Two-Dimensional Near-Infrared Correlation Spectroscopy Study of Premelting Behavior of Nylon 12

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ABSTRACT: The premelting behavior of Nylon 12 has been investigated by two-dimensional (2D) Fourier-transform (FT) near-infrared (NIR) correlation spectroscopy. FT-NIR spectra of Nylon 12 in a cast film have been measured over a temperature range of 30−150 °C. The 2D NIR correlation analysis reveals that there are at least eight bands in the 6800−6100 cm^{-1} region where the first overtone of an NH stretching mode of Nylon 12 is expected to appear. They may be ascribed to free- and hydrogen-bonded NH groups in various environments. The asynchronous 2D NIR correlation spectrum in the above region indicates that the amide group with a free carbonyl oxygen (structure C) appears first and then unassociated free amide (structure A) and amide with free NH (structure B) follow as the temperature is increased. In the 6000−5500 cm^{-1} region of the synchronous spectrum, four dominant autopeaks corresponding to the first overtones of the CH_2 stretching modes are observed at 5840, 5770, 5680, and 5640 cm^{-1}, and negative cross peaks are found between the 5770 cm^{-1} band and the rest. This observation, together with the careful inspection of the dynamic NIR spectra, suggests that the band at 5770 cm^{-1} is due to the contribution of the CH stretching vibration of an ordered or highly associated form of Nylon 12, which decreases with temperature, while other NIR bands correspond to more disordered forms. The corresponding asynchronous spectrum indicates that the intensity variation of the bands at 5840, 5680, and 5640 cm^{-1} actually occurs at a lower temperature compared to the onset of the intensity decrease of the 5770 cm^{-1} band. A substantial amount of disordered or dissociated components corresponding to the above three bands start appearing before the disappearance of more ordered components represented by the 5700 cm^{-1} band. Probably, they appear as the premelting precursors (or even possibly as the indirect cause) to the precipitous decrease of the ordered components associated with the melting of Nylon 12 occurring at a much higher temperature.

Introduction

When the temperature of a semicrystalline polymer system is raised near its melt temperature, several physical processes could be expected. The temperature-induced increase in molecular mobility, for example, could result in the relaxation of polymer segments frozen in higher energetic states. Such relaxation may sometimes cause the recrystallization of the uncrystallized portion, leading to the increased order of the system. At more localized submolecular levels, the increased temperature often results in the weakening of molecular interactions. Especially, polymers associated by hydrogen-bonding interactions undergo a complex premelting process induced by the gradual weakening of inter- as well as intramolecular interactions.

The premelting behavior of Nylon 12 has been a matter of keen interest from various points of view. However, the detailed process of the premelting has not been welll investigated probably because the sensitivity of existing techniques has not been satisfactory enough to monitor thermally induced subtle changes in hydrogen bonds of the amide groups and in conformations of the hydrocarbon chains. Infrared (IR) spectroscopy has often been employed to investigate the thermal behavior and hydrogen bonds of polyamides.[1−11] However, it has one serious problem; i.e., in an IR spectrum a stretching band due to the free NH group of an amide group is extremely weak and overlaps with a much stronger broad feature arising from the hydrogen-bonded species.[4,11] Its intensity is thus difficult to estimate with reasonable accuracy. IR spectroscopy also cannot discriminate four possible hydrogen-bonded structures of amide groups in polyamides shown in Figure 1.

Near-IR (NIR) spectroscopy is another important technique to explore the dissociation process of hydrogen-bonded systems.[11−21] In NIR spectroscopy, overtones of the stretching mode due to a free X-H group are clearly observed because the anharmonicity constant for the stretching mode of a free X−H group is large.[11] Recently, we studied the dissociation and thermodynamic properties of *N*-methylacetamide (NMA), which is the simplest model of a polyamide, by using Fourier-transform (FT) NIR spectroscopy.[19] Moreover, we introduced generalized two-dimensional (2D) NIR correlation spectroscopy to the same study.[21] It has turned out that the 2D NIR approach can monitor the complex sequence of events arising from the dissociation of hydrogen-bonded NMA oligomeric association complexes of various sizes.

In the present study we have applied generalized 2D FT-NIR correlation spectroscopy to explore the premelting behavior and hydrogen bonds of Nylon 12. FT-NIR spectra in the region of 9000−5000 cm^{-1} of Nylon 12 were measured over a temperature range of 30−150 °C where gradual weakening of inter- or intramolecular associative interactions and a decrease of local order leading to the eventual melting of Nylon 12 crystals are observed.

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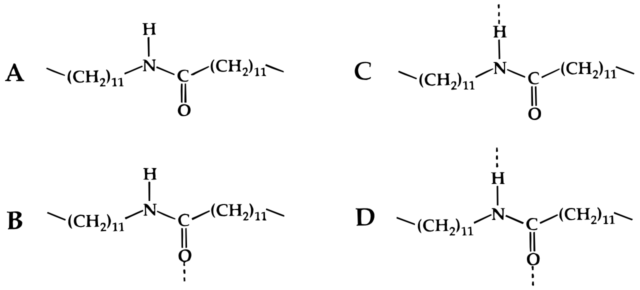


Figure 1. Structure of hydrogen bonds of amide groups in Nylon 12.

2D correlation spectra, which enhance similarities and differences of the variations of individual spectral intensities, are all derived directly from dynamic spectra.[22−25] In 2D correlation spectroscopy, deviations of spectral intensities from the expected value collected sequentially in the order of certain physical variables, such as time or temperature, are compared at two independent wavenumbers. The pairwise cross correlation analysis of such sequential spectral intensity variations yields two types of correlation spectra: *synchronous* and *asynchronous*.[22−25]

It has been expected that the 2D NIR approach elucidates temperature-dependent spectral changes of Nylon 12 in the regions of the first and second overtones of the CH_2 stretching modes and of the first overtone of the NH stretching mode. Therefore, it may provide new insight into the thermally induced dissociation of the amide groups and conformational changes in the hydrocarbon chains in Nylon 12. This is the first time that 2D NIR correlation spectroscopy has ever been applied to studies of polymers.

Background

The 2D NIR correlation spectra of Nylon 12 were derived from the set of FT-NIR spectra by using the generalized 2D correlation method described previously.[20,25] A synchronous 2D correlation spectrum characterizes the similarity between the sequential variations of spectral intensities.[22−25] Autopeaks located at the diagonal position represent the extent of dynamic variations of spectral intensity at different wavenumbers. Synchronous cross peaks appear at off-diagonal positions if the basic trends of dynamic variations observed at two different wavenumbers of the cross peak spectral coordinate are similar. Positive cross peaks indicate that intensities at both wavenumbers are either increasing or decreasing together, while negative peaks (usually marked by shading) show that one intensity is increasing and the other decreasing.

