In-Situ Monitoring of Emulsion Polymerisations of MMA and Styrene Using Conductimetry and Calorimetry

A. F. Santos,[1] *J. C. Pinto,*[2] *T. F. McKenna**[3]

[1]Instituto de Tecnologia e Pesquisa, Universidade Tiradentes, Av Murilo Dantas, 300, Farolândia, Aracaju, 49032-490 SE, Brasil
[2]Programa de Engenharia Quimica / COPPE, Universidade Federal do Rio de Janeiro, Cidade Universitária, CP: 68502, Rio de Janeiro, 21945-970 RJ, Brasil
[3]CNRS-LCPP/ESCPE, Université Claude Bernard Lyon 1, 43 Blvd du 11 Novembre 1918, Bât 308F, 69616 Villeurbanne, France
E-mail: mckenna@cpe.fr

Summary: In the present work, conductimetry is applied for on-line evaluation of anionic surfactant dynamics during emulsion polymerisation of methyl methacrylate and styrene and for on-line estimation of particle size and number. Reactor and jacket temperatures are used to perform energy balance computations on-line and to provide on-line evaluation of monomer conversion. The parameters of a previously proposed model are re-estimated in order to describe the conductivity signal during methyl methacrylate runs. Some important issues regarding the effects of the surfactant micelles over the conductivity signal are addressed. Finally, the model is inverted and combined with conversion and reactor temperature measurements, providing good predictions of the number of polymer particles in the latex, without needing of on-line measurements of particle size.

Keywords: conductivity; emulsion; monitoring; polymerisation; reactor

Introduction

Several of the different phenomena involved in particle formation during emulsion polymerisations are very rapid, making their observation a complicated task. In essence, the number of particles present at any time inside the reactor is the result of a competition between particle nucleation and particle coagulation. Therefore, in a certain sense, the role of the stabilizer is to shift this balance along one of these directions. In many situations, only in-situ and on-line measurements can provide useful information about the state of the particle size distribution (PSD) in the reactor. There are multiple reasons for this, including the fact that the use of sampling devices can alter the actual size distribution, which may lead to wrong interpretation of experimental results [1]. Particularly, light scattering devices generally

 DOI: 10.1002/masy.200550815

require that particle size analyses be performed in diluted conditions. This requires withdrawing samples from the reactor (or use of an in-line sampling loop), pumping and dilution of latex samples, which may produce delayed (and sometimes erroneous) results, as these operations can lead to redistribution of the surfactant among the many phases of the latex and consequently to "readjustment" of the measured PSD. This may not constitute a serious problem during the reaction stages when one would not expect significant modifications of the PSD (for instance, when significant rates of particle nucleation do not occur). However, when the rates of particle nucleation are high, manipulation of latex samples may constitute a serious problem [2] since the number of particles can vary rapidly, and in a manner that would not be detected through off-line analyses. Nevertheless, fast and reliable on-line measurement of the PSD cannot yet be performed with existing sensors. For instance, even though certain spectroscopic techniques can be adapted to monitor polymer properties on-line and in-situ, the use of spectral data for particle size monitoring during emulsion polymerisations is still a complex issue and merits further investigations[3]. For these reasons, there are many incentives for development of experimental procedures for in-situ and on-line measurement of the PSD.

On the other hand, monitoring techniques based on conductivity measurements and calorimetry are well suited to provide real-time data with simple hardware and software tools. For example, recent studies have shown that conductimetry offers a means to monitor the evolution of ionic surfactant concentrations in the latex [1,4]. Interpretation of the conductivity signal with the help of calibration models allows one to evaluate the concentration of free surfactant in the system and as a consequence to evaluate the surface area of the latex particles in the reaction. However, these studies focused only on styrene homopolymerisations (STY). It has therefore yet to be shown that these techniques can be applied with confidence in polymerisation reactions where at least one of the monomers is partially soluble in the aqueous phase, making the interpretation of the conductivity signal more complex. For this reason, in the present work conductimetry is applied for on-line evaluation of anionic surfactant dynamics during emulsion polymerisation of methyl methacrylate (MMA). Particular attention is given to the prediction of the number of particles in the latex. Conductivity measurements are coupled with a calorimetric technique in order to allow for on-line estimation of monomer conversion, which is of fundamental importance for proper evaluation of the number of particles in the system.

