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Detection of monomer droplets in a polymer latex by near-infrared spectroscopy

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Abstract

It is shown here that near-infrared spectroscopy (NIRS) may be used to detect the presence of monomer droplets in polymer lattices directly from spectra, without any kind of previous calibration. Experiments involving the addition of methyl methacrylate (MMA) and butyl acrylate (BuA) to monomer-free lattices indicated that there exists a specific wavelength (1620 nm) where, at some instant of the addition process, spectra are subject to a marked change. It is shown that this abrupt spectral change is caused by the formation of monomer droplets in the reaction medium. This finding may significantly improve the controllability of emulsion polymerization processes and the quality of its products, as shown by actual MMA/BuA emulsion polymerization experiments, which reinforces the potential of NIRS as a multipurpose analytic tool for in-line and in-situ simultaneous monitoring of different properties in emulsion polymerizations. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Near-infrared spectroscopy; Emulsion polymerization; In-line monitoring

1. Introduction

According to Downey [1], one of the areas that will have a quick development in near-infrared spectroscopy (NIRS) is the identification of products directly from spectra, without the need to perform any type of quantitative analysis. This branch of chemometrics has already found some applications in the pharmaceutical and food industries and may be used to detect process malfunctions in the chemical industry. This procedure is usually called 'process diagnosis'.

The presence of monomer droplets in emulsion polymerizations is an event that may cause degradation of the reactor controllability and may increase the risks of temperature runaways and specification drifts [2,3]. Therefore, it is often desired to circumvent the formation of monomer droplets in the reactor [2,4]. This may be accomplished through empirical trial-and-error procedure or through process modeling/optimization. In the first case, reaction recipes are developed to avoid the formation of monomer droplets. However, as recipes are insensitive to process disturbances, problems may arise during actual operation in face of unexpected and/or unknown modification of reaction conditions (contaminants, for instance). In the second case, the swelling limits of polymer particles may be predicted with the help of thermodynamic equilibrium models and material balances and then used as constraints for computation of feed policies. The main problems of this approach is the reliability of the thermodynamic parameters, which are available only for a limited set of systems and for a limited set of operation conditions, and the assumption of thermodynamic equilibrium, which sometimes may not be true. Besides, models would have to be solved in-line if continuous monitoring and disturbance rejection is to be accomplished. Therefore, the development of a simple and reliable method to detect the onset of droplet generation would be outstanding.

Santos et al. [5,6] observed that the spectra of suspension polymerization systems respond to changes of the mean particle diameter at specific NIR wavelengths. Analyzing the styrene suspension polymerization they verified that the most sensitive regions were comprised between 1630 and 1680 nm. These changes allowed them to use NIRS for in-line monitoring and control of the mean diameter of polystyrene particles produced in a batch reactor. Gossen

