

# Thermally induced conformational and structural disordering in polyethylene crystal studied by near-infrared spectroscopy

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Received 23 August 2007; received in revised form 9 December 2007; accepted 19 December 2007

Available online 23 December 2007

## Abstract

Thermally induced structural and conformational changes in polyethylene (PE) samples were explored by using near-infrared (NIR) spectroscopy. The differences in the temperature-dependent structural disordering process among six PE samples were depicted by monitoring the intensities of NIR bands characteristic of orthorhombic crystalline phase. The temperature dependency of bands in the NIR region that have been considered to be due to orthorhombic crystalline lattice was compared to that of a band at  $1378\text{ cm}^{-1}$  due to the methyl symmetric bending mode. The intensity decrease of the band in the mid-infrared (MIR) region seems to sensitively reflect the overall disordering of orthorhombic crystalline structure. As a result of this study, the intensity decrease of the bands in the NIR spectral region was found to proceed at lower temperature than that of the band at  $1378\text{ cm}^{-1}$ . This finding suggests the status of orthorhombic crystalline structure probed by the intensity of the band at  $1378\text{ cm}^{-1}$  and that by the “crystalline” bands in the NIR spectral region may not be identical. The NIR spectra were further analyzed by two-dimensional (2D) correlation spectroscopy to provide the in-depth analysis of NIR bands. The 2D correlation spectroscopy has detected the presence of two NIR bands at  $4342$  and  $4290\text{ cm}^{-1}$  due to orthorhombic crystalline phase and those at  $5840$  and  $5640\text{ cm}^{-1}$  due to amorphous phase. The hetero-spectral 2D correlation analysis was carried out between the NIR spectral region of  $4365$ – $4240\text{ cm}^{-1}$  and the well-established MIR spectral region for  $\text{CH}_2$  wagging deformation region of  $1390$ – $1240\text{ cm}^{-1}$ , where bands due to non-planar conformer are detected. This approach allowed us to determine NIR bands, which behave in a way similar to MIR bands originating from conformational defect sequences that exist in the orthorhombic crystalline lattice, the amorphous domain and the chain fold regions. As a result of the hetero-spectral 2D NIR–MIR correlation spectroscopic studies on the development of conformational defect sequence in three types of PE samples, it was concluded that the intensity of a band at  $4265\text{ cm}^{-1}$  changes in the same manner as the MIR bands at  $1368$ ,  $1353$  and  $1308\text{ cm}^{-1}$  assignable to *gtg*, *gg* and *gtg'* (*kink*) conformations. This finding means that the state of conformational disorder in PE crystal can be studied by monitoring the intensity of the NIR band at  $4265\text{ cm}^{-1}$ . The use of NIR spectroscopy makes it possible to directly probe the degree in the formation of conformational defect sequences in thick PE products typically produced in industry, which cannot be studied by MIR spectroscopy. This paper thus provides in-depth fundamental understandings on NIR spectra of PE as well as the results of our study regarding structural and conformational changes in PE crystals probed by NIR spectroscopy.

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**Keywords:** Polyethylene; Near-infrared (NIR); Conformational defects

## 1. Introduction

One of the characteristic features of the semicrystalline polymer species is the sensitive change of their structures and chain

conformations depending on the external conditions such as temperature, mechanical force, etc. [1]. Among the changes, the crystallization and the melting of ordered molecular chain segments have particularly been studied [2,3]. To study transition processes that happen in polymers, vibrational spectroscopy has played important roles because the vibrational spectroscopic features, such as intensity, width, and frequency

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of a band sensitively reflect such physical phenomena [4]. In this way, physical status in the structure of polymers can be studied in details.

Polyethylene (PE), which has the simplest chemical structure but is one of the most basic and important polymers has been extensively studied for a number of research and industrial purposes [3,5]. Particularly, PE's molecular structure, chain conformation and chain packing morphology have been the main research focus areas as they controls the mechanical properties of industrial importance. Within the crystalline structure of semicrystalline PE, some domains remain in the fully disordered or amorphous state, while some parts of the polymer chains have localized "defects" [6]. In the attempt to quantitatively measure conformationally disordered domains in PE, many researchers used mid-infrared (MIR) [7–16]. It is noted that the bands assigned to conformational defect sequence arise not only from that exist within crystalline lattice but also from that in amorphous domain and in the chain fold regions.

Thermally induced structural changes that happen in PE, especially those induced by the annealing treatment at a temperature lower than its melting temperature ( $T_m$ ), have been studied [17]. If PE is treated first at a temperature lower than its crystallization temperature, mainly three types of rearrangements take place in crystalline lattice: nucleation and growth of new crystals directly from the amorphous state [18], lateral growth of the preexistent crystals [18,19], and thickening of the crystals [19,20]. The structural changes in PE occurring during the temperature change have so far been studied mainly by using DSC, X-ray diffraction, infrared spectroscopy and Raman scattering techniques. We have recently reported the usefulness of near-infrared (NIR) spectroscopy [21]. Relatively low-absorption coefficient in NIR spectral region is particularly advantageous in its industrial applications, because it can handle thick and bulk specimen. An NIR spectrum on realistic form of industrial PE products, such as blow-molded bottles, injection molded sheets, and stretched tensile bar specimens, can be obtained with minimum sample preparation. Sato et al. established a calibration model for the prediction of physical properties of PE, such as density and crystallinity, by taking advantage of NIR spectroscopy in combination with multivariate data analysis [22]. Watari et al. reported the establishment of on-line monitoring NIR system that can measure the density of LDPE in combination with chemometric technique [23]. Amari and Ozaki reported the establishment of an *in situ* NIR method for the monitoring of oligomerization reaction of bis(hydroxyethyl terephthalate) (BHET) by quantitatively measuring the amount of hydroxyl end groups and that of ethylene glycol [24]. In this paper, we apply NIR spectroscopy to six different types of PEs, two samples from each group of LDPE, LLDPE and HDPE, as an extension of our previous study. In our previous study, we studied temperature dependency of NIR bands in HDPE and determined those NIR bands, which are characteristic of orthorhombic, hexagonal and amorphous phases [21]. In the present paper, the sensitivity of NIR spectroscopy for detecting the difference in structural

disordering processes among LDPE, LLDPE and HDPE is examined.

In particular, 2D correlation analysis is employed for the in-depth analysis of NIR spectra of PE. Generalized 2D correlation spectroscopy proposed by Noda in 1993 has become a powerful and versatile tool for elucidating subtle spectral changes induced by an external perturbation such as temperature, concentration and time [25–28]. Two-dimensional (2D) correlation spectroscopy has widely been applied to various spectroscopic data for two major reasons. One is that 2D correlation spectroscopy enhances apparent spectral resolution by deconvoluting highly overlapped bands into individual components. Another reason is that it gives the information about specific order of the spectral intensity changes from the analysis. The use of 2D correlation spectroscopy has been particularly useful for exploring physical changes occurring in polymer [29–32]. The technique made the relationships clearer among the overlapped bands and the physical changes, such as premelting phenomenon in Nylon 12 [29], or interactions between blended polymer species during the heating of a polymer alloy [30]. In the present study, 2D correlation spectroscopic technique was utilized for two separate research purposes. One is to detect the highly overlapped "hidden" bands in the NIR spectrum of PE. The other is to identify specific NIR bands originating from conformationally disordered sequences. For this purpose, hetero-spectral 2D correlation analysis was performed between NIR and MIR spectra, which had been simultaneously obtained during the heating of PE up to the melt temperature. The hetero-2D correlation analysis has been utilized as a powerful tool for studying a new spectroscopic region of interest while examining the relationship with other spectroscopic region where detailed understanding is already given. The usefulness of the hetero-2D correlation analysis has also been proved in studying physical changes that happen in polymer species [31,32]. The vibrational spectroscopic bands arising from the conformational defects in the crystalline structure of PE have so far been studied by MIR, and the bands due to conformationally disordered sequences are already well established in the MIR spectral region [6–16]. However, corresponding NIR bands to the MIR "conformational defect" bands have not been studied so far. Therefore, we carried out the MIR–NIR hetero-spectral 2D correlation study and successfully identified an NIR band due to conformationally disordered sequences for the first time.

