the particle nucleation in emulsion polymerizations is a very complex process that depends on the particular set of operation conditions, including the surfactant and initiator concentrations, the temperature, and the monomer solubility in the aqueous phase. The formation of the initial particles occurs very quickly, and different mechanisms must be taken into account simultaneously (Gilbert et al., 1991; Gilbert, 1995; El-Aasser and Sudol, 1997). The nucleation step obviously plays an important role in determining the PSD of the final latex, which in itself constitutes an important parameter to be controlled in the final product. Besides, it has been recognized that a well-defined PSD allows the synthesis of high solids content latices, with improved rheological properties and viscosity (Chu et al., 1998). By correctly manipulating the PSD of the final product, one can achieve polymer volume fractions of well over 65% (Schneider *et al.*, 2002). Actually, high solids content without undesirably high viscosity can be obtained when the PSD is multimodal. To achieve this, recent experimental studies have applied emulsion polymerization processes involving several stages with different experimental conditions (Schneider *et al.*, 2002; Boutti *et al.*, 2004). In the final polymer PSDs present a strong dependency on several different, but interdependent phenomena, including particle nucleation, kinetics, latex stability, monomer type and concentration. There has been an incentive for the development of mathematical models that provide a complete description of the emulsion polymerization process considering all of these phenomena. These mechanistic models generally involve several dozens of differential and algebraic equations, demanding high computational effort. Besides, these models generally include a great number of parameters that must be estimated through experimental data. Due to the complexity of the phenomena involved and the lack of experimental data, many simplifications and assumptions have been proposed, limiting the modeling scope (Immanuel *et al.*, 2002; Coen *et al.*, 1998). Consequently, these models offered only limited fidelity in describing and extrapolating behavior of industrial polymeric latices, especially with multimodal particle size distributions. The value of these models has been further diminished as they could only be used by model-developers.

Even though significant progress has been made in understanding the mechanisms of particle nucleation and stabilization, much work remains to be done in terms of generating robust mathematical models of emulsion polymerizations. In a related effort, Fortuny *et al*. (2004a) incorporated stability models based on the DLVO theory into a population balance equation (PBE) in order to describe the evolution of the PSD during the addition of electrolytes into the polymeric latex. Successful results were obtained for a non reacting system. The objective of the current work is to go beyond what was done by Fortuny *et al.* (2004a) and develop a general mathematical framework based on PBE, including particle coagulation, particle nucleation, the polymerization kinetics and monomer partitioning among the many phases of the system.

II. MATHEMATICAL MODEL

A mathematical model was built for batch emulsion copolymerizations stabilized by anionic surfactants. The main objective was the description of the evolution of monomer conversion coupled with that of the PSD, through a population balance equation (PBE) which takes into account the several physicochemical phenomena occurring in an emulsion polymerization. The model was applied to the emulsion copolymerization of butyl acrylate/methyl methacrylate (BuA/MMA). The following sections cover each of these important phenomenological aspects that occur during emulsion polymerization reactions. The model was built based on the following set of standard assumptions:

- the reactor is perfectly mixed.
- radical balances in the aqueous and particle phases are solved assuming pseudo steady-state conditions.
- monomer concentrations in the different phases are at thermodynamic equilibrium.
- kinetic constants are considered to be the same for both aqueous and polymer phases.
- radicals formed by initiator decomposition and by transfer reactions have similar kinetic behavior.
- particles are formed through both micellar and homogeneous nucleation.
- compartmentalization of radicals into polymer particles can be neglected (pseudo-bulk kinetics).

A. Kinetics

The kinetic mechanism used in the proposed model includes the polymerization rates in both aqueous and particle phases. The aqueous phase mechanism involves initiator decomposition, which forms radicals that can propagate, terminate or enter into polymer particles. Radical entry may occur if the degree of radical size is above a critical value for entry (z). Radicals with size higher than the critical degree of solubility (j_{crit}) precipitate and form a new particle. When radicals enter into polymer particles, they can propagate, terminate or desorb from the particle (if the radical activity is transferred to a monomer unit).

