Control and Design of Average Particle Size in Styrene Suspension Polymerizations Using NIRS

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ABSTRACT: In a previous paper, Santos et al. (J Appl Polym Sci 1998, 20, 1737) showed that NIRS may be used efficiently for in-line evaluation of average particle sizes in styrene suspension polymerizations if proper calibration is carried out with the help of both multivariate techniques and nonlinear models. In the present work, the technique presented by Santos et al. was used for in-line evaluation and for control and design of average particle sizes during styrene suspension polymerizations carried out in the batch mode. The effects of agitation speed and stabilizer concentration on the particle-size Distribution (PSD) were investigated. It is shown here that this technique allows the successful design and real-time control of particle sizes in lab-scale styrene suspension polymerization reactors. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 453–462, 2000

Key words: process control; NIRS; near infrared spectroscopy; particle; size; suspension; polymerization

INTRODUCTION

Polymer particle morphology (particle size, shape, and internal structure) affects resin performance in many important applications, consequently affecting the economical value of the polymer resin.[1] Besides compounding, processing and bulk-handling properties are affected by the particle size and particle-size distribution.[2] Thus, particle morphology of the final polymer resin is often a key quality parameter to be controlled. Usually, large particles with a relatively uniform size are more desirable. Fine particles may lead to dusting problems, both during bulk handling and processing, and may also be a cause of uneven absorption of plasticizers during dryblending. On the other hand, coarse particles may lead to flow problems during processing and may be a cause for the appearance of *fish eyes* in the finished product.[2] Finally, large resin particles sometimes do not melt completely during processing, which may spoil considerably the appearance and physical properties of the finished articles.

Recently, a relatively large number of publications presenting experimental in-line measurements of particle sizes in heterogeneous media have been reported in the literature. However, most of these investigations refer to systems suspended in diluted diluents without chemical reactions.[3–7] Very little is known about the in-line evaluation of particle sizes in suspension polymerizations.

Monitoring techniques based on near-infrared spectroscopy (NIRS) are very well suited to provide real-time data with simple hardware and software tools. A fiber optic probe can be inserted into an existing reactor system without time-consuming and/or expensive hardware modifications.

Nevertheless, NIR absorbances are mostly overtones or combination bands of fundamental absorbance bands of the IR region and are typically weaker than their corresponding fundamental transitions, so that NIR spectra do not present sharp bands for the different chemical groups. Because of this, the application of NIRS had not been widely used for analytical purposes in organic chemistry. However, the development of multivariate methods for the analysis of large data sets, for example, principal component analysis (PCA) and partial least squares (PLS), led to an exponential growth of the number of applications of NIRS for in-line evaluation of chemical and physical properties of complex chemical media.[8] The combination of NIRS and multivariate techniques was used for in-line monitoring of fermentation processes,[9–11] polymerization processes,[12–18] and the synthesis of organic compounds.[8,19] The successful implementation of these in-line monitoring techniques relies greatly on the proper development of calibration methods. Usually, calibration methods applied to NIRS are based on a linear model representation of the relationship between the desired property and the spectral absorbances of the chemical medium. Multiple linear regression (MLR) and PLS are the regression techniques used most often, although efforts to account for nonlinearities in the calibration model have also been described.[10,20–23]

In a previous article, Santos et al.[18] showed that NIRS may be used efficiently for in-line evaluation of average particle sizes in styrene suspension polymerizations if proper calibration is carried out with the help of both multivariate techniques and nonlinear models. In the present work, the technique presented by Santos et al. is used for in-line evaluation and for control and design of average particle sizes during styrene suspension polymerizations carried out in the batch mode. The effects of agitation speed and stabilizer concentration on the particle-size distribution (PSD) were investigated. It is shown here that this technique allows the successful design and real-time control of particle sizes in lab-scale styrene suspension polymerization reactors.

EXPERIMENTAL

Suspension styrene polymerization batches were carried out at 84°C in aqueous medium, using an 1-L stirred tank reactor and benzoyl peroxide

(BPO) as the initiator. Experimental procedures (determination of molecular weights, particle size distributions, monomer conversion, and spectral analysis) were described previously[18] and will not be described here to avoid repetition. The chemicals used were styrene (provided by Nitriflex Resinas S.A. with a minimum purity of 99%), BPO (provided by Quimibrás, with minimum purity of 95%), distilled tap water, sulfonated polystyrene (PES, provided as an aqueous suspension by Nitriflex Resinas S.A.), and poly(vinyl acetate) (PVA, provided by Fine Chemicals with a minimum degree of hydrolysis of 99%). PES and PVA were used as stabilizers. Chemicals were used as received, without any further purification, to simulate actual industrial operation.

The experimental setup is shown in Figure 1. The reactor used was a jacketed glass tank equipped with a reflux condenser, a temperature controller, a stainless-steel stirrer, a sampling device, and a liquid immersion probe for measurement of the NIR spectra. Nitrogen was fed continuously in all reactions to keep an inert atmosphere. The agitator used in the process was a FISATOM 713 T two-bladed airscrew, with a speed controller in the range between 90 and 6300 rpm. NIR spectra were collected at regular intervals of 3 min with an on-line NIRS-6500 spectrophotometer (NIRSystems Inc.), configured to scan the spectral region ranging from 400 to 2500 nm in the transmittance mode. Data acquisition, spectral mathematical treatments, and partial least-squares analysis were performed with the Near-infrared Spectral Analysis Software (NSAS)[24] supplied with the instrument. Agitation speed was measured and controlled with a process tachometer (Takotron TD2004-C) during polymerization batches.

