# In-Line Evaluation of Average Particle Size in Styrene Suspension Polymerizations Using Near-Infrared Spectroscopy

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ABSTRACT: The main objective of this article is evaluating the influence of average polystyrene particle size upon the near-infrared (NIR) spectra collected during suspension polymerization experiments and observing whether NIR spectroscopy may be used for in-line monitoring and control of average particle size. It is shown that NIR spectra are sensitive to changes of the average particle size, and that standard empirical models (PLS—partial least squares—and NN—neural networks) may be built to correlate average particle size and light absorbance at certain wavelengths fairly well. Finally, it is shown that these models allow the in-line evaluation of average particle size in styrene suspension polymerizations with NIR spectroscopy. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1737–1745, 1998

Key words: near-infrared; suspension polymerization; particle size

## INTRODUCTION

The increasing necessity to improve and assure the quality of industrial products (and particularly of polymer resins) led to the development of very sophisticated pieces of equipment and monitoring techniques for process control. However, the list of instruments and techniques available for in-line evaluation of polymer properties is relatively scarce in the polymer industry. According to Chien and Penlidis,<sup>1</sup> in-line instrumentation is the least-developed part of the technology needed to allow the proper control of polymerization processes. This is particularly true when in-line monitoring of particle size distributions in heterogeneous polymerization reactions is considered. According to Kiparissides and Morris,<sup>2</sup> on-line

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measurement of molecular properties is usually the weakest link in any polymerization closed-up control task. The presence of long measurement delay as well as poor reliability are two common problems associated with the on-line characterization of polymer quality.

The proper characterization and control of particle sizes in heterogeneous polymerizations is important for many reasons. In some systems, such as emulsion polymerizations, the dynamics of monomer consumption and particle size distributions are strongly coupled. In other processes, such as heterogeneous Ziegler-Natta and suspension polymerizations, the production of fractions of small particle diameter may lead to huge losses during the postreaction treatment of the polymer beads. Besides, particles of small diameter may get suspended in the air and spoil the quality of the work environment. Additionally, when the particle diameter is too large, the processing of the final polymer resin may be difficult. For all these reasons, in-line monitoring and control of average particle sizes is very important in heterogeneous polymerizations.

It is not aimed to present here a review of experimental methods for evaluation of particle size distributions in polymerization systems.<sup>1</sup> However, it is important to say that most of them rely on very sophisticated and expensive techniques, such as light scattering and electronic microscopy, and cannot be used for in-line measurements in industrial environments. Therefore, particle size measurements are usually carried out off-line in the lab and, due to the significant time delays that exist between sampling and obtaining the final results, cannot be used for tight control of the polymer process.

A lot of activity has been developed recently regarding the use of near-infrared (NIR) spectroscopy for in-line evaluation of polymer properties.<sup>3–8</sup> This is because the NIR spectrophotometer can be connected directly to the polymerization environment by using a bundle of optic fibers, which carry the light from the light source to the reaction environment and back to the light detector, so that the basic instrument may be placed at safe and controlled conditions even when the probe is installed at harsh ambients.

Generally, NIR spectra are the result of light absorption by organic molecules. All the absorption bands are the result of overtones or combinations of overtones originating in the fundamental midrange (2500 to 16000 nm) infrared region of the spectrum.<sup>9</sup> However, the same sample ground in different conditions gives rise to spectra of different intensities. The coarser samples have higher spectral values, and the effect is stronger for the highest absorbance values. This fact occurs because one part of the energy is reflected at the surface of the sample without being absorbed and, therefore, depends on the size and the shape of the particles. The other part of the energy penetrates the particles and is partially absorbed. This energy is diffracted or refracted into the particles and then reflected according to the different interfaces encountered. The amount of energy absorbed depends on the concentration and on the absorptivity of the chemical constituents present in particles. The final radiation is the sum of the reflection within the particles. Thus, particle size is an integral part of the NIR absorbance values at all wavelengths.<sup>10</sup>

Suspension polymerization is carried out heterogeneously by suspending the monomer (discontinuous phase) as droplets (50–500  $\mu$ m in diameter) in water (continuous phase). The mono-

