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Comparing Near Infrared and Raman Spectroscopy for On-Line Monitoring of Emulsion Copolymerization Reactions

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Summary: In this work, Raman and Near InfraRed (NIR) spectroscopies are evaluated for the monitoring of different semicontinuous emulsion homo- and co-polymerization reactions. Important process variables, namely monomer concentrations and average particle sizes, were monitored by both techniques under realistic conditions that would be found in an industrial environment (*e.g.* low signal/noise ratio, probe placed in the reaction medium). Results suggest that Raman and NIR are suitable for on-line monitoring of emulsion polymerization reactions and that the success of their application is mainly related to representative calibration models used for the estimation of the properties of interest.

Keywords: average particle sizes; emulsion polymerization; monomer concentrations; NIR spectroscopy; on-line monitoring; Raman spectroscopy

Introduction

On line monitoring, as a component of a computer integrated manufacturing, plays an important task on polymer manufacture (*e.g.* productivity and quality improvement, safer and more stable process control)[1]. In such case, the development of sensors for evaluating the polymer properties throughout the polymerization process has become a challenge. Among industrial polymerization processes, emulsion polymerization has great importance being used to produce a large variety of polymers for different uses (*e.g.* paints, adhesives, coatings, binders). One of the advantages of this process is its compartmentalized nature, which enables to obtain polymers of high molecular weight at high polymerization rates[2,3]. Several techniques have been used for monitoring emulsion polymerization, *e.g.*, calorimetry, densimetry, refractive index, sound attenuation measurements, viscosimetry, turbidimetry,

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dynamic light scattering, chromatographic methods. More recently, spectroscopic methods have been pointed out as promising for on line monitoring and this is being indeed confirmed in the last years[4,5,6,7]. Spectroscopic techniques have as advantages the easy handling, fast measurements and, last but not least, its multipurpose usage, since different polymer properties might be monitored simultaneously. Its implementation for monitoring, in general, requires a calibration model to estimate the property(ies) of interest. In emulsion polymerization, not only a wide range of process variability in the composition of the medium takes place (*i.e.* monomer consumption, polymer content increase, polymer particles growth, reaction temperature changes), but also several different phases, such as, monomer droplets, micelles and polymer particles, are present in the reaction medium and might appear or disappear along the reaction. On the other hand, the spectra of vibrational spectroscopies evaluated in this work, Raman and Near InfraRed (NIR), are affected by changes in composition and temperature of the medium as well as by the heterogeneity of the medium. Thus, calibration models are key factors for the implementation of spectroscopic monitoring of emulsion polymerizations.

This work shares some experience on implementing spectroscopic monitoring (Raman and NIR) of emulsion polymerization reactions in a polymer reaction engineering laboratory, which houses several projects on emulsion polymerization reactions. These spectroscopic techniques are being evaluated as tools for improving the process understanding as well as for the development of technology for their industrial implementation. It is presented, in this work, a comparison between univariate and multivariate models; the effect of laser power loss and the effect of the increase in noise level; the ability in monitoring monomer concentrations and average polymer particle size; and also the ability for fault detection, since spectroscopic measurements performed on line are subject to process variability, which can drive the process to a stage not considered in the calibration model fitting and may result in gross errors. Therefore, statistical tools (Hotteling T^2 and Q[8]) were used to detect outliers and to judge whether the spectra can be used in the monitoring.

Experimental

Emulsion polymerization reactions were performed with industrial-grade inhibited monomers: butyl acrylate (BA), vinyl acetate (VA), styrene (Sty). Two different reactors were used: a 600 ml jacketed glass reactor, and a 3000 ml jacketed stainless steel reactor, both connected to a condenser to avoid monomer losses due to evaporation during the reaction. The startup procedure in all reactions comprised filling the reactor with the initial charge (without the initiator) and heating it up until the reaction temperature was reached. The reactants were fed in two different streams: 1) an aqueous solution of the initiator and 2) the organic phase. In order to remove traces of dissolved oxygen, both feed tanks and the reactor were continuously purged with nitrogen.

