

# On-Line Monitoring of the Evolution of Number of Particles in Emulsion Polymerization by Conductivity Measurements. II. Model Validation

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**ABSTRACT:** A model to describe the evolution of conductivity measurements in emulsion polymerizations was presented in the first part of this work [Santos et al., *J Appl Polym Sci*, 2002]. The model was built on the assumption that surfactant is partitioned among the three principle phases of the polymerizing latex. Model parameters were estimated by fitting the model responses to experimental conductivity data obtained in different runs performed with similar solids content, reactor temperature, and initiator concentration. A soft-sensor strategy was then proposed for monitoring of the number of polymer particles ( $N_p$ ) by combining the conductivity model with the available conversion, temperature, and conductivity signals. The main objective of the current work is to validate the conductivity model in a broader range of operation conditions, to follow

the evolution of  $N_p$  (nucleation/coagulation) on-line under different reaction conditions. A series of batch and semi-batch polymerization runs were carried out aiming to evaluate the model performance when different solids content, surfactant concentration, and reactor temperatures are used. Additionally, simulation studies were performed to assess the model sensitivity to the fluctuations of the conversion and temperature signals. Results showed that the model is able to perform accurate predictions of  $N_p$ , even when disturbances of  $\pm 2^\circ\text{C}$  in temperature and  $\pm 0.03$  in monomer conversion take place during the polymerization process. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 941–952, 2004

**Key words:** emulsion polymerization; particle nucleation

## INTRODUCTION

Emulsion polymerization is a widely used industrial process for the production of synthetic polymer latexes. Many studies have been conducted to unveil the kinetics and mechanisms of emulsion polymerization reactions. Harkins<sup>2</sup> presented the first attempt to postulate the basis of emulsion polymerizations, by stating that the swollen polymer particles and micelles are the main reaction loci in emulsion polymerization, and that the monomer droplets serve as monomer

reservoirs for the growing particles. Smith and Ewart<sup>3</sup> treated the Harkins' theory quantitatively, providing fair description of emulsion polymerizations of water-insoluble monomers, such as styrene and butadiene. Since then, the batch emulsion polymerization has been generally viewed as a sequence of three intervals that involve particle generation by micellar nucleation, particle growth, and final monomer consumption inside swollen polymer particles. For slightly water-soluble monomers, alternative theories had to be built to describe the more complex particle nucleation mechanism. The possibility of producing polymer particles in the absence of micelles by homogeneous nucleation, was first verified by Priest<sup>4</sup> and Jacobi<sup>5</sup> for the vinyl acetate and vinyl chloride emulsion polymerizations, respectively. Further contributions were provided by different groups (Napper and Alexander,<sup>6</sup> Dunn and Chong,<sup>7</sup> Fitch and Tsai,<sup>8</sup> and Han-

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sen and Ugelstad<sup>9</sup>). The last two groups attempted to present a quantitative description of the homogeneous nucleation, which is known as the HUFT theory. According to the homogeneous nucleation theory, the formation of particles is due to the precipitation of the oligomeric radicals formed in the aqueous phase.

Citing a lack of unambiguous experimental evidence for previous theories, Feeney et al.<sup>10,11</sup> proposed an alternative theory, the so-called "coagulative nucleation theory," by assuming that the particle nucleation involves at least two mechanistic steps: the formation of colloidally unstable primary particles by homogeneous nucleation, and the coagulation of primary particles until attainment of colloidal stability, providing the so-called mature particles. Giannetti<sup>12</sup> presented an approach for description of particle formation by assembling aspects from the micellar, homogeneous, and coagulative nucleation theories, yielding the so-called "extended coagulative nucleation" model. General expressions for time evolution of the PSD moments were then proposed.

Due to their smaller surface area, monomer droplets have long been regarded solely as reservoirs of unpolymerized monomers rather than as sites for polymerization in all of the above-mentioned theories. However, strong stirring conditions and the presence of hydrophobic compounds lead to the formation of submicron monomer droplets, which provide a surface area that can be large enough to compete with the micelles for radicals. Ugelstad et al.<sup>13</sup> reported that the monomer droplets can become the predominant loci for particle nucleation in these cases. This mechanism has been called "droplet nucleation," and is the most important one in miniemulsion and microemulsion polymerization reactions.

It should be clear that particle nucleation in emulsion polymerizations is a very complex process, and that it 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 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. In addition, because the polymerization rate is directly proportional to the number of polymer particles, it is desirable to be able to monitor particle nucleation on-line during the emulsion polymerization. However, sensors currently available for this purpose, such as light-scattering devices, are both expensive and difficult to operate on-line. It is therefore of interest to develop an alternative on-line tool to monitor and control particle nucleation and/or  $N_p$

in emulsion polymerizations. For these reasons, our two laboratories have taken a special interest in developing techniques that are inexpensive, easy to implement and widely applicable, such as conductivity and calorimetry.

The main objective of this work is to validate the conductivity model, to follow the particle nucleation process on-line at different conditions. A series of batch polymerization runs were carried out to evaluate the model performance, and to extend its use to both seeded and unseeded semibatch processes. Finally, simulation studies are performed to test the model ability to predict  $N_p$  when both conversion and temperature data, used as model inputs, are subject to perturbations.

The use of conductivity measurements for monitoring and control of  $N_p$  constitutes a new area of study and is still in the early stages of development.<sup>1</sup> The concept is based on the fact that conductivity measurements allow us to monitor the evolution of concentrations of different species in the latex. In the first part of this work, a conductivity model was built to describe the evolution of conductivity measurements in emulsion polymerizations. The model was built by assuming that the surfactant is partitioned among the principle phases of the polymer latex (the aqueous phase, the micelles and polymer particles—it is assumed that the contribution of the surface area of any monomer droplets present is too small to influence how the surfactant is distributed). Model parameters were estimated by fitting the model responses to the experimental conductivity data obtained for different batch polymerization runs performed with similar solids content, reactor temperature, and initiator concentration. However, our main interest is to apply the conductivity model on-line during emulsion polymerizations, and to demonstrate that it can be used for control purposes, which necessarily involves the analysis of semibatch processes using monomer and emulsified monomer feed policies. Furthermore, the great majority of the industrial emulsion copolymerization/terpolymerization processes are carried out through semibatch operations. It is therefore of great interest to verify the ability of the model previously developed to perform proper predictions of  $N_p$  for emulsion polymerization systems at different conditions, such as solids content and the surfactant concentrations, and to show that the model parameters estimated from a base set of conditions can be applied to a moderately wide range of solid contents, temperatures, and surfactant concentrations.

