

In-Line and *In Situ* Monitoring of Semi-Batch Emulsion Copolymerizations Using Near-Infrared Spectroscopy

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ABSTRACT: This article shows that near-infrared spectroscopy (NIRS) can be used efficiently for the simultaneous in-line and *in situ* monitoring of monomer (methyl methacrylate, MMA, and butyl acrylate, BuA) and polymer concentrations in the reaction medium during seeded semibatch emulsion copolymerizations. A series of actual reaction experiments was planned to allow the proper obtainment and selection of calibrating samples. Partial least squares (PLS) was used to build three independent calibration equations in the range of 1100–1900 nm, which were used to successfully monitor some disturbed reactions in-line. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2670–2682, 2002

Key words: emulsion polymerization; in-line monitoring; monomer and polymer concentrations; near infrared spectroscopy (NIRS); sensors

INTRODUCTION

One of the main barriers to implement closed-loop control schemes in polymerization reactions is the lack of reliable, robust and truly real-time monitoring technologies capable of providing the necessary feedback of the process status. An important cause of this difficulty is the intrinsic complex nature of polymerization processes, a situation that becomes worse for emulsion systems due to their heterogeneous and unstable nature.¹

In-line monitoring techniques presented in the open literature are most often some sort of adaptation of the more traditional off-line approaches. Examples are in-line densimetry,² viscometry,³ and gas chromatography.^{3–5} This practice has the

disadvantage of not eliminating problems already present in their ancestral off-line methods, such as laborious sample preparation, time-consuming analysis, and troublesome maintenance.

Because of their nondestructive and *in situ* monitoring capabilities, some vibrational spectroscopic techniques received much attention of the scientific community in the last two decades. The most prominent are those that explore the mid-infrared (MIR) region, the near-infrared (NIR) region and the Raman effect.

Vibrational spectroscopy involves the absorption of radiation by matter due to matching of energy intensities found in the incident electromagnetic waves and in the electrical field of vibrating molecular bonds. This electrical field appears when covalently bonded atoms of distinct electronegativities naturally oscillate. According to the laws of physics, every charge (dipolar moment) in movement generates an electrical field with a certain amount of associated energy. This

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resonance phenomenon causes the increase of the amplitude of oscillations and, as the magnitude of permanent dipolar moments depends upon the characteristics of the linked atoms, energy up-takes occur at specific wavelengths.⁶

Changes of vibrational levels generated by MIR absorption are called fundamental transitions. These transitions take place where the vibrational quantum number changes by unity and where covalent bonds behave like harmonic oscillators. Sharp bands are found and the assignment of peaks to specific bond vibrations is a common practice.^{6,7}

Raman spectroscopy is based on the so called Raman effect or Raman shift, described as the increase of wavelength (inelastic scattering) suffered by a monochromatic incident beam due to the absorption of energy by matter. The usual procedure is to illuminate the sample with a monochromatic radiation and analyze the scattered spectra generated by the Raman effect, after proper filtering of the reflected light. Several different Raman shifted signals may often be observed, each being associated with distinct vibrational or rotational motions of the molecules in the sample. The particular molecule and its environment determine the Raman signals that may be observed. This effect is very weak. Approximately one photon out of a million (0.0001%) will scatter from the sample at a wavelength slightly shifted from the original wavelengths. The incident light is generally in the near-infrared region to avoid fluorescence phenomena, which degrade the detection of the weak Raman signals.⁸

MIR and Raman spectroscopies, although possessing more distinguishable bands, more easily related to specific vibrating bonds, have some inconveniences for in-line process monitoring applications. MIR radiation, for example, is not transmitted by the most common communication-grade fiber optics. In addition, the strong water absorption in this region makes the use of narrow optical pathlengths imperious for measurements on an aqueous medium, like the one encountered in conventional emulsion polymerizations. Together, these two characteristics make the implementation of MIR spectroscopic remote-monitoring techniques prohibitive for real polymerization processes, even nowadays. Raman vibrational spectroscopy signal-to-noise ratios are usually low, diminishing its sensitivity. In spite of this, encouraging results are described in the literature regarding the use of both MIR and Raman spectroscopy for real-time monitoring of emulsion

polymerizations.⁸⁻¹⁴ The development of the underlying hardware will probably encourage the use of technologies based on MIR and Raman spectroscopies in the near future.

Near-infrared spectroscopy (NIRS) is based on the inharmonic behavior of molecular vibrations, leading to transitions that contain multiples of the energy of a single vibration quantum number. Such transitions are called overtones and appear at frequencies approximately two or three times higher than that of the fundamental absorptions. In spite of being more energetic, the probability of occurrence of such transitions is lower than that of fundamental ones. The net result is that NIRS bands have lower intensity, allowing thicker pathlengths to be used in real process environments without degrading signal-to-noise ratios. Another important characteristic is that peaks are broad and overlapped, as vibrations in the NIR region are assigned to bonds found in almost all chemical compounds (in practice, C, N, O, S covalently linked to hydrogen). The consequence is the indispensable aid of empirical multivariate modeling methods, like principal components analysis (PCA) and partial least squares (PLS), to reduce the dimensionality of multivariate data. These methods use information of the full spectrum, thus eliminating undesirable correlation of data obtained at distinct wavelengths and minimizing matrix effects in complex samples.¹⁵ Furthermore, differently from what was previously exposed for MIR, NIR radiation may be transmitted by common fiber optics, which guarantees its use in remote monitoring. The most delicate parts of the spectrometer may be positioned far away from the harsh process environment, while special probes perform *in situ* measurements.

Another important characteristic that should be emphasized is that NIRS may be used as a multipurpose monitoring tool in polymerization reactions, providing different and simultaneous information. Santos et al.^{16,17} used NIRS to monitor and control the average particle size in styrene suspension polymerizations. In this case, Santos et al. were unable to monitor monomer conversion during the polymerization, probably due to the more important scattering and surface effects observed in oil-in-water suspensions. Wu et al.^{18,19} monitored semibatch emulsion styrene homopolymerizations with short-wavelength near-infrared spectroscopy (SW-NIRS) during normal runs and process upsets. In this case, a single measurement (polymer content) could provide information about the remaining state vari-

ables, due to the mass balance constraints. Gosse et al.²⁰ developed calibration models for residual monomers, polymer holdup and mean particle size in order to monitor the emulsion copolymerization of methyl methacrylate and styrene using NIRS. However, models were built after preparation of synthetic samples and results for *in situ* and in-line monitoring of actual reactions were not presented. The authors acknowledge that some of the models were unable to predict the properties of extra samples, not used for model calibration. Therefore, the viability to use NIRS for *in situ* and in-line monitoring of actual emulsion copolymerizations has yet to be shown. It is also interesting to observe that styrene was one of the monomers used in almost all of the previous studies.^{8,10–20} The only exception is the study of Özpozan et al.,⁹ which analyzed vinyl acetate homopolymerizations. When styrene is used as a monomer, monitoring of monomer compositions becomes much easier, because the aromatic ring leads to the development of very characteristic spectral responses.

