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Beyers, C.P.; Boelens, H.F.M.; Klumperman, L.; Westerhuis, J.A.

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In-Line Reaction Monitoring of a Methyl Methacrylate and *N,N*-Dimethylacrylamide Copolymerization Reaction Using Near-Infrared Spectroscopy

C. P. BEYERS, H. F. M. BOELEN, L. KLUMPERMAN, and J. A. WESTERHUIS*

Polymer Research Division, BASF-AG, D-67056 Ludwigshafen, Germany (C.P.B.); Process Analysis and Chemometrics, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands (H.F.M.B., J.A.W.); and Dutch Polymer Institute, Laboratory of Polymer Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands (L.K.)

Fast and accurate monitoring of monomer concentration during copolymerization reactions is of much interest. It is known that near-infrared spectroscopy (NIRS) can be used to monitor polymerization reactions. Here, a free radical solution copolymerization reaction between methyl methacrylate and *N,N*-dimethylacrylamide is considered. NIR spectra were measured in-line with a transreflectance probe. The spectra of both involved monomers are very similar, making monitoring with NIRS challenging. It is shown that the NIRS calibration can be set up with only a few (5) off-line measured mixtures. Several validation methods for such a NIRS calibration model are discussed and tested. NIRS is used to follow conversion of the two monomers in a copolymerization reaction on-line.

Index Headings: Near-infrared spectroscopy; Multivariate calibration; Partial least squares; PLS; Net analyte signal; Copolymerization; Methyl methacrylate; *N,N*-Dimethylacrylamide; Validation.

INTRODUCTION

Our final purpose is to control the end properties of the products resulting from copolymerization reactions. These properties depend strongly on the molecular weight, molecular weight distribution, amount of branching, and the inter-molecular as well as the intra-molecular chemical composition distribution (CCD) of the copolymer molecules.¹ It is well established in the literature that the terminal unit model (TUM)² gives a good description of the CCD of the copolymers formed, even though it does not give a fully adequate description of the average propagation rate constant when using the same set of rate parameters. According to the TUM, the ability to control the CCD of copolymer molecules is directly dependent on the ability to control the instantaneous monomer concentrations in the reactor. To accomplish this goal, the first step was to set up a calibration model for the on-line monitoring of the monomer concentrations. This article deals with the best way to set up and validate the monitoring of individual monomer concentrations in a copolymerization reaction using near-infrared spectroscopy (NIRS).

To control the CCD, a closed-loop control strategy with in-line NIRS instead of an open-loop control was selected. Open-loop control is inferior since the monomer addition rate strategies depend on an assumed true kinetic model. However, the kinetics of copolymerization reactions are complex and the kinetic coefficients such as the

termination rate coefficient are mostly not constant, but depend on a number of properties such as the chain length of the polymer molecules.³ In contrast, a closed-loop control strategy uses an in-line sensor that provides close to real-time information about the concentrations of reactants and products in the reactor. A prerequisite is that the sampling rate should be faster than the kinetics of the reaction.

Different techniques are described in the literature to control chemical reactions via closed-loop control strategies.⁴ With recent advances in gas chromatography (GC) columns it is possible to perform fast measurements that are ten times faster than with mainstream technology. However, analyzing the reaction mixture in GC is cumbersome since the high viscosities involved in not only this particular reaction, but these reactions in general, may cause fouling and eventual clogging of the sampling lines. Of all the in-line methods, vibrational spectroscopy not only allows the quantification of individual concentrations, but the analysis time is on the order of a minute. Therefore, it is possible to follow the kinetics of chemical reactions even if the reaction rates are high. Furthermore, with fiber optics it is also possible to measure with a probe inside the reaction mixture. A very thorough overview of on-line reaction monitoring using spectroscopic sensors is given in several references.^{5–8}

