Macromol. Symp. **2004**, *206*, 135—148

On-line Monitoring of All-Acrylic Emulsion Polymerization Reactors by Raman Spectroscopy

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Summary: Fourier Transform Raman spectroscopy was used as an on-line sensor in order to monitor high solids content (50 wt%) n-BA/MMA emulsion copolymerization reactions. Due to the similarity of the chemical structure of the monomers, no separate bands could be detected for each monomer, and therefore a multivariate calibration technique was required (Partial Least Squares Regression, PLSR). Using experimental data from several semi-batch reactions independent PLSR models were built for the solids content, cumulative copolymer composition and unreacted amounts of n-BA and MMA. Those models were experimentally validated by monitoring reactions not used for calibration. It is demonstrated that FT-Raman spectroscopy can be successfully applied to on-line monitor emulsion polymerization reactors. This technique also shows a high potential for process control purposes because independent information about several molecular properties can be obtained from a single apparatus.

Keywords: emulsion polymerization; on-line monitoring; Raman spectroscopy; Partial Least Squares Regression; acrylic monomers; high solids

Introduction

Emulsion polymerization has a large number of applications in the chemical and process industry and presents many advantages compared to other polymerization processes. It offers the possibility to obtain products with unique properties, and therefore, it is one of the predominant processes for the commercial manufacture of polymeric materials used in a great variety of applications such as paints, adhesives, and coatings. Due to the increasing demand of the market regarding product quality control, substantial efforts are being devoted to control the processes used to produce them. The control of the polymerization reactor is essential because it is during the reaction when the final properties of the products are defined. In spite of the economical importance of emulsion polymerization, the control of emulsion polymerization reactors is still a pending task.

DOI: 10.1002/masy.200450211

The control of the molecular properties during the process demands an efficient on-line monitoring method. The difficulties to control emulsion polymerizations are in many cases associated to the lack of efficient and robust on-line measurements of the molecular properties[1,2]. There are very few instruments and techniques to evaluate on-line the polymer properties and they usually present problems due to long measurement delays and poor reliability. The complexity and high viscosity of the polymerization systems increase the difficulty to perform on-line measurements. Due to the lower viscosity of the emulsion polymerization compared to other polymerization processes, the development of on-line measurement techniques for emulsion may seem simpler. However, it is actually more difficult because of the risk of coagulation of the latex particles, which may block the pipes, valves and pumps used in the on-line instrumentation sampling devices[3,4].

Reaction calorimetry[5-8] has been widely used for the monitoring and control of emulsion polymerization reactors. Calorimetric measurements are easy to apply, robust, fast and universal (they can be easily applied to any industrial reactor). However, reaction calorimetry does not provide a direct measurement of the amount of unreacted monomer in the reactor, and this variable is estimated from the amount of polymer produced in the system using an overall material balance. In practice, this presents a serious limitation for the monitoring of the unreacted monomer in processes carried out under starved conditions because error propagation due to noisy temperature measurements and inaccuracies of the parameters (e.g., polymerization heats) may lead to errors in monomer conversion that at high conversions result in substantial errors in the amount of unreacted monomer. Reaction calorimetry also presents problems in very slow polymerizations where the heat generation rate is small.

In the last decade, there has been plently of activity regarding the use of spectroscopic techniques for on-line evaluation of polymer properties[9-16]. The recent development of fiber-optic probes suitable for remotely collecting spectra via optical fibers has given rise to the possibility of making *in situ* measurements in remote and harsh environments[12] (high temperatures, pressures, toxic environments etc...). The spectroscopic techniques coupled with fiber optics have a high potential for on-line monitoring and can provide important information about the state and nature of the samples under analysis. An additional advantage is that a fiber-optic probe can be installed in an existing reactor without time consuming and expensive modifications.

Styrene/butadiene[13,14] and Styrene/n-butyl acrylate[15] copolymerizations have been monitored by means of Raman spectroscopy. For systems containing styrene, usually the peak associated with the ring-breathing mode of styrene at 1000 cm^{-1} is used to normalize the spectral intensity, and the calibration stage does not present especial difficulties[12]. All acrylic copolymerizations are much more complex because the bands of the main functional groups of the different acrylic monomers of the formulation overlap due to the similarity in the chemical structure. Therefore, univariate calibration methods[17] are not appropriate and multivariate calibration techniques such as Partial Least Squares Regression[18-19] (PLSR) are required.