The main objective of this article is to show that NIRS can be used very successfully for the in-line and *in situ* monitoring of actual semibatch emulsion copolymerizations. MMA and BuA are used as comonomers, as this copolymer system finds many applications in the industry of paints and adhesives. It is shown here that the residual concentration of these two chemically similar monomers and the polymer holdup can be independently tracked by NIR spectroscopy combined with a multivariate calibration technique (PLS), providing important information for both kinetic studies or process control decision-taking. Calibration models are built first, based on reaction samples collected during actual reaction runs, so that preparation of synthetic samples is avoided and a more representative picture of the reaction process can be captured. Afterwards, calibration models are used to monitor disturbed reactions, not used for calibration, allowing very good description of the dynamic trajectories of monomer concentrations and polymer holdup.

EXPERIMENTAL

Reaction and Analytic Apparatuses

An automatic reaction unit, schematically shown in Figure 1, was mounted to perform the semibatch emulsion polymerizations. It consisted of a

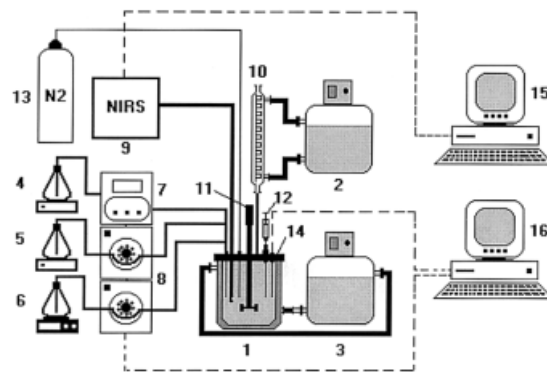


Figure 1 Schematic drawing of the semibatch polymerization unit. (1) Reactor, (2) cold bath; (3) hot bath, (4,5) preemulsified feed streams, (6) net monomer feed stream, (7,8) precision dosing pumps, (9) NIRS and probe, (10) condenser, (11) agitator/turbine, (12) syringe for sample withdrawal, (13) N₂ purge, (14) thermocouple, (15) NIRS computer, (16) data acquisition and logging computer.

1 L jacketed glass tank reactor (FGG Equipamentos Científicos); a hot thermostatic bath (Haake DC-3), to provide hot water to the reactor jacket; a cold thermostatic bath (Polyscience KR-30A), to provide cold fluid (water/glycol ethylene, 50 wt %) to the condenser; a thermocouple type J/Iron Constantan (Ecil); a mechanical agitator (Fisaton 713-T), equipped with a six-blade turbine; a tachometer (Takotron TD2004-C), to monitor the agitation speed; two mixing plates, to homogenize the preemulsified feed streams (Corning PC-420); one digital balance (Helmec HM 1000), to register the amounts fed by each stream along the batch; three computer-controlled precision dosing pumps (Masterflex 7550-60 / 7550-90; Prominent Gamma Gala 1000 SST); and two computers, one dedicated to acquire and treat NIR spectra and another one to monitor the reaction and control the pumps. This second computer was equipped with a plug-in data acquisition board (National Instruments Lab PC +), which contained the A/D and D/A converters. Before reaching the board, the thermocouple analog signal was filtered, amplified and cold-junction compensated by a previous conditioning module (National Instruments SCXI 1100). LabVIEW/NIDAQ (National Instruments) were used as application software and drivers to develop data acquisition and logging interfaces respectively. The spectrometer used in the experiments was a NIRSystems 6500 on-line (NIRSystems), equipped with two concentric fiber optic bundles to illuminate and collect NIR radi-

Table I Formulation of Reaction Runs in Group I (R1–R3)^a

Reagent	Initial Charge (g)	Feed Stream 1 (g)	Feed Stream 2 (g)
MMA	—	123.66	—
BuA	—	147.56	—
H ₂ O	255.60	—	340.78
SLS	1.1306	—	6.4914
K ₂ S ₂ O ₈	0.0597	—	0.4758
NaHCO ₃	0.0534	—	0.4856

^a Feed streams 1 (0.82 mL/min) and 2 (0.96 mL/min) were added simultaneously for 6 h.

ation. An interactance immersion probe was connected to the end of the fiber bundles and its tip was properly positioned to provide a total path-length 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 and data acquisition. Mathematical pretreatment and calibration procedures were performed with the help of proprietary software named NSAS (Near-Infrared Spectral Analysis Software).⁷

Gas chromatography (GC) was chosen as the reference method to calibrate the spectrometer. The chromatographer was equipped with a GS-Q PLOT column (J & W Scientific) and with a small glass liner, which was filled with silanized glass wool and positioned at the injection port to avoid clogging of the stationary phase with polymer. The temperature of the injector (180°C) was carefully chosen to allow fast vaporization of residual monomers and circumvent eventual (de)polymer-

ization problems. Other important analysis parameters are the column temperature (200°C), the detector temperature (230°C) and the carrier gas employed (N₂). No sample split was used in order to minimize experimental errors. Internal standardization with 2-butanone was used to develop calibration curves and sample analysis. Chromatographic calibration samples were synthesized to mimic real samples. For this reason, polymer latex, free of residual monomers and containing 100 ppm of hydroquinone, was added to calibration samples in order to homogenize samples (avoid the generation of monomer droplets) and to prevent polymerization at the injector port.

All reagents were used as received. Methyl methacrylate (Metacril) and butyl acrylate (Rhodia do Brasil) were the monomers; sodium lauryl sulphate-SLS (Rhodia do Brasil), the anionic emulsifier; potassium persulfate (Merck), the initiator; sodium bicarbonate (Isofar), the buffer; distilled water, the continuous medium; *t*-dodecyl mercaptan (Rhodia do Brasil), the chain transfer agent (CTA); and hydroquinone (Vetec), the polymerization short-stopper.

