

# Inline Monitoring of Styrene/Butyl Acrylate Miniemulsion Polymerization with Attenuated Total Reflectance/Fourier Transform Infrared Spectroscopy

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**ABSTRACT:** The copolymerization of styrene/butyl acrylate in a miniemulsion was monitored inline with an attenuated total reflectance/Fourier transform infrared (ATR-FTIR) probe. ATR-FTIR spectroscopy was used to track the concentration of the monomers, thereby providing conversion and polymer composition data. Offline gravimetry and  $^1\text{H-NMR}$  spectroscopy were used to provide a comparison with the ATR-FTIR data. Because of inconsistent results with a univariate method, a multivariate or partial least squares calibration method using the full spectra of the reac-

tions was selected and gave excellent results. No statistically significant differences were found between the offline and ATR-FTIR spectroscopy data coupled with multivariate statistics, and this confirmed that ATR-FTIR spectroscopy is a reliable tool for monitoring the conversion and polymer composition in miniemulsion polymerizations. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 46–52, 2007

**Key words:** emulsion polymerization; infrared spectroscopy; radical polymerization

## INTRODUCTION

Traditional polymerization monitoring is often carried out with offline characterization of samples from a process flow line. A disadvantage of offline techniques for conversion and composition monitoring, such as gravimetry and  $^1\text{H-NMR}$  spectroscopy, is the time lag between the sampling and results. Despite their accuracy, these techniques can rarely be used for real-time process monitoring and control. Spectroscopic techniques such as mid- and near-infrared and Raman spectroscopy are especially suitable for real-time reaction monitoring.<sup>1</sup> These techniques can provide structural and kinetic information without costly modifications to existing process equipment. Infrared spectroscopy is particularly attractive because of the high information content in the infrared spectrum and the various options available for sample measurement. Infrared spectroscopy has become one of the most important analytical methods for preparative and analytical chemistry.<sup>2</sup>

In conventional infrared spectroscopy, the intense absorption of water overlaps the majority of the mid-infrared spectral region. This makes it very difficult to

collect any kind of information in this region. Applying the principle of internal reflection spectroscopy, attenuated total reflectance (ATR) is a versatile, non-destructive technique for obtaining the infrared spectrum of materials either too thick or too strongly absorbing. In this technique, the sample is placed in contact with an internal reflection element (IRE) with a high refractive index and low infrared absorption in the region of interest. Diamonds are the most commonly used IREs.<sup>2</sup> When the infrared beam enters the IRE below an angle that exceeds the critical angle for total internal reflection, an evanescent wave is set up that penetrates a small distance beyond the IRE surface into space. A sample brought into intimate contact with the IRE can interact with the evanescent wave by absorbing specific infrared frequencies. The penetration depth of this evanescent wave can be designed to be well suited for quantitative analysis and is generally in the range of 1–10  $\mu\text{m}$ . What makes ATR a powerful technique is the fact that the intensity of the evanescent wave decays exponentially with the distance from the surface of the IRE. As the effective penetration depth is usually a fraction of the wavelength, the total internal reflectance is generally insensitive to the sample thickness and allows thick or strongly absorbing samples (e.g., water) to be analyzed.

Recent technological advancements have enabled the use of attenuated total reflectance/Fourier transform infrared (ATR-FTIR) spectroscopy for the monitoring of polymerizations.<sup>3</sup> The technology has been

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successfully implemented in the monitoring of the conversion and composition for a variety of polymerizations. For example, Full et al.<sup>4</sup> followed the kinetics of a microemulsion with internal reflectance infrared spectroscopy. Storey and coworkers<sup>5,6</sup> monitored the kinetics of a living cationic polymerization. Recently, we reported the successful use of ATR-FTIR spectroscopy to monitor solution and emulsion homo-, co- and terpolymerizations inline.<sup>7-10</sup> Spectral measurements were obtained directly in the process stream without the need for sampling devices for on-line analysis.