The objective of this work was to develop an on-line monitoring technique based on FT-Raman for all acrylics high solids content (50 wt%) emulsion copolymerization. The method was applied to a system containing n-butyl acrylate (n-BA) and methyl methacrylate (MMA). Unreacted monomer amounts, solids content and cumulative copolymer compositions were the variables monitored.

Experimental

The experimental setup employed to run the reactions was a commercial reactor (RC1, Mettler-Toledo) equipped with a stainless steel HP60 reactor. The reactor was also equipped with a Raman dip-probe (Bruker RamProbe) that was directly immersed into the reaction mixture, making possible *in-situ* measurements along the reaction.

The spectrometer used in the experiments was a near infrared Fourier Transform Raman spectrometer, RFS 100/S (Bruker), equipped with a 1064nm wavelength Nd:YAG laser, with a maximum power of 1.5 W. The spectral coverage is from 50 to 3500 cm^{-1}, corresponding to the Stokes interval. The spectrometer uses a germanium detector (D481-TU) optimized for FT-Raman measurements that is cooled down with liquid nitrogen. The Raman dip-probe is connected to the equipment through two optical fibers (5 meters long), one to carry the laser signal to the reaction mixture, and the other to carry the scattered radiation back to the spectrometer.

All the n-BA/MMA latexes had a solids content of 50 wt% and a molar composition of 50/50. Doubly deionized water was used in all polymerizations. All reactants, monomers (n-BA and

MMA, Quimidroga), emulsifier (Dowfax), initiator ($K_2S_2O_8$, Fluka) and buffer ($NaHCO_3$, Panreac) were used as supplied. Table 1 contains the formulation that was employed in the series of reactions Cal 1-5, used to construct the calibration models, and in the reaction Val 1 used for model validation. The amounts of initiator and buffer were varied in the experiments and the monomers and an emulsifier solution were fed into the reactor at constant flow rates, varying the feeding time (2 and 3 hours). Nitrogen was fed continuously during the reactions to keep an inert atmosphere.

Table 1. Formulation of the n-BA/MMA emulsion copolymerizations employed in the calibration reactions Cal 1-5 and the validation reaction Val 1.

Ingredients	**Initial Charge (g)**	**Stream 1 (g)**	**Stream 2 (g)**
n-BA	-	337	-
MMA	-	263	-
H_2O	617	-	32.55
Seed	63	-	-
$K_2S_2O_8$	Variable	-	-
$NaHCO_3$	Variable	-	-
Dowfax	-	-	9.45
Temperature	70	-	-

Raman spectra were collected from the start of the reaction, at regular intervals of 10 minutes. Each spectrum consisted in the accumulation of 200 scans, and was taken with a spectral resolution of 4 cm^{-1}, using a laser power of 1000 mW. Considering the time required to switch the laser on and off before and after each measurement (due to security reasons) and the data acquisition time, the time required to get the Raman measurement was approximately 4 minutes. OPUS software (supplied with the instrument by Bruker) was used for data acquisition and pre-processing. Figure 1 shows the spectra evolution along one of the reactions. During the acquisition of the Raman spectra a sample was withdrawn from the reaction mixture (after a Raman acquisition time of 2 minutes) for off-line analysis. The withdrawn samples were analyzed off-line by gas chromatography (GC) to determine the residual monomer concentrations in the reaction mixture. The conversion of monomer to polymer was determined by gravimetric analysis. For these analyses, immediately after collecting the samples, the reaction was quenched by addition of an inhibitor (hydroquinone).