The purpose of this paper is to establish a scientific basis for studying both structural and conformational changes that happen in PE crystal by using NIR. The technique allows the study of structural and conformational changes in thick and bulky PE specimens that represent a realistic physical state of industrially produced PE products. Monitoring the intensity of NIR bands due to orthorhombic crystalline structure has shown that it can clearly differentiate characteristic disordering process of LDPE, LLDPE and HDPE during heating. To explore the formation of conformational defects in PE crystal, an NIR band due to nonplanar conformer is determined, and the difference in the formation of such defect sequences has been studied among LDPE, LLDPE and HDPE.

Table 1  
Density, crystallinity and melting point of six PE samples

	Density (g/cm <sup>3</sup> )	Crystallinity (%)	Melting point (°C)
<i>HDPE</i>			
HDPE-L	0.952	68.3	128.4
HDPE-H	0.964	74.7	132.4
<i>LLDPE</i>			
LLDPE-L	0.921	31.2	123.2
LLDPE-H	0.937	52.2	127.5
<i>LDPE</i>			
LDPE-L	0.918	26.1	106.1
LDPE-H	0.923	33.1	111.0

## 2. Experimental

### 2.1. Materials

Six PE samples with different structures and crystallinities were used in this study. Specifically, two high-density polyethylenes (HDPEs), two linear low-density polyethylenes (LLDPEs) and two low-density polyethylenes (LDPEs) were

kindly supplied by Japan Polyethylene Corporation, Japan. Table 1 shows the crystallinity and the melting point estimated from DSC traces provided by the courtesy of Japan Polyethylene Corporation. All the samples were supplied in the form of pellets. In order to prepare a film sample for NIR measurements and also for the sake of adjusting thermal history of the samples, ca. 0.9 g of PE pellet samples was sandwiched in-between a pair of polyimide film and melted at approximately 10 °C higher than their  $T_m$ . The samples were kept for more than 10 min at the same temperature under the pressure of ca. 2 MPa using a *Shindo* hot press YS-5. The samples were then cooled to the ambient temperature at  $-2.0$  °C/min by using a Mettler FP800. The spectroscopic studies were completed within 1 week from the sample preparation.

### 2.2. Spectral measurements

NIR spectral measurements of PE samples were performed with a spectral resolution of 2 cm<sup>-1</sup> by means of a Thermo

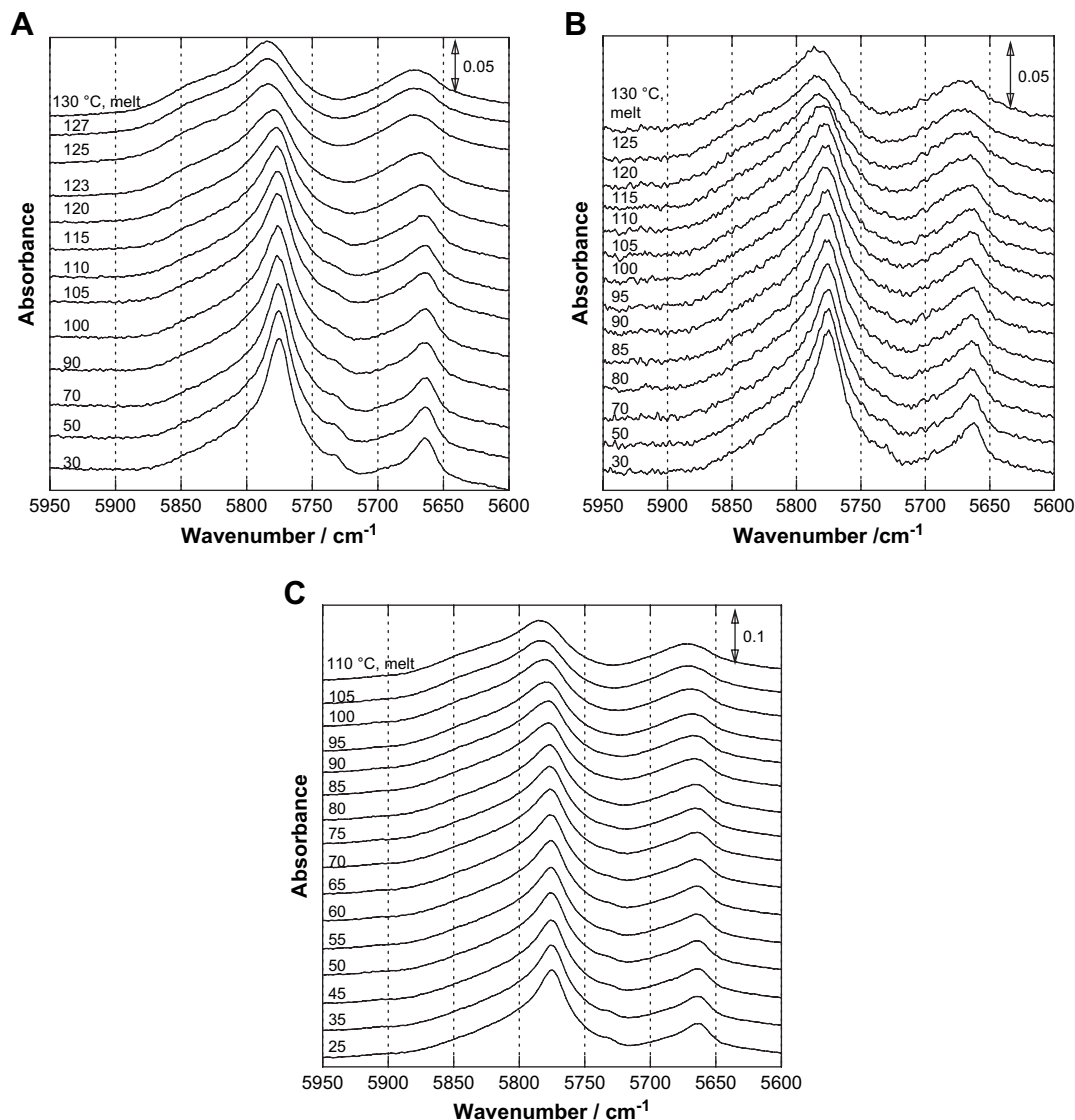


Fig. 1. NIR spectra in the 5950–5600 cm<sup>-1</sup> region of HDPE-L (A), LLDPE-H (B) and LDPE-L (C) in the temperature range of 25 °C to  $T_m$ .