Based on this standard kinetic mechanism, mass balances for radical species in the aqueous phase were described and solved for the steady-state conditions. For the sake of brevity, the radical balances will not be shown here and the detailed approach can be found in Fortuny (2002). For polymer particles, the kinetic model influences the computation of the average number of radicals per particle (Gilbert, 1995). As reported by Unzueta and Forcada (1997), the pseudo-bulk approximation can be used for BuA-MMA emulsion copolymerizations, and computed using the equation developed by Ugelstad *et al.* (1967).

B. Monomer Partitioning

The amount of monomer which should be in the aqueous or polymer phases is calculated from the semi-empirical approach proposed by Maxwell *et al.* (1993), as follows:

$$[M_i]_k = \phi_{Mi}[M_i]_{k,sat}(h)\,, \tag{1}$$

where ϕ_{Mi} is the volume fraction of monomer of type ‘i’ in the reactor, $[M_i]_{k,sat}(h)$ is the monomer concentration of type ‘i’ in the ‘k’ phase for homopolymerizations (indicated by h) at saturation conditions.

For non-saturation conditions, the partitioning of monomers is modeled using the following equations:

$$[M_i]^{aq} = \frac{V^p_{M_i}\rho_{M_i}}{(V_p)^2 MW_{M_i}}\frac{\phi^{aq}_{M_i,sat}(s)}{\phi^p_{M_i,sat}(s)}V_{aq}\times \exp\left(\phi^p_{Pol} - \phi^p_{Pol,sat}(s)\right) \tag{2}$$

$$[M_i]^p = \frac{V_{M_i}\rho_{M_i}}{V_p MW_{M_i} + V_{aq}MW_{M_i}\dfrac{\phi^{aq}_{M_i,sat}(s)}{\phi^p_{M_i,sat}(s)}\exp\left(\phi^p_{Pol} - \phi^p_{Pol,sat}(s)\right)} \tag{3}$$

where $V^p_{M_i}$ is the volume of monomer of type ‘*i*’ in the polymer particles, V_p is the volume of swollen polymer particles, ρ_{Mi} is the density of the monomer type ‘*i*’, MW_{Mi} is the molecular weight of the monomer type ‘*i*’, $\phi^k_{M_i,sat}(s)$ is the volume fraction of monomer type ‘*i*’ in the ‘k’ phase at saturation conditions, s represents the molar ratio between monomers in the copolymer, $\phi^k_{pol,sat}(s)$ is the volume fraction of polymer in the ‘*k*’ phase at saturation conditions. A complete study of the partitioning of mixtures of MMA and BuA in BuA-MMA copolymers can be found in Fortuny *et al.* (2004b).

C. Nucleation

The mathematical representation of the nucleation step was based on the competition of both micellar and homogeneous nucleation mechanisms. For micellar mechanism, the nucleation rate was computed as a function of the micelle concentration (R_{mic}) as follows:

$$R_{mic} = k_{mic}N_{mic}[R_{ent}]_{aq}\,, \tag{4}$$

where the term $[R_{ent}]_{aq}$ is the concentration of radicals in the aqueous phase that can enter into particles and k_{mic} is the rate constant for radical entry into micelles, which is based on the diffusion theory (Gao and Penlidis, 2002)

For the homogeneous mechanism, the nucleation rate is related to the rate of formation of radicals with size j_{crit}. The homogeneous nucleation rate is then expressed as:

$$R_h = N_A V_{aq}\left(\left(k_{pii}P_i^{aq} + k_{pij}P_j^{aq}\right)\left[M_i\right]_{aq} + \left(k_{pjj}P_j^{aq} + k_{pji}P_i^{aq}\right)\left[M_j\right]_{aq}\right)\left[R_{j_{crit}-1}\right]_{aq}, \quad (5)$$

$$P_i^{aq} = \frac{k_{pji}[M_i]_{aq}}{k_{pji}[M_i]_{aq} + k_{pij}[M_j]_{aq}}, \quad (6)$$

where N_A is the Avogadro constant, V_{aq} is the volume of the aqueous phase, k_{pij} is the propagation rate constant of monomer of type 'i' with monomer of type 'j', $[M_i]_{aq}$ is the concentration of the monomer of type 'i' in the aqueous phase, $[R_{jcrit-1}]_{aq}$ is the radical concentration of size j_{crit}-1, P_i^k is the probability that a radical is of type 'i' in the 'k' phase, being expressed as a function of the cross- propagation rate coefficients.