Experimental

Methyl methacrylate, styrene, potassium persulfate (KPS) and sodium dodecyl sulfate (SDS) were obtained from Acros Organics and were used without further purification. Emulsion homopolymerisations of MMA and Styrene were carried out with a solids content of 10% (mass monomer with respect to total reaction mass). The initiator concentration (KPS) was maintained at 0.25 g/L_{H2O} for the MMA runs and 1.0 g/L_{H2O} for the styrene runs. The total reaction mass was equal to 1820 g (182 g monomer, 1640 g water, KPS, SDS) in all cases. Only the SDS concentration was allowed to vary in the experiments. A platinum sensor connected to a conductivity meter (TACUSSEL CD 810) was employed for conductivity measurements. This sensor was inserted into a 3-litre jacketed glass reactor (calorimetric reactor), connected to a heating bath [1] and equipped with a sampling valve at the bottom. Reactor was heated with water at a constant temperature of 60°C. A condenser was used to minimize the loss of reactants through evaporation. Platinum resistance probes (PT100 – precision = 0.1°C) were used to measure water inlet and outlet temperatures. The reactor temperature was measured with the help of a high precision probe inserted into the agitator axis. Temperature and conductivity measurements were acquired in real-time through a standard data acquisition board. The sampling interval was equal to 10 seconds. Latex sampling was performed during the reaction for off-line analyses of conversion (x, gravimetry) and average particle size (d_p, dynamic laser light scattering, S7032-Malvern Instruments Lo-C). These pieces of information were used to validate the proposed measurement procedures and to allow for off-line calculation of the number of polymer particles in the latex (N_p), of the latex surface (S_L) and of the surface coverage by surfactant (θ, %), which is dependent on the specific adsorption coverage area of surfactant on the polymer particle (as).

Modelling Approach

The semi-empirical mathematical model proposed previously for the conductivity signal of styrene emulsion polymerisations [1] was recalibrated for the MMA runs. The model assumes that the conductivity signal is the sum of contributions from free surfactant molecules, micelles and polymer particles, according to Equation (1).

$$\sigma = \sigma_0 + (\xi_0)\frac{m_e^{aq}}{V^{aq}} + (\xi_1)\frac{m_e^{mic}}{V^{aq}} + (\xi_2)\left(\frac{1}{m_p}\right)\frac{m_e^{ads}}{V^{aq}} \quad (1)$$

It is important to emphasize that the last term of Equation (1) implicitly accounts for the effects of the latex surface area upon the conductivity signal. Besides, it explicitly considers the surfactant partitioning among the many phases of the latex and requires that monomer conversion be known. It should be noted that the amount of surfactant absorbed by the monomer droplets is assumed to be negligible. However, one might reconsider this assumption when monomer droplets are small enough (as in miniemulsion and microemulsion polymerisations). In the current work, model parameters were estimated by fitting the model responses to experimental conductivity signal of 4 different MMA polymerisation runs (see Figure 1). Temperature and ionic strength effects are inserted into the calibration model in accordance with Equation (2).

$$\begin{bmatrix} \sigma_0 \\ \xi_0 \\ \xi_1 \\ \xi_2 \end{bmatrix} = \begin{bmatrix} \hat{\sigma}_0 & \sigma_0^T & \sigma_0^E & \sigma_0^{ET} & \sigma_0^{EE} & \sigma_0^{EET} \\ \hat{\xi}_0 & \xi_0^T & \xi_0^E & \xi_0^{ET} & \xi_0^{EE} & 0 \\ \hat{\xi}_1 & \xi_1^T & \xi_1^E & \xi_1^{ET} & \xi_1^{EE} & \xi_1^{EET} \\ \hat{\xi}_2 & \xi_2^T & \xi_2^E & \xi_2^{ET} & \xi_2^{EE} & 0 \end{bmatrix} \cdot \begin{bmatrix} 1 \\ (T_0 - T_r) \\ [SDS] \\ (T_0 - T_r)[SDS] \\ [SDS]^2 \\ (T_0 - T_r)[SDS]^2 \end{bmatrix} \quad (2)$$

