Online monitoring of the particle size in semi-batch emulsion co-polymerization using spatially resolved spectroscopy and Raman spectroscopy

Manis Gheghiani1, Noémie Caillol2, Timothy McKenna3, Nida Sheibat-Othman1\*

*1 University of Lyon, University Claude Bernard Lyon 1, CNRS, LAGEPP UMR 5007, F-69100, Villeurbanne, France*

*2 Axel’One, Solaize, France*

*3 University of Lyon, University Claude Bernard Lyon 1, CPE Lyon, CNRS, UMR 5265, C2P2-LCPP group, Villeurbanne, France*

*\*Corresponding author:* *nida.othman@univ-lyon1.fr*

Abstract

Spatially resolved spectroscopy (SRS), based on near infrared, is better adapted to extract physical information than classical spectroscopy. It was employed in order to monitor the particle size in emulsion copolymerization. The physical information, in the form of particles size, was distinguishable from the chemical information, in the form of polymer content, by their different impact on the spectra with respectively scattering and absorption phenomena. Different types of particle mean diameters were studied to explore the sensitivity of the SRS and the possibility to reconstruct the particle size distribution. A model based on partial least square regression was developed. Raman spectroscopy was also investigated to detect the variations in the particle size and how far it can be quantitative.

Keywords: Spatially resolved spectroscopy, Raman spectroscopy, emulsion polymerization, scattering, particle size distribution

# Introduction

Both emulsion and suspension polymerizations are heterogeneous processes, with the reaction taking place in the dispersed phase. A wide variety of polymers with different properties can be obtained by these processes, such as adhesives, rubbers and plastics. However, heterogeneous reactions are more complex, which makes them more challenging to control and ensure product quality criteria. ~~Monitoring the process then becomes an import challenge to control the final product properties and the process productivity~~.

Monitoring the progress of the reaction, such as the monomer conversion or the reaction rate, is the first step towards a good control of the process [1]. Concerning the quality of the product, it may be affected by both chemical and physical properties that are important to monitor. For instance, monitoring the polymer molecular weight is essential as it affects the polymer mechanical properties and its viscosity [2], [3]. Also, several processes involve more than one monomer in order to modulate the product properties, such as the glass transition temperature, by changing the chemical composition[4]. For instance, polymer composition was monitored by spectroscopy [5]–[7].

In heterogeneous polymerizations, also the particle size distribution (PSD) may affect the polymer quality as well as the progression of the reaction (e.g. mass and heat transfer, viscosity, stability, etc.). The particle size can be measured by different offline techniques, such as optical or electron microscopy [8], dynamic light scattering (DLS) [9] mainly for nanometer scale particles, or laser diffraction [10] for micrometer and nanometer scale particles. These techniques require however sampling and dilution.

Based on the light-matter interaction, spectroscopy is expected to contain physical information besides chemical information, as in DLS or laser diffraction. Frequently, to consider only the chemical information, this information is removed from the spectral data using different pre-processing methods, like multiplicative scatter correction or standard normal variate transformation [11], [12]. This makes it possible to apply Beer-Lambert law to quantify the chemical composition. More recently, some works have employed spectroscopy to focus on the particle size. In the case of Raman spectroscopy, studies have been done offline in order to quantify or find a qualitative correlation with the particle size for styrene, butadiene, methyl methacrylate and acrylonitrile latexes [13]. Online studies have also been done using styrene/acrylic acid [14] or styrene/butyl acrylate emulsion co-polymerizations [15]. A good agreement was shown but for a limited range of particle size, going from 50 to a maximum of 150 nm.

Many studies have also employed near infrared spectroscopy (NIR) to predict particle size. For instance, this was done in the emulsion copolymerization of styrene/butyl acrylate [16], [17], styrene suspension polymerizations [18] and vinyl chloride suspension polymerization [19]. These works demonstrated that the NIR spectrum is affected by the particle size distribution. In these works, the spectrum was treated to remove other chemical effects and only focus on the particle diameter.

The ability to predict the particle diameter with infrared spectroscopy can be explained by different phenomena related to the light-matter interaction, and affect the collected data. First of all, the different chemical species present in the particles can absorb part of the energy (i.e. photons) of the incident light. This affects both the transmitted and reflected energy. The absorption of light at different wavelengths is a function of the nature of the species, and thus contains important chemical information. A second phenomenon appears in heterogeneous systems causing light deflection, and is called the scattering phenomenon. Different cases of scattering can be observed according to the properties of the particles (size and shape among others). In the case of a spherical particle with a size smaller than the wavelength of excitation (λ),Rayleigh theory (an approximation of Mie’s theory) describes the scattering cross section. This cross section, corresponding to the probability of a particle to scatter the light, is dependent on 1/λ4. It can be applied to study the effect of particle size in the light-matter interaction [20],[21].

When absorption and scattering phenomena of light by particles are significant, only a fraction of the incident light is transmitted, and so transmission spectroscopy only contains part of the information of the medium. Therefore, different technical solutions have been proposed to collect both transmission and scattering information, like the integrating sphere [22] or temporal resolved spectroscopy [23]. Another solution, that is considered in this work, is the spatially resolved spectroscopy (SRS) [24], [25]. In this technology, the light is collected at different angles from the incident light, enabling to collect both the transmission and scattering information. The aim of this work is to evaluate the potential of the SRS, based on NIR spectroscopy, in order to determine physical properties in emulsion copolymerization. Different mean diameters are investigated to identify to which one the SRS is more sensitive, and eventually reconstruct the particle size distribution from these diameters.

The paper is organized as follows: In the first part, the potential of SRS spectroscopy is investigated. An offline study is first used to investigate the impact of the particle diameter and bimodality of the particle size distribution (PSD) on the spectra. Then, polymerization experiments are designed to ensure decoupling between the particle size and polymer content. A predictive model based on Partial Least Squares is developed using a selection of training samples. Different types of mean diameters are considered. Then, a predictive model is evaluated using external data and under specific conditions, including particle renucleation, to evaluate the limits and the potential of the model and the technology more generally. Rebuilding of the full particle size distribution is also investigated.