The relative importance of each nucleation mechanism is influenced by the experimental conditions. According to standard nucleation models, when the surfactant concentration is above the critical micellar concentration (CMC), micelles are formed and micellar nucleation is the dominant mechanism. The standard nucleation model predicts that the homogeneous mechanism may become important when polymer particles are nucleated and absorb surfactant molecules from the reaction media to become colloidally stable, reducing the micelle concentration in the system and consequently the rate of micellar nucleation.

D. Coagulation

In an earlier study (Fortuny *et al.*, 2004a), an electrostatic stability model based on the DLVO theory (Deryaguin *et al.*, 1995) was incorporated into the population balances for non-reacting systems and was successfully validated for coagulation experiments where polymer particles were destabilized by electrolyte addition. Based on these results, the model in question can be used for the theoretical description of the coagulation between particles in the reacting systems with confidence. The coagulation rate between two polymer particles was calculated as a function of the radius (r) of each polymer particle as described by the following equation:

$$B_{ij} = B_{ji} = \frac{2k_B T}{3\eta W_{ij}}\frac{\left(r_i + r_j\right)^2}{r_i r_j}, \quad (7)$$

where k_B is the Boltzmann constant, T is the medium temperature, η is the latex viscosity and W_{ij} is the Fuch's stability ratio. The details about this model can be found in Fortuny *et al.* (2004a).

E. Population Balances

The Population Balance Equation (PBE) includes the most important phenomena that can influence the evolution of the number of individual particles, such as nucleation, coagulation and growth of polymer particles. The number density of the particle size distribution was denoted as $N(m_i,t)$, where the polymer mass (m) was taken as the characteristic dimension of the polymer particles. The general form of the PBE was derived by Araújo *et al.* (2001) and adapted in this work for batch processes as described by the following equation:

$$\begin{aligned}
&Np\frac{\partial f(m_i,t)}{\partial t} + f(m_i,t)\frac{\partial Np}{\partial t} + Np\frac{\partial\left[cr(m_i)f(m_i,t)\right]}{\partial m_i} = \\
&-\frac{f(m_i,t)}{V_R}N_p^2\int_{m_0}^{m_f} B_{ij}(m_i,m_j)f(m_i,t)\,dm_j + \\
&+\frac{N_P^2}{2V_R}\int_{m_0}^{m_i-m_0} B_{ij}(m_i-m_j,m_j)f(m_i-m_j,t)f(m_i,t)\,dm_j + \\
&+R_{mic}(m_i) + R_h(m_i)
\end{aligned}\quad , \quad (8)$$

where Np is the total number of polymer particles, $f(m_i,t)$ is the number fraction density of the PSD, V_R is the reaction volume, $B_{ij}(m_i,m_j)$ is the coagulation rate between two polymer particles of mass m_i and m_j (which are related to the radius of each particle), and $cr(m_i)$ is the mass growth rate of polymer particles due to the polymerization reaction.