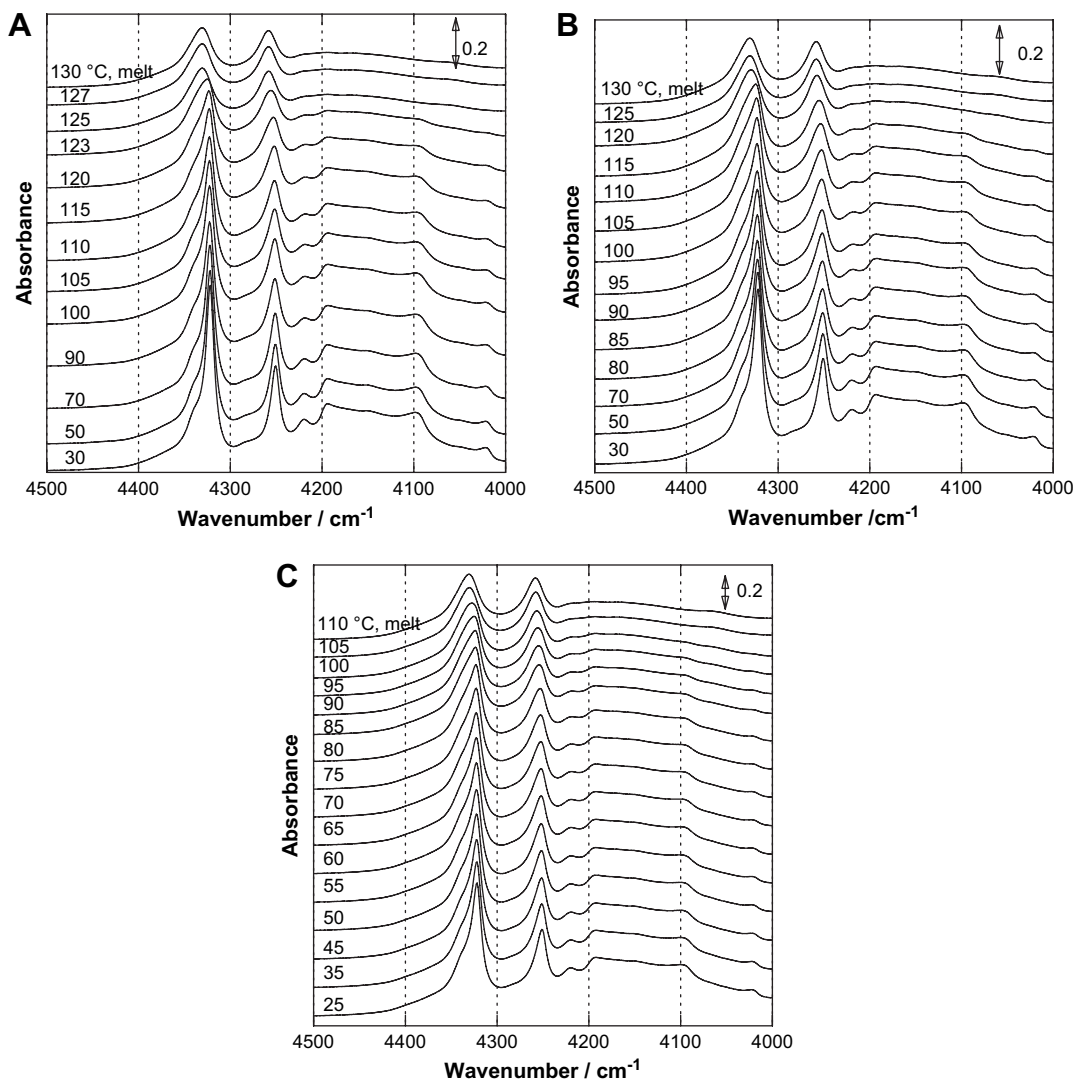


Fig. 2. NIR spectra in the 4500–4000  $\text{cm}^{-1}$  region of HDPE-L (A), LLDPE-H (B) and LDPE-L (C) in the temperature range of 25 °C to  $T_m$ .

Nicolet Nexus 870 FT-IR/NIR spectrometer. An MCT detector and an extended KBr beam splitter were used for the simultaneous measurements of both NIR (6000–4000  $\text{cm}^{-1}$ ) and MIR (4000–1200  $\text{cm}^{-1}$ ) spectra. Total of 32 spectra were co-added in each measurement. The spectra were measured for approximate dimensions of ca.  $10 \times 10 \times 0.3 \text{ mm}^3$  of the specimens. The sample was sandwiched with a pair of  $\text{CaF}_2$  plates ( $30 \times 15 \times 4 \text{ mm}$ ) and then placed in a heating block. The temperature was controlled by a CHINO temperature controller while its sensor was directly inserted into the sample set. In the temperature-dependent measurements, temperature was increased at a constant rate of 2 °C/min up to 100 °C and then 1 °C/min to the melt.

### 2.3. Curve fitting, spectral subtraction and second derivative calculation

In order to estimate integrated intensities of overlapped bands, curve fitting was carried out by using Grams/32 ver 4.2, Galactic Industries Corp against NIR spectra as needed. In this process, Lorentzian curve fitting function was adopted

and the integrated intensities of individual bands were estimated separately. The second derivative of a spectrum was calculated by Savitsky–Golay method (second-order polynomial with 15 data points).

### 2.4 Two-dimensional (2D) correlation analysis

To obtain 2D spectra, 2D Shige ver. 1.3 developed by Dr. Shigeaki Morita of Nagoya University was used. In the 2D correlation maps, unshaded regions indicate positive correlation intensities, while shaded regions indicate negative correlation intensities.

## 3. Results and discussion

### 3.1. Difference in the structural disordering process among six PE samples studied by NIR

Figs. 1 and 2 show the temperature-dependent NIR spectra in the 5950–5600 and 4500–4000  $\text{cm}^{-1}$  regions of the three types of PE samples representing HDPE, LLDPE and LDPE

collected during the heating process up to each melt temperature. We previously studied the temperature dependency of NIR bands in these spectral regions of HDPE. As a result, bands due to orthorhombic crystalline phase and those from disordered amorphous phase are identified in both of the spectral regions [21]. A decrease in the intensity of orthorhombic bands during the heating process is compensated by an increase in the intensity of bands due to amorphous phase. This gradual change manifests itself on the series of spectra as the apparent shift of the peak positions. In the present study, the sensitivity of the NIR spectroscopy to the structural disordering process is examined by analyzing six different PE specimens. In order to quantitatively measure the disordering process of the crystalline structure, the areas of the bands due to orthorhombic phase appearing in the 4500–4000  $\text{cm}^{-1}$  region are measured.

