Off-line monitoring of styrene/butyl acrylate copolymerizations in toluene using ATR-FTIR spectroscopy

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Abstract

The solution copolymerization of styrene/butyl acrylate in toluene was monitored off-line using an ATR-FTIR probe. The probe was used to track the concentration of the starting materials, thereby providing conversion and polymer composition data. Off-line gravimetry and ^{1}H NMR spectroscopy were used as standard methods to provide a comparison to the ATR-FTIR data. A non-calibrated univariate method was first used to calculate individual monomer conversions by monitoring the peak height of characteristic IR absorbances for each monomer. An alternative, calibrated method using partial least squares (PLS) regression to relate the whole IR spectral changes to monomer concentration was also attempted. The ATR-FTIR spectroscopy with multivariate analysis showed improvement in monitoring the monomer conversion compared to the univariate method. The results agreed with those determined by traditional gravimetric and ^{1}H NMR spectroscopy analysis.

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1. Introduction

Real-time monitoring of polymerization reactions is crucial to the production of tailor-made polymers with pre-specified properties and the improvement of process control policies. It requires the development of robust and accurate on-line sensors to provide correct information on the state and evolution of the on-going reaction [1,2].

In our previous work, an attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy technique was used to monitor solution and emulsion polymerizations of butyl acrylate (BA), methyl methacrylate (MMA), and vinyl acetate (VAc) homo-co- and terpolymers [3–5]. Following a univariate approach similar to that used by Chatzi et al. [6], individual characteristic infrared absorbances for each monomer were chosen to estimate monomer conversions and polymer compositions. The data acquired through ATR-FTIR spectroscopy showed good agreement with data from conventional gravimetric and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy analyses.

Multivariate statistical analysis has proven to be advantageous for monitoring multicomponent and/or heterogeneous reaction systems, which pose additional challenges when semi-batch processes are involved. A variety of vibrational spectroscopic techniques such as near-infrared (NIR), mid-infrared (MIR) and Raman spectroscopy have been used to monitor polymerizations [7]. NIR spectroscopy uses overtones of the fundamental absorbance bands in the MIR region. The NIR spectroscopy bands usually have lower intensities and its peaks are broad and overlapped. Raman spectroscopy is based on the very weak Raman effect. Its signal-to-noise ratio is usually low, diminishing its sensitivity. Thus, multivariate methods such as principal component analysis (PCA) and partial least squares (PLS) regression can help correlate the process variables of the reaction spectra with the quality and productivity variables of the polymerizations. While the combination of NIR and Raman spectroscopy with multivariate techniques has been successfully applied in-line to several polymerization processes, the required use of spectral manipulation to circumvent instrument limitations made the data analysis less straightforward [8–11]. Recently with the implementation of commercially available chemometrics software packages, multivariate data analysis has become easier to perform. Cherfi et al. [12] and Vieira et al. [13] described

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the use of NIR spectroscopy in combination with multi-variate data analysis to monitor polymerization reactions in-line. Vieira et al. [13] used the seeded semi-continuous emulsion copolymerization of MMA/BA as an example. Off-line gravimetry and gas chromatography (GC) were used as reference measurements for the monomer and polymer concentrations. It was found that the disagreement between the model predictions and the GC data became significant when monomer concentrations increased. Similarly, Cherfi et al. [12] used NIR spectroscopy with a PLS calibration method to monitor batch and semi-batch solution homopolymerizations of MMA in toluene. Off-line gravimetry and gel permeation chromatography (GPC) measurements were correlated to NIR spectral data to predict the monomer conversion and polymer molecular weight profiles during the reaction under different conditions. In both cases, strong correlations were reported between the NIR spectroscopy and the off-line measurements.

MIR spectroscopy possesses more easily distinguishable bands corresponding to specific functional groups and inter-actions between them, which can improve our ability for qualitative and quantitative analysis compared to NIR and Raman spectroscopy. Stavropoulos et al. [14] monitored the batch emulsion copolymerization of styrene (St) and 2-ethylhexyl acrylate (2-EHA) and described the PCA and PLS regression algorithm that was developed to analyze the IR spectral data from the polymerization process under different conditions. Model predictions of the monomer conversion and the copolymer composition compared favorably with the direct off-line measurements through gravimetry, thermogravimetry, ultra-violet (UV) and IR analysis.

Pollard et al. [15] reported the use of the ReactIR™ 1000 reaction analysis system for a fermentation process, in which the numerous medium components gave rise to complex IR spectra that were difficult to interpret. The multivariate data analysis based on a PLS algorithm was completed in conjunction with other measurements to build a calibration model and gave satisfactory predictions compared to off-line results. Amari et al. [16] used the same equipment on a step growth polymerization process producing polyester. A PLS regression-based multivariate calibration model was developed to predict both the reagent and the by-product concentrations during the polymerization reaction. The predicted values from the ATR-FTIR spectroscopy measurements agreed well with results from ^{1}H NMR analysis.