The first two terms on the left-hand side of this equation describe the time rate of change of the number of polymer particles of mass m_i, while the third term represents the mass change of the number density function due to the polymerization reaction. The terms on the right-hand side of the PBE take into account the rates of formation of particles of mass m_i+dm_i due to the coagulation of particles of mass m_i, the rate of formation of particles of mass m_i due to the coagulation of smaller polymer particles and the nucleation rates of particles of mass m_i through the micellar and homogeneous mechanisms respectively. Therefore, the overall balance of polymer particles can be written as:

$$\begin{aligned}
&\frac{\partial Np}{\partial t} = \\
&-\frac{1}{4}N_p^2\int_{m_0}^{m_f}\int_{m_0}^{m_f} B_{ij}(m_i,m_j)f(m_j,t)f(m_i,t)\,dm_j\,dm_i + \\
&+R_{mic} + R_h
\end{aligned}, \quad (9)$$

The PBE can be solved after introduction of the coagulation and nucleation rate expressions, of the differential mass balance equations for all chemical species (initiator, monomers, surfactant and polymer), definition of the reaction volume and the determination of the kinetic parameter $\bar{n}$, as proposed by Ugelstad *et al.* (1967), based on the pseudo-bulk approach. In order to solve the PBE, the entering domain of mass polymer particles is discretized into 200 mesh points using regular central finite differences. Numerical integrations were performed with the help of the DASSL procedures (Petzold, 1982).

It is important to point out here that what is essential in this approach is that the different terms in the PBE are separately validated in order to eliminate as much correlation as possible between the terms. In other words, the kinetic model is validated (see below) in the absence of nucleation and coagulation, and the model for coagulation (and the relevant parameters) was validated in the absence of reaction. This allows us to use the mathematical tool to infer more detailed information about the process of nucleation than would be possible if we simply fit the parameters needed for Eq. 8 to off-line data obtained during a batch polymerization run.

III. EXPERIMENTAL

Batch and semibatch emulsion copolymerizations were performed with a monomer composition of 80% butyl acrylate (BuA) and 20% methyl methacrylate (MMA) by weight. Ammonium persulfate (APS) was used as initiator. These reagents were obtained from Acros Organics and used as received. The anionic electrosteric surfactant Disponil® FES 32 IS (sodium salt of the sulfate of a polyglycol ether, abbreviated here as ‘TA’) and the non-ionic Disponil® A3065 (mixture of linear ethoxylated fatty acids, abbreviated here as ‘TN’) were used to stabilize polymer particles. The surfactants were supplied by Cognis (Meaux, France) and used as received.

Latexes were prepared in a 3-L jacketed glass vessel connected to a condenser to avoid the loss of monomers through evaporation. For semibatch runs a preemulsion formed by water, non-ionic surfactant, initiator and monomers were continuously added into the reactor. The reactor temperature was tightly controlled at 70°C through manipulations of the flow of cooling water. Samples were collected at regular intervals and monomer conversion and average particle diameter (Dp) were measured. Overall monomer conversion (X) was determined by gravimetry and Dp was measured using a Malvern LoC and Malvern Multiangle apparatus (Autosizer 4800), both based on quasi-elastic-light-scattering technique. The latter apparatus is preferentially used for identifying latexes with large or multimodal distributions, which could not be correctly identified by the Malvern LoC. Nevertheless, concerning multimodal latexes, the quasi-elastic-light scattering techniques are not appropriated to quantify the moments of the particle size distribution. As shown by Schneider and McKenna (2002) CHDF (Capillary Hydrodynamic Fractionation) is very well suited to evaluate multimodal particle size distribution. Then, for proper characterization of those bimodal latexes previously analyzed by quasi-elastic-light techniques, CHDF technique (Matec CHDF 2000) was applied to confirm the distributions observed in this study, according to the experimental procedures described by Schneider and McKenna (2002).

IV. RESULTS AND DISCUSSIONS

A. Kinetic Model Validation

The description of the kinetic mechanism of this copolymerization system includes a large set of kinetic parameters. The validation of the kinetic model for batch emulsion polymerization is a difficult task because nucleation, coagulation and polymerization can take place simultaneously. In order to isolate the “kinetics” from coagulation and nucleation-related phenomena, the model was validated for seeded semibatch reactions under well controlled conditions of stabilization in order to avoid secondary nucleation (so far as possible) and coagulation between polymer particles. The semibatch step was conducted with addition of water, monomers, surfactant and initiator (only for long reactions). All these components were previously emulsified and added into the reactor through a single feed stream. The feed flow rate was deliberately modified from run to run in order to keep starved or non-starved conditions. The temperature was kept constant at 70°C during the reaction. Tables 1 and 2 show recipes and experimental conditions for batch and seeded semibatch reactions, used to validate the kinetic model.

