

On-Line Determination of the Conversion in a Styrene Bulk Polymerization Batch Reactor Using Near-Infrared Spectroscopy

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ABSTRACT: A fast on-line method for measuring the monomer conversion of a styrene batch polymerization reaction with near-infrared spectroscopy (NIR) has been developed. Multivariate calibration was performed, using polymer samples having temperatures around the set point of the batch reactor (75–85°C) and monomer conversions up to 35%. The calibration model was built in such a way that the effect of the temperature on the predicted conversion of the sample was minimized. The method was validated in a number of batch runs. In these runs, the batch temperature and molar mass distributions of the polymer were varied. At-line size-exclusion chromatography was used as a reference method for measuring the monomer conversion. Results show that on-line conversion monitoring with NIR offered overall an excellent accuracy (~ 0.32% conversion). For high and low monomer conversions a small bias in the predicted conversion is present. The method proved to be insensitive to both relative large changes (10°C) of the batch temperature and to considerable changes of the molar mass distribution of the polymer. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 90–98, 2002; DOI 10.1002/app.10241

Key words: degree of polymerization; polystyrene; near-infrared spectroscopy; sensors; modeling

INTRODUCTION

Over the years the use of polymers has expanded significantly, a tendency that urged for higher quality of polymers, which are produced in large-scale batch reactors. A very challenging way to improve polymer product quality is the monitoring of the batch polymerization process itself.¹ This will facilitate end-point determination of the

polymerization reaction. In the case of bulk polymerization, two main variables have to be controlled: viz., the monomer conversion and the molar mass distribution of the produced polymer. Of these variables the monomer conversion is the most accessible for on-line measurement. Several on-line methods for determination of monomer conversion, based on fast measurement of density,² rheological properties,³ reactor heat fluxes, for example, determined by calorimetry,⁴ ultrasound propagation velocity,⁵ or on-line GC⁶ have been proposed in literature. Except for the on-line GC, these methods are based on fast measurements of process variables that are only indirectly

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related to the monomer conversion. Because of this indirect relation with the conversion, these methods offer only poor selectivity and accuracy. This will hamper the use of these on-line measurements for control purposes. On-line GC-methods have an analysis time of about 10 min, which is rather slow, and may have a sampling interface to the batch process that is rather cumbersome.

Direct and easy measurement of the monomer conversion is possible with spectroscopic techniques. It is known that in general (short-wave) near infrared spectroscopy (SW-NIR) is very suitable for monitoring polymer reactions.⁷ Aldridge et al.,⁸ for example, showed the potential of SW-NIR for monitoring the conversion of bulk polymerization of Methylmethacrylate.

The scope of this work is to develop and validate a NIR spectroscopy method, as a tool for on-line conversion monitoring of a styrene polymerization. In general, this method would be applicable to batch, semibatch, or continuous styrene bulk polymerization processes. Here, the method is specifically developed and tested for a styrene batch polymerization process.

A multivariate calibration model is constructed based on calibration experiments in which the NIR spectra of polymer–monomer mixtures are measured at different temperatures. These mixtures have different known monomer conversion levels. For the purpose of validating the developed method and establishing its robustness, several free-radical bulk polymerization reactions initiated with AIBN are monitored. These batch experiments are performed according to an experimental design in which the polymer properties were varied. The reference method for determining the monomer conversion in these experiments is a modified and thoroughly tested, at-line size-exclusion chromatographic (SEC) method.

THEORY

Calibration

The basic spectral quantity that is used throughout this work is given in eq. (1).

$$D(\sigma) = -10 \log \left(\frac{\text{SB}_{\text{mixture}}(\sigma)}{\text{SB}_{\text{styrene}}(\sigma)} \right) \quad (1)$$

where σ is the wave number [cm^{-1}].

Equation (1) relates the single-beam spectrum of the polystyrene–styrene reaction mixture, $\text{SB}_{\text{mixture}}(\sigma)$, to the single-beam spectrum of styrene, $\text{SB}_{\text{styrene}}(\sigma)$. The spectral quantity $D(\sigma)$ is, in fact, equal to the difference between the absorbance spectrum of pure styrene and the absorbance spectrum of the reaction mixture. To prevent confusion with absorbance spectra this quantity is called the D -spectrum from now on. The reason to use this D -spectrum as the spectral quantity for calibration is that at the start of the batch reaction, when the reactor is filled with styrene monomer, the styrene single beam spectrum can easily be measured. During the batch reaction the single beam spectra of the reaction mixture can also be recorded easily. Measuring a nonabsorbing reference, a blank, during the reaction would be impractical and is not necessary. Moreover, the difference between spectrum of the reaction mixture and the spectrum of styrene is exactly the quantity that is of interest.