Raman spectra were collected in a FRA 106/S FT-Raman accessory attached to a IFS 28/N spectrometer from Bruker, equipped with a quartz beamsplitter. The laser frequency is 1064 nm. Laser power was set to 450 mW (or 510mW, when indicated). Glass tubes with 6 mm diameter were used to measure the spectra at room temperature (~25 °C), and a probe connected to reactor window was used to collect spectra directly during the reactions. NIR spectra were collected in a IFS 28/N Bruker spectrometer using a probe (Hellma 661.622-NIR, with a transflection system with a 1 mm overall light path) immersed into the reaction medium. These spectroscopic techniques differ in the spectral region and in the principle of light-matter interaction.[9, 10, 11]. Figures 1a and b show typical water and monomer (vinyl acetate and butyl acrylate) spectra measured by Raman and NIR spectroscopies. In these figures is possible to observe that water is strong absorbing in NIR overlaping with monomer spectra and a very weak scattering in Raman (only at about 3200-3400 cm^{-1}).

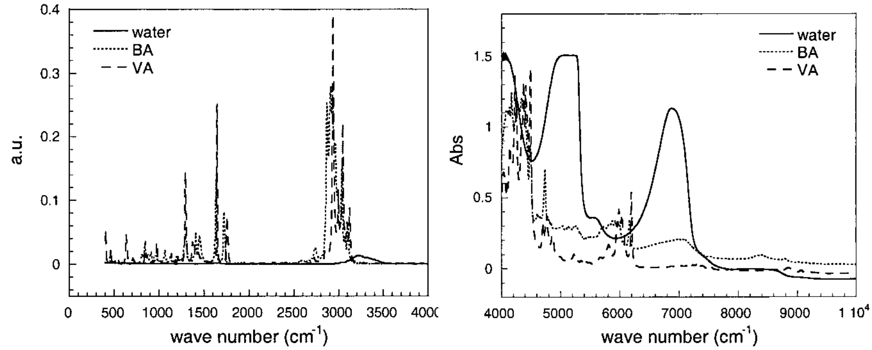

Figure 1. Spectra of water, VA and BA measured by Raman in (a) and by NIR in (b).

The Summary of the experiments and calibration models are described in the Tables 1 and 2. Reference methods used for measuring residual monomer concentrations and average particle sizes were, respectively, head-space gas chromatography (GC, HS-GC17A Shimadzu) and photon correlation spectroscopy (Coulter N4-Plus).

Table 1. Summary of the experiments (semicontinuous runs)

Run Name	Sampling technique	Type of samples for model fitting	Model*	Reaction** conditions	Estimated property	Technique
MVA	Samples collected from the reaction	Synthetic samples obtained by dispersing a known concentration of monomer in a polymeric emulsion	Models 2 and 3	VA s.c.=20% T = 60 °C GR	Monomer concentration	Raman
MBA	Samples collected from the reaction	Synthetic samples obtained by dispersing a known concentration of monomer in a polymeric emulsion	Models 1 and 4	BA s.c.=20% T = 60 °C GR	Monomer concentration	Raman
CBAVA2	Samples collected from the reaction	Samples from the reaction	Models 5 and 6	VA/BA (15/85) s.c.=20% T = 60 °C GR	Monomer concentration	Raman
CBAVA1	Samples collected from the reaction	Synthetic samples obtained by dispersing a known concentration of monomer in a polymeric emulsion plus samples from a different reaction	Models 5 and 6	VA/BA (50/50) s.c.=20% T = 60 °C GR	Monomer concentration	Raman
Msty1	Diluted samples from the reaction (to s.c.~ 7.2 wt%)	Synthetic samples obtained by dispersing a known concentration of monomer in a polymeric emulsion plus samples from the reaction	Model 8	Sty s.c.=46% T = 75 °C GR	Particle diameter	Raman
Msty2	Samples collected from the reaction	Synthetic samples obtained by dispersing a known concentration of monomer in a polymeric emulsion plus samples from the reaction	Model 8	Sty s.c.=46% T = 80 °C GR	Particle diameter	Raman
CBAVAR	Raman-Probe (placed at reactor window)	Reaction medium (from window probe)	Model 7	VA/BA (15/85) s.c.=24% T = 60 °C SSR	Monomer concentration	Raman
CBAVAN	NIR-probe placed in the reaction medium	Reaction medium (from immersion probe)	Model 9, T^2 and Q.	VA/BA (15/85) s.c.=24% T = 60 °C SSR	Monomer concentration	NIR
CBASty (1, 2, 3, 4)	NIR-probe placed in the reaction medium	Reaction medium (from immersion probe)	Model 11 T^2 and Q. Model 10	Sty/BA (50/50) s.c.=33% T = 70 °C SSR	Monomer concentration Particle diameter	NIR