The copolymerization reaction of methyl methacrylate (MMA) and *N,N*-dimethylacrylamide (DMAAm) (shown in Scheme 1) in toluene is considered here. Monitoring such a copolymerization reaction with NIRS is particularly challenging because both monomers have very similar NIR spectra. Furthermore, there were a number of interfering substances (solvents and copolymer) present whose concentrations were not constant during the reaction. The aim of this study is to illustrate how to set up a calibration model for the quantification of individual monomers in a solution copolymerization reaction using NIR spectroscopy. A partial least-squares (PLS) calibration model was built for each monomer. It is shown that by applying the net analyte signal (NAS), initial wave-number ranges of interest for the determination of monomer concentrations can be determined quickly. Furthermore, it will be shown that, even though it is believed that making a calibration model for NIR is an elaborate task, only a few measurements were needed to set up a robust model. Attention is also paid to the best way to validate the calibration model. A reaction in which both monomers were individually spiked was experimentally

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* Author to whom correspondence should be sent. E-mail: westerhuis@science.uva.nl.

Scheme 1. The structure of (a) MMA and (b) DMAAm.

performed especially for validation purposes. Such an experiment is an excellent way to validate the calibration model for these kinds of reactions.

THEORY

Calibration. To relate the NIR absorbance spectrum of a process sample to the amount of monomer in the reactor, a first-order calibration model⁹ is needed. For each monomer, an inverse least-squares model (ILS) was used. In this model the $(I \times 1)$ column vector $\mathbf{c}_{\text{cal}}$, containing the concentration of monomers in the calibration samples, is described by Eq. 1:

$$\mathbf{c}_{\text{cal}} = \mathbf{R}_{\text{cal}}^T \mathbf{b} + \mathbf{e}_c \quad (1)$$

In this equation the $(J \times I)$ matrix $\mathbf{R}_{\text{cal}}$ contains the measured NIR absorbances at J wavenumbers for the I calibration mixtures, the $(I \times 1)$ vector $\mathbf{e}_c$ contains the concentration errors, and the $(J \times 1)$ vector $\mathbf{b}$ contains the regression coefficients. These regression coefficients were estimated by PLS. The number of latent variables (LV) needed in the PLS model was determined by a leave-one-out-cross-validation. For each number of LVs in the model the prediction error of all samples and the root mean square error of cross-validation (RMSECV) was calculated. The number of LVs for which the first local minimum of the RMSECV occurred is used.

The regression vector $\mathbf{b}$ for the selected PLS model can be used to predict the monomer concentration for unknown samples with Eq. 2:

$$\hat{c}_{\text{un}} = \mathbf{b}^T \mathbf{r}_{\text{un}} \quad (2)$$

in which the $(J \times 1)$ vector $\mathbf{r}_{\text{un}}$ is the NIR spectrum of the unknown mixture to be analyzed, and the scalar $\hat{c}_{\text{un}}$ is the predicted concentration of the monomer in the mixture.

Internal Validation. Two types of validation were used to evaluate the calibration models thoroughly. We like to distinguish between “internal” and “external” validation of the calibration model. The internal validation consists of the prediction of the monomer concentration of *prepared* samples, measured offline, which were *not* used for the calibration model. The physical properties of these M samples are much like those of the calibration samples that were used to build the model. The RMSEP as defined by Eq. 3 was used to measure the performance of the calibration model:

$$\text{RMSEP} = \left[\frac{1}{M} \sum_{i=1}^M (c_i - \hat{c}_i)^2 \right]^{0.5} \quad (3)$$

in which c_i is the known monomer concentration of the validation sample and $\hat{c}_i$ is the predicted monomer con-

centration according to the calibration model. A lower RMSEP value means a better calibration model. The RMSEP is a good indicator of standard deviation of the lowest prediction errors that may be achieved by the monomer calibration model. Because the reaction mixture will have other physical properties (viscosity, etc.) than the prepared samples, the physical properties of the reaction mixture may be altered. In general, higher prediction errors are therefore expected.