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**TABLE I**  
**Estimated Model Parameters and the 95% Confidence Interval for the General Model**

Parameter	Estimates	$\pm 2^*STD$	Units
$\hat{\sigma}_0$	0.4090	$\pm 0.0371$	mS/cm
$\sigma_0^T$	-0.3265	$\pm 0.0138$	mS/cm/°C
$\sigma_0^E$	130.57	$\pm 4.19$	(mS/cm)/(g/L)
$\sigma_0^{ET}$	19.14	$\pm 1.29$	(mS/cm)/(g/L)/°C
$\sigma_0^{EE}$	-2.49E + 04	$\pm 1.60E + 03$	(mS/cm)/(g/L) <sup>2</sup>
$\sigma_0^{EET}$	372.42	$\pm 25.21$	(mS/cm)/(g/L) <sup>2</sup> /°C
$\xi_0$	0.1111	$\pm 0.0072$	(mS/cm)/(g/L)
$\xi_0^T$	0.0463	$\pm 0.0036$	(mS/cm)/(g/L)/°C
$\xi_0^E$	-9.94	$\pm 0.67$	(mS/cm)/(g/L) <sup>2</sup>
$\xi_0^{ET}$	0.1978	$\pm 0.0949$	(mS/cm)/(g/L) <sup>2</sup> /°C
$\xi_0^{EE}$	348.96	$\pm 13.72$	(mS/cm)/(g/L) <sup>3</sup>
$\xi_1$	-0.0168	$\pm 0.0265$	(mS/cm)/(g/L)
$\xi_1^T$	-0.0618	$\pm 0.0266$	(mS/cm)/(g/L)/°C
$\xi_1^E$	-3.771	$\pm 1.329$	(mS/cm)/(g/L) <sup>2</sup>
$\xi_1^{ET}$	3.619	$\pm 1.236$	(mS/cm)/(g/L) <sup>2</sup> /°C
$\xi_1^{EE}$	-2.22E + 03	$\pm 8.66E + 02$	(mS/cm)/(g/L) <sup>3</sup>
$\xi_1^{EET}$	39.3339	$\pm 14.1925$	(mS/cm)/(g/L) <sup>3</sup> /°C
$\xi_2$	-0.4953	$\pm 0.0141$	1-(mS/cm)
$\xi_2^T$	0.0116	$\pm 0.0021$	1-(mS/cm)/°C
$\xi_2^E$	24.4	$\pm 0.7$	1-(mS/cm)/(g/L)
$\xi_2^{ET}$	-0.0830	$\pm 0.0493$	1-(mS/cm)/(g/L)/°C
$\xi_2^{EE}$	-255.28	$\pm 7.20$	(mS/cm)/(g/L) <sup>3</sup>

Parameters estimated for an ensemble of four runs.  
 KPS = 1.0 g/L,  $T_r$  = 60°C, solids contents—10%, [SDS]  $\varepsilon$  0.01–0.04 M. CMC of SDS = 0.01 M at 60°C.

both seeded and unseeded semibatch processes. Finally, simulation studies are performed to test the model ability to predict  $N_p$  when both conversion and temperature data, used as model inputs, are subject to perturbations.

### BRIEF MODEL DESCRIPTION

The semiempirical mathematical model proposed previously for the conductivity signal<sup>1</sup> is briefly described in this section. The model was built by assuming the conductivity signal is the sum of contributions from surfactant molecules present in the latex as free molecules, as micelles, and as adsorbed species, according to eq. (1):

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

The number of particles is related to the conductivity signal through the last term in eq. (1), which gives the contribution of surfactant absorbed on the particle surface. More details of this are discussed by Santos et al.<sup>1</sup> Model parameters were estimated by fitting the model responses to experimental conductivity data obtained

for different polymerization runs. The final set of model parameters [eq. (2)] was very large because it was necessary to include the effects of temperature and ionic strength in the conductivity signal as discussed by Santos et al.<sup>1</sup> The set of model parameters is presented in Table I. These global parameters were fit for a set of four batch runs as described in the previous work. Note that because all of our experiments were performed at the same initiator concentration, this parameter was not taken into account in the original model, and any contribution from the KPS is thus included in the baseline.

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

### EXPERIMENTAL

A series of Styrene (99+%, ACROS, France) emulsion polymerization runs were carried out at different sur-

**TABLE II**  
**Styrene Polymerization Batches with 20% w/w Solids**  
**Content  $T_r = 60^\circ\text{C}$ ; KPS = 1.00 g/L**

Exp	[SDS]	Final $N_p$	Comments
S16	0.01 M	8.1E + 17	Low SDS content
S14	0.02 M	8.5E + 17	
S13	0.03 M	1.3E + 18	
S17	0.03 M	3.8E + 17	Shot of Hydroquinone at $t = 28$ min

factant concentrations (SDS, 99+%, ACROS, France), using potassium persulfate (KPS, 99+%, ACROS, France) as initiator. Two main operation conditions were employed during the tests: 20% solids content with  $60^\circ\text{C}$  as the reaction set-point temperature and 10% solids content with  $70^\circ\text{C}$  as the reaction set-point temperature.