Fig. 3 plots the integrated intensities of the bands at 4322 and 4250  $\text{cm}^{-1}$  as a function of temperature, where the band components were separated by curve fitting method based on the band positions determined previously [21]. These bands are ascribed to combinations of  $\nu_{\text{as}}(\text{CH}_2) + \delta(\text{CH}_2)$  and  $\nu_{\text{s}}(\text{CH}_2) + \delta(\text{CH}_2)$ , respectively, of the orthorhombic crystalline phase [33]. As temperature increases, the unit cell parameter  $a$  increases due to thermal pressure. This expansion provides the onset of PE chains mobility, leading to the structural disordering of orthorhombic crystalline phase. Intensities of bands due to the orthorhombic phase decrease during the heating. However, it is well known that the disordering process proceeds differently among various types of PEs with different structures or crystallinities. In HDPE, as we have already reported [21], the intensity of NIR bands arising from orthorhombic phase abruptly decreases when the temperature exceeds 120 °C or so. This phenomenon in HDPE was also reported by using SAXS measurement [34]. The structural disordering process in LLDPE proceeds over a relatively wide temperature range as shown in Fig. 3. LLDPE has been developed to achieve desirable physical properties by introducing short chain side branches. These branches disturb crystalline lattice structure and result in relatively broad distribution of the thickness and degree of perfection of lamellar crystals [35]. The structural disordering process in LLDPE during the heating process thus proceeds over a wide temperature range. Because of the introduction of longer polymer branches of varying length, crystallite size distribution in LDPE is considerably broad [36,37]. Due to this reason, structural disordering and rearrangement process undergo at even far lower temperature than  $T_m$  [17].

Fig. 4A–C shows the temperature dependence of the integrated intensities of bands in the NIR (4322 and 4250  $\text{cm}^{-1}$ ) and MIR (1378  $\text{cm}^{-1}$ ) spectral regions characteristic of the orthorhombic phases in HDPE-L, LLDPE-H and LDPE-L. As shown, the intensity decrease, which indicates the disordering of the orthorhombic crystalline structure of the bands in the NIR spectral region, proceeds at lower temperature than that of the band at 1378  $\text{cm}^{-1}$ . This finding suggests that the status of crystalline structure probed by the intensity of the band at 1378  $\text{cm}^{-1}$  and that by the “crystalline” bands in the NIR spectral region may not be identical.

The assignments of NIR “crystalline” bands at 4322 and 4250  $\text{cm}^{-1}$  have been reported as combinations of  $\nu_{\text{as}}(\text{CH}_2) + \delta(\text{CH}_2)$  and  $\nu_{\text{s}}(\text{CH}_2) + \delta(\text{CH}_2)$ , respectively [33]. The difference in the temperature dependency of the NIR bands and that of the band at 1378  $\text{cm}^{-1}$  may be considered due to the involvement of methylene stretching vibration in the NIR bands.

Hence, one has to be careful about this difference when studying the structural changes of orthorhombic crystalline structure based on the change in the intensities of NIR crystalline bands.

### 3.2. Elucidation of overlapping bands by 2D NIR correlation spectroscopy

We previously determined NIR bands originating from the orthorhombic crystalline phase and those from amorphous domain in HDPE by spectral subtraction technique [21]. Specifically, the bands were identified based on a difference spectrum that was constructed by subtracting a spectrum on quenched HDPE from that of annealed HDPE [21]. In order to further probe spectral changes during the heating process up to the melt, 2D correlation analysis has been carried out. Fig. 5A shows the contour map representation of the 2D NIR synchronous spectrum  $\Phi(\nu_1, \nu_2)$  of HDPE-H in the 5875–5600  $\text{cm}^{-1}$  region. The spectrum represents the coupled or coordinated temperature-dependent spectral intensity variations of NIR from 100 °C to the melting temperature (132 °C). Six cross-peaks are associated with the autopeak at 5775  $\text{cm}^{-1}$ , which is assigned to  $2\nu_{\text{as}}$  of the  $\text{CH}_2$  groups of the orthorhombic crystalline phase [33,38]. The appearance of two positive cross-peaks at 5775, 5732 and 5775, 5665  $\text{cm}^{-1}$  are expected as the presence of bands due to orthorhombic crystalline phase has already been reported at 5732 and 5665  $\text{cm}^{-1}$  [21]. The appearance of negative crosspeaks with the band at 5775  $\text{cm}^{-1}$

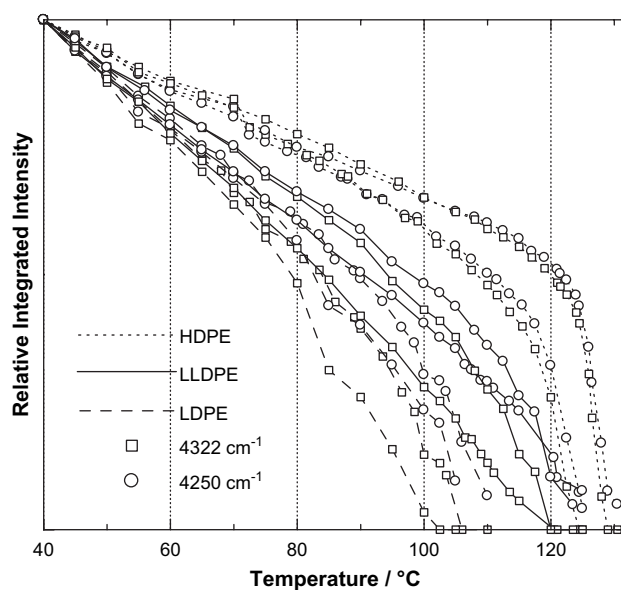


Fig. 3. Temperature dependence of the integrated intensities of bands in NIR 4322  $\text{cm}^{-1}$  (A), 4250  $\text{cm}^{-1}$  (B); and MIR 1378  $\text{cm}^{-1}$  (C) spectral region in HDPE, LLDPE and LDPE characteristic of the orthorhombic phases in the temperature range of 40 °C to its  $T_m$ .