Reaction Planning and Procedures

In order to calibrate the spectrometer and build independent calibration models for the residual monomer concentrations and polymer holdup, nine reaction runs were performed, divided into three groups. The dry polymer content was limited to 30 wt % to avoid polymer sticking to the probe window. Formulations used for reaction runs are shown in Tables I, II, and III. Experimental design follows heuristic procedures described in the open literature.^{7,15,21} The first heuristic procedure states that NIRS calibration sam-

Table II A Formulation of Reaction Runs in Group II (R4–R7)^a

Reagent	Initial Charge (g)	Feed Stream 1 (g)	Feed Stream 2 (g)	Feed Stream 3 (g)
MMA	—	—	59.23	86.13
BuA	—	186.00	—	—
H ₂ O	391.10	—	43.35	64.27
SLS	0.2509	—	0.4879	0.8576
K ₂ S ₂ O ₈	0.9271	—	—	—
NaHCO ₃	0.9088	—	—	—
CTA	—	—	—	3.8100
Seed latex ^b	94.4200	—	—	—

^a Feed streams 1, 2, and 3 were added simultaneously and were designed to keep copolymer composition constant and equal to 50 mol % (Sayer et al.)²²

^b $N_{\text{pseed}} = 5.0 \cdot 10^{15}$ particles/g seed latex.

Table IIB Optimum Feed Flow Rates for Reaction Runs in Group II

Time (min)	Flow Rate 1 (mL/min)	Flow Rate 2 (mL/min)	Flow Rate 3 (mL/min)
0	2.87	2.19	0.98
6	0.87	2.09	0.36
12	3.59	0.97	0.83
18	5.99	1.10	1.04
24	3.08	1.54	1.93
30	4.18	0.77	1.44
36	2.08	0.07	3.46
42	2.17	0.36	2.50
48	2.42	0.26	2.57
54	0.40	1.89	3.18
60	0.00	0.00	0.00

ples should be obtained from the real process, as it is impossible to reproduce generally complex matrix effects with synthetic samples. The second heuristic procedure says that the entire range of operation conditions expected in the real process should be covered by the calibration samples. The third heuristic procedure recommends that a large number of samples (20–30) should be included in the calibration set per modeled property in order to improve the robustness of the models obtained and allow proper filtering of unexpected process variances. Based on the heuristic procedures just presented, reaction runs in Group I (R1–R3) were designed to generate samples with low residual monomers concentrations. Reaction runs were carried out under starved conditions, with feeding periods of about 6 h. The final latex of R3 was used in the following runs (R4–R12) as polymer seeds. Reaction runs in Group II (R4–R7) were performed under monomer-flooded conditions, with feeding periods of about 1 h, and were designed to generate samples with high residual monomer concentrations. MMA and BuA concentrations in this case were 3 to 4 times larger than those observed in Group I. Feed flow rates were designed to keep the copolymer composition constant, as described by Sayer et al.,²² and are also shown in Table II. Reaction runs in Group III (R8 and R9) were designed to allow the independent identification of MMA and BuA residual concentrations through the introduction of homopolymerization periods during monomer feed. In reaction R8, a stream of pure MMA was initially fed to the reactor, followed by feeding of an equimolar mixture of MMA and BuA and finally by feeding of pure BuA. This order was inverted in reaction R9.

In order to carry out reaction runs, the initial charge and feed stocks were purged with 99 % pure nitrogen (AGA) for 30 min to avoid polymerization inhibition by dissolved oxygen. The nitrogen flux was maintained during the whole batch. When the temperature inside the reactor reached 80°C, monomer feeding was started in accordance with the specified feed profiles. Feed profiles were stored in the data acquisition system in order to monitor the reaction course and control the automatic pumps. The speed of the agitator was kept at 200 rpm. For runs in Group I, samples were withdrawn at intervals of 20 min and put into flasks containing aqueous hydroquinone solutions, so that the final hydroquinone latex concentration would be equal to 100 ppm. For runs in Group II and III, the sampling interval was shorter (6 min), as the monomer feed period was also much shorter (1 h). All samples were analyzed chromatographically to determine the residual MMA and BuA concentrations. Polymer holdup was measured gravimetrically by drying at 45°C in a vacuum oven and weighing to constant weight. Polymer holdup was also inferred through the overall reactor material balance, using residual monomer concentrations as inputs, to check for consistency. In all cases, results obtained were very similar.

In order to unequivocally show that NIRS can be used to monitor emulsion copolymerization reactions in-line and *in situ*, three additional exper-

Table III Formulation of Reaction Runs in Group III (R8–R9)^a

Reagent	Initial Charge (g)	Feed Stream 1 (g)	Feed Stream 2 (g)
MMA	—	^c	—
BuA	—	^d	—
H ₂ O	390.99	—	121.19
SLS	0.2698	—	1.4003
K ₂ S ₂ O ₈	0.9020	—	—
NaHCO ₃	0.9355	—	—
CTA	—	—	3.6700
Seed latex ^b	89.0100	—	—

^a Feed streams 1 (3.15 mL/min) and 2 (1.05 mL/min) were added simultaneously for 1 h.

^b $N_{\text{pseed}} = 5.0 \cdot 10^{15}$ particles/g seed latex.

^c Feed stream 1 for reaction R8: pure MMA up to 20 min; MMA/BuA equimolar mixture up to 40 min; pure BuA up to reaction end.

^d Feed stream 1 for reaction R9: pure BuA up to 20 min; MMA/BuA equimolar mixture up to 40 min; pure MMA up to reaction end.

Table IVA Formulation of Reaction Runs Used for Model Validation (R10–R12)^a

Reagent	Initial Charge (g)	Feed Stream 1 (g)	Feed Stream 2 (g)	Feed Stream 3 (g)
MMA	—	—	90.48	127.26
BuA	—	278.00	—	—
H ₂ O	389.65	—	68.74	98.05
SLS	0.2554	—	0.6741	1.2897
K ₂ S ₂ O ₈	0.9280	—	—	—
NaHCO ₃	0.9403	—	—	—
CTA	—	—	—	5.7000
Seed latex ^b	80.7400	—	—	—

^a Feed streams 1, 2, and 3 were added simultaneously and were designed to keep copolymer composition constant and equal to 50 mol % (Sayer et al.)²²

^b $N_{\text{pseed}} = 5.0 \cdot 10^{15}$ particles/g seed latex.

iments were performed to validate the calibration models. Process disturbances were deliberately applied to show that calibration models were able to detect process upsets by independently measuring MMA, BuA, and polymer concentrations in the reaction medium. Process disturbances used for model validation were the momentary interruption of the BuA feed flow rate (R10) and the addition of high (R11) and low (R12) amounts of inhibitor (hydroquinone) to the initial charge of the reactor. In reaction R10 the main objective was to observe whether calibration models would detect the composition drift during the batch. In reaction R12, the main objective was to observe whether calibration models would detect the initial induction period and monomer buildup before polymerization takes place. In reaction R11 the main objective was to observe the performance of calibration models when monomer droplets are formed. Reaction recipes are shown in Table IV. Feed flow rates were designed to keep the copolymer composition constant, as described by Sayer et al.,²² and are also shown in Table IV.