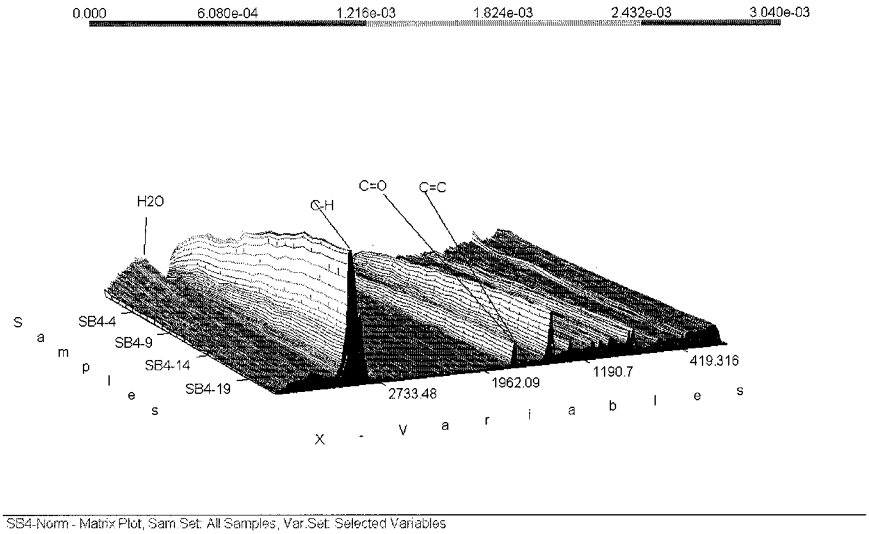

Figure 1. Spectra evolution during a semi-batch n-BA/MMA reaction.

Calibration

As mentioned before, the quantitative analysis of acrylic systems is not feasible by means of univariate calibration techniques, and the use full-spectra techniques is necessary. Raman spectroscopy has been used in combination with multivariate techniques for the monitoring of very different processes, such as curing reactions[20] and polymerization processes[21-23].The successful implementation of on-line monitoring techniques heavily relies on an adequate development of calibration methods. Usually, calibration methods applied to Raman are based on a linear model describing the relationship between the desired property and the spectral intensities of the reaction mixture. Among the multivariate calibration methods, PLSR is likely the most frequently used.

Partial Least Squares Regression (PLSR) analyses were performed using the Unscrambler software (CAMO ASA, Norway). The calibration models for the different properties are based on a set of five semi-batch reactions (Cal 1-5). PLSR models were built for the solids content, the cumulative copolymer composition and unreacted monomer amounts. For both monomers, n-BA and MMA, models to predict the unreacted monomer-to-solids content ratio and the unreacted monomer-to-total reactor weight ratio were developed.

Models were built using raw and normalized spectra (normalized to unit area, namely, dividing the y axis of each spectrum by its own area) and in all the cases better results were obtained with normalized spectra. Normalization also helps to overcome effects of instrumental variation. Several spectral pre-treatment techniques were also applied to the normalized spectra, and models were developed using the transformed spectra. Models were built with 1^{st} and 2^{nd} derivative spectra, with smoothed spectra and using only some parts of the spectra. In the best case, similar results to the ones obtained only with normalized spectra were achieved, and in many cases, the prediction error was increased with spectra pre-treatment. Therefore, only the models built up with the complete normalized spectra will be shown in this work.

In order to optimize the PLSR models, the optimal number of factors to be retained must be considered. In order to choose the optimal number of PCs, the root mean square error of validation (RMSEV) was plotted versus the number of principal components. In this case, the RMSEV was calculated using the leave-one-out cross validation method, because no separate validation sample set was available. The curve showing the evolution of the RMSEV is the sum of two opposite trends. One hand, the modeling error always decreases as more factors are added. On the other hand, the error associated with estimating the regression parameters, always increases as more factors are included in the model, and therefore, the prediction errors increase. The result is a curve with a more or less well defined minimum that corresponds to the optimal number of principal components. Figure 2 shows the RMSEV vs. the number of PCs plot for the solids content model and the model for the ratio of unreacted n-BA (n-BA grams) to the total reactor content (emulsion grams). For the solids content, a minimum is found at 3 PCs, and for the n-BA/Wreactor ratio at 4 PCs. Similar plots were constructed for the other properties, obtaining the optimal number of PCs required for each property that are summarized in Table 2. This table also includes the number of calibration samples (spectra taken at different times) employed in each model.

Table 2. Number of calibration samples employed in each PLSR model and the optimal number of principal components (PC) required for each property.

