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Two-dimensional near-infrared correlation temperature studies of an amorphous polyamide

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Abstract

Near-infrared spectra of a totally amorphous polyamide measured over the temperature range 25–200°C was analyzed using generalized two-dimensional (2D) correlation spectroscopy. At least, five distinct bands at 5690, 5810, 5900, 5980 and 6010 cm^{-1} were identified in the region of the CH overtones (5200–6200 cm^{-1}). Among them, two bands at 5810 (aliphatic) and 6010 cm^{-1} (aromatic) are found to be very sensitive to the temperature-induced structural changes of the polyamide under examination. In the ν(NH) overtone region (6300–6800 cm^{-1}), the asynchronicity of the bands assigned to the vibrations of the free and hydrogen-bonded NH groups indicate a complicated dissociation mechanism and the existence of different hydrogen-bonded species in the investigated totally amorphous polyamide sample. Owing to the spectral resolution enhancement in 2D correlation spectra, a splitting of the first overtone of the free NH stretching vibration into two components at 6780 (totally free) and 6740 cm^{-1} (free-end) can be observed. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Nylon; Near infrared spectroscopy; 2D correlation analysis

1. Introduction

The role played by the hydrogen bonds in the structure and properties of polyamides and polyurethanes has been the subject of numerous infrared (IR) spectroscopic investigations [1–10]. Although the energies of hydrogen bonds are weak (20–50 kJ mol^{-1}) in comparison to the covalent bonds (of the order of 400 kJ mol^{-1}), this type of molecular interaction is large enough to produce appreciable wavenumber and intensity changes in the vibrational spectra of the polymer under examination. In fact, the spectral effects are so significant that IR spectroscopy provides one of the most informative source of criteria for changes in the state of hydrogen bonding [11].

Valuable information regarding the temperature dependence of hydrogen bonding may be derived from IR studies at elevated temperature [1–10]. Most of the IR spectroscopic studies concentrate on the amide (–CONH–) group. Trifan and Terenzi [5] concluded from the absence of bands in the IR spectra above 3300 cm^{-1}, that at room temperature there is essentially 100% hydrogen bonding in linear, aliphatic homopolyamides. However, in structurally irregular copolyamides and in linear homopolyamides at elevated temperatures, an absorption at about 3450 cm^{-1} was observed and assigned to the stretching mode of the free N–H groups ($\nu(\text{NH})_f$). Using a complicated mathematical analysis, Bessler and Bier [6] attempted to estimate the percentage of free and bonded N–H groups from the corresponding ν(NH) peak maxima absorbances at various temperatures for different polyamides. In an elegant work, Coleman et al. [2–4] curve-fitted the ν(C=O) (Amide I) region and evaluated the population of the free and bonded carbonyl groups in different polyamides.

However, the temperature changes not only influence the hydrogen bonding between amide groups but also the structure of the hydrocarbon chains. Thus, it has been observed [12] that the peak maximum wavenumber of the $\nu_{as}(\text{CH}_2)$ absorption band in the spectrum of a polyesterurethane shows a linear decrease as a function of elevated temperature. Ozaki [9] showed that the first overtone of the CH_2 stretching mode of polyamide 12 splits into several components due to different ordered and disordered forms.

Although most of the IR studies of hydrogen bonding in polyamides were carried out in the mid-infrared (MIR) (4000–400 cm^{-1}) region, near-infrared (NIR) spectroscopy (12,500–4000 cm^{-1}) has also been recognized as a valuable tool to study the hydrogen bonding of compounds containing

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amide group [13–17]. In the MIR region, the $\nu(\mathrm{NH})_\mathrm{f}$ band is usually extremely weak and overlaps with a much stronger broad band arising from the stretching vibration of the NH groups associated through hydrogen bonds ($\nu(\mathrm{NH})_\mathrm{b}$). It is thus quite difficult to estimate the intensity of the $\nu(\mathrm{NH})_\mathrm{f}$ band with reasonable accuracy in the MIR region. In the NIR region, the stretching mode due to the free and hydrogen bonded NH groups are much better resolved. The overtone of the $\nu(\mathrm{NH})_\mathrm{f}$ absorption can be clearly observed even at room temperature, because the anharmonicity constant for this stretching mode due to the free N–H groups is relatively large [17] and leads to an enhancement of the overtone intensity.