The experimental procedure and set-up were described elsewhere.<sup>1</sup> A platinum sensor connected to the conductivity meter was inserted into the reactor to provide *in situ* measurements of latex conductivity. Both temperature and conductivity were measured every 10 s. Samples were regularly collected during the reaction for off-line analysis of conversion ( $x$ )—by gravimetry, and average particle size ( $dp$ , nm) by dynamic laser light scattering (S7032-Malvern Instruments Lo-C). These pieces of information were then used to calculate the number of polymer particles in the latex ( $N_p$ ) in accordance with eq. (3).

$$N_p = \frac{6 \cdot m_m \cdot x \cdot 10^{21}}{\pi \cdot \rho_{\text{pol}} \cdot dp^3} \quad (3)$$

#### Effect of solids content: unseeded batch reactions

Styrene emulsion polymerization runs were carried out using 20% (w/w) solids contents. Experimental conditions are reported in Table II. It must be pointed out that in experiment S16 the surfactant concentration was lower than the concentrations used in the calibration data set. Another important aspect is the sudden addition of hydroquinone during experiment S17 to halt the reaction. Experiment S17 is similar to experiment S13, but includes a shot of hydroquinone (HQ), reaching a concentration of 3.0g/L of HQ in the reactor. This test was performed to stop the particle nucleation quickly and verify whether the conductivity model response would describe the reactor response properly.

Figure 1 summarizes the results obtained for the batches carried out with 20% (w/w) of solids content. Basically, the  $N_p$  estimates agree well with the experimental values, particularly for those runs carried out with higher surfactant concentrations. Model deviations are of the order of the experimental error. This test shows that the model is able to perform predictions outside the calibration ranges used for surfactant concentrations and solids content. Moreover, both the conductivity and the temperature profiles were quite different from those observed previously in the calibration data set, which supports the model adequacy to describe the conductivity measurements.

In all cases, the model provides very good estimate of the measured values of  $N_p$  during the nucleation period. When the shot of hydroquinone was performed (S17), the reaction stopped immediately, as one can observe following both the temperature and conversion profiles. Furthermore, the typical decrease of the conductivity signal during the nucleation period is suddenly stopped after the HQ addition, and the model was able to capture the nucleation interruption.

Figure 1 also shows that the conductivity model performs correctly when the solids content in the recipe is changed from 10 to 20%. Thus, it would appear that the parameters estimated at 10% solids are still valid at 20%. This is comforting, as it implies that we can use one set of calibration data for a moderate range of experimental conditions (of course, how wide this range is needs to be verified). It can be observed that the conductivity model delivers reliable predictions on  $N_p$  under different conditions.

#### Effect of temperature: unseeded batch reactions

Most conductivity meter devices also measure the reactor temperature at the same time as the conductivity to compensate for temperature deviations of the conductivity signal. This compensation is generally accomplished by using an internal calibration law that relates the conductivity measured at a given temperature to the conductivity measured at the set point. In this study, the conductivity measurements were not compensated by the temperature drift because it was assumed that the conductivity model would be able to capture the deviations induced by changes in the reactor temperature. To verify the applicability of the conductivity model at higher temperatures, styrene emulsion polymerization runs were carried out at  $70^\circ\text{C}$ . Experimental conditions for these tests are reported in Table III.