St/BA copolymers are commercially important binders in many paints and coatings. Extensive reaction kinetics studies of this system have been carried out in bulk, solution, and emulsion [17,18]. Due to their differing monomer reactivity ratios, polymer composition drift can occur during a batch polymerization. The final product would thus contain a distribution of compositions and microstructure. Semi-batch policies are often used to produce polymers with homogeneous properties. These policies employ monomer feed control coupled with in-line monitoring of the

monomer conversion using GC, densimetry, and/or calorimetry [19–23]. In these cases, traditional off-line methods such as gravimetry and ^{1}H NMR spectroscopy were unable to monitor the polymerization in an adequate time frame when composition drifts occurred during the process. Other sensing techniques posed either sampling difficulties or time-consuming analysis [24]. Vibrational spectroscopy techniques such as MIR, NIR and Raman spectroscopy offer more help because of their non-destructive and on-line monitoring capabilities. Al-Khanbashi et al. [11] performed St/BA emulsion copolymerization monitoring using Raman spectroscopy.

In this paper, we report the results of solution copolymerizations of St/BA in toluene (50 and 65 wt%) initiated with 2,2′-azobisisobutyronitrile (AIBN) at 60 °C. The ReactIR™1000 reaction analysis system was used for off-line analysis of our samples to identify characteristic peaks, to follow the reaction kinetics and to evaluate its ability to estimate monomer conversion and polymer composition from spectral changes. Both univariate and multivariate analysis approaches were used. Kinetic data obtained through IR analysis were compared to results from traditional gravimetric and ^{1}H NMR methods. The objectives of this work were two-fold. One was to test the ability of the ReactIR™1000 to monitor the copolymerization off-line, and the other was to verify the ability of IR spectroscopy, combined with a multivariate calibration model, to follow the monomer concentration changes under different conditions. In particular, the potential to monitor semi-batch St/BA emulsion copolymerizations in-line was investigated.

2. Experimental section

2.1. Materials

Purification of reagents was performed by classical methods. Inhibitor was removed from BA (Aldrich Chemical Co., Inc.) and St (Aldrich Chemical Co., Inc.) according to previously described procedures [25]. The initiator, AIBN (DuPont Canada Inc.), was recrystallized three times from absolute methanol. The chain transfer agent (CTA), 1-dodecanethiol (Aldrich Chemical Co., Inc.), was used as received. All of the solvents used in these experiments and for characterization of the copolymers (i.e. toluene, ethanol, deuterated chloroform, tetrahydrofuran (THF)) were also used as packaged.

2.2. Instrumentation

A ReactIR™ 1000 reaction analysis system equipped with a light conduit and DiComp (diamond composite) insertion probe was used to collect mid-FTIR spectra of the polymerization components. These spectra were used to calculate monomer conversion and copolymer composition.

Table 1
St/BA solution copolymerizations in 50 and 65 wt% toluene (all monomer values in parts per hundred parts monomer)

	St20BA80		St40BA60		St60BA40		St80BA20	
	T50	T65	T50	T65	T50	T65	T50	T65
Toluene (wt%)	50	65	50	65	50	65	50	65
St	20	20	40	40	60	60	80	80
BA	80	80	60	60	40	40	20	20
AIBN (mol/l)	0.10	0.098	0.10	0.097	0.10	0.074	0.099	0.10
CTA (mol/l)	0.025	0.026	0.025	0.025	0.025	0.027	0.028	0.026

Resulting polymer compositions were also obtained through ^{1}H NMR spectra taken by a Bruker AMX500 Fourier-transform ^{1}H NMR spectrometer.

2.3. Experimental planning and procedures

High conversion solution polymerizations of St/BA were conducted at 60 °C in both 50 and 65 wt% toluene solutions (Table 1). Polymerization experiments were designed so that the entire range of reaction conditions expected during the process should be covered by the calibration samples. The IR samples used as standards for calibration were directly obtained from the reaction processes instead of being prepared from mixtures of pure chemicals.

Polymerizations were carried out in glass ampoules of length 20 cm and outer diameter 0.8 cm. The monomers and initiators, together with solvent and CTA, were weighed into a flask to prepare the initial feed and an amount of about 2.7 ml was then pipetted into several numbered ampoules. Next, the ampoules were degassed through several vacuum freeze–thaw cycles and subsequently submerged in a water bath for a recorded time interval with the temperature controlled at 60 °C.

Each ampoule was taken out at a pre-determined time interval. The contents of each ampoule were poured into an 18.5-ml vial and were analyzed using the ATR-FTIR insertion probe. After collecting the spectrum of air as a background, the probe tip was immersed in the vial to record the spectra of the polymerization contents. The standard acquisition mode of the ReactIR™ 1000 was used to collect the IR spectra from 128 scans, over the spectral range of 4000–700 cm^{-1}, with a resolution of 4 cm^{-1}. The spectra were recorded and further analyzed using the ReactIR™ (version 2.2) software.

After the spectrum was collected, all the contents were poured into a pre-weighed crystallizing dish and a 10-fold excess of ethanol was added to precipitate the produced polymer. Mass conversion based on the total polymer in the reaction mixture was measured using gravimetry. The resulting isolated polymers were analyzed for cumulative polymer composition by ^{1}H NMR spectroscopy. Analysis was carried out at room temperature in deuterated chloroform ($\sim 2\%$ (w/v) solutions), which was used as both the solvent and the reference. Acquisition time was 4.6 s, and 16 scans were performed per readout (for averaging). All spectra exhibited good peak separations for a straightforward interpretation of the results. The relative amounts of monomer bound in the copolymer were estimated from the areas under the appropriate absorption peaks of the spectra. For St/BA copolymers, the five protons on the aromatic ring of St absorb at approximately 6.5 ppm and the two protons of the methylene closest to the oxygen in the ester portion of the BA absorb at approximately 3.5 ppm (the –OCH$_2$ group). The copolymer compositions were determined by comparison of the integrated intensities of the resonance signals due to the phenyl proton of St and that of the methylene group in the BA. The individual conversion profile for each monomer was obtained by combining results from the overall conversions through gravimetry and each monomer's corresponding mole fraction in the copolymer chain through ^{1}H NMR spectroscopy.