Generalized 2D correlation spectroscopy was originally proposed by Noda [18] in 1993 as an extension of his original 2D correlation spectroscopy [19–21]. Generalized 2D correlation spectroscopy allows us to monitor spectral intensity fluctuation as a function of any physical variable, e.g. time, temperature, pressure, distance or concentration. Thus, the temperature dependence of vibrational spectra can be studied in much greater detail than has previously been possible [9,10,22–24]. Owing to the enhancement of the spectral resolution by spreading the peaks over the second dimension, it is possible to identify the bands not readily seen in the original data set. Additionally, 2D correlation spectra provide information about the sequential order of the spectral intensity changes of different molecular segments in the course of the external perturbation.

The structure of the semicrystalline polyamides is complex and the hydrogen bonds are affected by several morphological factors, including the degree of crystallinity; the size, shape and perfection of crystals and spherulites; the size and perfection of lamellae and the amount of intercrystalline links and tie molecules [25]. Therefore, in an attempt to understand these phenomena, it is better to study a totally amorphous polyamide to avoid the complications of crystallinity. In this paper, we present 2D FT-NIR spectroscopic correlation studies of temperature-induced variations of hydrogen bonding in a completely amorphous polyamide.

2. Experimental

The amorphous polyamide used in this study was obtained from E.I. du Pont de Numours and Co. The polymer was synthesized from *n*-hexamethylenediamine and a mixture of the isomers of phthalic acid. The random placement of the latter isomers in the polymer chain prevents crystallization. Differential scanning calorimetry (DSC) measurements reveal a glass transition temperature of 135°C and there is no evidence of a crystalline melting point.

The sample for NIR analysis was prepared by casting a film from a 10% (m/v) solution of the polymer in dimethylacetamide (DMAc) onto a surface-roughed glass plate (to avoid interference fringes in the spectra). The samples were then dried at 50°C under vacuum overnight. After evaporation of the majority of the solvent, the sample was peeled from the glass plate under water and placed under vacuum for several hours at 105°C to remove residual solvent and water. The sample was then immediately sandwiched between KBr windows and transferred to a temperature cell in the spectrometer.

The FT-NIR measurements were performed at a resolution of 4 cm^{-1} with a Bruker IFS 88 FTMIR/FTNIR/Raman spectrometer. To obtain an acceptable signal-to-noise ratio, 256 scans were accumulated. Spectra were recorded in a variable-temperature cell with a reported accuracy of ±0.1°C between 25 and 200°C in intervals of 5°C.

3. Data treatment

The data treatment was performed using MATLAB software (The Math Works Inc.). During the calculation, we applied the generalized 2D correlation formalism developed and modified by Noda [18]. The temperature-averaged spectrum was applied as a reference. Since 2D correlation is a function of two independent wavenumbers, the correlation peaks are represented as pairs ($\nu1$,$\nu2$). In all 2D correlation plots, the negative peaks are shaded, thus, the remaining (unshaded) peaks are positive. The peaks in 2D correlation spectra which developed before the noise peaks appear are considered as significant.

4. Results and discussion

Fig. 1 shows the MIR and NIR spectra recorded at room temperature in the ranges 400–4000 and 4000–7000 cm^{-1}, respectively. The assignments of the absorption bands in NIR region were made on the basis of the MIR band assignments of Coleman [2] and are summarized in Table 1. The NIR spectra of the sample in the region 5400–7000 cm^{-1}, recorded as a function of increasing temperature, are shown in Fig. 2. It is noted that the spectral changes of the $\nu(\mathrm{CH})$ overtone and combination bands are small as the temperature increase, while the intensities and shapes of the absorption bands of amide-functionality in the ranges 6300–6800 cm^{-1} changes significantly with temperature. The spectrum at 25°C is characterized by a relatively wide band at about 6535 cm^{-1} and a relatively weak band at 6765 cm^{-1}. The band at 6765 cm^{-1} may be due to the first overtone of the $\nu(\mathrm{NH_f})$ mode, as this frequency is very close to the reported overtone $2^*\nu(\mathrm{NH_f})$ of *N*-methyl acetamide in dilute $\mathrm{CCl_4}$ solution [16].