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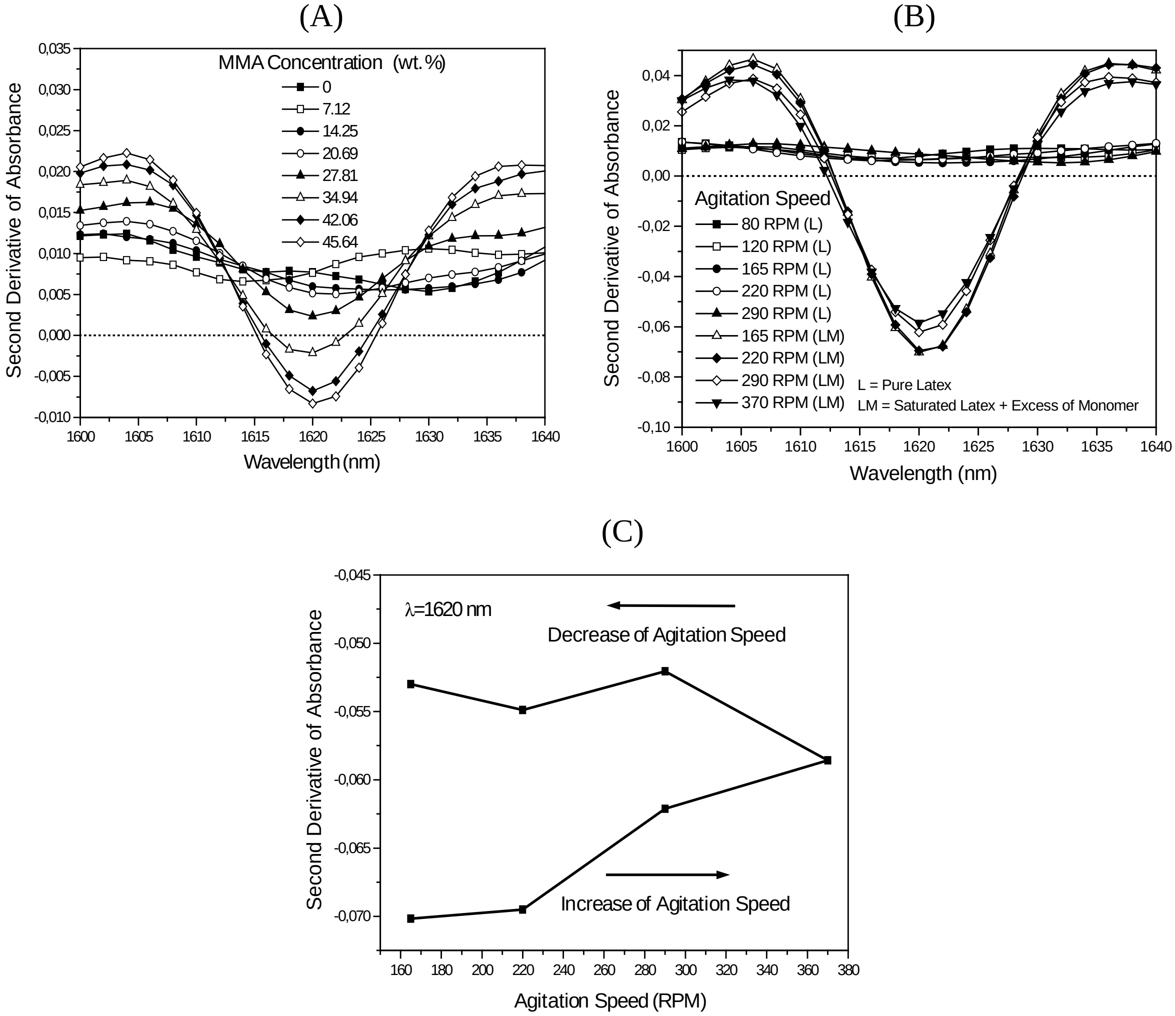

Fig. 1. Spectral changes observed during MMA addition (A) and during change of the agitation speed (B, C).

et al. [7] also reported the existence of strong correlation between NIR spectra and mean polymer particle diameters measured with light scattering techniques in emulsion polymerizations of methyl methacrylate and styrene. (In this case, though, it was not clear whether NIR spectra responded to changes of the particle size or to changes of other related variables, such as monomer conversion.) Both works employed partial least squares (PLS) for model building and in-line monitoring of particle size.

Based on the results available, it may be wondered whether it would be possible to detect the onset of monomer droplets generation in emulsion polymerization systems. As significant morphological changes will occur in the latex after the appearance of monomer droplets, droplet generation may perturb the NIR spectra of the original latex through additional scattering of the NIR light and introduction of different surface phenomena. It is shown below that this sort of reasoning is correct indeed and that it is possible to detect the generation of monomer droplets with the help of NIRS without any sort of previous calibration in the region analyzed by Santos et al. [5,6].