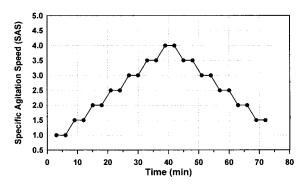
mer droplets (subsequently converted to polymer particles) are prevented from coalescing by agitation and the presence of suspension stabilizers (which may be water-soluble polymers or waterinsoluble inorganic powders), leading to the development of particles of different sizes. As discussed previously, the average particle size may be regarded as an important process variable. The reaction usually follows the classical free radical polymerization kinetics, so that the initiator used in suspension polymerizations are soluble in the monomer droplets, and each monomer droplet may be viewed as a minibulk polymerization system. The kinetics of polymerization within each droplet is, therefore, similar to the corresponding bulk polymerization.<sup>11</sup>

Suspension polymerizations are among the most important polymerization processes, especially regarding styrene homo and copolymerizations,<sup>12</sup> as most styrene-based polymers are produced in suspension processes. Therefore, developing techniques for monitoring suspension reactors is of fundamental practical importance. In spite of that, the operation of such reactors is almost always monitored by simply measuring global variables such as reactor temperature and pressure. Very little is usually known about the quality of the polymer resin until the batch is finished or the lab provides a result, with delays that may reach 10 h.

The main objective of this article is evaluating the influence of polystyrene particle size upon NIR spectra obtained in-line and observing whether NIR spectra may be used for in-line monitoring and control of the average particle size. It is shown here that NIR spectra are sensitive to changes of the average particle size and that standard empirical models, such as those obtained through partial least squares (PLS) techniques and training of neural networks (NN), may be built to correlate average particle size and light absorbance at certain wavelengths fairly well. Finally, it is shown that these models allow the in-line evaluation of average particle size in styrene suspension polymerizations with NIR spectroscopy.

## **EXPERIMENTAL**

Two different types of experiments were performed. The first one consisted of measuring NIR spectra of styrene–water and styrene–water–PES [calcium phosphate grafted into poly(styrene sul-



**Figure 1** SAS values during the recording of NIR spectra in the first set of experiments.

fonate), used as a stabilizer] suspensions in a 1-L stirred tank reactor. Agitation speed was manipulated to change the size of the monomer droplets suspended in the suspension medium. During the tests, NIR spectra were collected at regular intervals of 3 min for each level of specific agitation speed (SAS) used, as sketched in Figure 1. (The specific agitation speed means the stirrer dial position in the range 0-10, which is proportional to the actual agitation speed of the stirrer, which is in the range 90-6300 rpm. The use of the SAS value is preferred in this text because the actual agitation speed was not measured and controlled independently with additional measuring devices.) The SAS was varied as a series of step perturbations with magnitude of 0.5 (approximately 300 rpm), between a minimum of 1.0 and a maximum of 4.0. Higher values of SAS did not allow proper operation of the reactor vessel.

The reactor used was a jacketed glass tank, with temperature control. 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. Measurements were made at room temperature to avoid espontaneous thermal polymerization. NIR spectra were collected with an in-line NIRS-6500 spectrophotometer (NIRSystems Inc.), configured to scan the spectral region ranging from 400 to 2500 nm, in transmittance mode. The instrument was connected to the stirred tank by using a bundle of optic fibers terminated with an 1-in. diameter liquid immersion probe. Data acquisition, spectral mathematical treatments, and partial least squares regression analysis were performed by using the Near-infrared Spectral Analysis Software (NSAS) supplied with the instrument. For the first type of experiments, automatic acquisition of NIR spectra was performed at regular

intervals of 3 min. Reagents were provided by Nitriflex Resinas SA and used as received. PES was suspended in water at concentrations of 18 g/L. Water was distilled before use. Figure 2 illustrates the experimental set-up configuration.