As the temperature is increased from 25 to 200°C, the position of the 6765 cm^{-1} band is quite constant and the intensity of this band increases drastically, indicating the increase in the proposition of free NH groups. The band at about 6535 cm^{-1} slightly shifts to high frequencies and decreases in intensity, whereas bands around 6650 cm^{-1}

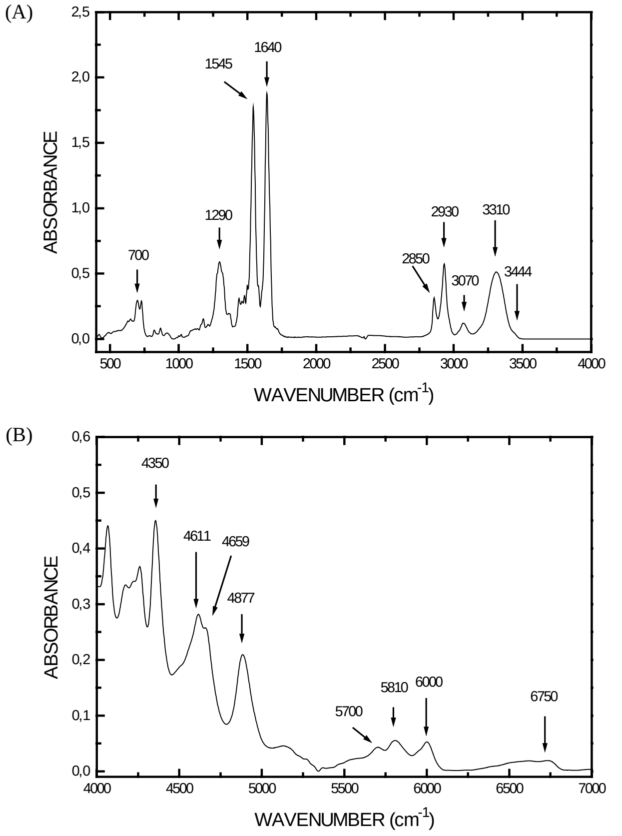

Fig. 1. FTMIR (A) and FTNIR (B) spectra of the investigated amorphous polyamide recorded at room temperature.

show a slight increase in intensity. Therefore, we assign the band at 6535 cm^{-1} to the first overtone of the $\nu(NH_b)$ mode.

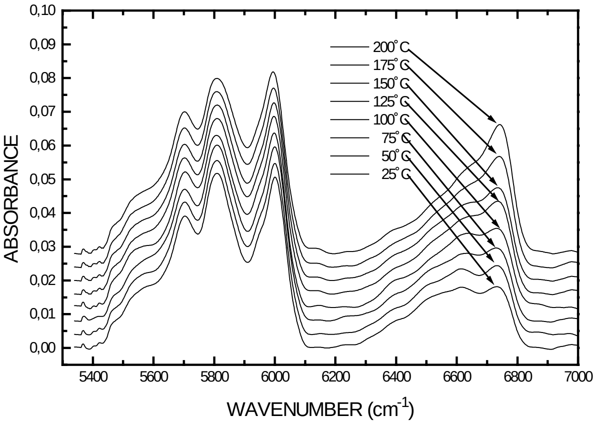

Fig. 2. Temperature-dependent FTNIR spectra obtained from 25 to 200°C of the investigated amorphous polyamide in the spectral range 5400–7000 cm^{-1}.

The four characteristic hydrogen-bonded structures of amide groups in polyamides are shown in Fig. 3. Upon a temperature increase, the fraction of the weaker hydrogen bonds increases. This observation agrees with the results derived from the MIR data [2].

Table 1
Band assignment of the investigated amorphous polyamide

Wavenumber (cm^{-1})	Intensity	Tentative assignment
3444	w	$\nu(NH)_f$
3310	s	$\nu(NH)_b$
3080	w	$\nu_{ar}(CH)/2^*$ Amide II
2930	s	$\nu_{as}(CH_2)$
2850	s	$\nu_{as}(CH_2)$
1640	s	Amide I
1545	s	Amide II
1290	m	Amide III
700	m	Amide V
6765	w	$2^*\nu(NH)_f$
6520	m	$2^*\nu(NH)_b$
6010	m	$2^*\nu_{ar}(CH)$
5980	m	$2^*\nu_{ar}(CH)$
5900	m	$2^*\nu_{ar}(CH)$
5810	m	$2^*\nu_{as}(CH_2)$
5690	m	$2^*\nu_s(CH_2)$
4877	m	$\nu(NH)_b$ + Amide II
4659	m	3^*Amide II
4611	m	$\nu(NH)_b$ + Amide III
4350	s	$\nu_s(CH_2) + \nu_{as}(CH_2)$