To relate these D -spectra of the styrene–poly(styrene) mixtures to the conversion a calibration model is needed.⁹ The inverse least-squares model (ILS) is made by modeling the $(I \times 1)$ column vector x , which contains the conversions of the I styrene–poly(styrene) calibration mixtures, by using the measured NIR spectra of the mixtures:

$$\mathbf{x} = \mathbf{R}\mathbf{p} + \mathbf{e} \quad (2)$$

In eq. (2) the rows of the $(I \times J)$ matrix \mathbf{R} contain the measured NIR spectra (J wave numbers) of calibration mixtures. The vector \mathbf{e} ($I \times 1$) contains the modeling errors and \mathbf{p} is a $(J \times 1)$ column vector with the regression coefficients of the calibration model. These coefficients are estimated by partial least squares (PLS).¹⁰

Validation

The conversion of the reaction mixture is estimated with the scalar \hat{x}_{NIR} that is calculated using:

$$\hat{x}_{\text{NIR}} = \mathbf{r}_{\text{un}}^T \mathbf{p} \quad (3)$$

In this expression the $(J \times 1)$ column vector \mathbf{r}_{un} is the D -spectrum of the reaction mixture. The $(J \times 1)$ column vector \mathbf{p} contains the regression coefficients of the PLS calibration model that was obtained in the calibration phase.

The prediction performance of NIR calibration model is characterized for each batch reaction by the root-mean-square error of prediction RMSEP:

$$\text{RMSEP} = \sqrt{\frac{1}{M} \sum_{m=1}^M (\hat{x}_{\text{NIR},m} - \hat{x}_{\text{REF},m})^2} \quad (4)$$

In eq. (4), the index m is running over the M samples taken from the reactor at M different points in time during the batch reaction. The value $\hat{x}_{\text{NIR},m}$ is the predicted conversion for the reaction mixture and $\hat{x}_{\text{REF},m}$ is the conversion of the sample, drawn from the reactor at the same point in time and analyzed with the at-line SEC reference method.

Also, the systematic difference between the at-line reference method and the on-line NIR method during a batch run is calculated as

$$\text{SDIFF} = \frac{1}{M} \sum_{m=1}^M (\hat{x}_{\text{NIR},m} - \hat{x}_{\text{REF},m}) \quad (5)$$

The meaning of the symbols in this equation is the same as in eq. (4).

EXPERIMENTAL

Chemicals

Nonreacting calibration mixtures were prepared from Styrene 99+% (Acros Organics) and Polystyrene (Acros Organics, $M_w = 1.4 \times 10^5$ g/mol, PDI = 2.6). Reaction mixtures for polymerization monitoring were prepared from dissolving the initiator AIBN (2,2'-Azobis(2-methyl-propionitrile) 98%, Acros Organics) in styrene p.a. (Acros Organics, 99.9%), after removal of the inhibitor by adsorption with Al_2O_3 (Riedel-Dehaën, basic activity for column chromatography).

Reactor Setup

In Figure 1 the experimental setup is shown schematically. From the 80-mL stirred reactor (A) of which the temperature is controlled by a separate temperature control system ($\pm 0.1^\circ\text{C}$), the reaction mixture was transported through a jacketed sample loop by a micro gear pump (B; Ismatec, Z-1830 with PEEK gears). The selected flow rate is 90 mL/min, which amounts to an average residence time of the reaction mixture in the sample

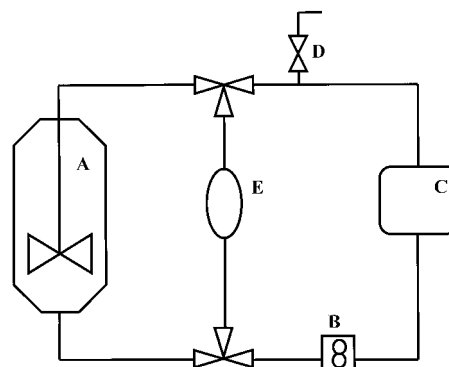


Figure 1 Experimental setup: (A) stirred polymerization batch reactor; (B) microgear pump; (C) flow cell and FT-NIR spectrometer; (D) sample port; (E) reservoir.

loop of less than 2 min. In the sample loop a dedicated, in-house made spectroscopic flow cell (C), having Quartz (Hellma, Benelux) windows is present. This flow cell (optical path length: 2.0 mm) is placed in a Fourier Transform Near Infrared spectrometer (BOMEM, Quebec, Canada, MB155) that contained an InAs detector module. A spectral resolution of 4 cm^{-1} was selected. The temperature of the flow cell and sample loop is controlled ($\pm 0.1^\circ\text{C}$) independent of the temperature of the batch reactor. In the recycled part of the sample loop a sample port (D) enables the drawing of samples from the reaction mixture. These samples were analyzed at-line. The portable sample reservoir (E) facilitates running the calibration experiments. It was also used to fill the reactor setup with monomer prior to each batch run.