2. Results

The spectrometer used in the experiments was a NIR Systems 6500 in-line (NIRSystems), equipped with two concentric fiber optic bundles to illuminate and collect NIR radiation. An interactance immersion probe was connected to the end of the fiber bundles and its tip was properly positioned to provide a total pathlength of 4 mm. The scanned wavelengths varied from 1100 to 2500 nm in transmittance mode. To enhance the signal-to-noise ratio, 32 spectra were collected for each sample. Data acquisition and mathematical pretreatment were performed with a proprietary software, named Near-Infrared Spectral Analysis Software (NSAS) [8].

First, methyl methacrylate (MMA) and butyl acrylate (BuA) were separately and slowly (0.17 ml/min) added to a monomer-free polymer latex, whose polymer (equimolar MMA/BuA) hold-up was equal to 30 wt%. This latex was kept at 80°C, which is the temperature commonly employed to perform polymerizations of MMA and BuA with thermal initiators. The agitation speed was kept at 200 rpm. To avoid

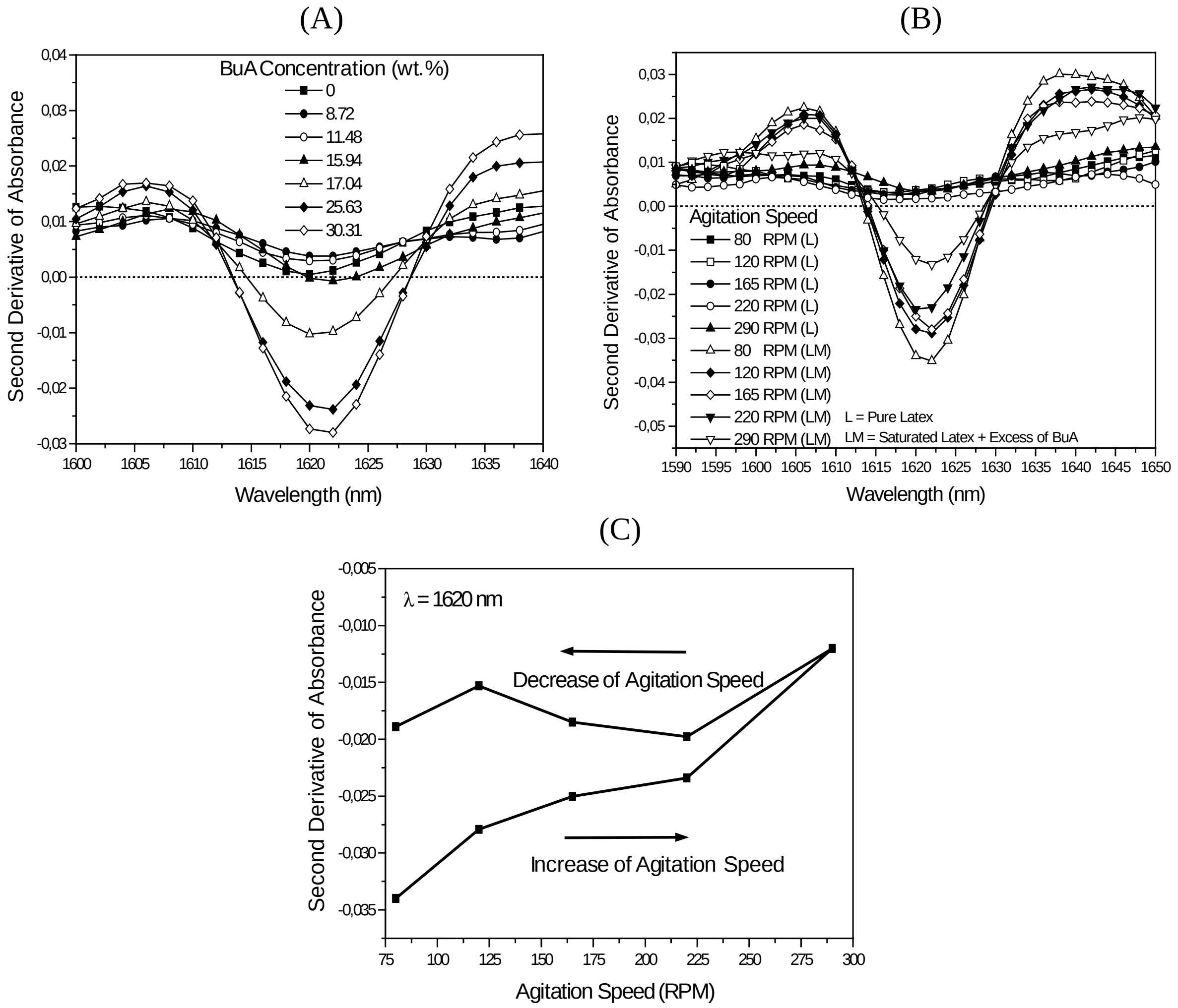

Fig. 2. Spectral changes observed during BuA addition (A) and during change of the agitation speed (B, C).

the risk of undesirable reaction, the polymer latex contained 200 ppm of hydroquinone. As soon as monomer feed was started, collection of NIR spectra was also started at regular intervals of 2 min. Figs. 1A and 2A show that a consistent change of the NIR spectra might be observed for both monomers at 1620 nm, indicating the increase of the monomer concentration. When the concentrations of MMA and BuA reached 27 and 17 wt% (water free basis), respectively, a strong negative peak appeared in the second derivative spectra at 1620 nm. The appearance of this peak was followed closely by the visual identification of monomer droplets in the medium (Table 1). As the wavelength where the phenomenon occurred was very similar to the one described in the literature [5,6] and used for monitoring of particle sizes in styrene suspension polymerizations, it seems that the phenomenon may be related to the scattering of NIR radiation caused by large particles in the micrometer domain.

Table 1
Saturation points of monomer-swollen polymer

	MMA (wt%)		BuA (wt%)	
	Polymer	Latex	Polymer	Latex
Visual saturation	20.69	1.84	15.94	1.11
NIRS saturation	27.81	2.45	17.04	1.53