The presence of water and the heterogeneity of emulsion polymerizations make them particularly challenging to monitor with infrared spectroscopy. In conventional emulsion polymerizations, the main ingredients are the monomer(s), water, surfactant, and initiator. Chain-transfer agents (CTAs) and buffers are often added to control the molecular weight and pH, respectively. When the concentration of the surfactant exceeds its critical micelle concentration, the excess surfactant molecules aggregate together to form small colloidal clusters called micelles. In principle, polymer particles can be formed by the entry of radicals into the micelle (heterogeneous nucleation), the precipitation of growing oligomers in the aqueous phase (homogeneous nucleation), and radical entry in monomer droplets. In conventional emulsion polymerization, monomer droplets are relatively large (1–10  $\mu\text{m}$ ) in comparison with monomer-swollen micelles (10–20 nm), and hence the surface area of the micelles is much greater than that of the monomer droplets.<sup>11</sup> Consequently, the probability of a radical entering into the monomer droplets is very low, and most particles are formed by homogeneous and heterogeneous nucleation.

The basis for miniemulsion polymerization is an energetic homogenization process to reduce the size of the monomer droplets, with the ingredients being basically the same as those found in a conventional emulsion, with the exception of a cosurfactant. The droplets can range from 50 to 500 nm in diameter, and the latex produced by a miniemulsion is characterized by a broader particle size distribution ranging from 50 to 1000 nm in diameter.<sup>11-13</sup> If one manages to reduce the size of the droplets sufficiently, the resulting large surface area of the droplets allows them to compete effectively against the micelles to capture the oligomeric radicals and to become the main loci of polymerization. The presence of micelles in miniemulsions is dependent on the amount of the surfactant used in the formulation and on the homogenization procedure. The ideal situation, in which no micelles are formed, is obtained when the surfactant concentration does not exceed the critical micelle concentration and the homogenization procedure gives sufficiently small monomer droplets.

In this article, we describe the application of ATR-FTIR spectroscopy to the inline monitoring of the miniemulsion copolymerization of styrene (St) and butyl acrylate (BA).

## EXPERIMENTAL

### Reagents

The reagents St, BA, acrylic acid (AA), and octadecyl acrylate (ODA), the CTA *n*-dodecyl mercaptan, sodium dodecyl sulfate (SDS; EM Science), Triton X-405, sodium bicarbonate ( $\text{NaHCO}_3$ ), and potassium persulfate (KPS) were purchased from Aldrich Chemical Co. (unless otherwise indicated) and were used without any further purification. All components used to perform the characterizations, that is, toluene, ethanol, methanol, chloroform-*d*, tetrahydrofuran, sodium hydroxide (NaOH), and calcium chloride ( $\text{CaCl}_2$ ), were used as received.

### Experimental procedure

The reactions were performed in a jacketed, 1.2-L, stainless steel reactor with a Labmax setup (Mettler-Toledo, Millersville, MD) and stirred at 200 rpm. The reactor was equipped with a nitrogen-purging/pressurizing line, reflux condenser, sampling line, and port for the ATR-FTIR insertion probe. The stirring speed and temperature were automatically controlled with Camille software (Mettler-Toledo).

St, BA, and ODA were mixed for 15 min in a beaker, whereas water, Triton X-405, and SDS were mixed for 15 min in a separate vessel. The two solutions were then combined and mixed for 1 h with a magnetic stirrer. The mixture was then sonicated with a Fisher Scientific 550 sonic dismembrator for 3 min at level 6. The mixture was simultaneously cooled in an ice bath and well mixed while undergoing sonication.

The polymerizations were run at 80°C. The air background spectrum was recorded before the mixture was poured into the reactor. The reaction mixture was then heated and purged of oxygen by  $\text{N}_2$  bubbling through it for at least 40 min. When the set point temperature was reached, a deoxygenated initiator solution made with KPS and distilled deionized water was charged into the reactor. This corresponded to time zero for the polymerization. At suitable time intervals, samples were taken through the sampling port for offline analysis by gravimetry and <sup>1</sup>H-NMR spectroscopy.