Property	**Number of calibration samples**	**Number of PCs**
Solids Content (SC)	106	3
Cumulative Composition	106	3
Unreacted n-BA/SC	101	3
Unreacted n-BA/WReactor	101	4
Unreacted MMA/SC	99	3
Unreacted MMA/WReactor	99	3

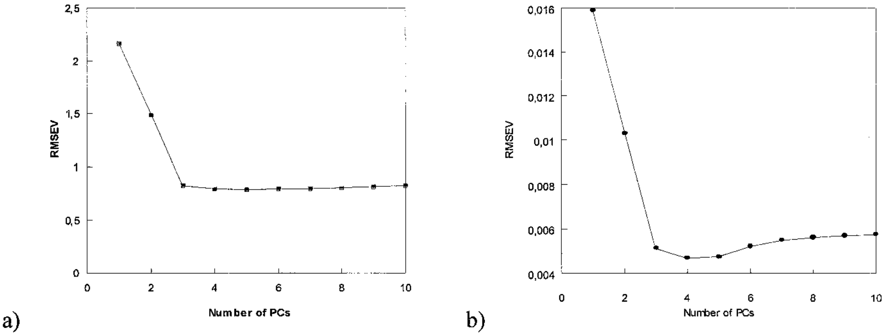

Figure 2. Root Mean Square Error of Validation (RMSEV) versus the number of principal components for: (a) the model of the solids content and (b) the ratio of the unreacted BA t.o the total content of the reactor.

Another useful piece of information in order to correctly interpret the PLSR models is the loading plots. These plots contain the coefficients of the PCs and show the relationships between the original variables (Raman wavelengths and property of interest) in the data set. Analyzing them, the parts of the spectra correlated with the property of interest can be identified. Figure 3 shows the loading plots for the first four PCs of the model for the solids content. Since the solids content has a positive loading value for the four PCs, wavelengths with positive loadings will be directly related to the solids content, and the ones with negative values will be inversely related to the solids content. Wavelengths with loading values around zero are not relevant for the property under study.

Looking at the loading plot for the first PC (Figure 3), a broad band in the 3500-3000 cm^{-1} with negative loading values can be observed. This means that this band is inversely proportional to the solids content, which is completely logical since it corresponds to water absorption. On the other hand, the group of bands in the 3000-2800 cm^{-1} region has large and positive values, and therefore, it is directly proportional to the solids content. This result is again what one should expect because those bands correspond to the vibration of the C-H bonds in the polymer.

Considering the loading plots for the different PCs and the percentage of X (Raman wavelengths) and Y (property of interest) variables explained by each PC (Table 3), it is possible to get an idea about the optimal number of principal components. Most of the variations in the solids content can be explained with the first PC. The next two PCs add further information about the changes in the solids content, therefore they still contribute to lowering the prediction error. But the 4th PC only adds noise and no relevant information to the model, and therefore, should not be considered.

A similar analysis can be made for the other properties, in order to optimize and interpret properly the PLSR models.

Table 3. The percentage of X (Raman) and Y (solids content) variables explained by each PC.