3. Results and discussion

3.1. Univariate analysis

ATR-FTIR results from St homopolymerizations in toluene showed that several characteristic absorbance bands at 1576, 992, 907, and 775 cm^{-1} could be used to follow the reaction. These wavelengths correspond to a ring quadrant stretch, –CH= wag, =CH$_2$ wag, and ring C–H wag, respectively. BA homopolymerizations in toluene revealed that peaks at 1409, 984, 969, and 810 cm^{-1} were appropriate for the quantitative estimation of monomer conversion [5]. These wavelengths correspond to a =CH$_2$ deformation, trans –CH wag, =CH$_2$ wag, and =CH$_2$ twist, respectively.

Reaction mixture spectra from the copolymerization reactions were collected and distinct changes as a consequence of the polymerization reaction were observed (see Fig. 1). Characteristic absorbance bands for both monomers were identified at 777 cm^{-1} for the St ring C–H wagging and 810 cm^{-1} for the BA =CH$_2$ twist, which diminished with increasing reaction time. According to our previous approach, because there was neither interference from the polymer nor from the solvent absorbances at or around these
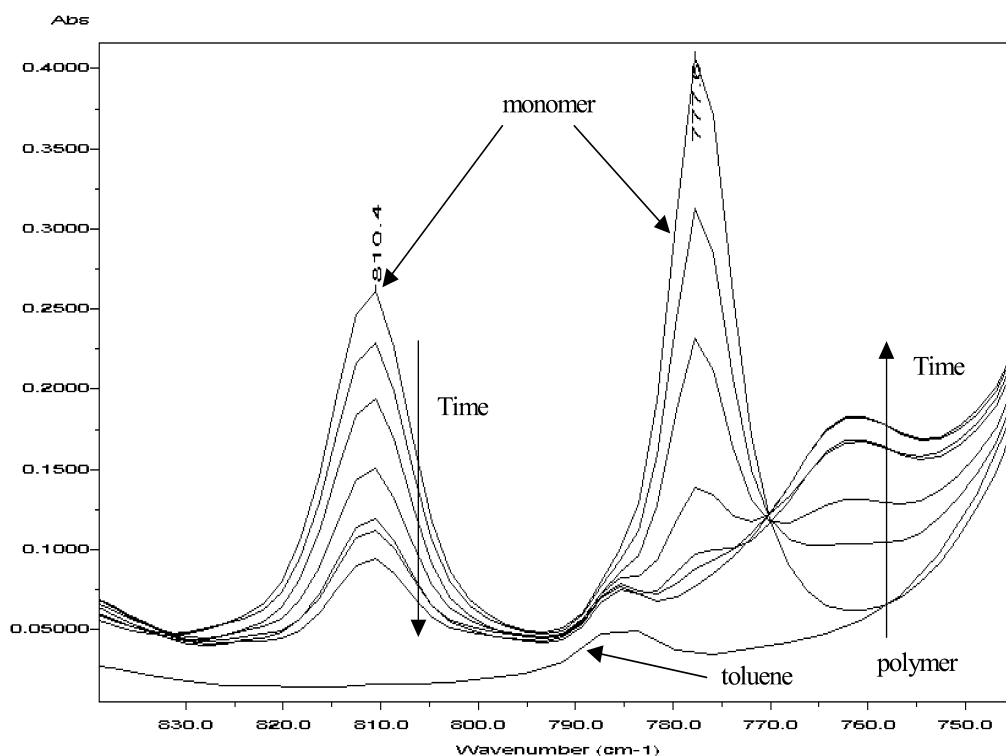
Fig. 1. ATR-FTIR spectra of run St40BA60T50 in toluene (50 wt%).

wavenumbers, these two peaks were used for tracking the reaction [3–5].

According to Beer's law, the concentrations of the various reaction components are proportional to the absorbances measured as the corresponding peak heights [3–6]. Thus, the individual conversions, x, of both monomers were estimated by calculating the ratio of the absorbances (peak height referenced to a two-point baseline) of the 777 and 810 cm^{-1} characteristic bands, for St and BA, respectively, at reaction time t to those corresponding bands at the start of the polymerization reaction ($t = 0$), according to

$$x(\text{mol}\%) = 1 - \frac{\text{peak height at time } t}{\text{peak height at time } t = 0} \qquad (1)$$

The overall weight percentage conversion, X, of the copolymerization was calculated using

$$X(\text{wt}\%) = \frac{w_i}{w_i + w_j} x_i(\text{mol}\%) + \frac{w_j}{w_i + w_j} x_j(\text{mol}\%) \qquad (2)$$

where $w_i/(w_i + w_j)$ is the weight fraction of monomers i fed into the reactor at time $t = 0$.

Fig. 2 shows a typical example of the agreement achieved between the overall and individual monomer conversion data obtained by traditional gravimetry and ^{1}H NMR spectroscopy techniques and ATR-FTIR spectroscopy. While the agreement seems reasonable from a purely visual inspection, when all eight runs were analyzed using a paired comparison of the differences between the gravimetry and ^{1}H NMR spectroscopy results and the

ATR-FTIR results, significant differences were found at both 95 and 99% confidence levels.