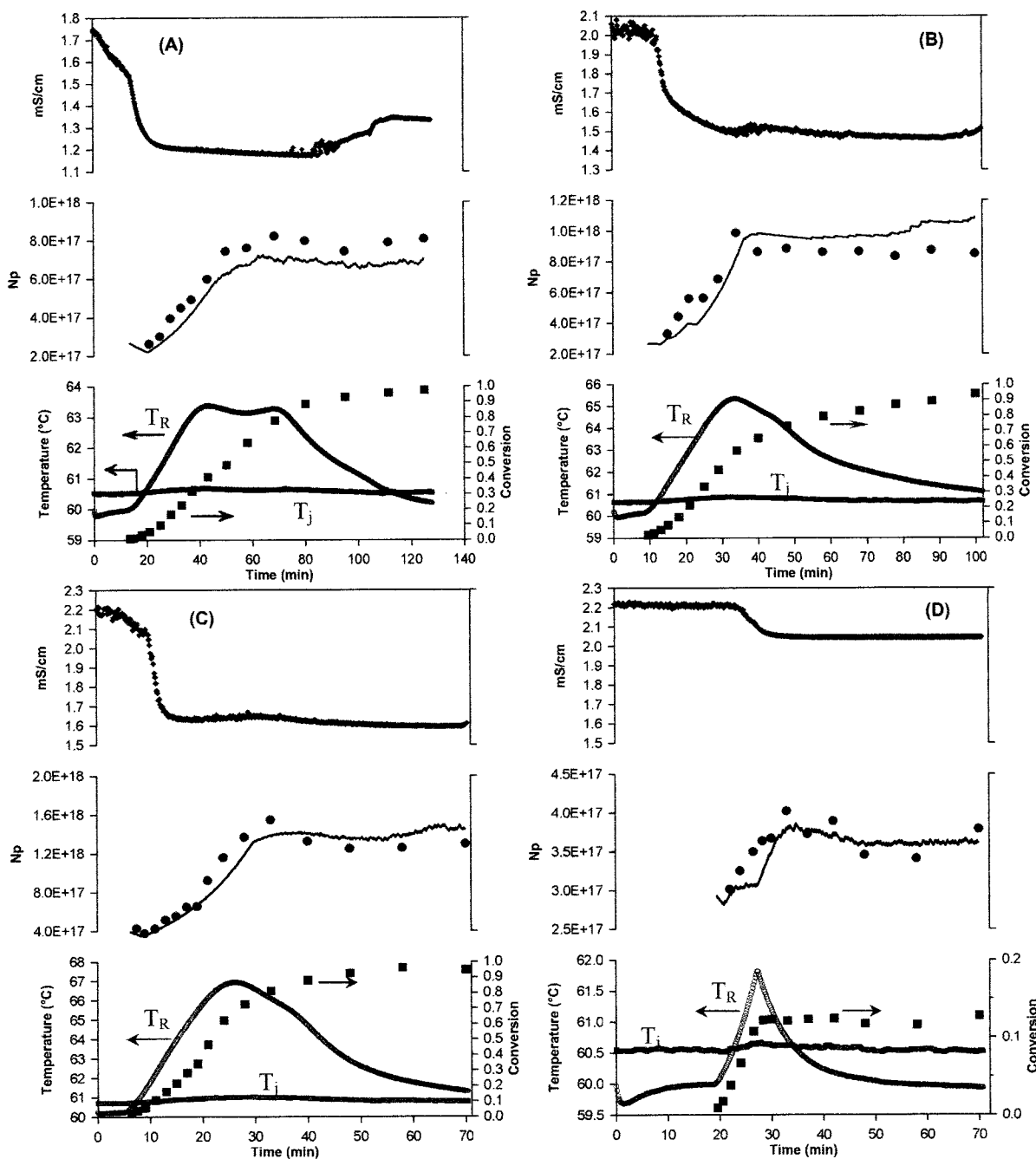


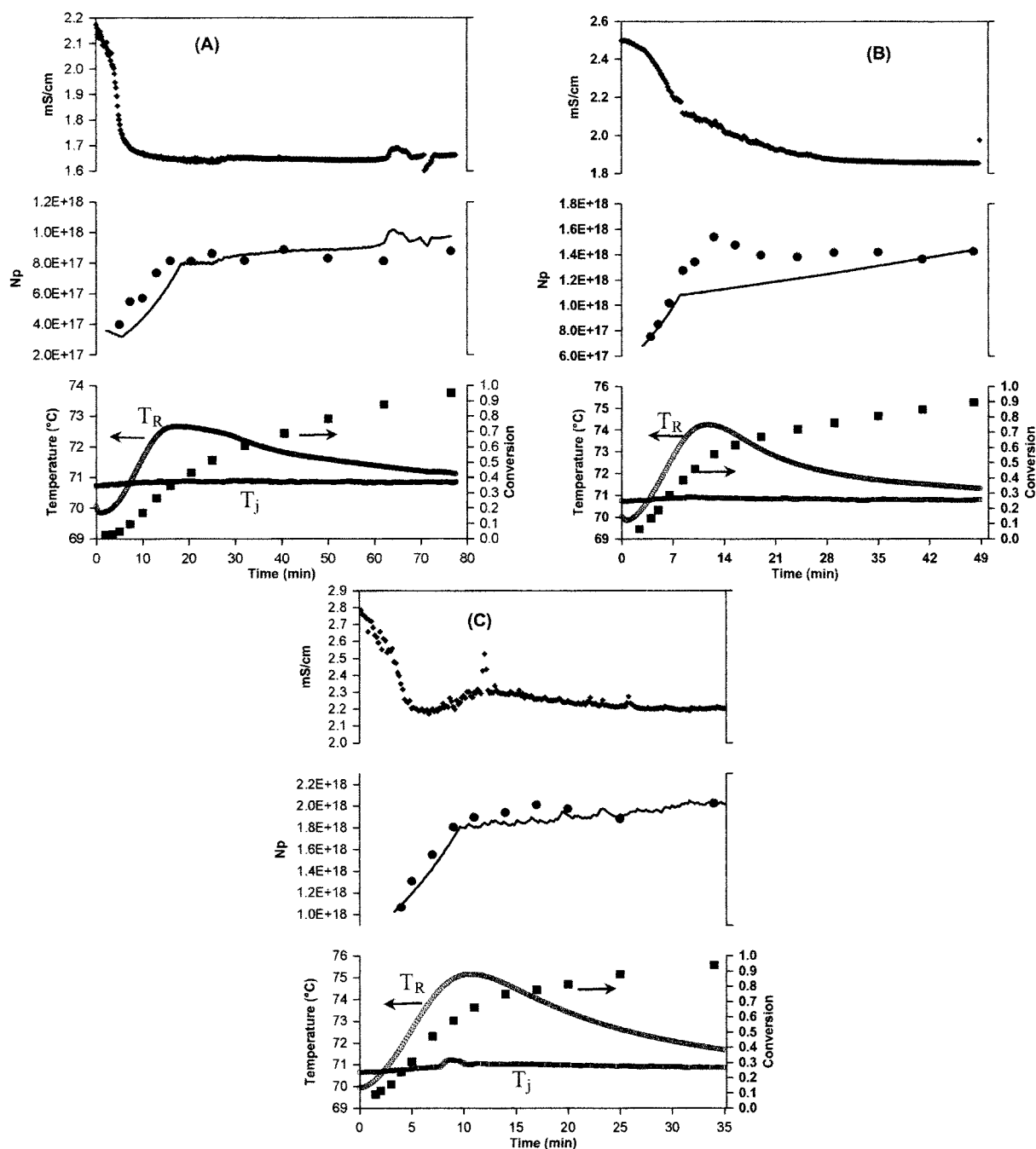
Figure 1 Experimental off-line latex properties, on-line measurements, and model results for  $N_p$  during batches with 20% (w/w) solids content: validation results for S16 (A), S14 (B), S13 (C), and S17 (D). N.B. Two temperature curves are shown: Reactor temperature ( $T_R$ ) and jacket temperature (no label).

The results obtained for the experiments reported in Table III are exhibited in c. The batch S7 (SDS = 0.02 M) was the only case where  $N_p$  estimates are not in good agreement with the experimental data. In this run, numerical difficulties were encountered during computation of model predictions, just after the interruption in the conductivity signal due to a brief loss of

TABLE III  
Styrene Polymerization Batches at  $T_r = 70^\circ\text{C}$

Exp	SDS	Final $N_p$
S9	0.01 M	8.8E + 17
S7	0.02 M	1.4E + 18
S8	0.03 M	2.0E + 18

Solids content = 10% (w/w); KPS = 1.00 g/L.