PC	Explained X percentage	Explained Y percentage
1	90	96
2	4	2
3	1	1
4	0	0

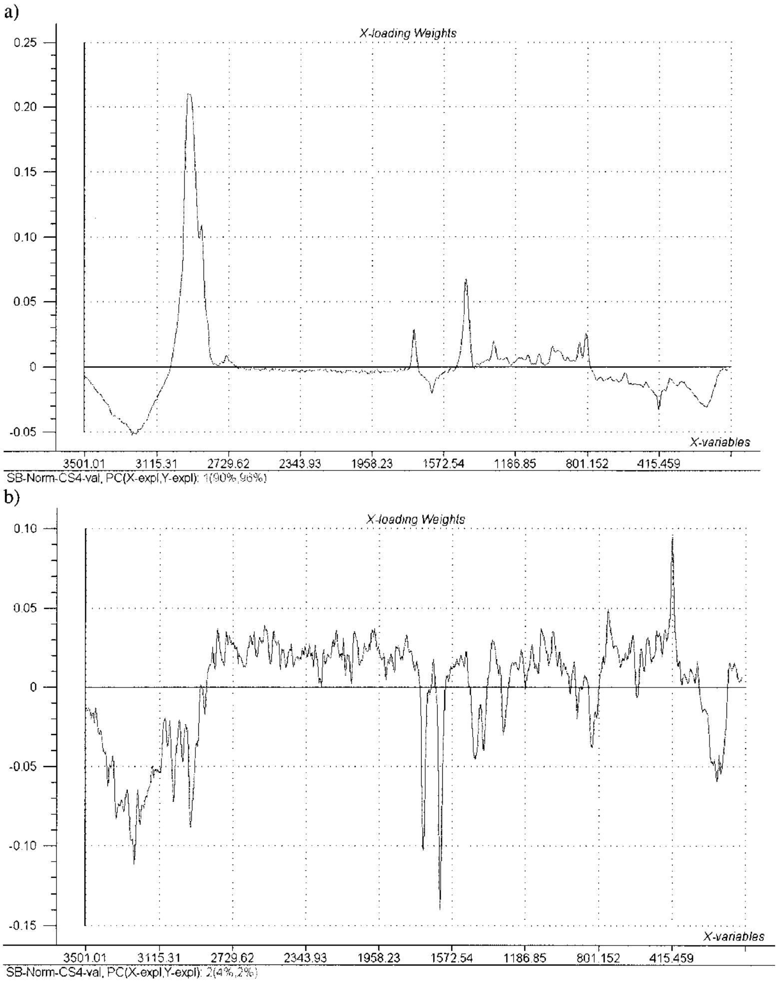

Figure 3. Loading plots for the first four PCs of the model for the solids content of the n-BA/MMA copolymerization: a) 1st PC; b) 2nd PC.

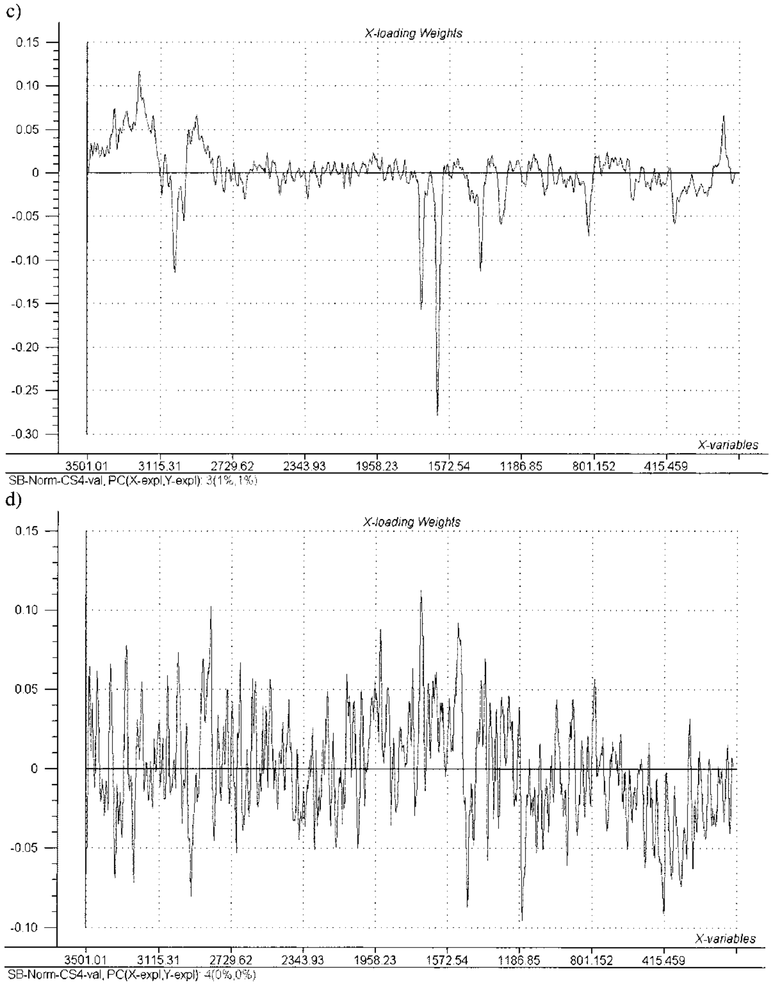

Figure 3. Loading plots for the first four PCs of the model for the solids content of the n-BA/MMA copolymerization: c) 3rd PC; d) 4th PC.