3.2. Multivariate analysis

Twenty-nine samples from runs St20BA80T50, St20BA80T65, St80BA20T50, and St80BA20T65 were used as standards to build a calibration model for multivariate analysis. In order to develop a good calibration equation, it was necessary to use these representative samples directly from the reaction as standards instead of using prepared mixtures of pure monomers. The monomer concentration ranges were from 0 to 3.366 mol/l for St and from 0 to 2.729 mol/l for BA (see Fig. 3). The monomer concentration varied within these ranges during the polymerization process under different operation conditions. Monomer concentrations during the polymerization were calculated using data from gravimetry and ^{1}H NMR analysis. The spectral variations recorded from these samples were related to different monomer concentrations. Samples from runs at two different toluene concentrations were used because the PLS method can implicitly account for unknown process variations such as polymer and solvent concentrations that are not included in the calibration set as long as their levels are sufficiently varied in the standards [26].

IR absorbances at 1100 wavenumbers from the spectral region 1800–700 cm^{-1} were included in the analysis. A large amount of calculation was involved due to the use of the full spectra instead of several distinct characteristic
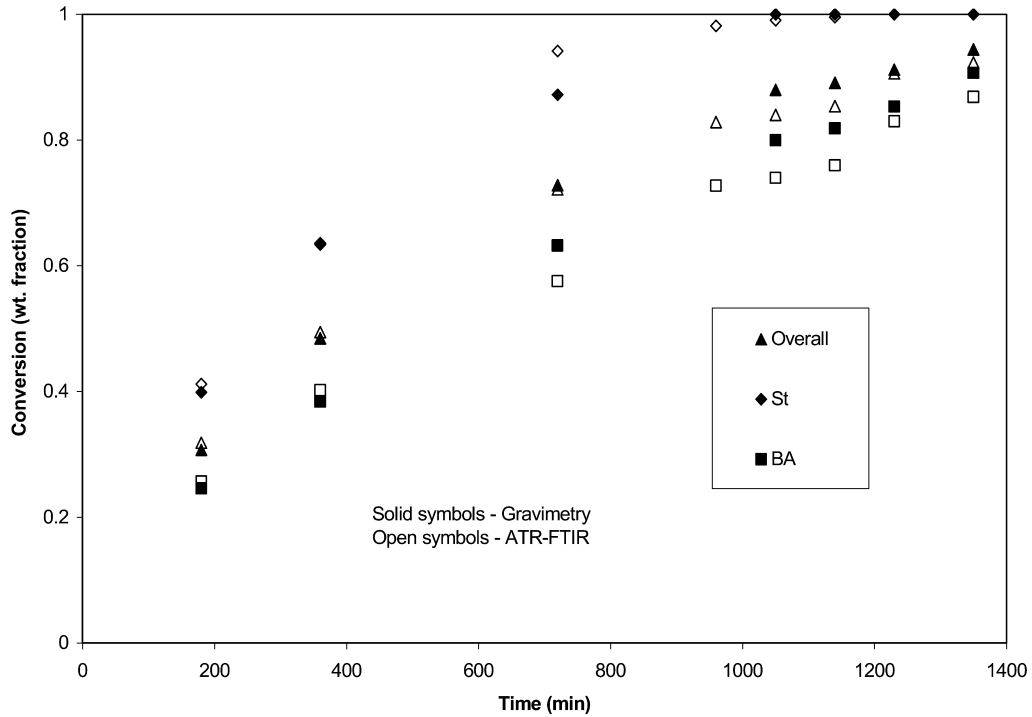
Fig. 2. Run St40BA60T65: conversion vs. time.

peaks. In the PLS approach, the set of calibration spectra was reduced to a smaller number of key spectra (called factors) that can, when taken in linear combination, approximate the original spectral data set. Factor analysis was used to determine the optimal number of factor spectra, which explained most of the variance within the data set.