The synchronous 2D FTNIR spectrum (Fig. 4A) of the sample in the 6200–6900 cm^{-1} range shows a strong autopeak at 6765 cm^{-1} and two negative crosspeaks at 6535/6765 and 6250/6765 cm^{-1}. In the 2D NIR representation, the temperature-induced spectral changes are compared to each other rather than to the temperature. In the synchronous plot, diagonal peaks are referred to as autopeaks. The intensity of autopeaks is always positive, and they represent the overall extent of the temperature-induced fluctuation of spectral intensity with respect to the reference spectrum. Thus, regions of a spectrum which change the intensity to a greater extent show stronger autopeaks, while those remaining constant do not yield an autopeak. Hence, the strong autopeak at 6765 cm^{-1} indicates the significant temperature-dependent intensity variation of the first overtone of the $\nu(NH)_f$ absorption (see also Fig. 2). The off-diagonal peaks are called crosspeaks and their presence indicates that simultaneous changes occur at two different wavenumbers. Positive synchronous crosspeaks indicate that the intensity variations upon temperature increase at wavenumber $\nu1$ and $\nu2$ proceed in the same direction, while negative synchronous crosspeaks show that the changes are in opposite direction, i.e. the intensity of one

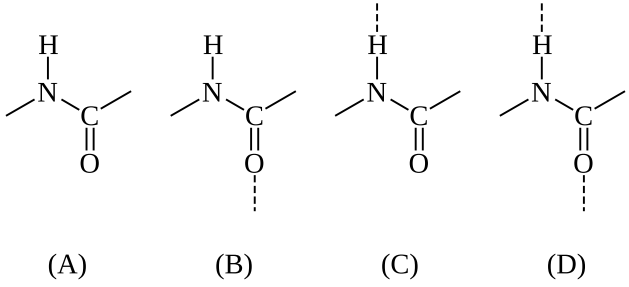

Fig. 3. Structure of hydrogen bonds of amide groups in polyamide.

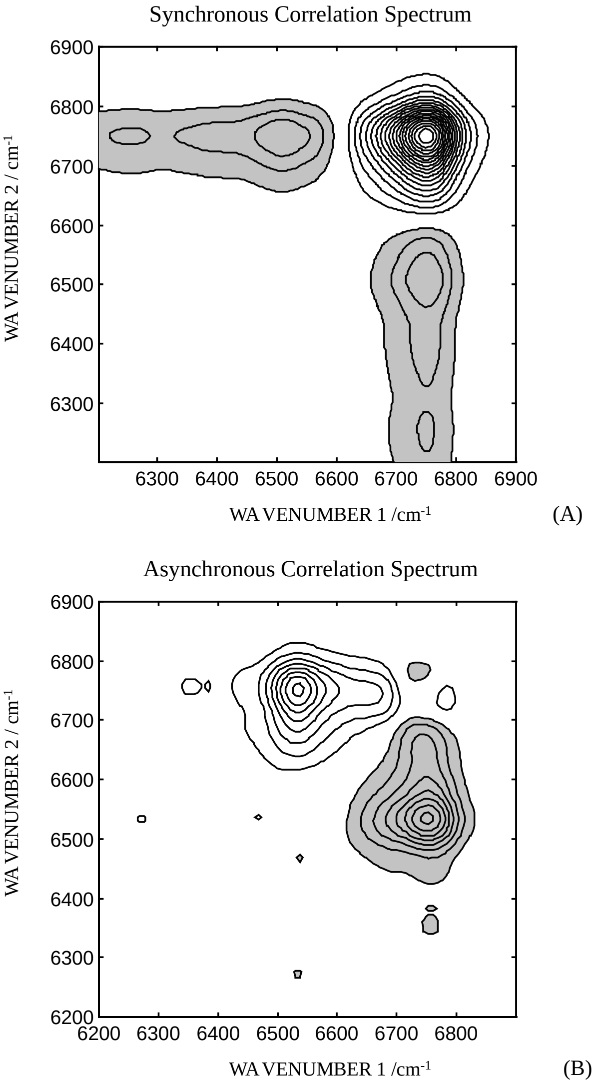

Fig. 4. Synchronous (A) and asynchronous (B) 2D FTNIR correlation spectra of the investigated amorphous polyamide obtained from 25 to 200°C in the 6200–6900 cm^{-1} range.