**Figure 2** Experimental off-line latex properties, on-line measurements, and model results for  $N_p$  during batches at 70°C: validation results for S9 (A), S7 (B), and S8 (C).

information caused by an unidentified (but temporary) process malfunction. This interruption took place in the middle of the particle nucleation period. From this point on, the model no longer predicts the data well. If one observes Figure 2 with care it can be seen that the conductivity signal profile is discontinuous because of the temporary sensor failure. The

perturbation step, however, is of the order of 5% of the overall change of conductivity signal along the batch. This indicates that model responses may be quite sensitive to certain loss of information. Therefore, it might be interesting to study how sensitive results are to changes of certain key process variables, such as the reactor temperature and monomer conversion.

TABLE IV  
Unseeded Semibatch Reactions with Monomer  
and Surfactant Feedings

Variable	S22	S24
$\tau_o$ (%)	10	20
$\tau_f$ (%)	17	30
$[\text{SDS}]_o$	0.02 M	0.02 M
$[\text{SDS}]_f$	0.047 M	0.05 M
$dp_o$	< 40 nm	< 40 nm
$dp_f$	71 nm	81 nm
$F_e$	2.66 g/min	2.90 g/min
${}^a F_m$	3.20 g/min	6.80 g/min

<sup>a</sup> Not kept constant; KPS = 1.00 g/L.

$F_m$ ,  $F_e$ —feeding flow-rate of monomer and surfactant;  
 $\tau$ —solids content

#### Effect of solids content: unseeded semibatch reactions

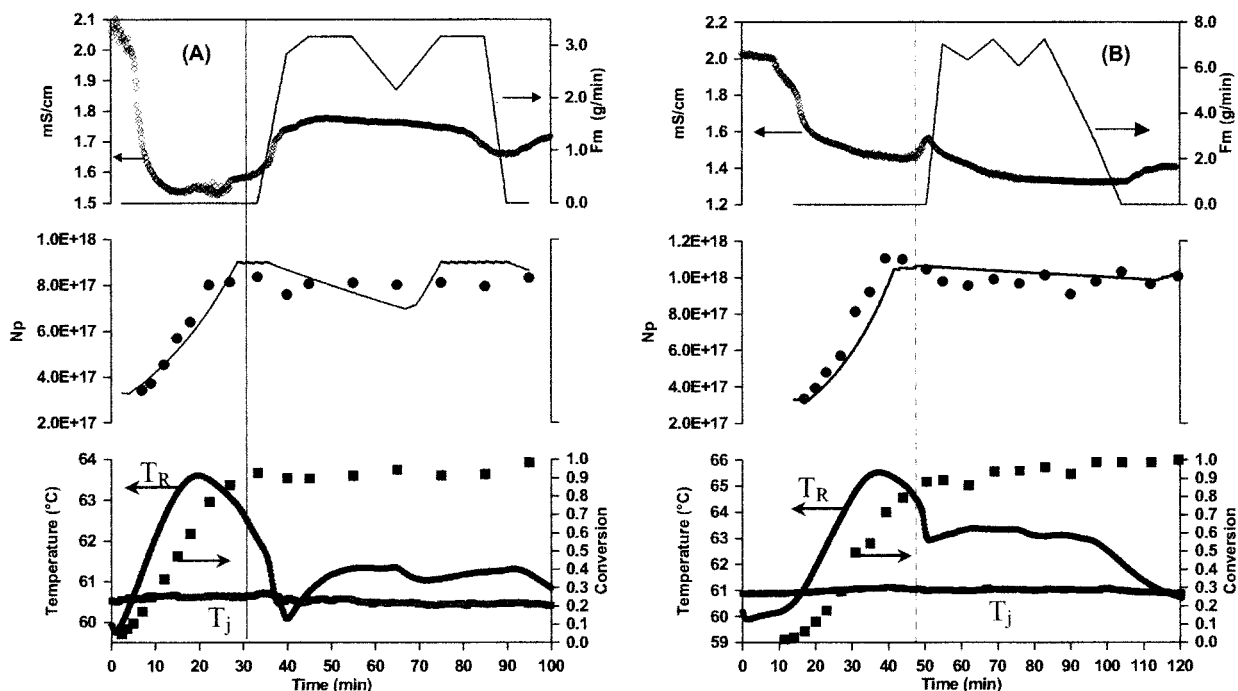
Unseeded semibatch emulsion polymerization reactions of styrene were also carried out using the experimental setup described previously. A solenoid dosing pump (ProMinent) was included in the apparatus to feed the monomer into reactor. A small burette containing a concentrated surfactant solution installed on the reactor lid provided the surfactant feed. The burette valve was operated in different positions depending on the experiment to provide either constant or time-varying feed flow rates of surfactant to reactor. The surfactant feed flow-rate values were calculated by considering the volume read in the burette and the time interval between successive readings. Usually, the monomer feed flow rate was not kept constant; instead, it was deliberately varied to provide a good test to the conductivity monitoring strategy. Table IV summarizes the experimental conditions used for the unseeded semibatch emulsion polymerization reactions. Basically, these reactions started in batch following the same procedure described previously<sup>1</sup> with 10 or 20% solids content, and after nucleation is finished, the surfactant and monomer feed streams were turned on, starting the semibatch period. Even though the model was not applied on-line during such experiments, the moment at which the semibatch feed stream was introduced was actually identified by the conductivity measurements because it is easy to identify the minimum in the conductivity signal that corresponds to the end of the nucleation period in a batch polymerization reaction. According to the light scattering analysis of particle size distribution, all of the experiments summarized in Table IV presented monodispersed PSD. This allowed us to make computations of  $N_p$  accurately.