Fig. 4 shows the amount of variance explained for both the spectral and the concentration data set as a function of the number of factors included in the model. A maximum of 15 factors was initially chosen to establish the model with the first four factors accounting for more than 95% of the total variance in the spectral data. The remaining factors
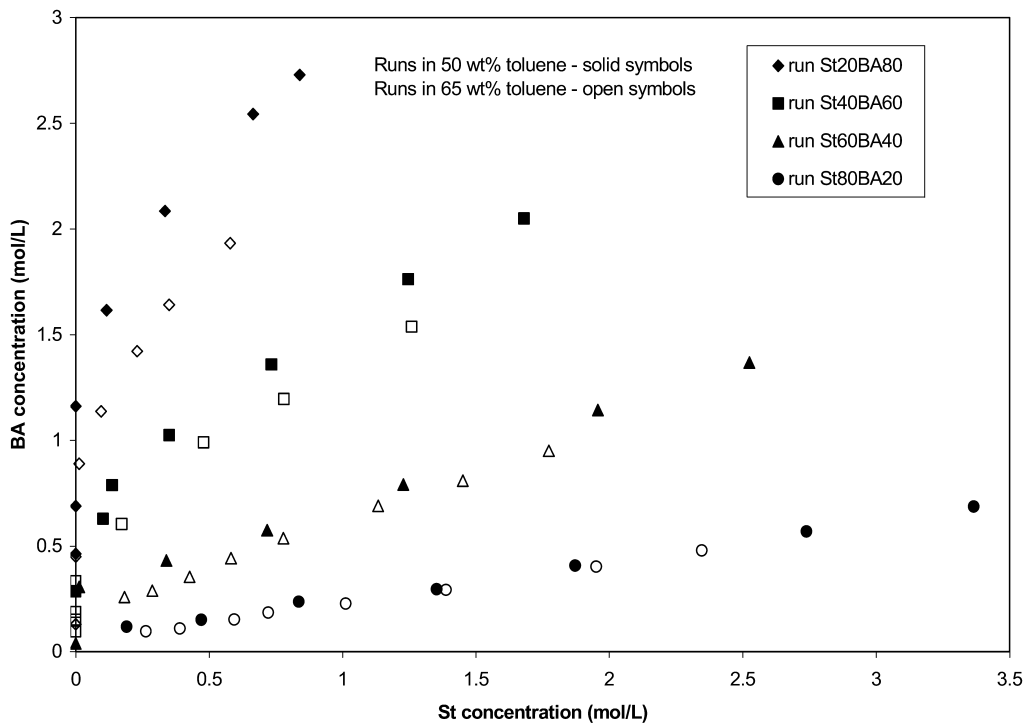

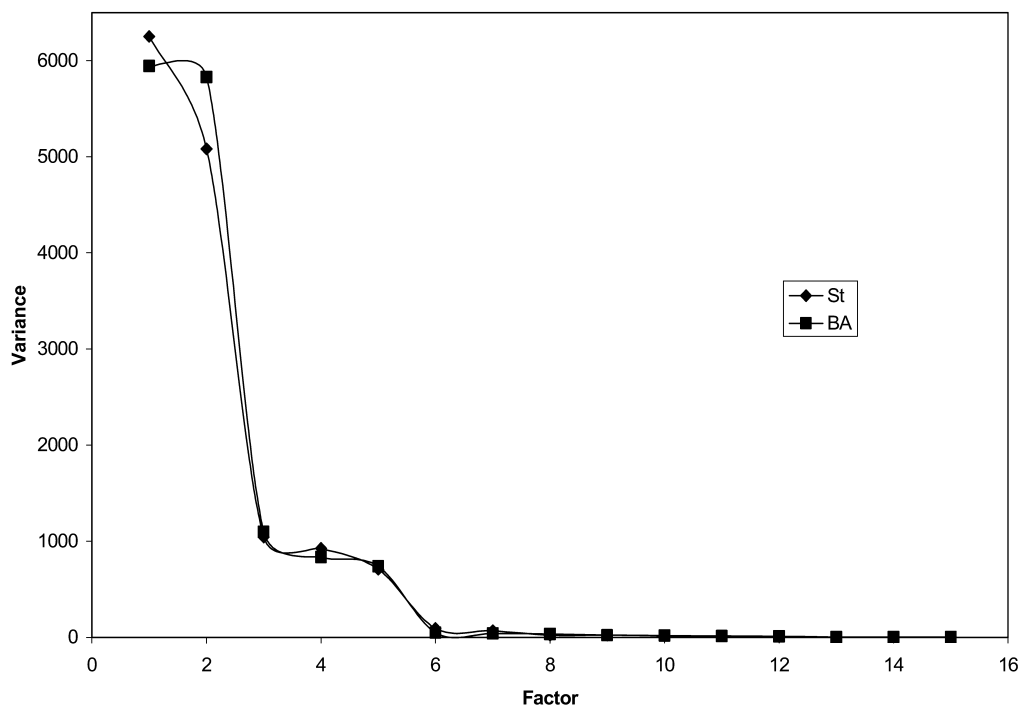Fig. 3. Monomer concentrations in all experimental runs.

Fig. 4. The variance plot of components St and BA.

contributed very little variance to the model and were typically attributed to either noise or spectral variations not related to concentration. As a result, the model used the modified spectral data set expressed as the linear combination of the first four factors; other factors were discarded so that noise or minor variation effects were eliminated from the analysis. The use of a 4-factor PLS model provided significant improvement to the monomer concentration predictions. Increasing the number of factors to five resulted in a slight deterioration of the predictions. Increasing the number of factors to six offered only a slight improvement.

The absolute intensity at different wave numbers in each factor's spectrum is called the loading. The original spectra were expressed as a linear combination of four factors. Thus, the magnitude of the loading for the individual absorbances in each of the four spectra defines how that absorbance contributes to the original spectra [26]. For example, positive loadings were observed around 775, 916 and 1576 cm^{-1} attributed to the St monomer in the first factor spectrum for the PLS model of the St monomer concentration while negative loadings appeared around 810 cm^{-1} attributed to the monomer BA. Similarly, in the first factor spectrum for the PLS model of the BA monomer concentration, positive loadings appear at 810, 1063, 1621, 1638, and 1726 cm^{-1} attributed to BA and negative loadings around 775 cm^{-1} are attributed to St. Compared to the spectra of the pure monomers and reaction mixture discussed previously (Fig. 1), the factor spectra confirmed the choice of characteristic absorbance bands used in the univariate non-calibrated method.