An asynchronous 2D correlation spectrum, which consists exclusively of off-diagonal cross peaks, characterizes the difference between the temperature dependent sequential variations of NIR spectral intensities.[20−23] Asynchronous cross peaks appear if the basic trends of dynamic variations observed at two different wavenumbers of the cross peak spectral coordinate are dissimilar. This feature of the asynchronous spectrum is especially useful in enhancing the spectral resolution of highly overlapped NIR bands. Even for a band located in a highly overlapped NIR spectral region, as long as the band intensity varies in a characteristic way different from others, it could be distinguished by the presence of asynchronous cross peaks. From the sign of an asynchronous peak, it is possible to assign the specific sequence of events occurring at different times (or temperatures in the present case), as long as the changes observed are of relatively monotonic nature. By convention, a shaded asynchronous cross peak indicates that the event (increase or decrease of intensity) observed at wavenumber ν_1 occurs later (i.e., at a higher temperature in the present NIR study) compared to the event observed at wavenumber ν_2. An unshaded asynchronous cross peak indicates the opposite.

Experimental Section

Nylon 12 and *m*-cresol employed in the present study were purchased from commercial sources and used without further purification. The samples for FT-NIR measurements were prepared by casting films from a 4% (w/v) solution of the polymer in *m*-cresol onto CaF_2 windows at room temperature. After evaporation of the majority of the solvent, the sample was placed in a vacuum at 60 °C overnight before spectral measurements.

The FT-NIR spectra were obtained at a resolution of 8 cm^{-1} by using a JEOL JRS 6500N FT-NIR/Raman spectrophotometer equipped with a TGS detector. The light source used was a halogen lamp. Two hundred scans were coadded to ensure an acceptable signal-to-noise ratio. The equipment used for the temperature control with the precision of ±1 °C was the same as that described previously.[24] We recorded absorbance spectra of a CaF_2 window on which the sample was cast and of an identical window without the sample at each temperature. Then, the background was eliminated by subtracting the spectrum of the window cell from that of the sample on the window.

Results and Discussion

Figure 2A shows the temperature-dependent FT-NIR spectra of Nylon 12 observed in the spectral region between 9000 and 5000 cm^{-1}. These spectra are collected between 30 and 150 °C with an increment of 20 deg. In addition, a measurement at 140 °C is also incorporated. Nylon 12 is known to exhibit a melt temperature well above 170 °C.[26] The temperature range studied here between 30 and 150 °C, therefore, probes the “premelting” phenomena, where gradual weakening of inter- or intramolecular associative interactions and a decrease of local order leading to the eventual fusion of Nylon 12 crystals are observed. In certain semicrystalline polymer systems, increased mobility of molecular chains near the melt temperature actually enhances the degree of order by inducing additional crystallization.[27]

Band assignments in the 9000−5000 cm^{-1} region can be made roughly as follows.[11,19,21,28,29] Intense bands in the 5950−5500 cm^{-1} region are due to the first overtones of the CH_2 stretching modes of Nylon 12, while their second overtones are identified in the region of 8800−8100 cm^{-1}. Weak features in the 6800−6100 cm^{-1} region are assignable to the first overtones of stretching modes of free and hydrogen-bonded NH groups of Nylon 12, respectively. Since Nylon 12 can take several hygrogen-bonded forms, as shown in Figure 1, the 6800−6100 cm^{-1} region should be very complicated. Bands in the 7300−6900 cm^{-1} region are ascribed to combination bands of CH_2 vibrations.

It is usually difficult to pick out subtle changes of spectral intensities from a stack of spectral traces, as given in Figure 2A. Difference spectra are often used to accentuate the changing features of such spectra. Figure 2B shows the so-called *dynamic NIR spectra* corresponding to the temperature-dependent variations of original FT-NIR spectra in Figure 2A. Each dynamic spectrum could be regarded as a difference (or more strictly speaking *deviation*) spectrum between the in-

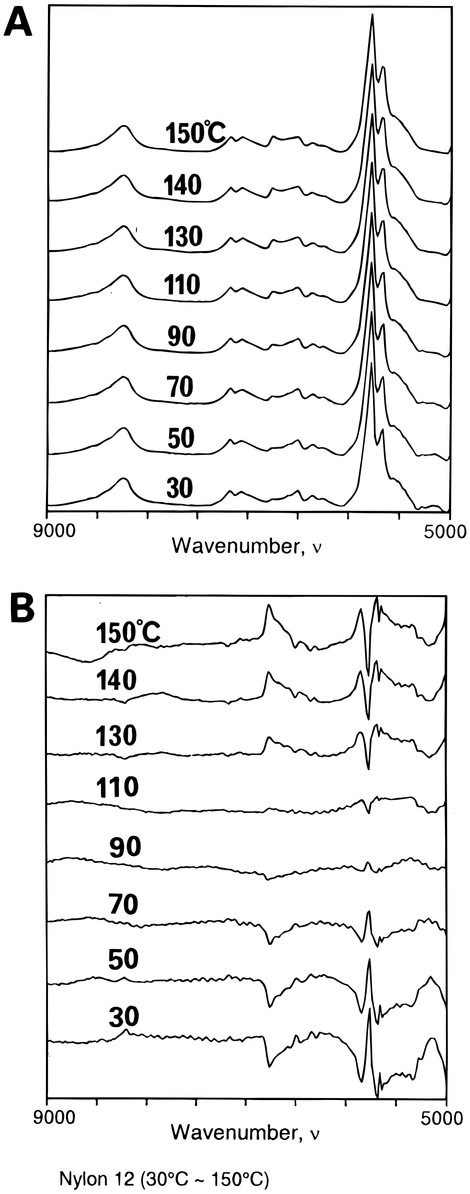


Figure 2. (A) Temperature-dependent FT-NIR spectra in the 9000−5000 cm^{-1} region of Nylon 12 obtained from 30 to 150 °C. (B) Dynamic NIR spectra corresponding to the temperature dependent variations of original FT-NIR spectra shown in A.

dividual FT-NIR spectrum and a preselected *reference spectrum*. By following the normal convention used in the field of time-series analysis, the reference spectrum is selected as the average (expected value) of all spectral data sampled during the entire temperature scan. Compared to the original FT-NIR spectral set in Figure 2A, the dynamic spectra given in Figure 2B depict more clearly the complex trends of variations of FT-NIR spectra of Nylon 12 induced by the temperature change.

The synchronous 2D FT-NIR spectrum of thermally induced intensity variations of Nylon 12 in the spectral range between 9000 and 5000 cm^{-1} is shown in Figure 3. The pseudo-three-dimensional fishnet representation used here provides the best view of the overall feature of the 2D spectrum. Fishnet plots are especially suited for the comparison of relative intensities of various correlation peaks. This plot of a synchronous spectrum, for example, shows that the spectrum is dominated by rich features in the spectral region between 5000 and 7000 cm^{-1}, where most of the thermally induced intensity changes of NIR spectra are observed. Interestingly, even though substantial NIR peak intensity is observed for the second harmonic contributions from CH stretching vibrations above 7000 cm^{-1} in Figure 2A, the corresponding peak intensities for the 2D NIR spectrum are much weaker. This is due to the fact that the extent of temperature-induced variations of spectral intensities is actually much smaller above 7000 cm^{-1} compared to the individual NIR intensity itself.