Acquisition and Processing of NIR Spectra

In all batch experiments each minute a single-beam spectrum is recorded of the styrene–polystyrene mixture in the flow cell. Such a single-beam spectrum is based on 30 scans, and has a wave number range of 3500 to $10,000 \text{ cm}^{-1}$ (spectral resolution: 4 cm^{-1}). This task was performed by a dedicated Visual Basic 4.0 program running under Windows 3.11, making use of the BOMEM windows acquisition driver (Version 1.0, 1996). The collected single beam spectra were imported into MATLAB (The MathWorks, Inc.; Version 5.2, 1997), in which all further data processing was performed. Calibration models were built from the spectra, using the PLS Matlab toolbox (Eigenvector Research, Inc.; Version 2.01c 1999).

Table I The Validation Experimental Design for Six Validation Batch Runs

	$T = 70^{\circ}\text{C}$	$T = 75^{\circ}\text{C}$	$T = 80^{\circ}\text{C}$
$C_1 = 0.030 \text{ mol/L}$	$M_w = 70 \text{ kg/mol}$ $x = 22\%$ $t_{\text{run}} = 2 \text{ h}$ Batch: 3		$M_w = 48 \text{ kg/mol}$ $x = 27\%$ $t_{\text{run}} = 1 \text{ h}$ Batch: 4
$C_1 = 0.015 \text{ mol/L}$		$M_w = 80 \text{ kg/mol}$ $x = 40\%$ $t_{\text{run}} = 3 \text{ h}$ Batch: 1, 2	
$C_1 = 0.005 \text{ mol/L}$	$M_w = 184 \text{ kg/mol}$ $x = 13\%$ $t_{\text{run}} = 3 \text{ h}$ Batch: 5		$M_w = 130 \text{ kg/mol}$ $x = 29\%$ $t_{\text{run}} = 3 \text{ h}$ Batch: 6

The reactor temperature (T) and the initiator concentration (C_1) are varied. The final monomer conversion x and the number average molar mass M_w according to a kinetic model of the reaction are supplied. t_{run} is the batch run time.

Calibration Experiments

In these experiments a nonreacting styrene/polystyrene mixture with known conversion flowed through the sample loop. To build a calibration model that has a high sensitivity for conversion of the mixtures and is rather insensitive to temperature effects, the next calibration experimental design was chosen. Prepared nonreacting styrene-polystyrene mixtures having known conversions of 1.00, 2.01, 4.98, 5.01, 10.00, 14.81, 19.97, 24.99, 25.07, 29.96, and 34.42%, were all measured at three different temperatures (70, 75, and 80°C) in the experimental setup. The selected temperature range of 10°C covers the maximally expected temperature variation during a batch run. During a period of 11 min NIR spectra were recorded. The mean absorbance spectrum measured in these 11 min was used for calibration. After data processing, the obtained absorbance spectra were divided into 11 subsets. Each subset contained the absorbance spectra that were recorded from a single calibration mixture at three different temperatures.

Validation Experiments

Prior to each batch run the appropriate amount of AIBN was dissolved in 135 g of purified styrene. This monomer was transferred into the reservoir (E). The experimental setup was already heated to the desired batch temperature and flushed with nitrogen. The microgear pump (B) was used to pump the solution from the reservoir to the reactor. As soon as the reservoir was emptied, the recycling of the reactor mixture through the flow

cell was started. At this point in time the data-acquisition of the NIR spectra was started.

At regular time intervals during the batch run 15 samples ($\sim 1 \text{ mL}$) were taken of the reaction mixture using the sample port (D). These samples were dissolved in 50 mL THF to halt the polymerization reaction. For batches with a run time of 3 h this time interval was approximately 12.5 min. For batches with a smaller run time this interval was selected to be 4 or 8 min. These samples of the reaction mixtures were analyzed at-line for monomer conversion and off-line for the MMD of the polymer.