RESULTS AND DISCUSSION

NIRS Calibration and Model Validation

The first step to develop good calibration equations is the selection of representative samples. Samples were selected in order to cover the entire range of interest of operation conditions. To account for unknown process variations not explicitly described by the reference calibration method, such as temperature oscillations and fluctuations of the concentrations of additional

reaction additives, calibration samples were taken from all nine reaction runs in Groups I, II, and III for different batch times.

An important point regards the influence of polymer holdup upon the evaluation of monomer compositions. Significant polymer interference upon detection of residual monomers can be expected because of the turbidity imposed by the polymer latex particles, because of the large concentration of polymer particles in the reaction medium, and because of the variation of the polymer content along the reaction batch. For this reason, calibration procedures had to take polymer concentration into account. In order to minimize polymer interference upon the evaluation of monomer concentrations, three calibration procedures were implemented. First, model calibra-

Table IVB Optimum Feed Flow Rates for Reaction Runs Used for Model Validation

Time (min)	Flow Rate 1 (mL/min)	Flow Rate 2 (mL/min)	Flow Rate 3 (mL/min)
0	3.32	1.32	2.95
6	2.38	1.10	1.29
12	2.31 ^a	0.43	1.54
18	4.06 ^a	1.69	2.25
24	3.68	1.58	2.16
30	2.68	1.53	1.37
36	2.09	0.55	2.32
42	2.22	0.97	2.50
48	2.01	2.53	1.89
54	2.10	1.63	2.45
60	0.00	0.00	0.00

^a Feed flow rate was set to 0.00 in experiment R10.

tions were performed simultaneously for polymer content and residual monomer concentrations. This is required if one implicitly assumes that the NIR spectra are sensitive to variations of the polymer content and intends to take this influence into consideration during computation of monomer compositions. Second, calibration samples with similar amounts of MMA and/or BuA, but with very distinct polymer holdups, were included in the calibration set in order to allow the proper filtering of polymer interference during calibration model development. Third, samples were always collected in pairs to allow the detection of possible outliers and gross analytical errors. Besides, composition data were required to satisfy the global mass balances of the system within $\pm 2\%$, which is believed to be the maximum absolute error of the gravimetric method used to evaluate the polymer content. Composition data that did not satisfy the global mass balance within the experimental precision were discarded.

Two additional points regarding model calibration must be noticed. First, it is important to emphasize that reactions R4–R12 were seeded with the polymer latex prepared in reaction R3. As the polymer seed composition was equal to 50 mol% and feed profiles were designed to keep the copolymer composition close to 50% along the batches, polymer seed was regarded as regular polymer during model calibrations. Thus, efforts were not made to explicitly include seed data in the calibration model. Second, independent experimental studies carried out by Vieira²³ indicate that NIR spectra are not sensitive to changes of the particle size diameter in the system analyzed. Vieira²³ observed that the models developed previously for particle sizes in batch emulsion polymerizations^{18–20} are probably inferences based on the evolution of polymer and monomer compositions, as it is well known that reaction rates and particle sizes are very correlated in these systems. Therefore, particle size distributions were completely neglected during model calibration.

Selected samples are shown in Figure 2 and can be visualized graphically. In order to allow better visualization of the calibration data sets, experimental data were organized in order of increasing concentrations in all cases. Figure 2 shows that 64 samples were used for model calibration and that the experimental composition ranges analyzed were equal to [0,2] wt % for MMA, [0,2] wt % for BuA and [0,30] wt % for

polymer. Figure 2 shows that the experimental regions were covered uniformly in all cases. Figures 2(a), 2(c), and 2(e) also indicate the experimental ranges covered by each reaction run. For instance, if the residual MMA concentration is analyzed [Fig. 2(a)], it may be seen that reaction R1 covered the range [0,0.25] wt %, while reaction R9 covered the range [0,2] wt %. If the residual BuA concentration is analyzed [Fig. 2(c)], it may be seen that reaction R1 covered the range [0,0.50] wt %, while reaction R4 covered the range [1.5,2.5] wt %. If the polymer content is analyzed [Fig. 2(e)], it may be seen that all reaction runs covered uniformly the range [0,30] wt %, as reactions were performed in semibatch mode. Figures 2(b) and 2(d) indicate the experimental ranges covered by each reaction run in terms of polymer composition. In both cases the experimental ranges are covered very uniformly. Figure 2(b) indicates that samples that contain low amounts of polymer may contain either low or high residual MMA compositions. This is also true for intermediate and high polymer concentrations. A similar behavior is shown in Figure 2(d) for the residual BuA concentrations.

NIR spectra were collected in transmittance mode and represented as the fraction of the input energy returned to the light detector. Besides, sample spectra were pretreated to eliminate baseline drifts through computation of second derivatives. Standard multiple linear regression^{7,15} failed to generate good calibration models. As the number of wavelengths used for model building increased, the squared error of prediction decreased slowly, indicating that a full spectrum method was necessary. Then, partial least squares^{7,15} (PLS) was chosen for model calibration and cross validation was employed to evaluate the proper number of factors. The cross validation set was formed by 16 samples selected at random among the samples in the calibration set. In all cases the first three factors were responsible for most of the spectral variability and that the mean square error of the cross validation procedure increased when the number of factors was larger than seven (Fig. 3). Based also on the performance of the rival calibration models (using 3 to 7 factors) during reactions R10 to R12, not used for model building, the number of factors were set to 7 for MMA, 6 for BuA, and 7 for polymer.