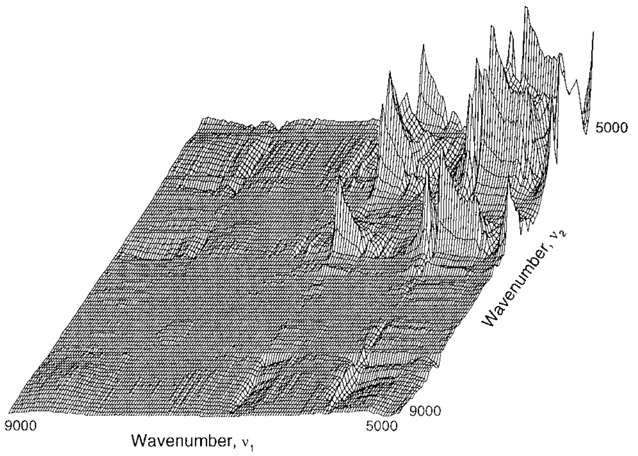
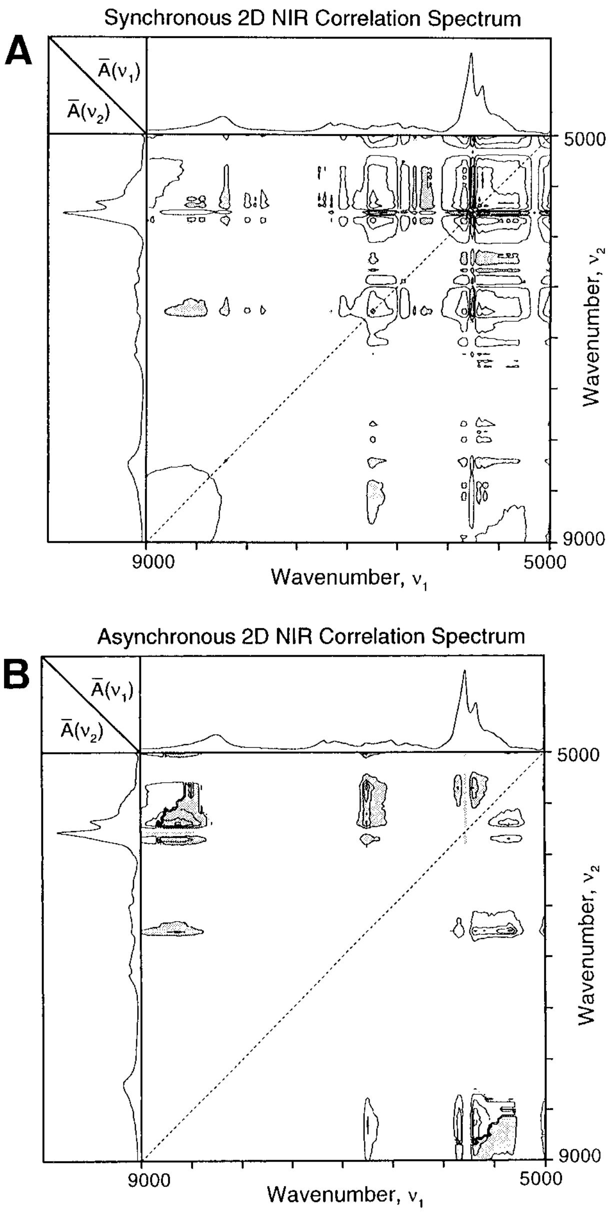


Figure 3. Full view of the psuedo-three dimensional staked trace representation of the 2D FT-NIR synchronous correlation spectrum of Nylon 12 obtained from 30 to 150 °C.

Figure 4A is the corresponding isointensity contour map representation of the same synchronous 2D NIR spectrum. For reference purposes, a pair of average NIR spectra are provided at the top and side of the correlation spectrum. The contour map representation as used in Figure 4A is much better suited for the identification of finer features of the correlation spectrum, as well as the accurate determination of the peak location. The negative peak intensity regions, i.e., troughs, are by convention indicated with shading. Many features hidden in Figure 3, especially the negative peaks surrounded by strong positive peaks, are now visible by using the contour map representation. Thus, this way of plotting 2D correlation spectra as contour maps is often chosen as the preferred method. It is, however, important to point out that some of the weaker peaks observed in Figure 3 (see, for example, the autopeak around 7500 cm^{-1}) are not clearly shown in Figure 4A. Such artificial omission is caused by the selection of the minimum level of the contour line. This is one of the limitations of the contour map representation of 2D correlation spectra.

The asynchronous 2D NIR spectrum of Nylon 12 in the same spectral region is given in Figure 4B. As stated previously, an asynchronous spectrum represents the dissimilarity between the variations of NIR spectra. In principle, we should be able to extract useful information about the temperature sequence of NIR intensity variations of the Nylon 12 system. It is, however, somewhat difficult to pick out the fine features of the spectrum when such a broad spectral region is displayed at once.

The full advantage of the contour map representation of 2D correlation spectra is realized when a relatively limited portion of the spectral map is displayed. Parts A and B of Figure 5 are the closeup view of the synchronous and asynchronous 2D NIR spectra in the spectral region between 6000 and 5500 cm^{-1}. A lot more detailed features become apparent. Parts A and B of



Nylon 12 (30°C ~ 150°C)

Figure 4. (A) Synchronous 2D FT-NIR correlation spectrum of Nylon 12 obtained from 30 to 150 °C in the 9000−5000 cm^{-1} region. (B) The corresponding asynchronous 2D FT-NIR correlation spectrum in the same spectral region.

Figures 6 show the actual NIR spectra and dynamic spectra in the same spectral region, respectively. Spectral features of Nylon 12 in this region are represented mainly by the contributions from the first overtone of the CH-stretching vibrations. The temperature-dependent variations of the NIR spectral intensities, which correspond to the changes in the population distribution of various submolecular components of Nylon 12 containing CH groups, manifest themselves as the intensity fluctuations of dynamic spectra.

The synchronous 2D FT-NIR spectrum of Nylon 12 shown in Figure 5A reveals several dominant autopeaks around 5840, 5770, 5680, and 5640 cm^{-1}. Other autopeaks, e.g. at 5480 cm^{-1}, are not clearly observed due to the artificial truncation imposed by the selected minimum level of the contour lines. Negative cross peaks marked by the shading are found at off-diagonal spectral coordinates between the 5770 cm^{-1} band and the rest of the NIR bands in this spectral region. This result implies that the thermally induced change in the NIR spectral intensity at 5770 cm^{-1} is in the opposite (i.e., decreasing) direction compared to the other NIR bands.

