REAL-TIME MONITORING OF POLYURETHANE PRODUCTION USING NEAR-INFRARED SPECTROSCOPY

FRANK A. DeTHOMAS

NIRSystems, Inc , 12101 Tech Road, Silver Spring, MD 20904, U S A

JEFFREY W HALL*

NIRSystems, Inc , 127 Farquharson Building, York University Campus, 4700 Keele Street, Toronto,
Ontario, Canada M3J 1P3
Department of Clinical Biochemistry, Mount Sinai Hospital, 600 University Avenue, Toronto,
Ontario, Canada M5G 1X5

STEPHEN L. MONFRE

NIRSystems, Inc , 12101 Tech Road, Silver Spring, MD 20904, U S A

Summary—A process near-infrared (NIR) spectrophotometer was interfaced directly to a reactor by using a fiber optic bundle interactance immersion probe This remote sensor configuration enables the production of polyurethanes to be monitored in real-time A Beer's Law model was derived for the quantitative determination of isocyanate in the urethane polymerization reaction Statistical process control was used to observe trends in the polymerization reaction The integration of NIR process analytical instrumentation directly into the process provides real-time chemical information that yields improvements in product quality and consistency, while minimizing reaction time

In the process environment, the time required to obtain pertinent information about the status of a process is critical. Conventional process parameters that provide real-time information such as temperature, pressure, flow and pH do not supply all the necessary information essential for process control. While providing relevant chemical information about the process, traditional wet chemical techniques are time-consuming and often require manipulation of the sample in environmentally harmful solvents.

Although rapid analytical methods of analysis are a clear advantage for the quality control laboratory, the delay in getting relevant chemical information from the laboratory to the process can have a tremendous impact upon product quality or consistency. In fact, the product is often made before the laboratory results are received. To optimize chemical production, analytical instrumentation must be installed directly into plants and where possible, into the process stream itself. In-process analysis places all the chemical information necessary for

process control directly into the hands of plant personnel who can react quickly to real-time process information.

The absorption of near-infrared (NIR) radiation (*i.e.* 700–2500 nm or 14,000–4000 cm^{-1}) is most often associated with the overtone and combination bands of the fundamental molecular vibrations of organic molecules that appear in the mid-infrared (400–4000 cm^{-1}) region of the electromagnetic spectrum. Near-infrared absorptions have low absorptivity, large bandwidths and are highly overlapped. As a result, the NIR region was initially perceived as being too complex for interpretation, and the absorption bands were considered too weak for practical application. In fact, the weak absorption of NIR radiation by organic molecules is advantageous for both the laboratory and process environments. Direct analysis of highly scattering or strongly absorbing matrices with traditional spectroscopic methods of analysis such as UV/Vis and mid-IR is impractical due to limited penetration depths, excessive scattering and interfering absorptions. By contrast, the low absorptivity of NIR absorptions provides

*Corresponding author

greater pathlength flexibility and permits intact sample analysis to be performed for percent levels (> 0.1%) of components by diffuse reflectance or transmittance measurements. Furthermore, improvements in instrumentation and advances in data analysis techniques, that can extract vast amounts of chemical information from NIR spectra, has led to a prosperous growth in the application of NIR spectroscopy in laboratory and process measurements. Historically, NIR spectroscopy has been used in the food processing and agricultural industries.[1] The benefits of NIR spectroscopy are now being exploited in the polymer,[2] petrochemical[3] and pharmaceutical[4] industries The implementation of NIR process analyzers for process monitoring and process control applications is developing rapidly [5]

The production of polyurethanes is an example of the need for real-time chemical information In a typical urethane polymerization reaction, a diisocyanate reacts with a polyol or glycol to produce a polyurethane [6] Due to the high reactivity of the isocyanate functionality, it is necessary to monitor the reaction closely to optimize product formation and to minimize side reactions Current physical and chemical process control procedures cannot provide adequate information in a timely fashion To facilitate efficient process monitoring and control, real-time chemical information is necessary

Reaction-injection molded polyurethane systems have been studied with NIR spectroscopy.[7] In this investigation, we provide an extension of this earlier work by using NIR spectroscopy to monitor a urethane polymerization process reaction in real-time. This study is composed of three parts. In the calibration or first stage, a spectroscopic model is derived for the quantitative determination of isocyanate in a pilot plant reaction mixture. Secondly, the empirically derived calibration model is validated by using a distinct set of samples not used in the calibration stage to ensure robustness Finally, the spectroscopic model is used to monitor the disappearance of isocyanate in an actual polymerization process reaction in real-time