Model predictions are compared with experimental off-line data and on-line measurements of temperature and conductivity shown in Figure 3. First of all, it should be noted that the conductivity signals in both experiments clearly respond to the different events observed in the reactor, such as the inhibition period during the higher solids content experiment (S24) and the nucleation stage during the batch period. Once the surfactant is added to reactor during the semibatch period, the conductivity signal increases. When the monomer feed stream is turned on, the conductivity measurements tend to decrease for two main reasons: (1) the increased concentration of nonconducting species like styrene; (2) the increased polymer surface area that demands more surfactant from the medium. Even though the drop in the temperature with the surfactant/monomer additions may also cause some decrease in the conductivity, the changes in temperature during the semibatch stage are small (1–2°C). Therefore, temperature effects seem to be of minor importance on the conductivity signal (see the following section). Nevertheless, model predictions are in very good agreement with the experimental values of  $N_p$  in both tests.

#### Effect of solids content: seeded semibatch reactions

Following the unseeded semibatch series, seeded semibatch emulsion polymerization reactions of styrene were conducted, using only monomer feeding (no surfactant feeding). For each test, known amounts of polystyrene latex (used as seeds), water, and SDS were charged to the reactor. When both the conductivity and temperature signals were stable, the initiator (KPS) was added. The seeds were used after the synthesis stage without further treatments. Table V shows the experimental conditions of each test, such as the initial (and final) solids content and average particle diameter associated to the polystyrene seeds introduced into the reactor, the monomer flow rate, and the theoretical final average particle diameter calculated supposing that the seeds' particles grow without suffering coagulation or renucleation during the reaction. Different conditions were tested to evaluate the conductivity model performance during reactions with solids content evolving from 10–15% to 35–40% solids.

Figure 4 shows results obtained when the conductivity model is inverted and applied to monitor  $N_p$  during seeded emulsion polymerization reactions. Monomer feed flow rate and off-line measurements of conversion for the different runs are also presented. In all four experiments, model predictions are in good agreement with the experimental values of  $N_p$ . Furthermore, the number of polymer particles



**Figure 3** Experimental off-line latex properties, on-line measurements, and model results for  $N_p$  for unseeded semibatch processes: validation results for S22 (A) and S24 (B). Vertical dashed lines indicate the beginning of the surfactant addition into the reactor.

at the end of each semibatch reaction is the same as the number at the start, indicating that coagulation or renucleation probably did not occur. This result is supported by Table V, which shows good agreement between calculated and experimental average particle size for the final polymer. This means that the styrene added has been consumed by the existing particles causing them to swell so that surface area is increased. The decrease in conductivity observed is therefore due to the adsorption of SDS from the aqueous medium to stabilize this new surface area.

It is interesting that the conductivity signal seems to be insensitive to the temperature drifts during the reactions,

even when high oscillations (2–3°C) occur. Regarding Table V, one can observe that the experiments S28 and S30 were conducted with the lowest monomer feed flow rate. As a consequence, these experiments show the slowest decreases in conductivity. This may explain why these two experiments presented the best monitoring results for  $N_p$ , as supported by Figure 4.

### PREDICTING $N_p$ FROM NOISY SENSOR MEASUREMENTS

In addition to the conductivity signal, the  $N_p$  prediction strategy evaluated herein relies on conver-

**TABLE V**  
Seeded Semibatch Reactions with Monomer Feeding

Variable	S25	S26	S28	S30
$\tau_o$	10	12	16	10
Seed	S24	S25	S26	S24
$\tau_f$	37	40	40	38
$[\text{SDS}]_o$	0.03 M	0.04 M	0.03 M	0.03 M
$dp_o$	85 nm	129 nm	205 nm	85 nm
$dp_f$	131 nm	205 nm	272 nm	140 nm
$^a dp_f(\text{calc.})$	131 nm	188 nm	276 nm	133 nm
$^b F_m$	7.0 g/min	3.5 g/min	3.0 g/min	2.0 g/min

<sup>a</sup> Final particle diameter calculated if no renucleation nor coagulation occur.

<sup>b</sup> Not kept constant.