Secondly Raman spectroscopy is considered, starting with a similar offline study. Then an online study, using the same experiments as the SRS, is done with the development of regression models based on Partial Least Squares.

# Materials and method

## Materials

The monomers used in this study are methyl methacrylate (MMA, Acros Organics, 99%, stabilized) and butyl acrylate (BuA, Acros Organics, 99+%, stabilized). The initiator is potassium persulfate (KPS, Acros Organics, 99+%). The monomers and initiator were stored in a fridge until used. Sodium dodecyl sulfate (SDS, Fisher Chemical) was used as ionic surfactant. Deionized water with an 18 MΩ cm resistivity was used throughout the work.

## *Seeded* semi-continuous polymerization experiments

A 1 L reactor was used with mechanical stirring at 300 rpm using a three blade Bohlender propeller. The standard seeded experiments protocol consisted in using a diluted latex, previously produced in *ab initio* or seeded experiments under similar conditions, for which the particle size, SDS content and solids content are known. The diluted latex was degassed using nitrogen for 30 min under stirring and heated to 70 °C using a thermostated bath. 200 g of a MMA/BuA mixture, with 70 % wt of MMA and 30 % wt of BA, was then put on a balance and semi-continuous monomer addition was started at a flow rate of 0.02 g/s. Simultaneously, 1.6 g of KPS was dissolved in the reaction medium to initiate the reaction. At the beginning of the reaction, the nitrogen gas flow was moved to the top of the reactor, to maintain saturation of the gaseous atmosphere with nitrogen. Temperature measurements in the reactor and the jacket were measured and a controller allowed maintaining the reactor temperature at 70°C. Also, the mass of monomer on the balance was measured to ensure constant monomer flow rate at 0.02 g/s by an automatic control of the pump. Samples were collected at specific time intervals to measure the solids content (*i.e.* mass fraction of solid) using a thermobalance (Mettler Toledo LJ16); with the mass of surfactant and initiator subtracted from the solid content to calculate the mass fraction of polymer. The particle size distribution was measured using dynamic light scattering (DLS, Malvern Nano ZS®).

## Design of experiments

A design of experiments was done to vary the particle size of the latex over a wide range of industrial interest. At the same time, tests were carried out to decorrelate variations in the size from variations in the solids content. Indeed, in emulsion polymerization the increase in the particle size is correlated with an increase in the solids content as the polymer production increases with the volume of the particles, once the nucleation process is finished (and the number of particles remains almost constant). Therefore, carrying out only *ab initio* experiments may not have allowed proper decoupling between these variables which may lead to big errors when developing predictive models based on spectroscopy. By carrying out seeded experiments, it is possible to start the reaction with any solids contend and any particle size. Such a choice of experiments should allow the model to predict the particle size independently of the solids content and progress of the reaction.

We therefore chose to run 12 experiments, and Table 1 shows the solids content and the mean particle diameter provided by the DLS (z-average) for each experiment. Note that in experiments 1-4, the particle size was varied from 48 to 550 nm with complete decoupling from the initial solids, which was varied from 2.2 to 25 % by weight. Part of the latex from previous experiments was diluted to restart the reaction and so on for the other experiments. To add further variety to the data, experiments 2, 9 and 10 were designed to have the same initial size (117 nm) but different initial solids content (4.3, 4.6 and 8.5 % wt), with experiment 2 being the most dilute and experiment 10 the most concentrated.

Finally, in experiments 11 and 12 a perturbation was caused on purpose at the middle of the reaction in order to simulate a renucleation. To do so, after 100 minutes of the reaction in experiment 11, the latex was partially emptied from the reactor (at this stage the particle size was about 280 nm and the solids content 20 % wt). Then, 400g of a latex, from experiment 5 (142 nm, at 22.8 % wt, previously heated to 70°C), with smaller particles was added to the reactor. As a result, the reactor contains approximately a 50-50 % mixture of latex with sizes 280 nm and 142 nm (with similar temperature and solids content). In experiment 12, the same modification in size was done but in such a way to have a different ratio of the number of small particles compared to big particles (about 45:55 %).

Table 1: Solids content range and z-average range for the different experiments realized

|  |  |  |
| --- | --- | --- |
| **Experiment** | **Solids content range (% wt)** | **Particle diameter range (z-average, nm)** |
| 1 | 2.2-13.6 | 48-73 |
| 2 | 4.3-22 | 117-195 |
| 3 | 4.4-23.4 | 195-345 |
| 4 | 9.7-23.9 | 345-550 |
| 5 | 5.6-22.8 | 73-142 |
| 6 | 6.6-25.4 | 195-372 |
| 7 | 5.5-23.6 | 195-338 |
| 8 | 7-26.2 | 195-381 |
| 9 | 4.6-20.8 | 117-210 |
| 10 | 8.5-20.4 | 117-167 |
| 11 | 3.8-16.4 | 210-280 |
| 12 | 5.5-17.2 | 167-246 |

## SRS spectroscopy

A multiangle probe Sam-Flex (Indatech®, Chauvin Arnoux) was connected to a spectrometer from Indatech® (Hyternity) which is composed of a NIR camera coupled with an InGaAs detector. The measurement is done simultaneously at four angles, with a 3mm pathlength. These measurement angles are positioned as follows: one angle in the transmission direction, i.e. at 180° (according to the light source), two angles in the scattering directions at 175° and 170°, and one angle in the backscattering direction at 30° described in another work [26]. From this configuration, the 175° angle can be thought to be more sensitive to simple scattering, while the angle at 170° is more sensitive to the multiple scattering and the angle at 30° is more sensitive to backscattering. The NIR spectral domain was from 871 nm to 1723 nm for each angle, with a 3 nm interval. For all the acquisitions, the integration time was 70 ms with 100 scans acquired, for a total acquisition time of 7s. The acquisition was made every 15s. The acquisition time was fixed in a way to maximize the intensity while avoiding saturation. As different intensity levels are measured at the four angles, attenuators are available to tune the intensity of light measured. Physical attenuators were thus set on manually at 180° and 175° in order to avoid saturation of the signal at the beginning of the reaction where the medium is diluted and the transmission signal is very strong.