* For details, see Table 3.

** VA = vinyl acetate, BA = butyl acrylate, Sty = styrene, s.c.=solids content (wt.%), for copolymerization, (50/50) or (15/85) indicates the comonomer composition (%wt/wt); GR = 600 ml glass reactor, SSR = 3000 ml stainless steel reactor.

Table 2. Summary of calibration models

Model	Spectra		Model type	Samples for model fitting			Reaction monitoring
	Pre-treatment	Region (cm^{-1})		Number of samples	Type	Spectroscopic setup	
Model 1	Each spectrum was normalized by dividing all its elements by the element corresponding to the wave number 427 cm^{-1}.	400-1941 and 2867-2906	SIMPLS 5 LVs	13	Synthetic samples	Raman- laser power set to 510mW, 32 scans with resolution of 8 cm^{-1}	Raman- laser power set to 510mW, 32 scans with resolution of 8 cm^{-1}
Model 2			SIMPLS 5 LVs	20			Raman- laser power set to 450 mW, 32 scans with resolution of 8 cm^{-1}
Model 3		1633-1662	Univariate linear model with the sum of the scattering intensities	20			
Model 4		1621-1652		13			Raman- laser power set to 510mW, 32 scans with resolution of 8 cm^{-1}
Model 5		400-1941	SIMPLS 6 LVs	13	reaction CBAVA2	Raman- laser power set to 450 mW, 32 scans with resolution of 8 cm^{-1}	Raman- laser power set to 450 mW, 8 scans with resolution of 8 cm^{-1}
				18	Synthetic samples		
Model 6			SIMPLS 8 LVs	13	reaction CBAVA2		
				15	Synthetic samples		
Model 7		400-4000	SIMPLS 10 LVs		reaction CBAVAR		Raman- laser power set to 450 mW, 32 scans with resolution of 8 cm^{-1}
Model 8 (Dp Raman)	NO	400-4000	SIMPLS 5 LVs	6	reaction Msty1 (~7.2 wt% s.c.#)	Raman- laser power set to 450 mW 32 scans with resolution of 8 cm^{-1}	
				7	reaction Msty2		
Model 9	Second derivative	7602-4902	SIMPLS 9 LVs	20	reaction CBAVAN	NIR 4 scans with resolution of 4 cm^{-1}	
Model 10 (Dp NIR)			SIMPLS 14 LVs	28	from 3 reactions similar to CBASty		
Model 11			SIMPLS 8 LVs	24	reaction CBASty		

* SIMPLS developed by de Jong was used[12].

\# 's.c.': solids content.

Results

Monitoring butyl acrylate emulsion homopolymerization reaction using off-line Raman Spectroscopy - comparison between univariate and multivariate models

In general terms, intensities of Raman bands can be expressed in an equation analogous to the Beer-Lambert law, where the intensity of Raman scattering at a given frequency is linear in relation to the concentration of the active compound(s)[10, 11]. FT Raman is an attractive method for monitoring polymerization reactions of vinylic monomers because the bands related to C=C stretching, which disappear during the reaction, are a strong scattering group[13,14,15]. Thus, as starting point, a simple univariate model (model 4 in Table 2) (using the area under the band due to C=C stretching) was compared to a multivariate linear model, the SIMPLS (model 1, Table 2) for monitoring a butyl acrylate homopolymerization reaction (MBA). Both calibration models were fitted from spectra collected of 13 synthetic samples. Run MBA was monitored by collecting samples from reactions, these samples were submitted immediately to spectra acquisition (two spectra were collected for each sample). Details about experimental and data handling procedures can be found in Reis et al. [16]. Figure 2a shows the evolution of butyl acrylate concentration during reaction MBA as estimated by both models. While results of the univariate linear model (model 4) present bias for samples corresponding to the beginning, compared to monomer concentration quantified by GC, the multivariate model, SIMPLS (model 1), results in good predictions. At the beginning of the reaction, the presence of monomer droplets in the reaction medium enhances its heterogeneity, what affects more adversely the univariate model (which is based on only one band) than the multivariate model.