In the next step, the PLS model was built to establish the predictive relationship between the modified spectral data set and the monomer concentrations. The corresponding calibration curves of the predicted vs. known concentrations are shown in Fig. 5a and b for the St and BA concentrations, respectively. For the standards, the correlation coefficients between the model predictions and gravimetric measurements were 0.9966 for St and 0.9961 for BA, suggesting a good agreement between the model prediction and the actual measurement.

The 4-factor PLS model was then used to predict the St and BA monomer concentrations from the other four run conditions: St40BA60T50, St60BA40T50, St40BA60T65, and St60BA40T65. Model predictions were compared to actual measurements and are plotted in Fig. 6a and b. The correlation coefficients between the model predictions and gravimetric measurements were 0.9865 for St and 0.9134 for BA. Model predictions of the BA concentration increasingly deviated from the actual measurement when the concentration was lower than 0.6 mol/l in the mixture, indicating a potential detection limit in the presence of higher polymer concentrations.

A paired comparison was carried out between the monomer concentrations obtained by gravimetry and ^{1}H NMR measurements and the PLS model predictions. For all of the samples from the runs used as standards, 99% confidence intervals for the difference in the concentration results between the two methods were found to be [−0.0256, 0.0244] for St and [−0.0205, 0.0205] for BA. This indicates that no significant difference exists between the two
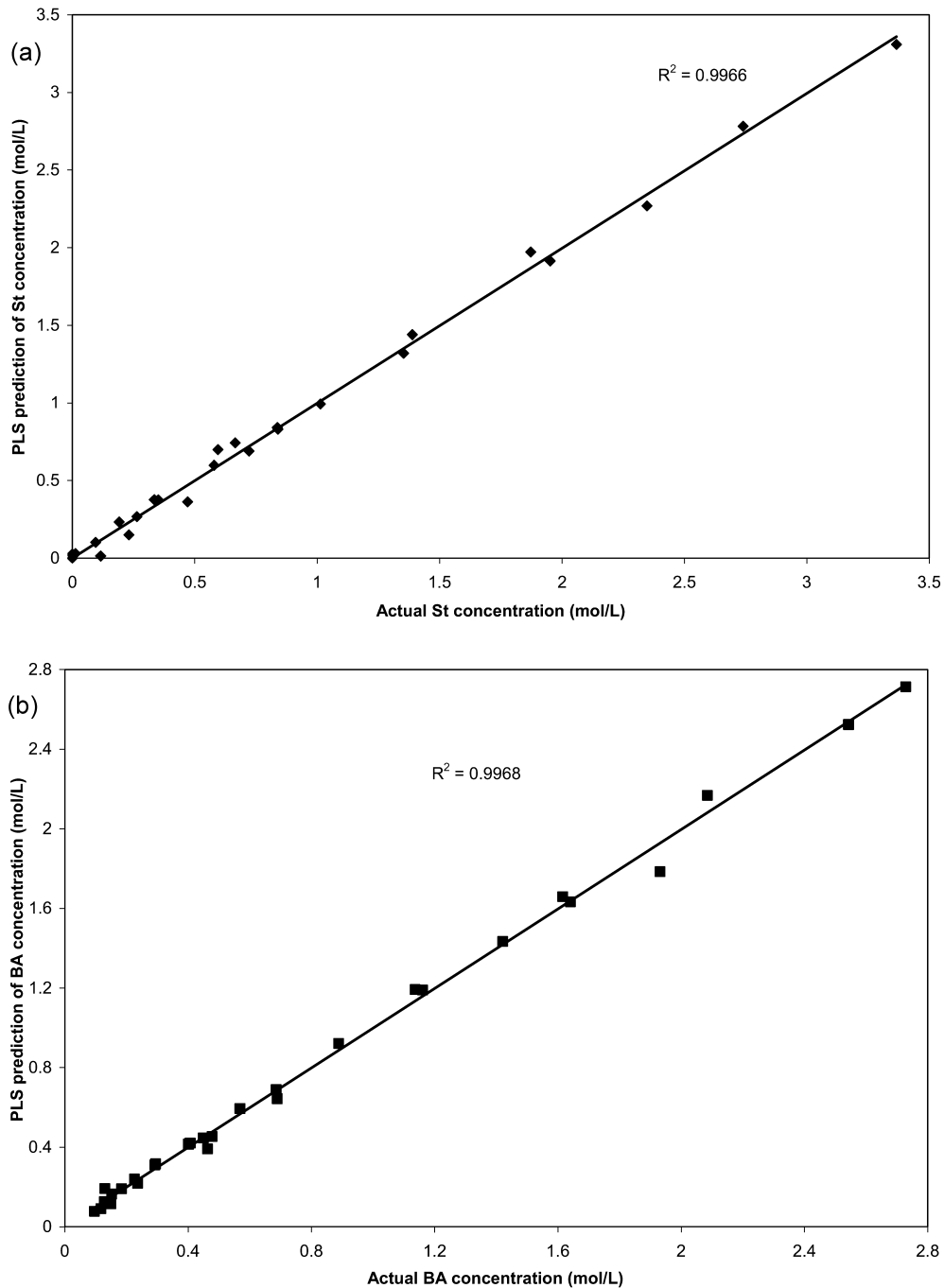
Fig. 5. (a) St concentration calibration: PLS predictions vs. actual measurements, (b) BA concentration calibration: PLS predictions vs. actual measurements.

methods. When the PLS model was used to predict the monomer concentrations of the four other runs, the 99% confidence intervals were found to be $[-0.0004, 0.0739]$ and $[-0.1665, -0.0627]$, respectively. This, however, implies that for BA, a significant difference does exist albeit a small one. A closer look reveals that two of these four experiments, St40BA60T65 and St60BA40T60, individually showed significant differences (see Fig. 6b). When the overall monomer conversion reached about 70 wt% and the BA concentration was lower than 0.6 mol/l, this deviation

became more and more significant. For all eight runs, 99% confidence intervals calculated for the difference in the results between the two methods were found to be $[-0.0192, 0.0552]$ for St concentrations and $[-0.1091, -0.0054]$ for BA concentrations, suggesting that the difference for the St concentration results between the two methods is not significant while a slight difference in the BA concentration results exists.