Due to, e.g., the instrumental noise, a calibration model never explains all measured spectral variation. The part of the spectrum ($\mathbf{r}$) of the sample, i , that is not explained by the model is called the spectral residual vector. For each sample, this vector ($\mathbf{e}_i$) was calculated using Eq. 4:

$$\mathbf{e}_i = \mathbf{r} - \mathbf{P} \mathbf{t} \quad (4)$$

in which $\mathbf{t}$ is the x-score matrix and $\mathbf{P}$ is the x-loading matrix of the PLS model used.¹⁰ The root mean square value (RMSE) of $\mathbf{e}_i$ was used as a measure of the spectral variation of the sample i not explained by the model.

External Validation. As already stated, during the copolymerization reactions, the physical properties of the reaction mixture are different from the prepared samples. Two polymerization reactions were performed for validation purposes to assess the impact these effects have on the prediction errors. The monomer concentrations as predicted by each calibration model during a normal copolymer reaction were compared to the monomer concentration measured in samples drawn from the reactor during the experiment. These drawn samples were analyzed with GC. An experiment was also performed to further validate the calibration models. In this reaction, two well-defined shots of MMA and DMAAm, respectively, were added to the reaction at two different times. The main purpose was to determine the sensitivity of the concentration predictions of the PLS model for one monomer when the other monomer was added.

Net Analyte Signal. The NAS for any analyte ($\mathbf{r}^{\text{nas}}$) is defined as that part of the spectrum of the analyte that is orthogonal to the space spanned by the spectra of all other compounds in the mixture. The NAS is, therefore, unique for the analyte of interest.¹¹

The NAS was of interest to us for two reasons. Firstly, we used NAS to find promising wavenumber ranges for the quantification of the monomers. The spectra of the pure compounds were used to calculate the NAS vector of each monomer with respect to the other monomer and the solvent. Wavenumbers that corresponded to high positive intensities in the NAS vector are unique for the specific monomer. At wavenumbers that have a high negative intensity, the interfering compounds dominate. Secondly, we used the NAS for the exact representation of the PLS model as a univariate graph as proposed by Faber.¹² The NAS direction ($\mathbf{r}^{\text{nas}}$) is proportional to the regression vector $\mathbf{b}$ of the PLS model defined in Eq. 5:

$$\mathbf{r}^{\text{nas}} = \frac{\mathbf{b}}{\|\mathbf{b}\|} \quad (5)$$

We project the spectra of calibration samples along this NAS direction. The length along this direction is called the NAS value ($y_{\text{cal}}^{\text{nas}}$) given by Eq. 6:

$$y_{\text{cal}}^{\text{nas}} = (\mathbf{r}^{\text{nas}})^T \mathbf{r}_{\text{cal}} \quad (6)$$

The plot of these NAS values against the known concentrations, c_{cal} , of the calibration samples yields a univariate representation of the PLS model. Visually, such a plot may be treated as a conventional univariate calibration plot. For example, points that are far from the calibration line are suspected outliers and the slope of the curve provides information about the sensitivity of the method for the monomer.

EXPERIMENTAL

Materials. The monomers, MMA and DMAAm (>99%, Aldrich), were purified from inhibitor by passing them over a basic Al_2O_3 column (Aldrich). Toluene (Bio-solve) and α - α' -azobis-isobutyronitril (AIBN, Fluka) were used as received.

Gas Chromatography Setup and Measurements. Monomer conversion of the copolymerization reaction mixtures was determined by GC using an HP 5890 series II gas chromatograph equipped with an HP Ultra 2 cross-linked 5% Me-Ph-Si column (25 m $\times$ 0.32 $\times$ 0.52 μm film thickness) and fitted with a split injector. Samples were diluted in tetrahydrofuran (THF) (1/10 v/v) before 1 μL of the solution was injected with an auto sampler. A constant helium flow was used as the mobile phase. A glass liner was used to retain the polymer. After injection the injector temperature was raised from 50 to 150 $^\circ\text{C}$ at 12 $^\circ\text{C}$ per minute. The flame ionization detector (FID) was kept at a constant temperature of 250 $^\circ\text{C}$. The oven temperature was started at 40 $^\circ\text{C}$ for 2 min, raised to 60 $^\circ\text{C}$ at 5 $^\circ\text{C}$ per min, and then raised to 150 $^\circ\text{C}$ at 10 $^\circ\text{C}$ per min. The total analysis time was 15 min. Toluene, the solvent for the reactions, was used as the internal standard. All samples were injected twice to improve the accuracy of these measurements.