Monitoring vinyl acetate emulsion homopolymerization reaction using off-line Raman Spectroscopy – effect of laser power loss

A vinyl acetate homopolymerization reaction MVA, that was performed to verify how the loss in laser power affects the predictions of calibration models, was monitored by collecting samples along the reaction. These samples were immediately submitted to spectra acquisition and two spectra were collected for each sample with laser power set to 450 mW. Calibration models, both univariate (model 3, Table 2) and multivariate (SIMPLS, model 2, Table 2), were fitted previously from spectra collected of 20 synthetic samples with the laser power set to a higher value, 510mW. A more complete description of reactions, data treatment and model development can be found elsewhere [16]. Results of MVA, shown in Figure 2b, indicate that these models are robust to the loss in the laser power and, again the SIMPLS model resulted in better predictions, as observed in the reaction MBA (Figure 2a).

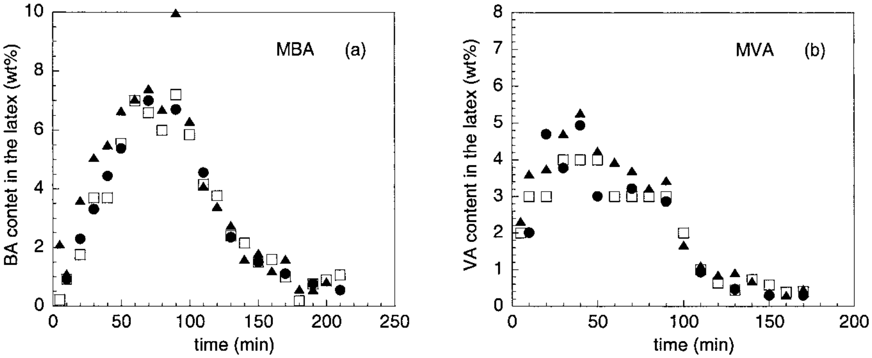

Figure 2. Concentration (wt%) of butyl acrylate in (a) and vinyl acetate in (b) predicted by the SIMPLS model (open squares '□') and the univariate linear model (full triangles '▲'). Full circles '●' correspond to CG measurements.

Monitoring vinyl acetate/butyl acrylate emulsion copolymerization reaction using off-line Raman Spectroscopy – effect of increase in noise level

There are situations in which the spectra collected during the monitoring has a higher noise level than the one present on the spectra used for calibration model fitting. Vinyl acetate/butyl acrylate copolymerization reactions CBAVA1 and CBAVA2 were performed in order to evaluate how deleterious an increase of the noise level would be. A complete description of these reactions can be found in Reis et al. [17]. Two SIMPLS models were fitted (one specific for vinyl acetate and another for butyl acrylate, models 5 and 6 in Table 2), using the data corresponding to 13 samples collected during reaction CBAVA2 (spectra and monomer concentrations quantified by GC), performed with a composition of the monomer feed stream of 15/85 VA/BA weight ratio and additional spectra corresponding to synthetic samples. These models were used to estimate the monomer concentration from spectra collected during another reaction, CBAVA1, with a different composition of the monomer feed stream (VA/BA 50/50 weight ratio). It must be noticed that the number of scans used to collect spectra during CBAVA1 was set to 8 (in fact an average of two spectra collected with 8 scans each), instead of 32 (the number of scans used for model fitting), leading to a higher noise level than the one present in the samples used for model fitting. The predictions of these models, as shown in Figure 3, are quite good, especially for vinyl acetate, that was present in a significantly higher concentration. Two different results are illustrated in Figures (3a and b). The first type shows the predictions of a model fitted with data from the same reaction (*i.e.,* the spectra were collected from samples obtained during the reaction, their monomer concentrations were quantified by GC and, after the reaction, a model was fitted from these data and was used to estimate the monomer concentration shown in this figure). The second type corresponds to results obtained from models fitted with data from another reaction (CBAVA2) with a completely different composition of the feed stream (Table 1) and from synthetic samples (model 5 and 6). The first type is described in this work to show that Raman spectroscopy is able to estimate relatively low monomer concentrations the reaction (about 5000 ppm for VA and 1500 for BA). The second type, which is realistic reaction monitoring, shows that it is possible to combine synthetic samples and data from former reactions to fit improved calibration models and that, in spite of the higher noise levels during reaction monitoring than during model fitting, good results can be obtained.