The predicted St and BA monomer concentrations from the PLS model were then used to calculate the individual
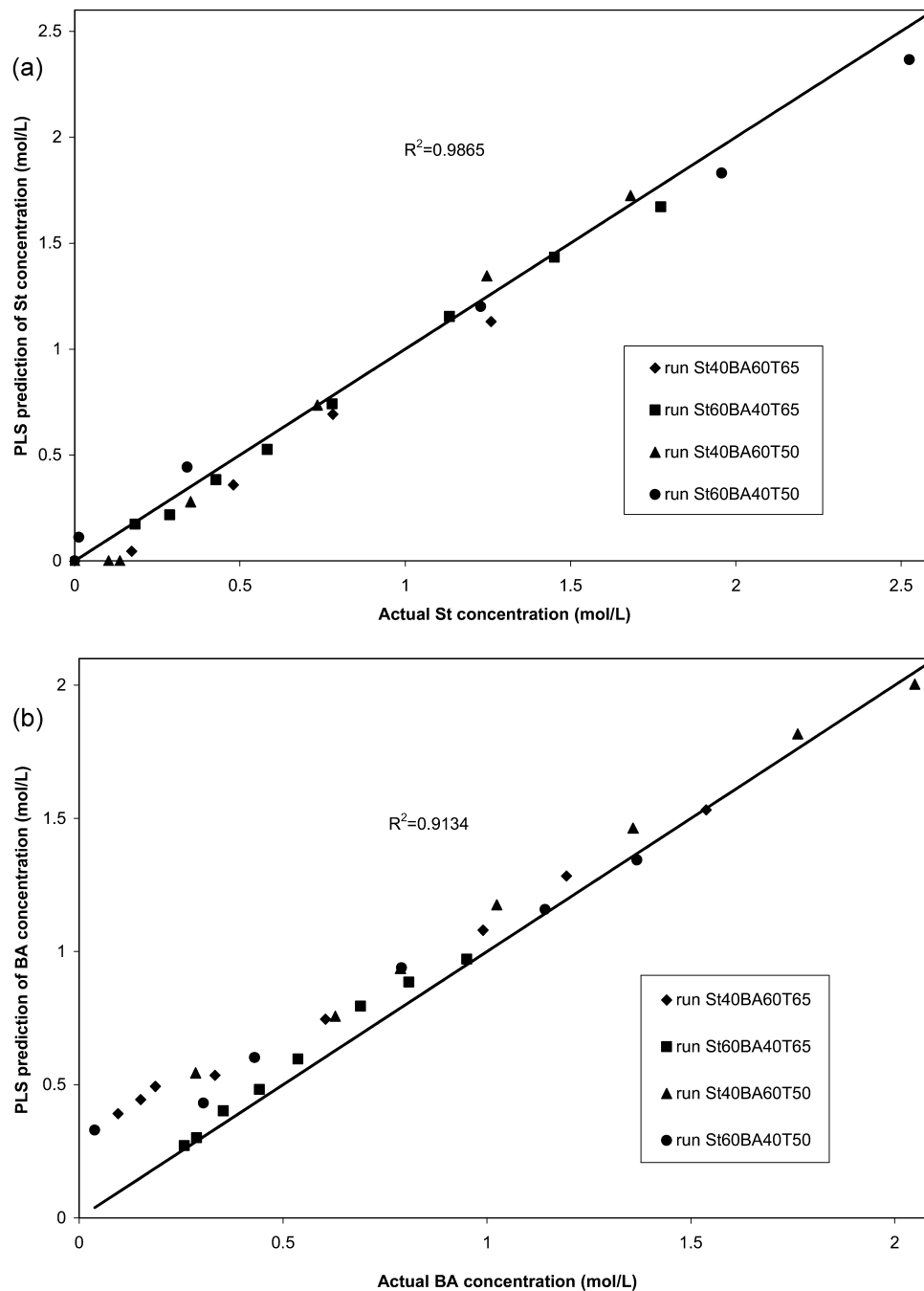
Fig. 6. (a) St concentration validation: PLS predictions vs. actual measurements, (b) BA concentration validation: PLS predictions vs. actual measurements.

monomer conversions. The calculated conversions agreed well with the actual measurements. One example is shown in Fig. 7 for the run St40BA60T50.

A local PLS model was also built based upon standards only from runs with 50 wt% toluene. Results from run St60BA40T65 in Fig. 8 show an example that such a local PLS model was not as effective in predicting the individual monomer conversions compared to the global PLS model, which was based upon standards from runs with different toluene concentrations.