The parameter σ_0 represents the baseline value of the conductivity signal. The remaining parameters are adjustable coefficients. The subscripts indicate the order of the effect, while the superscripts indicate the type of interaction (E for emulsifier, T for temperature). As N_p does not appear explicitly in the model, it is necessary to invert and solve the conductivity model iteratively as a function of N_p. For the sake of simplicity, a direct search method is employed here (golden section method [5]) as described previously [1]. N_p predicted here is the value that makes model predictions equal to the experimental values. When the iterative procedure is finished, one also obtains estimates of the surfactant partitioning among the many phases and of the latex surface. Such a strategy can be applied either on-line or off-line, depending on the availability of the temperature and conversion measurements.

Results and Discussion

Let us first consider monitoring of monomer conversion during the polymerisation of MMA.

During the batch reaction, the conductivity signal in Figure 1 clearly shows an inhibition period (given by an horizontal plateau in the beginning of the reaction), followed by a nucleation period (indicated by the continuous decrease of the signal up to 30% conversion) and, finally, a period of monomer consumption inside the polymer particles, with consequent release of surfactant molecules (sudden increase of the signal at a conversion of 30%). As very small amounts of SDS were employed in the experiments (SDS = 0.007M in the last experiment), micellar nucleation is unlikely. Thus, particles are formed essentially only by homogeneous nucleation. Indeed, particle nucleation and coagulation of small particles with bigger ones may occur during the whole batch, as the number of polymer particles increases continuously throughout the batches (Figure2).

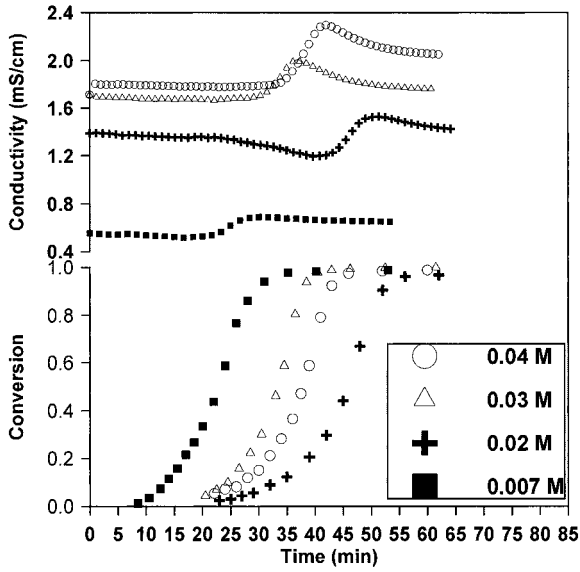

Figure 1. Evolution of the conductivity and conversion during emulsion polymerisation runs with MMA/KPS at different SDS concentrations (calibration data).

It should be pointed out that the conductivity results obtained for MMA homopolymerisations show some differences from the original values obtained for polystyrene [1] (see also below). This may be linked to the fact that the water solubility of MMA is higher than that of styrene, and that nucleation can occur throughout the reaction. This means that the evolution of the surface area is different for MMA, as is the redistribution of surfactant.

For SDS=0.03M (Figure 2), the presence of micelles is likely. In this case, the conductivity model provided reliable predictions of N_p. In spite of that, the model performs very well in all cases, which is an indication of the robustness of the proposed monitoring procedure. Actually, the model does not depend on the nucleation mechanism, but on the surfactant distribution among the many phases of the latex. Proper evaluation of monomer conversion is much more important than the nucleation mechanism that leads to formation of polymer particles [1].