Near-Infrared Setup and Measurements. All NIR measurements were performed with a BOMEM MB 155 spectrometer. The probe was connected to the spectrometer using optical fibers and a BOMEM optical interface. The open optical window of this setup runs from about 3850 cm^{-1} to 10000 cm^{-1} . A spectral resolution of 2 cm^{-1} was selected. In all measurements single-beam spectra based on 30 scans were recorded every 70 s. The transfectance probe (Hellma Ultra mini probe) had a 5 mm light path length (split width of 2.5 mm). The probe was washed extensively with THF and acetone before use. A spectrum of air was taken before each measurement to ensure that the probe was clean.

Near-Infrared Calibration and Internal Validation. One strategy to set up a calibration model consists of sampling a copolymerization reaction and measuring the samples by GC to obtain the concentrations of the monomers so they can be related to the NIR response. Another strategy is to prepare gravimetrically measured samples that can be used to set up a calibration model in an off-line way. Here, we selected the latter strategy since we believed that the amount of time spent on developing a calibration model is reduced. It was also possible to span the whole concentration range of interest more effectively.

To build a calibration model that has a high sensitivity, different concentrations of the monomers were individually measured in toluene. Samples of approximately 10

FIG. 1. Concentrations of the calibration and validation samples of MMA (black) and DMAAm (grey).

g were measured on a balance with an accuracy up to 0.5 mg. The sample concentration was varied beyond 2 mol/L, which was the maximum intended concentration to be used. For MMA and DMAAm five and six samples, respectively, were used to set up the calibration model. The samples used for the calibration and internal validation are given in Fig. 1.

The measurements were done in a sealed cuvette. The probe was inserted through a silicon rubber septum and submerged in the sample of known concentration. The temperature was measured using a temperature sensor that was placed in the solution. After the desired temperature of 80 ± 0.1 $^\circ\text{C}$ was reached, a single-beam spectrum was taken. For the calibration and internal validation samples, the spectra were recorded with WINBE Easy (BOMEM, version 3.01c, 1994).

Concentration calculations were made with density values measured at 25 $^\circ\text{C}$. All the mixtures contained the same amount of inhibitor to prevent unwanted polymerization during the measurements.

Reactor Experiments and External Validation. Each of the batch solution copolymerizations was performed in a cylindrical, jacketed, reactor of 250 mL. This reactor was filled with 100 mL of toluene. Subsequently, both monomers were added at concentrations of about 1.2 mol/L. When the temperature of the mixture reached 80 $^\circ\text{C}$, the initiator (AIBN) was added (0.02 mol/L). The reactor was fitted with a reflux condenser, the NIR probe, and a PT-100 temperature sensor in order to control the heating bath. The NIR probe was inserted through a silicon rubber septum and submerged into the reaction mixture. Samples (~1 mL) were taken from the reactor with a syringe and immediately diluted in 5 mL THF to which the inhibitor hydroquinone was added. These samples were analyzed by GC.

For data acquisition during the copolymerization reactions, a dedicated Visual Basic 4.0 program running under Windows 98, making use of the windows acquisition driver (BOMEM, version 1.0, 1996), was used. The collected single-beam spectra were imported into MATLAB (The MathWorks Inc., Natick, MA, version 6.1, 2001), in which all further data processing was performed. The PLS toolbox (Eigenvector Technologies,

FIG. 2. NIR absorbance spectra of (a) MMA, (b) DMAAm, and (c) toluene. The horizontal bars in the figure represent the wavenumber selections that are of interest for calibration purposes.

West Richland, VA, version 2.1, 2000) was used for the PLS modeling.

RESULTS AND DISCUSSION

Exploratory Analysis. During the initial experiments it was found that large changes in the fiber position would lead to small shape changes in the spectra. For this reason, the fibers were secured in a fixed position.