EXPERIMENTAL

Process configuration

NIR spectroscopic measurements were performed directly in a process stream by using fiber optics. Figure 1 illustrates a process configuration in which an NIR instrument is used as a remote sensor. In this configuration, the instrument is mounted close to the measurement point and uses relatively short lengths (1–15 m) of fiber optic bundle cables to interface the instrument to the process stream. This arrangement is essential as it allows for easy interface of the instrument to the process and more importantly enables the instrument to be isolated from the process. Chemical information about the process derived from the NIR spectrum can be monitored in the process control room, on the plant floor, or transferred to a process control computer via 4–20 mamp or RS232 outputs.
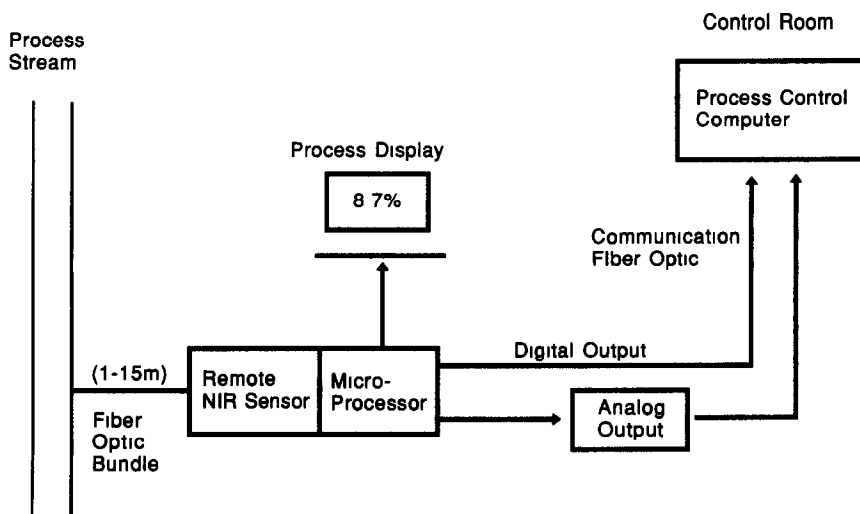

Fig 1 Near-infrared process analyzer configured as a remote sensor

Data acquisition and analysis

Studies were performed by using an NIRSystems, Inc., (Silver Spring, MD) Process Analytics^{tm} Interactance Immersion System in the spectral region from 1100 to 2500 nm. The spectrophotometer is protected from the process environment by using NEMA 4 (Hoffman, Anoka, MN) enclosures that meet the necessary process safety and temperature requirements (Class I, II, or III). The instrument was interfaced to the reactor by use of a 1 m interactance Anhydroguide (Fiberguide Industries, Stirling, NJ) fiber optic bundle terminated with a 1 inch diameter liquid immersion probe. The optical interface consists of a sapphire window fitted into the end of a 316 stainless steel probe with Kel-Rez (DuPont, Wilmington, DE) O-rings. This probe can withstand reaction pressures of 1000 psi and temperatures of 200°C. The fiber optic bundle contains concentric rings of illuminating (inner core, 420 fibers) and collecting (outer ring, 820 fibers) fiber optic bundles. The interactance immersion probe tip reflects light which passes through the sample (for translucent samples) from the illuminating bundle back to the collecting bundle providing a "double pass" through the sample. To ensure that the flow dynamics of the process stream were not disturbed and a representative sample was analysed, a 1 cm pathlength (0.5 cm gap) was used. Thirty-two coadded scans of each sample were referenced to 32 coadded scans of the reference channel. Total analysis time for each NIR spectrum was approximately 40 sec.

Communication with the instrument from the process control room was achieved through a RS232 modem and 30 m fiber optic communication cable.

Data acquisition, spectral mathematical treatments and linear least-squares regression analysis were performed by using the Near-infrared Spectral Analysis Software (NSAS) supplied with the instrument. Regression analysis was performed on the second-derivative of the absorbance data. The second-derivative calculation uses a moving average technique with segment size of 20 nm and gap size of 2 nm.