band is increasing and that of the other is decreasing. The negative crosspeaks at 6535/6765 and 6250/6765 cm^{-1} in Fig. 4A indicate that the intensity of the $2^*\nu(\mathrm{NH})_b$ overtone and the 6250 cm^{-1} band (possibly a $\nu(\mathrm{NH}) + \nu(\mathrm{CH})$ combination) decreases in the course of temperature variation. Fig. 4B shows the asynchronous plot for the same spectral region. An asynchronous plot has only off-diagonal peaks. The presence of asynchronous peaks indicates that the intensity responses of corresponding bands occur at different rates. A positive asynchronous peak at ($\nu1$, $\nu2$) means that the intensity at $\nu1$ changes faster compared to that at $\nu2$, while the negative asynchronous peak implies the opposite phenomenon. This feature is very useful in differentiating overlapped bands due to different spectral origin. The crosspeak at 6535/6765 cm^{-1} in Fig. 4B reveals that the decrease of population of the hydrogen-bonded NH species and the increase of population of the free NH groups occur at different rates. The positive sign of this peak in the left upper triangle indicates that the temperature-induced variations of spectral intensities occur earlier at 6535 cm^{-1} ($2^*\nu(\mathrm{NH})_b$) than those at 6765 cm^{-1} ($2^*\nu(\mathrm{NH})_f$). The obvious asymmetry of this crosspeak indicates the existence of a band at about 6650 cm^{-1}, probably due to the $2^*\nu(\mathrm{NH})_b$ overtone of weakly hydrogen bonded amide groups (see Fig. 3C). This result reveals that the intermolecular hydrogen bonding was gradually weakened upon heating.

The asynchronous crosspeak at 6740/6780 cm^{-1} suggest that the 6765 cm^{-1} band ($2^*\nu(\mathrm{NH})_f$) has two origins. The sign of this crosspeak indicates that intensity change at 6780 cm^{-1} band proceeds earlier than those at 6740 cm^{-1} band. The specific assignment of these two bands has not yet been fully determined. It is possible that the splitting of the two bands at 6740 and 6780 cm^{-1} arises from the free-end NH groups (Fig. 3B) and the totally free NH groups (Fig. 3A), respectively. The sign of the other crosspeaks at 6350/6535 cm^{-1}, in Fig. 4B indicates unambiguously that spectral change around 6350 cm^{-1} band (possibly a $\nu(\mathrm{NH}) + \nu(\mathrm{CH})$ combination) occurs at lower temperature than the intensity changes in the NH overtone regions (6765 cm^{-1}).

We now direct our attention to the first overtone region (5400–6200 cm^{-1}) of the aliphatic $\nu(\mathrm{CH_2})$ and the aromatic $\nu(\mathrm{CH})$ absorption bands. The synchronous 2D FT-NIR spectrum (Fig. 5A) of the sample in this region reveals several autopeaks at 6010, 5980, 5900, 5810 and 5690 cm^{-1}. The first three bands can be assigned to the first overtone of the aromatic $\nu(\mathrm{CH})$ absorption [26], the latter two bands to the first overtone of $\nu_{as}(\mathrm{CH_2})$ and $\nu_s(\mathrm{CH_2})$ absorption [26,27], respectively. The negative crosspeak at 5810/5690 cm^{-1} implies that the thermally induced change at 5810 cm^{-1} band is in the opposite direction compared to the 5690 cm^{-1} band. Careful inspection of NIR spectra in Fig. 2 reveals that the band intensity at 5810 cm^{-1} is steadily decreasing with the rising temperature, while the 5690 cm^{-1} band is slightly increasing. Jokl [27] reported that the intensity of the first overtones of $\mathrm{CH_2}$ stretching vibrations are very sensitive to the degree of order in polyamides. In the NIR spectrum of the polyamide 6 film (α form) the intensity ratio of two bands $I(5840\ \mathrm{cm}^{-1})/I(5740\ \mathrm{cm}^{-1})$ is about 5:3, however, this ratio is reversed (1:2) in a highly concentrated 2,2,3,3-tetrafuoropropanol solution of the same polyamide 6 sample. It is likely that the absorption at 5810 cm^{-1} can be assigned to a $\nu(\mathrm{CH_2})$ overtone of a highly associated form of the investigated polyamide. The sign of the 5690/5810 cm^{-1} crosspeaks in the asynchronous spectrum (Fig. 5B) reveal that the intensity variation at 5810 cm^{-1} (highly associated) occur earlier than those at the 5690 cm^{-1} (less associated).