The absorbance spectra of toluene, MMA, and DMAAm are shown in Fig. 2. It has been verified that the concentration of initiator, inhibitor, and chain transfer agent is too low to have any effect on the measured spectra.

The part of the spectrum below $\sim 3800\text{ cm}^{-1}$ is not usable because of the high noise level caused by the limited transmission of the equipment (optical interface probe fiber), already near zero. Moreover, the maximum absorbance value for this setup is around 1.4 A.U. This is due to the construction of the transreflectance probe that allows part of the light that leaves the input optical fiber to return directly through the output fiber. So, part of the light does not enter the sample at all. From 4000 cm^{-1} to 4500 cm^{-1} , the major part of the spectrum has an absorbance value of 1.4 A.U. Because of this clipping effect, this part of the spectrum is not usable. Above a wavenumber of about 6500 cm^{-1} , only very little chemical information seems to be present and only bands with low absorbances can be seen. For the rest of the exploratory analysis, the wavenumber range from 4500 cm^{-1} to 6500 cm^{-1} was selected. In Fig. 3 the absorbance spectra of the calibration samples can be seen.

Some of the spectra have an offset from the zero absorbance line that needed correction. The largest offset errors were observed in spectra from samples containing polymer. To correct for this, the average absorbance in the wavenumber range $6350\text{--}6400\text{ cm}^{-1}$ was subtracted from all measured spectra (Fig. 4).

This part of the spectra was chosen since no significant absorbance could be detected. Any other pretreatment of the data did not result in a significant improvement of the predictive ability of the calibration model.

Wavenumber Selection. From previous studies, it is

FIG. 3. NIR absorbance spectra of the calibration samples. Note the differences in offset between the samples.

known that for MMA the wavenumbers 6163 cm^{-1} ($2\nu(\text{CH}_2=)$) and 4746 cm^{-1} (combination band of $2\nu(\text{CH}_2=)$ and $\delta(\text{CH}_2=)$) are expected to reflect changes due to the conversion of monomer to polymer.⁹ The NAS was used to get a first impression of which wavenumber regions are useful. The NAS vector of MMA (dashed line) with respect to DMAAm and toluene and the NAS vector of DMAAm (solid line) with respect to MMA and toluene are shown in Fig. 5.

The largest intensities of both NAS vectors can be seen in the region around 6163 and 4746 cm^{-1} . Another promising region seems to be the 5720 to 5880 cm^{-1} region. These regions are also indicated in Fig. 2. However, the absorbances in these regions relate to the vibrations in the N,N-substituted amide group of DMAAm as well as the ester group of MMA that is also present in the copolymer. The result is that during a normal copolymerization reaction, the absorbances at these wavenumbers are nearly constant. Only if monomer is added during the reaction did these absorbances show changes that were not due to volume changes alone. This wavenumber range could not be used because our target was to monitor the total available amount of each individual monomer in the reaction mixture at any point in time.

FIG. 4. Offset-corrected NIR absorbance spectra of the calibration samples.

FIG. 5. NAS vectors for MMA (dashed) and DMAAm (solid).

Three PLS models for each monomer were made to determine which wavenumber range yields the best predictive ability. The wavenumber ranges are shown in Fig. 5, and Table I shows the results.

The predictive accuracy of the various models was compared using a randomization test, where the internal validation residuals were used in the calculations.¹³ The size of the spectral residuals was calculated using Eq. 4, and the RMSECV was calculated with Eq. 3. From Table I, it can be concluded that for both DMAAm and MMA the wavenumber range between 6100 and 6300 cm^{-1} should be preferred when PLS models are used. For this range, the prediction errors of the DMAAm and the MMA model are smaller (a factor 8 for DMAAm and a factor 1.5 for MMA). Spectral residuals are also lower, indicating that all major contributions are captured in the PLS model for that region. As can be seen in Fig. 2, for the 4700–4800 cm^{-1} region the pure spectra of toluene and the two monomers are much closer to the 1.4 A.U. clipping limit than at 6100–6300 cm^{-1} . Moreover, monomer bands are situated on the steep slope of the toluene band at 4666 cm^{-1} . Both of these effects might explain why PLS models based on this wavenumber region are worse. For now, we will only consider the region from 6100 to 6300 cm^{-1} .