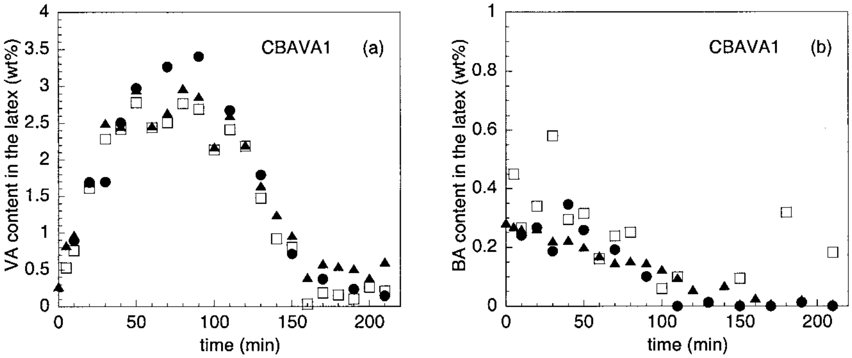

Figure 3. Concentration (wt%) of vinyl acetate VA in (a), butyl acrylate BA in (b) predicted by the SIMPLS model fitted with the data of reaction CBAVA2 and synthetic samples (open squares '□') and SIMPLS fitted with the data from the reaction CBAVA1 (full triangles '▲'). Full circles '●' correspond to CG measurements.

In-situ monitoring of vinyl acetate/butyl acrylate emulsion copolymerization reactions using Raman and NIR Spectroscopies

Monitoring reactions using probes placed at the reactor window (Raman measurements) and immersed into the reaction medium (NIR measurements) were also tested. For this purpose, two semicontinuous vinyl acetate/butyl acrylate emulsion copolymerization reactions

(CBAVAR and CBAVAN) were performed following almost the same formulation). This comonomer pair and formulation were chosen to compare the ability of both spectroscopic approaches for estimating low concentrations of monomers with relatively similar chemical structures. In this case, each calibration model was fitted with data from the monitored reaction.

Reaction CBAVAR was monitored with the Raman probe placed at the reactor window and a SIMPLS model (model 7 in Table 2) was fitted from spectra collected during the reaction. The average of every three spectra was used for model fitting as well as for the prediction of the reaction. Due to the width of the reactor window (15 mm), Raman spectra collected during CBAVAR presented a low signal/noise ratio and, therefore, a type of dynamic filter was used. So the estimated concentration profile was filtered with smoothing spline from the first value estimated to the actual value. In this case, the filter was applied after 21 minutes of reaction, and the 21 values of concentration estimated from the beginning of the reaction up to 21 minutes are used in the first application of the filter. This procedure is applied successively, in each instant the predicted value from the calibration model is corrected by the smoothing filter, using all the points available up to the time considered. It is important to emphasize that this filtering procedure was designed for on-line utilization, thus no correction is applied backwards. The use of this filter leads to a reduction of the variability of the estimation, as shown in Figure 4a and 4b. Finally, there is a good agreement between the reference measurements (GC) and the values estimated from Raman (model 7). This approach shows that, even under a low signal/noise ratio and low monomer concentrations, it is possible to monitor reactions with a Raman probe placed at the reactor window.