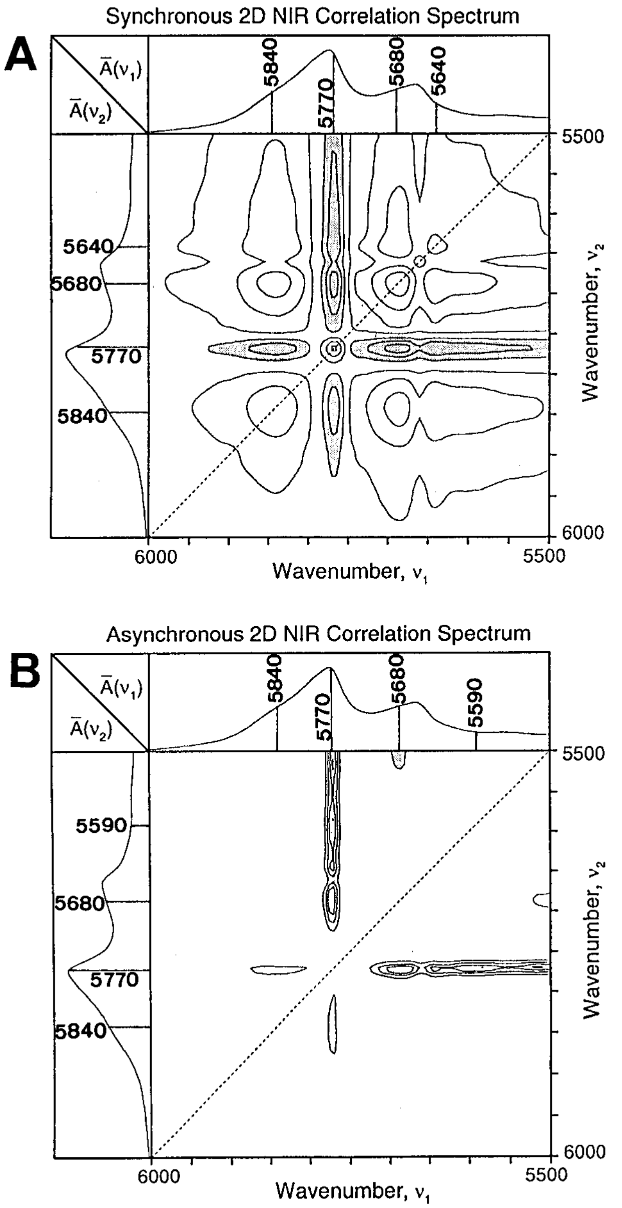


Figure 5. (A) Synchronous 2D FT-NIR correlation spectrum of Nylon 12 obtained from 30 to 150 °C in the 6000−5500 cm^{-1} region. (B) The corresponding asynchronous 2D FT-NIR correlation spectrum in the same spectral region.

Careful inspection of NIR spectra in Figure 6A, and more preferably the dynamic spectra in Figure 6B, reveals that the NIR peak intensity at 5770 cm^{-1} is steadily decreasing with the rising temperature, while other peaks located at 5840, 5680, and 5640 cm^{-1} are all increasing. It is, therefore, likely that the NIR band at 5770 cm^{-1} is assignable to the contribution of CH$_2$ stretching vibrations of an ordered or highly associated form of Nylon 12, which decreases with higher temperature. The intensity of this NIR band at 5770 cm^{-1} decreases dramatically around the melt temperature of Nylon 12. Other NIR bands probably correspond to more disordered forms created by the rising temperature.

Here, we point out one problem which may be encountered in the general application of the 2D representation of dynamic spectra. The intensity of the

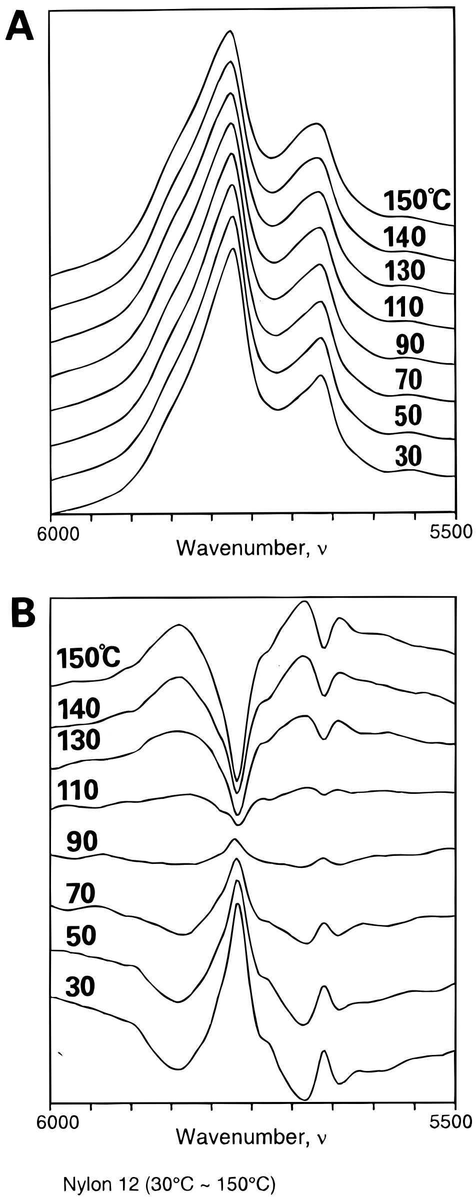


Figure 6. (A) Temperature-dependent FT-NIR spectra obtained from 30 to 150 °C in the 6000−5500 cm^{-1} region of Nylon 12. (B) Dynamic NIR spectra corresponding to the temperature dependent variations of original FT-NIR spectra shown in A.

band at 5770 cm^{-1} is decreasing as the temperature is raised, while those of the surrounding background and/or peaks are increasing (Figure 6B). This combination results in the maxima at 5840 and 5680 cm^{-1} in the dynamic spectra and, hence, the correlation peaks in the 2D spectra (Figure 5A,B). Therefore, a question may arise; to attribute absorption bands to these specific wavenumbers may not be correct. In the present case, it seems very likely that the bands are located at 5840 and 5680 cm^{-1} because the original spectra (Figure 6A) show a weak shoulder near these wavenumbers.

There are several strong and broad synchronous cross peaks correlating the NIR bands located at 5840, 5680, and 5640 cm^{-1} and those below 5600 cm^{-1}. The basic trends of temperature-dependent variations of NIR intensities among these bands, which all become stronger with increasing temperature, must be reasonably similar to each other. Interestingly, however, there is a small gap in these positive synchronous cross peaks around 5670 cm^{-1}. The NIR band intensity at 5670 cm^{-1} actually decreases with rising temperature, as in the case of the 5770 cm^{-1} band (Figure 6B) . Thus, this NIR band probably is also assignable to a more ordered crystalline form of Nylon 12.