A total of eight batch runs were performed. The validation experimental design for six of these runs is listed in Table I. The reactor temperature and the initiator concentration were varied in this design. According to the kinetic model of the reaction¹¹ this should result in considerable changes in the final weight average molar mass M_w and the final monomer conversion x . To study the effect from changing temperature and MMD on the on-line conversion measurement, during the batch reaction, two additional batch runs were performed. In one run (batch 7) the temperature of the reaction mixture was increased with 10°C after 1 h ($0.5^{\circ}\text{C}/\text{min}$). In the other experiment (batch 8) the initial AIBN concentration of 1 mmol/L was increased after 1 h to approximately 45 mmol/L.

At-Line Reference Method for Conversion

A modified size-exclusion chromatography method was used as the at-line reference method for the

determination of the conversion of the styrene–polystyrene mixture. The validation of this reference method showed¹² that the accuracy of the method is better than 0.30% conversion, and that no significant bias is present. Furthermore, it was established that the method is not sensitive to changes in the molar mass distribution of the styrene polymer.

Off-Line MMD Measurement

Size-Exclusion Chromatography (SEC) was performed in a setup that consisted of a solvent delivery system with an in-line eluent degasser, integrated injector, and a column oven (Waters, separation module model: 2690 chm/dg). Two separation columns were used in series (Waters, type: Styragel HR4E and HR5) at a temperature of 35°C. Tetrahydrofuran (Acros Organics, p.a.) was used as the eluent at a flow rate of 0.35 mL/min. A differential refractive index detector (Waters, model: 410) was used. Chromatograms were recorded with a personal computer with SEC-software (Waters, Millennium Chromatography Manager 2.0 with GPC add-in). From the measured MMD the weight averaged molar mass (M_w) and the polydispersity index (PDI) were calculated.

RESULTS AND DISCUSSION

Exploratory Analysis

The absorbance spectrum of styrene with nitrogen as a reference is shown in Figure 2(A). Some

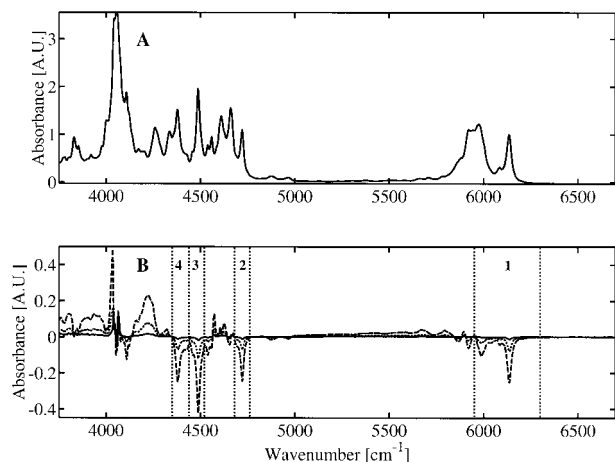


Figure 2 (A) Absorbance spectrum of styrene. N_2 is used as a reference. (B) D -spectra calculated using eq. (1). Conversion of the polystyrene mixtures: 2.01% (solid line), 10.00% (dotted line), and 29.96% (dashed line).

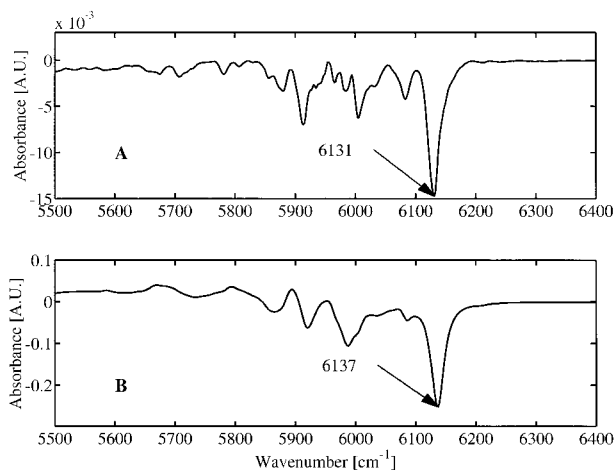


Figure 3 The relative impact of temperature on the NIR spectra. (A) Difference between the absorbance spectra of styrene at 80°C and at 70°C. (B) difference between absorbance spectrum of styrene/polystyrene mixture with conversion 34.42% and the absorbance spectrum of styrene. Wave numbers at which minima occur are indicated.