All process measurements were performed in a pilot plant reactor. Initially, the polyol was added to the reactor. When the temperature reached 55°C, the isocyanate (methylenedi-p-phenyldiisocyanate, MDI) was then added to the reactor. For calibration, samples ($n = 14$) were extracted from the reactor throughout the reaction and analyzed for isocyanate titrimetrically. Extraction of these samples was timed to correspond to the middle of the collection of an NIR spectrum. The model was validated by predicting the isocyanate concentration for samples ($n = 7$) extracted from another polymerization reaction and comparing the NIR result with the titrimetric assay. To aid in calibration development, spectra of the polyol, polyurethane and MDI were acquired by heating flasks containing the samples to 55°C and inserting the probe into the sample.

Process monitoring

The isocyanate concentration for a complete (~ 4 hr) polymerization reaction was determined every 2 min by using the Routine Analysis program contained in NSAS. This program autonomously applies the derived spectroscopic models to the acquired NIR spectra, reports the analytical results and provides statistical process control (SPC) capabilities.

SPC charts supply a graphical representation of the analytical results. The use of the SPC charts requires the selection of a group size for calculations and plotting. A group size of 2 was used for all analyses. The average change (AC $= (S_1 + S_2)/2$) is a plot of the average change for every two samples. The range plot ($R = S_1 - S_2$) is the difference between every two samples.

RESULTS AND DISCUSSION

Calibration

In order to isolate spectral features unique to MDI, the NIR absorbance ($\log(1/T)$) spectra of the isocyanate, polyol and final polyurethane
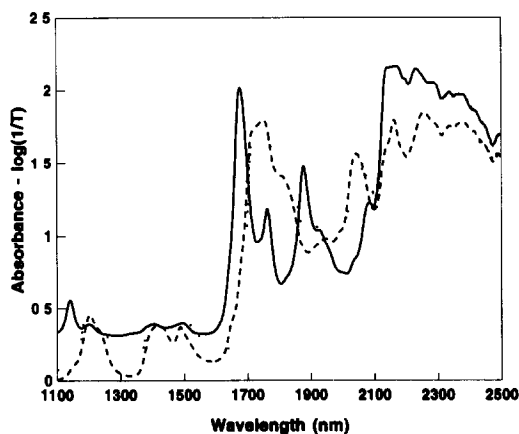

Fig 2 Near-infrared spectra of pure methylenedi-p-phenyldiisocyanate, MDI (——) polyol (·) and final polyurethane (– – – –)
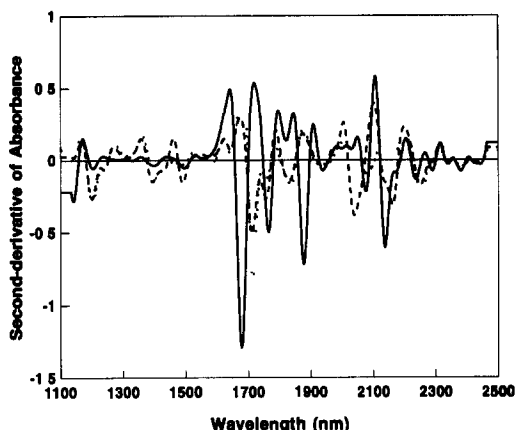
Fig 3 Second-derivative NIR spectra of pure MDI (——)
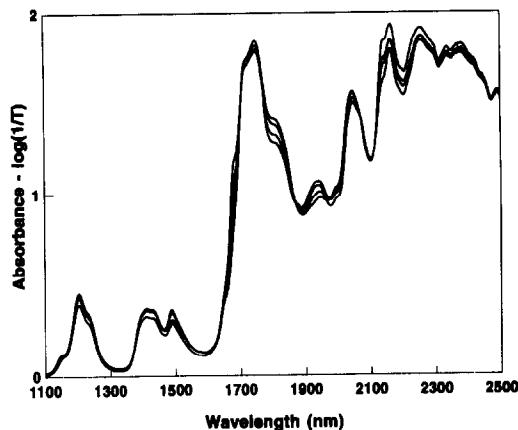   polyol (   ) and final polyurethane (– – – –)

Fig 5 Representative NIR spectra of polyurethane reaction
       samples with varying isocyanate levels.

were collected. The absorbance spectra are over-laid in Fig. 2. Due to the long optical pathlength necessary, high absorbance values are obtained and the signal is saturated beyond 2200 nm and not useful for quantitative purposes. It is difficult to isolate unique spectral features due to the broad, overlapping absorptions that occur in the NIR region. The baseline offsets are due to differences in the optical properties of the individual components.