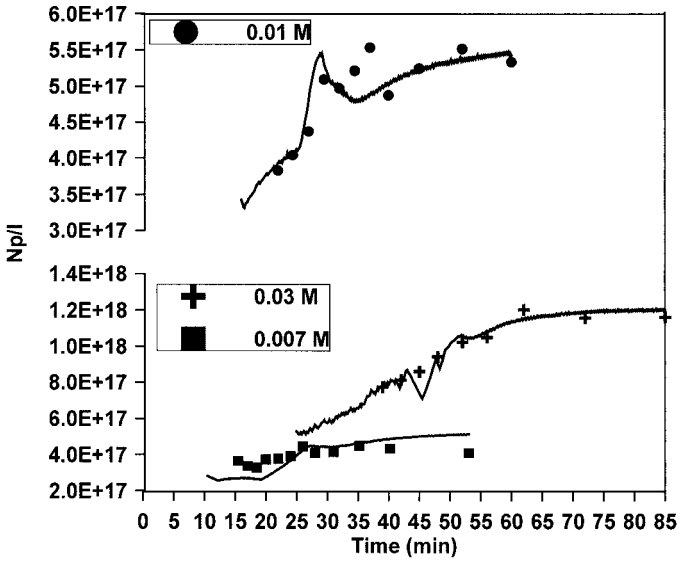

Figure 2. Experimental and predicted N_p for MMA runs with SDS = 0.007 M and 0.03 M; validation results for SDS = 0.01 M.

A series of experiments was carried out to determine the contribution of the initiator decomposition to the conductivity signal in aqueous solution containing surfactant or polymer particles. These solutions included KPS at 1.0 g/L in pure water, KPS at 1.0 g/L in a SDS solution (SDS = 0.02M) and KPS at 1.0 g/L in a polystyrene latex containing 10% of solids and SDS = 0.02M. In each case, the conductivity of the medium was measured at 60°C for four hours. The initiator decomposition rate can be evaluated by computing the slope of each conductivity curve (not shown here for the sake of brevity). It was found that that the initiator exerts a minimum effect on the conductivity signal when polymer particles and SDS are present in the reactor. This explains why one can neglect the initiator decomposition effect on

the conductivity signal during fast emulsion polymerisation reactions.

A series of 3 styrene polymerisations was carried with different SDS concentrations (0.01M, 0.02M and 0.03M: A, B, C). Figure 3 shows the on-line sensor measurements taken throughout the feed and the polymerisation stages in the three experiments. Conductivity changes along the feeding stage can be easily observed each case (A, B or C in Figure 3). Conductivity remains essentially constant when there is only water in the reactor, even when the reactor temperature rises. The addition of the surfactant (SDS) is performed in two steps: a first load of surfactant is charged when the reactor temperature reaches 40°C; while a second load of surfactant is added into the reactor when the reactor temperature reaches 60°C. SDS charges and heating lead to a large increase of the conductivity signal due to the increase of the ionic strength of the mixture.