Model performance can be evaluated in Figure 4, where only samples not included in the calibration set are used for additional model validation, including data collected in runs R10 to R12. The

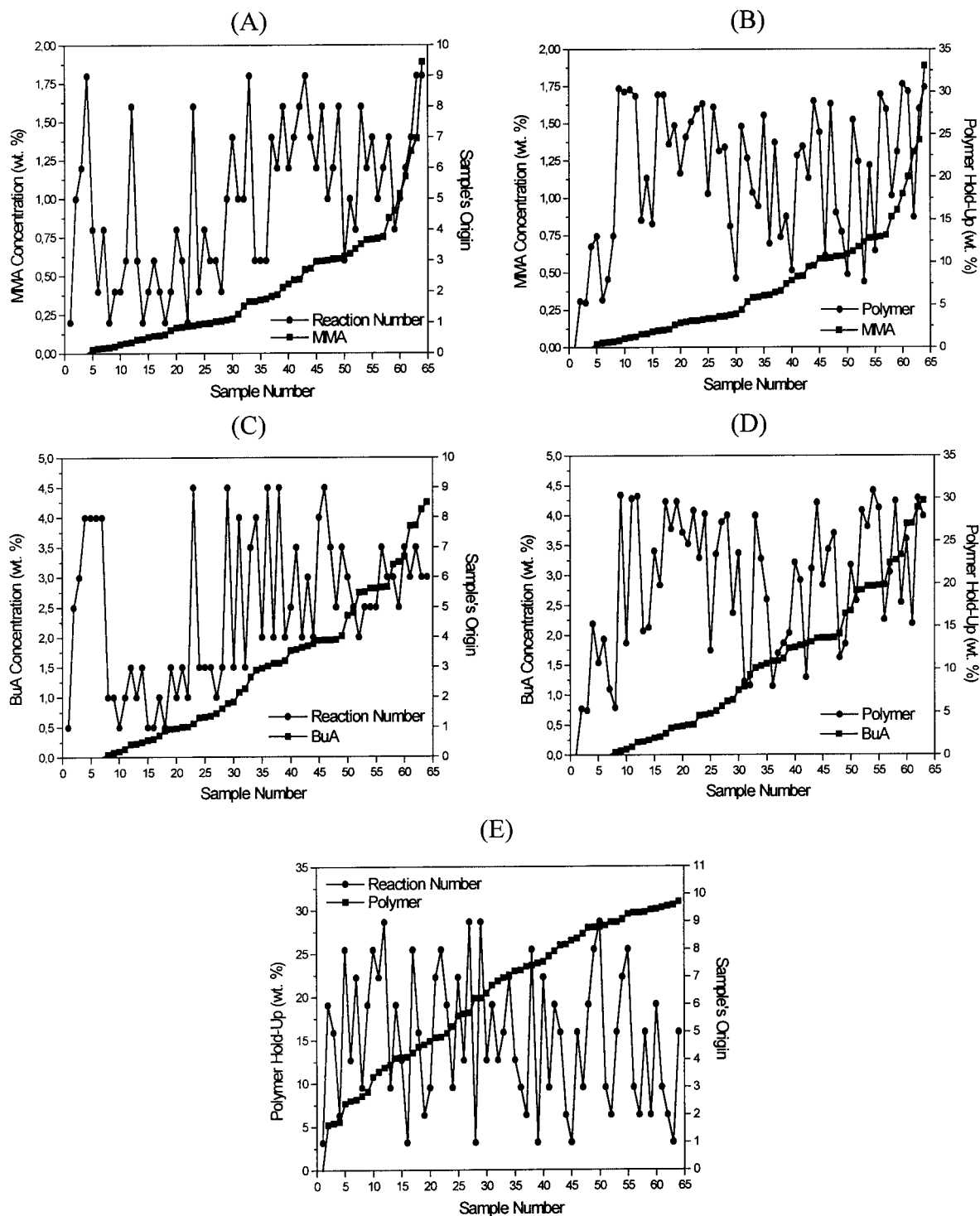


Figure 2 Samples selected for model building. (a,b) MMA, (c,d) BuA, and (e) polymer.

mean absolute errors observed were equal to 0.2 wt % for MMA, 0.4 wt % for BuA, and 1.0 % for polymer holdup and are comparable to the experimental errors of the chromatographic and gravi-

metric analysis. This result is consistent with previous works of Wu et al.^{18,19} and Riley and Crider,²⁴ where the observed relative errors increased as the component concentration dimin-