Reaction CBAVAN was monitored using NIR spectroscopy with the probe immersed into the reaction medium and a SIMPLS model (model 9 in Table 2) was fitted from spectra collected during the reaction (each spectrum is an average of 4 scans). Results are shown in the Figures 4c and 4d, where it is interesting to notice that the model fitted with 20 points resulted in a good estimation of more than 700 points (spectra) collected under the temperature oscillations. These results suggest that when the calibration model is fitted with spectra that represent the reaction stages, NIR spectroscopy is able to monitor reactions under process variability. In addition, both techniques, Raman spectroscopy with probe placed at the reactor window and NIR spectroscopy with immersion probe, are suitable to monitor low monomer concentrations of monomers with similar chemical structures like VA and BA.

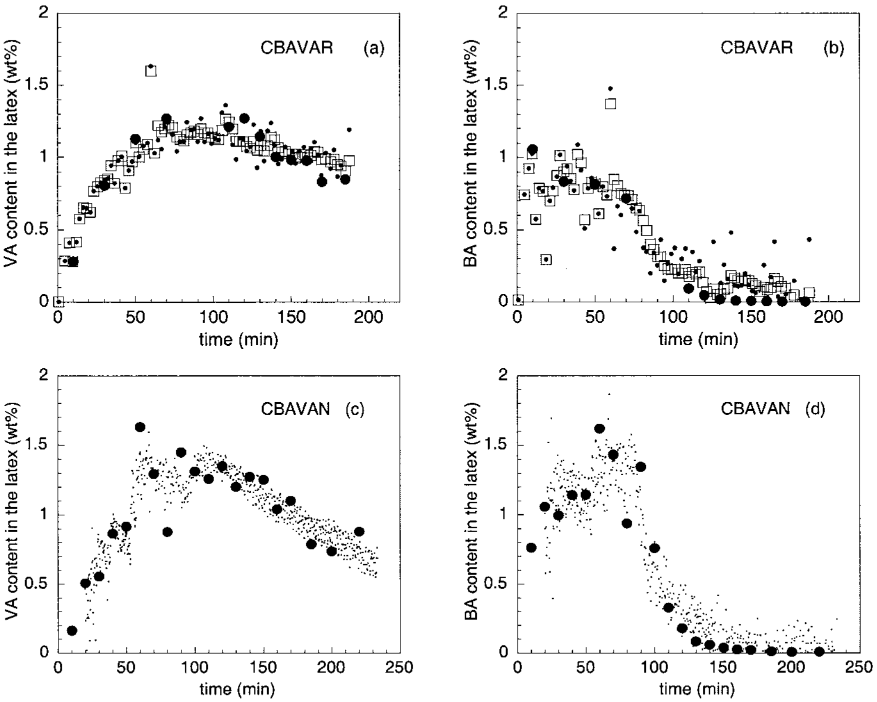

Figure 4. Estimations corresponding to measurements performed on line, Raman in (a) and (b), NIR in (c) and (d). Concentration (wt%) of vinyl acetate VA in (a) and (c), butyl acrylate BA in (b) and (d) predicted by the SIMPLS model fitted with the data from the corresponding reaction (small dot '.'). Open squares '□' correspond to the application of filter and full circles '●' correspond to CG measurements.

Monitoring average particle diameters during emulsion polymerization reactions using Raman and NIR Spectroscopies

As presented in very recent works, average polymer particle diameters might be estimated by both techniques, Raman[18] and NIR[19]. For Raman monitoring, in order to obtain a data set that describes all stages of the reaction, two reactions were performed and two approaches were tested. In the first one, the samples of reaction MSty1 were diluted in order to have always the same solids content (~ 7.2 wt. %), thus making the main difference among samples be due to only particle size. In the second approach, the samples collected during polymerization MSty2 were directly used. In this second case, particle size increases together with solids content as there is no renucleation along the reaction. The SIMPLS model (model 8 in Table 2) was fitted with 18 spectra from the diluted samples (triplicate of the 6 samples with ~7.2 wt. %) and 14 spectra from samples directly taken during reaction MSty2 (duplicate of the 7 samples) and no normalization of the spectra was applied. The predictions of this model for spectra of samples used in the model fitting and the others used as test data set are shown in Figure 5a. The predictions of this model are good for average polymer particle diameter, even though the predictions were rather poor when the same model was used to predict monomer concentration and solid content[18]. This suggests that the model does describe the variation due to polymer particle size and not a correlate property. On the other hand, if the estimation of monomer and polymer concentrations is done using normalized spectra, good estimates could also be obtained for these variables as this normalization would avoid the "interference" of the particle size[6].