## Raman spectroscopy

A RXN2 Raman spectrometer from Kaiser Optical Systems was used, with a laser at a power of 400 mW and an excitation wavelength of 785 nm. The spectrometer is equipped with an immersion probe with a diameter of 12.7 mm (1/2 inch) and a focal distance of 0.5 mm. The integration time was set to 15s, with 3 scans added for each spectrum, leading to a total acquisition time of 45 s. One spectrum per minute was acquired. The wavelength region was from 100 to 3425 cm-1.

## Dynamic light scattering (DLS)

A Malvern Nano ZS® was used to measure the particle size offline. This technology relies on photon correlation spectroscopy (PCS). The samples taken from the reactor were put in an ice bath to stop the reaction. They were then diluted with deionized water of 18 MΩ cm resistivity to reach an attenuation coefficient between 4 and 5 on the DLS. The mean diameter given by this device is the z-average, which is the intensity-based harmonic mean (2,3) calculated from the scattering intensity weighted distribution. The z-average and the particle size distribution (PSD) in volume and number were both collected. The number-weighted PSD was then used to calculate various types of particle mean diameters which will be discussed later on.

## Chemometrics

A data pre-processing approach was employed based on a previous work on SRS data [26], with data smoothing performed using a Savitzky-Golay filter [27] with 15 points averaged with a polynomial of second order, and a first order derivative to highlight the variations. A prediction model of the particle size was then developed based on Partial Least Square (PLS) regression using the Nonlinear Iterative Partial Least Square (NIPALS) algorithm [28].

In the case of Raman data, an offset correction of the baseline was first applied by subtracting the intensity at 2000 cm-1 to the whole spectrum. The same PLS regression was then applied. All the chemometric study was carried out using Matlab®.

# Results and discussions

## Types of mean diameters

The PSD plays an important role in determining many physical (e.g. viscosity) or end-use (e.g. visual aspect, coverage) properties of a latex. PCS provides an intensitweighted measurement of the PSD. From this distribution, the distributions in number and in volume are calculated, based on the Mie’s theory. These distributions are usually not easy to manipulate; it is thereofre convenient to calculate a mean diameter in order to characterize the latex. Namely, in the present paper, it is important to define a mean particle diameter to which the SRS spectra are most sensitive, so it can be well monitored. Several types of mean diameters can be calculated from the PSD in number ($f\_{i}$) by using equation 1. The volume-weighted mean diameter, *d*43, also called the De Brouckère mean, is obtained by dividing the 4th moment by the 3rd while the surface-weighted mean diameter *d*32, also called the Sauter mean diameter, is the ratio of the 3rd moment to the 2nd. The number mean diameter *d*10, the ratio of the 1st moment to 1 (moment 0), is also of interest mainly in order to reconstruct the PSD.

|  |  |
| --- | --- |
| $d\_{m,n}=\frac{\sum\_{}^{}f\_{i}d\_{i}^{m}}{\sum\_{}^{}f\_{i}d\_{i}^{n}}$  | (1) |

The PSD in volume is proportional to the volume of particles, so $f\_{vol\\_i}=f\_{i}πd\_{i}^{3}/6$ as the particles are considered to be spherical. Bigger particles have a higher impact in the volume distribution (also true for the intensity distribution). Generally, the median *d*v50 is used to describe the volume distribution, which corresponds to the diameter where half of the polymer volume has smaller particle size and the other half is larger. The *d*v10 and *d*v90, correspond respectively to diameters where 10 % and 90 % in volume of the particles have a smaller diameter.

The PSD by intensity obtained by the Nano ZS, is based on Rayleigh scattering and is proportional to *d*6. It gives even more weight to bigger particles compared to the volume distribution. The particle size distributions in number and volume are calculated based on this intensity distribution. The device also calculates the Z-average mean diameter (intensity-based harmonic mean) as a hydrodynamic diameter, *d*H, with the Stokes-Einstein equation (2), with *T* the temperature, *k* the Boltzmann’s constant and *η* the dynamic viscosity of the continuous medium. The translational diffusion coefficient *D* is calculated from an auto-correlation function based on the variations of intensity during the measurement [29].

|  |  |
| --- | --- |
| $d\_{H}=\frac{kT}{3πηD}$  | (2) |

In the case of monomodal and narrow distributions (see example in Figure 1 for a z-average of 73 nm), the different types of diameters are almost equivalent in terms of the importance given to a specific size and the difference between them during time. However, multimodal or wide distributions (Figure 1 with a z-average of 435 nm) generate bigger differences between the PSD in number, volume and intensity. Therefore, the difference between the different mean diameters, because of wider distribution, increases and it is important to decide which one is more descriptive. Note that the distribution can broaden during the reaction because the particles do not grow at the same rate and they do not undergo similar coagulation rates, due to different stochasticity or mixing issues.

|  |  |
| --- | --- |
|  | (b) |

Figure 1: Particle size distribution in number and volume indicating the mean diameters d10, d32, d43 and dv50 a), Z-average = 73 nm, b) Z-average = 435 nm

(a)

The SRS spectra are collected *in situ* in a concentrated media at different transmission and scattering angles, so it is important to determine to which mean diameter the SRS is more sensitive and which angle is the most useful for this purpose. In the following, the mean diameters *d*43, *d*v50, z-average, *d*10 and *d*32 are investigated.