Experimental validation

In order to experimentally check the model performance, a reaction, totally independent from the calibration data set (Cal 1-5), was carried out (Val 1). The formulation used in this reaction is shown in Table 1. As in the previous reactions, the solids content was 50wt% and the monomer molar composition 50/50. For this reaction, the monomers and an emulsifier solution were fed into the reactor during 3 hours at a constant flow rate. Spectra were recorded every 10 minutes, and during the required spectra acquisition time (4 minutes as before) samples were withdrawn from the reactor for their off-line analysis. After normalization, the spectra were introduced into the previously developed models for the prediction of the different properties.

Figure 4 shows the performance of the models for the solids content ((g solids/g emulsion)*100) and cumulative copolymer composition (molar, based on n-BA). As it can be observed, a very good agreement between off-line and Raman measurements was obtained for the solids content. For the evolution of the cumulative copolymer composition a fairly good agreement between Raman and chromatographic results was achieved with slight deviations at the beginning and at the end of the polymerization. These results are promising in terms of using the FT-Raman information for reactor control purposes.

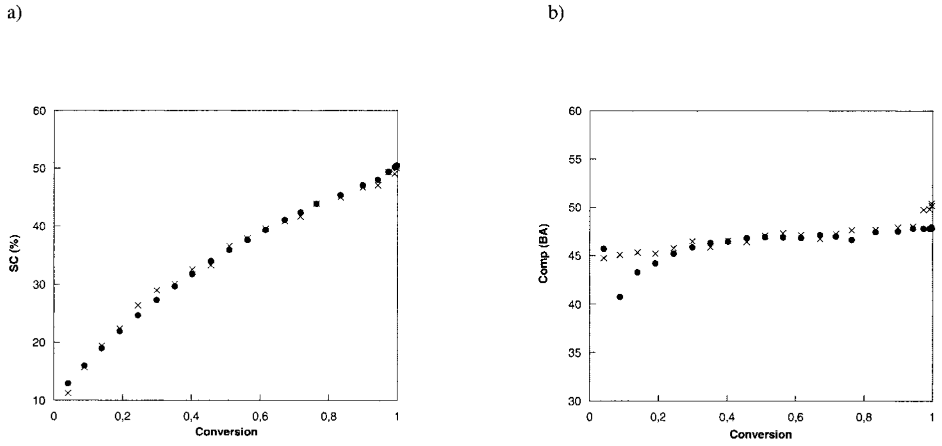

Figure 4. Evolution of the solids content (a) and cumulative copolymer composition (b) predictions during the semibatch emulsion copolymerization of n-BA/MMA. Legend: (•) gravimetry ; (x) FT-Raman spectroscopy.

Figures 5 and 6 show the evolution of unreacted n-BA and MMA amounts, followed by GC and FT-Raman. In both figures, two plots are shown. One for the monomer solids content ratio and the other one for the monomer reactor weight ratio. It can be observed, that on-line measurements agree pretty well with the off-line determination of the unreacted monomers. Considering the small amount of monomer present in the reaction mixture, the results are very satisfactory and can be extremely useful for later control strategies. It is important pointing out that under these conditions, the estimation of the amounts of unreacted monomer using reaction calorimetry leads to substantial errors.