Table 1. Recipe for batch emulsion copolymerization reaction.

	Mass
Water, g	728
TA, g	0.37
BuA, g	57
MMA, g	14
APS, g	0.22

Table 2. Recipes for seeded semibatch reactions

Seed synthesis	C2	C4
Water, g	2525	2525
TA, g	0.07	0.02
TN, g	13	7
BuA, g	200	200
MMA, g	50	50
APS, g	0.75	0.75
Preemulsion		
Addition time, min	72	298
Feed Rate, g.min^{-1}	7.8	1.7
Water, g	169	100
TN, g	12.1	12.3
BuA, g	306	434
MMA, g	77	109
APS, g	0	0.46

Fig.1 shows model simulation and experimental data for the evolution of the overall instantaneous monomer conversion and Dp as a function of time. The values of the kinetic constants used in the simulations are listed in Table 3. Note that the experimental conversion for the semibatch step was varied in a large range of 0.55 to

0.92, showing that the kinetic model is appropriate for starved and non-starved semibatch reactions. This way, the proposed kinetic model is well suited to provide good description of batch processes.

Table 3. Parameter values used in the kinetic model.

Parameter	Values	Reference
j_{crit}	10	Gilbert (1995)
z	5	Gilbert (1995)
$[M_{BuA}]_{aq,sat}$ (mol.dm^{-3})	0.064	Gilbert (1995)
$k_{pBuA\text{-}MMA}$	$k_p(BuA)/r_{BuA\text{-}MMA}$	Aerdts and German, (1994)
$k_{pMMA\text{-}BuA}$	$k_p(MMA)/r_{MMA\text{-}BuA}$	Aerdts and German, (1994)
k_{pBuA} (dm^3.mol^{-1}.s^{-1})	$7.40\times 10^7\,exp\left(-\frac{9600}{8.3144T}\right)$	Beuermann et al (1997)
k_{mic}	$4\pi D_{aq} r_{mic} N_A f_{mic}$	Gao and Penlidis (2002)
f_{mic}	0.6×10^{-4}	estimated
$[M_{BuA}]_{p,sat}$ (mol.dm^{-3})	5	Gilbert (1995)
$[M_{MMA}]_{aq,sat}$ (mol.dm^{-3})	0.15	Ballard *et al.* (1984)
$[M_{MMA}]_{p,sat}$ (mol.dm^{-3})	6.6	Ballard *et al.* (1984)
$k_{p\mathrm{MMA}}$ (dm^3.mol^{-1}.s^{-1})	$2.66\times 10^7\,exp\left(-\frac{22300}{8.3144T}\right)$	Beuermann *et al* (1997)
ρ_{MMA}	0.857	Gilbert (1995)
ρ_{BuA}	0.916	Gilbert (1995)

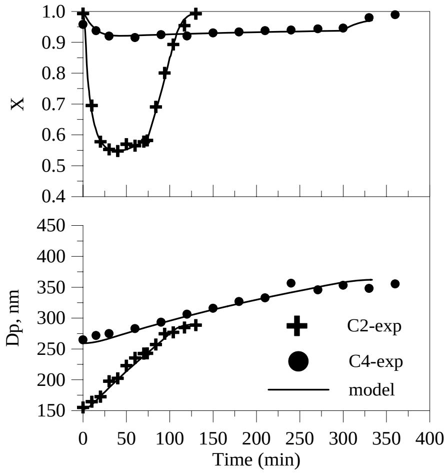

Figure 1. Evolution of overall instantaneous conversion and Dp for seeded semibatch runs (C2 and C4).