## Offline investigations of the SRS

Several latex samples were prepared at different sizes and solids content, and SRS spectra were collected for each one. The objective was to study the impact of the particle diameter at a known concentration on the spectra. Moreover, mixtures of latexes of different sizes were prepared to study the effect of the size bimodality on the SRS measurements. Samples were heated at 70°C to be representative of the process conditions, as the temperature is known to impact the spectra in the NIR region.

Figure 2a shows the SRS spectra of samples with the same solids content of 16 % wt but with different particle sizes, with a z-average varying from 70 nm to 550 nm. As a reminder, the angles at 180°, 175°, 170° and 30° from the light source correspond respectively to the transmission, simple scattering, multiple scattering and backscattering phenomena. It can be seen that the intensity of the spectra collected at 180°, 175° and 170° decreases when the particle size increases, with the intensity at 180° decreasing the fastest and the one at 170° the slowest. It can be deduced that the increase in the particle size first reduces the transmission and simple scattering to almost no signal when the z-average is equal or bigger than 195 nm (at a concentration of 16 % wt). Even if the multiple scattering signal (170°) also decreased, it was still non null when the particle size was 195 nm, but it then decreased significantly for particles of 345 nm. Concerning the signal at 30°, it had an opposite behavior as the intensity increased with the particle size. Indeed, big particles are more likely to reflect the light thus causing more backscattering. The difference in intensity between the spectrum for particles of 345 nm and 550 nm is smaller than between 195 nm and 345 nm. Scattering phenomenon is nonlinear [30] and depends on the difference between the size of the particle and the wavelength of the light. So the variations of the intensity are different at some levels. Also, in the experiment with 550 nm, the latex started to be non-uniform as some coagulum appeared, and therefore the offline measure with DLS might not be representative.

The offline study validates the fact that the SRS contains information about the particle size, independently of the latex concentration, that can be used for monitoring.

From Figure 2b, it can be seen that the spectra evolve when changing the solids content. In these samples, the z-average is at 195 nm, so an increase in the solids content is equivalent to an increase in the number of particles per unit volume. The signals at 180°, 175° and 170° decrease with the increase of the solids content while the signal at 30° increases such as for the particle size. However, the magnitude of the variations is different from the one observed with the particle size. The impact of concentration on the spectra is not investigated further here as monitoring of the solids content by SRS has already been studied in a previous work and its feasibility was demonstrated [26].



(b)

(a)

30°

170°

175°

180°

30°

170°

175°

180°

Figure 2: SRS spectra of samples with (a) 16 % wt of solids content and different particles sizes, (b) 195 nm and different solids content

Then, mixtures of latexes of different sizes, with a mass ratio of 1:1 at 16% wt, were prepared to study the impact of size bimodality on the SRS data. Figure 3a shows the SRS spectra of latexes with z-average of 70 nm, 550 nm and their 1:1 mixture, which represent the smallest and largest studied particles. It can be seen that for particles of 70 nm, the signal is non-null at all angles while for particles of 550 nm it is mainly present at 30° (with almost 6000 hits), a little at 170° (less than 200 hits) and null for the others angles, as big particles stop transmission and simple scattering at the studied concentration. As a result, the SRS spectra corresponding to the mixture of this two sizes show no signal at 180° and 175°, a small signal at 170° relatively close to the spectrum of 550 nm, and a maximum of intensity around 4 000 hits at the angle 30°. For this angle, the signal is in between the spectra of the unimodal latexes of sizes 70 and 550 nm. The observed phenomena in the mixture seem to be dominated by the biggest particles, because only the backscattering angle, 30°, shows a signal and not the others.

Figure 3b shows the SRS spectra with a z-average of 70 nm, 195 nm and their 1:1 mixture. It can be seen that the signal is present at every angle for each for the three products, as no big particle sizes are present. The spectra of the mixture are in between the unimodal spectra as observed previously. However, in this case all the phenomena (transmission, simple, multiple and backscattering scattering) are present (i.e. the intensity signal is non-null for all angles). The gap in the z-average is not as big as previously so the biggest particles do not totally govern the light-matter interaction. These observations indicate that the SRS can be sensitive to a second population of particles if it can be detected. This can be useful in emulsion polymerization for instance to detect renucleation or sudden particle coagulation if the gap between them is not too important.



(b)

(a)

30°

170°

175°

180°

180°

175°

170°

30°

Figure 3: SRS spectra at different angles for monomodal latexes of different sizes and their mixtures

## Online implementation of the SRS

### Building and comparison of the models for different types of diameters

As the angles 180°, 175° and 170° have no signal for almost half of the range of the particle size studied, they will not be included in the PLS prediction model. Only the 30° signal will be used, as it contains the biggest amount of information. The other angles can be useful for other ranges of sizes or concentrations or by changing the attenuator to avoid saturation and absence of the signal in the whole range. The calibration models were built based on the online experiments, for which a higher amount of data is available for training and validation. Experiments 3, 6 and 8 were used for external validation. The data from experiment 4 (z-average of 550 nm) were not included in the development of the calibration model due to the presence of some bubble in the probe and coagulation phenomenon. The other experiments were used as follows: 2/3rd to build the calibration model and 1/3rd for validation. A total of 66 samples were used, with 44 of them for the development of the calibration model and the 22 remaining for internal model validation. The experiments were organized from the one generating the smallest diameters to the one generating the biggest diameters and after that 2 samples out of every 3 were selected for calibration.

Figure 4 shows the z-average for the experiments used to build the calibration model (1, 2, 5, 7, 9 to 12) as a function of the solids content. It can be seen that the data are within the same range of solids content, from 2 to 25 % wt, while multiple z-average are available for one solids content (ranging from 48 nm to 350 nm). This is essential in order to ensure decoupling between these two variables.