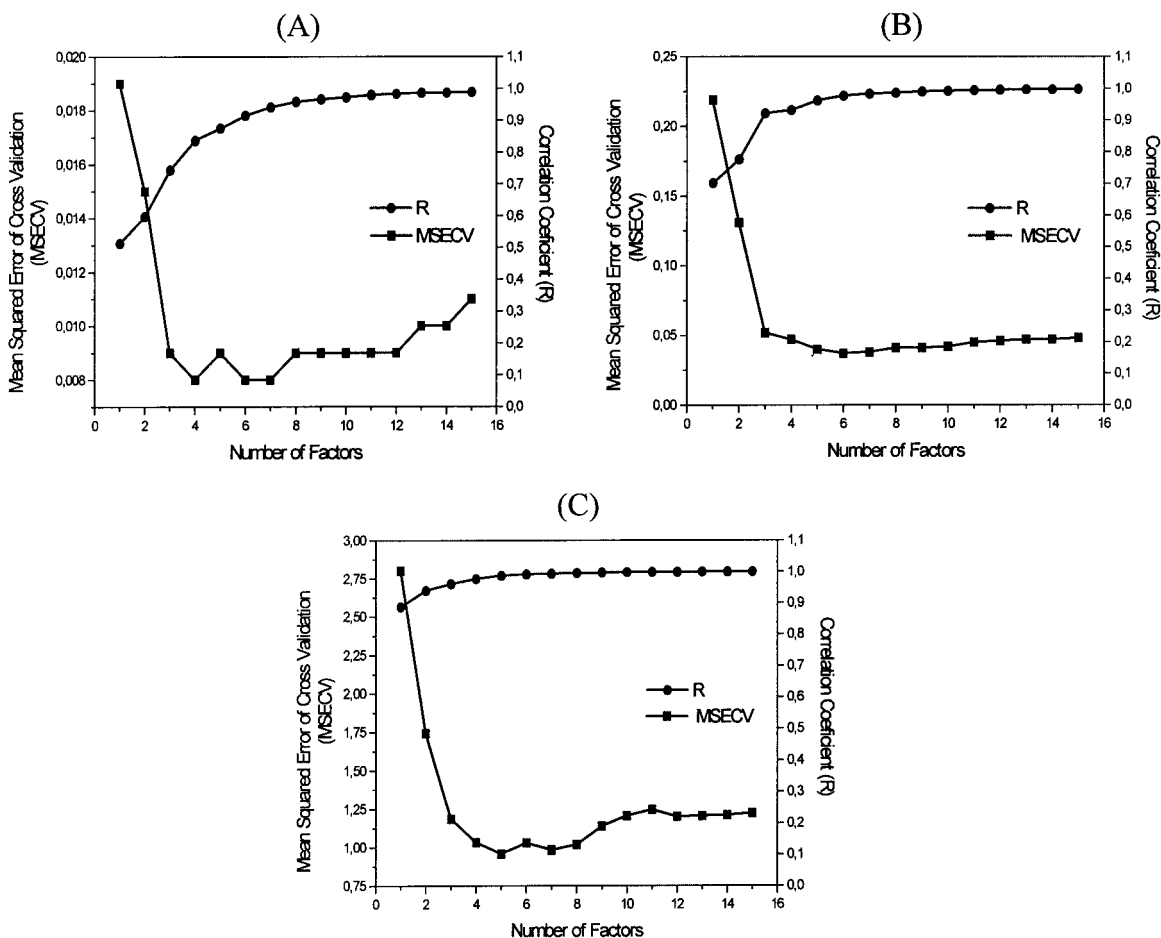


Figure 3 Selection of the number of factors for PLS through cross validation. (a) MMA, (b) BuA, (c) polymer.

ished in the reaction medium. These deviations are very similar to the ones obtained by Gossen et al.²⁰ for styrene and MMA, where polymer holdup was kept constant. Correlation coefficients between GC-measured and NIRS-predicted concentrations were high and statistically significant (0.940 for MMA, 0.977 for BuA, and 0.994 for polymer holdup). This indicates that the equipment is able to detect changes of both monomer concentrations and of polymer holdup simultaneously, thus presenting a great potential to perform in-line monitoring of polymerization reactions. The apparent spread of data in Figures 4(a) and 4(b) are due to the narrow ranges of compositions observed, which is consistent with the semibatch experiments performed. The prediction of negative compositions in Figure 4 should not be overemphasized, as this actually indicates that the concentration is very low and within the experimental detection limit. In practice, negative

values should be truncated to zero during actual applications. Therefore, it may be said that the detection limits for MMA, BuA, and polymer concentrations are equal to 0.2, 0.4, and 1 wt %, respectively, when the NIRS calibration models are used.

Figure 5 presents the performance of the calibration model during the in-line and *in situ* monitoring of reaction run R10, when the BuA feed flow rate was interrupted for 12 min, between 12 and 24 min from startup. GC and NIRS data agree very well, except for some discrepancies observed in the very beginning of the reaction. It is noteworthy that NIRS was able to independently detect the concentration drifts of both comonomers. As shown in Figure 5(b), BuA concentration decreases after feed interruption and increases again immediately after this period, while MMA concentration follows its normal increasing trajectory. The dotted lines mark the end

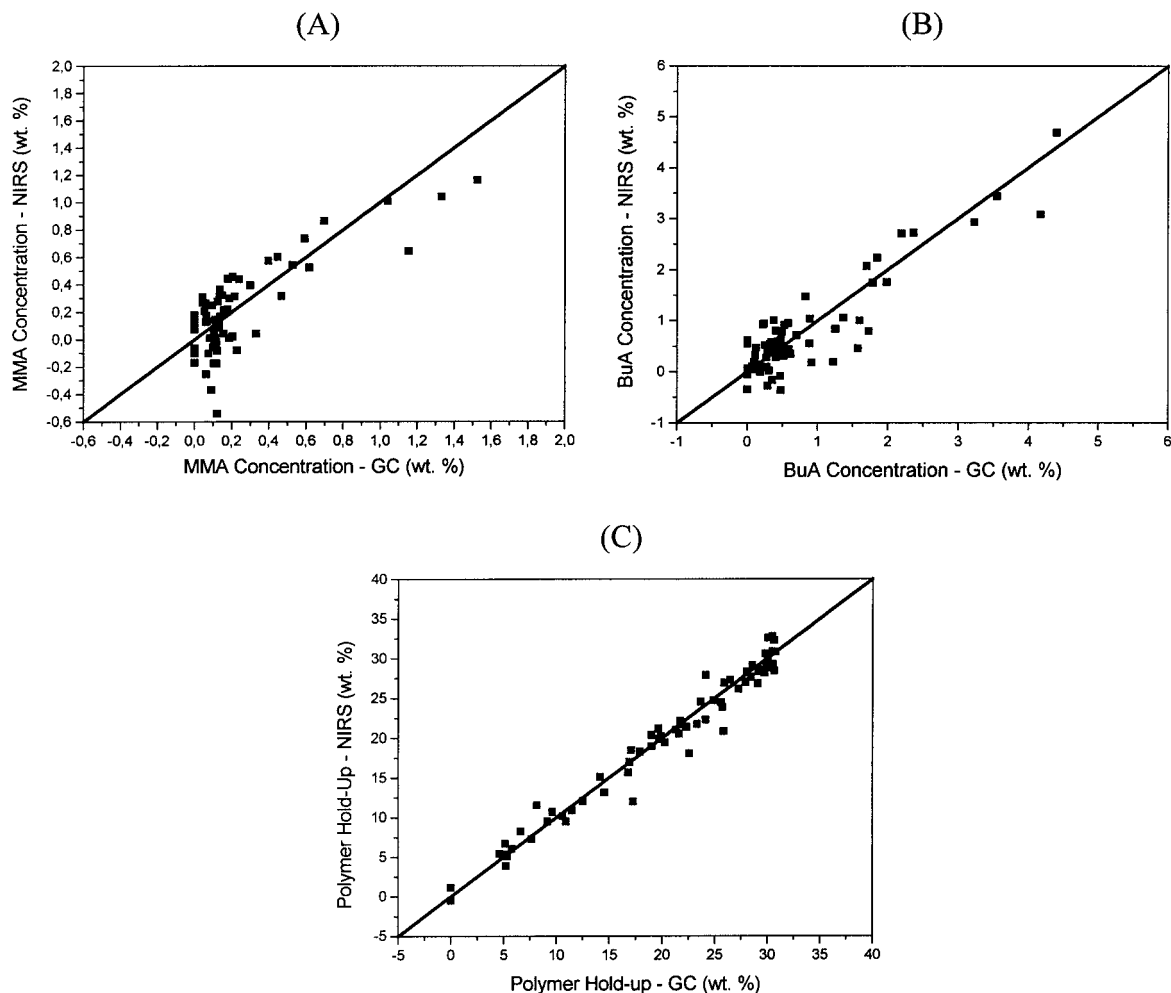


Figure 4 Model performance for samples not used for calibration. (a) MMA, (b) BuA, (c) polymer.

of monomer addition. Monomer concentrations start to decrease almost instantaneously, while polymer holdup still increases for additional 10 min, before reaching a maximum and constant value that indicates reaction halting.