B. Particle Nucleation during Unseeded Polymerization

A complete polymerization batch process was described including micellar and homogeneous nucleation and the growth of polymer particles on the PBE. The dynamic nature of the formation of new particles was investigated for batch system under micellar conditions. Figs. 2 and 3 show the shape of the experimental and simulated number of particles and overall conversion for a batch emulsion copolymerization of butyl acrylate and methyl methacrylate. Experimental values of Np were obtained through calculations involving measurements of X and Dp. A large number of moderately short-lived particles (several minutes at most) are formed during the early stages of nucleation in the presence of an initial population of particles. These particles contribute to an accelerated rate of polymerization during a short time before flocculating onto larger structures in the reactor.

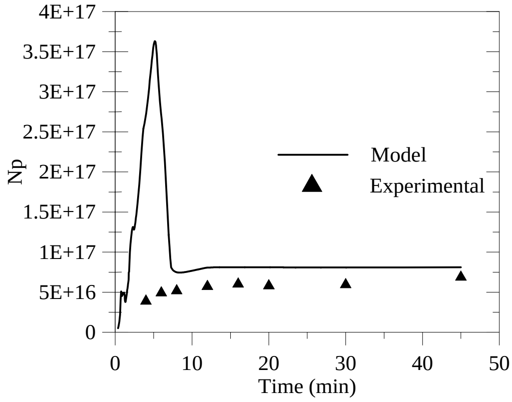

Figure 2. Experimental and simulated Np during batch emulsion copolymerization of BuA/MMA.

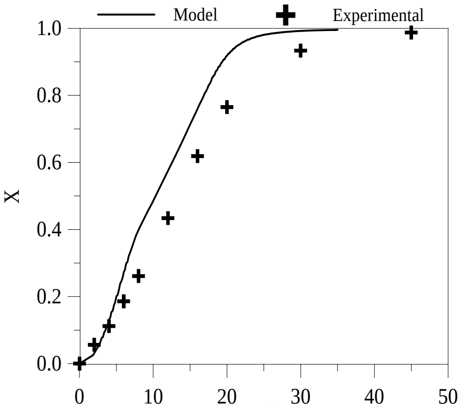

Figure 3. Experimental and simulated conversion during batch emulsion copolymerization of BuA/MMA.

These results shown in Fig. 2 differ from experimental data at the beginning of the reaction when particle nucleation occurs. It is important to note that experimental techniques are not adapted to measure particle diameter of these short-lived particles because of their small size and their rapid coagulation due to the low stability. Then, we have to be careful of the significance of experimental Np.

C. Competitive Growth of Particles during Seeded Semibatch Operation

The model was also used to predict the PSD during a seeded semibatch emulsion copolymerization reaction of BuA/MMA. The recipe and conditions of this semibatch reaction were already described by Schneider *et al.* (2002), who performed a deep experimental study on the synthesis of latices with multimodal PSDs. In this experiment (TR7), the seed was prepared through blending two seed latices of different sizes and ratios, with 91% for the large particles seed (Dp 535 nm) and 9% for the medium one (Dp = 290 nm). The reaction started after the addition of ammonium persulfate (used as initiator) accompanied by the introduction of a preemulsion, in order to produce a bimodal latex with final solids content around 65% solids.

Figs. 4 and 5 show the PSD model simulation results at the beginning (50% w/w solids content) and after 2 hours (57% solids) of reaction respectively, compared with experimental values measured through CHDF. Again, experimental results should be analyzed with care once they generally underestimate the medium size population in the beginning. The differences observed between the PSD model predictions and the PSD measured by CHDF are basically due to the experimental error of the CHDF technique. This is particularly true at time zero, where the copolymerization has not begun, and then the model output is very reliable as it is completely based in well-known initial conditions (average sizes and ratios) of the populations employed in the test, which are used as input to the model.

However, both model and experimental results for average values are in good accordance. Besides, the competitive growth of particle populations is well tracked by the model. The differences observed in the distributions may not be emphasized once the parameters were essentially taken from the literature. Results are therefore encouraging.