Figure 4: Z-average according to the solids content of the experiments used for model development (n°1 in dark blue and n°12 in light green)

As discussed before, different types of particle diameters can be calculated from the particle size distribution. To ensure the best model sensitivity, calibration models were developed for the z-average, *d*10, *d*32, *d*43 and *d*v50. The choice of the number of latent values (LVs) was made by using cross-validation with a leave-one out cross-validation and 3 repetitions with a Monte-Carlo cross-validation algorithm. Figure 5a shows the root mean square error of cross-validation (RMSECV) with a plateau for 5 LVs and a minimum for 10 LVs. In order to avoid overfitting and increasing sensitivity to noise, 5 LVs were chosen.

Figure 5b shows the parity diagram of PLS regression with 5 LVs. The obtained root mean square error of calibration (RMSEC) and prediction (RMSEP) are respectively 8 nm and 7 nm. The standard deviation of the DLS is 5 nm. A confidence interval of 95 % was chosen to validate the model as shown in Figure 5, so twice the standard deviation of the DLS, which makes 10 nm. The RMSEC and RMSEP are close to the DLS value so the uncertainty of the model is acceptable. It can be seen on the parity diagram that the majority of the data are within this interval.



(b)

(a)

Figure 5: (a) Root mean square error of cross-validation according to the number of latent values using leave-one out (black) and 3 iterations of Monte-Carlo algorithm (red, blue, green) and (b) Parity diagram of the data points predicted using partial least square (PLS) regression to predict z-average with 5 LVs

The same methodology was applied to the models based on *d*10, *d*32, *d*43 and *d*v50. Table 2 recaps the RMSEC and the RMSEP for these models, with 5 LVs. It can be seen that the RMSEC are quite similar for all models. However, the RMSEP shows some differences, with values of 7 nm, 6 nm, 9 nm, 15 nm and 10 nm respectively for the models based on z-average, *d*10, *d*32, *d*43 and *d*v50. A much higher RMSEP is obtained for *d*43 compared to the other diameters. As a reminder, only the 30° angle is used so it is difficult to predict a volume in that case. The use of other angles of SRS could provide better prediction of *d*43.

Table 2: Root mean square error of calibration (RMSEC) and prediction (RMSEP) obtained from the models based on z-average, d10, d32, d43 and dv50

|  |  |  |
| --- | --- | --- |
| **Diameter** | **RMSEC (nm)** | **RMSEP (nm)** |
| Z-average | 8 | 7 |
| *d10* | 9 | 6 |
| *d*32 | 9 | 9 |
| *d*43 | 9 | 15 |
| *d*v50 | 8 | 10 |

In order to compare the five models, the beta coefficients of the PLS regression are compared. Figure 6 shows that the beta coefficients, the contribution of the different wavelengths, for z-average and *d*32 are quite similar in shape all over the spectrum but they differ in the absolute value of the coefficient. The same observation can be made for *d*43 and *d*v50, which have the same trend but the coefficients of *d*43 show much bigger absolute value all over the spectral range. The *d*10 coefficients are not similar to the other coefficients, so it can be classified aside from the rest. The diameters do not evolve at the same rate when the particle size increases and this can explain why different coefficients are obtained. These observations show that different ways of calculating the mean diameters lead to different models and the diameter that is correlated to clear changes in the spectra needs to be chosen carefully.



Figure 6: Beta coefficients of the PLS regression models based on z-average, d10, d32, d43 and dv50

Figure 7 shows the prediction of the different mean diameters in experiments 1, 2, 5 and 7, for which part of the data was used to build the calibration model. First of all, all the predictions follow the trend of the reference measurements correctly. An overestimation of the particle diameter by the SRS compared to the DLS can be observed in some experiments. Namely, in experiments 2 and 5, the *d*43 prediction is less accurate than the other diameters. A first hint of this lack of accuracy for *d*43 was given in Table 2 with the high RMSEP.



Figure 7: Prediction of z-average (red), d10 (dark blue), d32 (green), d43 (black) and dv50 (cyan) for experiments 1, 2, 5 and 7 by the SRS models of prediction

The online monitoring is very interesting. It shows that the smaller the particle, the noisier the prediction can be. An external validation has also been done with the runs not used to build the calibration model. Figure 8 shows the predictions of all diameters for experiment 8. Some differences between the DLS values and SRS predictions are observed for all diameters, but in general the estimations remain acceptable. Some fluctuations of the SRS spectra (probably due to the presence of bubbles in the gap of the probe) occurred between 90 and 120 minutes, and therefore the spectra were deleted.

It can be concluded that the SRS data gives similar predictions of all the diameters, except the *d*43 which is less accurate. The other types of mean diameters are almost equivalent in terms of RMSEC and internal and external validation, and they all can be implemented.



Figure 8: Prediction of z-average (red), d10 (dark blue), d32 (green), d43 (black) and dv50 (cyan) for experiment 8 with the SRS models of prediction

### Online investigations of the size bimodality

The offline study indicated that the SRS is sensitive to bimodality. In this section, the developed model is evaluated in the case where perturbations are introduced in the experiment is done to simulate renucleation. The model using the z-average is used for the discussion in this section, knowing that the other diameters (*d*10, *d*32, *d*v50) give similar trends. Figure 9 shows the prediction of the z-average for experiments 11 and 12. As a reminder, at around 100 minutes a latex with smaller particles was added leading to a 50-50 % mixture latex with sizes 280 nm and 142 nm. In experiment 12, only the ratio of the number of big to small particles is slightly different (about 45:55 %). It can be seen that the model clearly detects a change in the medium, and the predictions move towards smaller particles, as smaller particles are added. No comparison with the DLS is shown after this modification, as it is incorrect to characterize a bimodal latex by one mean diameter.

Therefore, it can be expected that the SRS can detect particle renucleation or coagulation during the reaction. However, in these experiments half of the mixture had small particles, while when renucleation or coagulation occur they may not have a significant impact on the SRS. The offline study regarding size bimodality has also shown that the phenomena caused by small particles can be hidden by the bigger ones when the difference in size is important. So, the number of particles created from renucleation and the size of the particles already existing are key parameters for the detection of renucleation by the SRS.