In the second type of experiments, suspension styrene polymerizations were carried out in aqueous media, using PES as a stabilizer and benzoyl peroxide as an initiator, at specified agitation speeds to obtain different particle size distributions. Unless stated otherwise, the initial styrene concentration in the suspension was equal to 25%in volume, the initial initiator concentration was equal to 9.5 g/L of suspension, and the stabilizer concentration was equal to 1.5 g/L of suspension. The same reactor configuration presented before was used. Reactions were carried out at 84°C, under inert nitrogen atmosphere and in batch mode. Samples were collected at regular intervals of approximately 1 h, in duplicate, for determining conversion and particle sizes. NIR spectra were collected at regular intervals of 15 min for each polymerization batch. The average reaction time for each run was about 4 h 15 min. Polymer particles were obtained by centrifuging suspension samples and drying the wet powder to constant weight in vacuum ovens at approximately 40°C. Final polystyrene particle size distributions were evaluated by measuring particle diameters present in photographs obtained with a scanning electron microscope (JEOL JSM 5300 Scanning Microscope). A minimum of 200 particles were used to evaluate the average particle size of polymer samples. For conversion determination, samples of 10 mL were collected in glass flasks containing 0.2 mg of hydroquinone. Suspension samples were then weighed and dried to constant weight in vacuum ovens at temperatures around 40°C. Molecular weight distributions were obtained by gel permeation chromatography (Waters 410, Milipore Corporation). Distilled N-

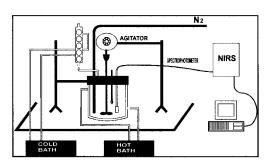
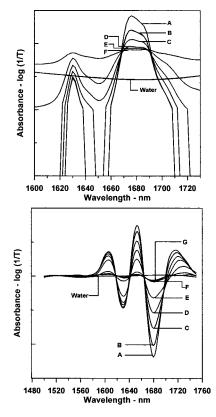


Figure 2 Experimental setup.

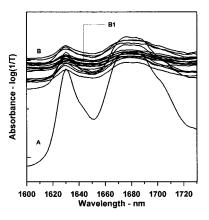


**Figure 3** NIR spectra of styrene–water suspensions: pure styrene (A); agitated styrene–water suspensions with SAS equal to 1.5 (B), 2.0 (C), 2.5 (D), 3.0 (E), and 3.5 (F); polystyrene powder (G). Below, the second derivative spectra are shown.

methylpyrrolidone was used as solvent. Benzoylperoxide was bought from Quimibrás with a purity of 99%+; nitrogen was provided by AGA with a purity of 99.9%+; *N*-methylpyrrolidone was bought from Aldrich with a purity of 99.9%+; and hydroquinone was bought from VETEC weith a purity of 99%+. These components were used as received, without additional purification. The other chemical species were supplied and used as described before.

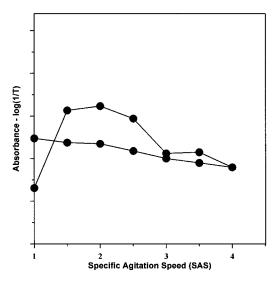
# RESULTS

Evaluation of the usefulness of spectra can be made on both a qualitative and a quantitative basis. Often, simple visual examination of spectra is used to determine whether some parameter has affected a spectrum. This point is especially true in initial efforts to study influences and effects.<sup>13</sup> For this reason, the NIR spectra for the first set of experiments are shown in Figure 3.

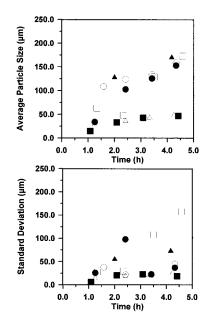


**Figure 4** Hysterisis during the recording of NIR spectra of agitated styrene–water–PES suspensions. SAS is equal to 1.0 (A), 4.0 (B), and 1.0 (B1).

The NIR spectra of stirred styrene-water suspensions and of stirred pure water for different SAS are overlaid in Figure 3(a). A simple visual analysis shows that in the wavelength range between 1600 to 1700 nm, the spectra of styrenewater suspensions are very sensitive to changes of the agitation speed. As this does not occur for pure water (and does not occur for pure styrene either), it may be concluded that the spectrophotometer is actually accusing changes of the morphology of the styrene-water suspensions, as the agitation speed grows. As it can be observed, there is an inverse relationship between SAS and absorbance peaks. As speed increases (according



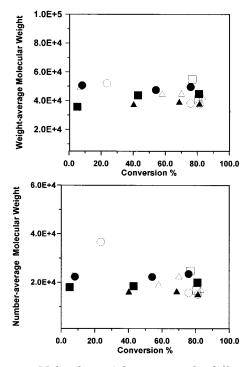
**Figure 5** Hysterisis during the recording of NIR spectra of agitated styrene–water–PES suspensions at the wavelength of 1630 nm.