Calibration Model and Internal Validation. In Fig. 6, the pure spectra of MMA, DMAAm, and toluene can be seen in the chosen wavenumber range. The monomer bands are severely overlapping. To get the best quantification of the individual monomers, the highest possible wavenumber resolution, namely 2 cm^{-1} for this spectrom-

FIG. 6. NIR absorbance spectra of MMA (dashed), DMAAm (dotted), and toluene (dash-dot) in the selected wavenumber range after offset correction.

eter, was used. The dots on the spectra in Fig. 6 show the individual intensities as obtained with a resolution of 2 cm^{-1} . Both monomers, but especially DMAAm, suffer from an interference of the tail of the toluene band located at 6116 cm^{-1} . In the mixtures that were used, the ratio between the toluene band and the monomer bands increased due to a reduction in the monomer concentrations, increasing the influence of the tail of the toluene band. These facts make it challenging to achieve optimal predictions for both monomers. Even the slightest spectral disturbance in this region could lead to large prediction errors.

The results of the PLS models of MMA and DMAAm are presented in Figs. 7–9 and Tables I and II. The model for MMA required three latent factors and the model for DMAAm required four (Fig. 7 and Table I).

A possible explanation for the four LVs for DMAAm is the larger impact of the interference of toluene on the DMAAm band. The NAS representation of the PLS models (Fig. 8b) shows that all calibration samples are very close to a straight line through the origin. The higher slope of MMA (0.389) for the calibration curve has a sensitivity that is 1.5 times higher than that of DMAAm (0.256). The RMSEP for DMAAm is 41×10^{-3} mol/L and 26×10^{-3} mol/L for MMA. The lower sensitivity of DMAAm in comparison to MMA can also be seen if the two models are compared in Fig. 7. At three LVs, MMA has a lower RMSE for the calibration samples than that of DMAAm at four LVs.

TABLE I. Number of LVs, spectral residuals, and RMSECV for MMA and DMAAm at different wavenumber ranges.

Wavenumber range (cm^{-1})	MMA			DMAAm		
	4700–4800 and 6100–6300	4700–4800	6100–6300	4700–4800 and 6100–6300	4700–4800	6100–6300
#LVs in PLS model	2	3	3	2	3	4
Spectral residuals (A.U.)	0.028	0.150	0.004	0.300	0.150	0.001
RMSECV (mol/L)	0.048	0.039	0.026	0.126	0.104	0.012

TABLE II. RMSEC of the calibration samples and the RMSEP for the internal and external validation samples of MMA and DMAAm and the STD values of GC.

Monomer	RMSEC (mol/L)	RMSEP (mol/L) (internal validation)	RMSEP (mol/L) (external validation)	GC STD (mol/L)
MMA	0.026	0.026	0.045	0.034
DMAAm	0.012	0.041	0.061	0.050

In Fig. 8a the concentration residuals are plotted against the individual monomer concentrations for the calibration samples. The data is well scattered around zero mol/L, indicating that there is no visible pattern relating to the concentrations of the two monomers. Except for the scattered data around zero mol/L, two possible outliers are detected. We believe these outliers are due to experimental error since they did not have a significant effect on the quality of the model.

The root mean square of the spectral residuals (RMSE) of each calibration and validation sample is plotted in Fig. 9. The line is the instrumental noise level, which was calculated as 0.58×10^{-3} A.U. using repeated measurements of the background spectra. The spectral residuals as seen in Fig. 9 are somewhat larger than the instrumental noise level, showing some variation of the measured calibration spectra that is not modeled.

In general, at near zero concentrations larger errors are expected. Figure 8a shows that prediction errors of the two monomers are larger than for higher concentrations. This fact should be taken into account during control at extremely high conversions.