The asynchronous 2D NIR spectrum shown in Figure 5B reveals an interesting asynchronous feature among the temperature-induced spectral intensity variations of Nylon 12 bands in the region of the first harmonic overtone of CH stretching vibrations. Asynchronous cross peaks correlating the 5770 cm^{-1} band with those at 5840, 5680, and 5590 cm^{-1} are observed. It clearly shows that the disappearance of the ordered component giving rise to the decrease in the 5770 cm^{-1} band is not directly coupled with the creation of other components, such as those contributing to the change in the 5840, 5680, and 5590 cm^{-1} bands, since these events are not occurring simultaneously.

The signs of cross peaks at 5840, 5680, and 5590 cm^{-1} indicate that the intensity variation of these bands actually occurs at a lower temperature compared to the onset of the intensity decrease in the 5770 cm^{-1} band. A substantial amount of disordered or dissociated components corresponding to the 5840, 5680, and 5590 cm^{-1} bands start appearing before the disappearance of more ordered components represented by the 5770 cm^{-1} band, as the temperature of the system is raised. They are, however, not created as the end product of the thermally induced disappearance of the more ordered component represented by the 5770 cm^{-1} band. Rather, they appear as the premelting precursors (or even possibly as the indirect cause) to the precipitous decrease of ordered components associated with the melting of Nylon 12 occurring at a much higher temperature.

It should be pointed out here that the asynchronicity revealed in Figure 5B among NIR bands for the overtone of CH stretching vibrations is a prime example of the true probing power of correlation spectroscopy. The sequential order of the occurrence of events, e.g., appearance and disappearance of certain species in the system induced by the externally imposed changes, provides valuable information on the exact mechanisms of the changes observed by a spectroscopic probe. Such definitive sequencing of different types of spectral intensity variations is often very difficult, unless the raw data are processed and presented in the form of a correlation spectrum. Even a close observation of the spectral intensity variations, as shown in Figure 6A,B, will most likely fail to detect such important information.

We now shift our attention to the NIR spectral region containing the information on amide NH groups of Nylon 12.[19,21] The synchronous and asynchronous 2D NIR spectra in the NH stretching region are shown, respectively, in Figures 7A,B. This region of the 2D NIR spectrum is one of the most interesting regions due to the presence of complex influence from hydrogen-bonding interactions which play important roles in the properties of Nylon 12.[19,21] Clearly, the most dominant autopeak of the synchronous 2D NIR spectrum in Figure 7A is located near 6750 cm^{-1}, with broad extension down to about 6500 cm^{-1}. This NIR band is assigned to the first overtone of the stretching vibration of free NH groups.[19,21] The raw NIR spectra and dynamic spectra previously shown in Figure 2A,B indicate a steady increase of the band intensity at this wavenumber. In other words, the population of free NH groups is increasing with the rising temperature.

Both structures A and B (Figure 1) have a free NH group. This means that “free” NH bands arise from the

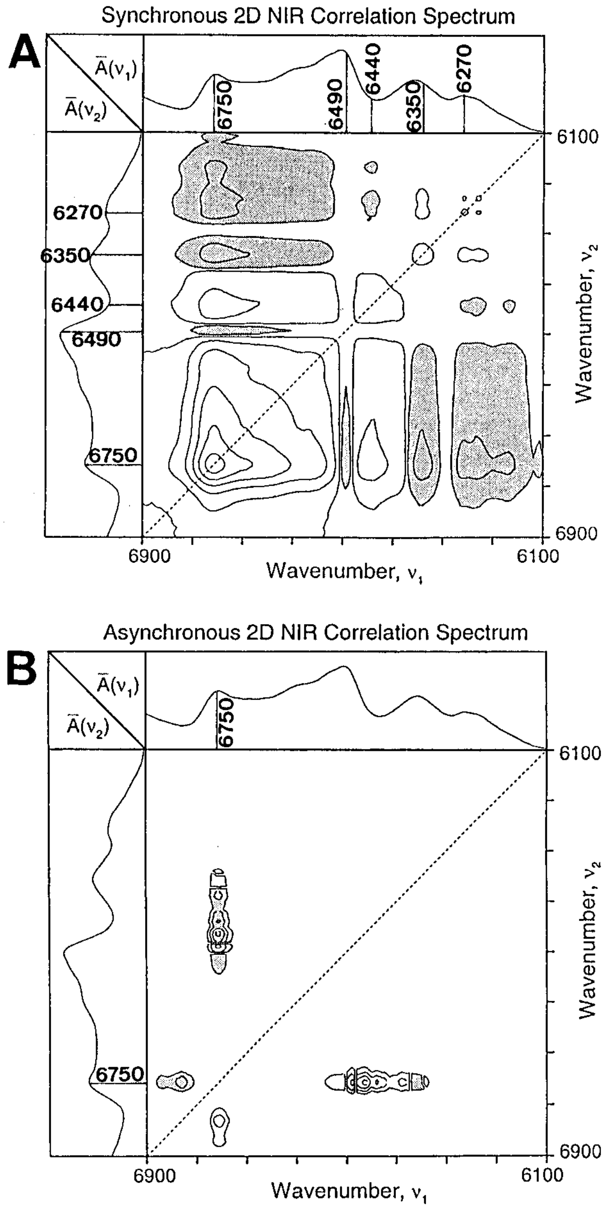


Figure 7. (A) Synchronous 2D FT-NIR correlation spectrum of Nylon 12 obtained from 30 to 150 °C in the 6900–6100 cm^{-1} region. (B) The corresponding asynchronous 2D FT-NIR correlation spectrum in the same spectral region.

two sources. It is clear from equilibrium considerations that the population of structure B exceeds that of structure A at ambient temperature. We assign the band at 6750 cm^{-1} to all the non-hydrogen-bonded NH groups (i.e., both structures A and B) because of the following reasons. First, only this band shows the systematic increase with temperature in the 6800–6500 cm^{-1} region where the band due to the free NH groups appears. Second, the frequency and thermal behavior of this band is consistent with the observations in the IR region.[3] Third, structure B should give a stronger band than structure B because the concentration of the former is lager than the latter. Thus, if we assigned the band at 6750 cm^{-1} solely to the free NH band of structure A, there would be no band assignable to that of structure B.

There are several other autopeaks and cross peaks located at different coordinates in this spectral region. For example, peaks are also found at 6490, 6440, 6350, 6270, 6220, and 6170 cm^{-1}. While the NIR intensities of the 6750 and 6440 cm^{-1} bands increase as the temperature of the system is raised from 30 to 150 °C, all other bands observed at 6490, 6350, 6270, 6220, and 6170 cm^{-1} decrease in their intensity.