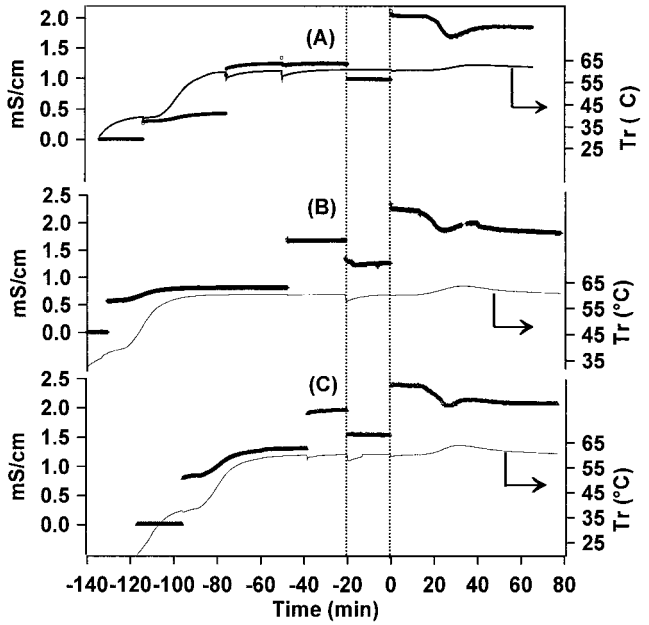

Figure 3. On-line sensor measurements during the feeding, heating and polymerisation stages involving 10% styrene, T_r=60°C and KPS=1.0g/L, with: (A) SDS = 0.01M, (B) SDS = 0.02M and (C) SDS = 0.03M. Dashed lines indicate monomer and initiator additions.

When styrene is charged into the reactor, a large decrease of the conductivity is observed (see the region between the 2 dashed lines in Figure 3). This can be explained by the

adsorption of SDS molecules onto the surface of the monomer droplets for stabilization, thereby reducing the mobility of the SDS molecules and decreasing their contribution to the conductivity. The conductivity increases again when the ionic initiator (KPS) is introduced into the reaction medium (time "zero" for the reaction). In the early stages of the reaction, an inhibition period can usually be detected (the conductivity signal tends to be constant for a few minutes). Then one can observe a period of conductivity decrease and temperature increase. The number of particles increases in this period, which indicates that nucleation is occurring. Due to the formation and growth of polymer particles, adsorption of surfactant from the aqueous phase occurs in order to stabilize the new-formed surface area. Conductivity therefore decreases due to the reduced mobility of the SDS molecules on the particle interface. After this point, a slight increase in the conductivity signal can be observed, probably due to the monomer consumption inside the polymer particles, leading to release of small quantities of surfactant into the continuous phase.

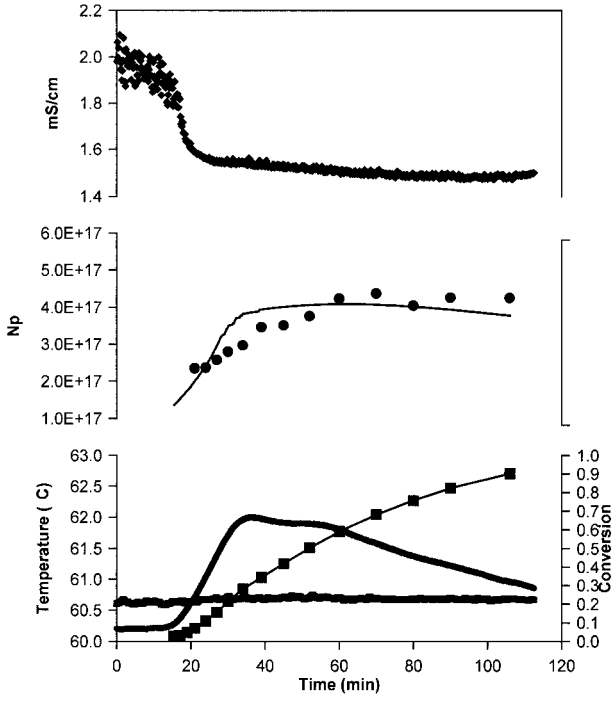

Figure 4. Experimental off-line latex properties, on-line measurements and model results for N_p: 10% solids (styrene), SDS = 0.01M, KPS =0.5 g/L.

To analyze whether the soft-sensor strategy for monitoring N_p remains valid when fewer initiator is introduced into the reactor, the series of experiments involving KPS at a concentration of 0.5 g/L was investigated in real-time. The conductivity baseline was measured and introduced into the model. The results obtained for the experiment carried out with SDS equal to 0.01M are exhibited in Figure 4. In all cases N_p estimates agree well with experimental values. One could consider that model predicts a faster formation of particles (nucleation) than that observed experimentally, and therefore, caution should be taken when we are to generalize this model.