Calculation of the second-derivative of the absorbance data with respect to wavelength eliminates baseline differences and resolves overlapping bands with no apparent increase in signal-to-noise response.[8] The second-derivative spectra for the polyol, polyurethane and MDI are displayed in Fig. 3. Note that this mathematical treatment inverts absorbance maxima to minima and each minima is flanked by positive side-lobes. Unique spectral bands can be isolated

for the polyol at 1422, 1574 and 2054 nm. The polyurethane exhibits unique spectral features at 1400 and 2160 nm. Unique MDI bands occur at 1680 nm, 1750, 1876 nm, and 2140 nm.

Although several unique regions can be isolated for the quantitative determination of the MDI, the ideal region to be used for quantitative purposes corresponds to a region where a unique feature exists in the second-derivative spectrum of MDI and minimal spectral information exists for the other matrix components. A second-derivative band suitable for quantitative analysis resides in the 1600–1800 nm region (Fig. 4). Here, MDI possesses a minima centred at 1680 nm that is flanked by positive side-lobes centred at 1640 nm and 1720 nm. Note that there is approximately 2% residual isocyanate in the final polyurethane.

Once unique spectral features were identified, a polymerization reaction was started in the
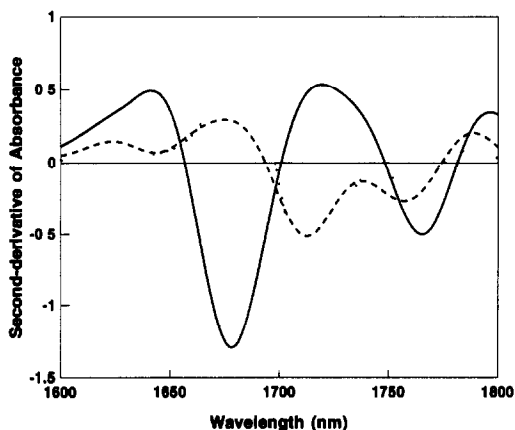

Fig 4 Expanded second-derivative NIR spectra of pure
MDI (——) polyol (   ) and final polyurethane (– – – –).
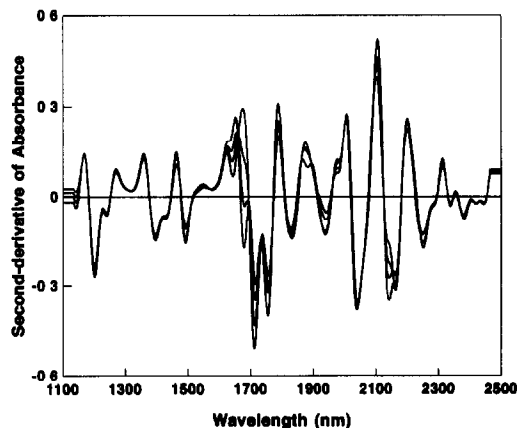Region that can be used for isocyanate determination

Fig 6 Second-derivative NIR spectra of polyurethane
reaction samples with varying isocyanate levels.

reactor. Spectra were acquired throughout the entire reaction and reference analyses were performed to determine the isocyanate content. The isocyanate content decreases from 7.9 to 2.1%. Representative NIR absorbance spectra are displayed in Fig. 5. Baseline offsets arise from light scatter caused by suspended particles within the reaction mixture (*e.g.* catalysts, precursors) and bubbles trapped within the highly viscous polymers. In these circumstances the polymer reaction mixture is strongly light scattering and signal collection is maximized by using a fiber optic bundle and an interactance immersion probe since both the diffusely reflected and transmitted radiation is collected.

The second-derivative spectra for the polymerization spectra are presented in Fig. 6. Since the baseline shifts are minimized and the spectra features are enhanced, compositional changes that occur during the polymerization reaction become apparent. By comparison with the reference material spectra (Fig. 3), bands due to the polyol, polyurethane and MDI are apparent in the polymerization spectra. The region selected to be used for the determination of isocyanate in the polyurethane reaction is isolated in Fig. 7. The apparent shift in the MDI band position is attributed to the interaction with other matrix components and concentration differences between the matrix components. A distinct trend is obvious between the second-derivative data in this region and the isocyanate concentration.

