



# Near-infrared (NIR) monitoring of Nylon 6 during quenching studied by projection two-dimensional (2D) correlation spectroscopy



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## ABSTRACT

Evolutionary change in supermolecular structure of Nylon 6 during its melt-quenched process was studied by Near-infrared (NIR) spectroscopy. Time-resolved NIR spectra was measured by taking the advantage of high-speed NIR monitoring based on an acousto-optic tunable filter (AOTF). Fine spectral features associated with the variation of crystalline and amorphous structure occurring in relatively short time scale were readily captured. For example, synchronous and asynchronous 2D correlation spectra reveal the initial decrease in the contribution of the NIR band at 1485 nm due to the amorphous structure, predominantly existing in the melt Nylon 6. This is then followed by the emerging contribution of the band intensity at 1535 nm associated with the crystalline structure. Consequently, the results clearly demonstrate a definite advantage of the high-speed NIR monitoring for analyzing fleeting phenomena.

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## 1. Introduction

This article provides an illustrative application example of high-speed near-infrared (NIR) spectroscopy for studying evolutionary change in supermolecular structure of Nylon 6 during its melt-quenched process. Spectroscopic monitoring of chemical reactions and product streams is an analytical tool of practical interest [1–4]. Near-infrared (NIR) spectroscopy is particularly suited for monitoring chemical reaction systems [1,5–8]. For example, each chemical functional group in a molecule vibrates at a unique frequency, providing a specific peak in spectrum. The transient variation of components in systems results in the change in the spectral feature. By analyzing the variation of the spectral feature, it is possible to sort out the chemically meaningful information on the system altered. In addition, the utilization of the NIR region with much less absorption compared to mid infrared region enables the light to penetrate much farther into a sample. In fact, the penetration depth of NIR beam can be on the scale of centimeters and this particularly becomes useful in probing bulk material.

Recent development of high-speed NIR spectrometer based on acousto-optic tunable filter (AOTF) opened up further perspectives for process analysis [1,9–11]. An AOTF consists of a birefringent crystal made of a tellurium oxide (TeO<sub>2</sub>) and a high-frequency

piezoelectric transducer. By applying a specific radio frequency to TeO<sub>2</sub> crystal, it produces acoustic vibrations that propagates through the crystal. As light goes through the crystal, interaction between the light waves and sound waves causes the crystal to act as a narrow-line band pass filter to separate a single wavelength of light from a broadband source. In other words, AOTF works as electronically tunable bandpass filter with no moving parts. The utilization of the AOTF provides a distinct advantage over the conventional grating-monochromator or interferometer based approach in terms of high speed data acquisition, especially when the variation of the system occurs in a relatively short time scale [10,11]. This is actually true to the development of supermolecular structures during polymer processing. Thus, the intrinsic properties of NIR light and AOTF brought together provide interesting opportunity to prove the even more in-depth understanding of polymer system of interest.

In this article, high-speed NIR monitoring of a seemingly simple Nylon 6 polymer undergoing melt-quenching is presented as an illustrative example of an application of this characterization technique in polymer analysis. Semicrystalline Nylon 6 prepared from the melt often show a complex polymer structure consisting of folded-chain crystal lamellae embedded in a liquid-like amorphous matrix [12]. The cooling rate substantially affects the crystalline growth, which eventually influences various properties of the polymer [13]. The high-speed NIR monitoring of the evolutionary change in polymer structure of Nylon 6 during its melt-

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quenched process promises a great deal of practical potential in process monitoring applications. The time-resolved NIR spectra were collected at an interval of 1 s during the early stage of the quenching. While the entire feature of the NIR spectra was overwhelmed by baseline change arising from the transition from liquid to solid states, detailed changes in the spectral feature was readily elucidated with an aid of the projection two-dimensional (2D) correlation analysis [10,11,14–19]. The 2D correlation spectra of Nylon 6 clearly revealed fine details of spectral intensity variations closely related to the consumption of the amorphous structure and subsequent development of the crystalline which occur in relatively short time scale.

## 2. Theory

### 2.1. Projection treatment

Projection operation is an especially useful pretreatment method to analyze NIR spectra showing exceptional baseline change [14,15]. It aims to selectively remove the specific signal contribution from spectra by sorting out dynamic spectra into two separate sets: one which is fully aligned with a chosen projecting vector and the other which is orthogonal to the same vector. For given vector  $\mathbf{y}$ , the projection matrix  $\mathbf{R}_y$  is defined as

$$\mathbf{R}_y = \mathbf{y}(\mathbf{y}^T \mathbf{y})^{-1} \mathbf{y} \quad (1)$$

The  $m$ -by- $m$  matrix  $\mathbf{R}_y$  acts as a projector for the space spanned by  $\mathbf{y}$ . The projected data matrix  $\mathbf{A}_p$  is obtained as

$$\mathbf{A}_p = \mathbf{R}_y \mathbf{A} \quad (2)$$

The projected data  $\mathbf{A}_p$  represents the projection of  $\mathbf{A}$  onto the abstract space spanned by  $\mathbf{y}$ . The portion of dynamic spectra projected onto the space spanned by such a projecting vector  $\mathbf{y}$  will have the same trend of  $\mathbf{y}$ . Thus, all signals contained in the projected data  $\mathbf{A}_p$  are fully synchronized.