of the D -spectra that were calculated according to eq. (1) are shown in Figure 2(B). This figure clearly shows that styrene–poly(styrene) mixtures with different conversions have a pronounced effect on the NIR spectrum. Several seemingly distinct bands at, for example, 4380, 4488, 4721, and 6137 cm^{-1} of which the intensity decreases with increasing conversion level can be distinguished. In some wider wave number ranges at, for example, 3850–4000 cm^{-1} or 4130–4300 cm^{-1} the intensity is increasing with increasing conversion. The impact of temperature on these spectra for the wave number range from 5500 to 6400 cm^{-1} is separately shown in Figure 3(A). Comparing this figure with Figure 3(B) it can be observed that the effect on the absorption of a 10°C increase of temperature is about an order of magnitude smaller than the effect on the absorption of a 30% increase of the conversion. Furthermore, the shape of spectral differences caused by temperature is similar but not the same as the shape of the spectral differences caused by conversion. Also, the minima of both difference spectra do not coincide, for example, the minima in the Figure 3(A) and Figure 3(B) do not coincide. A calibration model may take advantage of these differences between the concentration and the temperature effect on the NIR spectra, to make concentration estimates insensitive to temperature changes.

Table II Calculated RMSECV Values for Several Wave Number Ranges

Wave Number Range [cm ⁻¹]	Symbol in Figure 2	Number of Factors in PLS Model		
		3	4	5
5950–6300	1	0.34	0.13	0.15
4680–4760	2	0.25	0.31	0.69
4440–4520	3	1.26	1.06	0.92
4350–4440	4	1.27	1.19	0.83

Calibration Experiments

Inverse calibration models according to eq. (2) were built using the PLS algorithm. The mean centered D -spectra of the styrene–poly(styrene) mixtures of the calibration experimental design were used as the \mathbf{R} matrix, and the mean centered known conversions of the mixtures were used as the vector \mathbf{x} . The calibration set consists of 36 samples (3 temperatures and 11 conversion levels, one sample was measured in duplicate).

The aim is to calibrate for the conversion of the reaction mixture and make this calibration insensitive to temperature changes of the reaction mixture. A leave-more-out crossvalidation procedure was used to establish the number of latent vectors (LVs) that should be retained in the PLS calibration model. The subset left out in one crossvalidation cycle consists of D -spectra of a sample having the same conversion measured at different temperatures. Using a leaving-one-out crossvalidation instead would result in a too optimistic estimate of the prediction error.¹³ By using the measurements at all different temperatures a global¹⁴ calibration model is built. In such a global model the temperature of the reaction mixture is implicitly treated as an unknown interferent.

The RMSECV is calculated for each number of factors in the PLS model:

$$\text{RMSECV} = \sqrt{\frac{1}{I} \sum_{i=1}^I (\hat{x}_{\text{NIR},i} - x_{k,i})^2} \quad (6)$$

The index i is running over the samples. The symbol $\hat{x}_{\text{NIR},i}$ represents the predicted conversion for sample i using a calibration model that was built without using the spectra measured for sample i at different temperatures. Table II shows the

RMSECV as a function of the number of LVs (three to five) in the PLS model and as a function of some selected wave number ranges in which the absorbance decreases with increasing conversion. The wave number range around the band at 6130 cm⁻¹ has the lowest RMSECV for 4 LVs in the calibration model. In this wave number range it is known that several bands are caused by vibrations linked to the C=C bond of styrene.^{15,16} Figure 4 shows that when the wave number range from 5950 to 6300 cm⁻¹ is used a more parsimonious three-factor PLS model can be built for offset corrected spectra. The offset of each NIR spectrum was estimated by taking the mean absorption in the wave number range from 6492 to 6536 cm⁻¹. This offset in the NIR spectrum is probably caused by instrumental drift. When using offset-corrected NIR spectra for building a three-factor calibration model an RMSECV value of 0.13% was achieved. Using the uncorrected, raw spectra a four-factor calibration model was needed to get the same performance. The RMSECV curves for both models show an increase of the RMSECV when more than six factors are included. This increase is caused by overfitting of the calibration data by the multivariate model.

A plot of the scores against the conversion of the sample shows that the conversion effect is described by the first factor of the PLS model. The scores on the second factor neither seem to have a systematic relation with the conversion of the sample, nor with the temperature of the sample.

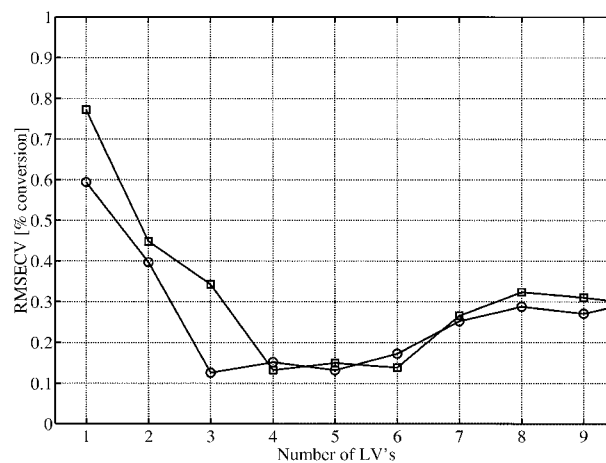


Figure 4 RMSECV values calculated with eq. (6) as a function of the number of LVs in the PLS model: \circ = offset corrected spectra; \square = nonoffset corrected, raw spectra. The wave number range 6492–6536 cm⁻¹ was used to estimate the offset.