The possibility of estimating polymer particle size during emulsion polymerization reactions using *in-situ* NIR measurements has also been evaluated. For this purpose, the data for fitting the calibration model were collected during three semicontinuous styrene/butyl acrylate copolymerization reactions with different particle sizes and similar polymer contents, in order to be able to verify whether it is possible to estimate particle sizes independently from the polymer content, since both these properties increase during the reaction. The second criterion, was the temperature, *i.e.* the spectra in the model should represent the range of temperature variation (67-80°C). Finally, the samples used in the calibration model fitting had to represent the overall reaction time, which was done by taking equally spaced data (spectra and the corresponding results of the reference methods) along the reaction time. On fitting the SIMPLS model (model 10 in Table 2), the data from these three reactions were divided into two sets: one for model fitting (28 spectra) and another to test the fitted model (25 spectra). The number of latent variables (LV = 14) was estimated by cross validation and is large due to the temperature range considered in the model fitting. The results for the calibration model fitting are shown in Figure 5b, where a very good agreement between the reference method measurements and the predictions of average particle diameters from NIR spectra is observed for both the model fitting data set and the model test data set.

These results are very important to show that there exists a correlation between Raman and NIR spectra and average particle diameter and that the average particle diameter might be estimated independently from other properties like polymer content or monomer concentrations. Details about the prediction of average polymer particle sizes by Raman and NIR spectroscopies can be found, respectively, in Reis et al. [18,19].

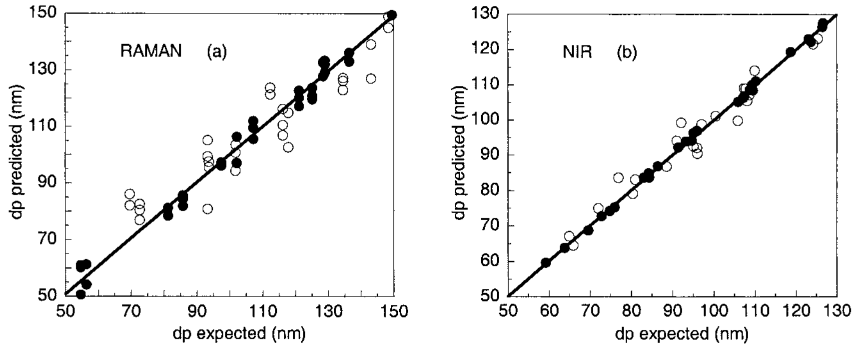

Figure 5. Prediction of average polymer particle diameter by Raman in (a) and NIR in (b). Full circles '•' correspond to samples used in the fitting of the calibration model and open circle'○', to samples used as test data set.

***In-situ* monitoring emulsion copolymerization reactions using NIR Spectroscopy – fault detection**

Reaction monitoring has, among its goals, the detection of abnormal changes during the reactions, which sometimes drives the reaction to stages not represented by the calibration models. In this case, the spectra collected during these reaction periods cannot be used for the estimation of properties. The detection of such situations has been identified by the statistic of Hotteling, 'T^2' and statistic Q[8]. Figure 6 shows the results of two copolymerizations, one of vinyl acetate and butyl acrylate (CBAVAN) and another of butyl acrylate and styrene (CBASty). This figure shows the identification of gross errors induced by the presence of monomer droplets in the reaction medium, presence of N_2 bubbles and/or the formation of polymer film in the probe. It can be observed that some behavior not present in the calibration model fitting, such as the presence of monomer droplets and the formation of polymer film in the probe, correspond to a special pattern of variation in the Q *versus* T^2 logarithmic plot, which allows the identification of such faults.