A series of reactions was selected to build and validate the calibration model for miniemulsion monitoring. Table I provides a list of reactions analyzed for this monitoring model. All recipes were performed as miniemulsions with a sonication time of 3 min, a reaction temperature of 80°C, and a solid

TABLE I  
Miniemulsion Polymerization Recipes

	Run	St (phm)	BA (phm)	Triton X-405 (phm)	SDS (phm)	ODA (phm)
Runs used for calibration model building	1	5	95	1	0.06	1
	2	5	95	2.5	0.15	2.5
	3	10	90	0.5	0.03	0.5
	4	10	90	1	0.06	1
	5	10	90	2.5	0.15	2.5
	6	15	85	1	0.06	1
	7	5	95	2.5	0.15	2.5
	8	5	95	2.5	0.15	2.5
Runs used for model validation	9	5	95	0.5	0.03	0.5
	10	10	90	1	0.06	1
	11	10	90	1	0.06	1
	12	15	85	0.5	0.03	0.5
	13	15	85	0.5	0.03	0.5

concentration of 50 wt %. The following concentrations of the ingredients were also kept constant: water = 90 phm,  $\text{NaHCO}_3$  = 1 phm, KPS = 0.75 phm, AA = 4 phm, and CTA = 0.25 phm (where phm represents parts per hundred parts of monomer).

### Characterization

The mass conversion, based on the total polymer in the reaction mixture, and the percentage of solids were measured with gravimetry.

$^1\text{H-NMR}$  spectroscopy was used to determine the average or cumulative composition of the copolymers. Analyses were carried out at room temperature in deuterated chloroform (ca. 2% w/v solution) with a Bruker AMX-500 Fourier transform  $^1\text{H-NMR}$  spectrometer. The acquisition time was 4.6 s, and 16 scans were performed per sample. The relative amounts of the monomers bound in the copolymer were estimated from the areas under the appropriate absorption peaks of the spectra. The spectral peaks for the  $-\text{OCH}_2$  group in BA were located at  $\sim 3.4$ – $4$  ppm, and the cyclic (5H) group in St was located at  $\sim 6.6$ – $7.2$  ppm.

The polymerizations were monitored inline with a ReactIR 1000 (ASI Applied Systems, Mettler-Toledo) with ATR-FTIR spectroscopy. The ReactIR 1000 is designed for inline monitoring of chemical reactions in the mid-infrared spectral region ( $4000$ – $650$   $\text{cm}^{-1}$ ). Rather than using a more traditional fiber-optic probe technology, the ReactIR 1000 employs light conduit technology, which consists of six mirrors and three tubes that provide a purged path through which the infrared beam travels to a remote sampling device and back to a detector. The sampling device is a diamond-composite insertion probe with a stainless steel body (18.42 cm long and 1.59 cm in diameter) and a six-reflection bilayer ATR element with a diamond surface element (6 mm in diameter and 0.25 mm thick) at the top. Interfacing with the diamond and

acting as a focusing element is an infrared transmitting optic (a focusing crystal made of a composite material). The design enables infrared radiation to enter the focusing crystal and then, in a controlled manner, the side of the diamond disk. Once inside the disk, it forms an evanescent wave that penetrates a finite distance (the depth of penetration) into a sample. The depth of penetration is analogous to the path length in transmission sampling techniques. The peaks are more intense at a low wave number than at a high wave number because the low-wave-number radiation penetrates further into the sample. A depth of penetration of at least 10  $\mu\text{m}$  was estimated for the conditions studied herein.<sup>10</sup> The data were collected over a spectral range of  $4000$ – $700$   $\text{cm}^{-1}$ , with 128 scans and a resolution of 4  $\text{cm}^{-1}$ . The number of scans and the resolution were selected to provide an adequate signal-to-noise ratio. To ensure continuous monitoring, the reaction spectra were acquired every 2 min.