In order to prove that the spectral changes observed were really related to the monomer droplet appearance and not to the increase of monomer concentration, different degrees of agitation were applied to the system, as performed by Santos et al. [5,6]. In our case, after the saturation of the polymer latex with monomer, the latex was submitted to increasing rotation speeds. (Latex saturation was confirmed visually to guarantee that monomer droplets were present in the system.) The same procedure was applied to an unsaturated latex sample. Figs. 1B and C and 2B and C show that the increase of agitation speed caused a significant change of the spectral information of the saturated latex in the region analyzed. On the other hand, the NIR spectra of the unsaturated latex sample did not respond to changes of the agitation speed. This is a strong indication that the peaks observed in the second derivative spectra of the latex samples are responding to changes of the latex morphology and particularly to the monomer droplet generation.

Finally, Figs. 1C and 2C show unequivocally that significant hysteresis can be observed when NIR spectra of saturated latex samples are collected during increasing and decreasing agitation speeds. As explained by Santos et al. [5,6], hysteresis is probably caused by stabilization of smaller particles by emulsifier during the increasing agitation period. Therefore, the average particle sizes are different during the increasing and decreasing agitation speed periods. As NIR spectra respond to the morphological changes of the latex sample, NIR spectra are subject to changes depending on whether the agitation speed is increasing or decreasing.

Based on the previous data, it can be proposed that NIRS be used for in-line monitoring of monomer droplet formation in emulsion polymerization reactions, to improve the robustness and controllability of industrial processes. As the proposed technique does not require any kind of previous calibration (if one is not interested in evaluating the droplet size), it may be easily implemented in-line with the simultaneous measurements of residual monomer concentrations [9–12], without any extra labor or computational efforts. Possible applications, for instance, could include the automatic halting of monomer feed flow rates whenever monomer droplets appear, reducing the risks of temperature runaways and polymer quality drifts. This may be a significant help to the safe operation of emulsion batch and semi-batch reactors, as most of the times monomer droplets cannot be detected directly by plant personnel. Besides, this technique does not depend either on parameter uncertainties or unknown disturbances and can indeed be used to provide rough estimates of partition parameters at lab conditions.