Conclusions

This work was focused on monitoring emulsion polymerization by two vibrational spectroscopic techniques: Raman and NIR, which differ on the spectral region as well as in their principle of light-matter interaction. Raman and NIR have in common the linearity between signal, scattered in Raman and absorbed in NIR, and the concentration of the

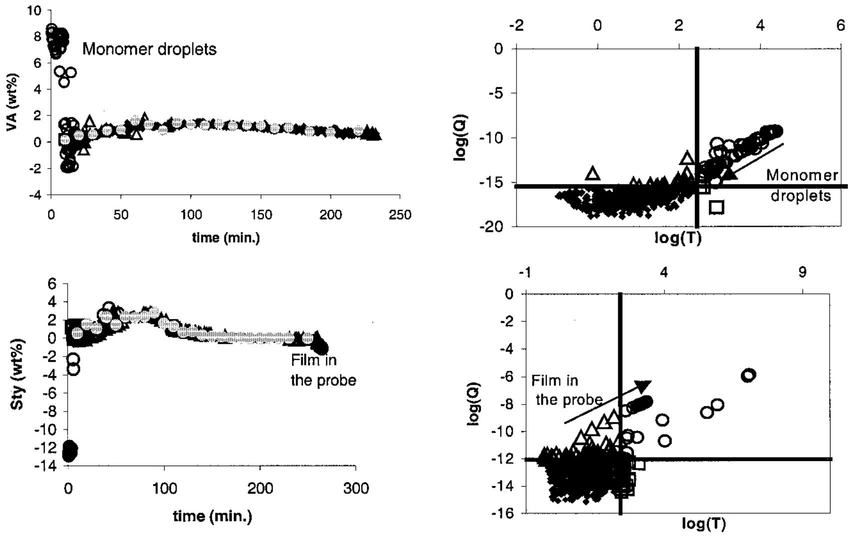

Figure 6. Estimations corresponding to measurements performed on line with NIR. In (a) and (c) concentration (wt%) of VA and Sty, respectively, predicted by SIMPLS model fitted with data from the corresponding reaction, CBAVAN and CBASty, respectively (small dots '.'). Open circles 'o' correspond to spectra over the T^2 and Q limits described in (b) and (d) as vertical and horizontal lines respectively. The arrows in (b) and (d) correspond to the time direction. Full grey circles '•' correspond to CG measurements.

scattering or absorbing species. Other important difference of these two techniques is the water molecule, which presents a weak scattering in Raman and strong absorption in NIR. As discussed before, both techniques require a calibration model to estimate the properties of interest (*e.g.* monomer concentration, polymer content, polymer particle size). Thus this work discussed the viability of estimating such properties by both techniques under realistic conditions (small number of scans for the acquisition of the spectra, spectra from the reaction medium with temperature variation). The results already discussed (based on different monomers systems) show that comparing Raman and NIR goes further than suggesting which approach is the best one for monitoring emulsion polymerization, but relies on evaluating which circumstances are more appropriate for their use. In general, both techniques presented good results on estimating composition variables, *i.e.* monomer concentration, this success is highly associated to how representative is the calibration model. This issue, fitting representative calibration models for on-line monitoring emulsion polymerizations, is far more complex than simply using a large composition range. One reason for that can be the correlation between polymer particle size and the signal of both spectrocopies, which allowed the fitting of models to estimate this important latex property.

Other important feature is the signal/noise ratio, which is usually low in Raman for rapid spectra acquisition, and seems to be the main variable effectively differing in the application of these two techniques. The sampling procedures for on-line monitoring, Raman probe placed at the reactor window and NIR probe in the reaction medium, were useful on estimating low monomer concentrations, even under low signal/noise ratio, the limitation due to low signal/noise ratio in Raman probe was overcome by a dynamic filter. Finally, faults during NIR measurements were successfully detected by statistical diagnosis, which also detected the presence of monomer droplets as well as the accumulation of polymer film in the NIR probe.

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