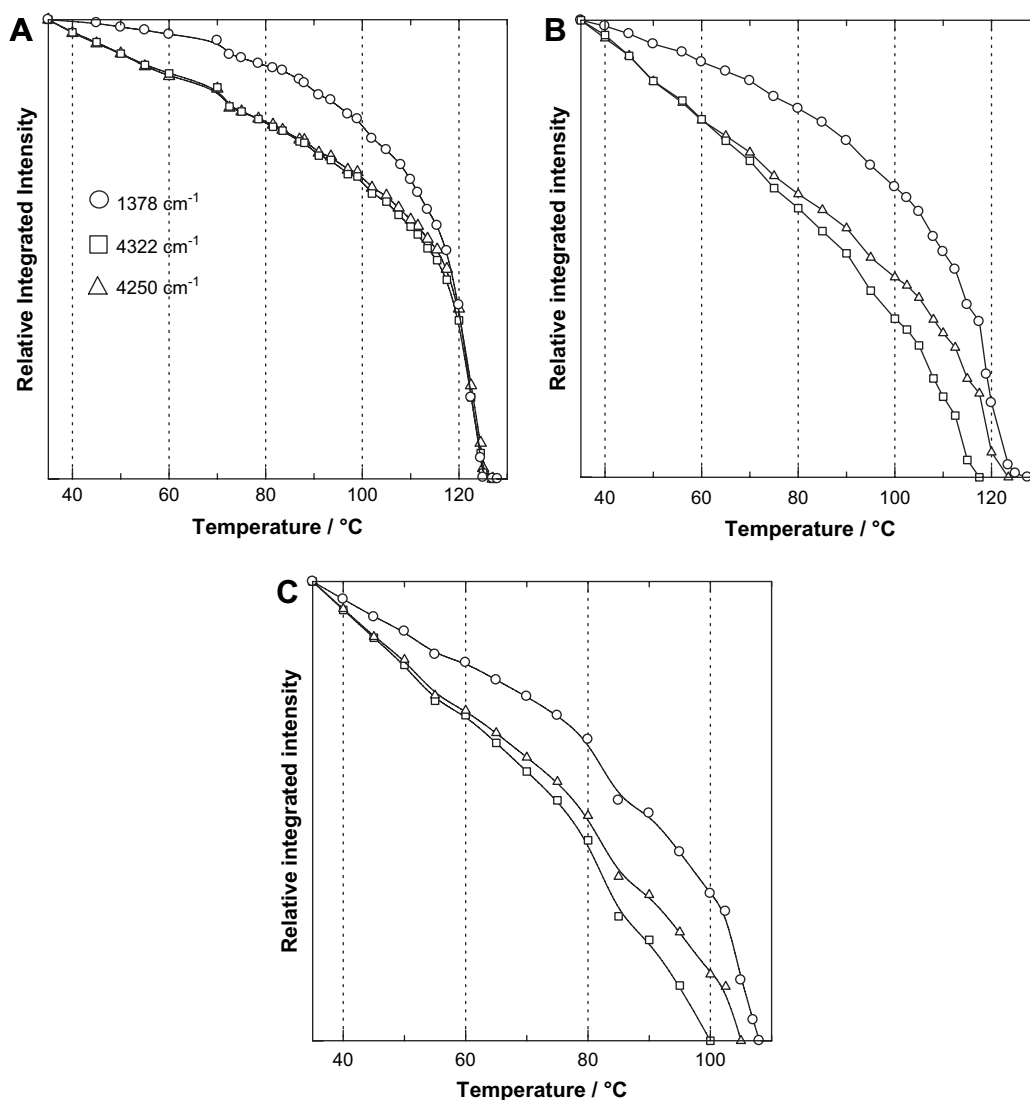


Fig. 4. Temperature dependence of the integrated intensities of bands in the NIR (4322 and 4250  $\text{cm}^{-1}$ ) and MIR (1378  $\text{cm}^{-1}$ ) spectral region in HDPE-L (A), LLDPE-H (B) and LDPE-L (C) characteristic of the orthorhombic phases in the temperature range of 35 °C to its  $T_m$ .

indicates the presence of bands due to the amorphous phase. Such negative crosspeaks are detected at 5775, 5840; 5775, 5680 and 5775, 5640  $\text{cm}^{-1}$ . Although we already reported the presence of a band at around 5810  $\text{cm}^{-1}$  that originates from the amorphous phase [21], an additional amorphous band in this spectral region is now identified at 5840  $\text{cm}^{-1}$ . It is reasonable to detect a negative crosspeak at around 5680  $\text{cm}^{-1}$ , because the existence of a band due to amorphous phase has previously been reported in this spectral region [21]. The presence of a negative crosspeak at around 5640  $\text{cm}^{-1}$  indicates the existence of an amorphous phase band in this spectral region, which has not been reported so far.

Fig. 5B shows an NIR spectrum obtained at 30 and 132 °C in the corresponding spectral region. The difference spectrum between the two spectra was obtained by adjusting the subtraction factor. In the difference spectrum, bands due to the amorphous phase should appear with negative intensities. The presence of amorphous bands is confirmed at 5840 and 5640  $\text{cm}^{-1}$  by this spectral subtraction technique as well.

Fig. 6A shows a synchronous 2D NIR correlation spectrum  $\Phi(\nu_1, \nu_2)$  of HDPE-H in the 4360–4250  $\text{cm}^{-1}$  region calculated from the spectra from 100 °C to the melting temperature. The minimum level of contour lines has been intentionally set very low so that we can observe the behavior of small bands in this spectral region. Among the detected crosspeaks, two negative crosspeaks at 4350, 4320; 4336, 4320  $\text{cm}^{-1}$  and one positive crosspeak at 4342, 4320  $\text{cm}^{-1}$  are of special interest. In our previous paper, we speculated the presence of amorphous bands at 4333 and 4259  $\text{cm}^{-1}$  based on the result of the spectral subtraction analysis [21]. The strong negative crosspeak at 4259, 4320  $\text{cm}^{-1}$  in Fig. 6A supports our original assignment, indicating that the band at 4259  $\text{cm}^{-1}$  arises from the amorphous phase, because the band at 4320  $\text{cm}^{-1}$  originates from the orthorhombic crystalline phase. Concerning the single broad amorphous band that we originally assumed at around 4333  $\text{cm}^{-1}$ , the result of the present study reveals that this spectral region actually consists of three bands: two independent amorphous bands and one band that is ascribed to the orthorhombic crystalline phase.

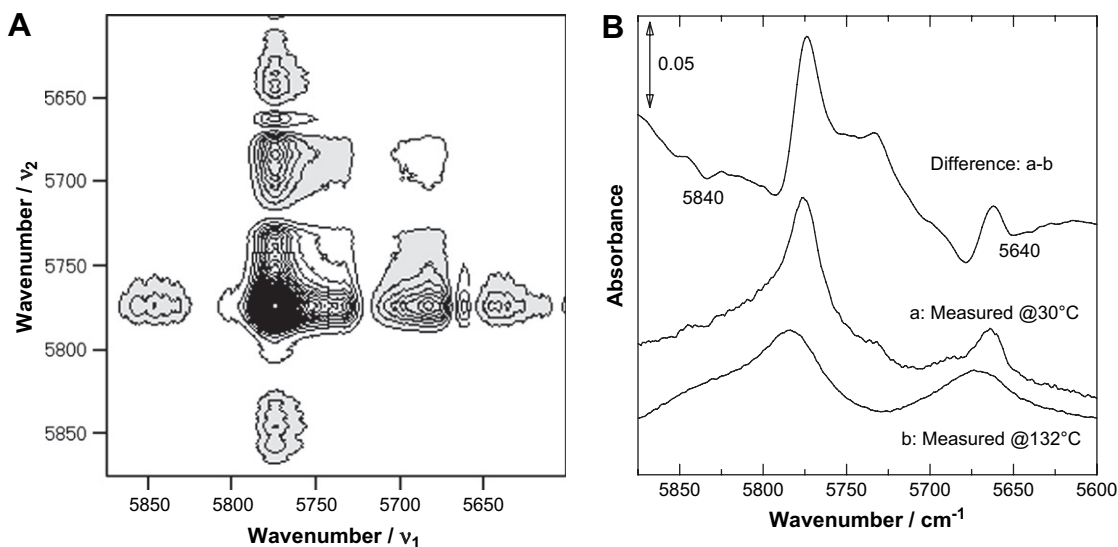


Fig. 5. The contour map representation of the 2D NIR synchronous correlation spectra of HDPE-H in the 5875–5600  $\text{cm}^{-1}$  region (A) and corresponding NIR spectra measured at 30 and 132  $^{\circ}\text{C}$  and their difference spectrum (B). Shading treatment of crosspeak at off-diagonal position in the 2D NIR synchronous correlation spectrum (A) indicates negative correlation while positive correlation is shown without shading.

Fig. 6B shows an NIR spectrum in the corresponding spectral region obtained at 30  $^{\circ}\text{C}$ . The orthorhombic crystalline structure is preserved well at this temperature. The second derivative of the spectrum was obtained with Savitsky–Golay method (second-order polynomial with 15 data points). The presence of orthorhombic bands at 4342 and 4290  $\text{cm}^{-1}$  is clearly depicted in the second derivative spectrum as well. In this way, the result of 2D correlation spectroscopy that detected the presence of the two orthorhombic bands at 4342 and 4290  $\text{cm}^{-1}$  is confirmed. Table 2 summarizes the NIR bands newly identified in the present study.