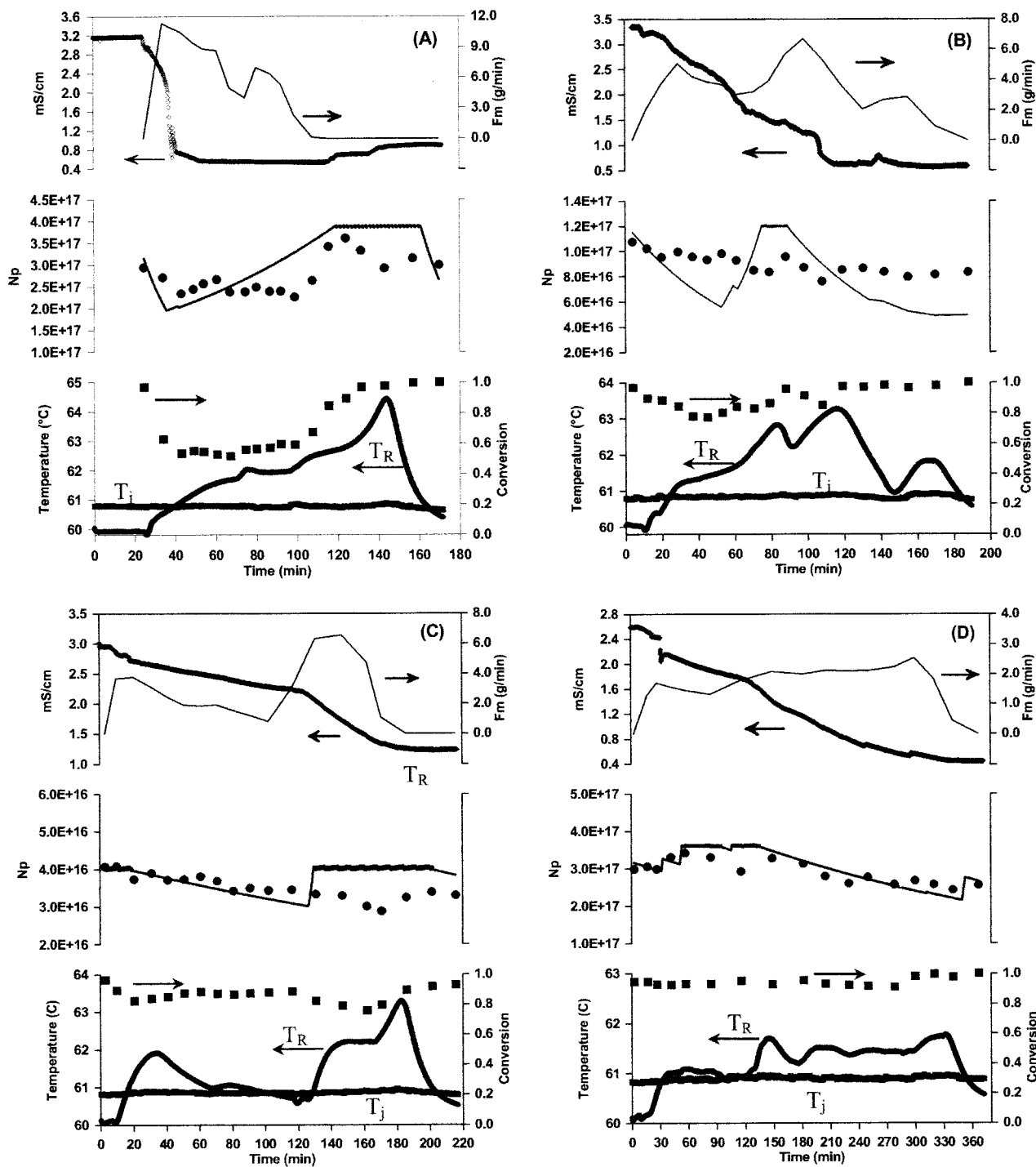
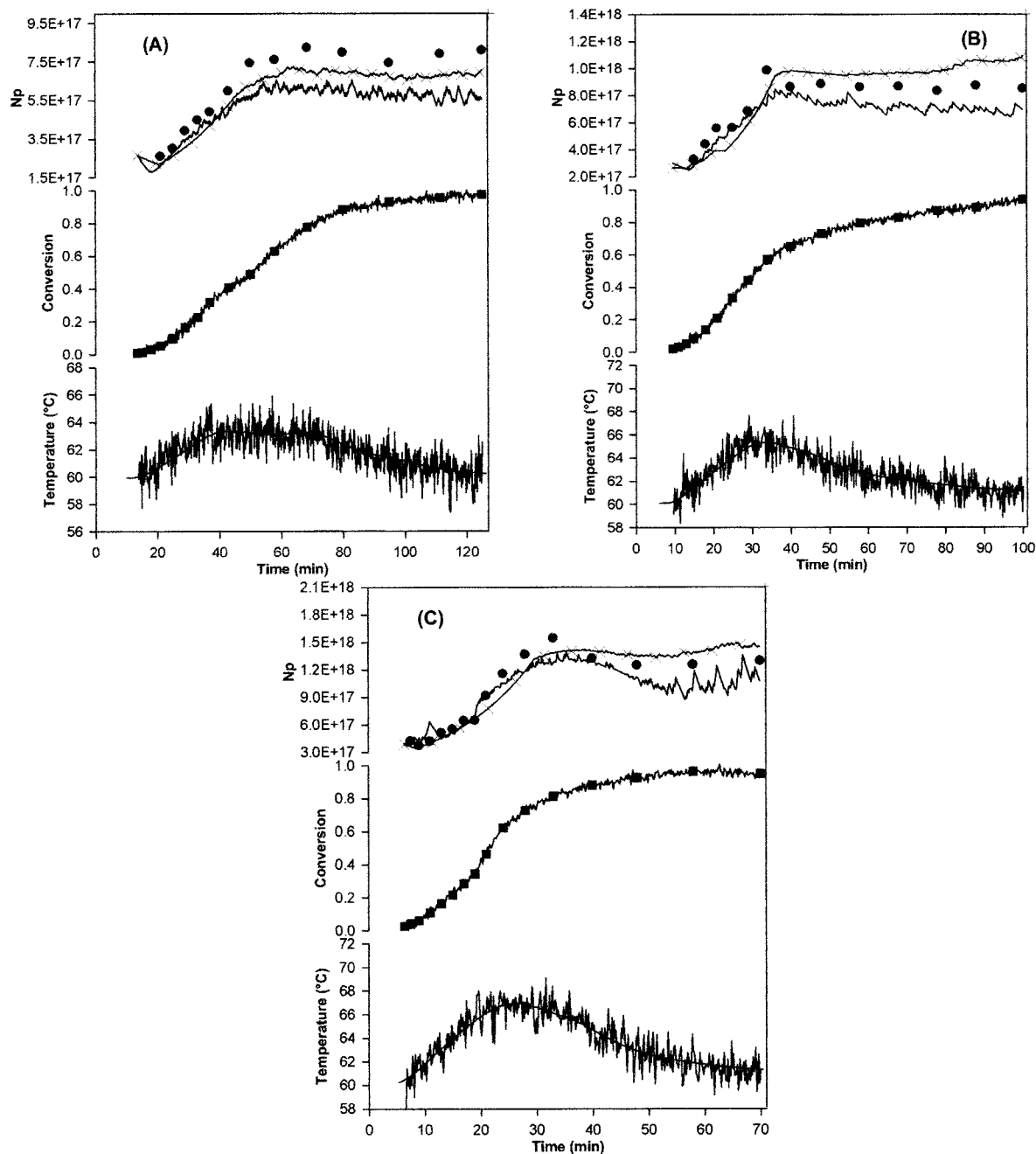


Figure 4 Experimental off-line latex properties, on-line measurements, and model results for  $N_p$  for seeded semibatch processes: validation results for S25 (A), S26 (B), S28 (C), and S30 (D).