The 6500–6150 cm^{-1} region of the synchronous 2D NIR correlation spectrum of Nylon 12 bears considerable resemblance to that of NMA in the pure liquid state.[21] Comparison of the 6500–6150 cm^{-1} region in Figure 7A with the corresponding region of NMA leads us to propose the following assignments: (i) The bands in the 6380–6100 cm^{-1} region arise from structure D. The appearances of several bands in this region suggest that there are a variety of environments or structures for structure D. (ii) The bands in the 6500–6400 cm^{-1} region are due to structure C. Note that one band in this region at 6490 cm^{-1} decreases with temperature while other bands in the 6470–6400 cm^{-1} increase. There may be at least two kinds of structure C; for example, one is surrounded by more ordered or associated parts while the other is located in the disordered or dissociated parts. The detailed band assignments in the 6500–6150 cm^{-1} region may be considered to be tentative, because the peak positions of the hydrogen-bonded NH bands shift to a higher frequency and broaden significantly as the temperature is raised. These shifts may complicate the interpretation of the data in the 6500–6150 cm^{-1} region.

The asynchronous 2D NIR spectrum shown in Figure 7B reveals several cross peaks. Most of the cross peaks are located at the spectral coordinate near 6750 cm^{-1}. The result suggests that the temperature dependence of the stretching vibration of free NH groups in Nylon 12 is quite different from those of other NH stretching bands. The signs of cross peaks appearing in the expanded view of the asynchronous 2D NIR spectra (Figure 8A,B) point to the following sequence of events: As the temperature of the system is raised from 30 to 150 °C, the NIR intensity at 6440 cm^{-1} increases slightly before any other bands in this spectral region. The intensity increase at 6440 cm^{-1} is followed by the marked increase of the intensity around 6750 cm^{-1}. The increase in this band assignable to the free NH groups indicates that there are significant amounts of the free amide groups even in the premelting process of Nylon 12. At higher temperatures, the decrease of band intensities at 6330 cm^{-1}, as well as the decrease at 6270 and 6220 cm^{-1}, detected (Figure 8B). These bands are related to the NH stretching vibrations of hydrogen-bonded NH groups. Note that the NIR spectra are collected at temperatures well below the melt temperature of Nylon 12. The system, therefore, is still dominated by the highly associated or crystalline form. In fact, in the IR region the free NH stretching band is essentially undetected until Nylon 12 is melted, and then it is only a small contribution at 3447 cm^{-1}.[3] Although the fraction of free NH groups is small, the intensity of the free NH band is enhanced in the NIR region due to anharmonicity caused by the large displacements of the "free" proton.[11] The preservation of the majority of hydrogen bonds below the melting point was also suggested by solid-state ^2H NMR for Nylon 66.[30,31]

Up to this point, 2D NIR spectra are obtained near the diagonal line where temperature-dependent variations of NIR band intensities arising from relatively similar molecular vibrations are compared. We now look at the cross peaks located further away from the diagonal, where signals from different modes of vibration are compared.

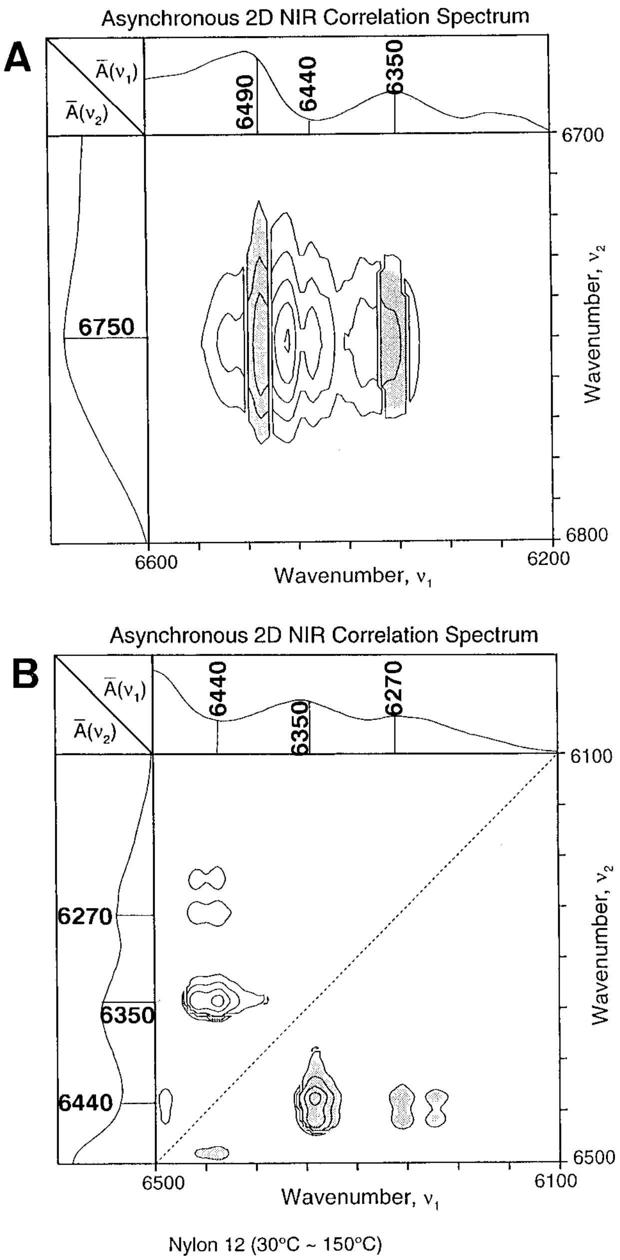


Figure 8. (A,B) Expanded view of the asynchronous 2D FT-NIR correlation spectrum of nylon 12 shown in Figure 7(B).

Parts A and B of Figure 9 compare the regions corresponding to the first overtones of CH and NH stretching vibrations. The strong negative synchronous cross peak correlates the decrease of intensity at 5770 cm^{-1} and the increase of NIR intensity associated with free NH groups of Nylon 12 at 6750 cm^{-1}. The positive cross peaks, on the other hand, are found between the 6750 cm^{-1} band and the rest of the CH stretching vibrations. The intensities of bands arising from the hydrogen-bonded NH groups all decrease so that they are showing negative correlation intensities with most of the CH stretching bands, except of course at 5770 cm^{-1}. The sign of asynchronous cross peaks shown in Figure 9B indicates that the observed intensity reduction of these CH stretching bands occurs at temperatures below the temperature where the intensity of the 6750 cm^{-1} band increases. Therefore, it seems that the premelting precursors appear before structures A and B are created.

The synchronous and asynchronous 2D NIR spectra shown in Figures 10A and B, respectively, are interesting because they compare regions corresponding to the first overtones and combination bands of CH stretching vibrations. A sharp and strong positive synchronous cross peak is found at the position correlating the temperature-dependent decrease of NIR band intensities at 7170 and 5770 cm^{-1} (Figure 10A). Similarly, several positive cross peaks are found at 7040 cm^{-1}, correlating the increase of band intensities at 5840, 5680, and 5640 cm^{-1}. These two types of positive cross peaks are in turn correlated by negative cross peaks, indicating that one represents bands with increasing intensities while the other those with decreasing intensities.