V. CONCLUSIONS

In this work a general mathematical model based on population balance equation was proposed to describe emulsion polymerization reactions. This model includes particle coagulation, particle nucleation, the polymerization kinetics and monomer partitioning among the many phases of the reaction system. Each particular phenomenon was studied independently both theoretically and experimentally in order to characterize the relative importance of each of them separately, and to eliminate any correlation between the model parameters. The model was applied to butyl acrylate (BuA) and methyl methacrylate (MMA) emulsion copolymerizations using anionic surfactant, providing good description on the kinetics and on the PSD for a number of cases.

As a final remark, it can be said that thr mathematical procedures provided rapid calculations, which may allow the proper application of this simulations to industrial sites. Further adaptations will be made in order to integrate the model into a simulation framework with user-friendly interface in the near future.

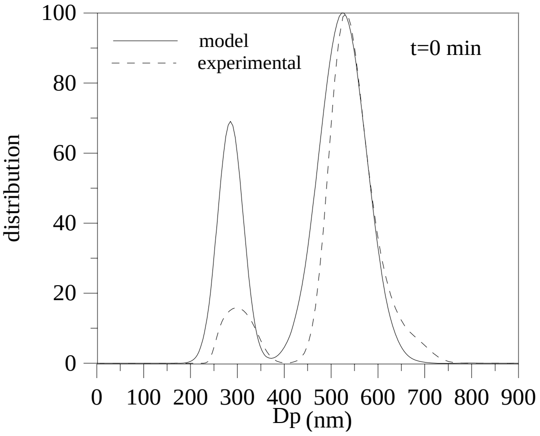

Figure 4. Experimental and simulated PSD during Exp TR7 (Schneider et al., 2002): t=0 min and 50% solids.

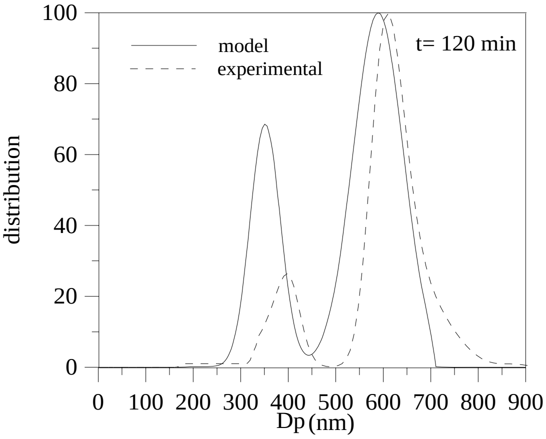

Figure 5. Experimental and simulated PSD during Exp TR7 (Schneider et al., 2002): t=120 min and 57% solids.

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REFERENCES

Aerdts, A. M. and A.L. German, “Determination of the reactivity ratios, sequence distribution and stereoregularity of butyl acrylate-methyl methacrylate copolymers by means of proton and carbon-13 NMR,” *Mag. Res. Chem.*, **32**, S80-S88 (1994).

Araújo, P. H. H., J. C. De La Cal, J. M. Asua and J. C. Pinto, “Modeling particle size distribution (PSD) in emulsion copolymerization reactions in a continuous loop reactor,” *Macromol. Theory Simul.*, **10**, 769-779 (2001)

Ballard, M. J., D. H. Napper and R. G. Gilbert, “Kinetics on emulsion polymerization of methyl methacrylate," *J. Polym. Sci. : Polym. Chem.*, **22**, 3225-3253 (1984)

Beuermann, S., M. Buback, T. P. Davis, R. G. Gilbert, R. A. Hutchinson, O. F. Olaj, G. T. Russell, J. Schweer and A. M. Van Herk, "Critically evaluated rate coefficients for free-radical polymerization, 2. Propagation rate coefficients for methyl methacrylate," *Macromol. Chem. Phys.*, **198**, 1545-1560 (1997).

Boutti, S., C. Graillat and T. F. McKenna, "New routes to high solid content latexes: A process for in situ particle nucleation and growth," *Macromol. Symp.,* 206, 383-398 (2004).

Chu, F., M., C. Graillat and A. Guyot, "High solid content multisized emulsion copolymerization of styrene, butyl acrylate, and methacrylic acid," *J. Appl. Polym. Sci.*, **70**, 2667-2677 (1998).