Figure 9: Prediction of the z-average in experiments 11 and 12 with addition of a latex with smaller particles size (142 nm) than the latex into the reactor

### Reconstruction of the particle size distribution

In this section we investigate the possibility of reconstructing the particle size distribution from the predictions. The PSD can be characterized by a normal distribution which can be expressed as a function of the standard deviation, σ, and, the mean of the distribution, $d\_{10}$, (where *x* is the diameter varying all along the distribution):

|  |  |
| --- | --- |
| $f(x)=\frac{1}{σ\sqrt{2π}}e^{-\frac{1}{2}\left(\frac{x-d\_{10}}{σ}\right)²}$  | (3) |

The mean diameter $d\_{10}$ is available by the SRS, but the standard deviation is unknown. As the standard deviation is not a physical property, it is not coherent to be estimated directly from the spectra, even though it is related to the fraction of particles with different sizes which do have an impact on the spectra. The standard deviation and the PSD can be estimated from the other predicted diameters indirectly. In order to do so, the PSD is assumed to be Gaussian and the standard deviation σ is estimated using an optimization algorithm. A function J (equation 4) is described:

$\min\_{σ}J=\left(d\_{10, model}-d\_{10, SRS}\right)^{2}+\left(d\_{32, model}-d\_{32, SRS}\right)^{2}+\left(d\_{43, model}-d\_{43, SRS}\right)²$ (4)

Where the values $d\_{10, model}$ $d\_{32, model}$ and $d\_{43, model}$ are obtained from the Gaussian distribution.

The sum of the square of the difference between the diameters obtained from SRS and the diameters obtained from the Gaussian distribution is defined by this function (diameters are *d10*, *d32*and *d43*). The standard deviation σ is then estimated by minimizing this function J. In order to have a better calculated PSD, the *d10* was also recalculated.

Figure 10 compares the distributions obtained using the DLS and the reconstructed distribution based on the SRS predictions, for different latexes with z-average of 48 nm, 142 nm, 210 nm and 295 nm. It can be seen that the recalculated PSD fits well the PSD obtained by DLS. However, for small particles, the peak is not well estimated, while when the particles get bigger, the recalculated PSD is closer to the real PSD. This is partly due to the fact that the real distribution is not exactly Gaussian. Also, as shown previously (Figure 1), when the particles are bigger, the distribution becomes larger and the distance between *d*10, *d*32 and *d*43 increases. This increase improves the distinction between the different mean diameters and gives more precise results when using equation 4. It can be concluded that the use of the diameters predicted with SRS allows to recalculate the PSD with satisfactory results, which allows predicting the PSD online without sampling.

  

Figure 10: PSD in number obtained from DLS and recalculated from SRS predictions with z-average of 48 nm, 142 nm, 210 nm and 295 nm

## Offline investigations of Raman data

In parallel to the SRS monitoring, Raman data were acquired first offline to study the effect of the particle size on the spectra and then online during the same experiments as presented in the design of experiments section.

Figure 11 shows the Raman spectra of different samples with similar solids content of 16 % wt and different z-average varying from 70 nm to 550 nm (at 70°C). It can be seen that the whole Raman spectrum varies with the particle size. Indeed, the intensity decreases at all Raman shift when the z-average of the particles increases, mainly the Rayleigh band at 127 cm-1 and the bands from 3000 cm-1 to the end. Note that this last area corresponds to the water band. Only two bands, at 417 cm-1 and 750 cm-1, do not evolve with the diameter of the particles because they are characteristic of the sapphire at the tip of the probe. Table 3 shows that less energy (the sum of the intensity) is received from the Raman when the particle diameter increases. It can be concluded that there is a clear effect of the diameter of particles on the Raman spectra. It is reminded here that the probe used has a working distance of 0.5 mm.



Figure 11: Raman spectra of samples with 16 % wt of solids content and different particle sizes with z-average of 70 nm, 117 nm, 195 nm, 345 nm and 550 nm

Table 3: Sum of intensity of the Raman spectra according to the z-average studied

|  |  |
| --- | --- |
| Z-average | Sum of intensity (hits) |
| 70 nm | 7.7 × 107 |
| 117 nm | 6.6 × 107 |
| 195 nm | 4.5 × 107 |
| 345 nm  | 3.0 × 107 |
| 550 nm | 2.4 × 107 |

Figure 12 shows the spectra of latexes with a z-average of 70 nm, 195 nm and their mixture. It can be seen that the spectrum of the mixture is in between the two unimodal spectra but closer to the one with a z-average of 70 nm. The figure also shows the spectra with a z-average of 70 nm, 550 nm and their mixture. In this case too, the spectrum of the mixture is closer to the spectrum with the bigger particles but with slightly lower intensity. When the difference in size is big, the impact of the big particles becomes dominant on the Raman spectrum (as is the case for the SRS).



Figure 12: Raman spectra for monomodal latexes of different sizes and their mixtures with solids content at 16 % wt

## Online implementation of Raman

The offline study has demonstrated that the diameter of particles affects the Raman spectra, but it is of interest to determine if this effect can be quantified. The z-average was chosen to develop the calibration model. The same data used for calibration, internal and external validation of SRS were used here.

PLS regression has been used, as done for the SRS data, with 7 LVs. Figure 13a shows the parity diagram for 7 LVs and it can be seen that the RMSEC and RMSEP are respectively at 14 nm and 19 nm, much higher than the confidence interval of 10 nm (twice the standard deviation of the DLS). Figure 13b shows the coefficients of the PLS regression model. It can be seen that the area from 100 cm-1 to 500 cm-1 contributes little although it had high variability. In fact, this region can suffer from instability of the notch filter that removes the Rayleigh band. The region between 500 cm-1 and 1600 cm-1 contributes directly to the model with the evolution of the spectral band. Between 1600 cm-1 and 2600 cm-1 an evolution of the baseline with a slope can be observed. The entire spectral domain thus contributes to the model. The highest coefficients are observed for the 2600-3000 cm-1 region.