CALIBRATION

The procedure presented previously[18] was used to perform the calibration of the empirical model which relates the average particle sizes with the NIR spectra. The data set used for calibration comprises the data presented in the previous article and additional data used to enlarge the range of the validity of the calibration model. The experimental conditions of the additional polymerization runs are shown in Tables I and II. Runs 1–6 and 18 were added to the previous data set and used for calibration, as discussed below. Runs 17 and 19 were used exclusively for valida-
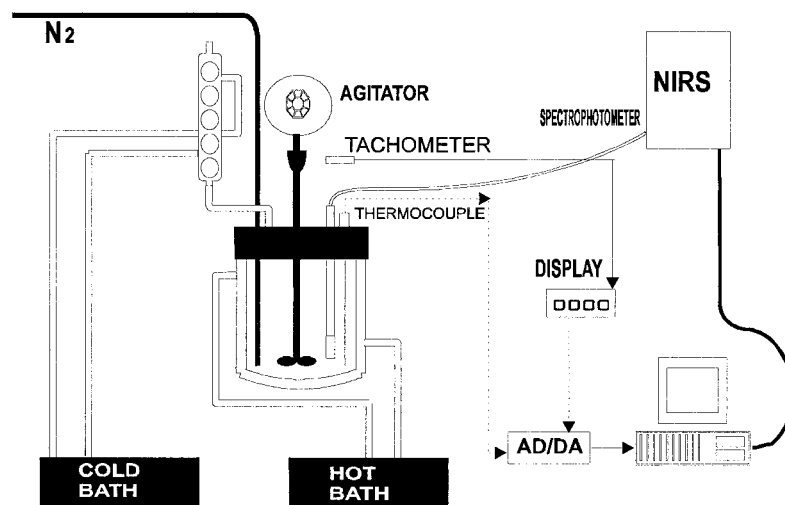
Figure 1   Experimental setup.

tion of the control scheme. The PLS technique was used to build the empirical calibration model.

Figure 2 shows the typical evolution of the standard deviations of the model predictions (using validation data sets) and correlation coefficients (using training data sets) when a cross validation test is performed. It can be observed that a minimum of eight factors must be used in the PLS model to allow the proper prediction of average particle sizes from the NIR data. The model obtained when eight factors are used was called NIRMOD1. Figure 3 shows that the prediction capability of the model for the new data set is

very similar to the prediction capability of models presented previously.[18]

It is very interesting to observe the evolution of particle sizes during run 18, where more complex operation conditions were used to generate data for model calibration. In this experiment, the suspension agent concentration was increased steadily during the batch. As shown in Figure 4, the calibration model is able to reproduce extremely well the general trends observed experimentally through electron microscopy. These results show, unequivocally, that the NIRS can be used for in-line monitoring and control of average

Table I   Additional Data Used for Calibration

Run	Agitation Speed (rpm)	Time (h)	Conversion (%)	$Dp \pm \sigma$ (μm)
1	1960	3.33	70	43 ± 21
1	1960	4.25	83	45 ± 25
2	1490	3.08	70	43 ± 23
2	1490	4.42	81	47 ± 19
3	1100	3.50	77	129 ± 108
3	1100	4.58	80	173 ± 158
4	850	3.42	76	146 ± 23
4	850	4.33	81	111 ± 85
5	514	3.42	76	134 ± 22
5	514	4.33	81	139 ± 82
6	405	3.00	69	—
6	405	4.17	81	171 ± 73

Styrene:water = 0.32 : 1.00; [BPO] = 37.40 g/L; [PES] = 1.5 g/L; T = 84°C.

Table II   Experimental Conditions for Additional Runs

Run	Agitation Speed (rpm)	Time (h)	[PES] (g/L)
17	2100	0.00–1.95	
	1300	1.95–2.95	1.50
	2200	2.95–3.78	
	1900	3.78–4.50	
18	1300	0.00–1.42	1.10
		1.42–1.75	1.40
		1.75–2.25	1.70
		2.25–4.67	2.00
19	500	0.00–1.10	1.00 ($t < 3.25$ h)
	650	1.10–1.83	2.00 ($t > 3.25$)
	1100	1.83–5.00	

Styrene/water = 0.32 : 1.00; [BPO] = 37.40 g/L; T = 84°C.
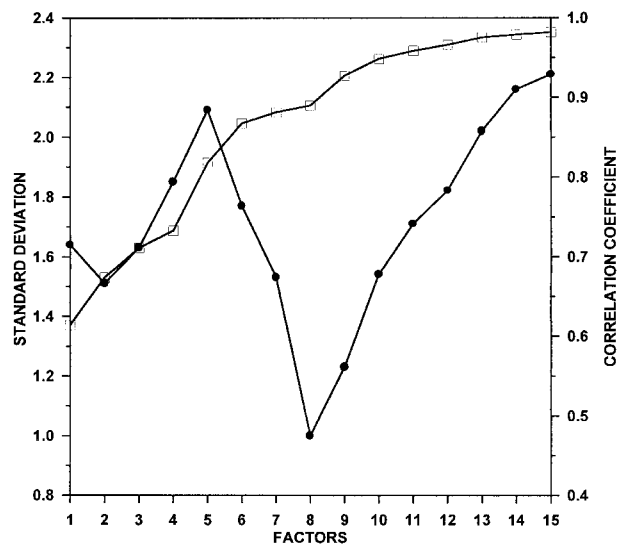
Figure 2 Cross-validation for NIRMOD1.

particle sizes of styrene suspension polymerizations.