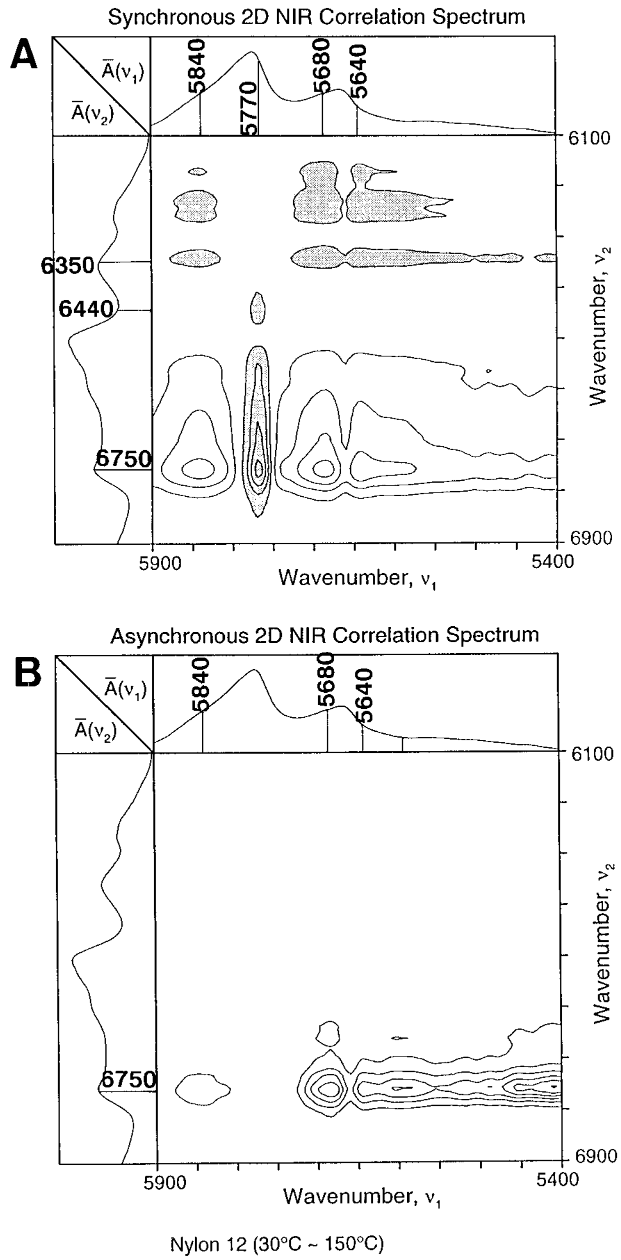


Figure 9. (A) Localized view of the off-diagonal position of a synchronous 2D FT-NIR correlation spectrum of Nylon 12 between the 6900–6100 and 5900–5400 cm^{-1} regions. (B) The corresponding asynchronous 2D FT-NIR correlation spectrum.

Figure 10B reveals the existence of asynchronicity among the temperature-dependent variations of intensities in these spectral regions. While the relatively weak temperature dependence, and consequently the increased noise level, of the combination bands makes the interpretation of the asynchronous spectrum in this region somewhat difficult, we may still deduce that some CH stretching combination bands of Nylon 12 behave

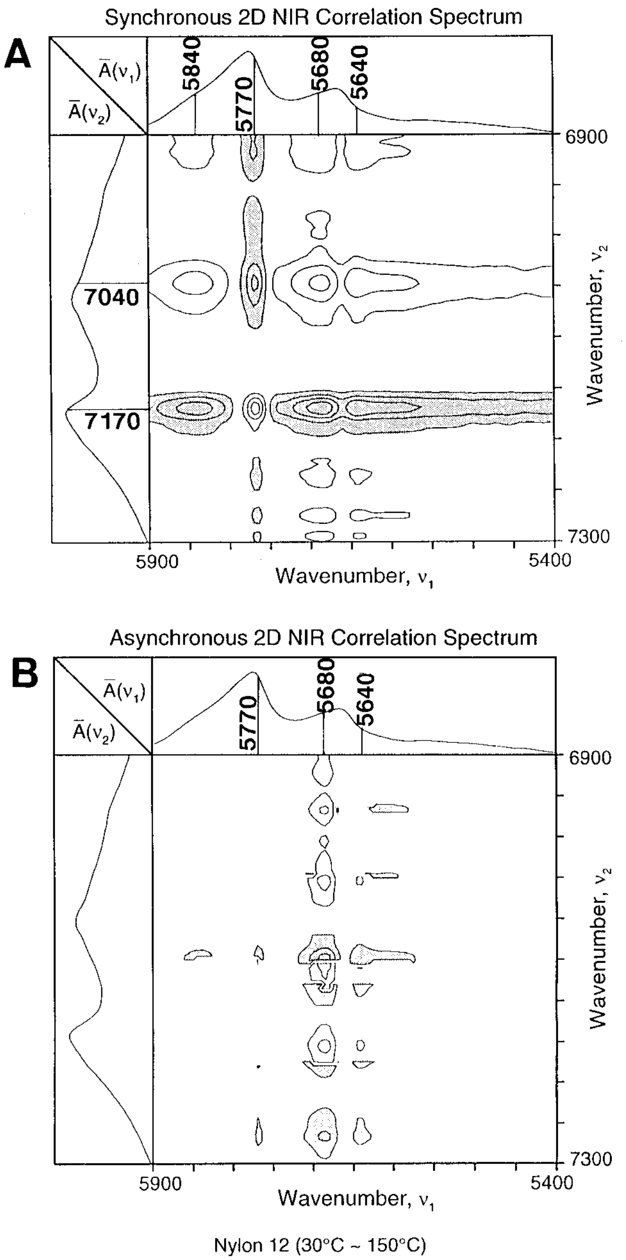


Figure 10. (A) Localized view of the off-diagonal position of a synchronous 2D FT-NIR correlation spectrum of Nylon 12 between the 7300–6900 and 5900–5400 cm^{-1} regions. (B) The corresponding asynchronous 2D FT-NIR correlation spectrum.

differently from the first overtone bands during the temperature scan between 30 and 150 °C. Obviously, this result suggests that there are numerous CH groups in Nylon 12, which are placed in very different molecular surroundings, each contributing to the molecular vibrations in a unique way. The observation in Figure 10B, at the same time, reveals the complexity of the combination band region.