Increasing the temperature of the sample for some conversion leads to an increase of the score on the second factor (at a conversion of 1, 5, 15, and 25), but may also to a decrease (at other conversions). Figure 5 shows a score plot for the third factor in the PLS model. A measurement on the *same* sample at a temperature of 80°C (symbol Δ) always results in a higher score on the third factor than a measurement at a lower temperature of 70°C (∇). The third factor in the PLS model thus (partly) describes the interfering temperature effect on the NIR spectra. It seems that, additionally, the third factor in the PLS model also accounts for a slight nonlinear dependence of absorbance of the NIR spectra on the conversion of the sample.

The three-factor PLS model, based on the offset-corrected NIR spectra (wave number range: 5950–6300 cm^{-1}), was further used for the prediction of monomer conversion during the batch experiments.

Validation Experiments

Before performing the validation experiments it was checked that the addition of the AIBN initiator to styrene did not have any measurable effect on the NIR spectra of styrene. For each of the eight batch runs the conversion values as determined by the at-line reference method and by the NIR method are compared. The RMSEP calculated according to eq. (4) is a measure for the accuracy of the NIR method. Because it is known that the at-line reference method is almost unbiased,¹⁴ the value of SDIFF gives an indication of the bias of the NIR method.

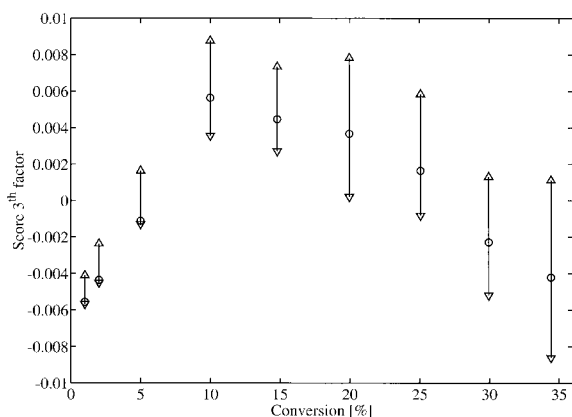


Figure 5 Scores on third factor of PLS model against known conversion of the sample. Δ : measurements at 80°C. \circ : measurements at 75°C. ∇ : measurements at 70°C.

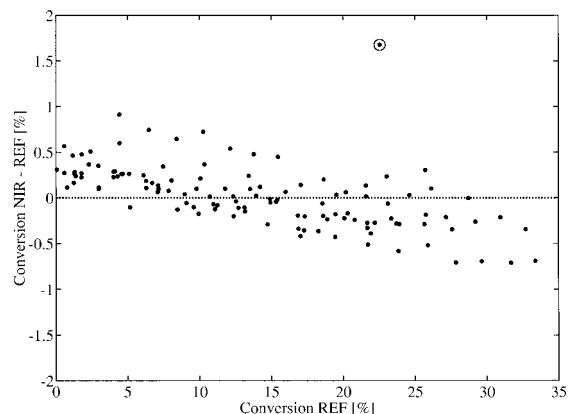


Figure 6 Difference in conversion value (NIR-REF) vs. conversion, as determined with the reference method (REF). The outlier of batch run 6 marked with a circle.

In Figure 6 the conversion residual, i.e., the conversion value as predicted by NIR method minus the conversion value as determined by the reference method, is plotted as a function of conversion determined by the reference method. The residuals for all batch reactions are plotted. In batch 6 one sample (marked by extra circle in Fig. 6) measured by the XSEC reference method is clearly deviating. This could be traced back to a sampling error for that particular sample. It can also be observed that overall a very slight downward trend is present. For lower conversions the NIR method tends to slightly overestimate, and for higher conversions to slightly underestimate the value produced by the at-line reference method.

In Table III the values for RMSEP and SDIFF are collected. The outlying reference measurement during batch 6 is removed before calculation. For most batches the SDIFF of the NIR method is very small, and the accuracy of the method is dominated by the random error. Only for batches 1 and 4 the SDIFF values are somewhat larger. The averaged RMSEP over all batch runs is 0.32% conversion. This value is comparable to the known accuracy of the at-line reference method (0.30% conversion). This shows that, overall, the NIR method hardly adds any uncertainty to the conversion measurement.