To implement the control scheme, it is interesting to enlarge the training data set as much as possible, to increase the model accuracy and reduce extrapolation errors. For practical applications, as many as 100–200 data points may be needed for a good calibration model to be developed. In the laboratory environment, sometimes it is impossible to generate so many experimental points for model calibration (although this constraint could be unimportant in an industrial en-
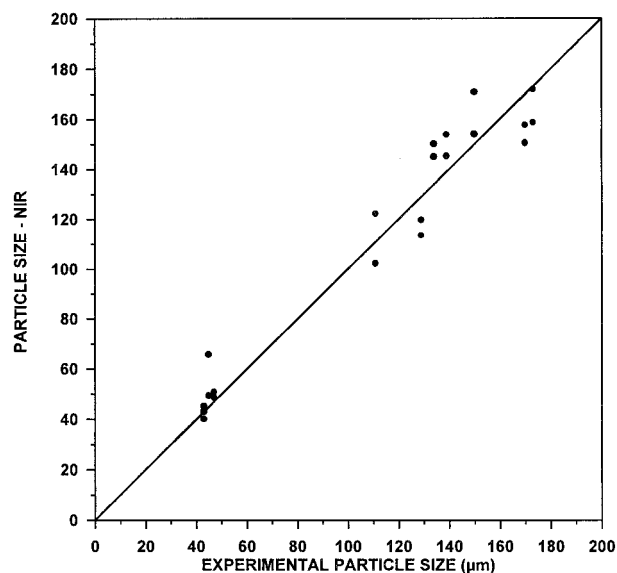
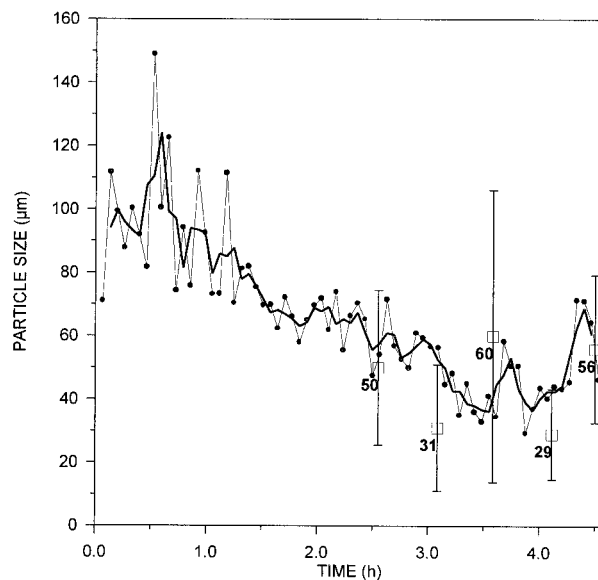**Figure 3** Prediction of additional data with NIRMOD1.

Figure 4 Monitoring of average particle size: run 18.

vironment). Given the excellent results obtained with the previous model, model predictions presented in Figure 4 for Run 18 were artificially added to the training data set, as if they had been obtained experimentally, and used for calibration, as suggested and performed successfully elsewhere.[25,26] If model predictions are sufficiently accurate, this procedure generally leads to significant improvement of the calibration model, because it introduces "experimental" data points in the range of interest uniformly. For instance, results presented in Figure 4 are uniformly distributed over the range 30–120 μm. A new PLS regression model was then built with the augmented data set. Calibration results obtained when eight factors were used are shown in Figure 5 for the same data points presented in Figure 3. One may observe the significant improvement of the model predictions. This augmented model, called NIRMOD2, was then used for control purposes.

CONTROL OF AVERAGE PARTICLE SIZES

Agitation speed and stabilizer concentration are natural manipulated variable choices for controlling particle morphology in suspension polymerization reactors. Although it is generally accepted that these variables do not cause any influence upon the kinetics of polymerization,[27] so that the control of PSDs and the control of monomer con-
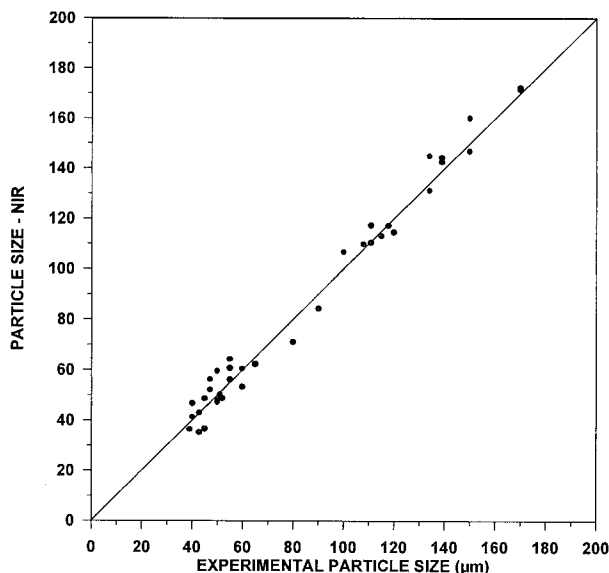
Figure 5 Prediction of additional data with NIRMOD2.