The first and second overtones of the CH stretching vibrations of Nylon 12 are now compared in Figure 11A–C. The positive synchronous cross peaks correlate the decrease of NIR band intensities around 8200 and 8600 cm^{-1} with the intensity decrease at 5770 cm^{-1}, while negative cross peaks are found for bands at 5840, 5680, and 5640 cm^{-1} with increasing intensities (Figure 11A). The temperature-dependent behaviors of the bands at 5770 and 8200 cm^{-1} are especially similar to each other, as there is little asynchronicity between these two bands (Figure 11C). Figure 11B provides the closeup view of the synchronous cross peak between these two bands, which most likely are originating from

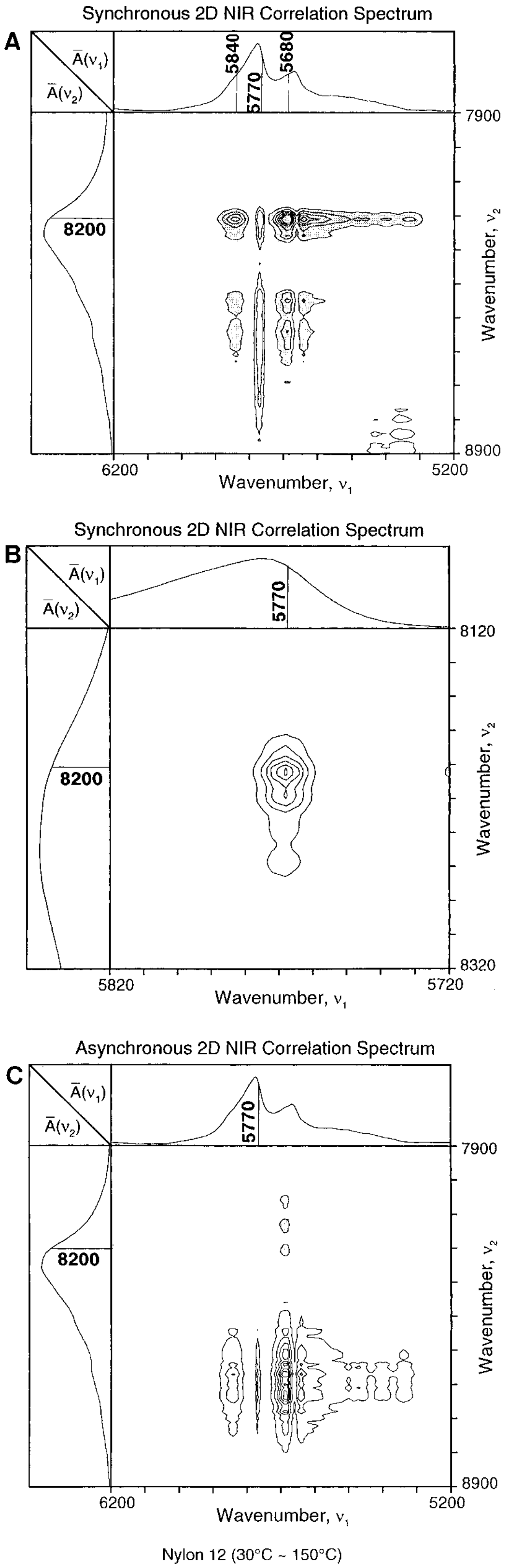


Figure 11. (A) Localized view of the off-diagonal position of a synchronous 2D FT-NIR correlation spectrum of Nylon 12 between the 6200–5200 and 8900–7900 cm^{-1} regions. (B) Localized view of the off-diagonal position of a synchronous 2D FT-NIR correlation spectrum between the 8320–8120 and 5820–5720 cm^{-1} regions. (C) Localized view of the off-diagonal position of an asynchronous FT-NIR correlation spectrum of Nylon 12 between the 8900–7900 and 6200–5200 cm^{-1} regions.

the same CH groups of the same species in this Nylon system. Probably, the bands at 8200 and 5770 cm^{-1} are due to the second and first overtones of the antisymmetric CH_2 stretching mode of the ordered hydrocarbon chains. The anharmonicity constant for an antisymmetric $X-H_n$ stretching mode is, in general, much larger than that for the corresponding symmetric $X-H_n$ stretching mode,[32,33] so that it is reasonable that they appear more prominently in the NIR region than others.

Conclusion

This paper has demonstrated for the first time the potential of generalized 2D FT-NIR correlation spectroscopy in studies of thermal behaviors and hydrogen bonds of polymers. A set of FT-NIR spectra of Nylon 12 under a temperature variation has been unraveled by the combination of the synchronous and asynchronous 2D NIR correlation spectra. The existence of a number of bands in the overtone and combination band regions of the CH and NH stretching modes and their assignments have been elucidated by the 2D technique. The following conclusions could be reached for the band assignments.

(1) There are at least five bands at 5840, 5770, 5680, 5640, and 5480 cm^{-1} in the region of the first overtone of CH_2 stretching modes (Figure 5A). The intensity of the 5770 cm^{-1} band increases with temperature, and there are negative cross peaks between this band and the rest, indicating that the band at 5770 cm^{-1} is due to a more ordered crystalline form of Nylon 12 while the rest are ascribed to disordered or dissociated forms.

(2) A number of bands are observed in the 6800−6100 cm^{-1}, region where the first overtone of the NH stretching modes of Nylon 12 is expected to appear (Figure 7A). The band at 6750 cm^{-1} arises from the free amide group of Nylon 12 (structures A and B, Figure 1). The bands in the 6510−6400 and 6380−6100 cm^{-1} regions are due to structures C and D, respectively (Figure 1).

(3) The strong correlation peak appears between the two strong bands at 5770 and 8200 cm^{-1}, showing that the two bands arise from the same groups of the same species (Figure 11B). They are probably due to the first and second overtones of antisymmetric CH_2 stretching modes, respectively.

On the basis of the above band assignments, the following mechanistic picture emerges for the premelting of Nylon 12.

(i) Disordered or dissociated components represented by the bands at 5840, 5680, and 5590 cm^{-1} appear as the premelting precursors before the disappearance of more ordered components corresponding to the 5770 cm^{-1} band, leading to the precipitous decrease in the ordered components associated with the melting of Nylon 12 occurring at a much higher temperature (Figure 5B).

(ii) The marked increase in the band intensity at 6750 cm^{-1} indicates that a significant number of free amide groups emerge in the course of premelting of Nylon 12 (Figures 3 and 7A). The asynchronous 2D NIR correlation spectrum in the region of the first overtones of the NH stretching mode indicates that structure C is created first and then structures A and B follow it (Figure 7B).

(iii) The localized view of the off-diagonal position of the asynchronous 2D FT-NIR spectrum of Nylon 12 between the 6900−6100 and 5900−5400 cm^{-1} regions (Figure 9B) shows that the precursers are created before the free amide groups are increased.

The general mechanistic picture of the premelting behavior of Nylon 12 appears to be compatible with that from NMR.[30,31] We are planning to extend our research on Nylon 12 to higher temperature ranges to investigate the melting behavior and molten Nylon 12. Not only 2D NIR but also 2D IR and 2D heterospectral NIR−IR correlation analysis may be undertaken. These studies should provide new insight into thermal behaviors of Nylon 12.

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