In order to prove the previous remarks and illustrate the use of the proposed technique at actual polymerization conditions, a series of MMA/BuA emulsion polymerization experiments was performed. The detailed description of reaction conditions and experimental set-up is presented in detail elsewhere [12]. For the purposes of this report, it is important to say though that one is interested in producing copolymer material with equimolar MMA/BuA composition and to keep composition constant throughout the batch. Besides, it is also necessary that a specified number average molecular weight be achieved at the end of the batch. In order to attend the required specifications, polymerization is carried out in semi-batch mode with the continuous feeding of a process stream containing pre-emulsified MMA and a chain transfer agent. A very detailed mathematical model is then used to provide the optimum feed policies for the whole run, as described by Sayer et al. [13].

During the actual implementation of optimum feed policies, one of the major process disturbances is the possible existence of unknown amounts of inhibitor in the monomer feeds and in the initial reactor charges. This usually happens because monomer feeds are stabilized in the feedstock through addition of inhibitors, in order to avoid ignition and/or spontaneous polymerization. However, due to practical reasons and to the relatively high costs of monomer purification, monomer feeds are frequently used as received. Therefore, monomer concentrations (reaction rates) must be monitored in situ and in line, while optimum trajectories must be recalculated during the whole batch, in order to guarantee that the desired specifications will be achieved. One of the main process constraints is assuring that monomer droplets will not be generated during the batch, so that monomers will not be partitioned among the monomer/polymer phases and reaction will occur in a single phase. Besides, given the relatively high reaction rates, formation of monomer droplets may significantly increase the risks of thermal runaway and loss of temperature control [13].

Two experiments are presented in Fig. 3. The initial monomer charge contained 100 ppm of hydroquinone, but this piece of information was not taken into consideration for formulation of optimum feed policies. In the first experiment (Fig. 3A, C and E) the information provided by NIRS was not used as feedback, while in the second experiment (Fig. 3B, D and F) the information provided by the spectrophotometer was used as feedback. The arrow shows the moment when the spectrophotometer indicated the appearance of monomer droplets. The addition of 100 ppm of hydroquinone to the initial monomer charge made the residual concentrations of MMA and BuA reach very high values, so that after about 3 sampling intervals the spectrophotometer indicated the formation of monomer droplets. When the controller was turned on, this additional piece of information indicated that something was going very wrong with the batch and that the feed flow rates had to be interrupted (Fig. 3B). When the controller was turned off, no in-line correction was possible (Fig. 3A). In order to guarantee the desired final polymer hold-up without the risk of sharp increase of monomer feed rates, the control algorithm automatically extended the batch time when formation of monomer droplets were detected and feed rates were interrupted. The intention was to avoid reaction runaways and guarantee the product quality, as already discussed.

The simulation of copolymer compositions with NIRS feedback was very bad in the first case (Fig. 3C). This result can be easily explained if one realizes that the appearance of monomer droplets exerts a tremendous effect upon the NIR spectra. This is confirmed independently by the extremely high monomer concentrations obtained with off-line GC analysis, as illustrated in Fig. 4. As the NIR model calibration for residual monomer concentrations was performed under conditions without monomer droplets [11], NIR composition data was not accurate at the reaction condition analyzed. This should not be considered a bad result, as the process is not supposed to operate at such conditions. As Fig. 3C shows, control of polymer composition was not possible without feedback and final composition offset was very high. Comparing Fig. 3C and D, it may be