version and molecular weight distributions are usually assumed to be decoupled, three polymerization runs were carried out using PES as a stabilizer (runs 17, 18, and 19 of Table II), at different agitation conditions, to guarantee that control of the average particle sizes might be implemented independently of the other relevant polymerization variables. Despite the small number of runs, Figures 6 and 7 show that monomer conversion and molecular weight distributions may be assumed not to depend on the levels of agitation speed and stabilizer concentrations used in the experiment, while Figure 8 shows that PSDs experience dramatic changes as agitation speeds and stabilizer concentrations are modified.

Figure 6 shows the evolution of monomer conversion for each run. Although some differences may be observed in the range of conversions between 70 and 90%, from a practical point of view, the reactions are finished after 4 h of reaction, as monomer conversions around 90% are attained at this point. We believe that the addition of the stabilizer suspension may introduce a certain amount of inhibitors in the reaction medium, as stabilizer suspensions were used as provided without any further purification. This may explain the reaction delay observed after addition of the stabilizer to the reaction medium. This effect should be avoided during actual operation, but is not important for our purposes here.

Figure 7 shows the evolution of the weight-average molecular weights (M_w) for each run. M_w

remains essentially constant throughout the batch in all cases, which indicates that changes of agitation speeds and stabilizer concentrations are not affecting the kinetics of polymerization significantly. Besides, M_w changes among the batches may be regarded as unimportant, given the fact that chemicals were not purified. Although it is not shown, the polydispersity index was always very close to 2.

Figure 8 shows the final PSD of the dry polymer powder, as obtained through electron microscopy. Different from the previous cases, changes are very significant. It may be observed that, as the agitation speed increases, the PSD becomes broader. On the other hand, as the stabilizer concentration increases, the PSD becomes narrower. It is particularly interesting to observe that the frequent modification of the agitation speed in run 17 led to bimodal PSDs, with large concentrations of fines in the number and large concentrations of coarse particles in the volume. However, for the purposes of this work, the most important thing is to observe that both agitation speeds and stabilizer concentrations are extremely effective to change the PSD of the final polymer powder, without introducing much change in the other polymerization variables.

Figures 9–11 show the evolution of the average particle sizes in runs 17–19, as evaluated by the spectrophotometer and measured through electron microscopy. Results may be regarded as excellent in all cases. The only exception is the final
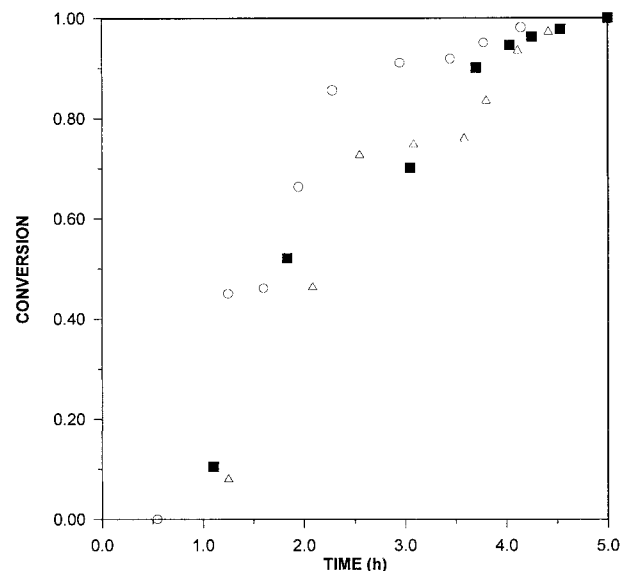

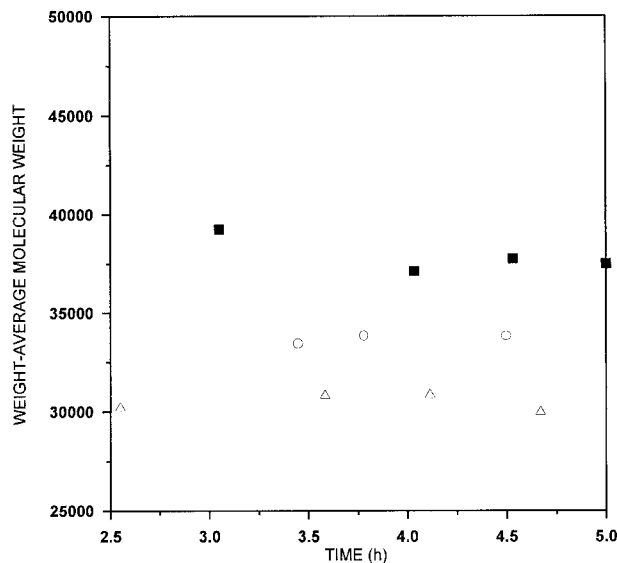**Figure 6** Evolution of monomer conversion for runs (○) 17, (△) 18, and (■) 19.