### RESULTS AND DISCUSSION

To assess the validity of ATR-FTIR spectroscopy for monitoring the polymerization, a number of potentially problematic factors were investigated. These included the use of an inappropriate background spectrum, a poor signal-to-noise ratio, probe fouling, the effect of temperature variations, and the assignment of appropriate spectral peaks.

To facilitate the monitoring of systems containing strongly absorbing substances such as water, a background spectrum was collected and subtracted from the reaction spectra. In our case, an air background was sufficient to follow the reaction because a background spectrum with water did not provide more information (or meaningful peaks). The signal-to-noise ratio was sufficiently large to allow the identification of many single-component peaks from the pure St spectrum. A visual inspection of the probe

after all reactions led to the conclusion that there was no probe fouling. The effect of temperature on absorbance was nonsignificant. It was calculated that temperature variations of 1°C would propagate an error of approximately 1% in the calculations for the conversion. Because the temperature of the reaction mixture never varied by much more than 1°C during the experiments, the temperature effect was deemed to be insignificant.

### Univariate method

In the univariate approach to monitoring polymerizations, the absorbance of different functional groups inside the monomers or polymers was monitored throughout the course of the reaction with the ReactIR 1000. Each functional group was associated with a characteristic peak, and its concentration was assumed to be proportional to its absorbance (according to Beer's law), which could be measured as a peak height. Real-time peak profiles of the monomers (changes in absorption for a specific component) were used to calculate the conversion, as previously done successfully for conventional emulsion and solution polymerization process monitoring.<sup>9,10</sup> With the univariate method, eq. (1) could be used to calculate the conversions of the monomers [ $x$  (molar fraction)] in the reaction mixture:

$$x = (\text{Peak}_{t=0} - \text{Peak}_{t=t}) / \text{Peak}_{t=0} \quad (1)$$

where  $\text{Peak}_{t=0}$  represents the peak height of one of the monomer peaks at the beginning of the polymeriza-

tion, and  $\text{peak}_{t=t}$  is the peak height at time  $t$ . With eq. (1), we could calculate the conversion at the beginning of the reaction. This method was applied to St and BA homopolymerizations as well as their copolymerization. The univariate method is a straightforward calibration technique that should be attempted first because of its simplicity.<sup>7-10</sup> One would always prefer to use the most straightforward methods for data analysis, but despite our previous successes with the univariate method,<sup>7-10</sup> it gave inconsistent results in this case, and we therefore decided to employ the more complex multivariate [partial least squares (PLS)] method.

### Multivariate method

Thirty-three samples from the runs shown in Table I were used as standards to build a calibration model for the multivariate analysis. To develop a good calibration model, it was necessary to use these samples directly from the reactions instead of preparing mixtures with pure monomers. The selection of infrared spectra was made such that the St/BA feed ratios ranged from 5/95 to 15/85 (w/w). Monomer concentrations during the polymerization were calculated offline with gravimetry and <sup>1</sup>H-NMR spectroscopy. The spectral variations recorded from these samples were related to different monomer concentrations. QuantIR version 2.1 software (ASI Applied Systems 1996, Mettler-Toledo) was used to perform the chemometric analysis. In the PLS approach, the set of calibration spectra was reduced to a smaller number of key spectra (called factors) that could, when taken in linear combination, approximate the