Figure 13: a) Parity diagram of the data points predicted using partial least square (PLS) regression to predict z-average with 7 LVs, b) Coefficients of the PLS regression model based on Raman data

Figure 14 shows the predictions of experiments 1, 2, 5 and 7. It can be seen that for experiments 2 and 7, the predictions follow the DLS reference values well. However, for experiments 1 and 5 the predictions differ from the DLS measurement. Some negative values can be observed for experiment 1 that have no significance and that might indicate a problem of robustness of the model and the trend of the prediction is hardly representative of the evolution of the particle size. Figure 15 shows the prediction of experiment 8, as external validation. A good agreement between DLS and the prediction model can be observed.



Figure 14: Prediction of z-average for experiments 1, 2, 5 and 7 by the Raman PLS model of calibration



Figure 15: Prediction of z-average for experiment 8 as external validation by using Raman PLS model of calibration

# Conclusion

The use of NIR spatially resolved spectroscopy and Raman were investigated for the monitoring of the particle size in emulsion copolymerization. The experiments were designed in a way to decouple variations in the particle size from the solids content. PLS was used for model development. Different mean particle sizes were predicted and compared.

Offline investigations demonstrated that the SRS is sensitive to changes in the particle size, particle concentration (or solids content) and the presence of a bimodal latex. Changes in the particle size had different effects on the spectra than for the solids content. The calibration was done using part of the online data. By keeping similar solids content for different ranges of diameter, and vice versa, we have ensured that the diameter of particle was totally decoupled from the solids content in the dataset.

Even though only the backscattering information at 30° was used, good predictions were obtained for all diameters (z-average, *d*10, *d*43, *d*32 and *d*v50) even though the *d*43 was slightly less accurate. The capacity to predict multiple diameters has allowed to recalculate the PSD in number which is a useful information to be monitored online using SRS. The study has also shown the ability to detect bimodality offline as well as online but within particular ranges of sizes and concentrations which would need to be investigated.

On the other hand, Raman spectroscopy has demonstrated its capacity to differentiate different diameters of particles. It could give acceptable predictions of the particle size, though with a lower sensitivity than the SRS. The SRS is therefore better adapted for the monitoring of the particle size.

# Acknowledgments

This work was funded by the pole Lyon Process Science and Engineering (LPSE).

# References

[1] A. Cherfi et G. Févotte, « On-line conversion monitoring of the solution polymerization of methyl methacrylate using near-infrared spectroscopy », *Macromolecular Chemistry and Physics*, vol. 203, no 9, p. 1188, juin 2002, doi: 10.1002/1521-3935(200206)203:9<1188::AID-MACP1188>3.0.CO;2-N.

[2] R. H. Colby, L. J. Fetters, et W. W. Graessley, « The melt viscosity-molecular weight relationship for linear polymers », *Macromolecules*, vol. 20, no 9, p. 2226‑2237, sept. 1987, doi: 10.1021/ma00175a030.

[3] J. M. Nölle, C. Jüngst, A. Zumbusch, et D. Wöll, « Monitoring of viscosity changes during free radical polymerization using fluorescence lifetime measurements », *Polym. Chem.*, vol. 5, no 8, p. 2700, 2014, doi: 10.1039/c3py01684f.

[4] L. A. Wood, « Glass transition temperatures of copolymers », *J. Polym. Sci.*, vol. 28, no 117, p. 319‑330, mars 1958, doi: 10.1002/pol.1958.1202811707.

[5] R. A. M. Vieira, C. Sayer, E. L. Lima, et J. C. Pinto, « In-line andin situ monitoring of semi-batch emulsion copolymerizations using near-infrared spectroscopy », *J. Appl. Polym. Sci.*, vol. 84, no 14, p. 2670‑2682, juin 2002, doi: 10.1002/app.10434.

[6] A. M. Alb, P. Enohnyaket, M. F. Drenski, A. Head, A. W. Reed, et W. F. Reed, « Online Monitoring of Copolymerization Involving Comonomers of Similar Spectral Characteristics », *Macromolecules*, vol. 39, no 17, p. 5705‑5713, août 2006, doi: 10.1021/ma060800f.

[7] S. E. Barnes, M. G. Sibley, H. G. M. Edwards, et P. D. Coates, « Process monitoring of polymer melts using in-line spectroscopy », *Transactions of the Institute of Measurement and Control*, vol. 29, no 5, p. 453‑465, déc. 2007, doi: 10.1177/0142331207084336.

[8] C. K. Ober, K. P. Lok, et M. L. Hair, « Monodispersed, micron-sized polystyrene particles by dispersion polymerization », *J. Polym. Sci. B Polym. Lett. Ed.*, vol. 23, no 2, p. 103‑108, févr. 1985, doi: 10.1002/pol.1985.130230209.

[9] K. Takahashi, H. Kato, T. Saito, S. Matsuyama, et S. Kinugasa, « Precise Measurement of the Size of Nanoparticles by Dynamic Light Scattering with Uncertainty Analysis », *Part. Part. Syst. Charact.*, vol. 25, no 1, p. 31‑38, avr. 2008, doi: 10.1002/ppsc.200700015.

[10] J. Qiu, S. G. Gaynor, et K. Matyjaszewski, « Emulsion Polymerization of *n* -Butyl Methacrylate by Reverse Atom Transfer Radical Polymerization », *Macromolecules*, vol. 32, no 9, p. 2872‑2875, mai 1999, doi: 10.1021/ma981695f.

[11] M. R. Maleki, A. M. Mouazen, H. Ramon, et J. De Baerdemaeker, « Multiplicative Scatter Correction during On-line Measurement with Near Infrared Spectroscopy », *Biosystems Engineering*, vol. 96, no 3, p. 427‑433, mars 2007, doi: 10.1016/j.biosystemseng.2006.11.014.