**Figure 6** Particle size averages for different agitation speeds. [SAS =  $3.5 (\triangle)$ , SAS =  $3.0 (\blacksquare)$ , SAS =  $2.5 (\Box)$ , SAS =  $2.0 (\bullet)$ , SAS =  $1.5 (\bigcirc)$ , SAS =  $1.0 (\blacktriangle)$ ].

to Fig. 1), absorbance peaks decrease. It is important to emphasize that NIR spectra does not depend on the direction of speed variation, which means that NIR spectra is determined by the degree of agitation only. Therefore, morphological transformations of the suspended droplets occur very fast.

When suspension stabilizer is added to the styrene–water suspension, a different behavior is observed, as shown in Figure 4. Increasing the SAS leads to permanent changes of the NIR spectra, as peaks become very similar and limited to a certain range (B) after a certain value of SAS (1.5) is reached. The NIR spectra do not change significantly even when the SAS is decreased continu-



**Figure 7** Molecular weight averages for different agitation speeds. [SAS = 3.5 ( $\triangle$ ), SAS = 3.0 ( $\blacksquare$ ), SAS = 2.5 ( $\Box$ ), SAS = 2.0 ( $\bullet$ ), SAS = 1.5 ( $\bigcirc$ ), SAS = 1.0 ( $\blacktriangle$ )].

ously to zero. This may be explained if the hysteresis observed when the suspension stabilizer is added to the system is assumed to be caused by the stabilization of the particle size distribution. Figure 5 displays the hysteresis observed for a specific wavelength of 1630 nm. Similar behavior can be observed for other wavelength values. Therefore, it may be concluded that NIR spectra are sensitive to changes of the particle size distributions, so that it may be possible to monitor particle sizes of suspended polymer particles by in-line NIR spectroscopy.

Exp.	Time (h)	Number of Spectra Collected	Suspension Stabilizer (g/L)	SAS	Size (µm)	Deviation (µm)
1	4.5	45	1.5	3.5	48	27
2	4.42	48	1.5	3.0	47	19
3	4.58	50	1.5	2.5	173	158
4	4.33	49	1.5	2.0	153	37
5	4.33	49	1.5	1.5	159	45
6	4.17	48	1.5	1.0	171	73
7	4.25	66	1.5	3.0	48	20

Table I Experimental Runs with PES as Stabilizer

Exp.	Time (h)	Number of Spectra Collected	Suspension Stabilizer (g/L)	SAS	Size (µm)	Deviation (µm)
8	4.50	82	5	2.5	32	16
9	4.30	60	1	2.5	275	162
10	4.35	80	2.5	2.5	106	38
11	4.42	90	2.5	2.5	124	50

Table II Experimental Runs with Poly(vinyl alcohol) (PVA) as Stabilizer

To evaluate the performance of the NIR spectroscopy during actual suspension polymerization batches (second set of experiments), the average particle sizes and standard deviations of the particle size distributions and average polymer molecular weight were evaluated for different SAS (Figs. 6 and 7). Figure 6 shows a sharp influence of SAS upon the average particle size. For the largest SAS values, both the final average particle size and the final standard deviation are smaller than 50  $\mu$ m. For the lowest SAS values, final average particle sizes and standard deviations are around 150  $\mu$ m. Figure 7 shows that the reaction kinetics is essentially the same in all batches, so that it may be said that differences between NIR spectra collected at different batches are mostly due to morphological changes of the suspended droplets and may be used to allow the development of a mathematical model to correlate the NIR spectra with the average particle size.

It is interesting to observe that the NIR spectra of the final dry polystyrene samples and of the original styrene-water-PES suspensions obtained with equal SAS values are very similar (Fig. 3), so that it seems that morphological changes are the most important source of NIR spectral variations during the suspension polymerizations analyzed. If this is true, then particle size distributions should not be expected to change significantly during the polymerizations, as spectra obtained for similar SAS values are alike.