In Figures 7 and 8 the conversion curves are shown for the batch runs 7 and 8, respectively. For batch 7 the disturbance in the conversion caused by the temperature change that starts at $t = 1$ h can be tracked well by the NIR method. In fact, tracking of detection of such disturbances by

Table III The RMSEP and the SDIFF for the Validation Experiments

Batch Number	T (°C)	C_1 (mmol/L)	Measured M_w (end of run) (kg/mol)	RMSEP (% conversion)	SDIFF (% conversion)
1	75	15	89	0.48	-0.35
2	75	15	89	0.24	-0.12
3	70	30	68	0.19	-0.06
4	80	30	46	0.48	0.40
5	70	5	161	0.26	0.18
6	80	5	112	0.24 ^a	0.06 ^a
7	70 ^b	5	139	0.19	-0.03
8	70	1 ^c	76	0.28	0.17

The reactor temperature (T) and the initiator concentration (C_1) at the start of the batch reaction are listed as well.

^a Outlier for reference method removed (see text).

^b Temperature was increased from 70°C to 80°C after 1-h run time (0.5°C/min).

^c After 1-h run time the initiator concentration was increased to 44 mmol/L.

NIR has improved compared to the reference method. In batch 7, some variations in the reactor temperature occur after $t = 1$ h. These variations can be ascribed to the interaction of the two temperature controllers that were used: the controller of the reactor temperature, and the controller of the flow cell/sample loop. Figure 7 shows that also these undesired temperature variations do not result in a deviation between the conversion as estimated by the NIR and by the reference method.

In batch 8, an extra amount of initiator was added at $t = 1$ h. Note how fast the increase of the conversion of the batch process can be monitored by the NIR method.

In Figure 9, the conversion residuals (NIR method minus reference method) are plotted as a

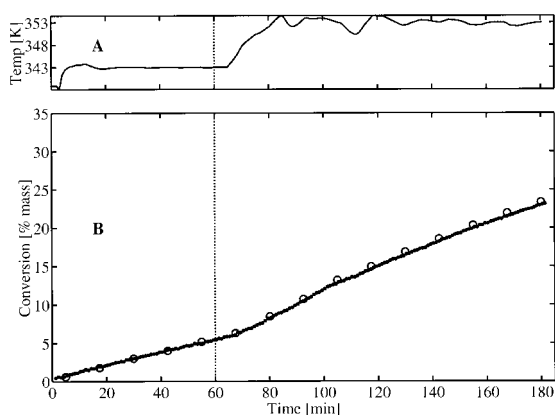


Figure 7 Results for batch run 7. (A) Measured reactor temperature; (B) \circ = conversion determined by the reference method; \bullet = conversion determined by the NIR method. Vertical dotted line indicates $t = 1$ h.

function of the measured weight average molecular weight (M_w) of the samples drawn at each batch. It can be observed that no pattern emerges as a function of M_w . This indicates that the size of the conversion residuals does not depend on the M_w .

All these results indicate that the developed NIR method only measures the monomer conversion, and that the method is neither sensitive to considerable changes in actual temperature of the reaction mixture nor to the actual molecular weight distribution of the polymer, and is able to pick up deviating batch behavior very quickly.

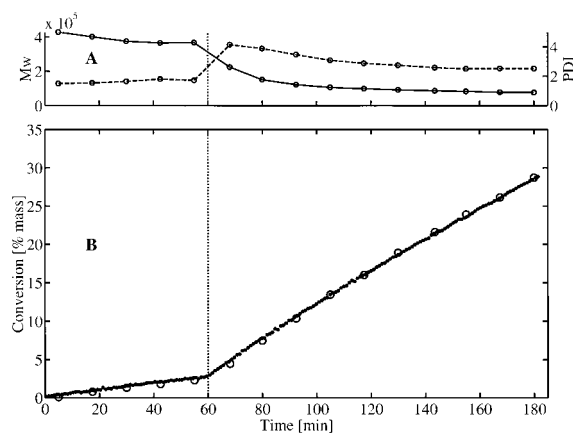


Figure 8 Results for batch run 8. (A) Solid line = measured weight average molecular weight of polymer (M_w , left y-axis); dashed line = measured polydispersity of polymer (PDI, right y-axis) (B) \circ = conversion determined by the reference method, \bullet = conversion determined by the NIR method. Vertical dotted line indicates $t = 1$ h.