The corresponding null-space projection is carried out as

$$\mathbf{A}_N = (\mathbf{I} - \mathbf{R}_y) \mathbf{A} = \mathbf{A} - \mathbf{A}_p \quad (3)$$

where  $\mathbf{I}$  means  $m$ -by- $m$  identity matrix. The null-space projected data matrix  $\mathbf{A}_N$  represents the projection of  $\mathbf{A}$  onto the space spanned by the vectors orthogonal to  $\mathbf{y}$ .  $\mathbf{A}_N$  is the residual after the removal of  $\mathbf{A}_p$  from  $\mathbf{A}$  by using the information contained within  $\mathbf{y}$ . In other words, the null-space projection selectively eliminates the portion of dynamic spectra which is synchronized with the projecting vector.

There are several options to choose the source of the projector. In most cases, a single column is selected as a projector vector  $\mathbf{y}$  from the data matrix [14,15,19]. By using a spectral intensity change at specific wavenumber where a peak is observed as the vector  $\mathbf{y}$ , it  $\mathbf{A}_N$  becomes free from the signal contribution from the trend associated with  $\mathbf{y}$ . Such an ability is suitable for the elimination of specific trend from spectra. In fact, baseline correction by the projection becomes especially important in the analysis of the spectra measured by the several NIR techniques where the baseline fluctuation of spectra can be caused necessarily by morphological changes of samples [10,11].

## 3. Experimental

### 3.1. Time-resolved NIR spectra

A schematic description of NIR monitoring of the melt-

quenching of Nylon 6 is depicted in Fig. 1. A temperature-controlled cell holder was equipped with an AOTF-NIR spectrometer (Systems Engineering Inc., Tokyo). The Nylon 6 provided by Sigma–Aldrich was placed in the cuvette cell with 10 mm pathlength. The sample was melted at 250 °C and then quenched by setting the temperature of the cell holder at 30 °C. During the quenching, a series of NIR transmittance spectra of the sample were measured for every 1 s by co-adding 16 scans. An input optical beam from broadband source is separated into wavelengths ranging 1100–1800 nm by an AOTF between crossed polarizers. The measurement of the time-resolved NIR spectra was carried out for 180 s. A background spectrum was measured with the empty cuvette cell prior to the collection.

## 4. Result and discussions

### 4.1. Time-resolved NIR spectra of Nylon 6

The time-resolved NIR spectra of Nylon 6 undergoing the quenching are represented in Fig. 2. Interestingly, entire feature changes from one spectrum to another, suggesting that the transient variation induced in such short time scale can be readily captured. NIR study of semicrystalline polymer samples is often complicated with the presence of overlapped contributions from coexisting crystalline and amorphous components. Fortunately, the NIR spectrum of amorphous component of Nylon 6 is approximated by the melt spectrum since the contribution of amorphous component is well represented by the initial spectrum of Nylon 6 undergoing the quenching. For example, variation of the band around 1485 nm suggests that the crystallization process is accompanied by a precipitous decrease in the intensity of the NIR band. This band is thus mostly assignable to the first overtone of the  $\text{NH}_2$  antisymmetric vibration arising from the amorphous component [12]. Another notable feature is that the decrease in the amorphous band is compensated by the rising contribution of the band around at 1530 nm due to the first overtone of the  $\text{NH}_2$  symmetric vibration associated with the crystalline component [12].

The quenching of the melt Nylon 6 results in the substantial variation in the spectral intensity. The difference in the spectral intensity change between the crystalline and amorphous bands will provide useful information to sort out the variation of the population. However, it is obvious that the change in the spectral intensity caused by the crystallization is overwhelmed by exceptionally predominant baseline changes to make the identification of the pertinent spectral intensity variations difficult. A major cause of the baseline fluctuation observed in the time-resolved NIR spectra is the change in the light scattering due to the transition from liquid to solid states. For example, the solid Nylon 6 scatters even more NIR light and the less light is then detected by the sensor. This, in turn, induces apparent increase in the light absorption by the sample to provide upward shift of the spectral baseline. Unfortunately, these changes are essentially inevitable to the NIR

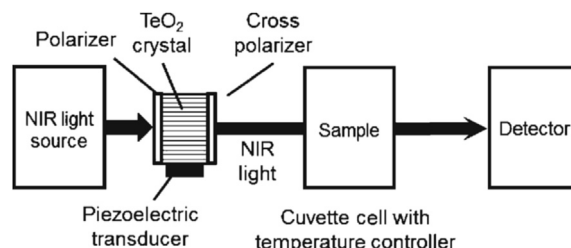


Fig. 1. A schematic illustration of NIR monitoring based on AOTF.

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