The aromatic $\nu(\mathrm{CH})$ absorption band of this amorphous polyamide is very weak compared with the aliphatic $\nu(\mathrm{CH_2})$ in the MIR region (see Fig. 1A). The first overtone of the $2^*\nu(\mathrm{CH})_{ar}$ absorption, however, shows almost the same intensity as the $2^*\nu(\mathrm{CH_2})$. The negative synchronous crosspeaks at 5900/6010 and 5980/6010 cm^{-1} in Fig. 5A

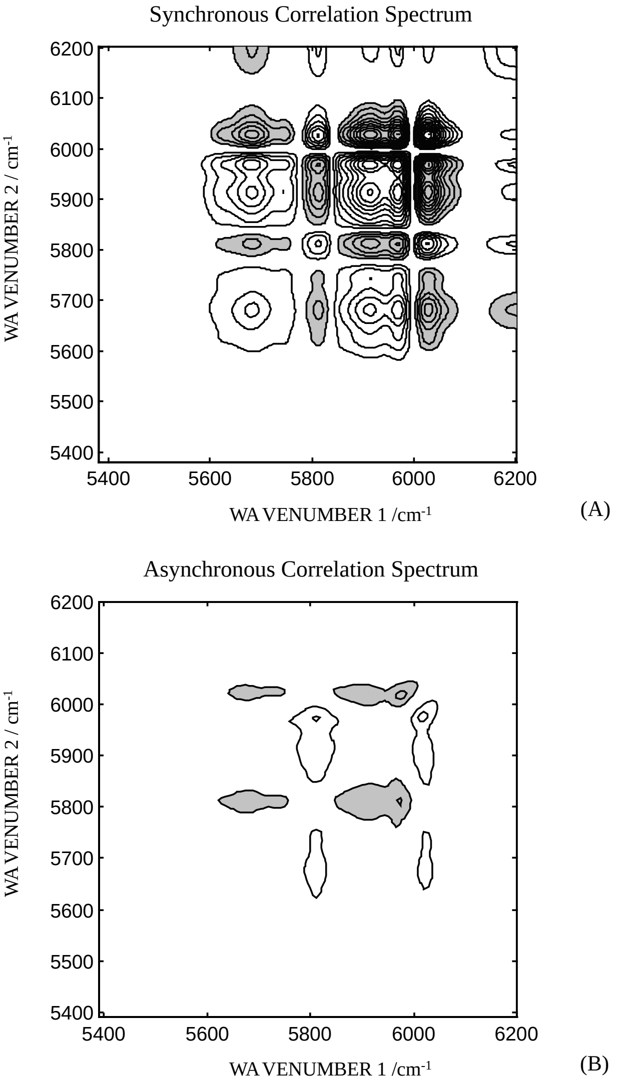

Fig. 5. Synchronous (A) and asynchronous (B) 2D FTNIR correlation spectra of the investigated amorphous polyamide between 5400 and 6200 cm^{-1}.

suggest that the thermally induced changes derived from the 6010 cm^{-1} band are in the opposite direction compared to the 5900 and 5980 cm^{-1} band.

Furthermore, the signs of the asynchronous crosspeaks between 6010 cm^{-1} band and the bands at 5900 and 5980 cm^{-1} in Fig. 5B reveal that the temperature-induced spectral changes reflected by the 6010 cm^{-1} band occurs earlier or at lower temperature than those at the 5900 and 5980 cm^{-1} bands. The strong synchronous and the absence of the asynchronous correlation between 6010 and 5810 cm^{-1} indicate that these two bands have the same origin in the highly associated form of the investigated polyamide. Similar relations can be derived for the 5690, 5990 and 5980 cm^{-1} bands and the 5810 cm^{-1} band.