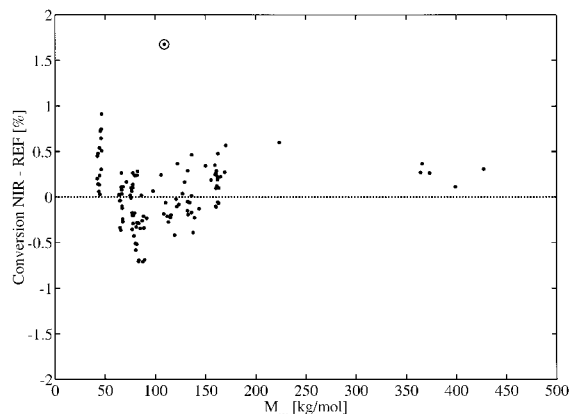


Figure 9 Difference in conversion value (conversion according to the NIR method minus conversion according to the reference method) vs. weight average molecular weight (M_w) of the reaction mixture for all batch reactions. Outlier of batch run 6 marked with a circle.

These properties of the NIR method allow a better operation of batch polymerization reactions.

CONCLUSIONS

The monomer conversion in a batch reactor was measured on-line with near infrared spectroscopy, during bulk polymerization of styrene with AIBN. The analysis time of this method is small (< 1 min) compared to the batch time (> 1 h) of the polymerization. The influence of the temperature of the reaction mixture on the predicted conversion was minimized by building a global multivariate calibration model.

In calibration experiments the range of wave numbers that yielded the lowest prediction errors was the range from 5950 to 6300 cm^{-1} . This range contains bands linked to vibrations of the C=C bond of styrene. The used calibration model is based on offset corrected NIR spectra and contains three LVs. It could be shown that the conversion effect on the NIR spectra is mainly modeled by the first factor, and that part of the temperature effect on the NIR spectra is partly modeled by the third factor of the calibration model.

In designed validation batch runs the monomer conversion could be predicted with an accuracy (viz. 0.32% conversion) that is comparable to the known accuracy of the at-line reference method.

These runs also showed that the method is insensitive to either changes of the MMD or of the temperature (changes of at least 10°C) of the reaction mixture and is able to detect abnormal behavior during a batch quickly. It is concluded that the proposed on-line NIR method is a fast, very robust, and accurate method for monitoring the conversion of styrene monomer.

The mechanical workshop of the Department of Chemical Engineering of the University of Amsterdam is greatly acknowledged for constructing the major parts of the experimental setup. We would like to dedicate the presented achievements to the remembrance of Erik Jongepier, who made an important contribution to this project.

REFERENCES

1. Yoo, K. Y.; Jeong, B.; Rhee, H. *Ind Eng Chem Res* 1999, 38, 4805.
2. Ellis, M. F.; Taylor, T. W.; Jensen, K. F. *AIChE J* 1994, 40, 445.
3. Gupta, S. K.; Mankar, R. B.; Saraf, D. N. *Ind Eng Chem Res* 1998, 37, 2436.
4. Arotçarena, M.; Armitage, P. D.; Asua, J. M.; Guigliotta, L. M.; Leiza, J. R. *Ind Eng Chem Res* 1995, 34, 3899.
5. Morbidelli, M.; Siani, A.; Storti, G. *J Appl Polym Sci* 1999, 72, 1451.
6. Leiza, J. R.; de la Cal, J. C.; Montes, M.; Asua, J. M. *Process Control Qual* 1993, 4, 197.
7. Dallin, P. *Process Control Qual* 1997, 9, 167.
8. Aldridge, P. K.; Burns, D. H.; Callis, J. B.; Kelly, J. J. *Anal Chem* 1993, 65, 3581.
9. Booksh, K. S.; Kowalski, B. R. *Anal Chem* 1994, 66, 782A.
10. Martens, H.; Naes, T. *Multivariate Calibration*; Wiley: New York, 1989.
11. Lousberg, H. H. A.; Hamersma, P. J.; Iedema, P. D.; Ruitenber, E. *Ind Eng Chem Res*, submitted.
12. Lousberg, H. H. A.; Boelens, H. F. M.; Hoefsloot, H. J. C.; Schoenmakers, P.; Smilde, A. K. *Int J Polym Anal Char*, accepted.
13. Shao, J. *J Am Stat Assoc* 1993, 88, 486.
14. Wulfert, F.; Kok, W. Th.; Smilde, A. K. *Anal Chem* 1998, 70, 1761.
15. Osborne, B. G.; Fearn, T.; Hindle, P. H. *Practical NIR Spectroscopy with Applications in Food and Beverage Analysis*; Longman Scientific Technical: UK, 1993.
16. Burns, D. A.; Ciuczak, E. W. *Handbook of Near-Infrared Analysis*; Marcel Dekker: New York, 1992.