External Validation. During the reaction, some potential disturbing effects could occur. A limited increase of the viscosity of the reaction mixture occurs when the polymer is formed. This increase may reduce the mass transfer through the probe. In addition, due to the dissociation of AIBN, N_2 bubbles were formed in the reaction mixture. These bubbles passed through the light path and could affect measurements. It was seen that, especially at the start of the reaction, the temperature rose about 2 °C for approximately seven minutes before the

FIG. 8. (a) Residuals for calibration samples (○) MMA and (◇) DMAAm, and validation samples (△) MMA and (□) DMAAm. **(b)** NAS calibration curves for calibration samples (○) MMA and (◇) DMAAm, and validation samples (△) MMA and (□) DMAAm.

water bath fully corrected for the sudden change in temperature. This temperature change was due to the strong exothermic nature of the dissociation of the initiator. Other smaller temperature fluctuations (<0.5 °C) may also occur during the reaction.

To further validate the calibration models, a copolymerization reaction was performed. Known amounts of MMA and DMAAm were added to the reaction mixtures at different times.

Figure 10 shows that the prediction of MMA is not affected by the addition of a considerable amount of DMAAm to the reaction mixture, except for a small concentration change that is caused by the increasing reaction mixture volume. The same observation can be made for the prediction of DMAAm when MMA is added. The concentration changes of both monomers were also in close agreement with the 4 mL of each monomer that was added. Furthermore, since the NIR spectroscopy measurements are very fast, changes in the rate of polymerization, immediately after the monomer additions, are well identified by NIR spectroscopy and less clearly by GC. This shows that NIR spectroscopy is superior to

FIG. 7. RMSECV values at the different number of latent variables for MMA (solid) and DMAAm (dotted), respectively.

FIG. 9. Spectral residuals for the validation samples for MMA (□) and samples for DMAAm (▽).

FIG. 10. Fractional concentrations of (a) MMA ($\square$) and (b) DMAAm ($\triangle$) in a spiked copolymerization reaction.

GC when small changes in the kinetics of a system are under investigation.

To assess the impact of the mentioned physical effects on the prediction of the monomer concentration, the RMSEP of the internal validation samples were compared to the RMSEP of the external validation samples taken during the polymer reactions identified in Table II. Even though the RMSEP values for the external validation are larger for both monomers than that of the internal validation, the two sets of RMSEP values compare well with each other as well as with the standard deviation of the GC, also seen in Table II. In Fig. 11 the fractional concentrations of MMA and DMAAm in an ordinary solution copolymerization reaction can be seen. The NIRS measured concentrations here are also in close agreement with the GC measured concentrations.

Although the prediction error in the case of the reaction is larger than that of off-line validation samples, it can be concluded that the accuracy of NIR in the reactor is only slightly affected by physical changes that occur during the reaction.

Another observation is that the conversion of monomer to polymer can only be followed accurately up to a limited conversion. It is difficult to determine this maximum conversion since the reference method, namely GC, is less accurate at high conversion than NIR. Taking the detection limits¹⁴ for both monomers into account, the maximum reliable measured conversion for MMA is 95.7% and for DMAAm is 93.3%. Even so, it is well known that the polymer conversions seldom continue to 100% due to onset of the glassy state, and therefore, a conversion of 95% is adequate for control actions.

CONCLUSION

In this paper we showed that robust NIR calibration models (PLS) for monitoring two monomers in a solution

FIG. 11. Fractional concentrations of MMA ($\square$) and DMAAm ($\triangle$) in a solution copolymerization reaction.

copolymerization reaction could be built from only a few prepared calibration samples. This shows that a fast external calibration is possible. The models were thoroughly validated. Internal validation was performed using additional prepared samples while external validation under reaction conditions was done using GC as the reference method. The initial wavenumber selection was obtained with the net analyte signal methodology. The models proved to be robust against increasing polymer concentration during the reaction and also against temperature differences caused by the exothermic initiation of the reaction.

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