Figure 7 Evolution of weight-average molecular weights for runs (○) 17, (△) 18, and (■) 19.

average particle size obtained for run 17. As discussed before, PSD was found to be bimodal in this case, which is also reflected through the extremely large range of the 95% confidence region of the PSD shown in Figure 9. It is important to observe that all trends observed with the spectrophotometer are confirmed by the micrograph results. In all cases, it seems that average particle sizes decrease during the first moments of poly-
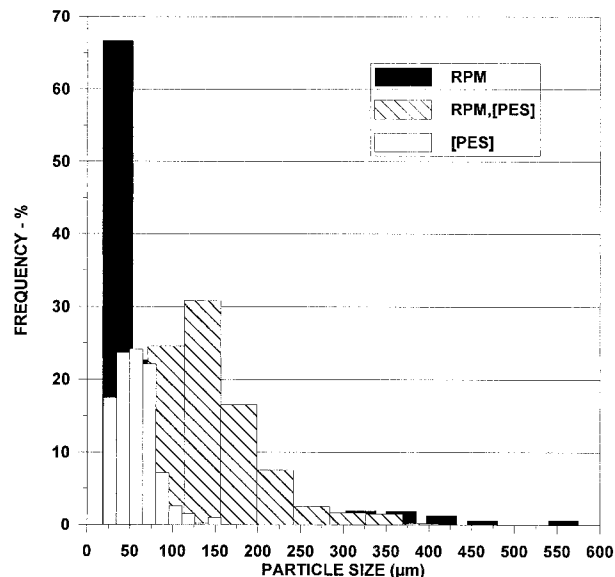

Figure 8 Final PSDs for runs 17 (changes of RPM), 18 (changes of PES), and 19 (changes of RPM and PES).
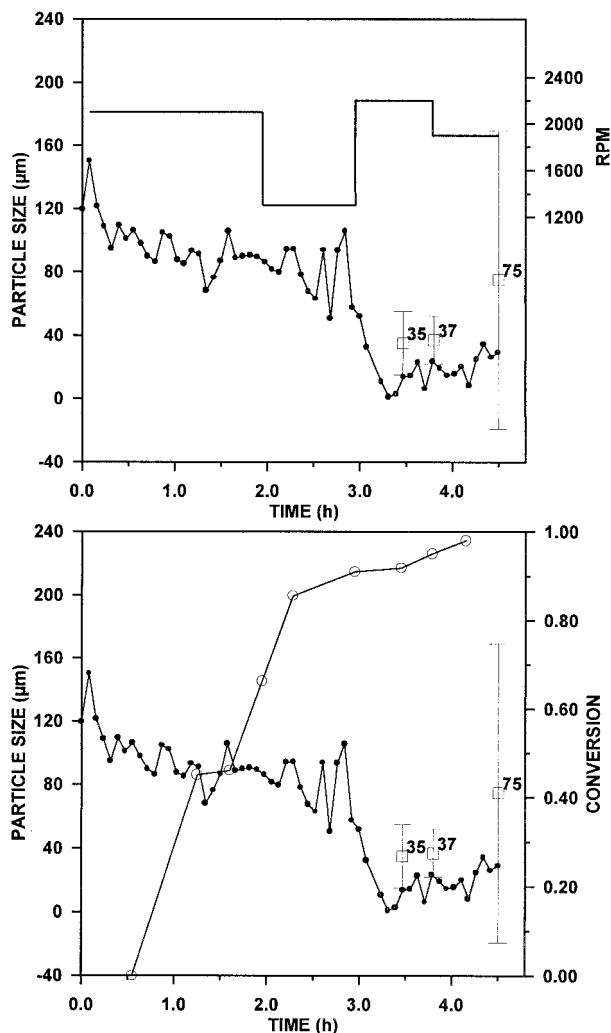

Figure 9 Evolution of average particle sizes for run 17.

merization (PSDs are governed by breakup phenomena) and increase during the last stages of the polymerization (PSDs are governed by coalescence phenomena, due to the high viscosities of the suspended droplets). This shows that PSDs evolve continuously during the batch and should be controlled if improved particle morphology is desired.