Using a paired comparison test for the univariate

approach indicates that both St and BA show significant differences between the gravimetric and ^{1}H NMR spectroscopy measurements and the ATR-FTIR results at a 99% confidence level. This clearly indicates that the use of the multivariate IR technique affords an improvement to the polymerization monitoring for the St/BA copolymerization.

5. Conclusions

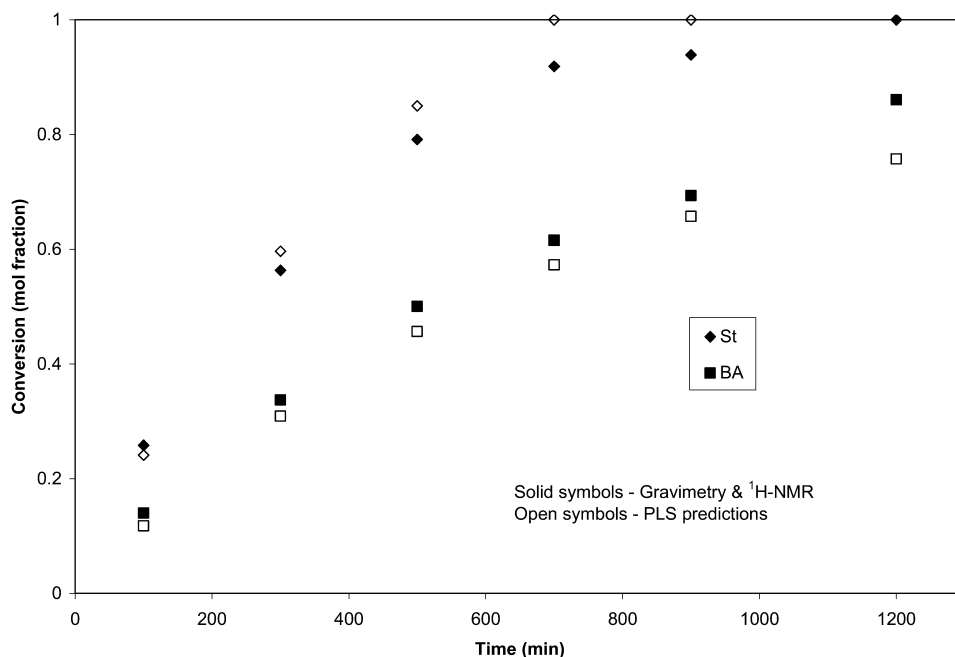The non-calibrated or univariate method, while adequate

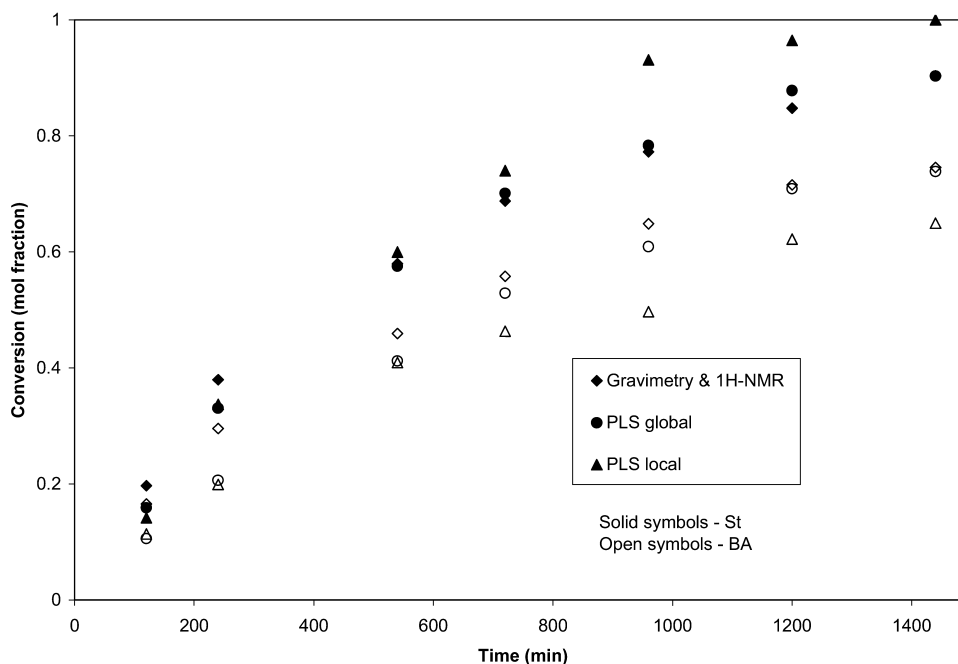Fig. 7. PLS predictions on run St40BA60T50: conversion vs. time.

Fig. 8. Global and local PLS model prediction comparison on run St60BA40T65: conversion vs. time.

for off-line solution polymerization monitoring of several other systems, was found to be inadequate for the St/BA copolymerization in toluene.

Calibration using a full spectra PLS method appears to be adequate for off-line solution polymerization monitoring of monomer concentrations and conversions. Factor analysis confirms our choice of characteristic absorbance bands used in the non-calibrated method. The use of a global PLS model rather than local PLS models (i.e. models built upon different solvent concentrations) is preferred. More

measurements taken at high conversion stages, when the monomer concentration is low, should improve the model predictions in these cases. Future work will examine the use of PLS methodology to monitor batch and semi-batch St/BA emulsion polymerizations in-line.

Acknowledgements

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