Figure 5 shows results obtained when the conductivity model is applied to monitor N_p during two experiments containing 0.5 g/L of KPS and also SDS = 0,02M or SDS=0.03M. As observed, model results are in good agreement with the experimental values, particularly for the run carried out with SDS=0.02M. From these results, it can be concluded that the conductivity model is still valid even when the initiator is varied in the recipe.

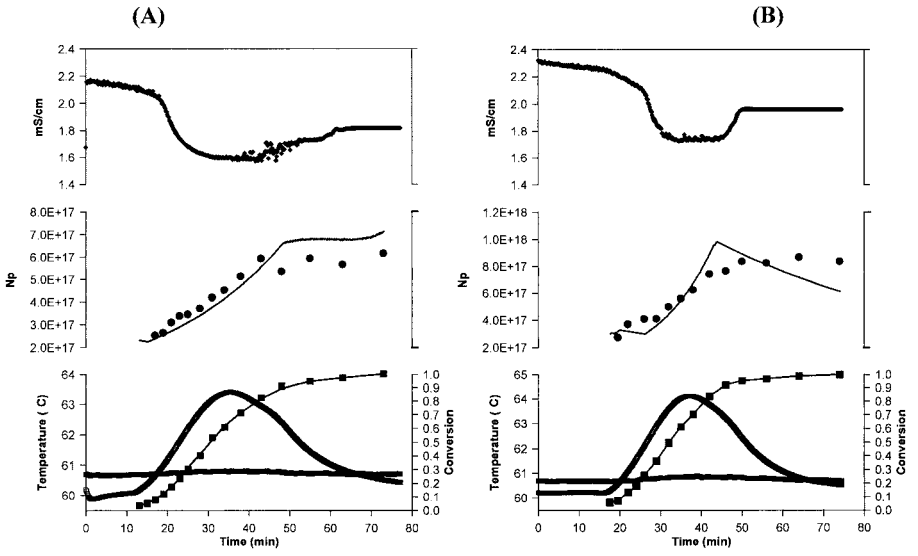

Figure 5. Experimental off-line latex properties, on-line measurements and model results for N_p: 10% solids (styrene), KPS =0.5 g/L, SDS = 0.02M (A) and SDS =0.03M (B).

Conclusions

Useful real-time information about emulsion polymerisations can be provided by the use of conductivity meters coupled with a calorimetric reactor. In addition to being inexpensive, both techniques are suited to industrial applications due to the ease of performing conductivity measurements and balance energy computations on large-scale reactors. A semi-empirical model based on conductivity, conversion and temperatures previously developed for styrene was recalibrated and applied to MMA emulsion polymerisations. In these cases, it was shown that the conductivity signal could be very different from the one obtained for polystyrene runs, according to the initial SDS concentration used in the reactor. Nevertheless, the same model structure developed before could also be applied with confidence to estimate the number of particles during MMA emulsion polymerisation. Additional experimental and simulation studies showed that nucleation could be monitored with the help of the proposed technique even when more complex operation strategies, involving multiple charges of reactants, are used.

Acknowledgments

The authors thank FAP-SE (Fundação de Amparo à Pesquisa de Sergipe, Brasil) for supporting this research. The authors also thank CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico, Brasil) and CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior, Brasil) for providing scholarships and supporting this work.

1. A.F. Santos, E.L. Lima, J.C. Pinto, C. Graillat, T.F. Mckenna, *J. of Appl. Pol. Sci.*, 2003, *90*, 1213
2. M. Fortuny, C. Graillat, P.H.H. Araújo, J.C. Pinto, T.F. McKenna, *AIChE J.*, 2005 (In press)
3. O. Kammona, E.G. Chatzi, C. Kiparissides, *J.M.S – Rev. Macromol. Chem. Phys.*, 1999, *C39(01)*, 57
4. A.F. Santos, E.L. Lima, J.C. Pinto, C. Graillat, T.F. Mckenna, *J. of Appl. Pol. Sci.*, 2004, *91*, 941
5. G.N. Vanderplaats, "Numerical optimization techniques for engineering design", McGraw Hill, New York, 1984