Chapter 9

Monitoring Polymerization Reactions by Near-IR Spectroscopy

Shih Ying Chang and Nam Sun Wang

Department of Chemical Engineering, University of Maryland, College Park, MD 20742

The following overview is an investigative survey on the feasibility of near-infrared (NIR) spectroscopy as an on-line process analytical technique for control and optimization. The review focuses on current developments in the field of polymerization monitoring. A brief background description on instrumentation and methods of data analysis leads to suggestions for further investigation. After NIR's introduction in the early 1950s, it remained unnoticed by polymer chemists and engineers through the 1960s and 1970s. NIR recaptured chemical engineers' attention in the late 1980s for two major reasons: (1) the development of advanced optical fiber materials and solid state detectors and (2) the incorporation of recent progress on multivariate data analysis algorithms. A review of the current trends in reactor monitoring strategies comprises the last section.

NIR spectra, like the mid-infrared spectra, are the result of light absorption by certain chemical bonds in molecules. In the NIR region of the spectrum, which covers the range from 780 nm (12,820 cm^{-1}) to 2500 nm (4,000 cm^{-1}), the absorption bands are the result of overtones or combinations originating in the fundamental mid-infrared region of the spectrum (4,000~600 cm^{-1}). Because of energy considerations, the majority of the overtone peaks seen in the NIR region arise from the R-H stretching modes with the fundamental vibrations located around 3000 cm^{-1} (O-H, C-H, N-H, S-H, etc.). Other fundamental vibrations manifest in the NIR region only as higher-order overtones that are generally too weak to provide useful analytical information. Another characteristic of NIR spectra is the large number of overlapping bands. For a given molecule, many active overtone and combination bands are typically present in a narrow NIR region and force the peaks to overlap significantly.

Because of the aforementioned weak absorptivity and highly overlapping peaks in the NIR region, NIR analysis, in comparison to its mid-IR counterpart, was largely

neglected by spectroscopists before the 1960's. After the 1960's, as NIR spectroscopy was emerging as a rapid, nondestructive method in the agricultural field, relatively few investigations in NIR applications dealt with polymers. Probable reasons for the lack of interest included difficulties in resolving overlapping bands and complex band assignments in the NIR region and the establishment of mid-IR spectroscopy as a standard and reliable polymer analysis technique.

Currently, agricultural analyses comprise the majority of established NIR applications. Other applications are found in pharmaceutical, biomedical, textile, and petrochemical industries. For a pertinent review, some references are available (*1-6*).

INSTRUMENTATION AND DATA ANALYSIS

NIR Instrumentation

Recent advances in NIR instrumentation have undoubtedly contributed to its increased use in quality analysis and process monitoring. Since the first NIR spectrophotometer of Dickey-John and Neotec in 1971, tremendous progress has been made in several aspects of instrument design towards a high signal-to-noise ratio and a stable spectral measurement. Improved design features include better optical configuration, faster scan rate, superior detector, implementation of sample averaging, and simplified sample presentation. These features are summarized in Table I (*7*).

Figure 1 displays the primary building blocks of a typical NIR spectrophotometer. It is a predispersive, single monochromator-based instrument in which light is dispersed prior to striking the sample. It employs a tungsten-halogen lamp as the light source, a single monochromator with a holographic diffraction grating, and an uncooled lead sulfide (PbS) detector. Interchangeable gratings allow experimentation with different holographic diffraction to achieve wavelengths from 400 to 2500 nm. The wavelength resolution is approximately 1~10 nm. Both transmittance and reflectance modes are offered in most instruments. Because of different requirements, some contemporary spectrophotometers incorporate advanced diode array detectors, NIR emitting diode sources, Hadamard mask exit slits, acousto-optical tunable filters (AOTF), ultrafast spinning interference filter wheels, tunable laser sources, and interferometers with no moving parts (*7*).

Modern NIR-based on-line process monitoring often benefits from advances in optical fiber techniques. Several types of optical fibers that can efficiently transmit light throughout the entire NIR region are presently available. As a result, remote sampling is now feasible with an NIR spectrophotometer coupled with optical fibers. A specific type of measurement configuration is called *transflectance*. In this configuration, light travels through a relatively thin layer of sample where a reflecting surface such as a ceramic disc or a metallic mirror forms the opposite physical boundary. After reflection, light subsequently transmits through the sample back toward the detector. This type of measurement is generally suitable for liquid samples or slurries.

Spectral Pretreatment

In the measurement process, a spectrophotometer records as raw data the fraction of the transmitted or reflected energy of the sample. The signal level is generally referenced to