Coen, E. M., R. G. Gilbert, B. R. Morrison, H. Leube and S. Peach, "Modelling particle size distribution and secondary particle formation in emulsion polymerization," *Polymer*, **39**, 7099-7112 (1998).

Deryaguin, B. V. and L.D. Landau, In J. Lyklema, "Fundamentals of interface and colloid science. Vol I. Solid-liquid interfaces," London Academic Press, London (1995).

El-Aasser, M.S. and E. D. Sudol, "Features of emulsion polymerization" In: P. A. Lovell and M. S. El-Aasser (Eds.), *Emulsion polymerization and emulsion polymers*, Jonh Wiley & Sons, Chichester, **38** (1997).

Flores-Cerrillo, J. and J. F. MacGregor, "Control of particle size distributions in emulsion semibatch polymerization using mid-course correction policies." *Ind. Eng. Chem. Res*., **41**, 1805-1814 (2002).

Fortuny, M., "Modélisation de procédés pour la synthèse de latex multipopulés," Ph.D. Thesis, Université Claude Bernard Lyon I, Lyon (*in French*) (2002).

Fortuny, M., C. Graillat and T. F. McKenna, "Coagulation of polymer particles stabilized electrosterically," *Ind. Eng. Chem. Res.*, **43**. 7210-7219 (2004a)

Fortuny, M., C. Graillat and T. F. McKenna, "A new technique for the experimental measurement of monomer partition coefficients," *Macromol. Chem. Phys.*, **205**, 1309-1319 (2004b).

Gao, J. and A. Penlidis, "Mathematical modeling and computer simulator/database for emulsion polymerization," *Prog. Polym. Sci.*, **27**, 403-535 (2002).

Gilbert, R. G., B. R. Morrison and D. H. Napper, "The status of nucleation models in emulsion polymerization," *Polym. Mater. Sci. Eng*., **64**, 308-309 (1991).

Gilbert, R. G., *Emulsion polymerization: a mechanistic approach*, Academic Press, London, (1995).

Immanuel, C.D., C. F. Cordeiro, S. S. Sundaram, E. S. Meadows, T. J. Crowley and F. J. Doyle, " Modeling of particle size distribution in emulsion copolymerization: comparison with experimental data and parametric sensitivity studies," *Comp. Chem Eng.*, **26**, 1133-1152 (2002).

Maxwell, I. A., L. F. J. Noël, H. A. S. Schoonbrood and A. L. German, "Thermodynamics of swelling of latex particles with two monomers: a sensitivity analysis," *Makromol. Chem. Theory Simul*., **2**, 269-274 (1993).

Petzold, L. R. "A differential algebraic system solver," Sandia National Laboratories, Report # SAND82-8637 (1982).

Schneider, M. and T. F. McKenna. "Comparative study of methods for the measurement of particle size and size distribution of polymeric emulsions," *Part. Part. Syst. Charact*, **19**, 28-37 (2002).

Schneider, M., C. Graillat, A. Guyot, A., I. Betrémieux and T. F. McKenna, "High solids content emulsions. IV. Improved strategies for producing concentrated lattices," *J. Appl. Polym. Sci.*, **84**, 1935-1948 (2002).

Stickler, M. and G. Meyerhoff, "Die thermische polymerisation von methylmethacrylat, 1. Polymerisation in substanz," *Makromol. Chem*., **179**, 2729-2745 (1978).

Ugelstad, J., P. C. Mork and J. O. Aasen, "Kinetics of emulsion polymerization," *J. Polym. Sci.: Part A*-1, **5**, 2281-2288 (1967).

Unzueta, E. and J. Forcada, "Modeling the effect of mixed emulsifier systems in emulsion copolymerization," *J. Appl. Polym. Sci.*, **66**, 445-458 (1997).

Verwey, E. J. W. and J. Th. G. Overbeek, *Theory of the stability of lyophobic colloids*, Dover Publications, New York (1999).

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