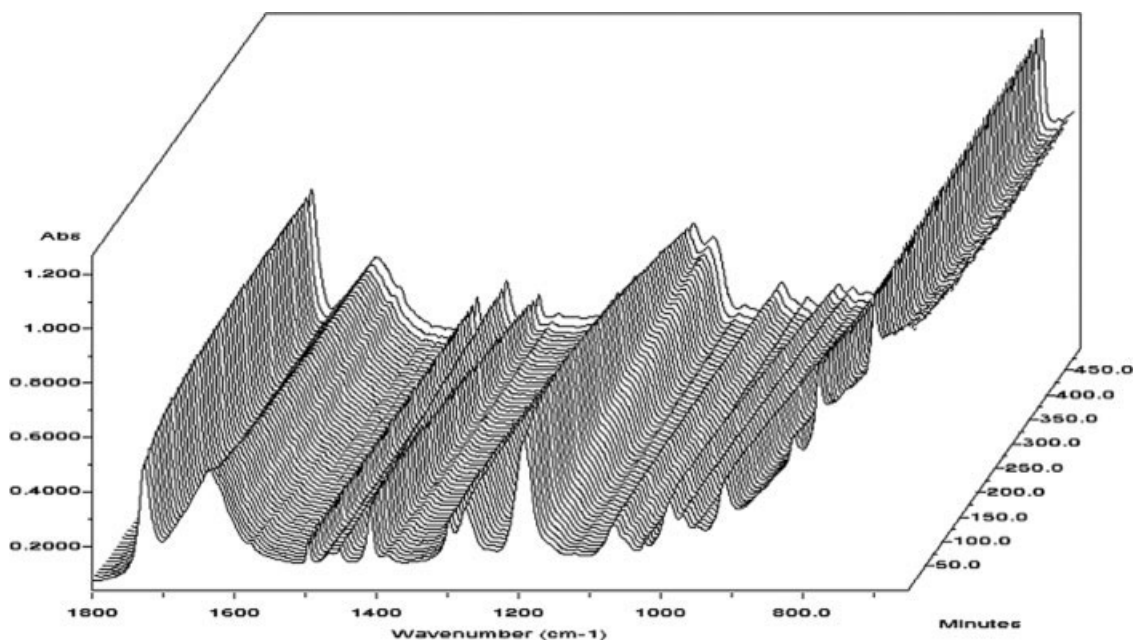
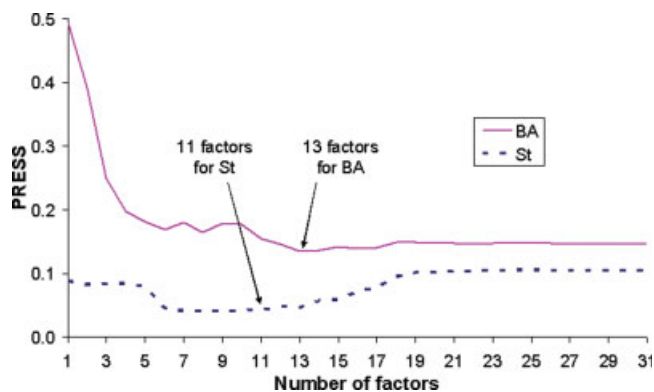


Figure 1 Typical copolymerization spectra of an St/BA miniemulsion.



**Figure 2** PRESS analysis for the PLS model. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

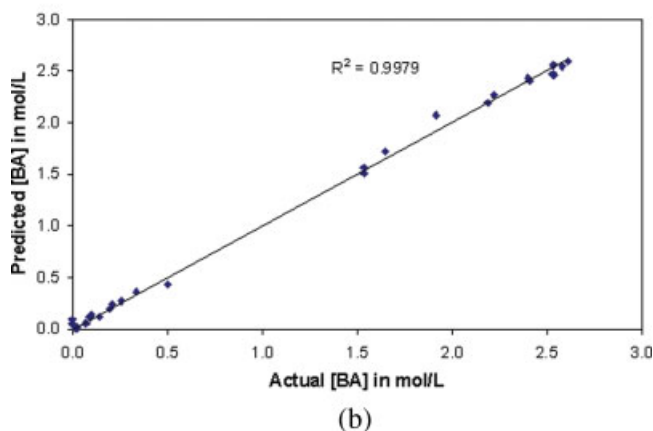
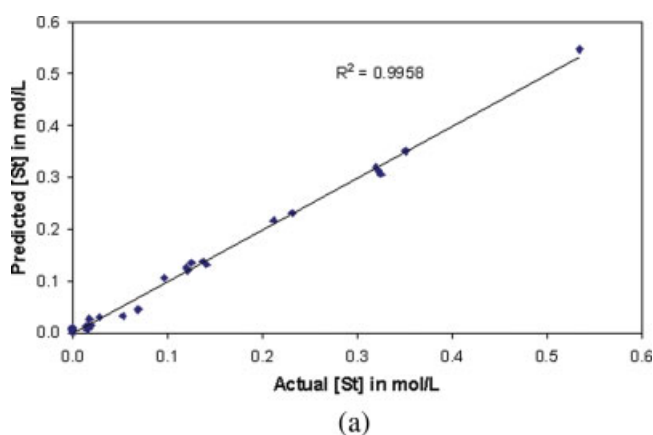
original spectral data. Each one of those factors was composed of multiple peaks within the same spectral region. A predicted residual error sum of squares (PRESS) analysis was used to select the optimum number of factors for each component (St and BA). As factors that represent useful information were added to the analysis, the PRESS value decreased, and this indicated improvement in the PLS calibration error. At some point, the factors added noise or other information unrelated to the concentration; the PRESS value then leveled off or increased. The correct number of factors to select was associated with the minimum PRESS value. Several spectral regions were tested for the calibration, but the spectral region of  $650\text{--}1800\text{ cm}^{-1}$  gave superior results. For this chosen spectral region, typical spectra of St/BA copolymerization in a miniemulsion can be seen in Figure 1.