### 3.3. Conformational defect bands in NIR spectral region

In order to explore the presence of NIR bands that are characteristic of conformational defect sequences in the crystalline

structure of PE, the hetero-spectral 2D correlation analysis was carried out for the spectra collected in the NIR and MIR spectral regions at the same time. This approach has been particularly useful in providing spectral assignments to highly overlapping NIR bands, by referring to the bands in MIR, where detailed spectral assignments have already been established [39]. Fig. 7 shows synchronous 2D NIR–MIR correlation spectra  $\Phi(\nu_1, \nu_2)$  of HDPE-H, LLDPE-L and LDPE-H. These 2D NIR–MIR spectra were constructed on NIR spectra and corresponding MIR spectra, which were simultaneously collected during the NIR measurements.

Negative crosspeaks are detected between the MIR bands at 1368, 1353 and 1308  $\text{cm}^{-1}$  and NIR bands at 4322 and 4250  $\text{cm}^{-1}$ . In the MIR spectral region, bands due to conformational defect sequences are known to give a rise at 1368, 1353 and 1308  $\text{cm}^{-1}$ . Specifically, the vibrational assignments

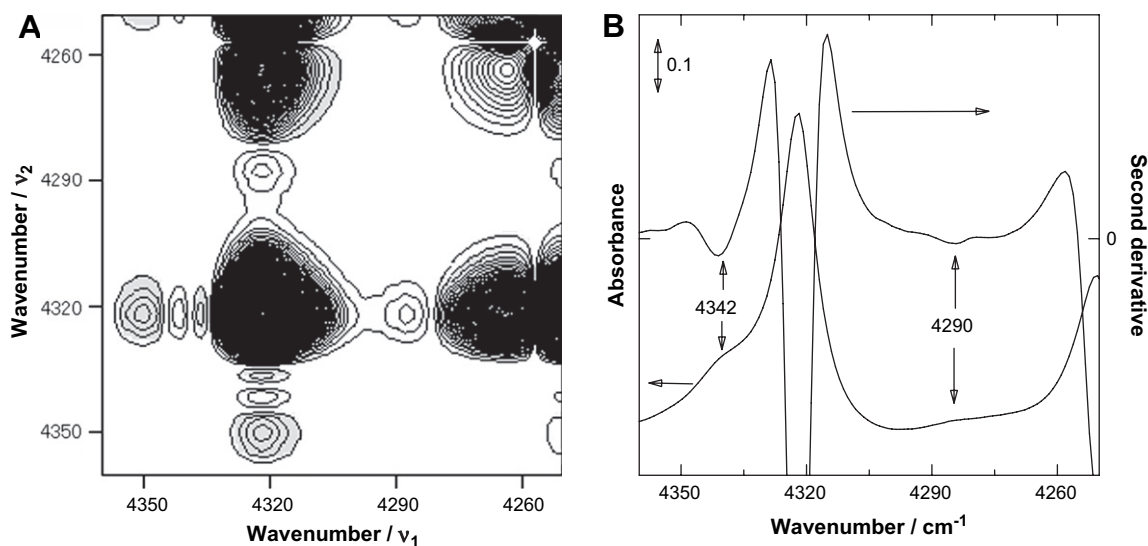


Fig. 6. The contour map representation of the 2D NIR synchronous correlation spectra of HDPE-H in the 4360–4250  $\text{cm}^{-1}$  region (A) and the corresponding NIR spectra measured at 30  $^{\circ}\text{C}$  and its second derivative spectrum (B).

Table 2  
Newly identified NIR bands of PE

Wavenumber ( $\text{cm}^{-1}$ )	Phase <sup>a</sup>
5840	Amr
5640	Amr
4342	Orth
4290	Orth
4265	Conf

<sup>a</sup> Amr: amorphous; Orth: orthorhombic; Conf: conformational defect.

on these bands are traditionally given as *kink* + *gtg* conformation (1368 and 1308  $\text{cm}^{-1}$ ) and *gg'* sequences (1353  $\text{cm}^{-1}$ ) based on MD calculations [14–16]. However, Clavell-Grunbaum et al. have amended the assignments on these bands as *gtg* conformation (1366  $\text{cm}^{-1}$ ), *gg* (1353  $\text{cm}^{-1}$ ) and *gtg'* (1306  $\text{cm}^{-1}$ ) [40]. The intensities of bands assignable to nonplanar conformer sequences are increased as the temperature

approaches to the  $T_m$  due to enhanced molecular mobility [41]. On the other hand, the intensities of the bands at 4322 and 4250  $\text{cm}^{-1}$  in the NIR spectral region decrease as temperature increases, because the bands are due to orthorhombic crystalline phase [21]. In this way, the presence of the negative correlation with the MIR bands due to conformational defects is reasonably explained. A positive crosspeak is detected between the NIR band at 4265  $\text{cm}^{-1}$  and the MIR vibration frequencies due to nonplanar conformers at 1368, 1353 and 1308  $\text{cm}^{-1}$ . This means that the temperature dependency of the NIR band at 4265  $\text{cm}^{-1}$  is very similar to the MIR bands due to conformational defect sequences. This result opens up the intriguing possibility of employing NIR spectroscopy to study conformational defect sequences in PE crystal using thick specimens.

The temperature dependence of the integrated intensity for the band at 4265  $\text{cm}^{-1}$  in the six PE specimens is shown in Fig. 8. As the temperature approaches to the  $T_m$ , the intensity