Results presented in Figures 9–11 agree extremely well with the qualitative trends presented by Kiparissides.[28] According to his observations, the polymer suspension usually undergoes an initial size-reduction period, where the droplet size distribution is narrowed. Afterward, a sticky period, characterized by an accelerated viscosity increase of the dispersed phase and a corresponding reduction of the breakage rates,
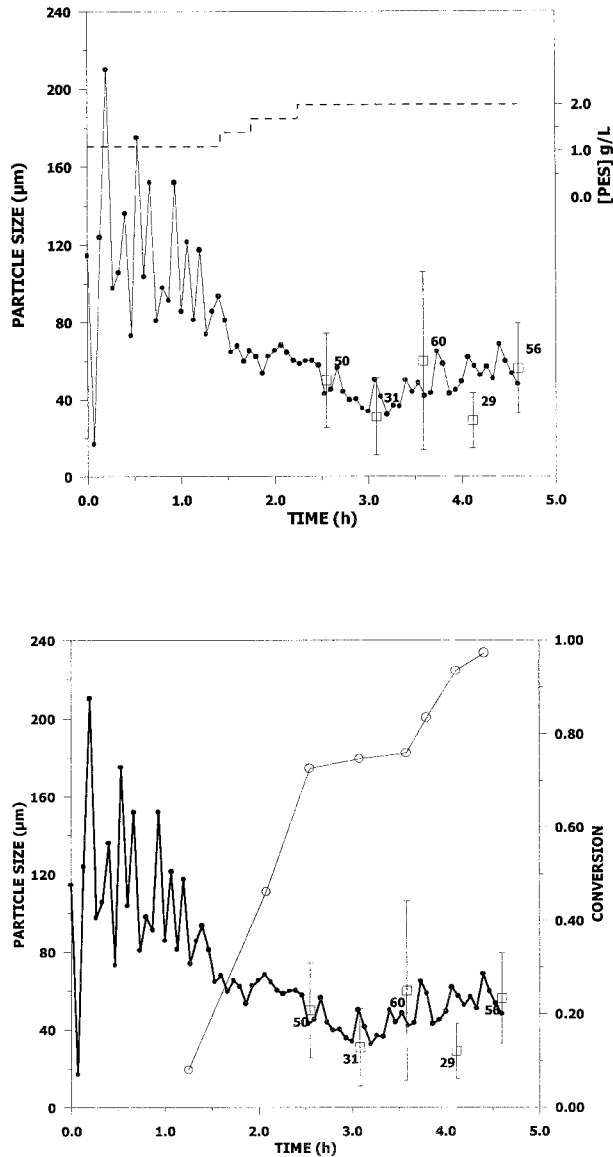
changes of the stabilizer concentration, the results presented previously show that addition of a stabilizer to the reaction environment may cause some sort of coupling between the dynamics of monomer consumption and the dynamics of the PSD. Besides, the experiments seem to indicate that it may be necessary both to add a stabilizer (during the coalescence period) and to reduce the stabilizer concentration (when droplet breakup dominates the dynamics of PSD) along the polymerization batch. The second operation is virtually impossible, unless additional pure water is added to the system, which may cause significant perturbation of the reaction environment and of the PSD.
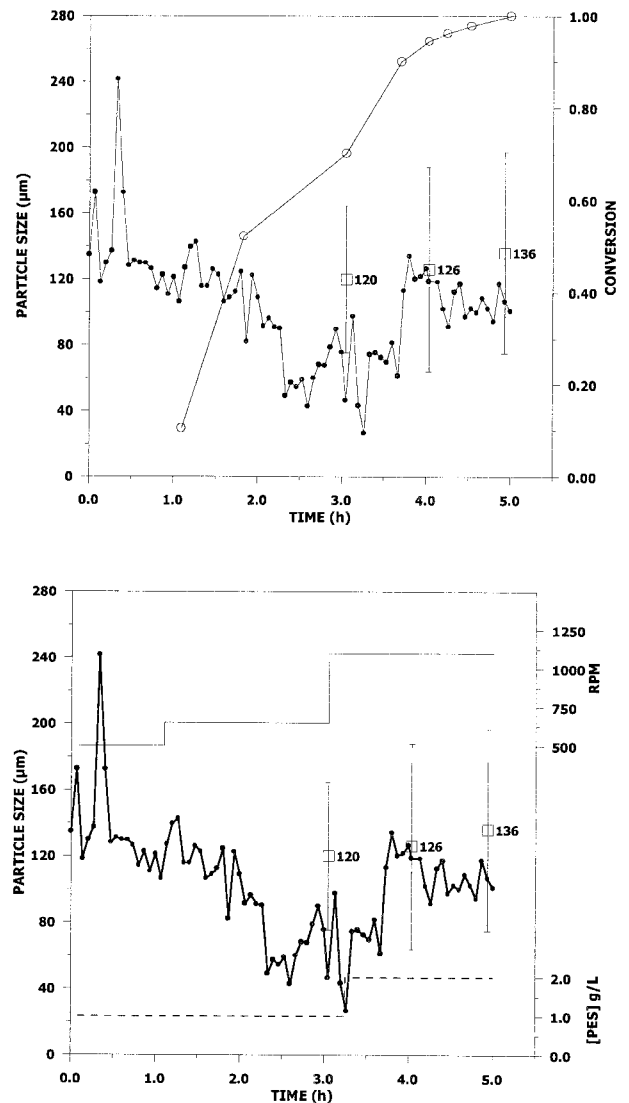

Figure 10   Evolution of average particle sizes for run 18.

leads to PSD broadening and shifting to larger particle sizes. This occurs because coalescence rates during this period are much higher than are breakage rates. This trend is maintained until the PSD reaches its particle identification point (PIP), where breakage and coalescence cease and the PSD acquires its final shape. This behavior is qualitatively described in all runs, which highlights the adequacy of the NIR spectrophotometer to control the final polymer particle size.