Another disturbance applied to the emulsion copolymerization of MMA and BuA was the addition of hydroquinone to the initial charge of the reactor (R11 and R12). When 100 ppm of hydroquinone was added to the initial monomer charge (R11), the spectrometer detected strong accumulation of monomers in the medium (Fig. 6). However, differences observed between NIRS and GC data during the first moments of reaction were much bigger than observed in the previous experiments. These differences might be attributed to two facts: first, to the existence of much higher residual monomer concentrations, which extrap-

olated the region for which the spectrometer was trained; and second, to the formation of monomer droplets and appearance of additional scattering phenomena,^{16,17} as polymer latex was not formed. In spite of that, NIRS unequivocally indicated abnormal increase of monomer concentration. After halting all feed flow rates for 18 min (the time period marked by the first two dashed lines of Fig. 6), NIRS indicated that both MMA and BuA concentrations started to decrease and returned back to the region included in the calibration set. Then, as it might be expected, NIRS and GC data become similar again. Figure 6(a) also shows that reaction rates increase after interruption of feed flow rates, probably due to consumption of the initial charge of hydroquinone and to the composition drifts in the reaction medium, as MMA and BuA reactivities are quite different. Figure 7

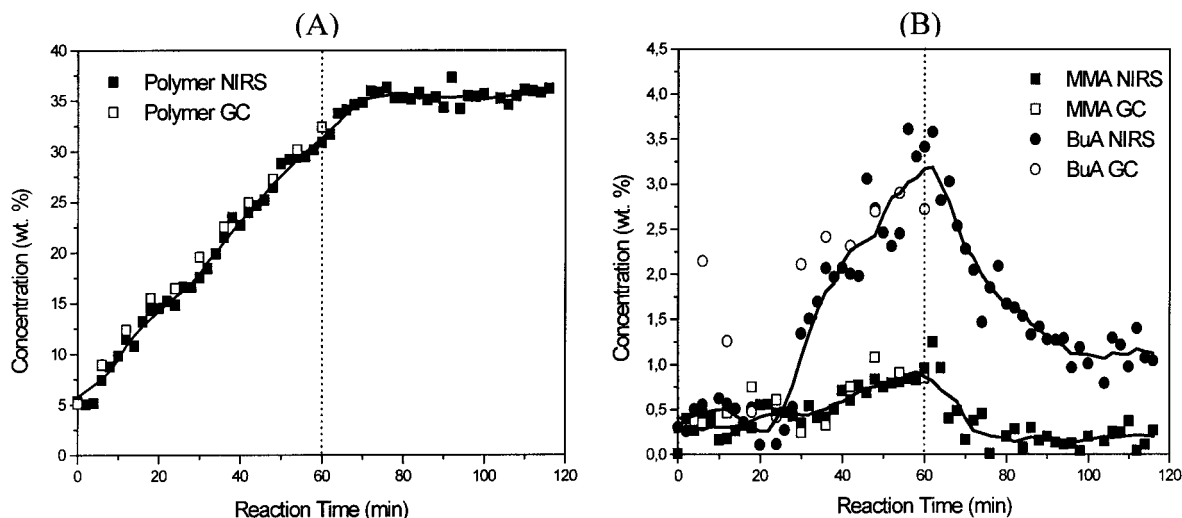


Figure 5 Monitoring of (a) polymer holdup, and (b) residual monomers in reaction run R10. Continuous lines are moving averages of three adjacent points.

shows results obtained for a replicate of reaction run R11, without interruption of the feed flow rates. Monomer concentrations increased very significantly and that disagreement between NIRS and GC data became more pronounced. This seems to reinforce the analysis already presented.

In reaction run R11 the amount of hydroquinone used was about 5 times greater than usually encountered in industrial feedstocks to avoid pre-polymerization of monomers. In order to verify whether the spectrometer would be able to detect the slighter effects of inhibition agents on the

reaction rate, just 20 ppm of hydroquinone were added to the reactor initial charge (R12). The initial accumulation of MMA and BuA was captured by NIRS again, (Fig. 8) although the accumulation peaks observed were less pronounced than in the previous case. Monomer accumulation can be verified by comparing concentration profiles in Figures 5 and 8. It is interesting to observe once more that the reaction rates decreased with the increase of the BuA concentration, given the very different reactivities of the monomer species analyzed.

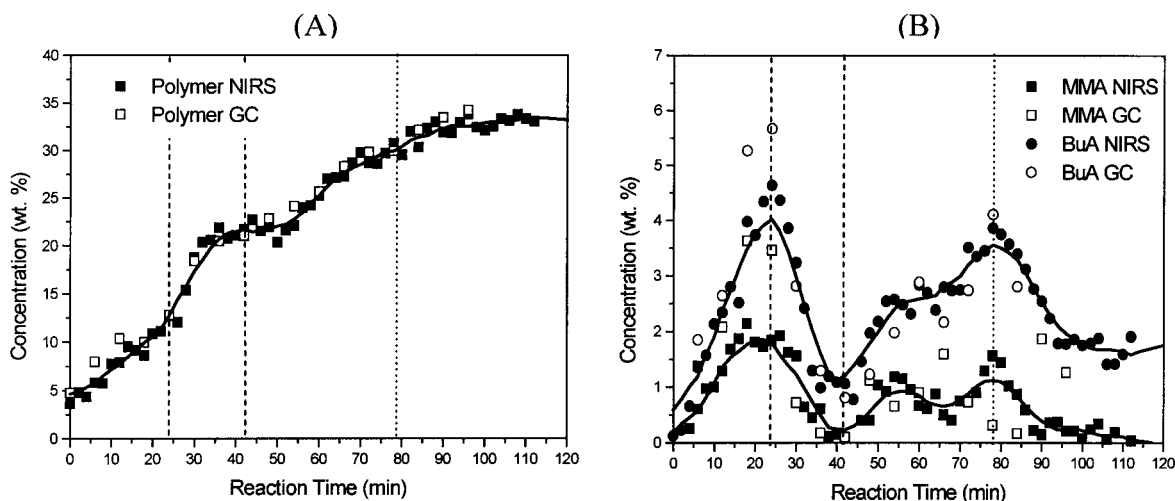


Figure 6 Monitoring of (a) polymer holdup, and (b) residual monomers in reaction run R11 with feed interruption. Continuous lines are moving averages of three adjacent points.