Fig. 6 compares the regions corresponding to the first overtones of CH and NH stretching vibrations. The negative synchronous crosspeaks in Fig. 6A correlate the decrease of intensity at 5810 and 6010 cm^{-1} with the increase of intensity of the 6765 cm^{-1} band ($2^*\nu(\text{NH})_f$). On the other hand, positive synchronous crosspeaks can be found between 6765 cm^{-1} band and the rest of the aliphatic and aromatic ν(CH) overtone vibrations.

The signs of asynchronous crosspeaks shown in Fig. 6B indicate that the observed intensity variations at 6535 cm^{-1} band occur earlier than those at 5690, 5900 and 5980 cm^{-1} bands, while the intensity changes at all the CH bands (both aromatic and aliphatic) take place at lower temperature than those at 6765 cm^{-1}. No asynchronous crosspeaks can be observed between 5810, 6010 and 6535 cm^{-1}, indicating that these bands may have a common origin in the highly associated form in the polyamide.

5. Conclusion

The asynchronicity of the bands assigned to the vibrations

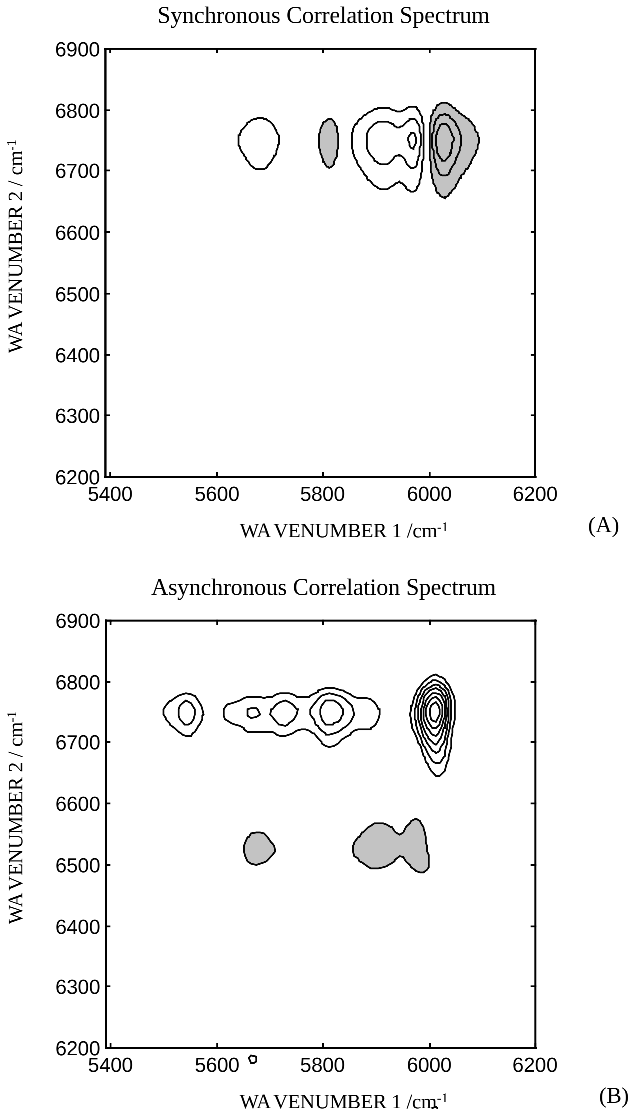

Fig. 6. Synchronous (A) and asynchronous (B) 2D FTNIR correlation spectra of the investigated amorphous polyamide between 5400–6200 and 6200–6900 cm^{-1} ranges.

of the free and hydrogen-bonded NH groups indicates a complicated mechanism of the dissociation and the existence of different hydrogen-bonded species in the investigated totally amorphous polyamide sample. The presence of the asynchronous peak at 6740/6780 cm^{-1} indicates the splitting of the $2^{*}\nu(\text{NH})_{\text{f}}$ band in a totally free (Fig. 3A) and a free-end (Fig. 3B) component. In the CH overtone region, two bands at 5810 (aliphatic) and 6010 cm^{-1} (aromatic) are found to be very sensitive to temperature induced structure in the investigated amorphous polyamide.

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