According to these preliminary results, it may be said that the monitoring of the average particle size during suspension polymerization reactions by NIR spectroscopy is possible. Besides, according to Figures 3 and 4, the region comprised between 1600 and 1750 nm seems to be an adequate region to develop a calibration model, given the higher sensitivity of the NIR spectra to changes of the SAS values.

## CALIBRATION

Different polymerization runs were carried out to allow the production of particles with different particle size distributions and to evaluate the importance of monomer conversion on the NIR spectra obtained. For the sake of model implementation and calibration, suspended droplets were assumed to have the same size distribution of the final dried polymer particles, sampled when monomer conversions were larger than 95%, which may be supported by experimental data presented in the previous section. We are aware that dried polymer particles and suspended droplets may present different size distributions, but it is assumed that the model will also be able to take into account changes that occur during the particle drying process. Besides, the target prop-

Table III	Experimental Run	s with Polyvinylpyrrolidone	e (PVP) as Stabilizer

Exp.	Time (h)	Number of Spectra Collected	Suspension Stabilizer g/L	SAS	Size (µm)	Deviation (µm)
12	4.41	75	5	2.5	44	23
13	4.25	80	1	2.5	144	151
14	4.35	70	2.5	2.5	192	250
15	4.42	70	$2.5^{\mathrm{a}}$	2.5	52	36

<sup>a</sup>The initial initiator charge was 30% larger than in the other experiments.

Exp.	Time (h)	Number of Spectra Collected	Suspension Stabilizer (g/L)	SAS	Size (µm)	Deviation (µm)
16	4.51	73	5	2.5	61	44
17	4.33	97	1	2.5	152	100
18	4.41	85	2.5	2.5	254	153
19	4.25	80	$2.5^{\mathrm{a}}$	2.5	217	110

Table IV Experimental Runs with Tricalcium Phosphate (TCP) as Stabilizer

<sup>a</sup>The initial initiator charge was 30% larger than in the other experiments.

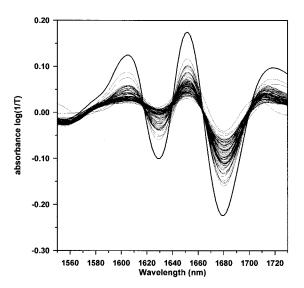
erty that must be controlled at actual industrial operation is the final dried particle size. The experimental results used to calibrate the NIR spectrophotometer are shown in Tables I to IV. Different suspension stabilizers were used to improve the consistency and applicability of the mathematical model. The suspension stabilizers used were polyvinylpyrrolidone (PVP), provided by Fluka Chemica, with an average molecular weight of 10,000, poly(vinyl alcohol) (PVA) 99%+ hydrolized, provided by Fine Chemicals, and tricalcium phosphate (TCP), provided by Nitriflex SA.

The second derivative spectra of the original NIR spectra were used for calibration, as it was verified that the raw data set did not allow adequate modeling of the average particle size. Different types of regression techniques provided by NSAS were tested, but the best results were obtained when linear models were used and parameters were computed according to the partial least squares (PLS) technique.<sup>9</sup> In this case, the regression factors are obtained as linear combinations of the absobances observed at different wavelengths of the NIR spectra.

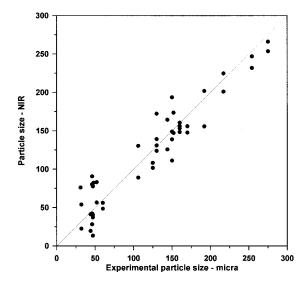
Eight experimental runs selected at random were always saved to allow the independent crossvalidation of the mathematical model and were not used for modeling purposes. The number of parameters used in the empirical linear model was established by minimizing the summation of the squared residuals obtained when the model was used to predict the average particle size of the final polymer powder of the validation set of experiments, as obtained by electron microscopy. This way, model overfitting could be avoided.

Figure 8 shows a typical set of NIR spectra collected during a polymerization batch. Variations are observed at random, so that spectral changes should not be assigned to changes of monomer conversion. These random variations could be assigned to various sources, but the main sources of variation are the natural distribution of sizes inside the reactor (at each sampling time a different and small particle population is observed at the sampling window) and sticking of polymer particles to the sampling window, which may eventually lead to gross measurement errors.