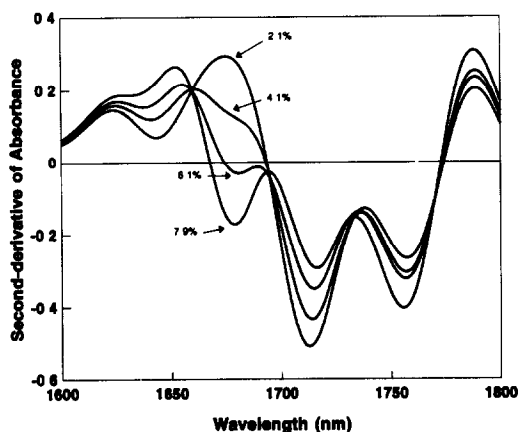There are a variety of calibration methods such as multiple linear least-squares (MLR), partial-least squares (PLS) and principal component regression (PCR) available for correlating chemical and physical properties to NIR spectra. The differences between these algorithms as well as their advantages and disadvantages are described in detail elsewhere.[9,10] In MLR discrete wavelengths are used to relate the intensity at specific wavelengths to analyte concentration and compensate for interfering bands or scattering differences. PLS and PCR extract spectral factors that relate the spectral variation to analyte concentration and inherent matrix variability. A good general rule to follow is to apply simple regression techniques (MLR) to simple calibration problems such as when unique spectral features for the analyte of interest are readily identifiable and reserve the more advanced techniques (PLS and PCR) for applications where analyte bands are highly overlapped by the bands of the other matrix components or when properties being correlated to NIR spectra are related to several chemical components within the matrix.[2] In industry, it is difficult to include all sources of process variation to be encountered in the calibration model. As only a few spectroscopically selected wavelengths are used in MLR, this technique should be less sensitive to spectral variations due to subtle differences in the product formulation or unmodeled sources of spectral variations.

As unique MDI absorption bands could be identified by comparing the reference spectra (Figs 2–4) and spectral differences associated with the changing isocyanate concentration are seen in the polymer reaction spectra (Figs 5–7) that are assignable to variations in the MDI band intensity, an MLR calibration approach was used. In this approach, a variety of empirical Beer's Law relationships between the isocyanate concentration and the second-derivative data in the 1600 nm to 1800 nm region are derived. This produces a series of spectroscopic models for the determination of isocyanate in the polyurethane reaction of which the equation

$$\%NCO(w/w) = K(0) + K(1) \cdot A\,(\lambda_{1648}) \quad (1)$$

where the intercept $K(0) = 3.125$, the slope $K(1) = 15.016$ and $A\,(\lambda_{1648})$ is the second-derivative data at 1648 nm provided the best agreement between the two methods. A correlation coefficient r of 0.98 and standard error of calibration SEC of 0.25% were obtained. Since r approaches ± 1 and the SEC approaches the standard error of the reference method (*i.e.* 0.2%) we can conclude that a strong relationship exists between the second-derivative intensity at 1648 nm and the isocyanate concentration for
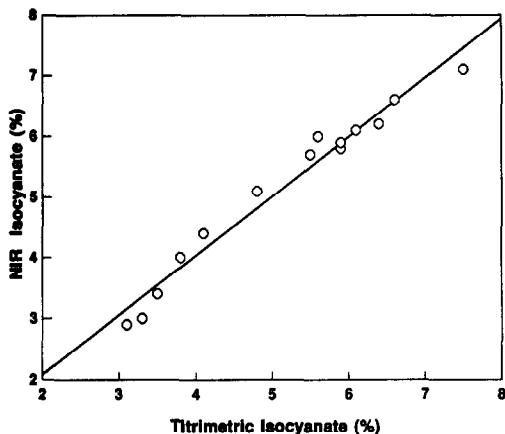

Fig 7 Expanded second-derivative NIR spectra of polyurethane reaction samples and corresponding isocyanate levels.

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Fig. 8. NIR calculated against titrimetric isocyanate level for a single-wavelength (1648 nm) linear least-squares calibration model ($r = 0.98$, SEC $= 0.25\%$)

the production of this polyurethane. The scatter plot of the NIR calculated versus the reference isocyanate concentration presented in Fig. 8 indicates that the model is linear for the entire isocyanate concentration range even with the high absorbance (>1 OD) values common to process spectroscopic measurements.