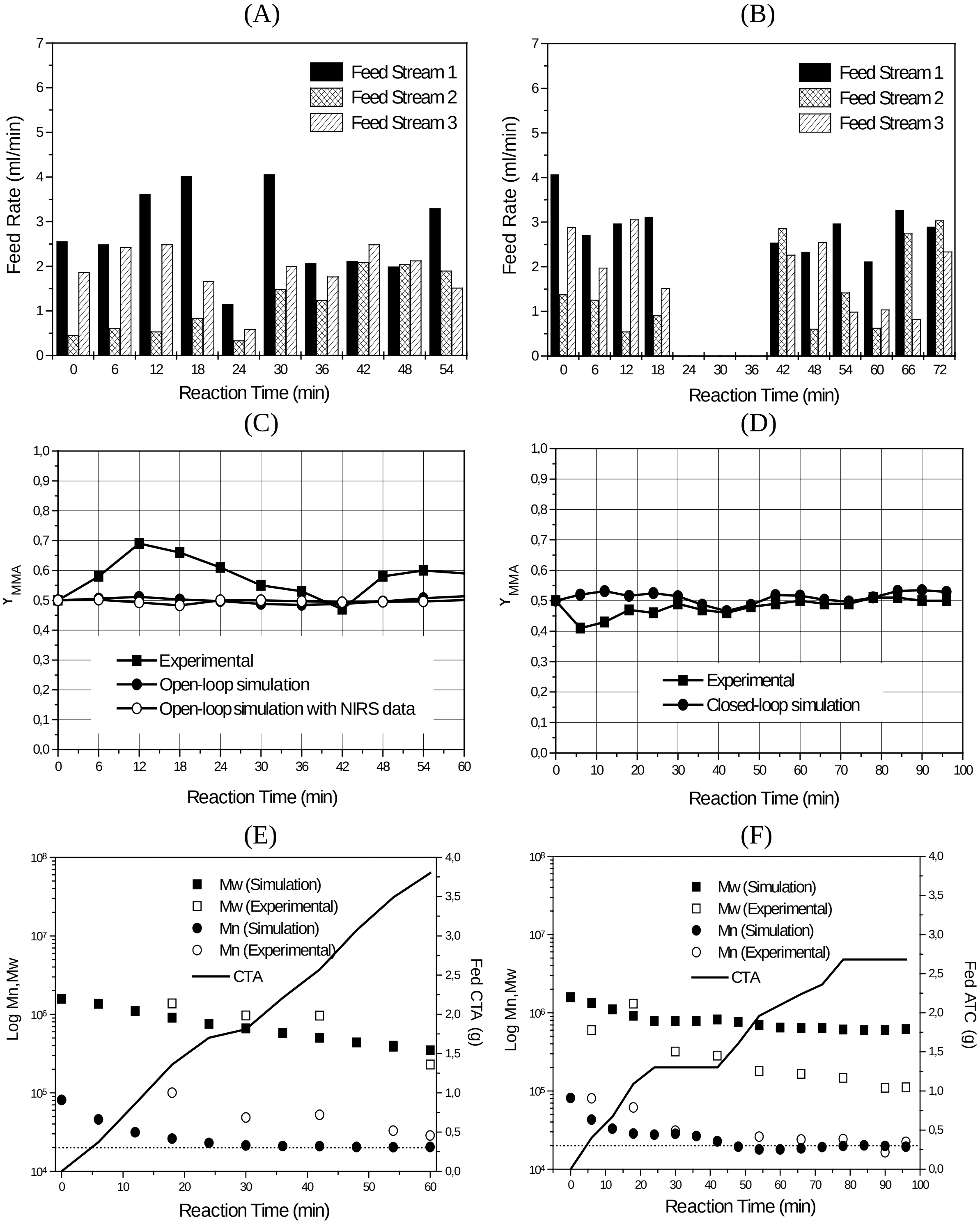

Fig. 3. Feed rates (A, B), cumulative copolymer composition (C, D) and average molecular weights (E, F) of open-loop and closed-loop reactions, respectively.

observed that the difference between process performances obtained with open-loop and closed-loop operation was remarkable. The identification of the appearance of monomer droplets allowed the tight control of the copolymer composition, despite the huge induction time caused by the initial charge of hydroquinone. Particularly, no offset was observed in the final copolymer composition.