Figure 9 shows a typical comparison between experimental and predicted results, when PLS is used with a linear model containing 10 factors. The model correlation to experimental data is 0.95, which may be regarded as very good. The model may then be used to allow the monitoring of the average particle size continuously during the polymerization run, as shown in Figure 10. As it can be seen, variations along the batch are very small and within the 95% range of variation of the particle size distribution, as measured by electron microscopy However, sometimes noisy measurements are obtained as the model output, as shown



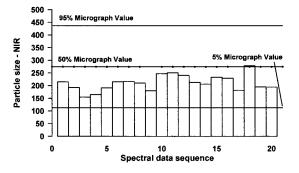
**Figure 8** Second derivative spectra of styrene–water suspensions during reaction.



**Figure 9** Experimental and predicted particle sizes after calibration with a PLS model (10 factors).

in Figure 11. As observed, these responses are caused by permanent sticking of polymer particles on the sampling window. Most of the time this can be used as a signal that the suspension is losing its stability or that the suspension is close to unstable conditions. However, at the present stage, cleaning of the sampling window after each run is finished is of fundamental importance for adequate monitoring of the reaction.

To analyze whether the inclusion of nonlinear effects might lead to better modeling of the average particle size, empirical neural networks (NN) were used to calibrate the spectroscopy results. NN are nonlinear models built by summing up nonlinear transformations of the linear combinations of the input variables. The nonlinear transformations may be implemented iteratively, according to the architecture presented in Figure



**Figure 10** Continuous monitoring of particle size with the PLS model. Polymer batch with a PVA concentration of 1 g/L (Experiment 9).

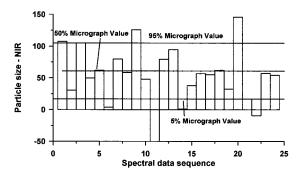


Figure 11 Typical response obtained when polymer sticks to the probe.

12, usually named as the feedforward architecture. All NN used in this study contained three different layers: the input layer, the hidden layer, and the output layer. The input layer was fed by the NIR absorption at specified wavelengths (1604, 1630, 1652, 1680, and 1724 nm), where the absorption peaks were shown to depend significantly on the SAS. The output layer provided the average particle size. The usual backpropagation procedure was used to train the NN.<sup>14</sup> In this study, the training data sets of input and output variables were normalized between 0.1 and 0.9, and the nonlinear transformations used were the sigmoidal activation functions, defined as

$$f(x_1, x_2, \ldots, x_n) = \frac{1}{1 + e^{(w_1 x_1 + \ldots + w_n x_n + b)}} \quad (1)$$

where  $w_i$  and b, are parameters to be determined.

Figure 13 shows typical results obtained with the neural network modeling. It may be seen that results are very similar to those obtained with the linear models and the PLS technique. Therefore, given the relatively small number of experiments, it seems that the ability to capture nonlinear responses is not fundamental to model the NIR size function and that the main sources of variations

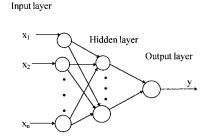
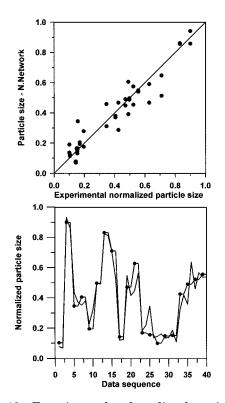


Figure 12 Neural network architecture.



**Figure 13** Experimental and predicted particle sizes after calibration with a neural network (5-10-1)  $((-\bullet-\bullet-\bullet-)$  experimental; (—) NN output).

are definetely linked to the experimental procedure.

## **CONCLUSIONS**

NIR spectroscopy may be used successfully to allow the in-line monitoring of average particle sizes in styrene suspension polymerizations. As shown experimentally, NIR spectra are sensitive to changes of the particle size distributions, so that empirical models may be built to correlate the NIR spectra with the average particle size. Model results are subject to small random variations that are due to polymer sticking to sampling devices and to fluctuations of the sampled particle population. Based on the experimental results available, the inclusion of nonlinear effects by using a neural network approach did not lead to any significant improvement of the empirical model, so that empirical linear models and the PLS may be recommended for practical applications.

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