The reason why 1648 nm provides the best results for the estimation of isocyanate is not immediately obvious, 1648 nm corresponds to the positive side-lobe for the MDI second-derivative band centred at 1680 nm and resides in a region where both the polyol and the polyurethane are non-absorbing (Fig. 4). The shift observed for the isocyanate band in the reaction spectra (Fig. 7) accounts for the shift from 1640 nm to 1648 nm for analytical wavelength. While the strong band at 1680 nm would be expected to provide better results, the positive

side-lobe at 1680 nm for the polyol band centred at 1720 nm interferes with the spectroscopic measurement for MDI at 1680 nm. The same spectral interference is experienced by the MDI side-lobe at 1720 nm. Hence, the second-derivative intensity at 1648 nm can be used to monitor the isocyanate concentration with minimal spectral interference from the other polymer reaction components.

Validation

It is necessary to ensure that the empirically derived spectroscopic model is representative of the isocyanate content in the polyurethane reaction and not unique to the calibration data set only. To validate the model, the isocyanate concentration was predicted for a subsequent polyurethane reaction. The NIR predicted results were compared to the titrimetrically determined isocyanate levels by using linear least-squares regression analysis. The validation regression equation $y = 0.99x - 0.02$ provided an $r = 0.99$ and standard error of prediction (SEP) of 0.19%. A satisfactory validation equation will have an intercept that approaches zero and a slope and correlation coefficient that approach one. The SEP should be of the same order of magnitude as both the SEC and error of the reference method used to derive the model.

Process monitoring

Monitoring of the polymerization reaction was performed by collecting sample spectra at 2 min intervals for a production run (~ 4 hr). Predicted results were produced by application of the isocyanate calibration to the collected NIR spectra.
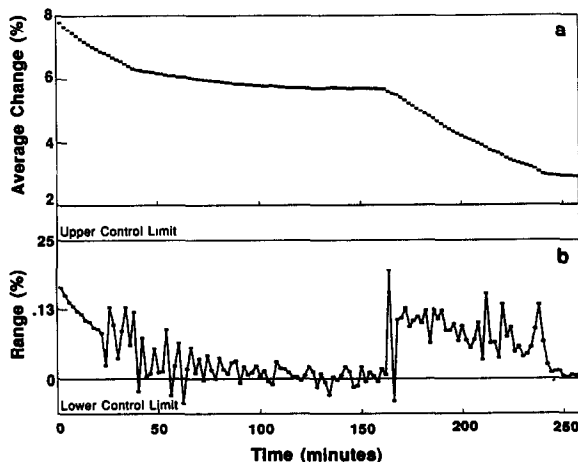

Fig 9. Statistical process control charts for another polymerization reaction. Average change chart (a) indicates process trends and range chart (b) indicates short-term process variation. Spike in the range chart indicates when chain-extender was added. Note 60 min plateau prior to chain extender addition

The statistical process control (SPC) charts are presented in Fig. 9. The average change chart (Fig. 9a) is used to observe trends in the process, while the range chart (Fig. 9b) is used to observe short term variations in the process. For the urethane batch reaction the average change chart demonstrates the extent of reaction for each of the reaction steps. The slowing of the first reaction is followed by an acceleration after the addition of the chain extender It is noteworthy that the 60 min (i e from 100 to 160 min) plateau in the average change chart before the chain extender was added by using a pre-determined time-dependent reaction end-point. In fact, much of the initial reaction occurs in the first 25 min. The spike in the range chart indicates when the chain extender was added. During this time, the initial polyol has been consumed and no further reaction is occurring. Therefore energy, time and production capacity are being wasted Had real-time chemical process information been used, the chain extender could have been added much earlier in the reaction sequence.

CONCLUSIONS

With NIR spectroscopy, real-time chemical process monitoring can provide simultaneous chemical information in less than 1 min about reactants, intermediates, products and side-reactions.

The benefits of real-time chemical analysis are best utilized by observing SPC charts. Using these control charts, extent and rate of reaction for a polymerization can be determined.

Real-time chemical process information allows the operator to optimize the process conditions and minimize reactor time. This time saving translates into an increase in production capacity, decreases in energy consumption and significant cost-savings

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