sion and temperature measurements. Reliable conversion and temperature measurements can be easily obtained in lab-scale reactors. However, in industrial plants, these measurements can be disturbed to a certain extent. To evaluate how noise, or variations in the temperature and conversion inputs

can affect the model ability to predict  $N_p$ , simulation studies were performed by perturbing conversion and temperature measurements at random within specific ranges, using  $\pm 2^\circ\text{C}$  for the temperature signal and  $\pm 0.03$  for conversion. These noisy measurements were combined with the actual conduc-

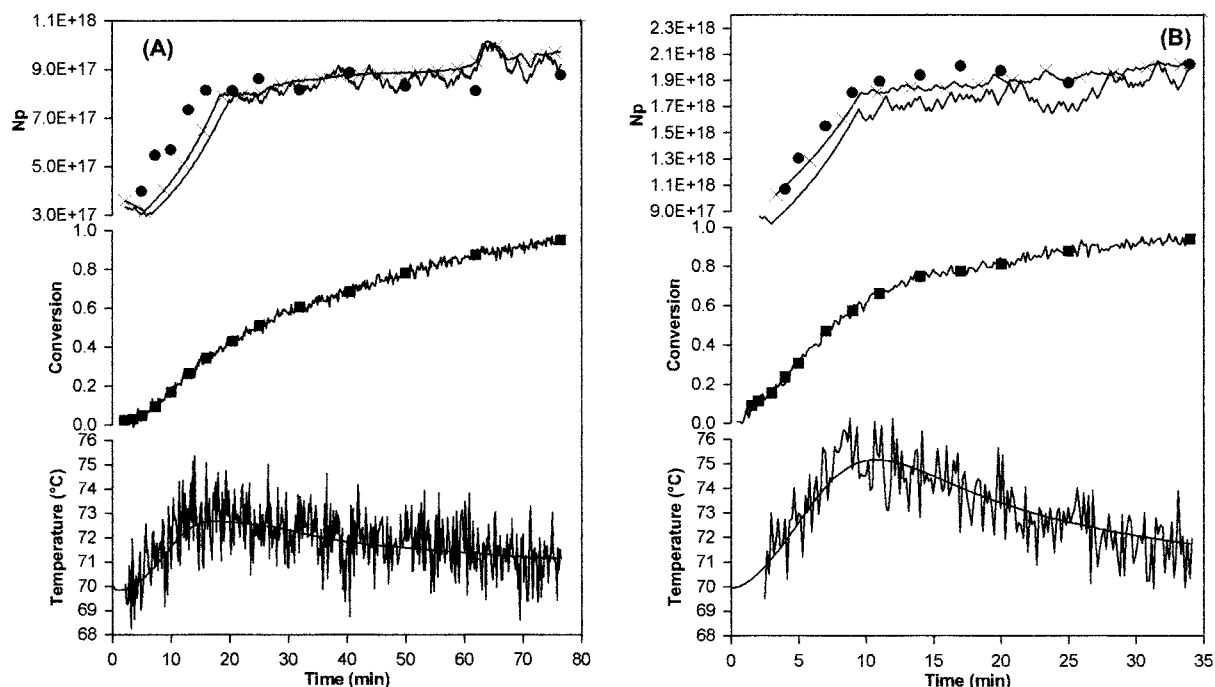


**Figure 5** Model results for  $N_p$  under normal conditions (-x-) and model predictions under on-line noisy measurements (-) during batches with 20% (w/w) solids content: S16 (A), S14 (B), and S13 (C).

tivity signal and used as input to the conductivity model.

The simulation results obtained for polymerization runs with 20% solids content (Table II) are shown in Figure 5. Experimental values for monomer conversion and actual temperature signal are also plotted, and can be compared with the artificial noisy inputs. The evolution of experimental  $N_p$  values can be compared with the  $N_p$  model predictions

when the model is fed by actual data and by simulated noisy data input. As one can observe in Figure 5, the model predictions based on the noisy input data are different from the model predictions based on actual data. The largest differences between the prediction curves are observed at the end of the polymerization runs due to the temperature deviations, which may be regarded as the most influential perturbation. However, even in these cases, conduc-



**Figure 6** Model results for  $N_p$  under normal conditions (-x-) and model predictions under on-line noisy measurements (-) during batches at  $70^{\circ}\text{C}$ : S9 (A) and S8 (B).

tivity responses can be regarded as very good and robust, as temperature deviations are not expected to be so large at plant sites.

Figure 6 shows the simulation results for two runs carried out at  $70^{\circ}\text{C}$ . Similar to the previous results, the model predictions for  $N_p$  based on noisy inputs are in good accordance with the experimental results. Moreover, the model seems to be well suited to predict the  $N_p$  during the nucleation period, even when conversion and temperature signals are subjected to fluctuations of  $\pm 0.03$  and  $\pm 2^{\circ}\text{C}$ , respectively. This may be seen as a further proof of the reliability of the conductivity model.

## CONCLUSIONS

The use of conductivity measurements as a tool to determine  $N_p$  on-line is an original area of study. In the first article of this series, a semiempirical model was proposed to describe the conductivity signal as a function of the latex composition and of the reactor temperature. The model was inverted and combined with conversion and reactor temperature measurements, being able to perform good prediction of  $N_p$ . In this second article of this series, the model is validated at different conditions of solids content and temperature. Results show that model

parameters estimated for batch runs with 10% solids are still valid for distinct reactions with 20% solids (and up to 40% in the semibatch runs). Polymerization runs involving surfactant concentration lower than those used during model calibration were also included in the analysis with satisfactory results. Reliable predictions of  $N_p$  during additional unseeded and seeded semibatch reactions were also provided by the conductivity model. Simulation studies revealed that disturbances in the monomer conversion and reactor temperature measurements lead to slightly corrupted values of  $N_p$  (with respect to base case measurement), but only to a small extent. Therefore, besides being inexpensive, the conductivity strategy presented shows little sensitivity to the disturbances generally encountered during actual emulsion polymerization processes. Consequently, these results are encouraging, and show that the conductivity strategy presented is robust enough and can be applied at industrial sites.

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