Fig. 3E shows that the formation of monomer droplets during the open-loop operation perturbed the average molecular weights considerably, leading to larger number

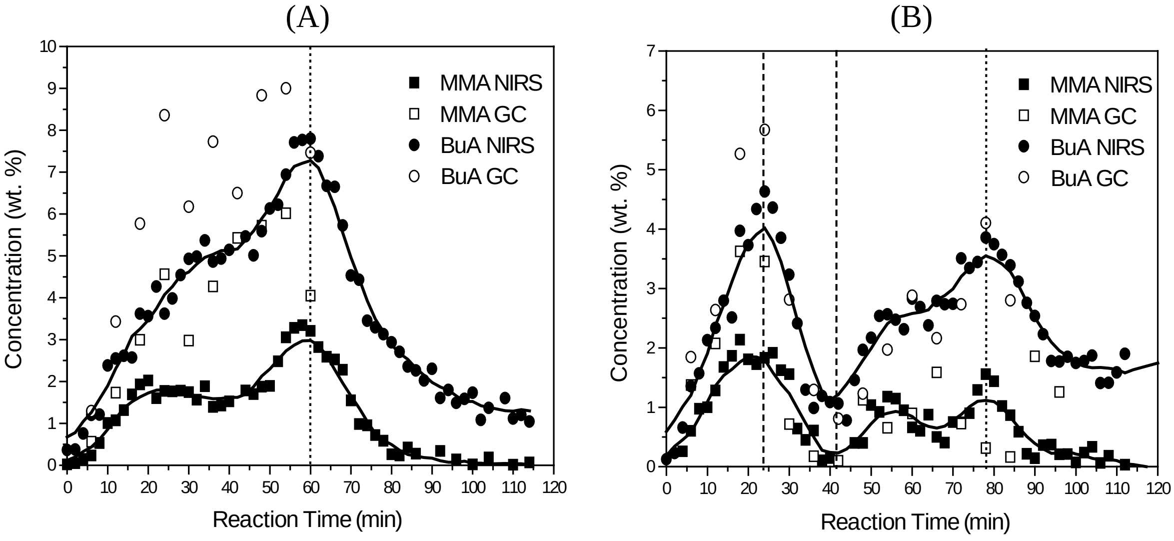

Fig. 4. NIRS and GC monitoring of open-loop (A) and closed-loop (B) controlled reactions. Dashed and dotted lines mark interruption periods of all feedings along the batch. Continuous lines represent a smoothing of NIRS measurements by averaging three adjacent points.

average molecular weights. However, when the controllers was turned on, the flow rates of both monomers and of chain transfer agent were manipulated accordingly to guarantee the proper control of Mn, despite the large changes of the monomer feed flow rates. Once more, the feed policies were corrected in-line without any significant perturbation of the desired value of Mn. While in the open-loop reaction Mn^f presented a deviation of 42% in relation to Mn_d^f, in the closed-loop reaction this deviation was reduced to 12%.

3. Conclusion

It was shown that NIR spectra of polymer latex of MMA/BuA polymerization systems are subject to sharp changes when monomer is continuously added to monomer-free latex samples. It was shown that these sharp changes, which occur in the range of 1620 nm, previously used for monitoring of particle sizes in styrene suspension polymerizations, are due to the saturation of the polymer latex and formation of monomer droplets. Experiments were performed to show that this additional piece of information could greatly improve the capacity to control actual emulsion polymerization reactions. Particularly, when 100 ppm of hydroquinone was added to the additional monomer charge, the spectrophotometer was able to detect the moment when droplets were formed and to inform the controller that monomer feed should be halted. In this case, the desired specifications could be reached, while uncontrolled reaction conditions developed when no feedback from the spectrophotometer was available. Therefore, it is possible to use NIRS for in-line detection of monomer droplet generation during emulsion polymerization reactions and substantially improve the safety and quality of the process operation.

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