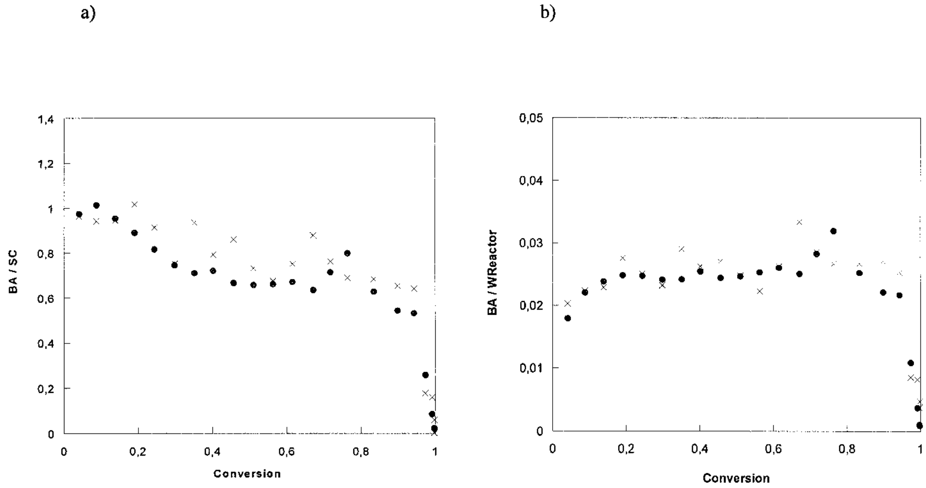

Figure 5. Monitoring of the n-BA/SC (g n-BA/SC) (a) and n-BA/reactor weight (g n-BA/g emulsion) (b) reaction Val 1. Legend: GC (•) and FT-Raman (x).

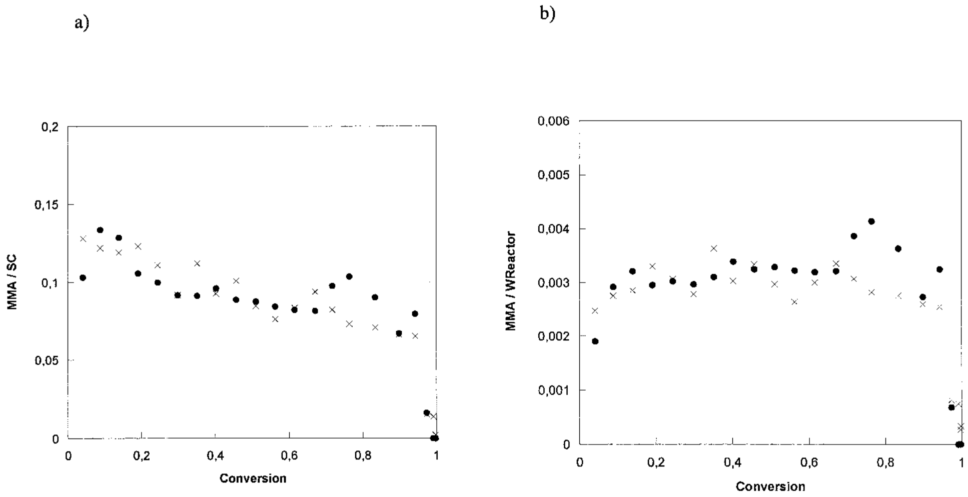

Figure 6. Monitoring of the MMA/SC (g MMA/SC) (a) and MMA/Wreactor (g MMA/g emulsion) (b) ratios for Val 1. Legend: GC (•) and Raman (x).

From the results shown in figures 5 and 6, it can be concluded that the predictions for the unreacted monomer to SC ratio and for the unreacted monomer to the total reactor content ratio were very similar. Since the ratios to the SC do not have direct physical meanings and in addition, they require measurements or predictions of the SC to get the total amounts of unreacted monomers, it is recommended to use the ratios to the total reactor content.

Conclusions

In this work, an on-line monitoring technique for high solids content all acrylic emulsion copolymerizations based on FT-Raman was developed. Despite the wide use of these emulsion polymers in the chemical industry, the on-line monitoring of these copolymerization systems by Raman spectroscopy had not been reported before. Models for the prediction of the solids content, the cumulative copolymer composition and unreacted monomer amounts were developed using partial least squares regression and experimentally validated, obtaining satisfactory results. The models worked very well even under starved conditions, where very little monomer was present in the reactor.

The obtained results show that FT-Raman spectroscopy offers the possibility to monitor several molecular properties from a single measurement, which makes this technique suitable for multipurpose on-line monitoring. This opens the possibility for application of FT-Raman to process control.

Acknowledgements

O. Elizalde acknowledges Ministerio de Educación y Ciencia for the scholarship. The authors acknowledge the financial support from the University of the Basque Country (Grant UPV 00221.215-13594/2001) and CICYT (project PP02000-1185).

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