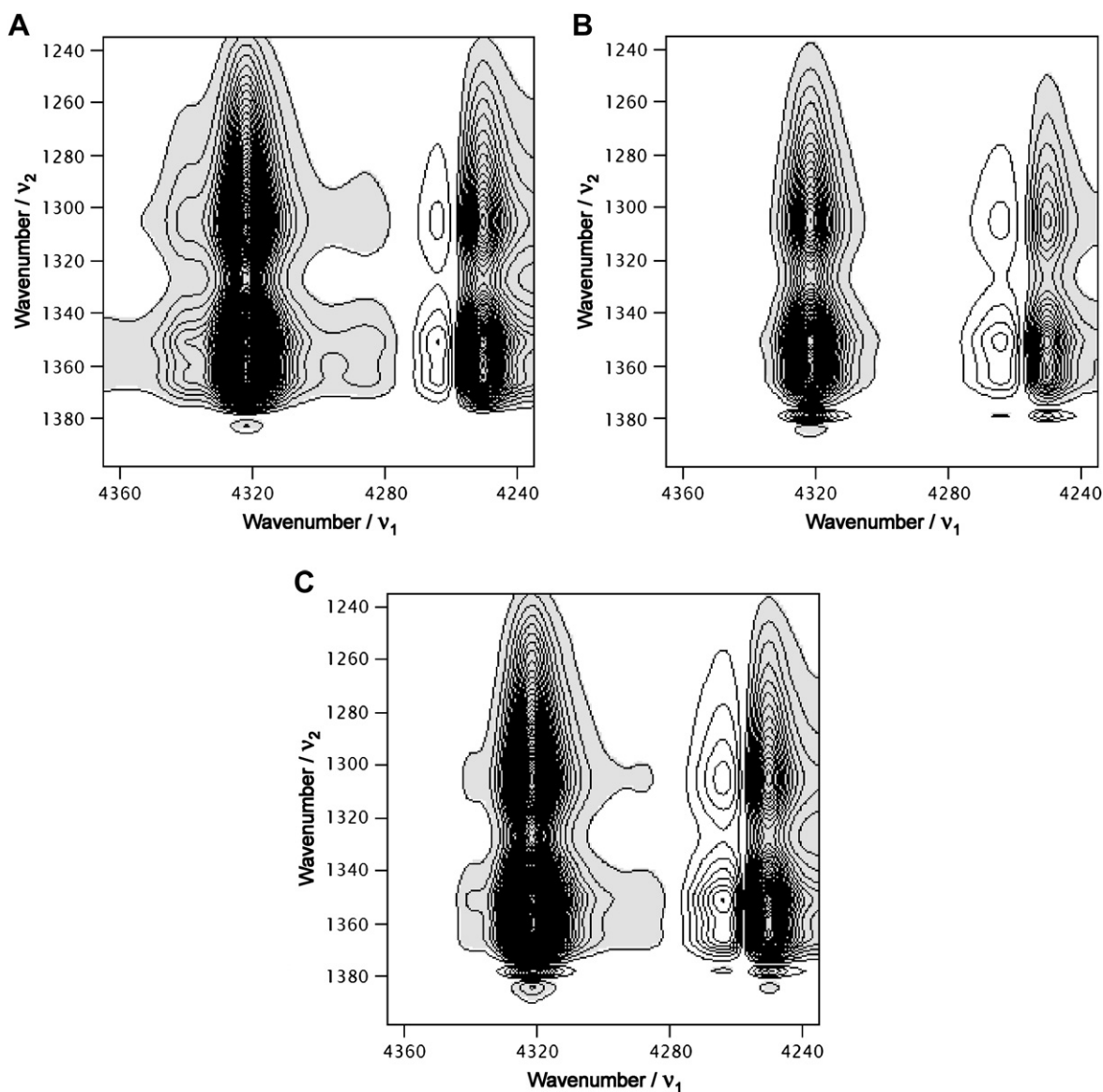


Fig. 7. The contour map representation of the 2D NIR–MIR synchronous correlation spectra of HDPE-H (A), LLDPE-L (B) and LDPE-H (C) between 4365–4235 and 1390–1235  $\text{cm}^{-1}$  regions.



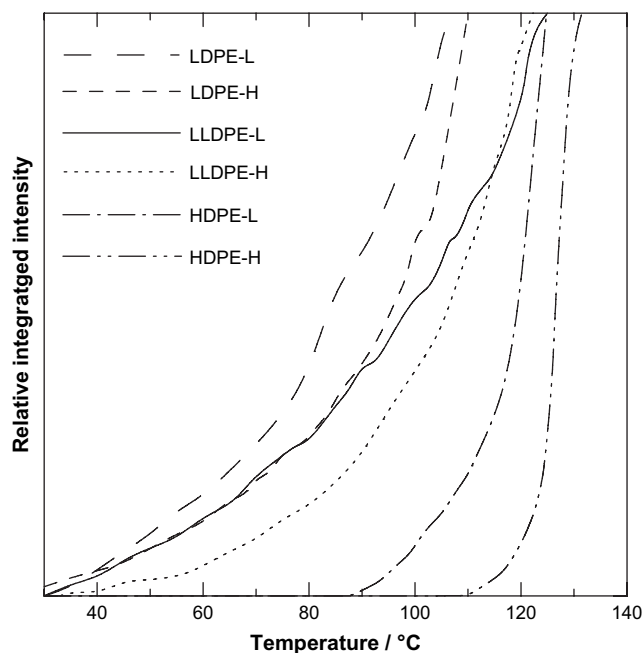


Fig. 8. Temperature dependence of the integrated intensities of a band at  $4265\text{ cm}^{-1}$  in HDPE, LLDPE and LDPE in the temperature range of  $30\text{ }^{\circ}\text{C}$  to its  $T_m$ .

of the NIR band at  $4265\text{ cm}^{-1}$  rapidly increases in HDPE. On the other hand, in LDPE, the increment undergoes continuously starting from the room temperature. The temperature dependency in the intensity of  $4265\text{ cm}^{-1}$  in LLDPE-H is similar to that in HDPE as it has an “on-set” of disordering. However, the temperature dependency of LLDPE-L has been found quite distinct such that the increment in the intensity of this band has nearly a linear correlation against temperature.

In our previous study on the temperature dependency of the MIR conformational defect mode bands at  $1368$ ,  $1353$  and  $1308\text{ cm}^{-1}$ , we detected the same temperature dependency in the intensity of the bands in LLDPE-L [42]. The 2D correlation

spectroscopic study was also carried out to explore the temperature dependency of the bands due to nonplanar conformers and that of methyl symmetric deformation “umbrella” vibration at  $1378\text{ cm}^{-1}$ . As a result, the conformational disorder sequence was detected in LLDPE-L even at a relatively low temperature, where orthorhombic crystalline structure is preserved well [42]. In order to examine the similarity in the temperature dependency of the NIR band at  $4265\text{ cm}^{-1}$  to the symmetric methyl deformation band in the MIR region, 2D NIR–MIR correlation spectroscopy has been performed. Fig. 9 shows 2D NIR–MIR synchronous  $\Phi(\nu_1, \nu_2)$  and asynchronous  $\Psi(\nu_1, \nu_2)$  correlation spectra for LLDPE-L. In the asynchronous 2D spectrum shown in Fig. 9B, the NIR band at  $4265\text{ cm}^{-1}$  against the band at  $1378\text{ cm}^{-1}$  develops a positive (unshaded) crosspeak. Since the correlation intensity of the corresponding spectral region in the synchronous spectrum (Fig. 9A) is negative, i.e.,  $\Phi(\nu_1, \nu_2) < 0$ , the change of the band at  $1378\text{ cm}^{-1}$  occurs later at a higher temperature compared with that of the band at  $4265\text{ cm}^{-1}$  in LLDPE-L. This result suggests that the formation of local nonplanar conformers proceeds ahead of the orientational and positional disordering of orthorhombic crystalline phase during the heating. Fig. 10 shows 2D NIR–MIR spectra for LDPE-H as a reference. As shown, the correlation between the band at  $4265\text{ cm}^{-1}$  and that of  $1378\text{ cm}^{-1}$  is reversed compared to the result of LLDPE-L. In other words, the decrease in the intensity of the band at  $1378\text{ cm}^{-1}$  proceeds prior to the increment of that of  $4265\text{ cm}^{-1}$  in LDPE-H. This “reversed” sequential relationship has also been confirmed in the temperature-dependent intensity change of MIR conformational defect bands at  $1368$ ,  $1353$  and  $1308\text{ cm}^{-1}$  and that of  $1378\text{ cm}^{-1}$  [42]. This strong similarity in the temperature-dependent intensity change of the NIR band at  $4265\text{ cm}^{-1}$  and that of MIR bands originating from *gtg*, *gg* and *gtg'* conformational defect sequences supports our proposal of considering this NIR band originates from conformation defect sequences exist in the structure of PE.