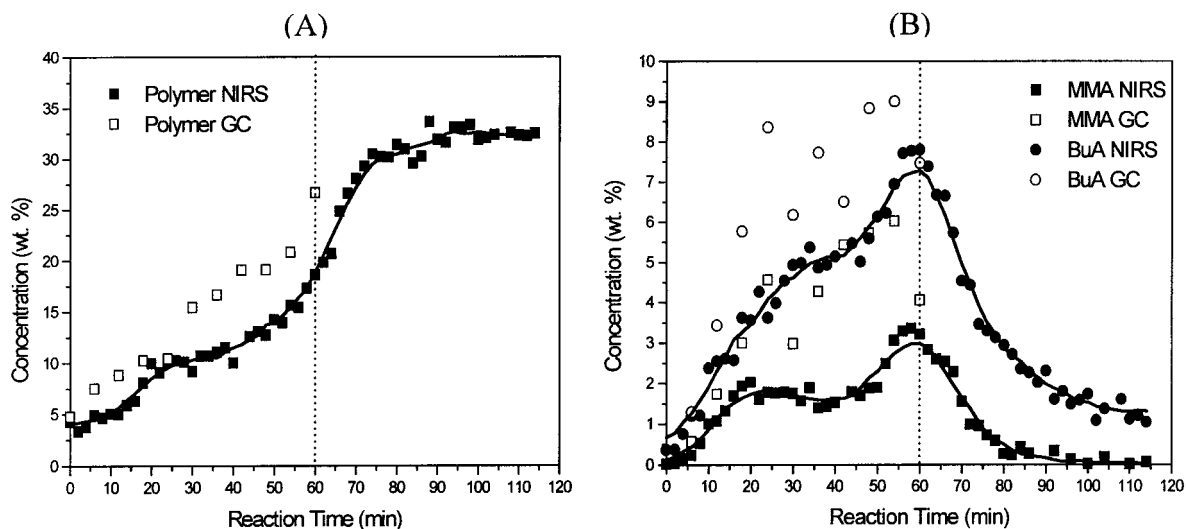


Figure 7 Monitoring of (a) polymer holdup, and (b) residual monomers in reaction run R11 without feed interruption. Continuous lines are moving averages of three adjacent points.

Figure 9 shows the temperature profiles obtained for the perturbed reaction batches. Effective temperature control becomes very difficult at certain operation conditions. For instance, monomer buildup clearly led reaction run R11, without feed interruption, to runaway conditions. Reaction runaway might have been avoided if monomer feed had been interrupted, as NIRS monomer concentration measurements seemed to recommend. This certainly illustrates how important the continuous in-line and *in situ* monitoring of

residual monomers can be to guarantee the safe process operation.

CONCLUSIONS

Near-infrared spectroscopy is a powerful tool for in-line and *in situ* monitoring of some important latex properties during actual emulsion polymerizations, such as residual monomer concentrations and polymer holdup. Using the MMA/BuA

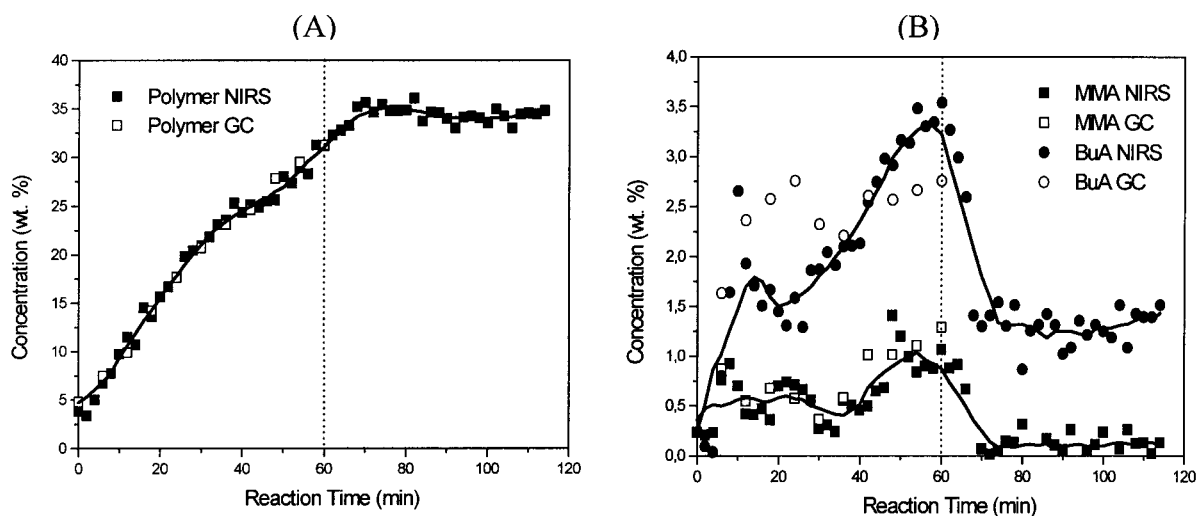


Figure 8 Monitoring of (a) polymer holdup, and (b) residual monomers in reaction run R12. Continuous lines are moving averages of three adjacent points.

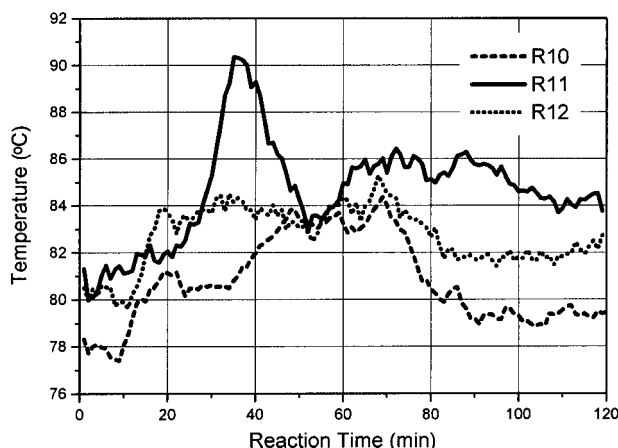


Figure 9 Temperature profiles of disturbed reactions (R10–R12).

copolymerization as the example, the cautious development of calibration equations using a full spectra multivariate statistical method (PLS) can provide empirical models that are able to keep track of compositions of different latex constituents simultaneously in real time. Monitoring of actual semibatch emulsion polymerizations showed that NIRS data are consistent, agree very well with chromatographic measurements, and may provide in-line diagnosis of process malfunctions.

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