Initially, a maximum of 30 factors for each component was chosen to establish the calibration model. After the PRESS analysis, 11 factors were chosen for the concentration of St, and 13 factors were chosen for the concentration of BA. Different scenarios were also explored with 6 or 9 factors for each component but without success. The PRESS analysis is shown in Figure 2.

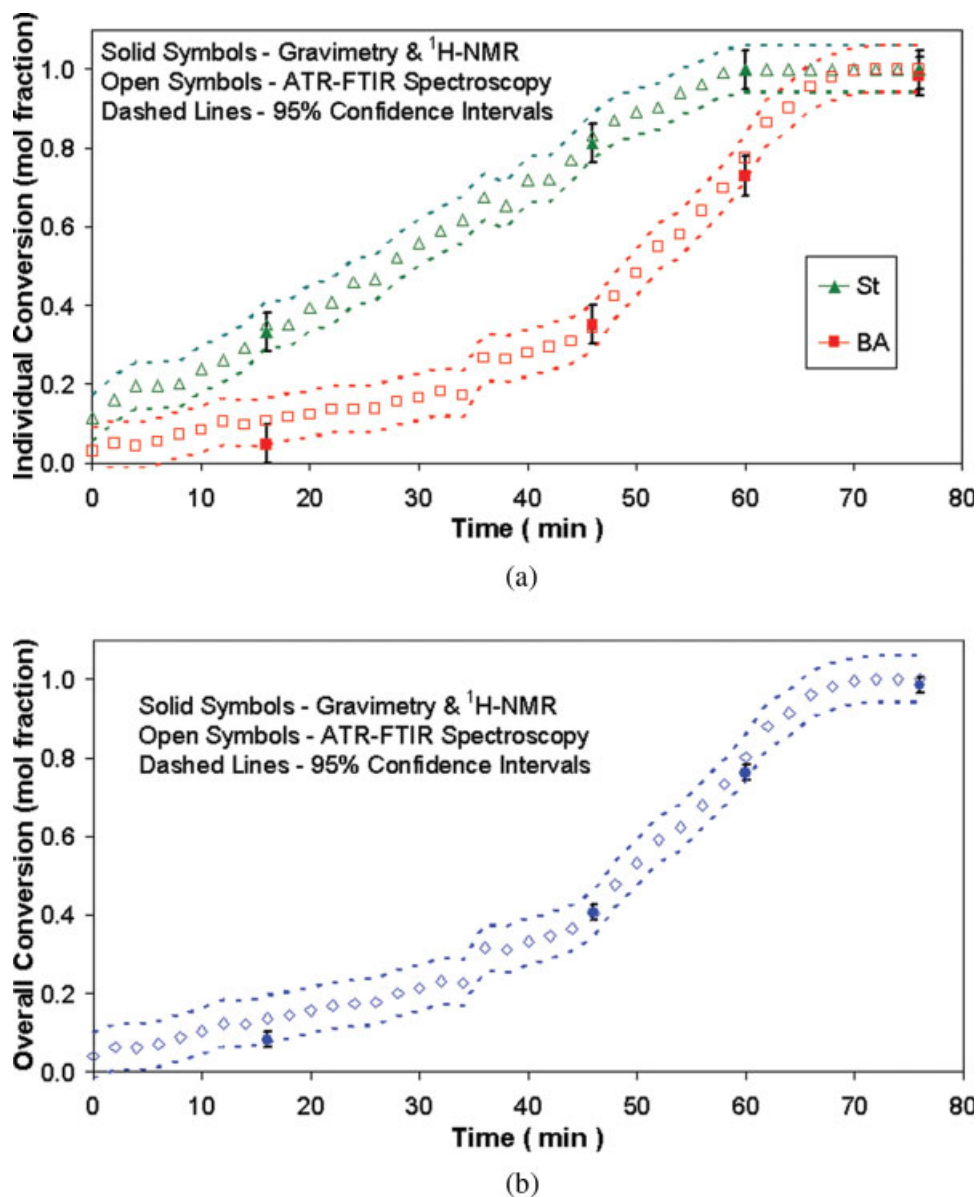
A PLS model was then built to establish a predictive relationship between the factors and the monomer concentrations from offline measurements. The corresponding calibration curves of the PLS predictions versus the known or offline concentrations are shown in Figure 3(a,b). With correlation coefficients of 0.9958 for St and 0.9979 for BA, the PLS model showed adequacy in predicting the known concentrations. The PLS model was then used to predict the St and BA concentrations from five additional runs shown in Table I. Model predictions were compared with offline measurements and with correlation coefficients of 0.9909 for St and 0.9908 for BA, which suggested a successful model.