[12] Å. Rinnan, F. van den Berg, et S. B. Engelsen, « Review of the most common pre-processing techniques for near-infrared spectra », *TrAC Trends in Analytical Chemistry*, vol. 28, no 10, p. 1201‑1222, nov. 2009, doi: 10.1016/j.trac.2009.07.007.

[13] K. Ito, T. Kato, et T. Ona, « Non-destructive method for the quantification of the average particle diameter of latex as water-based emulsions by near-infrared Fourier transform Raman spectroscopy », *J. Raman Spectrosc.*, vol. 33, no 6, p. 466‑470, juin 2002, doi: 10.1002/jrs.860.

[14] M. M. Reis, P. H. H. Araújo, C. Sayer, et R. Giudici, « Evidences of correlation between polymer particle size and Raman scattering », *Polymer*, vol. 44, no 20, p. 6123‑6128, sept. 2003, doi: 10.1016/S0032-3861(03)00669-4.

[15] C. Houben, G. Nurumbetov, D. Haddleton, et A. A. Lapkin, « Feasibility of the Simultaneous Determination of Monomer Concentrations and Particle Size in Emulsion Polymerization Using in Situ Raman Spectroscopy », *Ind. Eng. Chem. Res.*, vol. 54, no 51, p. 12867‑12876, déc. 2015, doi: 10.1021/acs.iecr.5b02759.

[16] P. D. Gossen, J. F. Macgregor, et R. H. Pelton, « Composition and Particle Diameter for Styrene/Methyl Methacrylate Copolymer Latex Using UV and NIR Spectroscopy », *Applied Spectroscopy*, vol. 47, no 11, p. 1852‑1870, nov. 1993, doi: 10.1366/0003702934066154.

[17] M. M. Reis, P. H. H. Araújo, C. Sayer, et R. Giudici, « Correlation between Polymer Particle Size and in-situ NIR Spectra », *Macromolecular Rapid Communications*, vol. 24, no 10, p. 620‑624, juill. 2003, doi: 10.1002/marc.200350004.

[18] A. F. Santos, E. L. Lima, et J. C. Pinto, « Control and design of average particle size in styrene suspension polymerizations using NIRS », p. 10.

[19] J. M. de Faria, F. Machado, E. L. Lima, et J. C. Pinto, « In-Line Monitoring of Vinyl Chloride Suspension Polymerization with Near-Infrared Spectroscopy, 1 - Analysis of Morphological Properties », *Macromol. React. Eng.*, vol. 4, no 1, p. 11‑24, janv. 2010, doi: 10.1002/mren.200900035.

[20] Q. Fu et W. Sun, « Mie theory for light scattering by a spherical particle in an absorbing medium », *Appl. Opt.*, vol. 40, no 9, p. 1354, mars 2001, doi: 10.1364/AO.40.001354.

[21] A. J. Cox, A. J. DeWeerd, et J. Linden, « An experiment to measure Mie and Rayleigh total scattering cross sections », *American Journal of Physics*, vol. 70, no 6, p. 620‑625, juin 2002, doi: 10.1119/1.1466815.

[22] E. Dzhongova, C. R. Harwood, et S. N. Thennadil, « Changes in the Absorption and Scattering Properties in the Near-Infrared Region during the Growth of *Bacillus Subtilis* in Liquid Culture », *Appl Spectrosc*, vol. 63, no 1, p. 25‑32, janv. 2009, doi: 10.1366/000370209787169777.

[23] R. Cubeddu *et al.*, « Nondestructive quantification of chemical and physical properties of fruits by time-resolved reflectance spectroscopy in the wavelength range 650–1000 nm », *Appl. Opt.*, vol. 40, no 4, p. 538, févr. 2001, doi: 10.1364/AO.40.000538.

[24] B. Igne, S. Talwar, H. Feng, J. K. Drennen, et C. A. Anderson, « Near-Infrared Spatially Resolved Spectroscopy for Tablet Quality Determination », *Journal of Pharmaceutical Sciences*, vol. 104, no 12, p. 4074‑4081, déc. 2015, doi: 10.1002/jps.24618.

[25] M. Rey-Bayle, R. Bendoula, N. Caillol, et J.-M. Roger, « Multiangle near infrared spectroscopy associated with common components and specific weights analysis for in line monitoring », *Journal of Near Infrared Spectroscopy*, p. 096703351983006, févr. 2019, doi: 10.1177/0967033519830062.

[26] M. Gheghiani, N. Caillol, S. Henrot, T. F. L. McKenna, et N. Sheibat‐Othman, « Monitoring of polymer content in an emulsion polymerization using spatially resolved spectroscopy in the near infrared region and Raman spectroscopy », *Polym Eng Sci*, p. pen.25467, juill. 2020, doi: 10.1002/pen.25467.

[27] A. Savitzky et M. J. E. Golay, « Smoothing and Differentiation of Data by Simplified Least Squares Procedures. », *Anal. Chem.*, vol. 36, no 8, p. 1627‑1639, juill. 1964, doi: 10.1021/ac60214a047.

[28] P. Geladi et B. R. Kowalski, « Partial least-squares regression: a tutorial », *Analytica Chimica Acta*, vol. 185, p. 1‑17, 1986, doi: 10.1016/0003-2670(86)80028-9.

[29] « Z-Average Particle Size: An Explanation - HORIBA ». http://www.horiba.com/scientific/products/particle-characterization/education/sz-100/particle-size-by-dynamic-light-scattering-resources/what-is-z-average/ (consulté le août 16, 2019).

[30] V. Joudrier, P. Bourdon, F. Hache, et C. Flytzanis, « Characterization of nonlinear scattering in colloidal suspensions of silica particles », *Applied Physics B: Lasers and Optics*, vol. 70, no 1, p. 105‑109, janv. 2000, doi: 10.1007/s003400050016.