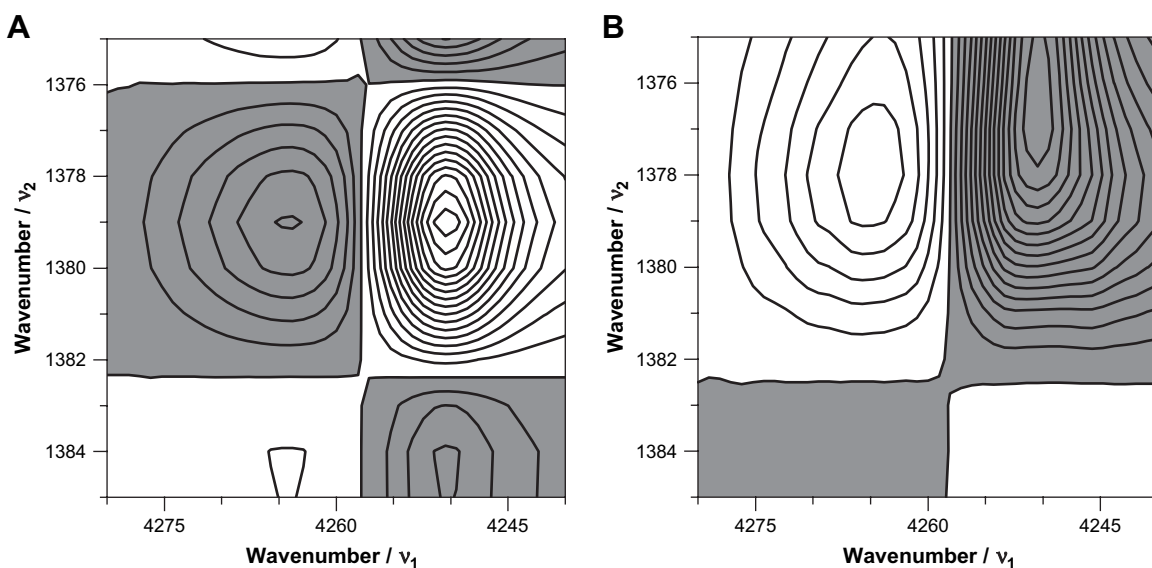


Fig. 9. The contour map representation of the 2D NIR–MIR synchronous (A) and asynchronous (B) correlation spectrum of LLDPE-L between  $4280\text{--}4240$  and  $1385\text{--}1374\text{ cm}^{-1}$ .

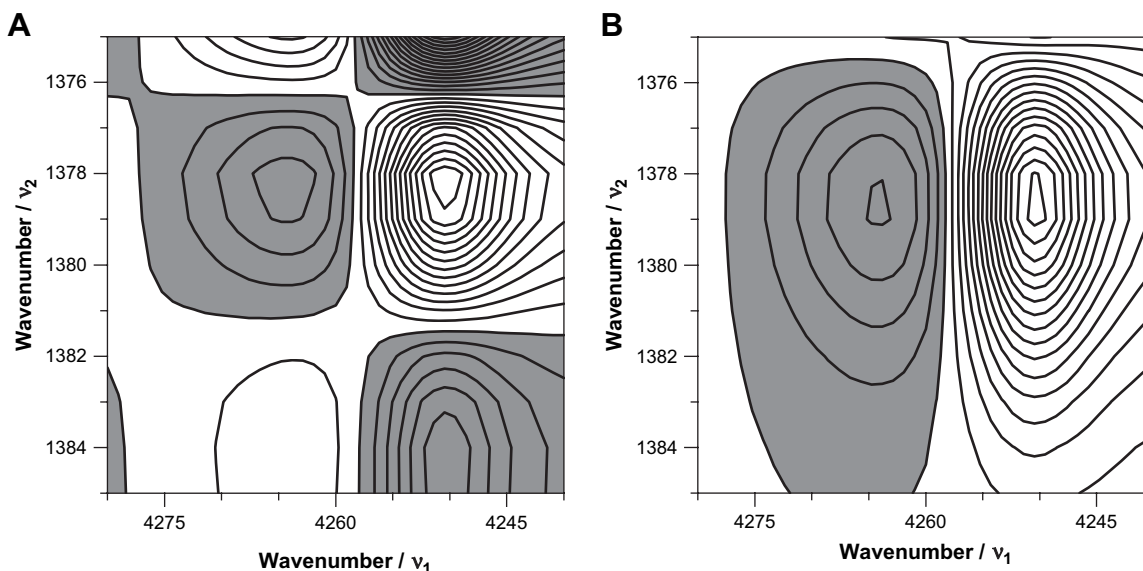


Fig. 10. The contour map representation of the 2D NIR–MIR synchronous (A) and asynchronous (B) correlation spectrum of LDPE-H between 4280–4240 and 1385–1374  $\text{cm}^{-1}$ .

This is probably the first description of the existence of an NIR band due to conformational defect sequences. The finding opens up a new and exciting approach to exploring conformational defects in the crystalline structure of PE by taking advantage of NIR spectroscopy applicable to a much thicker specimen of practical interest.

#### 4. Conclusion

We have investigated structural disordering process in the six different types of PE by means of NIR spectroscopy. Our results have demonstrated the applicability of NIR spectroscopy in investigating the structural transition behavior of different types of PE crystals. We introduced 2D correlation technique and carried out detailed spectral analysis for NIR spectra of PE during the heating process up to the melt temperature in order to elucidate “hidden” bands in the NIR spectrum. We also carried out 2D hetero-NIR–MIR spectroscopy in an attempt to detect a band due to conformational defect sequences. As a result, the presence of a band due to nonplanar conformer was identified in the NIR spectral region for the first time. This finding opens up a new way to directly study conformational transitions in PE by using NIR spectroscopy, while taking advantage of its applicability to thick specimens such as industrially produced blow-molded bottles, injection molded sheets and stretched tensile bars. The following conclusions have been reached in the present study.

(1) Two-dimensional (2D) hetero-NIR–MIR correlation spectroscopy has revealed that the temperature-dependent behavior in the intensity of an NIR band at 4265  $\text{cm}^{-1}$  undergoes the change in the same way as bands detected in the MIR spectral region (1390–1240  $\text{cm}^{-1}$ ), originating from conformational defects of *gtg*, *gg* and *gtg'* sequences. One can probe the formation and disappearance of

conformational defects in the crystalline structure of PE by studying the behavior of this NIR band.

- (2) The difference in the temperature dependency of structural disordering process among HDPE, LLDPE and LDPE has clearly been depicted by NIR spectroscopy. The thermally induced structural disordering process in orthorhombic crystalline structure of HDPE mostly happens about 10 °C below its  $T_m$ , while that in LLDPE and LDPE continuously undergoes above ambient.
- (3) The intensity decrease of “crystalline” bands in the NIR spectral region proceeds at lower temperature than that of the band at 1378  $\text{cm}^{-1}$ . This finding suggests that the status of crystalline structure probed by the intensity of the band at 1378  $\text{cm}^{-1}$  and that by the “crystalline” bands in the NIR spectral region may not be identical.
- (4) Two-dimensional (2D) NIR correlation spectroscopic study of HDPE revealed the presence of two bands at 4342 and 4290  $\text{cm}^{-1}$  due to orthorhombic crystalline phase and two bands at 5840 and 5640  $\text{cm}^{-1}$  due to amorphous phase.

#### Acknowledgements

The authors are grateful to Japan Polyethylene Corporation for supplying the specimens used in this study. The authors also thank Dr. Shigeaki Morita (Nagoya University) for his help in preparing figures.

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