A paired comparison was carried out between the monomer concentrations obtained by offline measurements (gravimetry and  $^1\text{H-NMR}$  spectroscopy) and the model predictions. For all the samples used in the calibration, the 95% confidence intervals for the difference between the two methods were found to be  $[-0.0077, 0.0078]$  (mol/L) for St and  $[-0.0203, 0.0203]$  (mol/L) for BA. This showed that no significant differences existed between the two methods. For all the samples used in the validation (five additional runs), the 95% confidence intervals were found to be  $[-0.0051, 0.0113]$  (mol/L) for St and  $[-0.0545, 0.0236]$  (mol/L) for BA, further confirming that a successful calibration model was calculated and that the concentrations could be predicted with ATR-FTIR spectroscopy.

The predicted concentrations of St and BA from the PLS model were then used to calculate the individual and overall monomer conversions. The calculated conversions agreed well with the actual measurements. Examples are shown in Figure 4(a) for individual conversions and in Figure 4(b) for overall conversions. Similar results were obtained for all other runs.



**Figure 3** (a) St and (b) BA concentration calibration results. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 4** (a) Individual and (b) overall PLS conversion predictions for run 11. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

## CONCLUSIONS

A series of St/BA miniemulsion copolymerizations were carried out in a 1.2-L, stainless steel reactor. The conversions were monitored offline with gravimetry, and inline monitoring was performed with ATR-FTIR spectroscopy. The air background and the signal-to-noise ratio were both appropriate for this kind of system. No significant probe fouling was observed, and the temperature effects were deemed to be negligible. The use of a univariate method to quantify the monomer or polymer concentrations in the reaction mixture gave inconsistent results; this was in contrast to our previous experience with other polymer systems.<sup>7-10</sup> A multivariate or PLS method

using the full spectra of the reactions gave much more promising results for inline miniemulsion polymerization monitoring. No significant differences were found between the offline (gravimetry and <sup>1</sup>H-NMR spectroscopy) results and the ATR-FTIR spectroscopy data coupled with the PLS method, and this confirmed that ATR-FTIR spectroscopy is a reliable tool for monitoring individual monomer concentrations and conversions.

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