To implement the control scheme, agitation speed was then selected as the proper control variable. Although the PSD also responds to

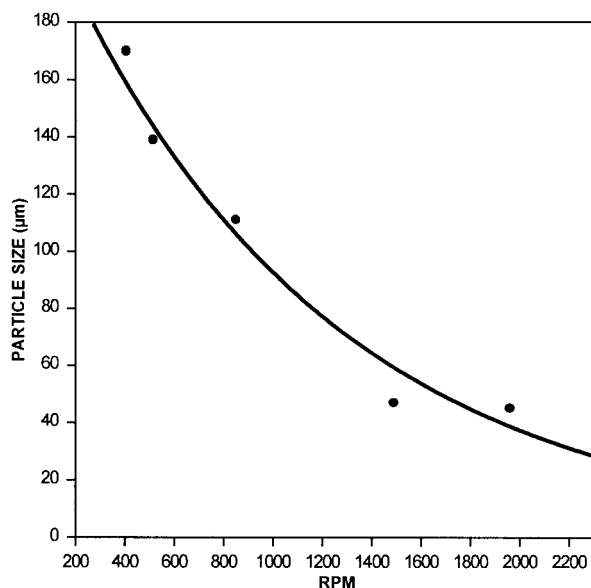**Figure 11**   Evolution of average particle sizes for run 19.

Figure 12   Control design curve.

The control algorithm used is a slight modification of the well-known proportional-integral controller. The main objective here was not to implement a novel controller algorithm, but to show that the NIRS might be used successfully to close the control loop of the average particle size. The controller depends on a design curve, built with the calibration model and the experiments available, which shows how average particle sizes depend on the agitation speed. The design curve is shown in Figure 12. Obviously, this design curve is of limited value, because it is based solely on the sizes of the final polymer particles, does not take into consideration the dynamics of the reactor operation conditions, and cannot be used for batches carried out with different amounts of stabilizer concentration. However, it may be used as a reference for control purposes as follows: First, the NIR spectra are collected by the spectrophotometer and then are transformed into the instantaneous average particle size (D^{exp}). D^{exp} is then used as an input in Figure 12, so that a reference agitation speed at stationary conditions may be obtained (w^{exp}). The procedure is repeated, using the desired average particle size (D^{set}) as input, which leads to the reference agitation speed at stationary conditions (w^{set}). The proportional action is then implemented as

$$w^{k+1} = w^k + K_p(w^{\mathrm{set}} - w^{\mathrm{exp}}) \qquad (1)$$

where the superscript k refers to the kth sampling time and K_p is the proportional gain, made equal

to 1 in all the experiments presented below. The sampling time interval was equal to 10 min in all experiments presented below. The continuous repetition of the procedure described by eq. (1) introduces the desired integral action. We are aware that significant improvements may be introduced in the control scheme, but this is beyond the scope of this text.

To produce a polymer resin with an average particle size within the range of Figure 12, a polymerization batch was carried out with a closed control loop, using PES as a stabilizer and setting the target average particle size to 60 μm. According to the design curve, the agitation speed should be kept constant around 1300 rpm. To force changes of the agitation speed and test the effectiveness of the control scheme, the initial stabilizer concentration was fixed at 1.10 g/L, which is 30% lower than the amount of the stabilizer used in the design curve (1.5 g/L) and tends to produce larger polymer particles. Similarly, the initial agitation speed was fixed at 1300 rpm. The evolution of average particle sizes for this run can be visualized in Figure 13.

Figure 13 shows that during the first hour of the reaction predicted values are highly oscillatory, probably due to the extreme sensitivity of the average droplet size to changes of agitation speed during the first moments of the reaction. For this reason, averages of five predictions (sampling time of 2 min) were used to feed the control-
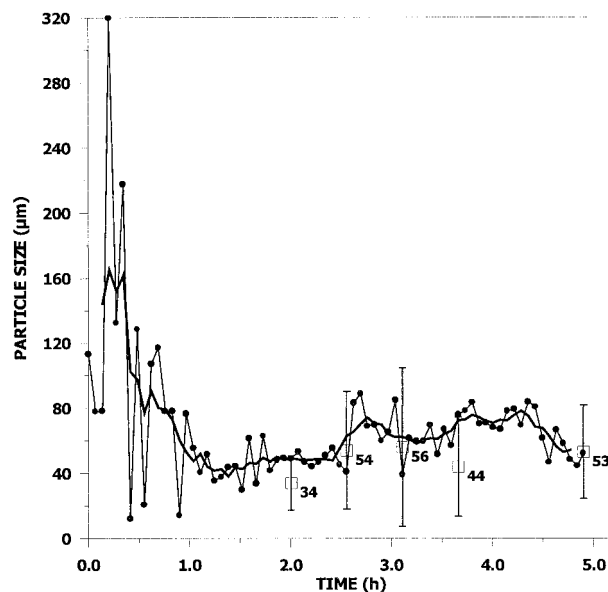

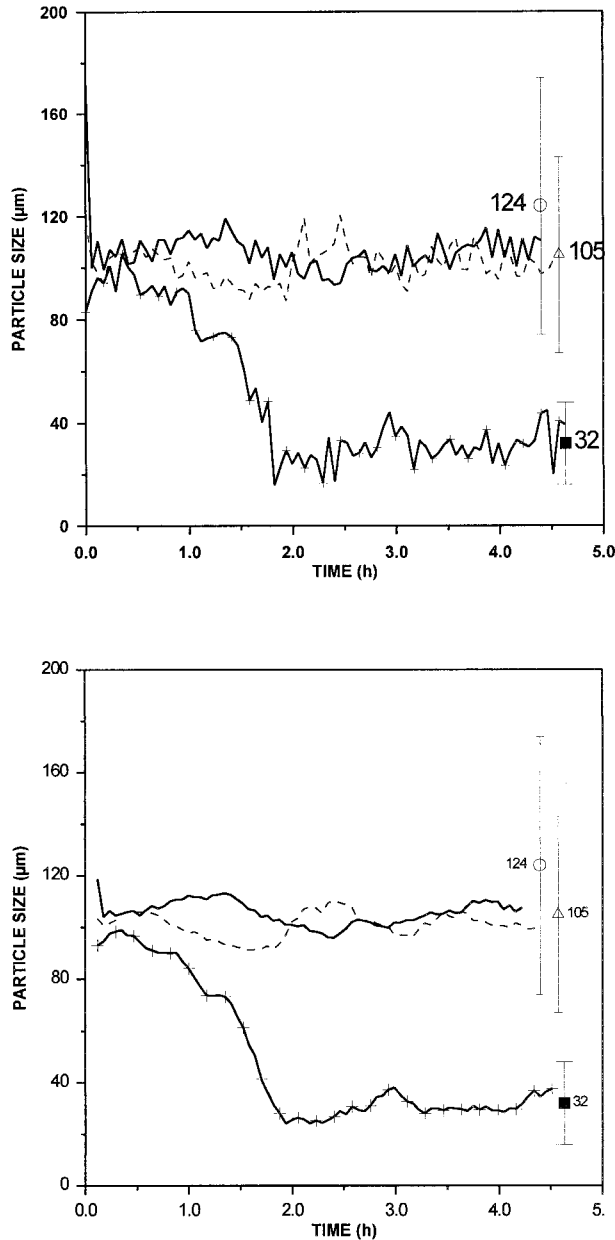**Figure 13**   Closed-loop response of average particle sizes with PES.

Figure 14 Closed-loop response of average particle sizes with PVA at (solid line) 2.0 g/L, (dashed line) 2.5 g/L, and (plus-marked line) 5.0 g/L.

ler. Changes of less than 100 rpm were sufficient to keep the average size around the desired value of 60 μm. During the second hour of the reaction, the NIRS predictions became much more stable, indicating a bias toward smaller-size values, between 50 and 60 μm. The controller decreased the agitation speed slightly and continuously until a value of 1000 rpm. The reduction of agitation speed and the increase of the coalescence rates led to average particle sizes values around 60 μm

during the third hour of the reaction. In fact, between 2.5 and 3.0 h, the predicted sizes increased to values in the range between 60 and 70 μm, which led to an increase of the agitation speed (1300 rpm) and a stable operation. At the fifth hour of the reaction, the system experienced a subtle decrease of the average particle sizes, which did not respond to the controller anymore because the control actions were small (the final average particle size—53 μm—was very close to the target value—60 μm) and because the particles had already reached the form of hard beads. Independent average particle sizes obtained through electron microscopy confirm all trends observed with the NIRS, within the 95% confidence region of the PSD.

Although the control experiment may be regarded as very successful, some points must be emphasized: First, the experiment shows that the best strategy during the first moments of the polymerization seems to be to turn off the controller. The monomer droplets are too sensitive to small changes of the agitation speed, which leads to excessive oscillation of prediction values. In-line evaluation of monomer conversion may provide the exact point where the PSD controller must be turned on. According to Figure 6, the styrene conversion value should be in the range between 20 and 30%. Second, the final fall of the average particle size shows that the controller may become ineffective after a certain point where the particle becomes rigid. If additional control action is necessary after this point, the final result obtained will be biased in relation to the desired value. Therefore, the control objective must be attained before the end of the batch. Third, changes of agitation speed necessary to keep the system under control are smooth and small after the initial 20% monomer conversion.

A final test of the controller scheme was carried out with a different stabilizer. According to Santos et al.,[18] the calibration model might be used to monitor the average particle sizes even when the stabilizer was changed. Therefore, PES was replaced by PVA and different runs were carried out with different targets, using different stabilizer concentrations. Two runs were carried out with PVA, at concentrations of 2.0 and 2.5 g/L, fixing the desired particle size at 110 μm. A third run was carried out with PVA at 5.0 g/L, to reach a target value of 30 μm. The stabilizer concentration was increased because the agitation speed to reach 30 μm when 2.5 g/L of PVA is used is excessively high and causes operation problems.

Experimental results obtained are shown in Figure 14. The controller is turned on after the first hour of the reaction. Results may be regarded as excellent, as confirmed by electron microscopy. Dynamic profiles presented in Figures 4 and 14 may be compared with each other to show that the average sizes predicted by the NIRS are much more stable in the second case.

CONCLUSIONS

This work shows that the combination of an NIRS and the PLS technique allows real-time monitoring of average particle sizes in suspension styrene polymerization reactors, permitting a better comprehension of droplet dynamics and of the effect of operational variables upon the evolution of the PSD. The use of this technique for the design and control of average particle sizes was carried out successfully, even when the stabilizer used for calibration (PES) was replaced by another one (PVA). It can be concluded that the NIRS can be used for the in-line control of average particle sizes in suspension styrene polymerizations effectively.

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